POLYMER SOLUTION

Criteria For Polymer Solubility

The Solution Process

Dissolving a polymer is a slow process that occurs in two stages First, solvent molecules slowly diffuse into the polymer to produce a swollen gel. This may be all that happens if, for example, the polymer-polymer intermolecular forces are high because of crosslinking, crystallinity, or strong hydrogen bonding. But if these forces can be overcome by the introduction of strong polymer solvent interactions, the second stage of solution can take place. Here the gel gradually disintegrates into a true solution Only this stage can be materially speeded by agitation. Even so, the solution process can be quite slow (days or weeks) for materials of very high molecular weight.

Polymer Texture and Solubility

Solubility relations in polymer systems are more complex than those among low-molecular-weight compounds, because of the size differences between polymer and solvent molecules, the viscosity of the system, and the effects of the texture and molecular weight of the polymer. In turn, the presence or absence of solubility as conditions (such as the nature of the solvent, or the temperature) are varied can give much information about the polymer; this is in fact the topic of most of this chapter. From what has already been said, it is clear that the topology of the polymer is highly important in determining its solubility. Crosslinked polymers do not dissolve, but only swell if indeed they interact with the solvent at all. In part, at least, the degree of this interaction is determined by the extent of crosslinking: Lightly crosslinked rubbers swell extensively in solvents in which the unvulcanized material would dissolve, but hard rubbers, like many thermosetting resins, may not swell appreciably in contact with any solvent

The absence of solubility does not imply crosslinking, however. Other features may give rise to sufficiently high intermolecular forces to prevent solubility. The presence of crystallinity is the common example. Many crystalline polymers, particularly nonpolar ones, do not dissolve except at temperatures near their crystalline melting points. Because crystallinity decreases as the melting point is approached and the melting point is itself' depressed by the presence of the solvent, solubility can often be achieved at temperatures significantly below the melting point. Thus linear polyethylene, with crystalline melting point T_m = 135 °C, is soluble in many liquids at temperatures above 100 °C, while even polytetrafluoroethylene, T_m = 325 °C, is soluble in some of the few liquids that exist above 300 °C More polar crystalline polymers, such as 66-nylon, T_m = 265 °C, can dis,- solve at room temperature in solvents that interact strongly with them (for example, to form hydrogen bonds).

There is little quantitative information about the influence of branching on solubility; in general, branched species appear to be more readily soluble than their linear counterparts of the same chemical type and molecular weight.

Of all these systems, the theory of solubility, based on the thermodynamics of polymer solutions, is highly developed only for linear polymers in the absence of crystallinity. Here the chemical nature of the polymer is by far the most important determinant of solubility, as is elucidated in the remainder of this section. The influence of molecular weight (within the polymer range) is far less, but it is of great importance to fractionation processes, which yield information about the distribution of molecular weights in polymer samples.

Solubility Parameters

Mixing can be described in terms of free energy. Free energy has two terms, an energy-related term and one related to order/disorder. The energy-related term is called enthalpy, H, and the order/ disorder term called entropy, S.

For mixing to occur and for polymers to be dissolved it is essential that the change in free energy, ΔG, which is the driving force in the solution and mixing processes, decrease to below zero, that is, be negative. ΔH and ΔS are equal to the change in enthalpy and change in entropy and for constant temperature the relationship is the classical Gibbs equation.

$$\Delta G = \Delta H - T\,\Delta S$$

“Like-likes-like best of all” is a description that is useful at appropriate times in science. It is true of solubility. Thus, water-likes-water best of all and is infinitely soluble in itself. Hexane-likes hexane best of all and is infinitely soluble in itself. Hexane and water are not soluble in one another because hexane is nonpolar and water is polar; thus they are not “like one another.” In solubility, and in fact all of mixing, the ΔH term is always unfavorable when mixing or when solubility occurs. (Shortly, we will deal with attempts such as the cohesive energy density (CED) and solubility parameter to minimize the unfavorable aspect of the ΔH

term.) Thus, it is the Δ*S* term that allows mixing and solubility to occur. As seen in **Figure 1** the amount of randomness or disorder gain is great when pure materials such as water and ethanol is changed from the ordered pure materials to the disordered mixture.

By comparison, the increase in randomness, Δ*S*, is much smaller if one of the materials is a polymer since the possible arrangement of the polymer chains is much more limited because the polymer units are attached to one another and not free to simply move about on their own. **Figure 2** illustrates this with water and poly(ethylene glycol), PEG. We notice several aspects. First, as noted above, the number of arrangements of the PEG units is limited. Second, as in the case of an onion, each layer of PEG chains must be peeled back allowing water molecules to approach inner layers before entire solubility occurs and causes swelling. This results in polymer solubility often requiring a longer period of time, sometimes hours to week to months, in comparison to the solubility of smaller molecules where solubility can occur in seconds. Polymer solubility, in comparison to small molecules, is

a. More limited with respect to the number of solvents as a result of the lower increase in randomness;

b. It is more limited with respect to the extent of solubility; and

c. Takes a longer time to occur.

Physical properties of polymers, including solubility, are related to the strength of covalent bonds, the stiffness of the segments in the polymer backbone, the amount of crystallinity/amorphous, and the intermolecular forces between the polymer chains. The strength of the intermolecular forces is directly related to the cohesive energy density (CED), which is the molar energy of vaporization per unit volume. Since intermolecular attractions of solvent and solute must be overcome when a solute (here the polymer) dissolves, cohesive energy density (CED) values may be used to predict solubility.

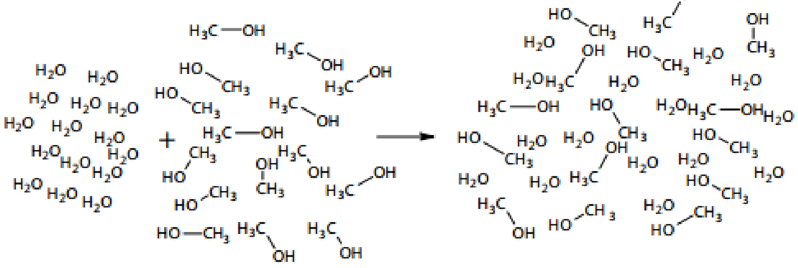

Fig 1. Illustration of the mixing of small molecules

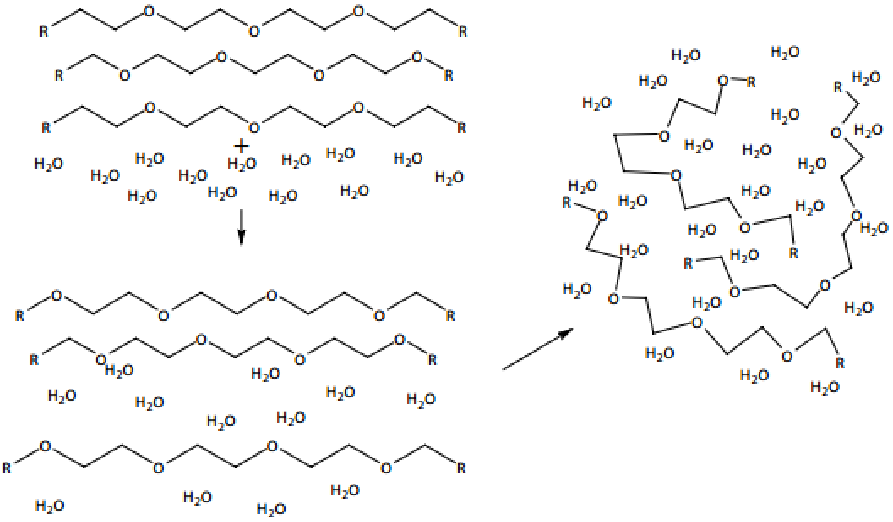

Fig 2 Illustration of water dissolving poly(ethylene glycol) (PEG).

When a polymer dissolves, the first step is often a slow-swelling process called *solvation* in which the polymer molecules swell by a factor δ, which is related to cohesive energy density (CED). Linear and branched polymers dissolve in a second step, but network polymers remain in a swollen condition. In the dissolving process, external polymers are initially "dissolved" exposing additional polymer chains to the solvent, and so on eventually resulting in the entire polymer mass being dissolved. Thus, polymer solubility often takes considerably longer than the solubility of smaller molecules.

As early as 1926, Hildebrand showed a relationship between solubility and the internal pressure of the solvent and in 1931, Scatchard incorporated the cohesive energy density (CED) concept into Hildebrand's equation. This led to the concept of a *solubility parameter, δ*, which is the square root of CED. Thus, as shown below, the solubility parameter, δ, for nonpolar solvents is equal to the square root of the heat of vaporization per unit volume.

$$\delta = \left(\frac{\Delta E}{V}\right)^{1/2} = (\mathrm{CED})^{1/2} \quad \text{or} \quad \delta^2 = \mathrm{CED}$$

According to Hildebrand, the heat of mixing a solute and a solvent is proportional to the square of the difference in solubility parameters, as shown below, where ϕ is the partial volume of each component, namely, solvent ϕ_1 and solute ϕ_2. Since, typically, the entropy term favors solution and the enthalpy term acts counter to the solution, the objective is to match solvent and solute so that the difference between their δ values is small, resulting in a small enthalpy acting against solubility occurring.

$$\Delta H_m = \phi_1 \phi_2 (\delta_1 - \delta_2)^2$$

The solubility parameter concept predicts the heat of mixing liquids and amorphous polymers. It has been experimentally found that generally any nonpolar amorphous polymer will dissolve in a liquid or mixture of liquids having a solubility parameter that generally does not differ by more than ±1.8 $(\text{cal/cc})^{1/2}$. The Hildebrand with units of $(\text{cal/cc})^{1/2}$ is preferred over these complex units giving for the previous expression ±1.8 H.

The solubility parameter concept is based on obtaining a negative Gibbs' free energy. Thus, as the term ΔH_m approaches zero, ΔG will have the negative value required for solution to occur because the entropy term favors solution occurring. As noted before, the entropy (S) increases in the solution process hence the emphasis is on achieving low values of ΔH_m.

For nonpolar solvents, which were called regular solvents by Hildebrand, the solubility parameter is equal to the square root of the difference between the enthalpy of evaporation (H_v) and the product of the ideal gas constant (R) and the Kelvin (or Absolute) temperature (T) divided by the molar volume (V), as shown in the following equation:

$$\delta = \left(\frac{\Delta E}{V}\right)^{1/2} = \left(\frac{\Delta H_v - RT}{V}\right)^{1/2}$$

Since it is difficult to measure the molar volume, its equivalent the molecular weight (M) divided by density (D), is substituted for V as shown in the following equation:

$$\delta = D\left(\frac{\Delta H_v - RT}{M}\right)^{1/2}$$

Because the law of mixtures applies to the solubility parameter, it is possible to easily calculate the solubility parameter of blended liquids forming mixtures that can serve as solvents. For example, an equal molar mixture of *n*-pentane (δ = 7.1 H) and *n*-octant (δ = 7.6 H) will have a solubility parameter value of 7.35 H (simply [7.1 + 7.6]/2).

The solubility parameter of a polymer is generally determined by noting the extent of swelling or actual solution of small amounts of polymer in a series of solvents and comparing the solubility values of the ones that swell or dissolve the polymer and assigning the polymer a solubility parameter value that is close to the solvents that dissolve/swell the polymer. The solubility parameter can also be determined by adding a nonsolvent to a polymer solution and by noting the amount of nonsolvent needed to begin to precipitate the polymers.

Since polar forces are present in polar solvents and polar molecules, this must be considered when estimating solubilities with such “nonregular” solvents and polymers. Hydrogen bonding, a special case of secondary polar bonding, is also important for some solvents and polymers and again will influence the solubility parameters. Thus, special solubility values have been developed for polar and hydrogen-bonding solvents (**Tables 1**).

Plasticizers help the flexibility of polymers and are chosen so that they do not dissolve the polymer but rather allow segmental mobility to occur. Through experience, it is found that the solubility

Table 1 Solubility Parameters (δ) for Typical Solvents

Poor Hydrogen Bonding		Moderate Hydrogen Bonding		Strong Hydrogen Bonding	
Dimethylsiloxane	5.5	Diisopropyl ether	6.9	Diethylamine	8.0
Difluorodichloromethane	5.5	Diethylether	7.4	*n*-Amylamine	8.7
Neopentane	6.3	Isoamyl acetate	7.8	2-Ethylhexanol	9.5
Nitro-*n*-octane	7.0	Diisobutyl ketone	7.8	Isoamyl alcohol	10.0
n-Pentane	7.0	Di-*n*-propylether	7.8	Acetic acid	10.1
n-Octane	7.6	*sec*-Butyl acetate	8.2	*m*-Cresol	10.2
Turpentine	8.1	Isopropyl acetate	8.4	Analine	10.3
Cyclohexane	8.2	Methylamyl ketone	8.5	*n*-Octyl alcohol	10.3
Cymene	8.2	Ethyl acetate	9.0	*t*-Butyl alcohol	10.9
Carbon tetrachloride	8.6	Methyl ethyl ketone	9.3	*n*-Amyl alcohol	10.9
n-Propylbenzene	8.6	Butyl cellosolve	9.5	*n*-Butyl alcohol	11.4
p-Chlorotoluene	8.8	Methyl acetate	9.6	Isopropyl alcohol	11.5
Decalin	8.8	Dichloroethylether	9.8	Diethylene glycol	12.1
Xylene	8.8	Acetone	9.9	Furfuryl alcohol	12.5
Benzene	9.2	Dioxane	10.0	Ethanol	12.7
Styrene	9.3	Cyclopentanone	10.4	*N*-Ethylformamide	13.9
Tetraline	9.4	Cellosolve	10.5	Methanol	14.5
Chlorobenzene	9.5	*N,N*-Dimethylacetamide	10.8	Ethylene glycol	14.6
Ethylene dichloride	9.8	1,2-Propylene carbonate	13.3	Glycerol	16.5
p-Dichlorobenzene	10.0	Ethylene carbonate	14.7	Water	23.4
Nitroethane	11.1				
Acetronitrile	11.9				
Nitroethane	12.7				

THERMODYNAMICS OF POLYMER SOLUTIONS

It was recognized in the 1940s that the thermodynamics of polymeric systems needs to be treated in a special way. In 1942, Gee and Treloar reported that even dilute polymer solutions deviated strongly from ideal-solution behavior. In these early experiments, a high-molecular-weight rubber was equilibrated with benzene vapour in a closed system and the partial pressure of the benzene (the solvent), p_1, was measured. The solvent activity, a_1, was calculated as the ratio of p_1 to the saturated vapor pressure of pure benzene, $p_1°$, at the system temperature as

$$a_1 = \frac{p_1}{p_1^{o}} \tag{1}$$

Experimental benzene activity is plotted as a function of the *volume fraction* of rubber, ϕ_2, in **Figure 3**. These data are compared with predictions of *Raoult's law* for an ideal solution given as

$$p_1 = x_1 p_1^{o} \tag{2}$$

where x_1 is the mole fraction of the solvent. Substitution of eq. (1) into eq. (2) yields the result that $a_1 = x_1$ for an ideal solution. As the experimental data (**Figure 3**) show, polymer-solution behavior follows a strong *negative* deviation from Raoult's ideal-solution law.

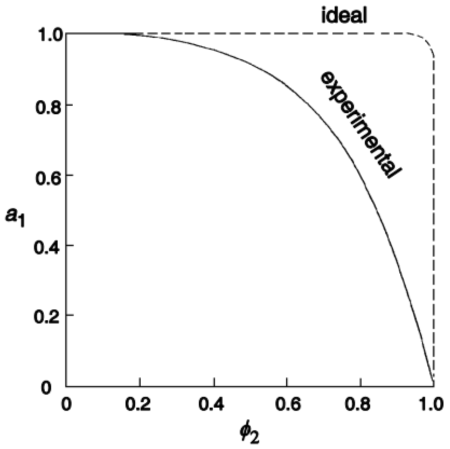

Figure 3. Plot of benzene activity, a_1, versus volume fraction of rubber, ϕ_2. Dashed line represents ideal-solution behavior.

Deviations From Ideal Behavior:

Polymer solutions invariably exhibit large deviations from Raoult's law, except at extreme dilutions, where ideal behavior is approached as an asymptotic limit At concentrations above a few percent, deviations from ideality are so great that the ideal law is of little value for predicting or correlating the thermodynamic properties of polymer solutions Even if the mole fraction is replaced with the volume fraction, in view of the different sizes of the polymer and solvent molecules, there is not a good correlation with the experimental results.

The Flory–Huggins Theory

In the early 1940s, Paul Flory and Maurice Huggins, working independently, developed a theory based upon a simple lattice model that could be used to understand the non ideal nature of polymer solutions. An excellent review of the development of the lattice model has been given by Flory. In the *Flory– Huggins model*, the lattice sites, or holes, are chosen to be the size of the solvent molecule. As the simplest example, consider the mixing of a low-molecular-weight solvent (component 1) with a low-molecular-weight solute (component 2). The solute molecule is assumed to have the same size as a solvent molecule, and therefore only one solute or one solvent molecule can occupy a single lattice site at a given time. **A** two-dimensional representation of an arrangement of lattice model for this case is illustrated in **Figure 4**.

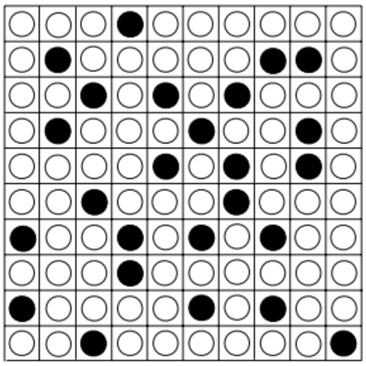

Figure 4. Representation of two-dimensional Flory–Huggins lattice containing solvent molecules (○) and a low-molecular-weight solute (●).

According to statistical thermodynamics, the entropy of mixing is determined by counting the number of possible arrangements in space that the molecules may assume, Ω. The entropy of mixing of a solvent and solute, ΔS_m is given by Boltzmann's relation.

$$\Delta S_{\mathrm{m}} = k \ln \Omega \tag{3}$$

where k is Boltzmann's constant (1.38 x 10^{-23} J K^{-1}) and Ω gives the total number of ways of arranging n_1 indistinguishable solvent molecules and indistinguishable n_2 solute molecules, where $N = n_1 + n_2$ is the total number of lattice sites. The probability function is given as

$$\Omega = \frac{N!}{n_1!n_2!} \tag{4}$$

Using the Stirling approximation

$$\ln n! = n\ln n - n \qquad 5$$

leads to the expression for the entropy of mixing *per molecule* as

$$\Delta S_{\mathrm{m}} = -k\left(n_1 \ln x_1 + n_2 \ln x_2\right). \qquad 6$$

Alternatively, the *molar* entropy of mixing can be written as

$$\boxed{\Delta S_{\mathrm{m}} = -R\left(x_1 \ln x_1 + x_2 \ln x_2\right)} \qquad 7$$

where *R* is the ideal gas constant (R= N_A k, where N_A is Avogadro's number.) and x_1 is the mole fraction of the solvent given as

$$x_1 = \frac{n_1}{n_1 + n_2} \qquad 8$$

The entropy of mixing a low-molecular-weight solvent with a *high*-molecular weight *polymer* is smaller than given by eq. (7) for a low-molecular-weight mixture. This is due to the loss in conformational entropy resulting from the linkage of individual repeating units along a polymer chain compared to the less ordered case of unassociated low-molecular-weight solute molecules dispersed in a low-molecular-weight solvent. In the development of an expression for ΔS_m for a high molecular-weight polymer in a solvent, the lattice is established by dividing the polymer chain into *r* segments, each the size of a solvent molecule, where *r* is the ratio of polymer volume to solvent volume (i.e., a lattice site). For n_2 polymer molecules, the total number of lattice sites is then $N = n_1 + rn_2$. It must be pointed out that ΔS_m is the combinatorial entropy computed by considering the possible arrangements of the molecules on the lattice in **Figure 5**, lattice containing low-molecular-weight solvent molecules and a single polymer chain is illustrated in **Figure 5**.

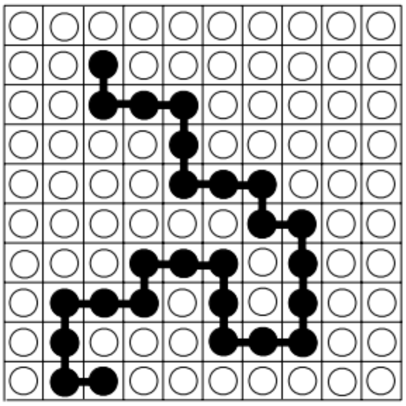

Figure 5. Lattice model for a polymer chain in solution. Symbols represent solvent molecules (○) and polymer-chain segments (●).

The expression for the entropy change due to mixing obtained by Flory and Huggins is given as

$$\Delta S_{\mathrm{m}} = -k\left(n_1 \ln \phi_1 + n_2 \ln \phi_2\right) \tag{9}$$

where ϕ_1 and ϕ_2 are the lattice *volume* fractions of solute (component 1) or polymer (component 2), respectively. These are given as

$$\phi_1 = \frac{n_1}{n_1 + rn_2} \tag{10}$$

$$\phi_2 = \frac{rn_2}{n_1 + rn_2} \tag{11}$$

For a polydisperse polymer, eq. (9) can be modified as

$$\Delta S_{\mathrm{m}} = -k\left(n_1 \ln \phi_1 + \sum_{i=2}^{N} n_i \ln \phi_i\right) \tag{12}$$

where the summation is over all polymer chains (N) in the molecular-weight distribution. For simplicity, the most commonly used form of the entropy expression, eq. (9), will be used in further discussion.

The Flory–Huggins theory introduces the unitless quantity χ_{12} as the Flory interaction parameter to represent the enthalpy of mixing, as

$$\Delta H_{\mathrm{m}} = kT\chi_{12} n_1 \phi_2 \tag{13}$$

The expression for the Gibbs free energy of mixing, ΔG_m, of a polymer solution given as

$$\Delta G_{\mathrm{m}} = \Delta H_{\mathrm{m}} - T\Delta S_{\mathrm{m}} \tag{14}$$

Combining the expression for the entropy (eq. 9) and enthalpy (eq. 13) of mixing in (eq. 14) gives the well-known Flory–Huggins expression for the Gibbs free energy of mixing

$$\boxed{\Delta G_{\mathrm{m}} = kT\left(n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi_{12} n_1 \phi_2\right)} \tag{15}$$

The first two terms of equation (15) are entropic, while the last term on the right is enthalpic. Again, incompressibility is assumed, meaning that the free volume in the system is constant. Equation (15) provides a starting point for many equations of interest. For example, by differentiating the expression with respect to n_1, the number of solvent molecules, and multiplying the result by Avogadro's number, the relative partial molar free energy $\overline{\Delta G_\iota}$ is obtained:

$$\overline{\Delta G_\iota} = RT[\ln(1-\emptyset_2) + \left(1-\tfrac{1}{r}\right)\emptyset_2 + \chi_{12}\emptyset_2^2] \tag{16}$$

We note that $\overline{\Delta G_\iota}$ is expressed on a per mole basis.

The osmotic pressure of the solution, π, are given by

$$\pi = \frac{\overline{\Delta G_1}}{v_1} \tag{17}$$

$$\pi = -\frac{RT}{V_1}[\ln(1-v_2) + \left(1-\tfrac{1}{r}\right)v_2 + \chi_{12}v_2^2] \tag{18}$$

where V_1 represents the molar volume of the solvent.

The activity of the solvent, a_1 is given by

$$\ln a_1 = \ln(1-\phi_2) + \left(1-\frac{1}{r}\right)\phi_2 + \chi_{12}\phi_2^2 \tag{19}$$

In the case of high-molecular-weight polymers for which the number of solvent equivalent segments, r, is large, the $1/r$ term within parentheses on the RHS of eq. (19) can be neglected to give

$$\boxed{\ln a_1 = \ln(1-\phi_2) + \phi_2 + \chi_{12}\phi_2^2} \qquad 20$$

The Flory–Huggins equation is still widely used and has been largely successful in describing the thermodynamics of polymer solutions; however, there are a number of important limitations of the original expression that should be emphasized. The most important are the following:

- Solutions are sufficiently concentrated that they have uniform segment density.
- There is no volume change of mixing (whereas favorable interactions between polymer and solvent molecules should result in a *negative* volume change).
- There are no energetically preferred arrangements of polymer segments and solvent molecules in the lattice.
- The Flory interaction parameter, χ_{12}, is independent of composition.

There have been a number of subsequent developments to extend the applicability of the original Flory–Huggins theory and to improve agreement between theoretical and experimental results.

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[The information, including the figures, are collected from the above references and will be used solely for academic purpose.]

POLYMER SOLUTION

Upper and lower Critical Solution Temperatures

Cloud-point or precipitation curves for different polymer-solvent systems have different shapes (Figures 6 & 7). The maxima and minima on these curves indicate the upper critical solution temperature (UCST) and lower critical solution temperature (LCST), respectively. As indicated in Figs 6 and 7 the phase diagram of a polymer solution has two regions of limited miscibility: (i) below UCST associated with the theta temperature and (ii) above LCST.

Different polymer-solvent systems may have completely different phase diagrams. For some systems, such as polystyrene-cyclohexane, UCST < LCST [Figs 7 (a)] but for others, e.g, highly polar systems like polyoxyethylene-water, UCST > LCST and closed solubility loop found [Figs 7 (b)].

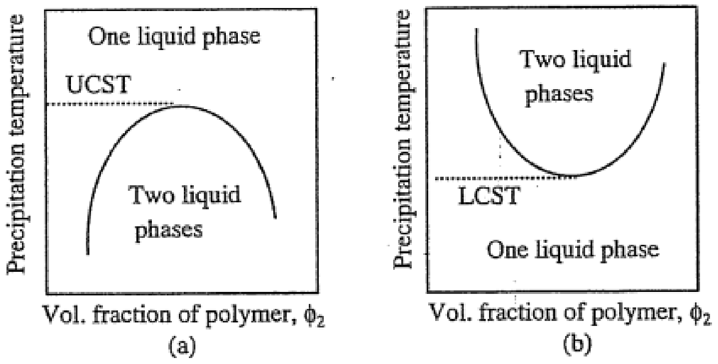

Figure 6. Schematic phase diagrams for polymer-solvent systems showing (a) UCST and (b) LCST.

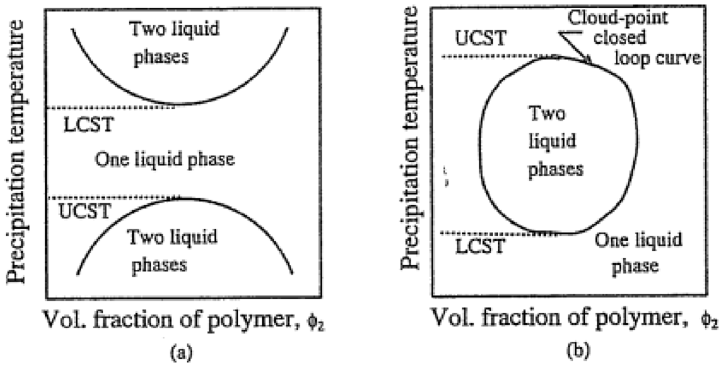

Figure 7. Schematic phase diagrams for polymer-solvent systems where (a) UCST < LCST and (b) UCST > LCST.

The solubility of a polymer in a solvent therefore depends on the temperature. If a single (homogeneously mixed) phase only exists above a certain temperature, this is referred to as an *upper critical solution temperature* (UCST). Here the separation below the UCST is an enthalpy-driven process—at lower temperatures the contribution of the enthalpy of mixing to the free enthalpy of mixing is greater than the effect of entropy (eq. 14).

However, if a solution is only thermodynamically stable below a certain temperature, the separation that occurs at this temperature must, by analogy, be driven by entropy. When a thermodynamically stable phase of the polymer–solvent-mixture occurs below a critical temperature, this is referred to as the LCST (*lower critical solution temperature*). This temperature denotes the maximum temperature at which the polymer still dissolves.

Formally, this behavior can be explained by interpreting the Gibbs–Helmholtz equation and considering the signs of the enthalpy and entropy terms. Assuming a negative enthalpy of mixing and a normal, positive entropy of mixing, the solution is completely miscible at all temperatures. An LCST occurs when the entropy and enthalpy of mixing take on negative values. As previously stated, because the entropy of mixing is usually positive, this case is rare and is only observed for a few polymers. If the signs of both the entropy and enthalpy of mixing are positive, the system has a UCST. This is often the case in reality. If the enthalpy of mixing is positive and the entropy of mixing negative, the system is not miscible at any temperature.

For real mixtures the situation is not so trivial, as both enthalpy and entropy of mixing are not monotonically dependent on the temperature. A detailed investigation shows that all polymer–solvent mixtures should display a UCST as well as an LCST. However, these are not always observable by experiment. This can often be explained by the UCST and LCST occurring at temperatures above or below the melting or the boiling point of the solvent.

PHASE EQUILIBRIA

Whether or not a polymer and solvent are mutually soluble, or *miscible*, is governed by the sign of the Gibbs free energy of mixing, ΔG_{m}, which is related to the enthalpy and entropy of mixing by eq. (14). Three different dependencies of ΔG_{m} on solution composition (i.e., volume fraction of polymer) at constant temperature are illustrated in **Figure 8**. If ΔG_m is positive over the entire composition range, as illustrated by curve I, the polymer and solvent are totally immiscible over the complete composition range and will coexist at equilibrium as two distinct phases. Two other possibilities are those of partial and total miscibility, as illustrated by curves II and III, respectively. For total miscibility, it is *necessary* that

$$\Delta G_m < 0 \qquad 21$$

and that the second derivative of ΔG_m with respect to the volume fraction of solvent (component 1) or polymer (component 2) be greater than zero over the entire composition range as formally expressed by

$$\left(\frac{\partial^2 \Delta G_m}{\partial \phi_2^2}\right)_{p,T} > 0 \qquad 22$$

Both conditions for miscibility are satisfied by curve III but not curve II, which exhibits two minima in ΔG_m, and therefore the derivative criterion expressed by eq. (22) is not satisfied at all points along the . ΔG_m–composition curve. A solution that exhibits such minima will phase-separate at equilibrium into two phases containing different compositions of both components. The compositions of the two phases are given by the points of common tangent as illustrated in **Figure 8**, where the composition of the solvent-rich phase is identified as ϕ_2^A and that of the polymer-rich phase as ϕ_2^B.

Phase equilibrium is strongly affected by solution temperature. In fact, any of three types of phase behavior illustrated in **Figure 8** may result from a change in the temperature (or pressure) of the system. Our usual experience with solutions of low-molecular-weight compounds is that solubility increases with an increase in temperature, as illustrated by the phase diagram shown in **Figure 9**. In this example, the solution is homogeneous (i.e., the two components are totally miscible) at temperatures above the point identified as UCST, which stands for the *upper critical solution temperature* as described below. At lower temperatures (i.e., below the UCST), phase separation may occur depending upon the overall composition of the mixture. At a given temperature below the UCST (e.g., T_1), compositions lying *outside* the curves are those constituting a homogeneous phase, while those lying inside the curves are thermodynamically unstable and, therefore, the solution will phase-separate at equilibrium. The compositions of the two phases, identified as phases A and B, are given by points lying along the curve called the *binodal*. The binodal is the locus of points that satisfy the conditions for thermodynamic equilibrium of a binary mixture given as

$$\mu_1^A = \mu_1^B \qquad 23$$

$$\mu_2^A = \mu_2^B \qquad 24$$

As the chemical potential is given by the derivative of the Gibbs free energy with respect to composition (eq. 25),

$$\Delta\mu_1 = \mu_1 - \mu_1^o = \overline{\Delta G}_m = \left(\frac{\partial \Delta G_m}{\partial n_1}\right)_{T,p} \qquad 25$$

the chemical potentials are obtained graphically from the intercepts of the common tangent drawn to curve II with the free energy axes as illustrated in **Figure 3-9**.

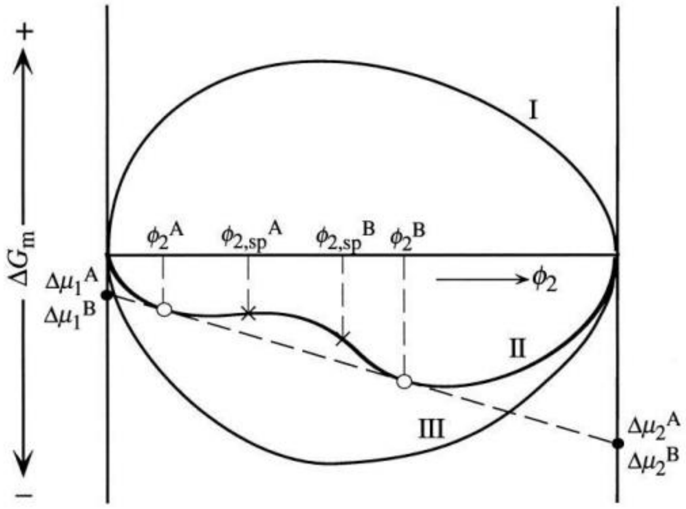

Figure 8. Dependence of the Gibbs free energy of mixing, ΔG_m, of a binary mixture on volume fraction of polymer, ϕ_2, at constant pressure and temperature. I. Total immiscibility. II. Partial miscibility. III. Total miscibility. In the case of partial miscibility (curve II), the mixture will separate into two phases whose compositions (○) are marked by the volume-fraction coordinates, ϕ_2^A and ϕ_2^B, corresponding to points of common tangent to the freeenergy curve. Spinodal points, compositions $\phi_{2,sp}^A$ and $\phi_{2,sp}^B$, occur at the points of inflection (x).

Between the binodal and the unstable region lies the *metastable* region, which is bounded by the *spinodal*. In the metastable region, the system can resist small concentration fluctuations but will eventually equilibrate to the stable two-phase state given by the binodal. Points lying along the spinodal correspond to the points of inflection identified in curve II of the free energy diagram (**Figure 3-9**) and satisfy the relationship

$$\left(\frac{\partial^2 \Delta G_m}{\partial \phi_2^2}\right)_{p,T} = 0 \qquad 26$$

The binodal and spinodal coincide at the *critical point*, which satisfies the following equality for the third derivative of the Gibbs free energy with respect to composition:

$$\left(\frac{\partial^3 \Delta G_{\mathrm{m}}}{\partial \phi_2^3}\right)_{p,T} = 0 \qquad (27)$$

In the case of the upper critical solution temperature (UCST), the critical point lies at the top of the phase diagram as shown in **Figure 3-10**.

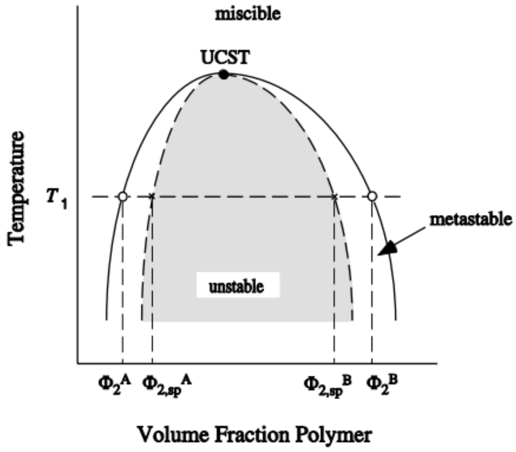

Figure 9. Representative phase diagrams for a polymer solution showing an upper critical solution temperature (UCST) (○), spinodal curve (– – – –), and binodal curve (_________).

Although the UCST behavior of dilute polymer solutions had been observed for many years, it was not until 1961 that phase separation of polymer solutions was first reported to occur with an *increase* in temperature. In this case, the bimodal and spinodal curves coincide at a temperature and composition called the *lower critical solution temperature* or LCST. One serious limitation of the Flory–Huggins theory is that it fails to predict LCST behavior.

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