THEORETICAL OBSERVATIONS ON SPINODAL DECOMPOSITION OF POLYMER SOLUTIONS

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Abstract—In systems showing spinodal decomposition, it is to be expected that a certain dimension D_m will be realized most frequently. Although most concentration fluctuations present increase in amplitude with time, the rate of increase depends upon the wavelength of the fluctuation, so that some fluctuations will grow much more rapidly than others; as a result, there will be a fairly uniform dimension throughout the system. In order to obtain an estimate of the dimensions to be expected in the system PPO®-caprolactam, some theoretical observations have been combined to yield D_m values of the order of 1 μ, depending upon the temperature below the spinodal where the decomposition sets in.

INTRODUCTION

LIQUID–LIQUID phase separation is possible as soon as the free energy of a homogeneous mixture is greater than the sum of the free energies of two phases of different composition which can grow from the original composition (see Fig. 1). For compositions between ϕ_1 and ϕ_s or between ϕ_s' and ϕ_1', this is only possible by nucleation of new phases with compositions in the neighbourhood of ϕ_1' or ϕ_1 respectively. Once these phases have been nucleated, they will continue to grow until the surrounding continuous phase has a composition ϕ_1 or ϕ_1'. If it is possible to cool down a homogeneous solution to such a temperature that its composition is between ϕ_s and ϕ_s' without appreciable nucleation and growth occurring in the meantime, the situation will be different. Every composition between ϕ_s and ϕ_s' is unstable to small fluctuations in composition, since this results in a gain in free energy. Such fluctuations, if present, will have a tendency to grow in amplitude, i.e., the difference in composition between neighbouring volume elements in the solution tends to increase. A theory for the initial stages of this process was developed by Cahn,[2] and we have here adapted this theory to polymer solutions in order to estimate the geometry of systems undergoing this kind of phase separation. Because the parameter K, connected with the course of the concentration gradient, plays an important role in this theory, it has also been necessary to try to make a reasonable estimate of K for solutions of high polymers. The result of this work, as applied to the system PPO® [poly(2,6-dimethyl-1,4-phenylene ether)]–caprolactam is presented in the following sections.

THEORY OF SPINODAL DECOMPOSITION FOR POLYMER SOLUTIONS

In order to give a description of the kinetics of spinodal decomposition in solutions of high polymers, it is necessary to have available a model of the solution and a thermodynamic theory of non-homogeneous solutions.
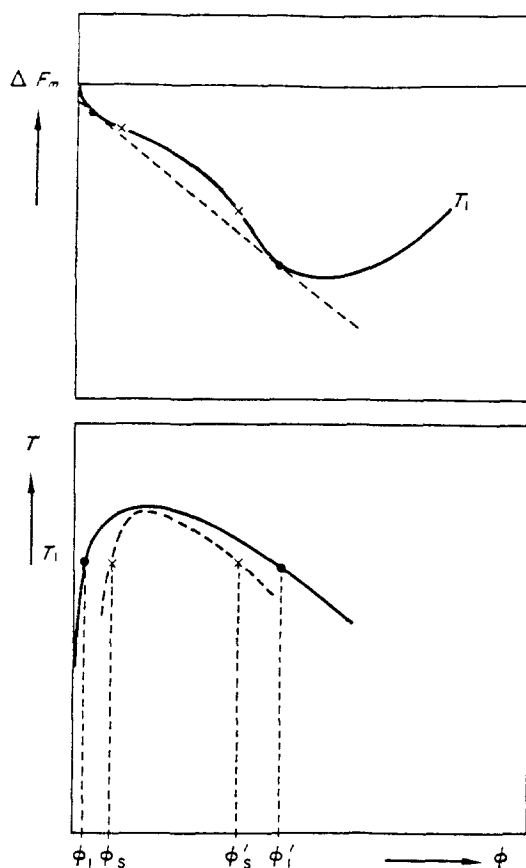
FIG. 1. Schematic representation of the free energy of mixing (ΔF_m) and the resulting phase diagram as a function of the volume fraction of polymer.

We are only interested in decomposition phenomena in rather concentrated solutions. Therefore we regard such a solution as a more or less homogeneous system in which there occur a number of small-amplitude fluctuations in solvent concentration. This means that the polymer is not treated as an assembly of individual molecules, but rather as a great number of segments mixed with solvent molecules. Properties of individual molecules are thus not directly detectable in such a solution. So it seems reasonable to use the Flory–Huggins expression for the free energy of mixing.

Thermodynamic theories of non-homogeneous solutions exist in two formulations as given by Debye[1] and Cahn.[2]

In the first place, the excess Helmholtz free energy, F^e, of a two-component system, assuming constant volume V, can be written according to Debye

$$F^e = kT \int_V d\tau \left[\left\{ \frac{\phi_1{}^0}{w_1} \ln \phi_1{}^0 + \frac{(1 - \phi_1{}^0)}{w_2} \ln (1 - \phi_1{}^0) + \frac{\Omega}{2kT} \phi_1{}^0(1 - \phi_1{}^0) \right\} \right.$$
$$\left. + \left(\frac{1}{w_1 \phi_1{}^0} + \frac{1}{w_2(1 - \phi_1{}^0)} - \frac{\Omega}{kT} \right) \frac{\eta^2}{2} + \frac{H}{2kT} \text{grad}^2\eta \right] \tag{1}$$
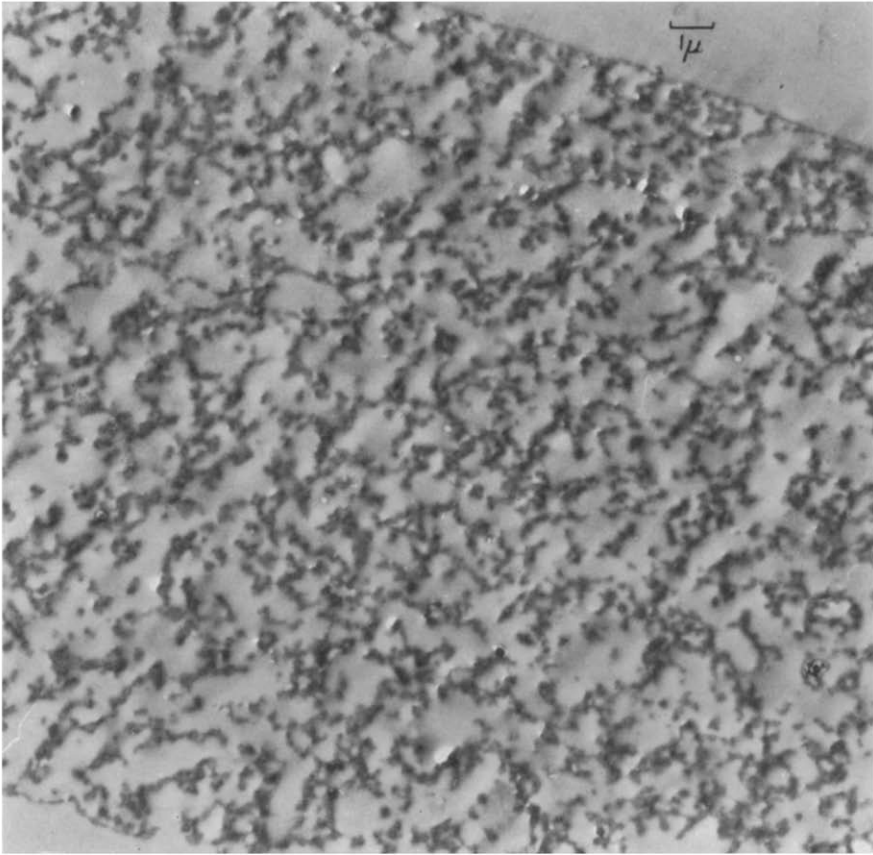
FIG. 2. Cross-section of a film of PPO solution (10 per cent weight) in caprolactam, quenched at 50° for 10 min, brought into liquid nitrogen and washed out with ethanol below 0°.

Preparation by embedding in Araldite resin was done before slicing. (By courtesy of B. J Spit, TNO-TH).

where $\eta = \phi_1 - \phi_1{}^0$ is the difference between the local concentration ϕ_1 and the average concentration $\phi_1{}^0$; $d\tau$ is a volume element, w_1 and w_2 are the molecular volumes of solvent and solute molecules, and Ω and H are interaction parameters.

This can also be written as

$$\Delta F = F^e - \Delta F_m = \int_V d\tau \left[\tfrac{1}{2} \left\{ \frac{\partial^2(\Delta F_m/V)}{\partial\phi_1{}^2} \right\}_{\phi_1{}^0} \eta^2 + \tfrac{1}{2}H \, \text{grad}^2\eta \right] \qquad (2$$

where ΔF_m is the free energy of mixing of a homogeneous solution (first term in the square brackets in (1)) and ΔF is the free energy contribution due to the concentration fluctuations.

A second expression for ΔF is given by Cahn;[2] it has been derived in quite a different way.

$$\Delta F = \int_V d\tau \left[\tfrac{1}{2} \left\{ \frac{\partial^2(\Delta F_m/V)}{\partial\phi_1{}^2} \right\}_{\phi_1{}^0} \eta^2 + K \, \text{grad}^2\eta \right]. \qquad (3)$$

Comparison between Eqns. (2) and (3) shows that these formulae are identical if $K = \tfrac{1}{2}H$.

It is seen from Eqns. (2) or (3) that ΔF is negative only if the first term in the brackets is negative and if it outweighs the second term in magnitude.

Now, from the theory of spinodal decomposition as given by Cahn,[2] it follows that all concentration fluctuations with wavenumber $\beta < \beta_c$ will spontaneously increase in amplitude with time, the rate of increase depending upon β. Furthermore there should be a tendency for the fluctuation with wavenumber β_m to be realized most frequently. This wavenumber β_m is given by

$$\beta_m = \frac{1}{\sqrt{2}} \left[-\frac{1}{2K} \left\{ \frac{\partial^2(\Delta F_m/V)}{\partial\phi_1{}^2} \right\}_{\phi_1{}^0} \right]^{\frac{1}{2}} \equiv 2^{-\frac{1}{2}} \beta_c. \qquad (4)$$

In order to make an estimate of the value of β_m for systems of interest, e.g. PPO®–caprolactam, we need an estimate of $(\Delta F_m/V)$. For this, we have chosen the well-known Flory–Huggins expression

$$(\Delta F_m/V) = RT \left[\frac{\phi_1}{\bar{V}_1} \ln \phi_1 + \frac{1 - \phi_1}{\bar{V}_2} \ln (1 - \phi_1) + \frac{\chi}{\bar{V}_1} \phi_1(1 - \phi_1) \right] \qquad (5)$$

$\bar{V}_1$ and $\bar{V}_2$ being the molar volumes of solvent and polymer respectively. We find from Eqn. (5)

$$\left\{ \frac{\partial^2(\Delta F_m/V)}{\partial\phi_1{}^2} \right\}_{\phi_1{}^0} = RT \left[\frac{1}{\bar{V}_1 \phi_1{}^0} + \frac{1}{\bar{V}_2(1 - \phi_1{}^0)} - \frac{2\chi}{\bar{V}_1} \right]. \qquad (6)$$

If we now assume for the interaction parameter $\chi = A + (BV_1/RT)$, which is a usual assumption (A and B being constants), and bear in mind that at a certain temperature T_s (the spinodal temperature) the expression (6) will be zero, we can write

$$\left\{ \frac{\partial^2(\Delta F_m/V)}{\partial\phi_1{}^2} \right\}_{\phi_1{}^0} = \frac{2RT}{\bar{V}_1} (\chi_{T_s} - \chi_T) = 2B \left(\frac{T}{T_s} - 1 \right). \qquad (7)$$

The temperature T_s is the spinodal temperature at the concentration $\phi_1{}^0$ and T_s will be equal to the critical temperature T_c as soon as $\phi_1{}^0$ happens to be the critical composition.

ESTIMATION OF K FROM A COMPARISON BETWEEN CRITICAL OPALESCENCE AND SPINODAL DECOMPOSITION

If we knew the value of K, it would be possible to calculate β_m from Eqns. (4) and (7), B being known. However, it seems that no estimate of K exists at the moment. Therefore we have tried to obtain a value of K from Debye's experiments on the critical opalescence of polymer solutions.

To this end, we have recalculated the light scattering to be expected from a system with concentration fluctuations at temperatures $T > T_s$. Starting again with a fluctuation $\eta(\beta) = \eta_0(\beta) \sin (\beta x)$, as done by Debye,[1] it is found that the intensity of scattered light will be proportional to $\overline{\eta_0{}^2 (\beta)}$ and will be scattered at such an angle that $\beta = (2\pi/\lambda) s = (4\pi/\lambda) \sin \theta/2$ using the same symbols as Debye.

The mean-square $\overline{\eta_0{}^2 (\beta)}$ can be found from

$$\overline{\eta_0{}^2 (\beta)} = \int_0^\infty \eta_0{}^2 \exp \left(-\frac{\Delta F}{VRT} \right) d\eta_0 \Big/ \int_0^\infty \exp \left(-\frac{\Delta F}{VRT} \right) d\eta_0$$

$$= 2RT \left[\left\{ \frac{\partial^2 (\Delta F_m/V)}{\partial \phi_1{}^2} \right\}_{\phi_1{}^0} + 2K \frac{4\pi^2}{\lambda^2} s^2 \right]^{-1}. \qquad (8)$$

Substitution of (7) into (8) leads to

$$\overline{\eta_0{}^2 (\beta)} = \frac{RT}{B} \left[\left(\frac{T}{T_s} - 1 \right) + \frac{K}{B} \cdot \frac{4\pi^2}{\lambda^2} s^2 \right]^{-1}. \qquad (9)$$

Comparing our Eqn. (9) with Eqns. (27) and (28) of Debye,[1] we see that

$$K/B = l^2/6 \qquad (10)$$

where l is a range of molecular interaction.

Combination of Eqns. (4), (7) and (10) immediately gives

$$\beta_m = l^{-1} \left[3 \left(1 - \frac{T}{T_s} \right) \right]^{+\frac{1}{2}} \qquad (11)$$

so that the dimension most frequently realized is the fluctuation wavelength

$$D_m = 2\pi \beta_m{}^{-1} = 2\pi l \left[3 \left(1 - \frac{T}{T_s} \right) \right]^{-\frac{1}{2}}. \qquad (12)$$

It is important to note here that D_m does not explicitly depend upon the interaction parameter χ, but nevertheless remains a function of the quality of the solvent through the value of l.

ACTUAL D_m VALUES TO BE EXPECTED

From Eqn. (12), it is possible to calculate D_m as a function of temperature with known values of l. There is much confusion about the l values in polymer solutions.[3, 4] However, it is evident that the value of l will depend on the thermodynamic quality of the solvent and through this on temperature, on the molecular weight of the polymer, and most probably on the concentration. This last point is especially important in the case of more concentrated solutions, as studied here, where individual molecular properties do not play such an important role.

For a 15 wt. per cent solution of PPO in caprolactam, with $T_s = 400°K$ and $\bar{M}_v = 2 \cdot 1 \times 10^5$, the value of l most probably is of the order of 200 Å, based on Debye's estimate that l should be equal to the radius of gyration of the polymer. This value also corresponds, at least in order of magnitude, with the average distance between the centres of the polymer coils in such a solution. In this way we find for D_m the values of Table 1.

TABLE 1. CALCULATED VALUES OF THE CHARACTERISTIC DIMENSION D_m AS A FUNCTION OF TEMPERATURE T FOR $T_s = 400°K$ AND $l = 200$ Å

$T(°K)$	$D_m(\mu)$
399	1·45
395	0·65
390	0·46
380	0·32
370	0·26
360	0·23

It should be realized that, for low molecular weight solutes with l of the order of 10 Å, the values of D_m at the same temperatures will be about 20 times smaller.

Although the D_m values calculated above are based on a rather crude approximation, the order of magnitude is most probably correct, and it is gratifying that the experimental values, as determined by microscopic observation $(2-0 \cdot 5 \, \mu)$[5] or by electron microscopy (Fig. 2), are in agreement with this estimate.

REFERENCES

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Résumé—Dans le cas des systèmes qui présentent une décomposition spinodale, on doit s'attendre à ce qu'une certaine dimension D_m soit la plus fréquemment réalisée. Bien que la plupart des fluctuations de concentration ont une amplitude qui s'accroît avec le temps, la vitesse d'accroissement dépend de la longueur d'onde de la fluctuation, de telle sorte que certaines fluctuations s'accroissent beaucoup plus rapidement que d'autres; il en résulte l'existence d'une dimension pratiquement uniforme au sein du système. Dans le but de pouvoir estimer les dimensions auxquelles on doit s'attendre pour le système PPO⁹–caprolactame, on a réussi quelques observations théoriques pour obtenir des valeurs de D_m de l'ordre du micron, en tenant compte de la température inférieure à la température spinodale à laquelle la décomposition a lieu.

Sommario—Nei sistemi che presentano decomposizione spinodale, ci si dovrebbe aspettare che una certa dimensione D_m si realizzi più di frequente. Sebbene molte fluttuazioni di concentrazione aumentino in ampiezza con il tempo, la velocità dell'aumento dipende dalla lunghezza d'onda della fluttuazione, così che alcune fluttuazioni aumentano più rapidamente di altre; come risultato ci dovrebbe essere una dimensione quasi uniforme attraverso il sistema. Per ottenere un'idea delle dimensioni da aspettarsi nel sistema PPO®–caprolattame, sono state combinate alcune osservazioni teoriche per ottenere valori D_m dell'ordine di un micron, dipendenti dalla temperatura al di sotto della quale ha luogo la decomposizione spinodale.

Zusammenfassung—In Systemen, die spinodale Zersetzung zeigen, ist zu erwarten, daß eine bestimmte Dimension D_m besonders häufig auftritt. Obwohl die meisten vorliegenden Konzentrationsschwankungen in ihrer Amplitude mit der Zeit zunehmen, hängt die Geschwindigkeit der Zunahme von der Wellenlänge der Schwankung ab, sodaß einige Schwankungen sehr viel rascher zunehmen als andere. Daraus ergibt sich eine ziemlich gleichmäßige Dimension im ganzen System. Um eine Abschätzung der zu erwartenden Dimensionen im System PPO®–Caprolactam zu erhalten, wurden einige theoretische Beobachtungen kombiniert und ergaben D_m Werte in der Größenordnung von 1μ, in Abhängigkeit von der Temperatur unterhalb der Spinodalen bei der die Zersetzung beginnt.