3 Dissolution and Precipitation of Polymers

3.1 Rules for Solubility of Polymers

Solubility of a polymer in a solvent, which is the most important property for polymer fractionation, depends generally on the chemical structures of both polymer and solvent. The old rule "similia similibis solventur" (solubility results from similarity) may give useful hints to select solvents for a polymer. This can be seen for the most solvent/polymer pairs listed in Table A 3 in the Appendix. Sometimes however, this rule also fails and this is illustrated by the following example: Water is a good solvent for poly(vinyl alcohol); poly(vinyl acetate) (from which poly(vinyl alcohol) usually is derived) is soluble in ketones. However, methanol or ethanol are nonsolvents for poly(vinyl alcohol) but solvents for poly(vinyl acetate).

Solubility decreases with increasing MW. A rise in temperature usually enhances the solubility, but, for a system with low critical solution temperature (LCST – see Glossary; one of a few examples is the system poly(vinyl alcohol)/water), the opposite holds good.

The solubility of copolymers depends mainly on CC and is generally better than expected from the solubilities of the parent homopolymers. For instance, both poly(styrene) and poly(acrylonitrile) are insoluble in acetone, but, a styrene/acrylonitrile copolymer with middle composition is soluble.

The structure of a polymer solution can depend on concentration. Often, molecular-disperse solutions exist only in a sufficiently diluted state whereas clusters (associates, aggregates) may be formed with increasing concentration. This is possible especially in the vicinity of the theta state (see Glossary) where interactions between the macromolecules become operative. Therefore, fractionations should be carried out at low concentrations.

Solubility problems arising from secondary structures in the polymer sample (supermolecular or ordered structures) have already been mentioned in Sect. 1.1. Ordered structures, especially crystallinity of a polymer, impede dissolution. Usually, the dissolution of a crystalline polymer only succeeds when the polymer/solvent system is heated to above the melting point of the crystallites.

The driving force for the solubility of a polymer in a solvent is provided by the difference in the chemical potentials of the two species. This reads in terms
of the Gibbs-Helmholtz equation

\[ \Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \]  

(3.1)

where \( \Delta G_{\text{mix}} < 0 \) is the free energy of mixing. The entropy of mixing, \( \Delta S_{\text{mix}} > 0 \), is large for low-MW substances but much smaller for polymers due to the size of polymer molecules and the repeat units maintaining their "linear-ordered structure" in solution. Thus, the dissolution of polymers requires a rather small value of the enthalpy of mixing. This is the reason why the solubility of polymers is much more restricted than that of respective low-MW compounds.

Let us turn to concepts for the quantitative description of the solubility of polymers.

**Solubility parameters:**

The enthalpy of mixing is according to Hildebrand [1] proportional to the square of the difference in the so-called solubility parameters for the solvent (S), \( \delta_S \), and the polymer (P), \( \delta_P \),

\[ \Delta H_{\text{mix}} \propto (\delta_S - \delta_P)^2 \]  

(3.2)

with

\[ \delta_S = (\Delta E_S/V_S)^{0.5} \]  

(3.3a)

and

\[ \delta_P = (\Delta E_P/V_P)^{0.5} \]  

(3.3b)

\( \Delta E_S \) and \( \Delta E_P \) are the values of the internal heat of evaporation, \( V_S \) and \( V_P \) are the molar volumes of solvent and polymer, respectively. Thus, solubility parameters represent the interactions in pure substances which must be overcome in the dissolution process.

Solubility parameters of solvents can be measured directly whereas for polymers, they must be determined in indirect ways. Estimation via additivity of increments for different structural units is also possible (see, for instance, [2] and Table A 1 in the Appendix). For copolymers and mixtures, the solubility parameters can be calculated assuming additivity of the respective components using volume fractions \( \varphi \):

\[ \delta = \varphi_A \delta_A + \varphi_B \delta_B \]  

(3.4)

where indices A and B represent parent homopolymers or two solvents (or solvent and nonsolvent), respectively.

As can be seen from Eq. (3.2), the enthalpy of mixing is a positive quantity. Its lowest value, which characterizes the best solubility, occurs for \( \delta_S = \delta_P \). The solubility parameters of common solvents and polymers have been tabulated (see, for instance, [2]). They are a useful tool for the estimation of