

Phase behavior of ordered polymer systems

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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 Lüdemann 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 (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, similar considerations are valid for solutions of liquid-crystalline polymers and for the formation of compounds (2). A simple molecular model is proposed which relates molecular aggregation of any kind to the appearance of a special type of phase behavior.

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).

There are more direct consequences of the laws of thermodynamics regarding equilibrium phase diagrams. For binary systems, for instance, we have:

- 1) two two-phase regions must be separated either by a bivalent one-phase range, or by a part of a nonvariant three-phase line;
- 2) two one-phase regions cannot be adjacent: they must be separated by a two-phase area;
- 3) 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;
- 4) 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 (3).

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 lamellar superstructures resembling micelles in surfactant 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, *lm*, 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.2, redrawn from work by Roe and Zin (4), 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 (5), viz., the system water/sodium oleate in which 10 nonvariant three-phase equilibria appear, apart from those in which solid water takes part (Fig.3). Besides arrow-shaped two-phase 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 (6), for metal alloys (7) and, recently, for aqueous solutions of block copolymers containing hydrophilic and hydrophobic blocks (8,9). An example of the latter system is shown in Fig.4.

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 detectable. Careful experimentation has indicated that such is the case (8) and Fig.5 illustrates the situation schematically. The system in Fig.4, if considered classically, must contain five nonvariant three-phase equilibria: *s*₁/*lm*₂/*s*₂, *s*₁/*lm*₁/*lm*₂, *s*₁/*l*/*lm*₁, *lm*₂/*l*/*s*₂ and *lm*₁/*l*/*lm*₂.

Molecular Modeling

Molecular models have been developed to understand or predict the molecular background of special types of phase behaviour. We mention Flory's theoretical treatment of solutions of rigid-rod molecules (10). A number of studies have appeared concerning mesophase formation in block copolymers (11-15). 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 (16). 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.6 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 (17-19) 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 *ym/ν*_{*p*} and their volume equals *ν*_{*p*}*mv*_{*p*} where *v*_{*p*} stands for the volume per repeating unit in the micelle. The 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 *ymνv*_{*p*}. The number of arrangements, *Ω*, for the *n* chains on the lattice with volume *V* is given by

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

where *V*^{*} is the volume to which every repeating unit of any chain is limited by chain connectivity, except the first unit (20-22), *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*_{*p*}), and the total interaction function *g* is supposed to add up the two contributions as follows

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

The temperature dependence of *g* has its usual form:

$$g_0 = g_{0s} + g_{0H}/T; \quad g_p = g_{ps} + g_{pH}/T \quad (4)$$

If the volume of a micelle is *ν*_{*p*}*mv*_{*p*}, its surface area is proportional to (*ν*_{*p*}*mv*_{*p*})^{2/3} and the total surface area of all micelles is proportional to *ymν*_{*p*}^{2/3}*v*_{*p*}^{2/3}. The contribution of the micellar surface area to the free enthalpy of the system is then

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

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:

$$\Delta G/(NRT) = \phi_0 \ln \phi_0 + (\phi/m) \ln \phi - (\phi/m) \{ y \ln(y\phi q) - y_0 \ln(y_0 q_0) \} + \{ g_0(1-y) + g_p y \} \phi_0 \phi + y \phi (\nu_p m)^{-2/3} B_s/T \quad (7)$$

and the chemical potentials

$$\Delta \mu_0/(RT) = \ln \phi_0 + (1-1/m)\phi + (\phi^2 y_\phi/m) \ln(y\phi q_p) + (\phi/m) (\phi y_\phi + y) + g_0 \phi^2 + (g_p - g_0) \phi^2 (y - \phi_0 y_\phi) - y_\phi \phi^2 (\nu_p m)^{-2/3} B_s/T; \quad (8)$$

$$\Delta \mu_p/(mRT) = (\ln \phi)/m - (1/m_0 - 1/m)\phi_0 - m^{-1} (y + \phi_0 \phi y_\phi) \ln(y\phi q_p) - (\phi_0/m) (y_\phi \phi + y) + (y_0/m) \ln(y_0 q_p) + g_0 \phi_0^2 + (g_p - g_0) \phi_0 (y + y_\phi \phi) + (y_\phi \phi_0 \phi + y) (\nu_p m)^{-2/3} B_s/T \quad (9)$$

where *y*_φ = ∂*y*/∂*φ*, and *q*_{*p*} = *v*_{*p*}/*v*₀.

At the maximum of the double sickle, (*T*_{*m*}, *φ*_{*m*}), the Δ*G*(*φ*) 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*_{*p*} - *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.10) which closely resembles the double-sickle type diagrams reported in literature. The values used in this particular calculation for the main double sickle are: *T*_{*m*} = 300 K; *φ*_{*m*} = 0.5; *φ*_{*iso*} = .35 and *φ*_{*meso*} = .3675 at 270 K; *m* = 10; *ν*_{*p*} = 6; *q*_{*p*} = 1. With *g*_{0*H*} = 400 K and *g*_{*pH*} = 100 K one finds *B*_{*s*} = 38.5 K; *g*_{0*s*} = - 1.438; *g*_{*ps*} = - 0.724. Further, *y*_{0*s*} = 2.163 and *y*_{0*H*} = 874.4 K. The calculation was carried out with *q*_{*p*} = 1; values larger than 1 do not change the phase diagram essentially. For the smaller double sickle we used: *T*_{*m*} = 290 K; *φ*_{*m*} = 0.36; *φ*_{*iso*} = 0.3 and *φ*_{*meso*} = 0.305 at 285 K; *m* = 10; *ν*_{*p*} = 6; *q*_{*p*} = 1. Keeping *g*_{0*s*} and *g*_{0*H*} at the same values as above one finds *B*_{*s*} = 113.4 K; *g*_{*ps*} = - 0.727; *g*_{*pH*} = 68.8 K. Further, *y*_{0*s*} = - 1.621 and *y*_{0*H*} = 716.6 K.

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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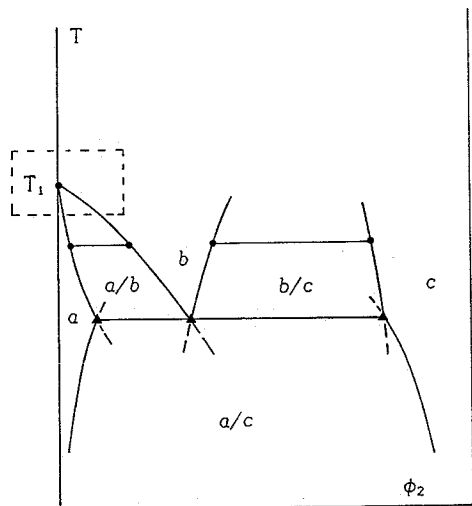


Fig. 1. Isobaric two-phase equilibria (a/b , b/c and a/c) in a binary (1/2) system. \bullet — \bullet : tie line connecting two coexisting phase compositions (\bullet), \blacktriangle — \blacktriangle : nonvariant three-phase equilibrium. ϕ_2 = volume fraction second component

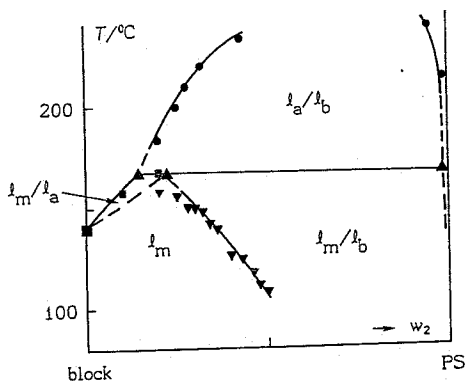


Fig. 2. Phase diagram for a mixture of a poly(styrene-co-butadiene) block copolymer with polystyrene (3). Dashed lines indicate estimated locations.

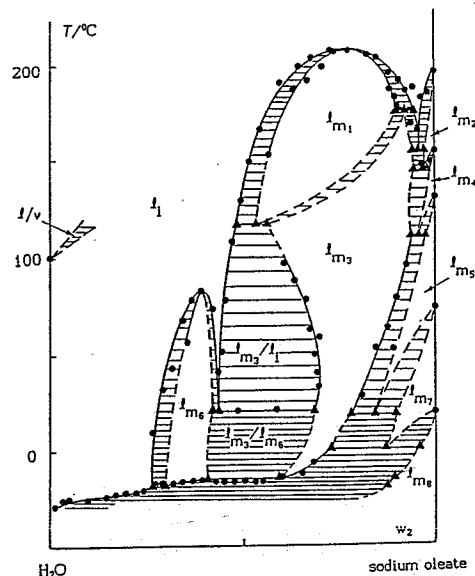


Fig. 3. Phase behavior of the system water/sodium oleate (redrawn from ref. 4). Mesophases indicated by l_{m1} , l_{m2} , etc.

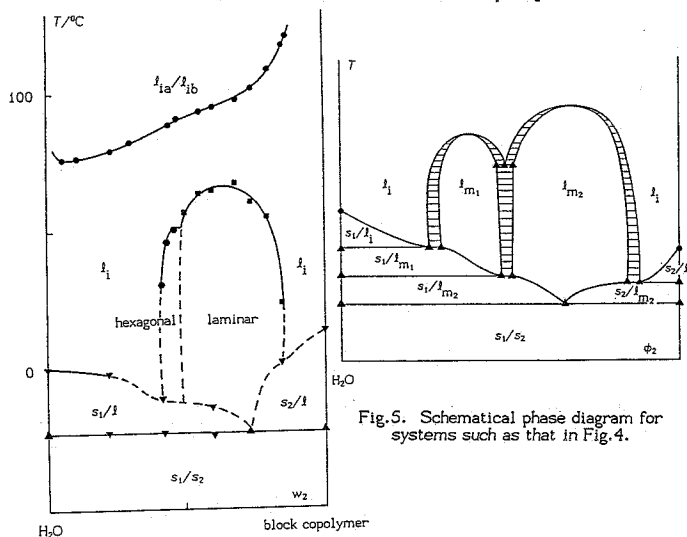


Fig. 4. Phase behavior in the system water/poly(dimethylsiloxane-co-ethylene oxide) (7,8). Block structure: 18 EO/14 DMS/18 EO.

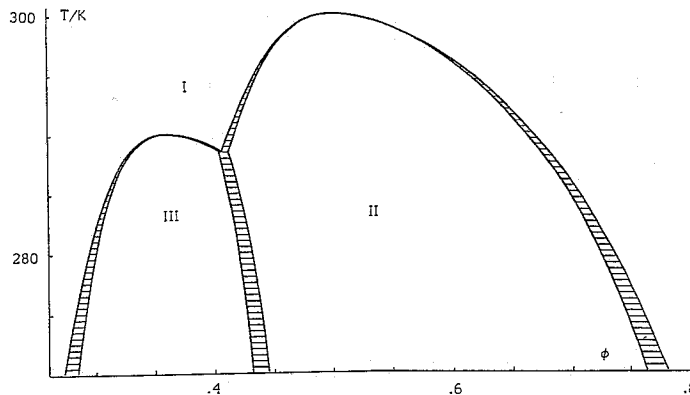


Fig. 6. Double-sickle phase behavior calculated with Eqs (7) - (9) (parameter values: see text). I: free chains, II, III: aggregated chains. ϕ = volume fraction of the second component