Solubility & Mixing

1 Properties of Polymers

1.1 Conformation of Polymer Chains

Polymers consist of a large number of (often C-C) bonds in a linear chain. However that chain is not rigid, and a polymer in the liquid or solution state can take on a large number of different arrangements, or conformations. These conformations arise from rotation about (C-C) single bonds along the backbone of the chain.

Consider first a typical addition (free-radical) polymer such as the poly(vinyl chloride).

$$\begin{align*}
\text{H-H-} & + \text{H-H} + \text{Cl-Cl} \\
& \rightarrow \text{H-H-Cl-Cl}
\end{align*}$$

A sketch of the polymer chain as shown below.

Some of the same features apply to condensation polymers such as poly(ethylene terephthalate)

$$\begin{align*}
\text{HO-} & + \text{HO} \\
& \rightarrow \text{HO-}
\end{align*}$$

This polymer chain can also take on a large number of different conformations.
We are now going to make a theoretical model (actually more than one) that describes the average conformation of a polymer in the liquid (also called the melt) or solution state. Our model will be kept as simple as possible, so we first need to identify the essential features of polymer chains. There are several things to notice of both examples of polymers.

- Every repeat unit is bonded to a neighbour on each side. The number of bonds along the backbone is thus

\[(\text{degree of polymerization, } n) \times (\text{number of bonds per repeat unit} + 1)\]

For vinyl monomers, the repeat unit is the monomer which has one bond in it, so the number of bonds in the chain is just \(2n\).

- Every bond between repeat units is a single bond that can rotate freely, so the polymer chain is made up of rigid units with flexible connections, and can take on many different arrangements (conformations).

  For vinyl monomers, all the bonds in the chain are C-C single bonds.

  For more complex polymers, the repeat units may contain rigid elements like double bonds or benzene rings.

To keep things simple, our model will be for a polymer chain consisting of \(2n\) identical segments (a vinyl polymer)

- Only one of all possible arrangement is for the bonds to be in an extended zig-zag (called “all trans”). It is very unlikely that a polymer will take up this arrangement.

The sum of the length of all bonds is called the contour length of the polymer, and it is slightly greater than the zig-zag length. The contour length is given by

\[(\text{number of bonds in the chain}) \times \text{length of one bond} \]

For vinyl monomers, this is just \(2n \times 1.54\) Å

The most probable arrangement of a polymer chain is called a random flight chain. In a random flight chain each rigid segment (bond) meets the next one at a random angle between 0 and 180°, so it is quite likely that the chain will fold back on itself many times. The average end-to-end length of such a chain (also called the coil diameter) is given by

\[R_{\text{end-to-end}} = (\text{number of rigid segments in the chain})^{1/2} \times \text{length of one segment} \]

\[= (2n)^{1/2} \times 1.54\text{Å}, \text{for vinyl polymers (with a C-C backbone)}.\]

This equation is an example of a scaling law that tells us the exponent or power that relates the number of bonds, \(2n\), to the end-to-end distance. In this case the exponent is 0.5.

Real polymers are not perfectly random walks. A more realistic model can be constructed that includes

- Fixed bond angles (rather than a freely jointed chain).

- Restricted rotation about the backbone bonds.

Restricted rotation is very sensitive to the structure of the monomer repeat unit. For example, compare polyethylene with polystyrene. It is more difficult to rotate segments of the chain containing the bulk phenyl ring, and this reduces the probability of forming a compact coil.
Both of the above effects increase the coil diameter of a polymer, but do not change the scaling law. The factor by which the diameter is increased is called the Characteristic ratio, and this is tabulated in reference and text books.

The third factor that affects the size of a polymer coil is the solvent. In the melt, every segment of a polymer chain is surrounded by segments of other identical chains. In solution, polymer chain segments are in contact with solvent molecules. The intermolecular interactions between the solvent and polymer can be

1. Attractive: In this case the chain swells, and the scaling exponent increases, this increasing contact between polymer segments and solvent.
2. Repulsive: In this case the chain collapses, and the polymer is insoluble in the solvent.
3. The same as between polymer segments: In this case the solvent is called a \( \theta \) or theta solvent, and the polymer behaves the same as it does in the melt.

The Characteristic Ratio describes a polymer solution in a theta solvent.

\[ R_{\text{end-to-end}, \theta} = C \frac{N^{1/2} l}{l} = C (2n)^{1/2} x 1.54 \text{ Å for a vinyl polymer} \]

Where \( N \) is the number of rigid segments, \( l \) is the segment length, and \( C \) is the characteristic ratio.

### Characteristic ratios of some linear polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( C )</th>
<th>Polymer</th>
<th>( C )</th>
<th>Polymer</th>
<th>( C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(vinyl chloride)</td>
<td>1.83</td>
<td>Poly(vinyl alcohol)</td>
<td>2.04</td>
<td>Polystyrene</td>
<td>2.44</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>2.20</td>
<td>Poly(acrylic acid)</td>
<td>1.96</td>
<td>polypropylene</td>
<td>1.85</td>
</tr>
<tr>
<td>polyethylene</td>
<td>1.63</td>
<td>polysisobutylene</td>
<td>1.80</td>
<td>poly(vinyl acetate)</td>
<td>2.12</td>
</tr>
</tbody>
</table>

#### Sample Problem.

Calculate the diameter of a molecule of poly(vinyl chloride) of molecular weight \( 1.25 \times 10^6 \) (i) using the random coil model, and (ii) in a theta solvent.

The molecular weight of a vinyl chloride monomer (CH\(_2\)CHCl) is

\[ 12.01 \times 2 + 1.008 \times 3 + 35.5 = 62.56 \]

The number of monomers in the chain is therefore \( 1.25 \times 10^6 / 62.56 = 20,000 \)

\[ R_{\text{end-to-end}} = (2 \times 20,000)^{1/2} \times 1.54 \text{ Å} = 310 \text{ Å} \]

In a theta solvent, we simply multiply this result by the characteristic ratio (see Table)

\[ R_{\text{end-to-end}} = 2.44 \times (2 \times 20,000)^{1/2} \times 1.54 \text{ Å} = 750 \text{ Å} \]
1.2 Polymer Solubility and Miscibility

1.2.1 Solubility and Dissolution

Why does one material dissolve in another? We can write a general solubility process as

\[ \text{X(solid)} \rightarrow \text{X(solution)} \]

and we can decide whether or not this is spontaneous using the Gibbs Free Energy

\[ \Delta G = \Delta H - T \Delta S \]

If \( \Delta G < 0 \), then dissolution will be spontaneous.

Entropy, \( S \), is related to the probability of a system being in a certain state. Probability can generally be defined as

\[ \text{Pr} = \frac{\text{number of outcomes of a particular type}}{\text{total number of outcomes}} \]

The classical example comes from cards; the probability of drawing a King from a deck is \( \frac{4}{52} \) (the number of “King” outcomes)/52 (the total number of outcomes).

In molecular systems, probability of being in a certain state is related to the number of different ways that molecules can arrange themselves and be in that state.

Consider the following cartoon of a crystal dissolving in a solvent:-

![Crystal Dissolving Cartoon]

There are many more ways the solute and solvent molecules can arrange themselves and be in solution than being separately arranged as solid + liquid. That is,

\[ \text{Pr(solution)} \gg \text{Pr(solid + liquid)}, \text{ or } \Delta S > 0, \text{ or } -T \Delta S < 0 \text{, so entropy always favours dissolution.} \]

In other words, solubility is determined by the sign and magnitude of \( \Delta H \).

In order that a solute dissolve in a particular solvent, \( T \Delta S \) must be greater in magnitude than \( \Delta H \) of solution.

We can make some general conclusions about solubility based on these simple observations.

- We expect solubility to increase with increasing temperature \( (-T \Delta S) \). [Sometimes this is not true, but it means something unusual is happening.]

\( \Delta H \) depends on the strength of intermolecular interactions, so we can make some conclusions about solubility based on these effects.
• Strong intermolecular attractions within the solute oppose solubility.
• Strong intermolecular attractions within the solvent oppose solubility.
• Strong intermolecular attractions between solute and solvent favour solubility.

e.g.1. Carbon tetrachloride has only weak intermolecular attractions (dispersion forces) within the solvent. What do you expect the solubility of the following solutes to be?

1. Benzene (C₆H₆). Weak (dispersion force) attractions within the solute, and weak interactions between benzene and CCl₄. Therefore expect high solubility.

2. Methanol (CH₃OH). Strong attractions (H-bonds) within the solute, but weak attractions with the solvent (dispersion forces). Therefore expect low solubility.

e.g.2. Water molecules form strong hydrogen bonds with each other (Strong intermolecular attractions within the solvent). What do you expect the solubility of the following solutes to be?

1. Benzene (C₆H₆). Weak (dispersion force) attractions within the solute, but no strong attractions between benzene and water. Therefore expect low solubility.

2. Methanol (CH₃OH). Strong attractions (H-bonds) within the solute, but also strong attractions with the solvent (H-bonds). Therefore expect high solubility.

1.2.2 Polymer Solubility

Consider again the cartoon of a dissolution process, but this time of a polymer chain consisting of many segments or monomer units:-

Although the number of arrangements (probability) still increases on dissolution, the gain in entropy is much smaller than for a small solute. This is because the segments of the monomer chain must remain connected with each other, and this reduces the number of arrangements it can adopt. In the language of probability, or more accurately number of arrangements (outcomes), we represent this as

\[ \text{arrangements(monomer solution)} >> \text{arrangements(polymer solution)} > \text{arrangements(solid + liquid)} \]

Even a small, positive enthalpy is therefore enough to make \( \Delta G \) positive overall.

As we noted for small molecules, enthalpy is related to intermolecular forces. A widespread model for the enthalpy of solution of a polymer makes the assumption of weak attractions between the polymer and the solvent. The intermolecular attractions are
measured using the cohesive energy density, $\delta$. This is calculated from the enthalpy of vaporization (= energy required to overcome intermolecular forces within the solvent) per unit volume.

$$\delta = \left( \frac{\Delta H_{\text{vap}}}{V} \right)^{\frac{1}{2}}$$

The enthalpy of solution of a polymer in a particular solvent is given by the following equation

$$\Delta H = n_{\text{solvent}} V_{\text{solute}} \phi_{\text{polymer}} (\delta_{\text{polymer}} - \delta_{\text{solvent}})^2$$

Note that all the quantities are positive, including the square of the $\delta$ parameter difference. Hence $\Delta H$ is positive and opposes dissolution. The bigger the magnitude of the $\delta$ parameter difference, the bigger $\Delta H$. $\Delta H$ increases with concentration, so that the free energy of solution should become positive at higher concentrations (the solubility limit).

This equation only considers the attractions between solvent molecules and between polymer segments, but not between polymer segments and solvent molecules. Similar $\delta$ parameters indicate similar intermolecular attractions, so the polymer and solvent will be indifferent to one another. Different $\delta$ parameters indicate different intermolecular attractions, so the polymer and solvent will each be preferentially attracted to itself.

In practice, a polymer is expected to be soluble in a solvent if their $\delta$ parameters lie within one unit of each other. Solubility parameters are tabulated in a variety of reference and polymer science textbooks. (For polymers it is not generally possible to measure the enthalpy of vaporization directly, as they decompose before they vaporize. Hence $\delta_{\text{polymer}}$ is usually determined by finding the solvent which gives the greatest solubility.)

Sample Calculation. Predict whether poly(vinyl chloride), PVC, will be soluble in (i) cyclohexanol or (ii) cyclohexanone?

$$\delta(\text{PVC}) = 9.7; \delta(\text{cyclohexanol}) = 11.4; \delta(\text{cyclohexanone}) = 9.3$$

(i) $|\delta(\text{PVC}) - \delta(\text{cyclohexanol})| = |9.7 - 11.4| = 1.7 > 1$. Insoluble

(ii) $|\delta(\text{PVC}) - \delta(\text{cyclohexanone})| = |9.7 - 9.3| = 0.4 < 1$. Soluble

### Solubility Parameters of Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\delta$</th>
<th>Polymer</th>
<th>$\delta$</th>
<th>Polymer</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose dinitrate</td>
<td>10.6</td>
<td>Poly(propylene)</td>
<td>8.1</td>
<td>Butadiene-acrylonitrile (70:30)</td>
<td>9.4</td>
</tr>
<tr>
<td>Cellulose lacquer nitrate</td>
<td>11.5</td>
<td>Poly(ethylene terephthalate)</td>
<td>10.7</td>
<td>Butadiene-styrene (72:28)</td>
<td>8.1</td>
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<tr>
<td>Solvent</td>
<td>δ</td>
<td>Solvent</td>
<td>δ</td>
<td>Solvent</td>
<td>δ</td>
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<td>Aniline</td>
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<td>Diphenyl</td>
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<td>Ethyl chloroformate</td>
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<td>Tri-n-butyl phosphate</td>
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<td>Benzenaldehyde</td>
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<td>Ethylene dichloride</td>
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<td>Butyl Acetate</td>
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<td>Ethyl ether</td>
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<td>Diacetone alcohol</td>
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<td>Chloroform</td>
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<td>Benzyl alcohol</td>
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<td>Cyclohexanone</td>
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<td>Styrene</td>
<td>9.3</td>
<td>Diethylene glycol</td>
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<td>Water</td>
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<td>Diethylsulfate</td>
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<td>Trichloroethane</td>
<td>9.6</td>
<td>Ethylene glycol</td>
<td>14.2</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>n-Hexane</td>
<td>7.3</td>
</tr>
</tbody>
</table>

### 1.2.2.1 Polymer Solubility: The Overlap Threshold Concentration

We have been thinking so far about dilute polymers. That is, the conformation of a single polymer chain in a theta solvent, or the dissolution of polymer chains into a dilute solution surrounded by solvent (not by other polymers). Dilute polymer solutions are physically pretty uninteresting and behave like other dilute solutions. However, once the polymer coils begin to overlap, the viscosity of the polymer solution increases abruptly by several orders of magnitude. This is called the semi-dilute concentration range, and it begins at the overlap concentration, \(c^*\).

We can calculate the scaling law for this concentration as follows. The concentration of polymer segments everywhere in solution at \(c^*\) will be about the same as the concentration of polymer segments in a single swollen polymer chain. That is

\[
c^* \cong N/R^3
\]
where $N$ is the number of polymer segments in a single chain, and $R^3$ is the volume of one chain. For a polymer in a good solvent, we already know the scaling law for the end-to-end distance $R$ is $R \sim N^{0.6}$, which gives

$$c^* \sim N^{-0.8}$$

This tells us how the overlap concentration depends on degree of polymerization or molecular weight of a particular polymer. The overlap concentration decreases as the molecular weight increases.

In fact the ratio $c/c^*$ is an example of a dimensionless group. Many flow and mechanical properties of polymer solutions such as viscosity depend on this ratio.

### 1.2.3 Polymer-Polymer Miscibility

The situation for mixing of two polymers is even worse. Just as the number of arrangements ($\Delta S$) for a polymer dissolving in a solvent is much smaller than for small molecules dissolving, polymers dissolving into another polymer would have extremely small, although still positive $\Delta S$ values. Even a tiny $\Delta H$ is enough to make $\Delta G$ positive and prevent mixing. As a result, most polymers do not mix with one another.

Polymer “blends” rarely contain polymers mixed on a molecular scale. They are not mixtures or solutions as we normally define them for small molecules. Instead they contain regions or “domains” of each component. Chemically the polymers are two separate phases. In order to create blends it is common to add a compatibiliser. This is a molecule with two chemically different ends, with each one attractive to one of the two polymers to be mixed. Addition of the compatibiliser reduces the size of the separated domains, creating a more homogeneous material.

**e.g. 1.** Polystyrene is often blended with poly(butadiene), as this rubbery polymer increases the impact strength and toughness. Simply mixing the two leads to poor mechanical properties. A block copolymer of polystyrene and poly(butadiene) can be used to improve blending and achieve the desired performance.

**e.g. 2.** Polyethylene is a major target for plastics recycling. Even after sorting, there are always some other polymers such as polystyrene, poly(vinyl chloride), and PET in the waste stream, and even a few percent of these can seriously reduce the breaking strain of recycled blends. Copolymers added as compatibilisers can restore mechanical properties to close to the original (pure) polymer.

### 1.2.4 Rubber Elasticity

Now that we have something of a molecular understanding of entropy as probability, we can combine this with our knowledge of polymer conformations.

The random coil conformation is the most probable conformation for the chain - There are more coiled conformations than extended ones. (In fact, we already know that there is only one all-trans conformation.) When a bulk piece of (rubbery) polymer is stretched, this elongates the random coil of each polymer in a particular direction. This is, of course, a lower entropy, more ordered arrangement of the coil. Hence it required external energy to perform the stretching (a non-spontaneous process).

The recovery of the rubber occurs because each polymer chain returns to its more disordered state. That is, entropy causes the rubber to contract.
If we raise the temperature, then we increase the entropy of the system. This means that a stretched rubber band will contract (coils forming the more probable, coiled conformation) as the temperature is raised.