# 8 Polymers in Solution

## 8.1 THERMODYNAMICS OF POLYMER SOLUTIONS

The interaction of long-chain molecules with liquids is of considerable interest from both a practical and theoretical viewpoint. For linear and branched polymers, liquids that will dissolve the polymer completely to form a homogeneous solution can usually be found, whereas cross-linked networks will only swell when in contact with compatible liquids. In this chapter, we shall deal with linear or branched polymers and treat the swelling of networks in Chapter 14.

When an amorphous polymer is mixed with a suitable solvent, it disperses in the solvent and behaves as though it too is a liquid. In a good solvent, classed as one that is highly compatible with the polymer, the liquid–polymer interactions expand the polymer coil from its unperturbed dimensions in proportion to the extent of these interactions. In a "poor" solvent, the interactions are fewer, and coil expansion or perturbation is restricted.

The fundamental thermodynamic equation used to describe these systems relates the Gibbs free-energy function G to the enthalpy H and entropy S; i.e., G = H - TS. A homogeneous solution is obtained when the Gibbs free energy of mixing  $\Delta G^{\rm M} < 0$ , i.e., when the Gibbs free energy of the solution  $G_{12}$  is lower than the Gibbs functions of the components of the mixture  $G_1$  and  $G_2$ .

$$\Delta G^{\rm M} = G_{12} - (G_1 + G_2) \tag{8.1}$$

## 8.2 IDEAL MIXTURES OF SMALL MOLECULES

To understand the behavior of polymers in solution more fully, knowledge of the enthalpic and entropic contributions to  $\Delta G^{M}$  is essential, and it is instructive to consider first mixtures of small molecules to establish some fundamental rules concerning ideal and nonideal behavior. Raoult's law is a useful starting point and defines an ideal solution as one in which the activity of each component in a mixture  $a_i$  is equal to its mole fraction  $x_i$ . This is valid only for components of comparable size and where the intermolecular forces acting between both like and unlike molecules are equal. The latter requirement means that component molecules of each species can interchange positions without altering the total energy of the system; i.e.,  $\Delta H^{M} = 0$  and, consequently, it only remains for the entropy contribution  $\Delta S^{M}$  to be calculated.

For a system in a given state, the entropy is related to the number of distinguishable arrangements the components in that state can adopt and can be calculated from the Boltzmann law,  $S = k \ln \Omega$ , where  $\Omega$  is the number of statistical microstates available to the system. We can begin by considering the mixing of  $N_1$  molecules of component

1 with  $N_2$  molecules of component 2, and this can be assumed to take place on a hypothetical lattice containing  $(N_1 + N_2) = N_0$  cells of equal size. Although this formalism is not strictly necessary for the analysis, the arrangement of spherical molecules of equal size in the liquid state will, to the first near-neighbor approximation, be similar to a regular lattice structure, and so it is a useful structure to use as a framework for the mixing process.

The total number of possible ways in which the component molecules can be arranged on the lattice increases when mixing takes place and is equal to  $(N_1 + N_2)! = N_0!$ , but as the interchanging of a molecule of component 1 with another molecule component 1, or component 2 with component 2 will be an indistinguishable process, the net number of distinguishable arrangements will be

$$\Omega = \frac{(N_1 + N_2)!}{N_1! N_2!} = \frac{N_0!}{\Pi N_i!}$$
(8.2)

The configurational (or combinatorial) entropy  $S_c$  can then be derived from the Boltzmann law and

$$S_{\rm c} = k \ln \frac{N_0!}{N_1! N_2!} = k \left( \ln N_0! - \ln N_1! - \ln N_2! \right)$$
(8.3)

For large values of  $N_i$ , Stirling's approximation can be used to deal with the factorials; i.e.,  $\ln N! = N \ln N - N$ , and Equation 8.3 becomes

$$S_{\rm c} = k(N_0 \ln N_0 - N_0 - N_1 \ln N_1 + N_1 - N_2 \ln N_2 + N_2)$$
(8.4)

which on dividing by  $N_0$  gives

$$S_{\rm c} = -k \left[ N_1 \ln \frac{N_1}{N_0} + N_2 \ln \frac{N_2}{N_0} \right]$$
(8.5)

If  $x_i = (N_i/N_0)$ , the mole fraction of component *i*, then

$$S_{\rm c} = -k[N_1 \ln x_1 + N_2 \ln x_2]$$
(8.6)

For pure components,  $x_i = 1$ , and as  $\Delta S^M$ , the change in entropy on mixing, is given by  $(S_c - S_1 - S_2)$ , we can write

$$S_{\rm c} = \Delta S_{\rm id}^{\rm M} = -k \sum N_i \ln x_{\rm i}$$

So for a two-component mixture,

$$\Delta S_{\rm id}^{\rm M} = -k[N_1 \ln x_1 + N_2 \ln x_2]$$
(8.7)

This expression is derived on the assumptions that (1) the volume change on mixing  $\Delta V^{\rm M} = 0$ , (2) the molecules are all of equal size, (3) all possible arrangements have the same energy,  $\Delta H^{\rm M} = 0$ , and (4) the motion of the components about their equilibrium positions remains unchanged on mixing. Thus, the free energy of mixing,  $\Delta G^{\rm M}$ , is

$$\Delta G^{\rm M} = -T\Delta S^{\rm M} = kT(N_1 \ln x_1 + N_2 \ln x_2)$$
(8.8)

which shows that mixing in ideal systems is an entropically driven, spontaneous process.

# 8.3 NONIDEAL SOLUTIONS

Any deviations from assumptions (1) to (4) will constitute a deviation from ideality - an ideal solution is a rare occurrence - and several more realistic types of solution can be identified:

- 1. Athermal solutions, where  $\Delta H^{M} = 0$  but  $\Delta S^{M}$  is not ideal
- 2. *Regular* solutions, where  $\Delta S^{M}$  is ideal but  $\Delta H^{M} \neq 0$
- 3. *Irregular* solutions, in which both  $\Delta S^{M}$  and  $\Delta H^{M}$  deviate from their ideal values

Polymer solutions tend to fall into category (3), and the nonideal behavior can be attributed not only to the existence of a finite heat of mixing but also to the large difference in size between the polymer and solvent molecules. The polymer chain can be regarded as a series of small segments covalently bonded together, and it is the effect of this chain connectivity that leads to deviations from an ideal entropy of mixing. The effect of connectivity can be assessed by calculating the entropy change associated with the different number of ways of arranging polymer chains and solvent molecules on a lattice and, as will be demonstrated, this differs from that calculated for the ideal solution. This is embodied in the theory developed by Flory and Huggins but still represents only the combinatorial contribution, whereas there are other (noncombinatorial) contributions to the entropy that come from the interaction of the polymer with the solvent and are much harder to quantify. Nevertheless, the Flory–Huggins theory forms the cornerstone of polymer solution thermodynamics and is worth considering further.

# 8.4 FLORY-HUGGINS THEORY: ENTROPY OF MIXING

The dissolution of a polymer in a solvent can be regarded as a two-stage process. The polymer exists initially in the solid state in which it is restricted to only one of the many conformations that are available to it as a free isolated molecule. On passing into the liquid solution, the chain achieves relative freedom and can now change rapidly among a multitude of possible equi-energetic conformations, dictated partly by the chain flexibility and partly by the interactions with the solvent.

Flory and Huggins considered that formation of the solution depends on (1) the transfer of the polymer chain from a pure, perfectly ordered state to a state of disorder, which has the necessary freedom to allow the chain to be placed randomly on a lattice, and (2) the mixing process of the flexible chains with solvent molecules (Figure 8.1).

The formalism of the lattice was used for convenience to calculate the combinatorial entropy of mixing according to the method outlined in Section 8.2 for small molecules, including the same starting assumptions and restrictions.

Consider a polymer chain consisting of r covalently bonded segments whose size is the same as the solvent molecules, i.e.,  $r = (V_2/V_1)$ , where  $V_i$  is the molar volume of component *i*. To calculate the number of ways this chain can be added to a lattice, the necessary restriction imposed is that the segments must occupy rcontiguous sites on the lattice because of the connectivity. The problem is to examine the mixing of  $N_1$  solvent molecules with  $N_2$  monodisperse polymer molecules comprising r segments; we can begin by adding i polymer molecules to an empty lattice with a total number of cells  $N_0$ .

$$N_0 = (N_1 + rN_2) \tag{8.9}$$

Thus, the number of vacant cells left, which can accommodate the next (i + 1) molecule, is given by

$$(N_0 - ri)$$
 (8.10)

The (i + 1) molecule can now be placed on the lattice, segment by segment, bearing in mind the restrictions imposed, i.e., the connectivity of the segments, which requires the placing of each segment in a cell adjoining the preceding one. This in turn will depend on the availability of a suitable vacancy. The first segment can be placed in any empty cell, but the second segment is restricted to the immediate near neighbors surrounding the first (see Figure 8.1). This can be given by the coordination number of the lattice *z*, but we must also know if a cell in the coordination shell is empty. If we let  $p_i$  be the probability that an adjacent cell is vacant, then, to a reasonable approximation, this can be equated with the fraction of cells occupied by *i* polymer chains on the lattice, i.e.,

$$p_{\rm i} = (N_0 - {\rm ri})/N_0$$
 (8.11)

which is valid for large values of z. So the expected number of empty cells available for the second segment is  $zp_i$ , and having removed one more vacant cell from the immediate vicinity, the third and each succeeding segment will have  $(z - 1)p_i$  empty cells to choose from. The total number of ways in which the (i + 1) molecule can be placed on the lattice is then

$$\omega_{(i+1)} = (N_0 - ri)z(z-1)^{r-2}[(N_0 - ri)/N_0]^{r-1} = (N_0 - ri)^r [(z-1)/N_0]^{r-1}$$
(8.12)



**FIGURE 8.1** Placement of polymer chains and solvent molecules on a lattice as required by the Flory–Huggins theory.

This gives the set of possible ways in which the (i + 1) molecule can be accommodated on the lattice. The total number of ways for all  $N_2$  molecules to be placed can then be obtained from the product of all possible ways, i.e.,

$$\omega_1 \omega_2 \dots \omega_i \dots \omega_{N_2} = \prod_{i=1}^{N_2} \omega_i$$

The polymer molecules are all identical and so, by analogy with Equation 8.2, the total number of distinguishable ways of adding  $N_2$  polymer molecules is

$$\Omega_p = \prod_{i=1}^{N_2} \omega_i / N_2 !$$
(8.13)

Substituting for  $\omega_i$  gives

$$\omega_{p} = \frac{1}{N_{2}!} \prod_{i=1}^{N_{2}} \{ [N_{0} - r(i-1)]^{r} [(z-1)/N_{0}]^{r-1} \}$$

$$= \left(\frac{1}{N_{2}!}\right) \left(\frac{z-1}{N_{0}}\right)^{N_{2}(r-1)} \prod_{i=1}^{N_{2}} \{N_{0} - r(i-1)\}^{r}$$
(8.14)

To evaluate the product term, we can multiply and divide by r

$$\prod_{i=1}^{N_2} \{N_0 - r(i-1)\}^r = r^{(N_2 r)} \prod_{i=1}^{N_2} \left\{ \frac{N_0}{r} - i + 1 \right\}^r$$
(8.15)

This can be converted into the more convenient factorial form by remembering that the product

$$\left(\frac{N_0}{r} + 1 - 1\right)^r \left(\frac{N_0}{r} + 1 - 2\right)^r \left(\frac{N_0}{r} + 1 - 3\right)^r \cdots \left(\frac{N_0}{r} + 1 - N_2\right)^r$$
(8.16)

is equivalent to

$$\left\{\frac{(N_0/\mathbf{r})!}{(N_0/\mathbf{r}-N_2)!}\right\}^{\mathbf{r}} = \left\{\frac{(N_0/\mathbf{r})!}{(N_1/\mathbf{r})!}\right\}^{\mathbf{r}}$$
(8.17)

and so Equation 8.14 can be written as

$$\Omega_{p} = \left(\frac{1}{N_{2}!}\right) r^{N_{2}r} \left\{\frac{(N_{0}/r)!}{(N_{1}/r)!}\right\}^{r} \left[\frac{z-1}{N_{0}}\right]^{N_{2}(r-1)}$$
(8.18)

The remaining empty cells on the lattice can now be filled by solvent molecules, but as there is only one distinguishable way in which this can be done,  $\Omega_s = 1$ , there is no further contribution to  $\Omega_p$  and the entropy of the system. The latter can now be calculated from the Boltzmann equation. The factorials can again be approximated using Stirling's relation and, although this requires considerable manipulation, which will be omitted here, it can eventually be shown that

$$S^{\rm M}/k = \ln \Omega_p = -N_1 \ln \left(\frac{N_1}{N_0}\right) - N_2 \ln \left(\frac{N_2}{N_0}\right) + N_2 \left\{ (r-1)\ln(z-1) - (r-1) \right\}$$
(8.19)

To convert this into a form that will allow us to express this in the correct site fraction form, we can add and subtract  $N_2 \ln R$  on the R.H.S. of Equation 8.19 to give

$$S^{M}/k = -N_{1} \ln\left[\frac{N_{1}}{N_{1} + rN_{2}}\right] - N_{2} \ln\left[\frac{rN_{2}}{N_{1} + rN_{2}}\right] + N_{2} \left\{(r-1)\ln\frac{(z-1)}{e} + \ln r\right\}$$
(8.20)

For the pure solvent,  $N_2 = 0$  and the entropy  $S_1 = 0$ . Similarly, the entropy of the pure polymer  $S_2$  can be obtained for  $N_1 = 0$ , which gives

$$S_2 = N_2 \left\{ (r-1) \ln \frac{(z-1)}{e} + \ln r \right\}$$
(8.21)

Equation 8.21 then represents the entropy associated with the disordered or amorphous polymer on the lattice in the absence of solvent.

It follows that the entropy change on mixing disordered polymer and solvent is

$$\Delta S^{\rm M} = S^{\rm M} - S_1 - S_2 = -k \{ N_1 \ln \phi_1 + N_2 \ln \phi_2 \}$$
(8.22)

where  $\phi_i$ , the volume fraction, can replace the site fraction if it is considered that the number of sites occupied by the polymer and solvent is proportional to their respective volumes.

Equation 8.22 is the expression for the combinatorial entropy of mixing of an athermal polymer solution, and comparison with Equation 8.7 shows that they are similar in form except for the fact that now the volume fraction is found to be the most convenient way of expressing the entropy change rather than the mole fraction used for small molecules. This change arises from the differences in size between the components, which would normally mean mole fractions close to unity for the solvent, especially when dilute solutions are being studied.

We can gain a further understanding of how the size of the polymer chain affects the magnitude of  $\Delta S^{M}$  and why it differs from  $\Delta S_{id}^{M}$  (Equation 8.7) by recasting Equation 8.22 in terms of the volume fractions  $\phi_{i} = (n_{i}V_{i}/V)$ , where  $n_{i}$  and  $V_{i}$  represent the number of moles and the volume of component *i*, respectively, and *V* is the total volume.

As  $V_i$  can conveniently be expressed as a function of a reference volume  $V_0$  such that  $V_i = r_i V_0$  and assuming that, without introducing significant error, r can be equated with the degree of polymerization for the polymer, then

$$\Delta S^{\mathrm{M}} = -\frac{RV}{V_0} \left[ \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 \right]$$
(8.23)

If the volume fraction form is retained, then for a simple liquid mixture,  $r_1 = r_2 = 1$ , but for a polymer solution,  $r_2 >> 1$  and the last term in Equation 8.23 will be smaller than the equivalent term calculated for small molecules. Consequently,  $\Delta S^{M}$  per mole of lattice sites (or equivalent volume) will be very much less than  $\Delta S_{id}^{M}$ , and the contribution of the combinatorial entropy to the mixing process in a polymer solution is not as large as that for solutions of small molecules when calculated in terms of volume fractions and expressed as per mole of sites.

#### 8.5 ENTHALPY CHANGE ON MIXING

The derivation of  $\Delta S^{M}$  from the lattice theory has been made on the assumption that no heat or energy change occurs on mixing. This is an uncommon situation as experimental experience suggests that the energy change is finite. We can make use of regular solution theory to obtain an expression for  $\Delta H^{M}$  where this change in energy is assumed to arise from the formation of new solvent–polymer (1–2) contacts on mixing, which replace some of the (1–1) and (2–2) contacts present in the pure solvent, and the pure polymer components, respectively. This can be represented by a quasi-chemical process

$$\frac{1}{2}(1-1) + \frac{1}{2}(2-2) \to (1-2) \tag{8.24}$$

where the formation of a solvent–polymer contact requires first the breaking of (1–1) and (2–2) contacts, and can be expressed as an interchange energy  $\Delta \varepsilon_{12}$  per contact, given by

$$\Delta U^{\mathrm{M}} = \Delta \varepsilon_{12} = \varepsilon_{12} - \frac{1}{2} (\varepsilon_{11} + \varepsilon_{22}) \tag{8.25}$$

Here,  $\varepsilon_{ii}$  and  $\varepsilon_{ij}$  are the contact energies for each species. The energy of mixing  $\Delta U^{M}$  can be replaced by  $\Delta H^{M}$  if no volume change takes place on mixing, and for q new contacts formed in solution

$$\Delta H^{\rm M} = q \Delta \varepsilon_{12} \tag{8.26}$$

The number of contacts can be estimated from the lattice model by assuming that the probability of having a lattice cell occupied by a solvent molecule is simply the volume fraction  $\phi_1$ . This means that each polymer molecule will be surrounded by ( $\phi_1$  rz) solvent molecules, and for  $N_2$  polymer molecules

$$\Delta H^{\rm M} = N_2 \phi_1 \ rz \ \Delta \varepsilon_{12} = N_1 \phi_2 \ z \ \Delta \varepsilon_{12} \tag{8.27}$$

considering the definition of  $\phi_2$ , i.e.,  $rN_2\phi_1 = N_1\phi_2$ .

This equation is the van Laar expression derived for regular solutions and shows that this approach can be applied to polymer systems. To eliminate *z*, a dimensionless parameter ( $\chi_1$ ) per solvent molecule is defined as

$$kT\chi_1 = z \ \Delta \varepsilon_{12} \tag{8.28}$$

which is the difference in energy between a solvent molecule when it is immersed in pure polymer and when in pure solvent. It can also be expressed in the alternative form  $RT\chi_1 = BV_1$ , where B is now an interaction density.

The final expression is

$$\Delta H^{\rm M} = kT \chi_1 N_1 \phi_2 \tag{8.29}$$

and the interaction parameter  $\chi_1$  is an important feature of polymer solution theory, which will be met with frequently. The Flory–Huggins interaction parameter is zero for athermal solutions, positive for endothermic, and negative for exothermic mixing.

#### 8.6 FREE ENERGY OF MIXING

Having calculated the entropy and enthalpy contributions to mixing, these can now be combined to give the expression for the free energy of mixing,  $\Delta G^{M} = \Delta H^{M} - T\Delta S^{M}$  as

$$\Delta G^{\rm M} = kT \underbrace{\left[ N_1 \ln \phi_1 + N_2 \ln \phi_2 \right]}_{\text{Combinatorial term}} + \underbrace{N_1 \phi_2 \chi_1}_{\text{Contact}}$$
(8.30)

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It is more useful to express Equation 8.30 in terms of the chemical potentials of the pure solvent ( $\mu_1^0$ ), by differentiating the expression with respect to the number of solvent molecules,  $N_1$ , to obtain the partial molar Gibbs free energy of dilution (after multiplying by Avogadro's number),

$$\frac{\partial \Delta G^{\mathrm{M}}}{\partial N_{1}} = (\mu_{1} - \mu_{1}^{0}) = RT \left[ \ln\left(1 - \phi_{2}\right) + \left(1 - \frac{1}{r}\right) \phi_{2} + \chi_{1} \phi_{2}^{2} \right]$$
(8.31)

This could also be carried out for the polymer  $(N_2)$ , but as it makes no difference which one is taken (both having started from  $\Delta G^M$ ), Equation 8.31 is more convenient to use. Although this expression is not strictly valid for the dilute solution regime, it can be converted into a structure that is extremely informative about deviations from ideal solution behavior encountered when measuring the molar mass by techniques such as osmotic pressure. If the logarithmic term is expanded using a Taylor series,

$$\ln(1-\phi_2) = -\phi_2 - \phi_2^2/2 - \phi_2^3/3...$$

but truncated after the squared term, assuming  $\phi_2$  is small, then

$$(\mu_1 - \mu_1^0) = -RT[(\phi_2/r) + (\frac{1}{2} - \chi_1)\phi_2^2]$$
(8.32)

This can be modified by remembering that  $\mathbf{r} = (V_2/V_1)$  and  $\phi_2 = c_2 \overline{v_2}$ , where  $\overline{v_2}$  is the partial specific volume of the polymer. This can be related to the polymer molecular weight  $M_2$  through  $\overline{v_2} = (V_2/M_2)$ , so that  $(\phi_2/\mathbf{r}) = c_2 V_1/M_2$  and, finally,

$$(\mu_1 - \mu_1^0) = -RT \left[ \frac{c_2 V_1}{M_2} + \overline{v}_2^2 (\frac{1}{2} - \chi_1) c_2^2 \right]$$
(8.33)

#### 8.7 LIMITATIONS OF THE FLORY-HUGGINS THEORY

The simple lattice theory does not describe the behavior of dilute polymer solutions particularly well because of the following invalid simplifications in the theoretical treatment: (1) it was assumed that the segment-locating process is purely statistical, but this would only be true if  $\Delta \varepsilon_{12}$  was zero; (2) the treatment assumed that the flexibility of the chain is unaltered on passing into the solution from the solid state this limits the calculation of  $\Delta S^{M}$  to the combinatorial contribution only and neglects any contribution from continual flexing of the chain in solution; (3) any possible specific solvent–polymer interactions that might lead to orientation of the solvent molecules in the vicinity of the polymer chain are neglected; i.e., polar solutions may be inadequately catered to by this theory; (4) a uniform density of lattice site occupation is assumed, but this will only apply to relatively concentrated solutions; and (5) the parameter  $\chi_1$  is often concentration dependent, but this is ignored. It is now accepted that a noncombinatorial entropy contribution arises from the formation of new (1–2) contacts in the mixture, which change the vibrational frequencies of the two components; i.e., assumption (4) in Section 8.2 must be relaxed. This can be allowed for by recognizing that  $\chi_1$  is actually a free-energy parameter comprising entropic  $\chi_H$  and enthalpic  $\chi_S$  contributions such that  $\chi_1 = \chi_H + \chi_S$ . These are defined by

$$\chi_H = -T(d\chi_1/dT)$$
 and  $\chi_S = d(T\chi_1)/dT$  (=  $-\Delta S/k$ )

Experiments tend to show that the major contribution comes from the  $\chi_s$  component, indicating that there is a large decrease in entropy (noncombinatorial), which is acting against the dissolution process of a polymer in a solvent.

In spite of much justifiable criticism, the Flory–Huggins theory can still generate considerable interest because of the limited success that can be claimed for it in relation to phase equilibria studies.

#### 8.8 PHASE EQUILIBRIA

The Flory–Huggins theory can be used to predict the equilibrium behavior of two liquid phases when both contain amorphous polymer and one or even two solvents.

Consider a two-component system consisting of a liquid (1) that is a poor solvent for a polymer (2). Complete miscibility occurs when the Gibbs free energy of mixing is less than the Gibbs free energies of the components, and the solution maintains its homogeneity only as long as  $\Delta G^{M}$  remains less than the Gibbs free energy of any two possible coexisting phases.

The situation is represented by curve  $T_4$  in Figure 8.2. The miscibility of this type of system is observed to be strongly temperature dependent, and as T decreases the solution separates into two phases. Thus, at any temperature, say,  $T_1$ , the Gibbs free energy of any mixture, composition  $x_2^{"'}$  in the composition range  $x_2'$  to  $x_2''$ , is higher than either of the two coexisting phases whose compositions are  $x_2'$  and  $x_2''$ , and phase separation takes place. The compositions of the two phases  $x_2'$  and  $x_2''$  do not correspond to the two minima but are measured from the points of contact of the double tangent AB with the Gibbs free-energy curve. The same is true of other temperatures lying below  $T_c$  ( $T_1$  to  $T_3$ ), and the inflexion points can be joined to bound an area representing the heterogeneous two-phase system, where there is limited solubility of component 2 in 1 and vice versa. This is called a *cloud-point curve*.

As the temperature is increased, the limits of this two-phase coexistence contract, until eventually they coalesce to produce a homogeneous, one-phase mixture at  $T_c$ , the *critical solution temperature*. This is sometimes referred to as the *critical consolute point*.

In general, we can say that if the free-energy-composition curve has a shape that allows a tangent to touch it at two points, phase separation will occur.

The critical solution temperature is an important quantity and can be accurately defined in terms of the chemical potential. It represents the point at which the inflexion points on the curve merge, and so it is the temperature where the first, second, and third derivatives of the Gibbs free energy with respect to mole fraction are zero.



**FIGURE 8.2** Schematic diagram of the Gibbs free energy of mixing  $\Delta G^{M}$  as a function of the mole fraction  $x_2$  of solute (top half), showing the transition from a system miscible in all proportions at a temperature  $T_4$  through the critical temperature  $T_c$ , to partially miscible systems at temperatures  $T_3$  to  $T_1$ . The contact points for the common tangents drawn to the minima are shown projected onto the temperature—mole fraction plane to form the binodal (cloud-point) curve, whereas projection of the inflexion points forms the spinodal curve. The lower part of the diagram indicates the one-phase stable region I, the metastable region II, and the unstable region III.

$$\partial (\Delta G^{\mathrm{M}}) / \partial x_2 = \partial^2 (\Delta G) / \partial x_2^2 = \partial^3 (\Delta G^{\mathrm{M}}) / \partial x_2^3 = 0$$
(8.34)

It is also true that the partial molar Gibbs free energies of each component are equal at this point, and it emerges that the conditions for incipient phase separation are

$$\partial \mu_1 / \partial \phi_2 = \partial^2 \mu_1 / \partial \phi_2^2 = \partial^3 \mu_1 / \partial \phi_2^3 = 0$$
(8.35)

By remembering that  $\Delta G_1 = (\mu_1 - \mu_1^0)$ , application of these criteria for equilibrium to Equation 8.31 leads to the first derivative of that equation

whereas the second derivative is

$$(1 - \phi_{2,c})^{-2} - 2\chi_{1,c} = 0 \tag{8.37}$$

where the subscript c denotes critical conditions. The critical composition at which phase separation is first detected is then

$$\phi_{2c} = 1/(1+x_n^{1/2}) \approx 1/x_n^{1/2} \tag{8.38}$$

and

$$\chi_{1,c} = \frac{1}{2} + \frac{1}{x_n^{1/2}} + \frac{1}{2x_n}$$
(8.39)

which indicates that  $\chi_{1,c} = 0.5$  at an infinitely large chain length.

The interaction parameter  $\chi_1$  is a useful measure of the solvent power. Poor solvents have values of  $\chi_1$  close to 0.5, whereas an improvement in solvent power lowers  $\chi_1$ . Generally, a variation from 0.5 to -1.0 can be observed, although for many synthetic polymer solutions the range is 0.6 to 0.3. A linear temperature dependence of the general form  $\chi_1 = a + b/T$  is also predicted for  $\chi_1$ , which suggests that as the temperature increases, the solvating power of the liquid should increase.

The relationship between chain length and solvent power as expressed by Equation 8.39 is illustrated in Figure 8.3. The implication is that if  $\chi_1$  can be carefully controlled, conditions could be attained that, for a polydisperse sample, would allow a given molecular species to precipitate, while leaving larger or smaller molecules in solution. This process is known as *fractionation*.

Experimentally, a polymer sample can be fractionated in a variety of ways; two in common use are (1) addition of a nonsolvent to a polymer solution and (2) lowering the temperature of the solution.

In the first method, the control of  $\chi_1$  is effected by adding a nonsolvent to the polymer solution. If the addition is slow,  $\chi_1$  increases gradually until the critical value for large molecules is reached. This first causes precipitation of the longest chains, which can be separated from the shorter chains that remain in solution. Successive additions of small quantities of nonsolvent to the solution allow a series of fractions of steadily decreasing molar mass to be separated.

In the second method,  $\chi_1$  is varied by altering the temperature, with similar results. For both techniques, it is useful to dissolve the polymer initially in a poor solvent with a large  $\chi_1$  value. This ensures that only small quantities of nonsolvent are required to precipitate the polymer in method 1 and that the temperature changes required in method 2 are small.

#### 8.9 FLORY-KRIGBAUM THEORY

To overcome the limitations of the lattice theory resulting from the discontinuous nature of a dilute polymer solution, Flory and Krigbaum discarded the idea of a



**FIGURE 8.3** Variation of  $\chi_1$  with volume fraction  $\phi_2$  of the polymer in solution, showing the effect of changing chain length  $x_n$ .

uniform distribution of chain segments in the liquid. Instead, they considered the solution to be composed of areas containing polymer separated by the solvent. In these areas, the polymer segments were assumed to possess a Gaussian distribution about the center of mass, but even with this distribution the chain segments still occupy a finite volume from which all other chain segments are excluded. It is within this excluded volume that the long-range interactions originate, as discussed more fully in Chapter 10.

Flory and Krigbaum defined an enthalpy  $(\kappa_1)$  parameter and an entropy of dilution  $(\psi_1)$  parameter such that the thermodynamic functions used to describe these long-range effects are given in terms of the excess partial molar quantities

$$\Delta H_1^{\rm E} = RT \kappa_1 \phi_2^2 \tag{8.40}$$

$$\Delta S_1^{\rm E} = R \psi_1 \phi_2^2 \tag{8.41}$$

From Equation 8.33 it can be seen that the excess free energy of dilution is

$$(\mu_1 - \mu_1^0)^{\rm E} = \Delta G_1^{\rm E} = -RT(\frac{1}{2} - \chi_1)\phi_2^2$$
(8.42)

Combination of these nonideal terms then yields

$$(\frac{1}{2} - \chi_1) = (\psi_1 - \kappa_1) \tag{8.43}$$

We will show in Chapter 9 that a relationship exists between the second virial coefficient *B* and the interaction parameter  $\chi_1$ 

$$B = RT \frac{\overline{v_2}}{V_1} (\frac{1}{2} - \chi_1)$$
(8.44)

When B = 0 and  $\chi_1 = \frac{1}{2}$ , the solution appears to behave as though it were ideal. The point at which this occurs is known as the *Flory* or *theta* point and is in some ways analogous to the Boyle point for a nonideal gas. Under these conditions,

$$\Psi_1 = \kappa$$
, that is,  $\Delta H_1^{\rm E} = T \Delta S_1^{\rm E}$ 

The temperature at which these conditions are obtained is the Flory or theta temperature  $\Theta$ , conveniently defined as  $\Theta = T\kappa_1/\psi_1$ . This tells us that  $\Theta$  will only have a meaningful value when  $\psi_1$  and  $\kappa_1$  have the same sign.

Substitution in Equation 8.42 followed by rearrangement gives

$$(\mu_{1} - \mu_{1}^{0})^{E} = -RT\psi_{1}\left(1 - \frac{\Theta}{T}\right)\phi_{2}^{2}$$
(8.45)

and shows that deviations from ideal behavior vanish when  $T = \Theta$ .

The theta temperature is a well-defined state of the polymer solution at which the excluded volume effects are eliminated and the polymer coil is in an unperturbed condition (see Chapter 10). Above the theta temperature, expansion of the coil takes place, caused by interactions with the solvent, whereas below  $\Theta$  the polymer segments attract one another, the excluded volume is negative, the coils tend to collapse, and eventual phase separation occurs.

#### 8.10 LOCATION OF THE THETA TEMPERATURE

The theta temperature of a polymer–solvent system can be measured from phase separation studies. The value of  $\chi_{1,c}$  at the critical concentration is related to the chain length of the polymer by Equation 8.39, and substitution in Equation 8.45 leads to

$$\Psi_1(\Theta/T_c - 1) = 1/x_n^{1/2} + 1/2x_n \tag{8.46}$$

where now we have replaced r with the equivalent degree of polymerization  $x_n$ . Rearrangement gives

$$1/T_{\rm c} = (1/\Theta)\{1 + (1/\psi_1)(1/x_n^{1/2} + 1/2x_n)\}$$
(8.47)

Remembering that  $x_n = (M\overline{v}_2/V_1)$ , where *M* and  $\overline{v}_2$  are the molar mass and partial specific volume of the polymer, respectively, and  $V_1$  is the molar volume of the solvent, the equation states that the critical temperature is a function of *M* and the value of  $T_c$  at infinite *M* is the theta temperature for the system.

Precipitation data for several systems have proved the validity of Equation 8.47. Linear plots are obtained with a positive slope from which the entropy parameter  $\psi_1$  can be calculated, as shown in Figure 8.4. Typical values are shown in Table 8.1, but  $\psi_1$  values measured for systems such as polystyrene-cyclohexane have been found to be almost ten times larger than those derived from other methods of measurement. This appears to arise from the assumption in the Flory-Huggins theory that  $\chi_1$  is concentration independent and improved values of  $\psi_1$  are obtained when this is rectified.



**FIGURE 8.4** Chain length  $x_n$  dependence of the upper critical consolute solution temperature  $T_c$  for (1) polystyrene in cyclohexane and (2) polyisobutylene in di-isobutyl ketone (data from Schultz, A.R. and Flory, P.J., *J. Am. Chem. Soc.*, 74, 4760, 1952), and the lower critical solution temperature for (3) polyoctene-1 in *n*-pentane (data from Kinsinger, J.B. and Ballard, L.E., *Polym. Lett.*, 2, 879, 1964).

TABLE 8.1		
Theta Temperatures and Entropy	Parameters for 9	Some Polymer-Solvent
Systems		

Polymer	Solvent	Θ(K)	$\Psi_1$
1. Polystyrene	Cyclohexane	307.2	1.056
2. Polyethylene	Nitrobenzene	503	1.090
3. Polyisobutene	Diisobutyl ketone	333.1	0.653
4. Poly(methylmethacrylate)	4-Heptanone	305	0.610
5. Poly(acrylic acid)	Dioxan	302.2	-0.310
6. Polymethacrylonitrile	Butanone	279	-0.630

*Note:* Values have been derived using Equation 8.47;  $\Theta$ =theta temperature,  $\psi$ = entropy of dilution.



**FIGURE 8.5** Location of the theta temperature  $\Theta$  for poly( $\alpha$ -methyl styrene) in cyclohexane. Values of A<sub>2</sub> are measured for (1)  $M_n = 8.6 \times 10^4$  g mol<sup>-1</sup>, (2)  $M_n = 3.8 \times 10^5$  g mol<sup>-1</sup>, and (3)  $M_n = 1.5 \times 10^6$  g mol<sup>-1</sup>.

The theta temperature, calculated from Equation 8.47 for each system, is in good agreement with that measured from the temperature variation of the second virial coefficient  $A_2$  (= B/RT, see Chapter 9). Curves of  $A_2$ , measured at various temperatures in the vicinity of  $\Theta$ , are constructed as a function of temperature for one or more molar masses as shown in Figure 8.5. Intersection of the curves with the *T*-axis occurs when  $A_2 = 0$  and  $T = \Theta$ . The curves for each molar mass of the same polymer should all intersect at  $T = \Theta$ .

# 8.11 LOWER CRITICAL SOLUTION TEMPERATURES

So far we have been concerned with nonpolar solutions of amorphous polymers, whose solubility is increased with rising temperature, because the additional thermal motion helps to decrease attractive forces between like molecules and encourages energetically less favorable contacts. The phase diagram for such a system, when the solvent is poor, is depicted by area A in Figure 8.6, where the critical temperature  $T_c$  occurs near the maximum of the cloud-point curve and is often referred to as the *upper critical solution temperature* (UCST). This behavior follows from that depicted in Figure 8.2.

For nonpolar systems  $\Delta S^{M}$  is normally positive but weighted heavily by *T*, and so solubility depends mainly on the magnitude of  $\Delta H^{M}$ , which is normally endothermic (positive). Consequently, as *T* decreases,  $\Delta G^{M}$  eventually becomes positive and phase separation takes place.

Values of  $\Theta$  and  $\psi_1$ , in Table 8.1, show that for systems 1 to 4 the entropy parameter is positive, as expected, but for poly(acrylic acid) in dioxan and polymethacrylonitrile in butanone,  $\psi_1$  is negative at the theta temperature. As  $\psi_1 = \kappa_1$  when  $T = \Theta$ , the enthalpy is also negative for these systems. This means that systems 5 and 6 exhibit an unusual decrease in solubility as temperature rises, and the cloud-point curve is now inverted as in area B. The corresponding critical temperature is located at the minimum of the miscibility curve and is known as the *lower critical solution temperature* (LCST).



**FIGURE 8.6** Schematic diagram of the two types of phase boundaries commonly encountered in polymer solutions: (A) the two-phase region characterized by the upper critical solution temperature and (B) the two-phase region giving the lower critical solution temperature, with a single-phase region lying between the two.

In systems 5 and 6, this phenomenon is a result of hydrogen-bond formation between the polymer and solvent, which enhances the solubility. As hydrogen bonds are thermally labile, a rise in T reduces the number of bonds and causes eventual phase separation. In solutions, which are stabilized in this way by secondary bonding, the LCST usually appears below the boiling temperature of the solvent, but it has been found experimentally that an LCST can be detected in nonpolar systems when these are examined at temperatures approaching the critical temperature of the solvent. Polyisobutylene in a series of n-alkanes, polystyrene in methyl acetate and cyclohexane, and cellulose acetate in acetone all exhibit LCSTs.

The separation of polymer–solvent systems into two phases as the temperature increases is now recognized to be a characteristic feature of all polymer solutions. This presents a problem of interpretation within the framework of regular solution theory, as the accepted form of  $\chi_1$  predicts a monotonic change with temperature and is incapable of dealing with two critical consolute points.

The problem of how to accommodate, in a theoretical framework, the existence of two miscibility gaps requires a new approach, and a more elaborate treatment by Prigogine and co-workers encompasses the difference in size between the components of a mixture, which cannot be ignored for polymer solutions. They replaced the rigid lattice model used by Flory and Huggins, which is valid only at absolute zero, with a flexible lattice whose cells change in volume with temperature and pressure. This allowed them to include in their theory dissimilarities in free volume between polymer and solvent together with the corresponding interactions. The same approach was extended by both Patterson and Flory to deal specifically with polymer systems.

The most important of the new parameters is the so-called structural effect, which is related to the number of degrees of freedom "3c" that a molecule possesses, divided by the number of external contacts q. This structural factor (c/q) is a measure of the number of external degrees of freedom per segment and changes with the length of the component. Thus, the ratio decreases as a liquid becomes increasingly polymeric.

The expansion and free volume can then be characterized by the ratio of the thermal energy arising from the external degrees of freedom available to the component,  $U_{\text{thermal}}$ , and the interaction energy between neighboring nonbonded segments,  $U_{\text{cohesive}}$ , which will oppose the thermal energy effects, i.e.,

$$\frac{U_{\text{thermal}}}{U_{\text{cohesive}}} = \left(\frac{ckT}{q}\right) \cdot \frac{1}{\epsilon^*}$$
(8.48)

where  $\varepsilon^*$  is the characteristic cohesive energy per contact.

For convenience q may be replaced by r, the number of chain segments, although q will actually be less than r because some of the external contacts are used in forming the covalent bonds in the chain.

Free-volume dissimilarities become increasingly important as the size of one component increases with respect to the second, as in polymer solutions, and when these differences are sufficiently large, phase separation can be observed at the LCST.

The differences in expansivity can be accounted for if the interaction parameter is now expressed as

$$\chi = -(U_1/RT)v^2 + (C_{n1}/2R)\tau^2$$
(8.49)

where the first term reflects the interchange energy on forming contacts of unlike type and includes segment size differences, whereas the second term is the new "structural" contribution coming from free-volume changes on mixing a dense polymer with an expanded solvent. This can be represented schematically as in Figure 8.7.

The first term in Equation 8.49, shown by curve 1 in Figure 8.7, is merely an expression of the Flory–Huggins theory where  $\chi$  decreases constantly with rising temperature, but now inclusion of the new free-volume term, shown by curve 2, modifies the behavior of  $\chi$ . The second term gains in importance as the expansivities of the two components become increasingly divergent with temperature, and the net effect is to increase  $\chi$  again until it once more attains its critical value at high temperature. The LCST that results is then a consequence of these free-volume differences and is an entropically controlled phenomenon.

This can be illustrated in the following ways. In terms of the flexible lattice model, one can imagine the polymer and liquid lattices expanding at different rates until a temperature is reached at which the highly expanded liquid lattice can no longer be distorted sufficiently to accommodate the less-expanded polymer lattice and form a solution; i.e., the loss in entropy during the distortion becomes so large and unfavorable that phase separation (LCST) takes place. Alternatively, a polymer solution can be thought of as a system formed by the condensation of solvent into a polymer. As the temperature increases, the entropy loss incurred during condensation becomes greater until eventually it is so unfavorable that condensation in the polymer is impossible and phase separation takes place. Neither picture is particularly rigorous, but they serve to emphasize the fact that the LCST is an entropically controlled phenomenon.



**FIGURE 8.7** Schematic diagram of  $\chi_1$  as a function of temperature, showing the composite curve of 1 (--), first term in Equation 8.49; and 2 (-•-), the free-volume contribution from the second term in Equation 8.49, which results in the observation of the LCST.