Phase behavior of ordered polymer solutions

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PHASE BEHAVIOUR OF ORDERED POLYMER SOLUTIONS

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Abstract: Rules for equilibrium phase behaviour, laid down long ago on the basis of the two laws of thermodynamics, appear to be valid also for many polymer systems in which aggregates of various topology occur. The phase rule offers a useful tool for the construction and understanding of phase diagrams for systems in which order of some kind is prevalent in certain ranges in the diagram. 'Double sickle' type phase diagrams, found for surfactant solutions, microemulsions as well as block-copolymer solutions can be traced back to the considerable loss of translational entropy which accompanies aggregation.

INTRODUCTION

The phase rule orders phase equilibria and is an essential tool in the construction of phase diagrams. This statement is valid also if the system contains macromolecules, even when kinetic effects, as in polymer crystallization, are important. Then, ordering reaches from a supermolecular to a macroscopic scale.

Other types of structure formation, limited to a supermolecular scale, may also occur in polymer solutions and mixtures. Such supermolecular structures may order themselves in many fashions, thus giving rise to a wide variety of phases differing in type of order. As a consequence, phase diagrams may become very complex but can still be understood in terms of the phase rule, though the phases involved do not quite conform to the classic definition of a phase. Recently, a striking case in point was presented in a study by Finkelmann, Rehage and Lühmann on aqueous solutions of monomeric and polymeric amphiphiles in which evidence was found for the existence of no less than ten nonvariant three-phase equilibria (Ref. 1).

In this paper we discuss phase diagrams for various types of structure formation in polymer solutions in terms of classic equilibrium thermodynamics. Examples are presented referring to block copolymer solutions and blends, solutions of liquid-crystalline polymers and other structures appearing in phase diagrams. A simple molecular model is proposed which relates molecular aggregation of any kind to the appearance of a special type of phase behaviour.

PHASE RULE PRINCIPLES

Gibbs' phase rule relates the number f of degrees of freedom of an equilibrium system to the number C of components and the number P of phases by

$$f = C + 2 - P \quad (1)$$

provided surface free-energy contributions are negligible and external fields are absent.

In the usual experiments one variable is fixed, e.g., the pressure p , and we see that two-phase equilibria in a single-component system are nonvariant ($P = 2$; $C = 1$). At the given pressure two phases can only coexist in equilibrium at one fixed temperature. Introducing a second component ($C = 2$) we add one degree of freedom and make the two-phase equilibrium monovariant. Thus, we expect in a binary phase diagram a two-phase curve to originate from the nonvariant point on the temperature axis representing the pure component. This point marks the single-component transition temperature T_1 (see Fig.1). The two-phase curve describes the change of the transition temperature with composition and consists of two branches since the two phases a and b will usually differ in composition. The two curves demarcate a two-phase region in the temperature-composition phase diagram. Nonvariant equilibria occur in a binary system when three phases coexist (Fig.1).

Fig.1. Isobaric two-phase equilibria (a/b , b/c and a/c) in a binary ($1/2$) system. $\bullet-\bullet$: tie line connecting two coexisting phase compositions ($\bullet$), $\blacktriangle-\blacktriangle-\blacktriangle$: nonvariant three-phase equilibrium.
 ϕ_2 = volume fraction second component

There are more direct consequences of the laws of thermodynamics regarding equilibrium phase diagrams. In binary systems, for instance, two two-phase regions must be separated either by a bivariant one-phase range or by part of a nonvariant three-phase line. Another, related rule states that two one-phase regions cannot be adjacent and must be separated by a two-phase area. Further, if there is one two-phase region on one side of a three-phase line, there must be two two-phase areas on the other side of that line. Finally, metastable extensions beyond the three-phase line must fall within the two-phase ranges in the area they extend into. Fig.1 schematically summarizes these general rules (Ref. 2).

POLYMER SOLUTIONS

Liquid-liquid and liquid-solid equilibria in polymer solutions exemplify the principles laid down above. The complete isobaric phase diagram will usually have the appearance of Fig.2 but in many experimental cases either only part of it has been reported or particular equilibria do not occur at all. Addition of solvent S decreases the melting point of polymer P and two curves spring from the nonvariant solid/liquid trans-

Fig.2. Phase diagram for a binary solvent/polymer (S/P) system showing equilibria occurring frequently in polymer solutions.

The dashed curve is the metastable extension of curve (1).

ition temperature T_{mp} on the pure polymer axis. One of these curves, the solubility curve, (1), represents the composition of mixed liquids that are in equilibrium with the pure solid polymer (s_2), so that the other curve, (2), coincides with the pure-polymer axis. Fig. 3. gives an example for the system *m*-cresol/poly(*N,N'*-sebacoyl piperazine) in which the polymer has a melting point of about 450 K at 1 bar (Ref.3).

We note the existence of another two-phase region, l_a/l_b , if S represents a poor solvent (diphenyl ether in Fig.3) which is partially miscible with the polymer. An increase of temperature increases miscibility and there is an upper critical solution temperature T_{cu} . When the solubility curve (1) meets the right-hand phase boundary of the miscibility gap l_a/l_b , three phases coexist, viz., l_a , l_b and s_2 (crystalline solid polymer), and the equilibrium is nonvariant. In accordance with equilibrium rules there are two two-phase regions above, and one under the horizontal three-phase line. When heated up above T_{cu} , most polymer solutions investigated so far will eventually demix again, a phenomenon known as lower critical miscibility behaviour (LCM). The system of Fig 3 has either not been investigated in this respect, or may decompose before the lower critical solution temperature, T_{CL} , is reached.

The objection may be raised that the example is not quite representative because polymers always consist of many components and the invariance criterion may therefore not apply. However, the differences in melting point among the various homologous components in the polymer are usually negligible, so that we effectively find a situation closely resembling nonvariance (Ref. 2).

The curvature of the solubility curve in Figs 2 and 3 (curves 1) is prescribed by the effective nonvariance of the three-phase equilibrium, $l_a/l_b/s_2$, which requires the

Fig.3. Isobaric phase equilibria in solutions of poly(*N,N'*-sebacoylpiperazine) in diphenyl ether (●), *o*-dinitrotoluene (■) and *m*-cresol (▼) (Ref.3)

curve to pass through the points A and B referring to the same temperature T_3 . A continuous curve can do so only by assuming a sigmoid shape with two extrema. The latter are found on the metastable extension of the solubility curve within the miscibility gap. They are not readily observable, if at all, because demixing is much less prone to supercooling than crystallization. The less poor solvent *o*-dinitrotoluene shows a sigmoidal solubility curve without extrema, which implies the proximity of a metastable miscibility gap. An increase of either the polymer molar mass or the pressure might produce a phase diagram like that with diphenyl ether.

In Fig.2 the lower and upper critical points at T_{cl} and T_{cu} , respectively, have been identified with the extrema of the two miscibility gaps. Molecular inhomogeneity in the polymer will shift the critical points away from the extrema and also have other effects in miscibility relationships that are well understood (Ref. 2,4,5). In the present context, however, such details are not important, since we shall be interested in qualitative features only.

The solubility curve for *o*-dinitrotoluene extends towards the pure-solvent axis and eutectic three-phase phase behaviour cannot be detected. The apparent absence of a eutectic is caused by the considerable disparity between the melting points of solvent and polymer (Fig.3). If they are brought closer together by a proper choice of constituents, eutectic behaviour obtains. An experimental example is given in Fig.4.

Fig.4. Eutectic phase diagram for the system
1,2,4,5-tetrachlorobenzene/polyethylene (Ref.6).
Crystallization temperatures at cooling rate 2°C/min: ▼.
Melting temperatures of quenched samples:
quenched to 81°C (●) and 105°C (■).
 w_2 = mass fraction of polymer

It is of interest to note that all examples obey the rules formulated in the preceding section. This remains true if data are taken under conditions such that severe kinetic limitations occur. In Fig.4 we see that the location of the solubility curve of the polymer (measured as melting temperature vs concentration) depends sensitively on the rate of crystallization. The eutectic temperature varies accordingly but the appearance of the diagram remains that of a eutectic. Similar observations have been made by Gryte, Berghmans and Smets (Ref. 7). Evidently, the driving forces for the phase transition are determined to a nontrivial extent by equilibrium conditions. Partially miscible systems are much less susceptible to supercooling, and equilibrium considerations can be expected to be quite meaningful.

MESOPHASES

When supermolecular structures have been formed they may be ordered in various topologies, each of which may be bound to a limited range in the phase diagram. Such temperature-concentration ranges do not represent phases according to the classical definition which requires any physical property not to depend on the location within the phase or at most to vary monotonically. Supermolecular structures have been observed to be ordered in various lattice topologies: as hexagonally packed cylinders, or in laminar superstructures resembling micelles in tenside solutions. Then, the classic definition is obviously not valid, yet phase relations often appear to follow the classic rules. The term 'mesophase' has become accepted for such systems. Evidently, the classic definition may be relaxed to include physical properties within the phase to vary periodically with the location. The 'wave length' of the periodic variation must be expected to be in some way related to the dimensions of the phase and to the interfacial free energy.

Block copolymers present a case in point. If composed of blocks that would be immiscible or partially miscible as free homopolymer chains, the covalent bonds between blocks force them to mix intimately. However, the repulsion between the blocks, responsible for segregation on a macromolecular scale, is still operative and gives rise to the formation of micellar structures containing a limited number of chains. The isotropic liquid, l , is transformed into a mesophase, l_m , at a well-defined temperature determined by the lengths of the two blocks and their repulsive interaction. Provided classic rules are obeyed, addition of a second substance should turn the single transition point into two curves demarcating the range of isotropic liquid/mesophase equilibrium, similar to the situation indicated by the framed part in Fig.1. Fig.5, taken from work by Roe and Zin (Ref. 8), clearly indicates that the above consideration is valid.

Micellar structures have been found in a wide variety of systems. A particularly interesting case has been documented some 50 years ago by Vold (Ref. 9), viz., the system water/sodium oleate in which 10 three-phase equilibria appear, apart from those in which solid water takes part (Fig.6). Besides arrow-shaped two-phase

Fig.5. Phase diagrams for mixtures of a poly(styrene-co-butadiene) block copolymer with polystyrene (top) and polybutadiene (bottom) (Ref.8).

Dashed lines indicate estimated locations.

regions like those discussed above we note two-phase ranges resembling two sickles touching at their points. Such shapes have also been reported for microemulsions, i.e., by Kahlweit and Strey (Ref. 10), for metal alloys (Ref. 11) and, recently, for aqueous solutions of block copolymers containing hydrophilic and hydrophobic blocks (Ref. 12-13). An example of the latter system is shown in Fig.7.

Classic rules require the seemingly adjacent one-phase regions to be separated by a two-phase range that, in the present example, is possibly too narrow to be easily

Fig.6. Phase behaviour of the system water/sodium oleate (Ref.9).

Mesophases indicated by l_{m1} , l_{m2} , etc.

detectable. Careful experimentation has indicated that such is the case (Ref. 12) and Fig.8 illustrates the situation schematically. The latter figure is based on the assumption that the mesophase and the isotropic phase can both be described by the same continuous free enthalpy function. Then, the solubility curve, which passes through two of the points on the three-phase line, must show two extremes and a point of inflection as explained above. If the two liquid phases cannot be described by the same free enthalpy function there will be two solubility curves, one for each of the liquid phases. In view of the nonvariance of binary three-phase equilibria at constant pressure, the points of intersection of solubility and liquid equilibrium curves must occur at the same temperature. Such situations are indicated in Fig.8 by three of the five horizontal lines, indicating three-phase equilibrium.

Fig.7. Phase behaviour in the system
water/poly(dimethylsiloxane-co-ethylene oxide) (Ref.12,13).
Block structure: 18 EO/14 DMS/18 EO.

Fig.8. Schematic phase diagram for systems such as that in Fig.7.

Fig.9. Isotropic/nematic phase transitions in the system $\text{CCl}_4/4,4'$ -dihexanoylazoxybenzene (Ref.14).

LIQUID-CRYSTAL STRUCTURES

Another type of order is illustrated in Fig 9 which refers to a substance forming nematic liquid crystals below 129.6°C . Addition of a solvent produces two curves encompassing the two-phase region isotropic/nematic which is very narrow and arrow-shaped. Narrow two-phase regions are quite common in liquid-crystalline systems. We refer to the funnel-shaped diagram predicted theoretically by Flory (Ref. 15, Fig 10) and experimentally verified in part by Miller *et al.* (Ref. 16).

The phase rule requires the narrow l_1/lc region and the broad l_1/lc_2 area to be separated by a three-phase line. Therefore we know that the jump in concentration from c_2 to c_3 upon a small decrease of the temperature proves the existence of a broad lc_1/lc_2 area, even if it escaped direct observation by Miller *et al.* because of its shallowness. The phase rule also prescribes that the l_1/lc funnel must eventually turn towards the axis of the solvent-free constituent 2 upon an increase of temperature, in the manner indicated by the dashed curves (see Fig.10).

Fig.10. Phase behaviour of solutions of rigid-rod molecules according to the phase rule (schematic)

OTHER TYPES OF ORDER

A type of order, so far seldom found in polymer systems, results from the formation of compounds. If the components in a binary system form a crystallizable compound s_{12} , not dissociating in either solid or liquid phase, the eutectic phase diagram is a simple combination of two binary systems, (component 1 + s_{12}) and (s_{12} + component 2). The compound will generally have a melting point deviating from that of either component. It will also differ in thermodynamic interaction with components 1 and 2 so that the two solubility curves of s_{12} do not have an identical initial slope (Fig.11a). Usually, the compound will dissociate and melt either congruently, when the liquid phase has the same composition as the compound or incongruently, if that is not the case. If the compound dissociates there is no discontinuity between the two solubility curves for s_{12} (Fig.11b).

Fig.11. Eutectic phase diagram for a system in which compound formation (s_{12}) occurs. Left: no dissociation of s_{12} , right: congruent dissociation

At first sight the diagram of Fig.11b might be mistaken to indicate partial miscibility in the liquid phase, like the example in Fig.12. Calorimetric or X-ray analysis will then easily remove the uncertainty. Fig.13 shows the phase diagram for the system *p*-dibromobenzene/poly(ethylene oxide), reported by Point and Coutelier (Ref. 18). The case for compound formation is very strong and is supported by the authors' X-ray results. The latter show a powder diagram of a new compound while the reflections of the original polymer are absent.

Fig.12. The system acetone/*n*-decane at 1 bar (Ref.17). x_2 = mole fraction of *n*-decane

Fig.13. The system *p*-dibromobenzene/poly(ethylene oxide) at 1 bar (Ref.18)

Another phase diagram that may readily be misinterpreted was presented recently by Arnouts and Berghmans (Ref. 19) and refers to the interference of the curve representing the glass transition of polystyrene as a function of the solvent concentration (trans-decalin) with the miscibility gap. The phase diagram (Fig.14) looks familiar and might be understood in terms of the system represented in Fig. 2. However, the dashed curve is not a solubility curve and the constant vitrification temperature T_g in a considerable concentration range is only indirectly related to the phase rule and nonvariant equilibrium. Here, the invariance is brought about by the liquid/liquid phase separation setting in when the concentration w_{2b} is reached upon addition of solvent to the polymer. At $T_{g,b}$ and $w_2 \leq w_{2b}$ the solution splits up into two phases. At polymer concentrations below w_{2b} one of the phases always has the composition w_{2b} and, consequently, vitrifies at $T_{g,b}$. The vitrification of the dilute phase occurs at very low temperature and has not been or cannot be observed. Molecular heterogeneity in the polymer does affect w_{2b} but to an extent that is negligible in the present context. The point of intersection of the liquid/liquid phase boundary and the T_g -concentration curve has been named the *Berghmans point* by Keller, who reported similar observations (Ref. 20).

Fig.14. Partial miscibility and vitrification in the system *tr*-decalin/polystyrene (Ref.19).

B = Berghmans point.

MOLECULAR MODELLING

Molecular models have been developed to understand or predict the molecular background of special types of phase behaviour. We have already mentioned Flory's theoretical treatment of solutions of rigid-rod molecules (Ref. 14). A number of studies have appeared concerning mesophase formation in block copolymers (Ref. 21-25). A recent addition to the field is the theoretical prediction and experimental verification of the existence of a three-phase line in the system *p*-azoxyanisole/*n*-tetracosane by Orendi and Ballauff (Ref. 26; Fig 15).

Fig.15. Phase diagram for a mixture of a nematic liquid crystal with a linear alkane, showing isotropic l_a/l_b and nematic liquid/isotropic liquid (l_n/l_a) two-phase regions (Ref.26). Left: predicted, right: *p*-azoxyanisole/*n*-tetracosane

Here we turn to the double-sickle shaped phase boundaries which have been observed in systems varying considerably in nature. Therefore, the question arises whether association of dissolved chain molecules, whatever the precise architecture of the aggregates, might be the cause of this peculiar phase behaviour. We present a simple analysis, which indicates that limitations in translational motion caused by aggregation of any kind may indeed explain the occurrence of double-sickle shaped phase boundaries. Fig.16 gives an example that we have calculated from the simple model described below.

We assume the isotropic solution to be described by the Flory-Huggins-Staverman rigid lattice theory (Ref. 27-29) and assume a fraction y of the n dissolved chain molecules to be associated in some way. Each of the chain molecules occupies m lattice sites (m = number of repeating units) and the aggregates each contain ν_p chains. The total number of aggregates, or micelles, is yn/ν_p and their volume equals $\nu_p m v_p$ where v_p stands for the volume per repeating unit in the micelle. The

Fig.16. Double-sickle phase diagram calculated with Eqs (7) - (9)
(parameter values: see text). I: free chains, II: aggregated chains.
 ϕ = volume fraction of the second component

latter might be a little larger than v_0 , the volume of the lattice unit, because of swelling of part of the micellar chains by the solvent. The total volume of the aggregates, V_m^* , thus equals ymv_p . The number of arrangements, Ω , for the n chains on the lattice with volume V is given by

$$\Omega = [N!/(n_0!n!)] (V^*/V)^{n(m-1)} (V_m^*/V)^{yn} \quad (2)$$

where V^* is the volume to which every repeating unit of any chain is limited by chain connectivity, except the first unit (Ref. 30-32), n_0 is the number of solvent molecules.

The solvent/repeating unit pair interaction parameter is assumed to be different for free chains (g_0) and those present in micelles (g_a), and the total interaction function g is supposed to add up the two contributions as follows

$$g = g_0(1 - y) + g_a y \quad (3)$$

The temperature dependence of g has its usual form:

$$g_0 = g_{0s} + g_{0h}/T; g_a = g_{as} + g_{ah}/T \quad (4)$$

If the volume of a micelle is $\nu_p m v_p$, its surface area is proportional to $(\nu_p m v_p)^{2/3}$ and the total surface area of all micelles is proportional to $ym^{2/3} \nu_p^{2/3} v_p^{2/3}$. The contribution of the micellar surface area to the free enthalpy of the system is then

$$\Delta G_s/(RT) = ym^{2/3} \nu_p^{2/3} B_s/T \quad (5)$$

where B_s contains the proportionality factor, the interface energy and v_p .

The degree of association, y , must be expected to depend on T and ϕ . We write arbitrarily

$$y = y_0\phi; \quad y_0 = y_{0s} + y_{0h}/T \quad (6)$$

where y_0 = degree of association in solvent-free polymer.

Standard procedures lead to the free enthalpy of mixing of the system:

$$\begin{aligned} \Delta G/(NRT) = & \phi_0 \ln \phi_0 + (\phi/m) \ln \phi - (\phi/m) \{ y \ln(y\phi q_p) - y_0 \ln(y_0 q_0) \} \\ & + \{ g_0(1-y) + g_a y \} \phi_0 \phi + y \phi (\nu_p m)^{-1} B_s / T \end{aligned} \quad (7)$$

and the chemical potentials

$$\begin{aligned} \Delta \mu_0/(RT) = & \ln \phi_0 + (1 - 1/m)\phi + (\phi^2 y_\phi / m) \ln(y\phi q_p) \\ & + (\phi/m)(\phi y_\phi + y) + g_0 \phi^2 + (g_a - g_0) \phi^2 (y - \phi_0 y_\phi) - y \phi \phi^2 (\nu_p m)^{-1} B_s / T; \end{aligned} \quad (8)$$

$$\begin{aligned} \Delta \mu_p/(mRT) = & (\ln \phi)/m - (1/m_0 - 1/m)\phi_0 - m^{-1}(y + \phi_0 \phi y_\phi) \ln(y\phi q_p) \\ & - (\phi_0/m)(y_\phi \phi + y) + (y_0/m) \ln(y_0 q_p) + g_0 \phi^2 \\ & + (g_a - g_0) \phi^2 (y + y_\phi \phi) + (y_\phi \phi_0 \phi + y) (\nu_p m)^{-1} B_s / T \end{aligned} \quad (9)$$

where $y_\phi = \partial y / \partial \phi$, and $q_p = v_p / v_0$.

At the maximum of the double sickle, (T_m, ϕ_m) , the $\Delta G(\phi)$ curves for the isotropic ($y = 0$) and micellar solutions have a common tangent. This condition can be used to calculate B_s and a value for $(g_a - g_0)$ at T_m , the temperature at which the maximum occurs. Choosing values for ϕ_{iso} and ϕ_{meso} , the volume fractions of polymer in isotropic liquid and mesophase, at a given temperature below T_m , we can calculate the complete phase diagram (Fig.16) which closely resembles the double-sickle type diagrams reported in literature. The values used in this particular calculation are: $T_m = 300$ K; $\phi_m = 0.5$; $\phi_{iso} = .35$ and $\phi_{meso} = .365$ at 270 K; $m = 10$; $\nu_p = 6$; $q_p = 1$. With $g_{0h} = 400$ K and $g_{ah} = 100$ K one finds $B_s = 38.5$ K; $g_{0s} = -1.438$; $g_{as} = -.724$. Further, $y_{0s} = 2.163$ and $y_{0h} = 874.4$ K. The calculation was carried out with $q_p = 1$; values larger than 1 do not change the phase diagram essentially.

This analysis strongly suggests that, quite generally, the formation of such peculiar narrow two-phase ranges can be related to the formation of mesophases, the nature of which evidently does not need to be specified.

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