

Solubility of polymers

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Abstract - Polymers differ from low molecular weight compounds in a number of ways; among them are (i) the comparatively low thermal expansivities and compressibilities of their melts at higher temperatures, (ii) the frequent occurrence of solidification to a glass instead of a crystal at low temperatures, and (iii) the fact that even chemically uniform polymer samples normally consist of a large number of species differing in molecular mass and architecture. The consequence of these peculiarities of polymers with respect to their solubility are discussed for the example of linear chain molecules. Firstly, the survey will review the experimental methods (some of which were specially developed for polymer solutions) for the determination of solubility limits and critical conditions. Then the general phenomena observed with systems containing high molecular weight material will be worked out and discussed theoretically. The main independent variables are: temperature, pressure, molar mass of the polymer and shear rate (for solubility in flowing systems). In addition, isotopic effects on the solubility will also be considered.

INTRODUCTION

To cover all types of macromolecular systems in this survey of the solubility of polymers is virtually impossible. Not only is there a large variety of linear synthetic and natural homopolymers, but it is easy to augment this diversity without limit by admitting variations in chemical composition and molecular architecture. For a fixed fraction of each kind of monomeric unit contained in a given polymer sample, each different way of assembly of these constituents leads to molecules of different length and stereoregularity, different branching and crosslinking characteristics, and different distribution of the comonomers (to yield in the extreme cases statistical or block copolymers). A further variable of drastic influence on the solubility lies in the content of charged units in ionomers or polyelectrolytes.

In view of the extra effects resulting from this diversity, which are not yet fully understood in many cases, the survey will be confined to linear uncharged molecules. Furthermore it will deal exclusively with the solubility of glassy polymers, i.e. equilibria between pure, partly crystalline polymers and their saturated solutions will be excluded. It should be noted, however, that the subsequent discussion also holds true for the liquid/liquid phase separation of such polymers, which is generally superimposed on the liquid/crystal equilibrium in the case of thermodynamically sufficiently poor solvents. The following statements will above all concentrate on systems containing one type of homopolymer only; in a more marginal way questions concerning the "incompatibility" of polymers will also be included. To illustrate the typical behavior of the systems of interest, experimental material is mainly taken from work done in the author's group, not because it is considered to be more important than other published material, but merely because of the easy access. The report is divided into two main sections. The first gives an overview of traditional and new methods for the measurement of demixing points and critical conditions. In the second, examples are presented and discussed theoretically for the typical dependence of the solubility on the variables of state, the molar mass and isotopic composition of the polymer, and on the rate of shear.

EXPERIMENTAL

Demixing points

For molecularly nonuniform polymer samples, no demixing curves constructed from independently measured points of incipient phase separation ever represent coexistence curves (Refs. 1 & 2). Except for critical phase separation conditions the composition of only one of the coexisting phases corresponds to a point on the demixing curve in the limit of incipient phase separation. This is because the molecular weight distribution of the residual polymer solution is practically identical with that of the initial, uniform solution, whereas that of the segregated phase is extremely different (polymer fractionation, cf. Fig. 14).

Visual determination. The oldest and simplest way to detect the entrance into the two-phase region is to observe, by means of the naked eye, the cloudiness that develops as the polymer solution demixes. In spite of the primitiveness of this method, the accuracy of the cloud point temperatures so determined is normally comparable with that of data resulting from much more sophisticated procedures, namely ca. $\pm 0,1\text{K}$. Problems arise whenever the components are nearly isorefractive and in cases where the solutions are colored.

Turbidimetric determination. If the development of cloudiness, associated with the approach of a miscibility gap, is measured quantitatively, additional information can be obtained, as will be demonstrated in the context of critical points. Fig. 1 shows an example for the variation in transmittance of a polymer solution with temperature (Ref. 3). Data obtained with flowing systems are also included, since shear influences will be the topic of the last section of the next chapter. The measurements were performed with an all-glass viscometer (concentric cylinders) using a laser beam. The individual data points were obtained from plots of the intensity I of the transmitted light as a function of time at constant temperature, in order to make sure that equilibrium (shear rate zero) or stationary conditions had been achieved.

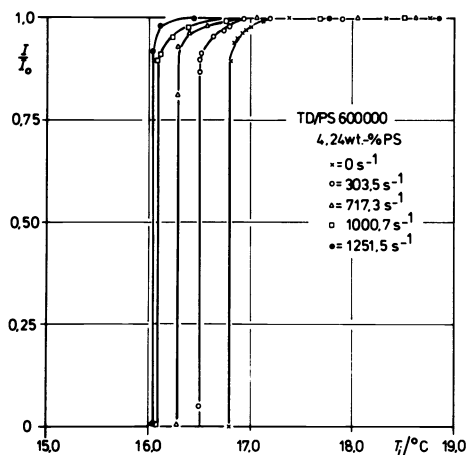


Fig. 1 I , the intensity of the light passing the solution, divided by I_0 , the intensity of the primary beam, as a function of temperature for a solution of 4,24 wt.% of polystyrene ($M=600\ 000$) in trans-decalin at the indicated shear rates (Ref. 3).

Viscometric determination. Whenever the components of a solution differ considerably in viscosity, it should be possible to monitor phase separation on the basis of a distinctly lower viscosity of the two-phase, as compared with the one-phase system. In the case of polymer solutions, the viscosity reduction observed upon entrance into the miscibility gap (Ref. 4) arises from the incorporation (i.e. viscometric desactivation) of polymer molecules into the droplets of the more concentrated phase suspended in the more dilute one.

The method is illustrated in Fig. 2 (Ref. 5), from which it can be seen that the discontinuity in the temperature dependence of the viscosity coefficient is the more pronounced, the closer one gets to the Newtonian region. Again the demixing conditions turn out to depend on shear rate; for sufficiently low values they coincide with the turbidimetrically determined equilibrium data (Ref. 3).

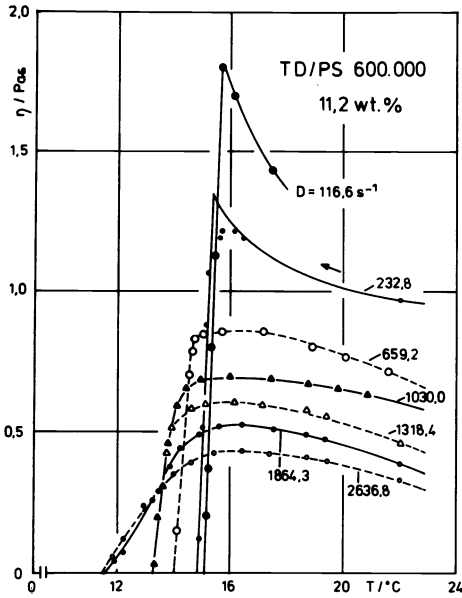


Fig. 2. Viscosity coefficient η as a function of temperature for a 11,2 wt. % solution of polystyrene ($M = 600\,000$) in trans-decalin at the different indicated rates of shear.

Calorimetric determination. Like all other thermodynamic excess functions which measure the deviation of an actual system from ideality, the heat of mixing can be used to fix the onset of phase separation. The heat of demixing (opposite in sign to the heat of mixing) is expressed to the extent that the coexisting phases become increasingly different in composition, as one penetrates into the miscibility gap.

Although the effects are quite small, the phase separation conditions of moderately concentrated polymer solutions can be detected with commercially available differential scanning calorimeters, by a change in the slope of the DSC trace (Ref. 6). However, at the present state of the method, great care must be exercised to avoid artifacts.

Other techniques. Any instrument that yields different signals for given kind of molecule, depending on the phase in which it is contained, can be used for the determination of demixing points. NMR measurements with polymer solutions are one example of such a procedure (Ref. 7).

Critical points

Methods for the determination of critical demixing data fall into two groups depending on whether they require macroscopic phase separation or not. With the turbidimetric and the viscometric methods, the experimental information for the determination of demixing points can be evaluated directly; no analysis is needed. In contrast, the methods of phase volume ratio and of equal composition are based on the direct investigation of the coexisting phases; consequently, they are normally much more time consuming and laborious, but also more reliable.

Turbidimetric determination. If the temperature dependence of the transmittance is evaluated according to Debye (Ref. 8) also for noncritical conditions (Ref. 9 & 10), both, binodal and spinodal points are accessible. Fig. 3 shows such an evaluation, in which $(\ln I_0/I)^{-1}$ (proportional to the inverse of the turbidity of the solution) is plotted as a function of T for the measurements of Fig. 1. The binodal point can be seen from the discontinuity, the spinodal from the intersect of the linear dependence, observed for the homogeneous system, with the abscissa (because of the vanishing transmittance under spinodal conditions). Since the critical point belongs to the binodal curve as well as to the spinodal curve, it should be possible (Ref. 11) to determine the critical data by plotting $(\ln I_0/I)^{-1}_{\text{bin}}$ (the value of the ordinate in Fig. 3 at the

binodal temperature) as a function of concentration and looking for the composition at which this quantity becomes zero, i.e. identical with the value for the spinodal conditions. Fig. 4 gives an example (Ref. 3) for such an evaluation, based on the results of Fig. 3. With the apparatus used for these measurements - specially constructed to avoid multiple scattering and reflections in the cell - it is possible to follow the transmittance down to practically zero (black square in Fig. 4). Even if a cruder experimental set-up is used - like light guides and a comparatively thick layer of the solution - a distinct minimum is observed in the curve of Fig. 4, which normally yields a good estimate of the critical data (Ref. 11).

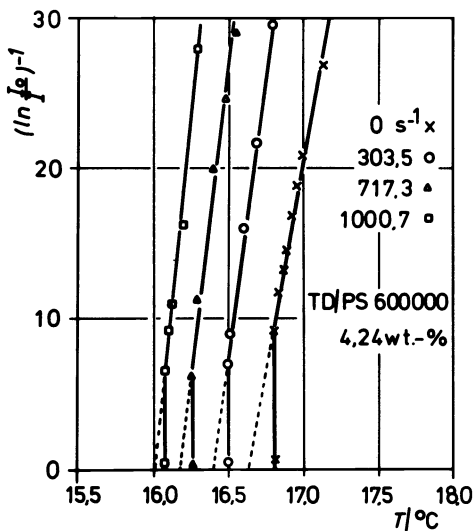


Fig. 3 Generalized Debye plot of the data of Fig. 1 (cf. text)

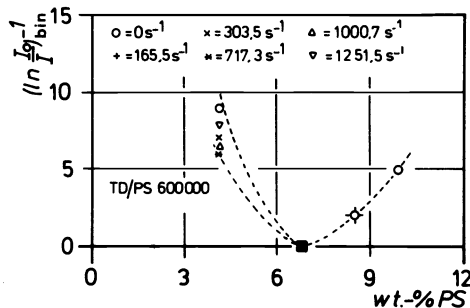


Fig. 4 Evaluation of the data available from generalized Debye plots to obtain the critical composition

Viscometric determination. As already reported, the demixing point of a given solution can be determined from a discontinuity of its viscosity coefficient. Further information is obtainable, if one also evaluates the stationary viscosity of the suspension of the more concentrated coexisting phase in the matrix of the more dilute one. Depending on the starting composition of the solution, the reduction in viscosity associated with a further penetration into the miscibility gap is more or less pronounced; for the critical composition it becomes most distinct (Ref. 4). This observation can be rationalized if one recalls that - for a given penetration into the two-phase regime - the coexisting phases show the greatest possible difference from the original solution, when the starting concentration is critical. Whenever the present method is applied to viscometric data referring to non-Newtonian conditions, the results should be treated with caution.

Determination of volumes. Measurements of phase volume ratios is probably the best known and most widely used rigorous method (Ref. 12). From plots of r , the ratio of the volume of the more dilute to the more concentrated coexisting polymer solution, versus the difference between the cloud point temperature and the equilibrium temperature, it can be seen whether a chosen starting concentration was sub- or supercritical. In the first case r approaches infinity, in the second zero, as the temperature difference becomes vanishingly small; the volumes of the coexisting phases only become identical ($r=1$) for commencing demixing when the composition is critical. By a proper selection of starting compositions and interpolation, the critical data can be determined with great accuracy.

Determination of concentrations. The most characteristic feature of a critical point is the fact that the coexisting phases become identical as the tie line degenerates into a point. This criterion can immediately be utilized (Ref. 13): To this end, the polymer concentrations w_2' and w_2'' of the coexisting phases are plotted as a function of the starting concentration w_2 , taking the variables of state as parameters.

Fig. 5 demonstrates how the method works for the determination of the critical demixing pressure of the system ethylene/polyethylene (Ref. 14). For a preselected temperature (160 °C) the polymer concentrations w_2' and w_2'' in the coexisting phases are determined as a function of w_2^0 for different pressures, yielding two lines that should be parallel to the abscissa in the case of molecularly uniform components. For the less concentrated phase these functions begin on the diagonal and for the more concentrated they end on it. This corresponds to the fact that the composition of the surplus phase is practically identical with w_2^0 as the demixing sets in. The limiting composition of the corresponding segregated phase can be obtained by extrapolating w_2' (w_2'') to the w_2^0 value at which $w_2'' = w_2'$ (full circles in Fig. 5) and proceeding analogously with w_2'' . In this manner a second line is obtained which gives the composition of the first segregated phases, whereas the diagonal represents the composition of the surplus phases at incipient demixing. Clearly the intersection of these curves yields the critical composition. The non-parallelism of the isobars of Fig. 5 arises from the pronounced non-uniformity ($U = M_w/M_n - 1 = 2,6$) of the present polyethylene.

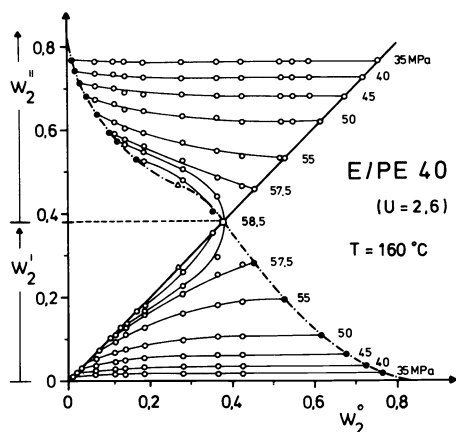


Fig. 5. Example (Ref. 14) for the determination of the critical composition by means of the method of equal concentrations (Ref. 13). The data refer to isothermal conditions and the system ethylene/polyethylene ($M_w = 4040$)

Depending on the particular system or question, either of the two rigorous methods just described may be preferable. The advantage of the method of equal volumes is that laborious concentration measurements are unnecessary, that of equal concentrations is that the solutions need not be visible (e.g. may be contained in windowless pressure cells) and that the critical concentration is accessible from an intersection instead of an interpolation.

GENERAL PHENOMENA

Temperature influences and mixed solvents

The most commonly observed effect of temperature on the solubility of polymers is probably the phase separation induced by cooling, like that shown in Fig. 6 for a binary system (Ref. 15). The most striking feature of such a demixing into two liquid coexisting phases is the pronounced asymmetry of the miscibility gap (weight or volume fractions as concentration variables) which increases as the molecular weight of the polymer is raised. The occurrence of upper critical solution temperatures (UCST) although frequently observed, is no phenomenon typical for all polymer solutions, in contrast to that of lower critical solution temperatures (LCST), i.e. the demixing upon heating.

For constant pressure and given molar mass of the polymer, two categories of liquids can be distinguished: **solvents**, characterized by complete miscibility with the polymer at least at some temperatures between freezing and boiling point, and **precipitants**, for which limited miscibility is observed at all temperatures. For atmospheric pressure, both, either or neither of the mentioned critical temperatures may be observed with solvents, but LCSTs almost inevitably show up as the temperature is raised above the normal pressure boiling point of the liquid. It should also be noted that precipitants can in some cases be transformed into solvents, when the parameter pressure is allowed to assume values different from 1 bar.

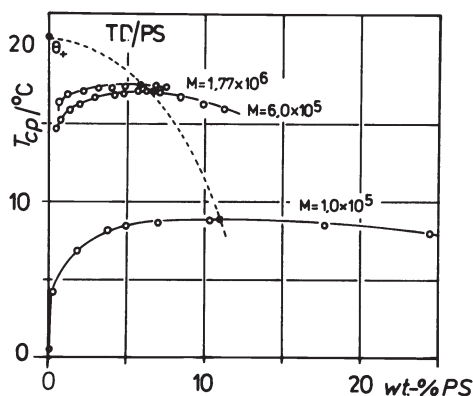


Fig. 6 Cloud point curves for solutions of narrowly distributed polystyrenes in trans-decalin; θ_+ : UCST extrapolated to infinite mol. wt. of the polymer

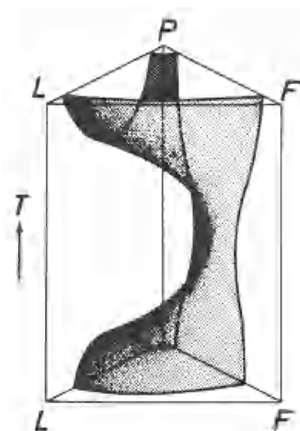


Fig. 7 Schematic representation of the isobaric binodal surface for ternary systems comprised of solvent + precipitant + polymer (for details see text)

For practical purposes it is rather inconvenient to work with variable pressure; it is therefore often preferred to use mixed solvents at 1 bar when certain thermodynamic conditions are to be tailored. Fig. 7 demonstrates how this can be done by combining a solvent (denoted by L and exhibiting an UCST and a LCST) and a precipitant (denoted by F). In the construction of this scheme it was assumed that the polymer is molecularly uniform and that the thermodynamic properties of the ternary system are built up from those of the two polymer containing subsystems L+P and F+P in a strictly additive manner. Under these premises it is possible to decrease the quality of the mixed solvent by adding increasing amounts of precipitant, i.e. increasing the UCST and decreasing the LCST until they coincide, whereupon the mixed solvent is transformed into a mixed precipitant. Naturally, different binodal surfaces would be obtained for different molecular weights of the polymer.

Simple additivity of the properties of the components of the mixed solvent is the exception rather than the rule. In extreme cases the polymer (given p and T) is completely miscible with the mixed solvent in a certain range of its composition, although this is not the case with the pure components (cosolvency), or a miscibility gap turns up with the ternary system, in spite of the fact that all three binary subsystems show complete miscibility (island curves, co-nonsolvency). An example of each extreme is given in the following.

With the system acetone/diethyl ether/polystyrene (AC/DEE/PS) the effect of cosolvency is particularly pronounced, since both, AC and DEE constitute precipitants, yet this polymer, irrespective of its molecular weight, is completely soluble in the mixed solvent over a wide range of composition and temperature. This special case, which has been called true cosolvency (Ref. 16), is shown in Fig. 8 for PS of molecular weight 110 000, at 1 bar and 0°C. The dashed line, parallel to the base of the Gibbs phase triangle, is the projection of the binodal edge (Ref. 16). As the temperature is lowered or raised, the two miscibility gaps, separated in Fig. 8, approach each other until they overlap at ca. - 70°C and + 60°C, respectively.

The system dimethyl formamide/cyclohexane/polystyrene (DMF/CH/PS) constitutes an example of co-nonsolvency (Ref. 17). As can be seen from Fig. 9, all binary pairs DMF+PS, PS+CH and CH+DMF are completely miscible above 49°C, and still a solubility gap, an island of inhomogeneity, is observed with the ternary system. It should be noted in this context that indirect information concerning the miscibility of two chemically different polymers, coming from an investigation of the phase separation behavior of their solutions in a common solvent, might be completely in error: Due to the occurrence of islands in the phase diagram one could erroneously conclude that the polymer pair is incompatible, i.e. practically immiscible, although this is not the case in reality.

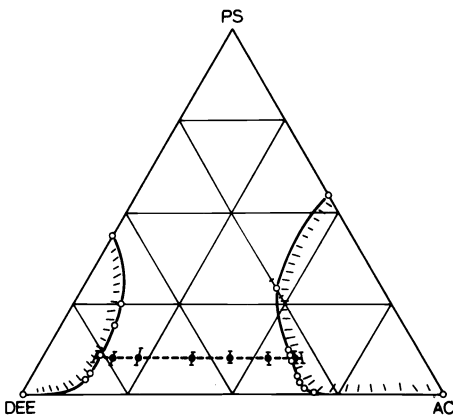


Fig. 8 Isothermal section through the binodal surface of the system diethyl ether/acetone/polystyrene ($M = 110\,000$) at 0°C (Ref. 16)

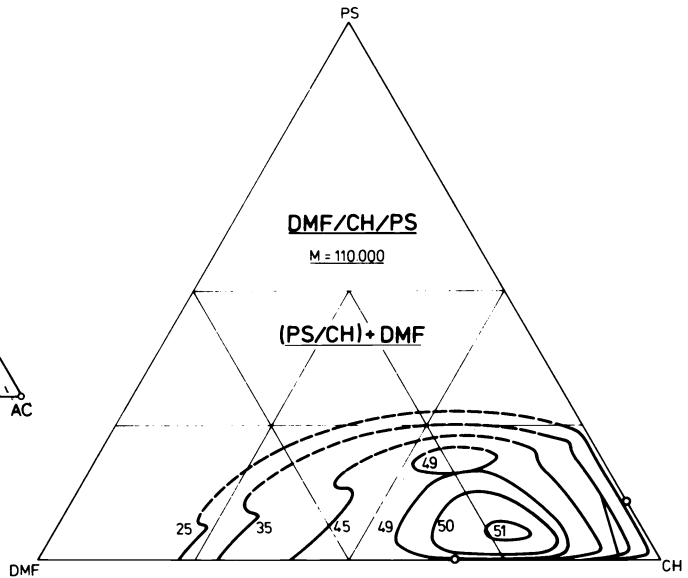


Fig. 9 Isothermal section through the binodal surface of the system dimethyl formamide/cyclohexane/polystyrene ($M=110\,000$) at the different indicated temperatures in $^\circ\text{C}$ (Ref. 17)

For the theoretical treatment of the reported isobaric temperature influences and of the behavior of mixed solvents, ΔG_M , the molar Gibbs (free) energy of mixing is the decisive thermodynamic function. If its variation with the mole fraction of the components of a system is known for different temperatures, it is possible to determine the composition of coexisting phases (binodal curve), the limits between the metastable and the unstable region (spinodal curve) and finally the values of temperature and concentration at which the composition of the coexisting phases becomes identical (critical point for constant pressure).

Introducing the reduced Gibbs energy of mixing \tilde{G} according to

$$\tilde{G} = \Delta G_M / RT, \quad (1)$$

the corresponding phenomenological thermodynamic equations can be written in the following form for the simplest case of a binary system, where $i = 1$ normally signifies the solvent and $i = 2$ the polymer, and primes denote the coexisting phases

$$\tilde{G}'_i = \tilde{G}''_i \quad (2)$$

(equality of chemical potentials, binodal conditions),

$$\partial^2 \tilde{G}'_i / \partial x_i^2 = \partial^2 \tilde{G}''_i / \partial x_i^2 = 0 \quad (3)$$

(vanishing concentration dependence of the chemical potential, spinodal conditions) and

$$\partial^3 \tilde{G}'_i / \partial x_i^3 = \partial^3 \tilde{G}''_i / \partial x_i^3 = 0 \quad (4)$$

(coincidence of spinodal and binodal conditions, critical point).

For polymer containing systems the Flory-Huggins equation, resulting from the lattice theory and specially designed to describe the behavior of chain molecules, is normally used as the analytical expression required for the calculation of phase equilibria (Ref. 18). In its general formulation for i components it reads

$$\tilde{G} = (\sum_i \phi_i N_i^{-1} \ln \phi_i + \sum_{i,j} g_{ij} \phi_i \phi_j) \sum_i x_i N_i \quad (5)$$

where N_i is the number of lattice sites a molecule of the species i can occupy (i.e. the number of its segments), ϕ_i the site fraction of this component in the mixture (closely related to the volume fraction), x_i its mol fraction and g_{ij} constitute the binary interaction parameters, measuring the reduced non-combinatorial Gibbs energy of mixing per contact of a segment of species i with a segment of species j .

For the special case of binary systems comprised of two types of chain molecules, Eq. 5 reads

$$\tilde{G} = x_1 \ln \phi_1 + x_2 \ln \phi_2 + g(x_1 N_1 + x_2 N_2) \phi_1 \phi_2 \quad (6)$$

For low molecular weight solvents ($N_1=1$) one obtains the Flory-Huggins equation in its original form

$$\tilde{G} = x_1 \ln \phi_1 + x_2 \ln \phi_2 + g x_1 \phi_2 \quad (7)$$

The index of g can be omitted in both equations, since only one type of intersegmental contact between chemically different molecules is possible.

Assuming that g does not vary with composition, one obtains the following conditions for the critical point from the Eqs. 6 and 4:

$$g_c = 0,5(N_1^{-0,5} + N_2^{-0,5})^2 \quad (8)$$

and

$$\phi_{2c} = N_1^{0,5} / (N_1^{0,5} + N_2^{0,5}) \quad (9)$$

Recalling that the mixing tendency of a real system is the less, the higher g becomes, the influence of chain length on the solubility can be discussed on the basis of Eq.8: For monomeric mixtures ($N_i=1$) the interaction parameter must exceed the value two, before phase separation commences. For a solution of an infinitely long chain polymer ($N_2 \rightarrow \infty$) in a monomeric solvent, the critical interaction parameter tends to 0.5, but for a mixture of chemically different polymers g_c approaches zero. According to these results, the thermodynamic conditions required for complete miscibility become more stringent, the longer the chains of the components become, in agreement with the observation that different polymers normally are incompatible.

A further experimental finding, the large asymmetry of the demixing curves in the case of polymer solutions can be rationalized on the basis of Eq. 9: For $N_1=1$ and rising N_2 , the critical polymer concentration is shifted towards lower values and tends to zero in the limit of infinite molecular weight of the polymer, whereas the miscibility gap remains more or less symmetric when both components are polymers.

The easiest approach to the influence of temperature on the solubility of the polymer is provided by the interpretation of g as a reduced non-combinatorial Gibbs energy for the contact formation between a solvent molecule and a polymer segment. If this Gibbs energy is subdivided into an enthalpy and an entropy contribution according to the Gibbs-Helmholtz equation, assuming the enthalpy and the non-combinatorial entropy to be independent of T , one obtains a dependence of the form

$$g = a + bT^{-1} \quad (10)$$

For a given solvent/polymer system with constant N_1 and variable N_2 , the critical temperature T_c measured for different molecular weights of the polymer can be evaluated to yield a and b (Ref. 18) by plotting $1/T_c$ as a function of the r.h.s. of Eq. 10 (Shultz-Flory plots); as a by-product one also obtains the critical temperature for infinite molecular weight (theta-temperature).

With ternary systems comprised of two low molecular weight liquids (indices a and b) and a polymer (index 2), Eq. 5 can be largely simplified if the pure mixed solvent (ms), characterized by $\phi_a + \phi_b = 1$, is treated as a single liquid and $N_a = N_b = 1$. For this case one obtains, under certain theoretical assumptions, (Ref. 19), a relation similar to Eq. 7, in which g is replaced by

$$g_{ms} = g_{a2} \phi_a + g_{b2} \phi_b - g_{ab} \phi_a \phi_b \quad (11)$$

and ϕ_1 by

$$\phi_{ms} = (\phi_a + \phi_b) / (\phi_a + \phi_b + \phi_2) \quad (12)$$

In the light of Eq. 11 the phenomena of cosolvency and co-nonsolvency can be rationalized as a consequence of the corresponding specific interactions between the components of the mixed solvent, measured by g_{ab} .

The results presented so far are in qualitative accord with many experiments. However, it was obvious from the very beginning that the parameters g_{ij} have to depend on composition, and in a much more complicated way on temperature than suggested by Eq. 10, in order to reproduce all experimental findings. Many attempts have been made to improve the theory; practically all of them allow for volume changes upon mixing, in contrast to the original lattice theory. The most elaborate approach stems from Flory and coworkers (Ref. 20). It rests on the corresponding states principle and makes it possible to calculate $g(\phi_2, T)$ from the knowledge of the pVT data of the pure components and a minimum of additional information. Since an adequate treatment of this theory would be beyond the scope of the present survey, the subsequent presentation will be confined to the special cases of $g(\phi_2)$ for constant T and to $g(T)$ for infinite dilution of the polymer.

For the concentration dependence of g , Koningsveld and Kleintjens (Ref. 21) have deduced the following expression on the basis of the lattice theory

$$g = \alpha + \beta(T) / (1 - \gamma\phi_2) \quad (13)$$

in which α and γ are constants and $\beta(T)$ is a parameter that varies with temperature. The allowance for a change of g with composition means that the experimentally accessible Flory-Huggins parameter χ , which refers to the differential Gibbs energy of the solvent, differs from g , referring to the integral Gibbs energy of mixing. χ and g are related by

$$\chi = g - (1 - \phi_2) \partial g / \partial \phi_2 \quad (14)$$

A concentration dependent g also implies that the differential interaction parameter for the polymer differs from that for the solvent. In the theoretical calculations this fact means that the polymer content of the coexisting phases, which would be by far too low on the basis of a concentration independent g , is reconciled with the experimental observation.

A more realistic relation than Eq. 10 for the temperature dependence of the interaction parameters has been given by Patterson and coworkers (Ref. 22), who have derived the following expression for χ_0 , the Flory-Huggins parameter in the limit of infinitely dilute solutions, on the basis of the corresponding states theory and the equation of state of Flory,

$$\chi_0 = \alpha_1 V_1^{-1} a' + V_1^{-1} b' T^{-1} \quad (15)$$

α_1 is the thermal expansivity of the pure solvent, V_1 its molar volume; a' and b' are parameters of theoretical significance, which can be calculated from the pVT data (reduction parameters) of the pure components. For low T Eq. 15 is almost equivalent to Eq. 10, as long as α_1 and V_1 do not vary strongly with temperature. At high T, however, the first term becomes very large as one approaches the liquid/gas critical temperature of the pure solvent. This effect, which is due to the difference in the free volume of solvent and polymer, gives a theoretical explanation for the general occurrence of high temperature demixing (LCST) with polymer solutions: As the temperature is raised, the solvent can expand to a much greater extent than the polymer, which is hindered by the chemical bonds linking the segments. In an oversimplified manner one could interpret this situation as a deterioration of the thermodynamic quality of the solvent by its thinning with vacuum. For the analytical description of experimentally measured temperature dependencies of χ , the tenor of Eq. 15 is often taken into account by extending Eq. 10 through the addition of a third term, proportional to T.

Pressure influences

For many purposes, such as the preparation of polymers from gaseous monomers, the pressure is an important variable and it is always the touchstone for the efficiency of a theory. The typical influences of this variable on the solubility of polymers can be seen from Fig. 10. Normally the UCSTs (low temperature demixing) are much less changed by p than the LCSTs (high temperature demixing). Whereas the application of pressure practically always extends the

homogeneous region in the latter case, there are also many examples known with the former, where the pressure enlarges the two-phase regime. Fig. 11 shows a (rare) instance of a low temperature demixing, for which a pressure of optimum miscibility is observed (Ref. 23). Fig. 12 can be taken to be typical of the pressure influences in the case of a high temperature demixing (Ref. 11)..

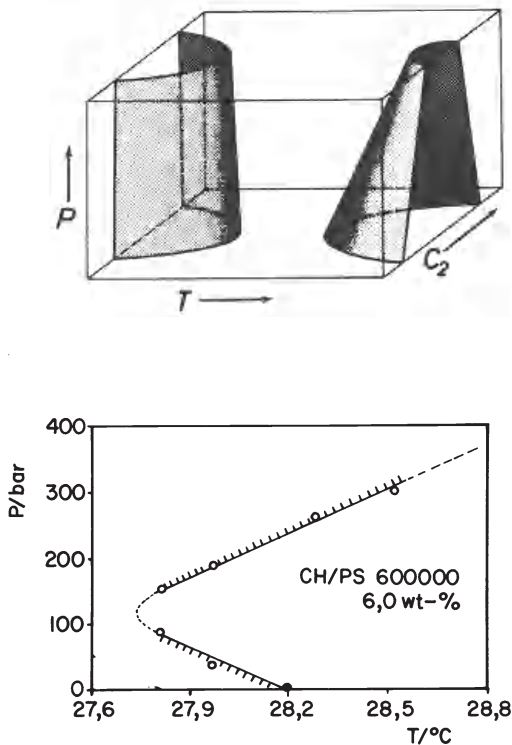


Fig. 11 Demixing curve for a 6 wt.% solution of polystyrene ($M=600\ 000$) in cyclohexane (Ref. 23); the two-phase region lies on the l.h.s. of the curve

+ Fig. 10 Scheme of the binodal surface of a binary system solvent/polymer (c_2 = polymer concentration)

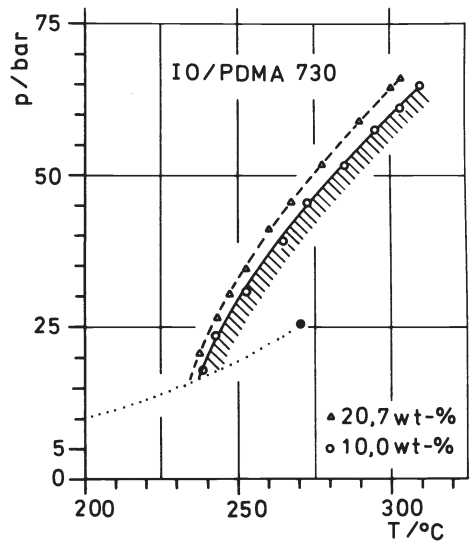


Fig. 12 Cloud point curves for the system iso-octane/polydecylmethacrylate ($M=730\ 000$) at the given polymer conc. (Ref. 24). Dotted line: Vapor pressure curve of the pure solvent

Phenomenological thermodynamics yields the following equation for the pressure dependence of critical temperatures

$$\left(\frac{\partial \ln T_c}{\partial p}\right) = \left\{ \frac{(\partial^2 V^E / \partial x^2)}{(\partial^2 H^E / \partial x^2)} \right\}_c \quad (16)$$

in which V^E is the molar excess volume and H^E the molar enthalpy of mixing. This relation reduces to

$$\left(\frac{\partial \ln T_c}{\partial p}\right) = (H^E / V^E)_c \quad (17)$$

in cases where Eq. 7 is applicable with concentration independent g . The inadequacy of this approximation is, however, already clearly demonstrated by the results of Fig. 11: The slope of the demixing curve (which is close to the critical line) changes sign, in contrast to the predictions of Eq. 17 (Ref. 25).

For a quantitative theoretical calculation of the pressure influences on the solubility of polymers it is indispensable to use an approach which considers non-zero excess volumes. The combination (Ref. 26) of Eq. 15 with the solubility parameter theory, using Flory's equation of state, gives probably the easiest access, particularly since extensive information concerning solubility parameters is available (Ref. 27). For UCSTs the results are, however, not even in qualitative accord with the experimental findings in many cases (Ref. 28). A simple (and theoretically intelligible) experimental rule turns out to

be more reliable: Whenever $(T_c - T_{mp})/T_{mp}$, the relative distance of the UCST from the melting point, T_{mp} of the pure solvent, exceeds ca. 0.25, the solubility is enhanced by pressure, if it falls below ca. 0.2, it is reduced (Ref. 28).

Extensive calculations concerning the miscibility of polymers, which also deal with the influence of pressure, have been performed by McMaster (Ref. 29) on the basis of a modified form of Flory's equation-of-state thermodynamics. The results demonstrate among others that LCSTs should generally be anticipated.

Molecular weight and isotopic influences

How the molar mass of a polymer of fixed chemical composition influences its solubility has already been shown in Fig. 6 for an UCST. With LCSTs or variable pressure, the effects are similar: In all cases the solubility is reduced as M increases. Two aspects have so far been neglected: (i) possible end-group effects and (ii) phase equilibria with polymers of broad molecular weight distribution.

Fig. 13 shows, as an example of (i), how many monomeric units N_2 the polyglycol must contain in order to make the influences of different end-groups on the UCSTs in mixtures with DMS-5 (pentamer of dimethylsiloxane) vanish (Ref. 30). OH stands for the original hydroxyl end-group, AC for acetyl, the single point denoted by ME for methyl and X for a hypothetical end-group possessing the same thermodynamic qualities as a middle group. For the present system it takes between 100 and 1000 monomeric units for the chemical nature of the endgroup to become inconsequential. The solid lines have been calculated on the basis of the solubility parameter theory, using the concept of group contributions to obtain the variation of the solubility parameter with N_2 (Ref. 30).

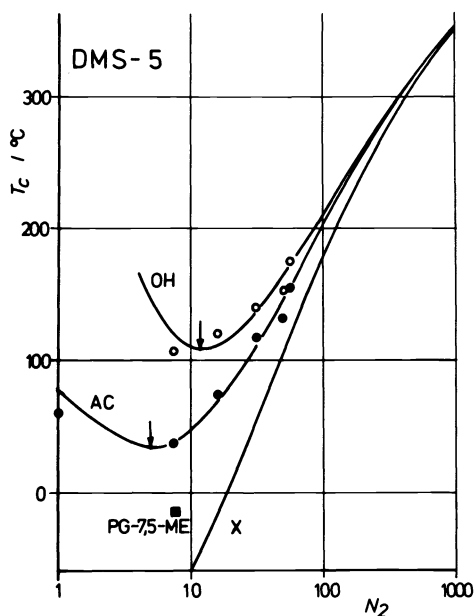


Fig. 13 UCSTs measured for mixtures of the pentamer of dimethylsiloxane and various N_2 -mers of polypropylene glycol as a function of N_2 for different end-groups. OH: hydroxyl, AC: acetyl, ME: methyl, X: hypothetic (cf. text). The solid lines are calculated theoretically.

Aspect (ii) can be discussed by means of Fig. 14 in terms of the corresponding differential weight distribution of degree of polymerization, which is denoted as P in this diagram. Fig. 14 shows how the polymer present in the homogeneous solution (Th 140) partitions between the more dilute (sol) and the more concentrated (gel) coexisting phases, when the conditions are chosen such that the ratio G of the total mass of the polymer in the sol to that in the gel is 0,43 (Ref. 31). This example demonstrates the general feature that the lower weight material is enriched in the sol and the higher in the gel phase. For a quantitative theoretical description of the partition coefficient as a function of chain length it is indispensable to allow for a concentration dependent interaction parameter g in Eq. 7. If phase equilibria of the present type are repeated many times, preferably in a continuous manner (Ref. 32), large scale fractionation of polymers can be achieved.

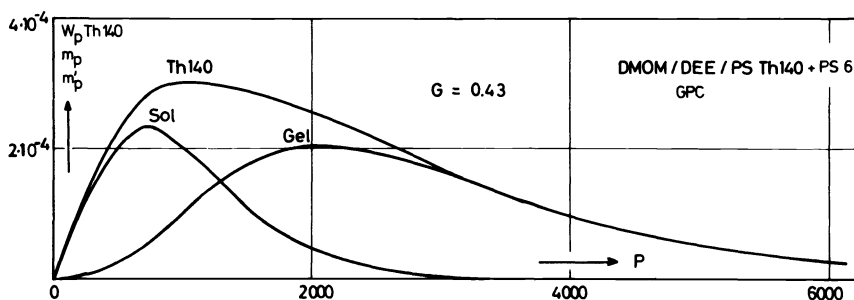


Fig. 14 Differential weight distribution of a thermally polymerized polystyrene (Th 140) and of the polymer contained in the coexisting phases (sol and gel) for $G=0.43$ (cf. text)

Differences in the isotopic composition constitute a special case of molecular weight influences. With the demixing of polymer solutions, measurable effects have been reported (Ref. 33) for the replacement of H by D in either of the components. With polymer mixtures the effects of deuteration are even more pronounced as is demonstrated by the recent results of Koningsveld and co-workers shown in Fig. 15; for the theoretical interpretation of these findings it has to be assumed that the deuterated and non-deuterated polymers do not mix athermally (Ref. 34).

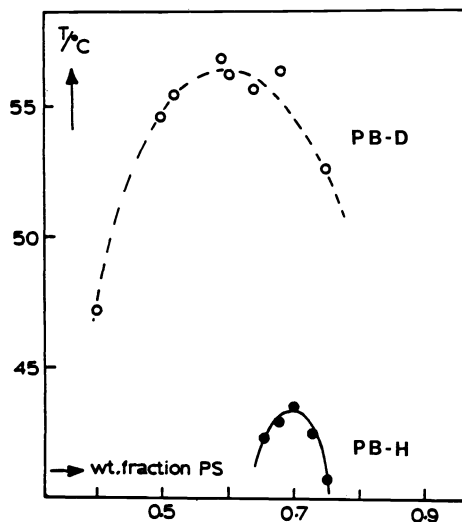


Fig. 15 Spinodal curves measured for mixtures of polystyrene with polybutadiene (PB-H) or with perdeuterated polybutadiene (PB-D) (Ref. 34)

Shear influences

For polymer containing systems it was discovered more than thirty years ago that the phase separation conditions may depend on the rate of shear $\dot{\gamma}$. With solutions of two incompatible polymers in a common solvent, the homogeneous region extends by ca. 10 K as the solutions flow (Ref. 35). With binary solvent/polymer systems, the effects are normally of the order of a few degrees; both phenomena, shear induced dissolution and shear induced phase separation, have been encountered (Ref. 36 & 37). Fig. 16 shows some measured changes of the binodal temperature of solutions of polystyrene in trans-decalin produced by laminar flow (Ref. 3). The results demonstrate that the effect of shear rate depends on the molecular weight of the polymer: It is practically absent for M less than 100 000, at higher values there follows a region of shear dissolution and at still higher M , shear demixing is observed. The pronounced influence of the polymer concentration can be seen from the example given for $M = 600\ 000$.

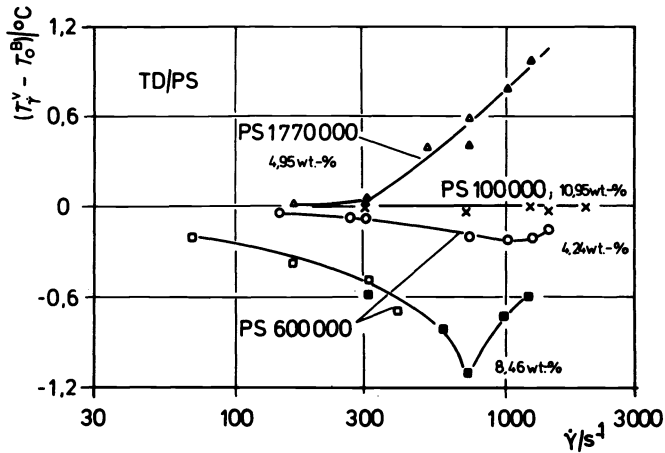


Fig 16 Differences between the viscometric demixing temperature and the binodal temperature of the system at rest, as a function of shear rate for the system trans-decalin/polystyrene and the indicated mol.wts. and conc. of the polymer (Ref. 3)

The observed phase separation of flowing solutions was discussed (Ref. 38) theoretically on the basis of two premises. Assumption (i) is that it is possible to define a generalized reduced Gibbs energy of a flowing system according to

$$\tilde{G} = \tilde{G}_z + \tilde{E}_s \quad (18)$$

where \tilde{G}_z is given by Eq. 7 (the index z indicating zero shear) and \tilde{E}_s , the reduced stored energy, by

$$\tilde{E}_s = V_1 (1 + (N_2 - 1)x_2) J_e^0 n^2 \dot{\gamma}^2 / (RT) \quad (19)$$

with J_e^0 being the stationary shear compliance and n the viscosity coefficient of the solution. Premise (ii), concerning the applicability of equilibrium thermodynamics to the stationary states of interest, seems justified in view of the fact that \tilde{E}_s is of the order of $10^{-3}\tilde{G}_z$.

The results of these calculations can be seen from Fig. 17, which shows the demixing curves for different shear rates. In accord with the experimental results presented in Fig. 16, for the molecular weight of 600 000 (comparable to the number of segments $N = 5000$ used in the calculation) the homogeneous region increases as the system flows. The most striking feature, however, concerns a shear-induced coexistence of three liquid phases under the conditions of most pronounced shear dissolution, which have been called eulytic (Ref. 38). Calculations based on the Eqs. 18 and 19 cannot reproduce the observed shear demixing. In order to modify the theory to cover this phenomenon too, it is either necessary to measure the stored energy (Ref. 39) instead of calculating it by means of Eq. 19, or to allow for a non-linear viscoelastic behavior of the polymer solutions (Ref. 3), which shows up whenever the molecular weight of the polymer and its concentration become sufficiently large.

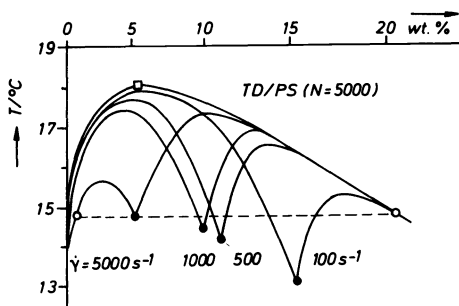


Fig. 17 Miscibility gap of the system trans-decalin/polystyrene (5000 segments) calculated for the different indicated shear rates; the concentration axis is linear for the mol fraction of the polymer (Ref. 38) for details cf. text

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