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# Flory−Huggins Theory for the Solubility of Heterogeneously Modified Polymers

**Patrick B. Warren***

*Unilever R&D Port Sunlight, Bebington, Wirral, CH63 3JW, UK*

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ABSTRACT: Many water-soluble polymers are chemically modified versions of insoluble base materials such as cellulose. A Flory−Huggins model is solved to determine the effects of heterogeneity in modification on the solubility of such polymers. It is found that heterogeneity leads to decreased solubility, with the effect increasing with increasing blockiness. In the limit of extreme blockiness, the nature of the phase coexistence crosses over to a polymer−polymer demixing transition. Some consequences are discussed for the synthesis of partially modified polymers and the experimental characterization of such systems.

Many water-soluble polymers are made by chemically modifying insoluble base materials such as starches and gums; for example, a wide class of water-soluble polymers is obtained from cellulose.[1,2] It is often possible to vary the degree of modification of the base polymer to obtain water-soluble polymers with, in principle, continuously variable properties. A basic characteristic of these polymers is their solubility, but given the essentially stochastic nature of the chemical modification step, what is the effect of heterogeneity in modification on the solubility of the resulting materials?

In the present paper, this question is approached from a theoretical point of view by setting up a Flory−Huggins model for the phase behavior of a polymer−solvent mixture,[3] where the polymers have a random degree of modification. In this approach, the issue of solubility is translated into the problem of determing the phase coexistence between a dissolved aqueous phase and an undissolved (water-poor) phase. The solubility is then formally given by the polymer concentration in the aqueous phase. Determination of the full phase behavior for a multicomponent Flory−Huggins theory is an onerous task though, and a simpler approach is to examine the spinodal stability of the system, which can be taken to be representative of the full phase behavior. This is the approach taken in the present paper. It is arguably more insightful than a full calculation of the phase behavior since closed-form analytic expressions can be obtained for the spinodal stability limit. The approach taken is similar to models for the phase behavior of random block copolymer melts which have been developed in the past.[4−7] There has been rather little work though on random copolymers which also include a solvent, apart from a brief example described by Sollich et al.[8] Also, the present approach does not allow for the possibility of microphase separation, although in principle it could be extended to encompass this.[4−7]

In the model, it is supposed that the system comprises a large number of species of polymers $i$ with differing degrees of modification $0 < \alpha_i < 1$ and concentrations $\rho_i$. For simplicity, length polydispersity is neglected, and all the polymers are assumed to have the same number $N$ of segments. The system is then described by the following (mean field) Flory−Huggins free energy density

$$f = \sum_i \rho_i \log \rho_i + (1-\phi)\log(1-\phi) + \chi(\phi-\eta)(1-\phi) \tag{1}$$

where $\phi$ is the total polymer segment concentration and $\eta$ is the concentration of chemically modified segments, given respectively by

$$\phi = N\sum_i \rho_i, \qquad \eta = N\sum_i \rho_i \alpha_i \tag{2}$$

The first term in eq 1 is the ideal free energy of mixing. The second term is the usual Flory−Huggins configurational chain entropy. The third term is the free energy cost of the unmodified polymer segments at a concentration $\phi - \eta$ coming into contact with solvent (water) at a concentration $1 - \phi$. Typically one expects $\chi > {}^1/_2$ for this interaction to represent the repulsion between unmodified segments and water which leads to phase separation of unmodified polymers. To keep the model simple, this is the only $\chi$-parameter that is retained in the problem.

Equation 1 has the structure of a *moment free energy*, since the excess free energy, comprising the second and third terms, only depends on $\phi$ and $\eta$, which are *moment densities*. Such a system can be analyzed using the methods developed by Sollich and co-workers.[8−11] In particular, ref 11 describes how the spinodal stability conditions for systems with an excess free energy can be expressed in terms of moment densities, generalizing various truncation theorems obtained by earlier workers.[12,13] I now summarize the relevant results, translated into terms suitable for the present problem. Let us consider such a system with a free energy $f = \sum_i \rho_i \log \rho_i + f^{(\mathrm{ex})}(\phi^{(1)} \dots \phi^{(n)})$, where the excess free energy depends on moment densities of the form $\phi^{(r)} = \sum_i \rho_i w_i^{(r)}$ $(r = 1 \dots n)$, with the $w_i^{(r)}$ being species-dependent weights. The fundamental idea is that the moment densities can be treated as effective species concentrations. In particular, it can be proved that spinodal stability corresponds to the positive-definiteness of the matrix $\mathbf{M}$ of second partial derivatives of the free energy with respect to the moment densities. In ref 11 it is shown that $\mathbf{M} = \mathbf{M}_{\mathrm{id}} + \mathbf{M}_{\mathrm{ex}}$ where $(\mathbf{M}_{\mathrm{id}}^{-1})_{rs} = \sum_i \rho_i w_i^{(r)} w_i^{(s)}$ and $(\mathbf{M}_{\mathrm{ex}})_{rs} = \partial^2 f^{(\mathrm{ex})}/\partial\phi^{(r)}\,\partial\phi^{(s)}$. The limit of spinodal stability is given by $\det \mathbf{M} = 0$. This condition usually corresponds to the vanishing of a single eigenvalue of $\mathbf{M}$, with an eigenvector $\Delta\phi^{(s)}$ that satisfies $\sum_s (\mathbf{M})_{rs}\Delta\phi^{(s)} = 0$. It is shown in ref 11 that the spinodal instability direction in the space of species concentrations is given by $\Delta\rho_i = \sum_{rs} \rho_i w_i^{(r)} (\mathbf{M}_{\mathrm{id}})_{rs} \Delta\phi^{(s)}$.

For the present problem, there are two moment densities $\phi$ and $\eta$, defined respectively with $w_i^{(1)} = N$ (a constant) and $w_i^{(2)}$

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* E-mail: patrick.warren@unilever.com.

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$= N\alpha_i$ (the number of modified groups on the $i$th species). Application of the above theory to eq 1 leads to

$$\mathbf{M}_{\mathrm{id}}^{-1} = N^2 \begin{pmatrix} \sum_i \rho_i & \sum_i \rho_i \alpha_i \\ \sum_i \rho_i \alpha_i & \sum_i \rho_i {\alpha_i}^2 \end{pmatrix} \tag{3}$$

and

$$\mathbf{M}_{\mathrm{ex}} = \begin{pmatrix} (1-\phi)^{-1} - 2\chi & \chi \\ \chi & 0 \end{pmatrix} \tag{4}$$

After some algebra the condition det $\mathbf{M} = 0$ reduces to

$$\frac{1}{N\phi} + \frac{1}{1-\phi} - 2\chi(1 - \langle\alpha\rangle) - \chi^2 N\phi(\langle\alpha^2\rangle - \langle\alpha^2\rangle) = 0 \tag{5}$$

where

$$\langle\alpha\rangle = \frac{\sum_i \rho_i \alpha_i}{\sum_i \rho_i}, \qquad \langle\alpha^2\rangle = \frac{\sum_i \rho_i {\alpha_i}^2}{\sum_i \rho_i} \tag{6}$$

I emphasize that, despite being remarkably simple, eq 5 is exact.

One already reaches a significant conclusion from this. The first three terms in eq 5 are what one would expect from standard Flory–Huggins theory,[3] with an effective $\chi$-parameter given by the product of the original $\chi$-parameter and the fraction $1 - \langle\alpha\rangle$ of unmodified segments. These terms therefore take account of the *mean* degree of modification. The final term in eq 5 is a correction due to the heterogeneity. Since the variance $\langle\alpha^2\rangle - \langle\alpha\rangle^2$ is positive, this term is always negative. The effect is that heterogeneity in modification *reduces* the solubility, over and above what would be expected from the mean degree of modification.

To make further progress, it is convenient to specify a model for the distribution of the $\alpha_i$. In particular, such a model can be used to examine the effect of blockiness in modification which is expected to play an important role. In previous work on random block copolymers,[5,6] a Markov model was used to characterize the correlations between different kinds of segments. While such a model may be appropriate for the stochastic nature of the synthetic route for such random block copolymers, I argue below that it is probably not appropriate in the present case. I therefore consider instead a very simple model for the heterogeneity in which the modified segments occur in blocks of size $M$, where $1 < M < N$. In this model, it is supposed that each block has an equal probability $p$ of being modified, and there are no further correlations. Then, for any particular species, $\alpha_i = (1/N)\sum_{j=1}^{N/M} M\epsilon_{ij}$, where $j$ labels the blocks and $\epsilon_{ij}$ is zero or one with probability $1 - p$ and $p$, respectively. Thus, the $\alpha_i$ are drawn from scaled binomial distribution, with

$$\langle\alpha\rangle = p, \qquad \langle\alpha^2\rangle - \langle\alpha^2\rangle = \frac{M}{N} p(1-p) \tag{7}$$

Equation 5 becomes

$$\frac{1}{N\phi} + \frac{1}{1-\phi} - 2\chi(1-p) - \chi^2 M\phi p(1-p) = 0 \tag{8}$$

This is a quadratic equation for $\chi$, and the appropriate root is

$$\chi = \frac{1}{M\phi p}\left[\left\{1 + \frac{M\phi p}{1-p}\left(\frac{1}{N\phi} + \frac{1}{1-\phi}\right)\right\}^{1/2} - 1\right] \tag{9}$$

I now examine the consequences of this result.

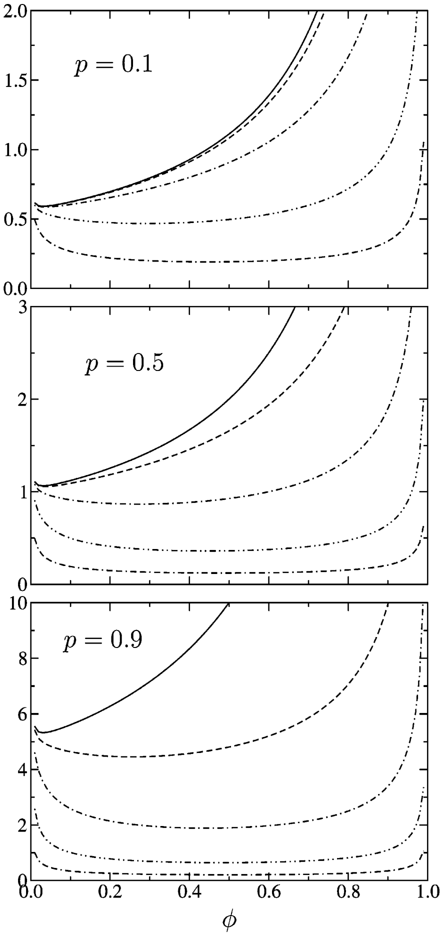

**Figure 1.** Spinodal curves calculated from eq 9 for polymers of length $N = 10^3$, for three values of the mean degree of modification $p$, and for block sizes $M \to 0$ (uniform limit, solid line), $M = 1$ (dashed line), $M = 10$ (dash–dot line), $M = 100$ (dash–dot–dot line), and $M = 10^3$ (dash–dash–dot line). The system is spinodally unstable above the indicated curves. Note the change in shape of the $M = 1$ curves: for $p = 0.1$ and 0.5 the minimum is at $\phi \to 0$, whereas for $p = 0.9$ the minimum is at $\phi \approx 0.25$.

The formal limit $M \to 0$ corresponds to a vanishing variance and a completely uniform distribution of modified segments, as though each monomer has undergone an identical fractional modification by a fraction $p$, rather than being modified or not with probability $p$ and $1 - p$. As noted already above, this limit corresponds to simple Flory–Huggins theory with an effective $\chi$-parameter equal to $\chi(1 - p)$. For large $N$, this indicates the absence of phase separation for $\chi(1 - p) < 1/2$ or $p > 1 - 1/(2\chi)$.

Now let us consider eq 9 for block size $M = 1$ . In this case, individual segments are modified randomly with no correlations. For $M = 1$ and large $N$ in eq 9, there are two behaviors depending on the value of $p$. For $p < 4/5$, there is an absence of phase separation for $\chi(1 - p) < 1/2$, just as for the $M \to 0$ limit. For $4/5 < p < 1$, the behavior is more complicated. To be precise, the location of the minimum value of the $\chi(\phi)$ spinodal shifts from $\phi_{\mathrm{min}} \sim N^{-1/2}$ for $p < 4/5$ to a nonvanishing $0 < \phi_{\mathrm{min}} < 1$ for $p > 4/5$. (It is the examination of eq 9 in the limit $\phi \sim N^{-1/2}$ that gives the crossover point $p = 4/5$.) The change in behavior can be seen for the $M = 1$ curves (dashed lines) in Figure 1 and is shown explicitly in the upper plot of Figure 2.

Let us next consider the limit of extreme blockiness $M = N$. This limit is strikingly different from the $M = 1$ case. For large $N$ and $p > 0$, one can show that there is an absence of

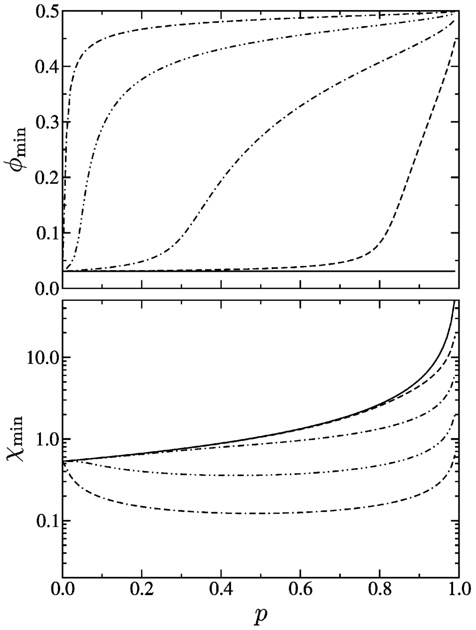

**Figure 2.** Location of the numerically determined minimum of the spinodal curves from eq 9 is plotted as a function of $p$, for polymers of length $N = 10^3$ and block sizes $M \rightarrow 0$ (uniform limit, solid line), $M = 1$ (dashed line), $M = 10$ (dash−dot line), $M = 100$ (dash−dot−dot line), and $M = 10^3$ (dash−dash−dot line). For $M = 1$ (dashed line) the upper plot shows clearly that $\phi_{\min} \approx N^{-1/2} \approx 0.03$ only holds for $p < 4/5 = 0.8$.

phase separation only for $\chi\sqrt{Np(1-p)} < 2$. In the large $N$ limit, this inequality is always violated, indicating that the system *always* has a tendency to undergo phase separation in the limit of extreme blockiness. Since the unmodified polymer system itself only phase separates for $\chi > 1/2$, this suggests that the phase separation has the nature of a polymer−polymer demixing transition rather than a solvent-driven phase separation. This insight is confirmed by analysis of the spinodal instability direction below.

For large $N$ and general $M$ in eq 9, one would expect that the above two cases represent the two classes of behavior. In the first case, the behavior for $M \ll N$ should be similar to the $M = 1$ limit where individual segments are randomly modified. In the second case, the behavior for $M \propto N$ should be similar to the $M = N$ limit of extreme blockiness. Figure 1 shows typical spinodal curves calculated from eq 9 for various values of $p$ and $M$. The location of the minimum ($\phi_{\min}$,$\chi_{\min}$) of the spinodal curves can be numerically determined, and Figure 2 shows how this depends on $p$.

The results show first that for $M \ll N$ increasing $p$ leads to increasing solubility as the value of $\chi$ required to reach the spinodal instability is increased. Moreover, a decrease in solubility between a uniform model ($M \rightarrow 0$) with no heterogeneity and a model with fine-grained blockiness ($M = 1$) is apparent. The major effect arises as $M \rightarrow N$ though, where the tendency for phase separation is greatly enhanced.

The above analysis is augmented considering the spinodal instability direction associated with the spinodal stability limit which can provide a useful mechanistic insight. As explained above, the spinodal instability direction is characterized by the eigenvector that corresponds to the vanishing eigenvalue responsible for the vanishing spinodal determinant. For the present problem, from eqs 3 and 4, one finds the instability direction is characterized by

$$\frac{\Delta\eta}{\Delta\phi} = \langle\alpha\rangle - \chi N\phi(\langle\alpha^2\rangle - \langle\alpha\rangle^2) \tag{10}$$

The corresponding spinodal instability direction in the space of species concentrations is

$$\begin{aligned}\frac{\Delta\rho_i}{\rho_i} &= \frac{\langle\alpha^2\rangle\Delta\phi - \langle\alpha\rangle\Delta\eta + \alpha_i(\Delta\eta - \langle\alpha\rangle\Delta\phi)}{\phi(\langle\alpha^2\rangle - \langle\alpha\rangle^2)} \\ &= \frac{\Delta\phi}{\phi}(1 + \chi N\phi(\langle\alpha\rangle - \alpha_i))\end{aligned} \tag{11}$$

where the second line follows by inserting the result for the ratio $\Delta\eta/\Delta\phi$. These results should be evaluated on the spinodal. They are all exact for an arbitrary distribution of $\alpha_i$.

For the instability direction to lie along a pure dilution line, one should have $\Delta\rho_i/\rho_i$ independent of species $i$. One can conclude that this only happens if $\Delta\eta/\Delta\phi = \langle\alpha\rangle$, in other words if the variance $\langle\alpha^2\rangle - \langle\alpha\rangle^2$ vanishes. In such a case, the phase transition is purely associative, or solvent-driven, meaning that the compositions of the coexisting phases remain the same ($\Delta\rho_i/\Delta\phi = \rho_i/\phi$).

If one specializes to the model of blockiness described above by inserting the value of $\chi$ corresponding to the spinodal stability limit, the instability direction becomes

$$\frac{\Delta\eta}{p\Delta\phi} = 1 - \frac{1-p}{p}\left[\left\{1 + \frac{M\phi p}{1-p}\left(\frac{1}{N\phi} + \frac{1}{1-\phi}\right)\right\}^{1/2} - 1\right] \tag{12}$$

This confirms that the spinodal instability lies along a dilution line ($\Delta\eta/\Delta\phi = \langle\alpha\rangle = p$) only in the limit $M \rightarrow 0$, which formally corresponds to a vanishing variance. For $M = 1$ (and $M \ll N$ in general) the phase transition has a mixed character. The interesting case occurs when $M = N$ (or $M \propto N$ in general) for which $\Delta\eta/\Delta\phi \sim (-)N^{1/2}$ in the limit of large $N$. One can write this as $\Delta\phi/\Delta\eta \rightarrow 0$ as $N \rightarrow \infty$. This shows that the phase transition tends toward being purely segregative, meaning that the overall polymer concentration in coexisting phases remains the same ($\Delta\phi = 0$). This confirms the suggestion above, that in the limit of extreme blockiness the system tends toward a segregative polymer−polymer demixing transition.

Let us now try to draw some conclusions. The main effect of randomness is to reduce the solubility of partially modified polymers beyond what would be expected from the mean degree of modification. The extent to which this occurs depends on the blockiness in substitution. For fine-grained blockiness, the phase behavior is expected to be similar to a system for which there is no randomness, albeit with a somewhat reduced solubility. For coarse-grained blockiness, where the block size is comparable to the polymer length, the nature of the phase transition changes to a polymer−polymer demixing transition. In this situation, one expects that the modified polymers (being almost fully modified) will partition into the aqueous phase, leaving the unmodified polymers behind.

The reason for considering the two extreme kinds of blockiness is now clearer: namely, one can envisage two different mechanisms of chemical modification. (This is the reason why a Markov model for the distribution of modified segments has not been used.) Fine-grained blockiness would arise if monomers are equally accessible to the modifying agent, irrespective of their surroundings. If this cannot be achieved in a one-step process (for the reason described below), it could perhaps be achieved in a two-step process, by fully modifying the polymers and then removing a random fraction of the derivative groups. Extreme blockiness on the scale of the polymer chain itself would arise if the modifying agent was present only in the aqueous phase and as such only able to access polymer which had already been solubilized. This would lead to a mixture of polymers which were either fully modified or remained unmodified and insoluble. The process of modification of insoluble polymers could still be initiated because the modifying agent is able to access the tiny proportion of the insoluble polymer segments which lie at the interface between the insoluble and aqueous phases. Experimentally, confirmation of the scenario of extreme blockiness would be given by measuring the mean degree of modification for the *dissolved* polymers. One should find that this is much in excess of the apparent mean degree of modification.

In the calculation, the major effect arises from interchain rather than intrachain heterogeneities. As mentioned in the introduction, the model is not sophisticated enough to allow for microphase separation. Such an effect would give the polymers a greater solubility than would be predicted from the present Flory−Huggins theory since the hydrophobic groups can be buried in micelles or other solution structures. The present theory could be extended to discuss these inhomogeneous situations using a Landau approach developed for random block copolymers.[4−7]

Finally, I note that in principle the above model for the phase behavior could be combined with a model for the chemical modification reaction to obtain a theory for reaction-induced solubility. However, one needs to take great care to capture the kinetics correctly.[14]

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