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# Polymer Blends

A Comprehensive Review

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## 2 Fundamentals of Polymer Blends

### 2.1 Thermodynamic Relationships

The most important characteristic of a polymer blend of two (or more) polymers is the phase behavior. Polymer blends (like low molecular weight solvents) can exhibit miscibility or phase separation and various levels of mixing in between the extremes (e.g., partial miscibility). The most important factor leading to miscibility in low molecular weight materials is the combinatorial entropy contribution which is very large compared to high molecular weight polymers. This contribution is the reason that solvent-solvent mixtures offer a much broader range of miscibility than polymer-solvent combinations. The range of miscible combinations involving polymer-polymer mixtures is even much smaller. As an example compare the miscibility of hexane-ethanol mixtures with their high molecular weight analogs of polyolefins and poly(vinyl alcohol). The former is miscible, whereas the latter is highly immiscible. This is well-demonstrated by the following discussion.

The most important relationship governing mixtures of dissimilar components 1 and 2 is:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (2.1)$$

where  $\Delta G_m$  is the free energy of mixing,  $\Delta H_m$  is the enthalpy of mixing (heat of mixing) and  $\Delta S_m$  is the entropy of mixing. For miscibility to occur,  $\Delta G_m$  must be smaller than 0. While this is a necessary requirement, it is not a sufficient requirement as the following expression must also be satisfied:

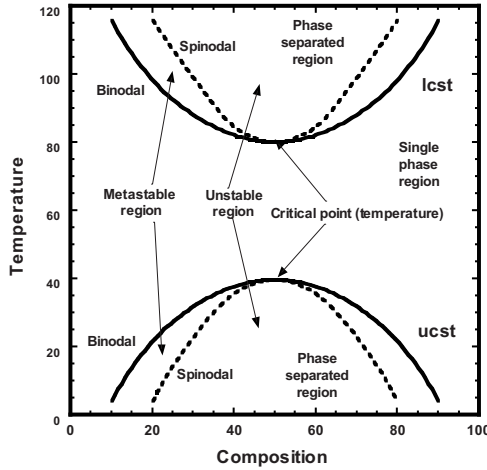
$$\left( \frac{\partial^2 \Delta G_m}{\partial \phi_i^2} \right)_{T,P} > 0 \quad (2.2)$$

Negative values of Eq. 2.2 (even though  $\Delta G_m < 0$ ) can yield an area of the phase diagram where the mixture will separate into a phase rich in component 1 and a phase rich in component 2.

For low molecular weight materials, increasing temperature generally leads to increasing miscibility as the  $T\Delta S_m$  term increases, thus driving  $\Delta G_m$  to more negative values. For higher molecular weight components, the  $T\Delta S_m$  term is small and other factors (such as non-combinatorial entropy contributions and temperature dependant  $\Delta H_m$  values) can dominate and lead to the reverse behavior, namely, decreasing miscibility with increasing temperature.

Thus, while liquid-liquid and polymer-solvent mixtures (that are borderline in miscibility) usually exhibit upper critical solution temperatures (*ucst*), polymer-polymer mixtures generally exhibit lower critical solution temperatures (*lcst*). This behavior is illustrated in Fig. 2.1 with an illustration of the free energy composition at key temperatures noted in Fig. 2.2. The binodal and spinodal curves (binodal and spinodal phase separation processes are discussed later in this chapter) are illustrated on the phase diagrams. The spinodal curve is related to the position where

$$\left( \frac{\partial^2 \Delta G_m}{\partial \phi_i^2} \right)_{T,P} = 0 \quad (2.3)$$



**Figure 2.1:** Phase diagram showing *lcst* and *ucst* behavior for polymer blends

The binodal curve is related to the equilibrium phase boundary between the single phase and the phase separated region. In a binary system, this is related to the chemical potentials of an individual component being equal in both phases as expressed by the following relationships:

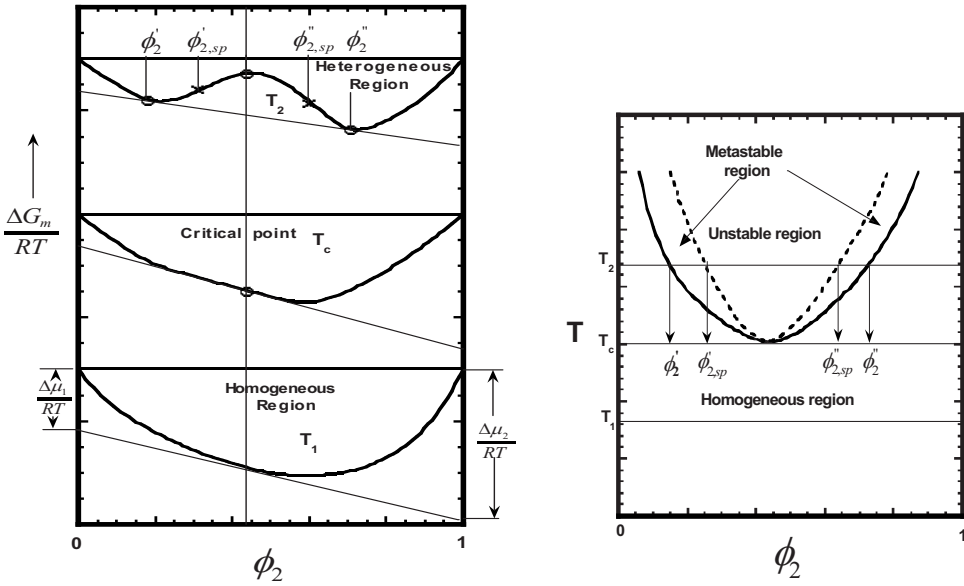
$$\Delta\mu_1^a = \Delta\mu_1^b \quad \Delta\mu_2^a = \Delta\mu_2^b \quad (2.4)$$

where 1,2 represent the two polymers and a,b represent the phases. The chemical potential is defined as the rate of change of the Gibbs function of the system with respect to the change in the number of moles of a specific component. The values of the binodal curve can be determined from the double tangent to the  $\Delta G_m$  curve shown in Fig. 2.2, as noted by Koningsveld [1]. The critical point, where the binodal and spinodal intersect, is determined from the expression:

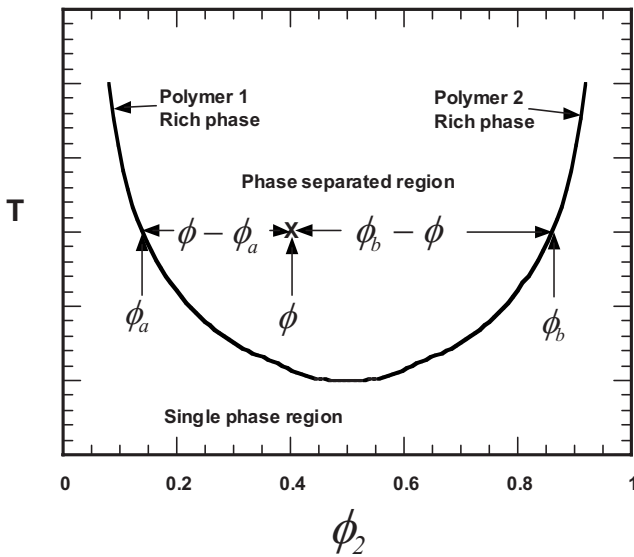
$$\left( \frac{\partial^3 \Delta G_m}{\partial \phi^3} \right)_{T,P} = 0 \quad (2.5)$$

The experimental phase diagrams are often not symmetrical, unless the molecular weights of the components are similar, and in the case of large differences in molecular weights, they can be highly non-symmetric. With phase separation, the binodal defines the composition of the component 1 rich phase and component 2 rich phase. The tie line noting temperature  $T_2$  between the binodal points can be employed to determine the relative amounts of each phase. The tie line is illustrated in Fig. 2.3. The volume fraction of component 1 rich phase,  $\phi_{1r}$ , and component 2 rich phase,  $\phi_{2r}$ , can be determined from the expression, with  $\phi$  representing the overall composition of the component noted in Fig. 2.3:

$$\frac{\phi_{1r}}{\phi_{2r}} = \frac{\phi_b - \phi}{\phi - \phi_a} \quad (2.6)$$



**Figure 2.2:** Free energy of mixing versus volume fraction generalized behavior for various positions on the phase diagram



**Figure 2.3:** Tie-line calculation of phase compositions

Highly miscible polymers exhibit single phase behavior over the entire temperature-volume fraction space available for experimental verification. If *ucst* or *lcst* behavior exists, it cannot be determined. At low temperatures, the *ucst* cannot be determined due to the glassy state restricting molecular motion (phase separation); and at higher temperatures, polymer degradation occurs before phase separation can be observed. With highly immiscible polymer blends, the phase diagram is virtually all in the two phase region with the binodal curves virtually overlapping the y axis at 0 and 1.0 volume fraction.

### 2.1.1 Combinatorial Entropy of Mixing

The entropy of mixing for mixtures of dissimilar components is an important contribution to the ability to achieve miscibility. The determination of the entropy of mixing begins with the Boltzmann relationship:

$$\Delta S_m = k \ln \Omega \quad (2.7)$$

where  $\Omega$  represent the summation of combinations of arranging  $N_1$  and  $N_2$  molecules into a regular lattice of  $N$  ( $N = N_1 + N_2$ ) cells.

$$\Omega = \frac{N!}{N_1!N_2!} \quad (2.8)$$

and application of Sterling's approximation yields:

$$\ln N! = N \ln N - N \quad (2.9)$$

Substitution of Eq. 2.9 into Eq. 2.8 and then Eq. 2.7 yields:

$$\Delta S_m = k(N \ln N - N_1 \ln N_1 - N_2 \ln N_2) = -k(N_1 \ln x_1 + N_2 \ln x_2) \quad (2.10)$$

where  $x_1 = N_1/N$  and  $x_2 = N_2/N$ . This equation is valid for equal sized low molecular weight molecules. For a mixture of solvent and polymer it was recognized that the above expression did not agree with experimental observations. Specifically for solvent (1), the term  $N_1 \ln x_1 \gg N_2 \ln x_2$ , and thus predicted that the presence of polymer would exhibit no change in the free energy of mixing as both the enthalpy and entropy would be dominated by the mole fraction,  $x_1$ , which would be  $\sim 1$  except in extremely low concentrations of solvent in the polymer. Vapor pressure measurements among other colligative property determinations showed that the free energy of mixing is changed and the value of mole fraction was replaced with volume fraction,  $\phi_i$ , to yield more realistic agreement.

For polymers, the assumption is made that the lattice is comprised of  $N$  cells with a volume of  $V$ . Each polymer molecule occupies volumes  $V_1$  and  $V_2$ , respectively, with each mer unit occupying a volume,  $V_{mer}$ . The molecular volume,  $V_i$ , is equal to the product of  $V_{mer}$  and the number of mer units. For solvents, the number of mer units is 1. The volume fractions  $\phi_1$  and  $\phi_2$  are represented by the equations:

$$\phi_1 = \frac{V_1 N_1}{V_1 N_1 + V_2 N_2}; \quad \phi_2 = \frac{V_2 N_2}{V_1 N_1 + V_2 N_2} \quad \text{and} \quad V = V_1 N_1 + V_2 N_2 \quad (2.11)$$

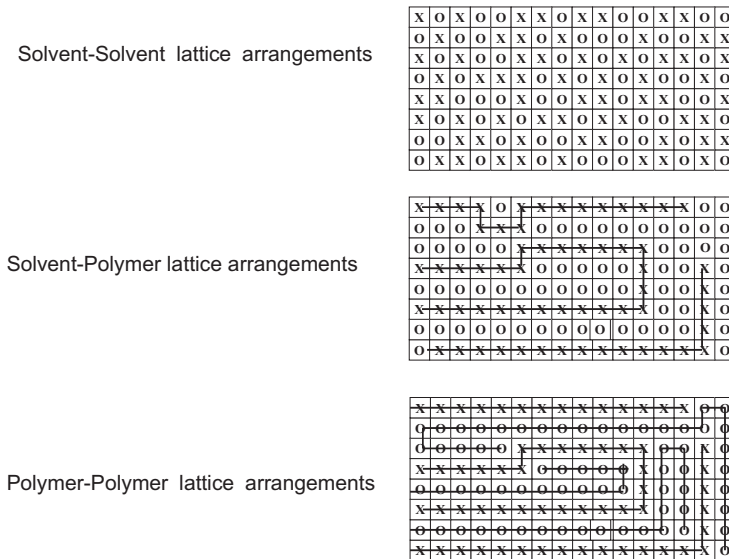
With the assumptions noted above for placement of polymers in the lattice, the substitution of the assumptions into Eq. 2.11 and Eq. 2.10 leads to:

$$\Delta S_m = -k(N_1 \ln \phi_1 + N_2 \ln \phi_2) = -kV \left[ \frac{\phi_1}{V_1} \ln \phi_1 + \frac{\phi_2}{V_2} \ln \phi_2 \right] \text{ or} \tag{2.12}$$

$$\Delta S_m = -RV \left( \frac{\phi_1}{v_1} \ln \phi_1 + \frac{\phi_2}{v_2} \ln \phi_2 \right)$$

for molecular volume or molar volume, respectively. Note that the change from mole fraction to volume fraction for  $x_1$  and  $x_2$  is valid if it is assumed that this ratio is expressed as the number of cells occupied by segments of 1 (or 2) over the total number of cells in the lattice. The one basic problem with this approach is the selection of the mer units such that the mer units of the different polymers occupy a similar volume. As with many theories, this approach is not ideal however, it allows for at least a qualitative assessment of the thermodynamics of polymer blends. The lattice arrangements for solvent-solvent, solvent-polymer and polymer-polymer combinations are illustrated in Fig. 2.4, demonstrating the combinations of arranging the molecules follows: solvent-solvent  $\gg$  solvent-polymer  $\gg$  polymer-polymer.

The combinatorial entropy of mixing (Eq. 2.12) is thus established for the Flory-Huggins theory which follows. As the  $\ln \phi_i$  value is negative,  $\Delta S_m$  is positive and the expression  $(-T\Delta S_m)$  in Eq. 2.1 leads to a negative contribution to  $\Delta G_m$ , thus improving the potential for miscibility. As noted with high molecular weight polymers, this contribution becomes negligible. A discussion of the lattice approach and derivation of the entropy of mixing can be found in [2].



**Figure 2.4:** Schematic of solvent-solvent, solvent-polymer and polymer-polymer arrangements in a lattice of N cells; visual illustration of combinatorial entropy

### 2.1.2 Enthalpy of Mixing

The enthalpy (heat) of mixing expression for Eq. 2.1 is derived from the relationship:

$$w_{12} = \frac{1}{2} (\epsilon_{11} + \epsilon_{22}) - \epsilon_{12} \quad (2.13)$$

where  $\epsilon_{ij}$  is the energy of contacts between components  $i$  and  $j$  and  $w_{12}$  is the exchange energy of interacting segments. The heat of mixing is related to  $w_{12}$  by the expression:

$$\frac{\Delta H_m}{V} = \frac{zw_{12}}{v_r} \phi_1 \phi_2 \quad (2.14)$$

where  $z$  is the coordination number (generally assumed as 8, but in the range of 6 to 12),  $v_r$  is the interacting segment volume and is often referred to as the reference volume. In this discussion,  $v_r$  can represent molecular or molar segment volumes, depending on whether molecular or molar parameters are employed in the analysis with the difference being the magnitude of the difference between  $k$  and  $R$  (Boltzmann's constant and the gas constant). A parameter termed the Flory-Huggins interaction parameter,  $\chi_{12}$ , has been typically employed, defined as:

$$\chi_{12} = \frac{zw_{12}}{kT} \quad \text{or} \quad \chi_{12} = \frac{zw_{12}}{RT} \quad (\text{for molar parameters}) \quad (2.15)$$

leading to

$$\Delta H_m = \phi_1 \phi_2 RTV \frac{\chi_{12}}{v_r} \quad (2.16)$$

For dispersive and non-polar (or modest polar) interactions,  $\epsilon_{12}$  can be estimated by a geometric mean:

$$\epsilon_{12} = (\epsilon_{11} \epsilon_{22})^{1/2} \quad \text{yielding} \quad w_{12} = \frac{1}{2} (\epsilon_{11}^{1/2} - \epsilon_{22}^{1/2})^2 \quad (2.17)$$

This leads to solubility parameter concepts (discussed later in this chapter), used by Hildebrand [3] to show that:

$$z (\epsilon_{11}^{1/2} - \epsilon_{22}^{1/2})^2 / 2v_r = (\delta_1 - \delta_2)^2 \quad (2.18)$$

Thus,

$$(\delta_1 - \delta_2)^2 = zw_{12}/v_r = \chi_{12}RT/v_r \quad \text{and} \quad \frac{\Delta H_m}{V} = (\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (2.19)$$

where  $\delta_i$  is the solubility parameter for component  $i$  (defined later in the chapter).

A discussion of the enthalpy of mixing and derivation of the above relationships can be found in [2, 3].

### 2.1.3 Flory-Huggins Theory

The most relevant theory for modeling the free energy of binary polymer mixtures is the Flory-Huggins theory, initially employed for solvent-solvent and polymer-solvent mixtures. This theory was independently derived by Flory [4, 5] and Huggins [6, 7]. The key equation (combined from discussions earlier in this chapter on entropy and enthalpy of mixing) is:

$$\Delta G_m = kTV \left[ \frac{\phi_1}{V_1} \ln \phi_1 + \frac{\phi_2}{V_2} \ln \phi_2 \right] + \phi_1 \phi_2 \chi_{12} kTV / v_r \quad (\text{molecular basis}) \quad (2.20a)$$

$$\Delta G_m = RTV \left[ \frac{\phi_1}{v_1} \ln \phi_1 + \frac{\phi_2}{v_2} \ln \phi_2 \right] + \phi_1 \phi_2 \chi_{12} RTV / v_r \quad (\text{molar basis}) \quad (2.20b)$$

where  $V$  = total volume,  $R$  = gas constant,  $\phi_i$  = volume fraction of component  $i$ ,  $V_i$  = molecular volume,  $v_i$  = molar volume of polymer chain  $i$ ,  $v_r$  = molecular or molar volume of a specific segment (depending on whether Eq. 2.20a or 2.20b is employed),  $\chi_{12}$  = Flory-Huggins interaction parameter and  $k$  is the Boltzmann's constant.  $v_r$  is often calculated as the square root of the product of the individual segmental unit molecular or molar volumes of the polymeric components ( $v_r = \sqrt{v_1 v_2}$ ).  $\chi'_{12}$  is further simplified to  $\chi_{12}$  (binary interaction parameter), defined as  $\chi'_{12} = \chi_{12}/v_r$  and often as a binary interaction density parameter,  $B$ , defined as  $B = \chi'_{12}RT$ . As the use of  $\chi_{12}$  and  $\chi'_{12}$  is often interchanged in the literature, some confusion may exist. The following discussion will employ the molar basis (Eq. 2.20b). From Eq. 2.12, it is apparent that the term in Eq. 2.20b:

$$RTV \left[ \frac{\phi_1}{v_1} \ln \phi_1 + \frac{\phi_2}{v_2} \ln \phi_2 \right] = -T\Delta S_m \quad (2.21)$$

Thus, from the relationship,  $\Delta G_m = \Delta H_m - T\Delta S_m$ , then

$$\Delta H_m = \phi_1 \phi_2 \chi_{12} RTV / v_r = \phi_1 \phi_2 B_{12} V \quad (2.22)$$

As  $v_i = M_i/\rho_i$ ; the following expression is also commonly utilized:

$$\Delta G_m = RTV \left[ \frac{\rho_1 \phi_1}{M_1} \ln \phi_1 + \frac{\rho_2 \phi_2}{M_2} \ln \phi_2 \right] + B_{12} \phi_1 \phi_2 V \quad (2.23)$$

where  $M_i$  = molecular weight of component  $i$  and  $\rho_i$  = density of component  $i$ . For simplicity, the volume is divided into both sides of the equation and some references also assume  $\rho_1 = \rho_2 = \rho$ ; allowing further simplification yielding the expression

$$\frac{\Delta G_m}{V} = \rho RT \left[ \frac{\phi_1}{M_1} \ln \phi_1 + \frac{\phi_2}{M_2} \ln \phi_2 \right] + B_{12} \phi_1 \phi_2 \quad (2.24)$$

In some references,  $\Delta G_m$  is expressed as the term  $\Delta G_m/V$  in Eq. 2.24, in those cases  $\Delta G_m$  has units of cal/cc. Unless noted otherwise,  $\Delta G_m$  in this text has units of cal. Also, in some cases,  $\rho$  is assumed to equal 1.0 g/cc and is eliminated from the equation; however, the units remain and must be accounted for.



The critical values for achieving miscibility are defined by Eqs. 2.3 and 2.5:

$$\chi'_{12,cr} = \frac{B_{12,cr}}{RT_{cr}} = \frac{1}{2} \left[ \frac{1}{v_1^{1/2}} + \frac{1}{v_2^{1/2}} \right]^2 \quad \text{and} \quad \phi_{cr} = \frac{v_1^{1/2}}{v_1^{1/2} + v_2^{1/2}} \quad (2.25)$$

or in terms of molecular weight (assuming density of the polymers is equal)

$$\chi'_{12,cr} = \frac{B_{12,cr}}{RT_{cr}} = \frac{1}{2} \rho \left[ \frac{1}{M_1^{1/2}} + \frac{1}{M_2^{1/2}} \right]^2 \quad \text{and} \quad \phi_{cr} = \frac{M_1^{1/2}}{M_1^{1/2} + M_2^{1/2}} \quad (2.26)$$

The miscibility region is therefore defined by the relationship

$$\chi'_{12} \text{ or } \frac{B_{12}}{RT} < \frac{1}{2} \left[ \frac{1}{v_1^{1/2}} + \frac{1}{v_2^{1/2}} \right]^2 \quad \text{or} \quad \chi'_{12} \text{ or } \frac{B_{12}}{RT} < \frac{1}{2} \rho \left[ \frac{1}{M_1^{1/2}} + \frac{1}{M_2^{1/2}} \right]^2 \quad (2.27)$$

As the molecular weights of the respective polymers increase,  $\chi'_{12,cr}$  and  $B_{12,cr} \rightarrow 0$ . Often, the density of both polymers is assumed = 1.0 g/cc, and  $\rho$  is eliminated from the equations (again units must be accounted for). With  $\rho = 1.0$  g/cc and equal molecular weight for the components,  $\chi'_{12,cr} = 2/M$  mole/cc and  $B_{12} = 2RT/M$  cal/cc.

For the spinodal condition (Eq. 2.3) to be satisfied, the second derivative of Eq. 2.23 yields:

$$\left( \frac{\partial^2 \Delta G_m}{\partial \phi_i^2} \right)_{T,p} = 0 = RTV \left( \frac{\rho_1}{\phi_1 M_1} + \frac{\rho_2}{\phi_2 M_2} \right) - 2B_{12}V \quad (2.28)$$

The first part of Eq. 2.20 (a and b) is the combinatorial entropy of mixing. As the molecular weight of component 1 and/or 2 increases, the negative value inherent with this expression becomes vanishingly small. For solvent-solvent and polymer-solvent mixtures, the combinatorial entropy of mixing is finite and an important contribution to the free energy of mixing. For such mixtures, strong positive values of the interaction density,  $B$ , will be required to yield phase separation. With high molecular weight polymers, the enthalpy of mixing term ( $B_{12}\phi_1\phi_2V$ ) determines the phase behavior of the polymer blend. As the magnitude and sign (positive or negative) of  $B_{12}$  is related to  $w_{12}$ , Eq. 2.13 illustrates the importance of interaction energies between unlike components compared to the averaged values of the like component interactions. In order to maximize  $\epsilon_{12}$ , specific interactions must exist between the components of the mixture.

The combinatorial entropy term is multiplied by temperature, thus illustrating improved miscibility with increasing temperature as is typically observed with solvent-solvent and polymer-solvent mixtures. With high molecular weight polymers, this term is very small, thus increasing temperature will have no significant effect. Heat of mixing experiments have shown a strong temperature dependence in cases of specific interactions (e.g., hydrogen bonding). These studies [8, 9] show an increasing (from negative to positive) heat of mixing or  $\chi_{12}$  with increasing temperature, implying that the value of  $\epsilon_{12}$  is temperature dependant. In order to provide clarity, it needs to be pointed out that negative values of  $w_{12}$ ,  $\chi'_{12}$ , and  $B_{12}$  are related to exothermic heats of mixing. It may seem confusing, but positive values for  $\Delta H_m$  indicate an endothermic heat of mixing leading to immiscibility. Negative values of  $\Delta H_m$ ,  $\chi'_{12}$ , and  $B_{12}$

for polymer-polymer mixtures invariably lead to single phase, miscible blends as the entropic contribution for the Flory-Huggins equation is always negative (assuming the expression in Eq. 2.2 is also satisfied). *The usual convention employed for polymer blends and utilized in this book is that a negative heat of mixing is exothermic and a positive heat of mixing is endothermic.* Other factors including non-combinatorial entropy of mixing terms not covered by the Flory-Huggins equation can also play a significant factor in the observed phase behavior as will be discussed briefly in the section on equation of state theories.

The Flory-Huggins approach is not directly capable of predicting *lcst* behavior unless a temperature dependent  $\chi_{12}$  value exhibiting increasing values (negative to positive) with increasing temperature is employed. The temperature dependence of  $\chi_{12}$  has often been expressed by  $\chi_{12} = a + (b/T)$ . For polymer-solvent mixtures,  $\chi_{12}$  has been expressed as a function of both temperature and concentration:  $\chi_{12} = a + (b/T) + c\phi_1 + d\phi_1^2$  [10].

### 2.1.4 Equation of State Theories

An equation of state (EOS) is basically a mathematical relationship between pressure, temperature and volume. There are many equation of state relationships employed for gases (e.g., van der Waals equation, Redlich-Kwong equation of state) as noted in the seminal book by Reid, Prausnitz and Sherwood [11]. Equation of state approaches can be applied to liquids and also polymeric systems.

The Flory-Huggins approach noted above is based on analysis of a lattice model of mixture components. This approach as an incompressible model does not allow for volume changes upon mixing, and additional entropic contributions as well as enthalpic contributions will exist for mixtures with non-additive volume-composition behavior. Equation of state models developed by Prigogine [12] for liquid mixtures in the 1950s have been applied to polymer-solvent solutions by Flory et al. in the 1960s [13]. Reduced variables of volume, temperature and pressure are employed for an equation of state from which the thermodynamic relationships are applied to determine the free energy of mixing, the binodal and spinodal curves, the critical points and thus the phase behavior. The specific equation of state and additivity rules allow for different equation of state approaches. While the equation of state theories offer improved quantitative information on the phase behavior of polymer mixtures, they are considerably more complex and require extensive work to compare theory with experimental results. The basis of the equation of state approach starts with the relationship:  $(\partial\mu_i/\partial P) = v_i$ , where  $v_i$  is the partial molar volume of component  $i$  and  $\mu_i$  is the chemical potential of component  $i$ . Thus, the PVT relationships for polymers can be related to the phase behavior as exemplified in the following discussion.

The Flory equation of state approach has been shown to be quite applicable to polymer mixtures (see McMaster [14]). The Flory equation of state approach involved the characterization of components by three parameters:  $v^*$  (the characteristic volume),  $T^*$  (the characteristic temperature) and  $P^*$  (the characteristic pressure). Reduced variables are defined as:

$$\tilde{v} = v/v^* \quad \tilde{P} = P/P^* \quad \tilde{T} = T/T^* \quad (2.29)$$

The volume,  $v^*$ , is the hard core volume of a polymer segment and  $v$  is the actual volume of the segment. The reduced volume,  $\tilde{v}$ , is then the reduced volume per segment.  $v^*$ ,  $\tilde{v}$ , and  $v$  are expressed as molar quantities in this discussion.

The corresponding equation of state (derivation given by Flory [13]) is:

$$\tilde{P}_i \tilde{v}_i / \tilde{T}_i = \tilde{v}_i^{1/3} / (\tilde{v}_i^{1/3} - 1) - 1 / \tilde{v}_i \tilde{T}_i \quad (2.30)$$

The key parameters of  $\tilde{v}$  and  $\tilde{P}$  can be determined from the thermal expansion coefficient,  $\alpha$ , and the thermal pressure coefficient,  $\gamma$

$$\alpha = (1/V)(\partial V/\partial T)_{P,N_i} \quad (2.31)$$

$$\tilde{v}^{1/3} = (3 + 4\alpha T)/(3 + 3\alpha T) \quad (2.32)$$

$$\gamma = (\partial P/\partial T)_{V,N_i} \quad \text{and} \quad P^* = \gamma T \tilde{v}^2 \quad (2.33)$$

$T^*$  is determined at the limit of zero pressure yielding:

$$T^* = T \left\{ \tilde{v}^{4/3} / (\tilde{v}^{1/3} - 1) \right\} \quad (2.34)$$

A constant interaction term  $X_{12}$  (similar to a binary interaction parameter) is defined and related by

$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \theta_2 X_{12} \quad (2.35)$$

$\phi_i$  = volume fraction of component  $i$  based on hard core volume;  $\theta_2$  = segment surface fraction.  $X_{12}$  is related to  $\chi_{12}$  as shown by Patterson and Robard [15]

$$\frac{\chi_{12}}{M_1 \tilde{v}_{1sp}} = \frac{P_1^*}{RT_1^*} \left[ \frac{\tilde{v}_1^{1/3} X_{12}}{(\tilde{v}_1^{1/3} - 1) P_1^*} \right] + \left[ \frac{\tilde{v}_1^{1/3}}{2(4/3 - \tilde{v}_1^{1/3})} \right] \left[ \left( 1 - \frac{T_1^*}{T_2^*} \right)^2 \right] \quad (2.36)$$

The mixing relationship is defined as:

$$\phi_1 = m_1 v_{1sp}^* / (m_1 v_{1sp}^* + m_2 v_{2sp}^*) \quad (2.37)$$

$\phi_2 = 1 - \phi_1$ ;  $m_i$  = mass of component I, where  $v_{isp}^*$  is based on hard core volume per unit mass (e.g., gram). The enthalpy change on mixing is equal to [16]:

$$\Delta H_m = \left( m_1 v_{1sp}^* + m_2 v_{2sp}^* \right) \left\{ (\phi_1 P_1^* \tilde{v}_1) + (\phi_2 P_2^* / \tilde{v}_2) - (P^* / \tilde{v}) \right\} \quad (2.38)$$

The determination of the free energy of mixing and the resultant binodal and spinodal curves (phase diagram) employing this approach has been detailed in various papers and reviews and is too complex to repeat here. These solutions were obtained from the expression

$$\Delta G_m = -kT \ln \left( \frac{Z}{\prod_{i=1}^n Z_i} \right) \quad \text{where } Z, (Z_i) \text{ is obtained from } Z = (Q) \left( \frac{2\pi m_i kT}{h^2} \right)^{3N_i c_i r_i / 2} \quad (2.39)$$

where

$$Q = \Omega_{comb} (\gamma v_i^*)^{N_i c_i r_i} (v_i^{1/3} - 1)^{3N_i c_i r_i} \exp(U_{oi}/kT) \quad (2.40)$$

and  $\gamma$  is the geometric factor,  $3c$  is the number of external degrees of freedom for one segment,  $r_i$  is the number of segments per chain. The origin of these equations and the formalism for their application to equation of state thermodynamics is noted in references [11–14, 17]. The binodal and spinodal relationships derived from this approach are complex relationships, expressed as a function of the many variables (e.g.,  $P^*$ ,  $T^*$ ,  $v^*$ ,  $v^{1/3}$ ,  $X_{12}$ ,  $Q_{12}$ ,  $\theta_i$ ), some of which are determined from PVT data and others comprising adjustable parameters.  $Q_{12}$  is related to additional entropy contributions of which one situation is a loss in entropy due to non-random mixing resulting from specific interactions.

$$\begin{aligned} \frac{\Delta G_m}{kT} = & \sum_{i=1}^n N_i \ln \psi_i + \sum_{i=1}^n 3r_i N_i (c_i - c) \ln [(2\pi m_i kT)^{1/2} / h] \\ & + 3\bar{r}N \sum_{j=2}^n \sum_{i=1}^{j-1} \psi_i \psi_j c_{ij} \ln [(\gamma v^*)^{1/3} (\bar{v}^{1/3} - 1)] + 3 \sum_{i=1}^n r_i N_i c_i \ln \left[ \frac{\bar{v}_i^{1/3} - 1}{\bar{v}^{1/3} - 1} \right] \\ & + \frac{\bar{r}Nv^*}{kT} \left[ \sum_{i=1}^n \psi_i E_i^* \left( \frac{1}{\bar{v}_i} - \frac{1}{\bar{v}} \right) \right] + \frac{\bar{r}Nv^*}{kT} \sum_{j=2}^n \sum_{i=1}^{j-1} \psi_i \theta_j \left( \frac{X_{ij}}{\bar{v}} - T\bar{v}_i Q_{ij} \right) \end{aligned} \quad (2.41)$$

where  $\psi_i$  is the segment fraction of component  $i$ ,  $\theta_i$  is the surface fraction of segment  $i$ , and  $c$  represents the total external degrees of freedom. The spinodal and binodal equations are even more complex, therefore the reader is directed to [14, 17].

One of the key results from application of the equation of state approach to predicting phase behavior is the observation that *lcst* behavior can be predicted based upon a non-combinatorial contribution to entropy inherent with this formalism. The Flory-Huggins lattice model theory is an incompressible model that does not allow for the compressibility effects on the system thermodynamics. For equation of state approaches that allow for compressibility effects, the miscibility condition expressed by Eq. 2.2 [18] becomes:

$$\left( \frac{\partial^2 \Delta G_m}{\partial \phi_i^2} \right)_V + \left( \frac{\partial V}{\partial P} \right)_{T, \phi_i} \left( \frac{\partial^2 \Delta G_m}{\partial \phi_i \partial V} \right)^2 > 0 \quad (2.42)$$

As  $\left( \frac{\partial V}{\partial P} \right)_{T, \phi_i} < 0$  and  $\left( \frac{\partial^2 \Delta G_m}{\partial \phi_i \partial V} \right) \geq 0$ , the compressibility nature is a negative contribution towards achieving miscibility. However, by allowing an interaction parameter which varies with temperature, the ability to predict *lcst* behavior offered considerable interest when initially recognized by McMaster [14]. The equation of state theories also allow a prediction of the effect of thermal pressure coefficient and thermal expansion coefficient differences on the resultant phase diagram. An increase in the thermal expansion coefficient difference ( $\alpha_1 - \alpha_2$ ) results in decreasing the free energy of mixing and shifting the miscibility curve downward. An increase in the thermal pressure coefficient difference ( $\gamma_1 - \gamma_2$ ) also shifts the miscibility curve down and shifts the critical composition. The generalized behavior of the phase diagram predicted by McMaster's analysis of the Flory equation of state as function of several variables is illustrated in Fig. 2.5 (a, b, c, d). Qualitative trends for achieving miscibility predicted by this analysis include the observation that  $T^*$  values should be similar for the components. If

$T_1^* > T_2^*$ , then  $P_1^* > P_2^*$  to balance the  $T_i^*$  mismatch to maintain miscibility. The  $\alpha$  (thermal coefficient of expansion) values should be similar to maintain miscibility. Different  $\alpha$  values are the primary cause for *lcst* behavior as predicted by the Flory equation of state. In the absence of specific interactions and when  $X_{12}$  and  $Q_{12}$  are essentially zero, miscibility will be observed when  $\alpha_1 = \alpha_2$  and  $\gamma_1 = \gamma_2$  [16]. This was noted to be the case for structurally similar blends of different polyethersulfones and polyetherimide/poly(ether ether ketone) blends. This situation would also be the case for structurally similar polymers such as the miscible blend of the isomeric polymers poly(methyl acrylate) and poly(vinyl acetate). This situation corresponds to matched solubility parameters for non-interacting polymeric components.

While *lcst* behavior has been generally considered to be a consequence of the non-combinatorial entropy of mixing predicted by equation-of-state models, the experimental observation that  $\Delta H_m$  for polymer blends with specific interactions increases to more positive values with increasing temperature implies that  $\chi_{12}$  (and  $B_{12}$ ) are indeed temperature dependent with the potential for *lcst* behavior. The Flory EOS approach does not adequately predict the phase behavior of polymer blends exhibiting specific interactions. Comparison of the Flory EOS with experimental data on hydrogen bonding blends (ethylene-vinyl acetate copolymer blends with chlorinated polyethylene and PVC with poly(n-butyl acrylate)) showed poor agreement with prediction of the *lcst* position [19]. A modification of the Flory EOS approach (termed oriented quasichemical approximation) to account for nonrandom orientation present for specific interactions was evaluated and showed good agreement with prediction of lower critical solution temperatures experimentally observed [19].

Additional examples of the application of the Flory EOS to polymer blends include polystyrene/poly(vinyl methyl ether) [15, 20, 21], oligomeric polystyrene/polybutadiene [22], ethylene-vinyl acetate/chlorinated polyethylene [23], poly( $\epsilon$ -caprolactone)/PVC [24], poly(ether sulfone)/poly(ethylene oxide) [25].

The other equation of state model widely noted is the Sanchez-Lacombe lattice fluid theory [26–28]. The Sanchez-Lacombe equation of state is:

$$\tilde{P}\tilde{v}\tilde{T} = -\tilde{v}[\ln(1 - \tilde{\rho}) + (1 - 1/r)\tilde{\rho}] - 1\tilde{T}\tilde{v} \quad (2.43)$$

where  $T^* = \varepsilon^*/k$  ( $\varepsilon^*$  is the characteristic interaction energy);  $kT^* = P^*V^*$ ;  $r = M(P^*/kT^*\rho^*)$  and  $\tilde{\rho} = 1/\tilde{v}\rho/\rho^*$  which reduces to:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1 - \tilde{\rho}) + (1 - 1/r)\tilde{\rho}] = 0 \quad (2.44)$$

as  $1/r$  goes to zero at high molecular weight then:

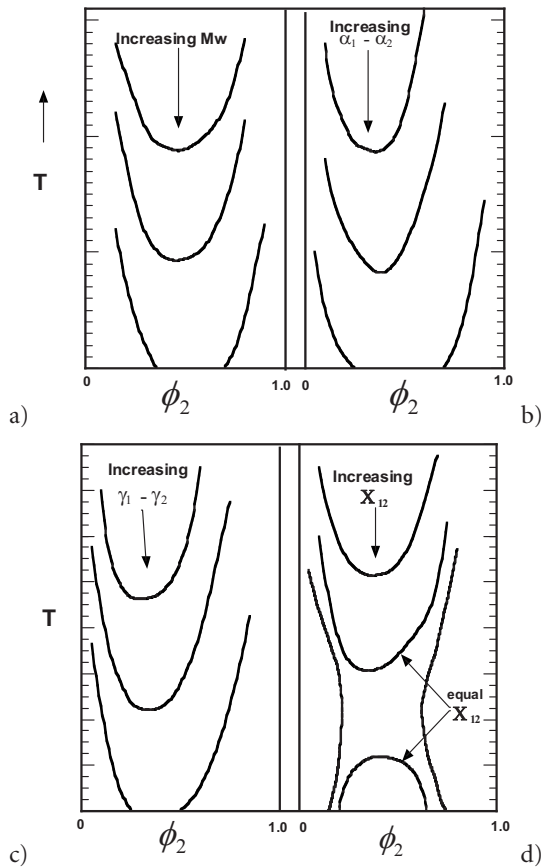
$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1 - \tilde{\rho}) + \tilde{\rho}] = 0 \quad (2.45)$$

The characteristic pressure for a binary mixture for the Sanchez-Lacombe EOS is expressed as:

$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \phi_2 \Delta P_{12}^* \quad (2.46)$$

where  $\Delta P_{12}^* = P_1^* + P_2^* - 2P_{12}^*$ .  $\Delta P_{12}^*$  has similarities to the binary interaction density parameter,  $B_{12}$ , and negative values of  $\Delta P_{12}^*$  predict miscibility.

The Sanchez-Lacombe EOS has been applied to PMMA/SAN [29], polycarbonate (PC), tetramethyl polycarbonate (TMPC) and poly( $\epsilon$ -caprolactone) binary and ternary blends [30],



**Figure 2.5:** Generalized phase diagrams from equation of state predictions involving key variables (adapted from reference: McMaster, L. P., *Macromolecules*, (1973) 6, p. 760, copyright (1973) American Chemical Society)

polystyrene/polyisoprene and polystyrene/poly(cyclohexyl methacrylate) [31] and styrene-maleic anhydride copolymers/polymethacrylates [32].

Additional examples of equation of state models include the lattice gas model (Kleintjens et al, [33, 34], Simha-Somcynsky hole theory [35], Patterson [36], the cell-hole theory (Jain and Simha [37-39], the perturbed hard-sphere-chain equation of state [40, 41] and the modified cell model (Dee and Walsh) [42]. A comparison of various models showed similar predictions of the phase behavior of polymer blends for the Patterson equation of state, the Dee and Walsh modified cell model and the Sanchez-Lacombe equation of state, but differences with the Simha-Somcynsky theory [43]. The measurement and tabulation of PVT data for polymers can be found in [44].

