CONCENTRATED SOLUTIONS, PHASE SEPARATION BEHAVIOR, AND DIFFUSION

- A wide range of modern research as well as a variety of engineering applications exist for polymers in solution.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Effect</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diblock copolymers</td>
<td>Motor oil</td>
<td>Colloidal suspensions dissolve at high temperatures, raising viscosity</td>
<td>Multiviscosity (constant viscosity) motor oil. Example: 10W-40</td>
</tr>
<tr>
<td>Poly(ethylene oxide) M = 10^6 g/mol</td>
<td>Water</td>
<td>Reduces turbulent flow</td>
<td>Heat exchange systems, reduces pumping costs</td>
</tr>
<tr>
<td>Poly(vinyl chloride) DOP</td>
<td></td>
<td></td>
<td>Viscosity control of motor oils with diblock copolymers.</td>
</tr>
</tbody>
</table>

Viscosity control of motor oils with diblock copolymers.
Phase separation

- Mixtures of polymers do not, generally, form thermodynamically stable single phase systems.
- Complete miscibility:

\[ \Delta G_m = \Delta H_m - T \Delta S_m < 0 \]

- An additional, necessary and sufficient condition for compatibility is given by

\[ \left[ \frac{\partial^2 \Delta G_m}{\partial \phi_i^2} \right]_{T, p} > 0 \]

- Where \( \phi_i \) is the volume fraction of the \( i \)th component.

Phase separation

- Free energy of mixing for binary mixtures as a function of their composition:
  - A) Incompatibility  
  - B) Total miscibility  
  - C) Partial miscibility

![Diagram of Phase Separation](image)
Phase separation

- The points B represent the points where the straight line shown is tangential to the curve and are called the **binodal** points.

- The points S are the points of inflection, where the curvature changes sign, and are called the **spinodal** points.

- Between $\phi = 0$ or 1 and the binodal points, a system forms homogeneous solutions and only one stable phase.

Phase separation

- The chemical potential of a component at binodal points is the same in each of the two phases in equilibrium because a common tangent line passes through them.

\[
\begin{align*}
\mu_1' &= \mu_1'' \\
\mu_2' &= \mu_2'' \\
\Delta\mu_1' &= \mu_1' - \mu_1^o = \mu_1'' - \mu_1^o = \Delta\mu_1'' \\
\Delta\mu_2' &= \mu_2' - \mu_2^o = \mu_2'' - \mu_2^o = \Delta\mu_2''
\end{align*}
\]
• The regions between binodal and spinodal points form metastable solutions.

• The regions between the spinodal points lead to unstable solutions.
Phase separation

- Curves of binodal and spinodal points can be drawn as a function of the temperature up to the critical temperature ($T_c$) where these two curves meet.

- Beyond $T_c$, the system forms only one phase (UCST). At this critical temperature, the partial first- and second-order derivatives of the chemical potential ($\Delta \mu_1$) are equal to zero:

$$\Delta \mu_1 = \frac{\partial \Delta G_{\text{mix}}}{\partial N_1} = RT \left[ \ln(1 - \Phi_2) + \left(1 - \frac{1}{X}\right) \Phi_2 + \chi_{1,2} \Phi_2^2 \right]$$

Phase separation

The following gives the relation for the critical volume fraction of phase 2:

$$\Phi_{2, \text{crit}} = \frac{1}{1 + \sqrt{X}}$$

$$\chi_{1,2, \text{crit}} = \frac{1}{2} \left(1 + \frac{1}{\sqrt{X}}\right)^2 \approx \frac{1}{2} + \frac{1}{\sqrt{X}}$$
Phase separation

- Phase diagrams for polystyrene fractions in cyclohexane. Circles and solid lines, experimental. Theoretical curves are shown for two of the fractions.
- The viscosity-average molecular weights are (g/mol)
  - PSA: 43,600
  - PSB: 89,000
  - PSC: 250,000
  - PSD: 1,270,000

REGIONS OF THE POLYMER–SOLVENT PHASE DIAGRAM

- A polymer dissolves in two stages. First, solvent molecules diffuse into the polymer, swelling it to a gel state.
- Then the gel gradually disintegrates, the molecules diffusing into the solvent-rich regions.
- Generally, linear amorphous polymers are assumed. Cross-linked polymers may reach the gel state, but they do not dissolve.
- In previous chapter the solutions were assumed to be dilute, generally below 1% concentration, because this is required to obtain molecular weights.
- However, many solutions are used in the 10% to 50% concentration range. More concentrated systems are better described as plasticized polymers.
Daoud and Jannink and others divided polymer–solvent space into several regions.

The θ temperature separates the poor solvent (bottom) half of the diagram from the good solvent (top) half. At this special temperature (T=θ) the interaction parameter χ = ½.

At very low concentrations, the polymers exist as isolated coils that are very far apart.

There is a special concentration that equals the overlap concentration.

\[ C^* = \frac{3M}{4\pi R_g^3 N_A} \]
An important quantity is the screening length, $\xi$, first introduced by Edwards. This quantity takes slightly different meanings in different regimes.

- In the dilute solution regime, $\xi = R_g$.
- In the semidilute regime, $\xi$ measures the distance between chain contacts.

The dependence of $\xi$ on $\phi$ follows the scaling law:

$$\xi_s \sim \phi^{-3/4}$$
Phase Separation Mechanisms

- Phase separation is induced, when a sample is transferred from the one phase region into a miscibility gap.

- This is accomplished by a change in temperature, pressure or concentration.

- Immediately after entering the two phase region, the structure is still homogeneous but, of course, no longer stable.

\[ \phi_0 \rightarrow \phi_0 + \delta\phi \]
\[ \phi_0 - \delta\phi \]

Local concentration fluctuation

Phase Separation Mechanisms

- The structure evolution in the early stages of demixing is generally controlled by either of Nucleation and growth (NG) or spinodal decomposition (SD).

- NG is associated with metastability, implying the existence of an energy barrier and the occurrence of large composition fluctuations.

- Domains of a minimum size (critical nuclei) are a necessary condition.
Phase Separation Mechanisms

• For example, NG is the usual mechanism of phase separation of salts from supersaturated aqueous solutions.

• The NG mechanism results in domain size increasing with time. The domains tend to be spherical in nature.

• SD, on the other hand, refers to phase separation under conditions in which the energy barrier is negligible, so even small fluctuations in composition grow.

Phase Separation Mechanisms

• For spinodal decomposition, interconnected cylinders tend to form. Their initial growth mechanism involves an exchange of mass across the boundary, purer phases forming with time.

• Thus the amplitude of the waves increases, but not necessarily the wavelength.
Phase Separation Mechanisms

- The domains are of about the same size as the original wavelength of the wavelike fluctuation during the early stages of phase separation.

- On annealing, both kinds of domains (NG and SD) may coalesce, forming larger and larger spheroidal structures.

Mixtures of polystyrene and partially brominated polystyrene ($PBr_xS$), with both species having equal degrees of polymerization ($N = 200$) and perfect miscibility at $T > 220 \, ^\circ C$.

- Nucleation and growth could be seen as tiny spheres, while spinodal decomposition looked like tiny overlapping worms.
Phase diagrams

- Phase separation and dissolution are controlled by three variables: temperature, pressure, and concentration.

The LCST behavior of a typical polymer blend, increasing pressure increases miscibility.

Ternary phase diagram
Phase diagrams

- Figure C illustrates the phase diagram of a solvent and two polymers, PI and PII.
- As the solvent is removed, the mixture becomes less miscible and undergoes phase separation on going from point A to point B.
- The case of a mutual solution of a polymer, PI, and a monomer MII is illustrated in Figure d.

Phase diagrams

- As monomer II polymerizes to form polymer II, the composition follows the trajectory A’ to B’. Here, phase separation occurs during polymerization.
- While this case is the most important industrially, encompassing such materials as high-impact polystyrene and ABS resins, it is the least understood.
- The reasons lie in the complexity of the thermodynamics of a system undergoing two simultaneous changes: (a) removal of the monomer solvent (as in Figure c) and (b) replacement of the solvent by polymer II.
- Grafting during the polymerization, if present, constitutes another complication. Generally, grafted polymers are more miscible than the corresponding blends.
Polymer Blend Characterization

- **SEM**: Electron microscopy is used to determine domain size and shape.
- **DSC**: measures the changes in heat capacity between the individual components and the blend.
- **DMA**: dynamic mechanical Analysis measures shifts in the glass transition temperatures.
- **FT-IR**: provides a measure of the specific interactions occurring between polymer segments.
- **SANS**: provides a measure of the second virial coefficient (thermodynamic interaction between the two polymers) in miscible blends.

Typical DSC curve for polymers

![Typical DSC curve for polymers](image)
Phase separation in copolymers and IPNs

- Most polymer blends, grafts, blocks, and IPNs exhibit phase separation.
- It must be emphasized that their wide application in commerce arises largely because of the synergistic properties exhibited by these materials.
- Applications have included impact-resistant plastics, thermoplastic elastomers, coatings, and adhesives.
- The presence of the chemical bond between the blocks definitely improves the mutual miscibility of the two polymers.

Phase separation in block copolymers

- The block copolymers are miscible to higher block molecular weight than their corresponding blends.
- If block copolymers phase-separate, the domains must be small enough that one block resides in one phase while the other block is in the neighboring phase.
- The junction, or bond between the blocks, tends to be in the interface between the two blocks.
- The morphology of the phases changes from spheres to cylinders to alternating lamellae depending on the relative length of the two blocks.
Phase separation in block copolymers

- Spheres containing the short blocks are formed within the continuous phase of the longer block.
- Alternating lamellae form when the blocks are about the same length.
- Cylinders are formed for intermediate cases.

The numbers give the phase boundaries in terms of the volume fraction of the A blocks.

Phase separation in block copolymers

- The triblock copolymer polystyrene–block–polybutadiene–block–polystyrene (SBS) as a rubbery shoe material.

- The long, rubbery block forms the continuous phase whereas the short, glassy polystyrene blocks form submicroscopic spheres.

- The hard domains constitute a type of physical cross-link, holding the whole mass together.
Permeation is the rate at which a gas or vapor passes through a polymer. The mechanism by which permeation takes place involves three steps:

- (a) absorption of the permeating species into the polymer
- (b) diffusion of the permeating species through the polymer, traveling, on average, along the concentration gradient
- (c) desorption of the permeating species from the polymer surface and evaporation or removal by other mechanisms

Factors affecting permeability include the solubility and diffusivity of the penetrant into the polymer, polymer packing and side-group complexity, polarity, crystallinity, orientation, fillers, humidity, and plasticization.

For example, polymers with high crystallinity usually are less permeable because their ordered structure has fewer holes through which gases may pass.

If the polymer is glassy, the solvent lowers the $T_g$ by a plasticizing action. Polymer molecular motion increases. Diffusion rates above $T_g$ are far higher than below $T_g$. 
DIFFUSION AND PERMEABILITY IN POLYMERS

- Often polymers, in the form of films, are used as barriers to keep out water and air. In the case of food wrappers, it is often desired to keep in water but keep out oxygen.

- The permeability coefficient, \( P \), is defined as the volume of vapor passing per unit time through unit area of polymer having unit thickness, with a unit pressure difference across the sample.

\[
P = D \cdot S
\]

Permeability Units

- There are many dimensions and units found in the literature for permeability. The preferred current dimensions are

\[
P = \frac{\text{quantity of permeant}}{\text{(area)} \times \text{(time)} \times \text{(pressure drop across the film)}} \times \text{(film thickness)}
\]

- The preferred SI unit of the permeability coefficient is

\[
\text{Units of } P = \frac{\text{cm}^3 \times \text{cm}}{\text{cm}^2 \times \text{s} \times \text{Pa}}
\]
Permeability Data

- Permeability coefficients range from $10^{-11}$ to $10^{-16}$ cm$^3$ × cm$^{-2}$ × s × Pa for many polymers.
- In general, permeability decreases from elastomers to amorphous plastics to semicrystalline plastics.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Permeant</th>
<th>$P \times 10^3$</th>
<th>$P_0 \times 10^7$</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene (LDPE)</td>
<td>He</td>
<td>2.2</td>
<td>66.5</td>
<td>42.7</td>
</tr>
<tr>
<td></td>
<td>N$_2$</td>
<td>0.73</td>
<td>329</td>
<td>49.9</td>
</tr>
<tr>
<td></td>
<td>CO$_2$</td>
<td>9.5</td>
<td>62</td>
<td>38.9</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>68</td>
<td>48.8</td>
<td>33.5</td>
</tr>
<tr>
<td>cis-1,4-Polybutadiene</td>
<td>N$_2$</td>
<td>14.4</td>
<td>0.078</td>
<td>21.3</td>
</tr>
<tr>
<td></td>
<td>He</td>
<td>24.5</td>
<td>0.0855</td>
<td>20.3</td>
</tr>
<tr>
<td>Polye(ethyl methacrylate)</td>
<td>O$_2$</td>
<td>0.889</td>
<td>2.1</td>
<td>36.4</td>
</tr>
<tr>
<td></td>
<td>CO$_2$</td>
<td>3.79</td>
<td>0.435</td>
<td>28.9</td>
</tr>
<tr>
<td>Polyethylene terephthalate$^a$</td>
<td>O$_2$</td>
<td>0.0444</td>
<td>0.227</td>
<td>37.7</td>
</tr>
<tr>
<td>(amorphous)</td>
<td>CO$_2$</td>
<td>0.227</td>
<td>0.00021</td>
<td>27.0</td>
</tr>
<tr>
<td></td>
<td>CH$_4$</td>
<td>0.0070</td>
<td>0.9232</td>
<td>24.7</td>
</tr>
<tr>
<td>Poly(vinylidene chloride)$^b$</td>
<td>N$_2$</td>
<td>0.00070</td>
<td>900</td>
<td>70.3</td>
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<tr>
<td></td>
<td>O$_2$</td>
<td>0.00383</td>
<td>825</td>
<td>66.6</td>
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<tr>
<td></td>
<td>CO$_2$</td>
<td>0.0218</td>
<td>24.8</td>
<td>51.5</td>
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<tr>
<td></td>
<td>H$_2$O</td>
<td>7.0</td>
<td>863</td>
<td>46.1</td>
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<tr>
<td></td>
<td>H$_2$O</td>
<td>18900</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Effect of Permeant Size

- For elastomers, concerted movements of several adjacent chain segments take place to provide rapid transport.
- Such motions are restricted in glassy polymers. Also free volume is much less in glasses than in elastomers.
- The size of the permeant is critical in determining its diffusion rate in polymers. Sizes range from 2 to 5 Å for many molecules.
- The larger the molecule, the smaller the diffusion rate.
Effect of Permeant Size