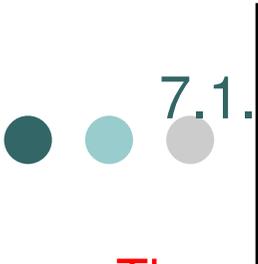# Chapter 7. Polymer solutions

7.1. Criteria for polymers solubility

7.2. Conformations of dissolved polymer chains

7.3. Thermodynamics of polymer solutions

7.4. Phase equilibrium in polymer solutions

7.5. Fractionation of polymers by solubility

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7.1. Criteria of polymer solubility

The solution process

The polymer dissolving occurs very slow and consists in 2 steps:

1. Solvent molecules slowly diffuse into the polymer
   $\longrightarrow$ a swolen gel.
   This process is very slow because of crosslinking, crytallinity, or strong hydrogen bonding.
2. The gel gradually disintegrates into a true solution.
   Agitation can speed up this process.

For very high molecular weight, the solution process takes days or weeks.

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Polymer texture and solubility

Solubility relations in polymer systems are complex, because of
- The size differences between polymer and solvent molecules,
- The viscosity of the system,
- The effects of the texture
- The molecular weight of the polymer.

Solubility depends on the nature of the solvent, the temperature of the solution, the topology of the polymer, and the crystallinity.

Cross-linked polymers do not dissolve, but only swell with the solvent when an interaction between the polymer and the solvent occurs.

Examples:
- Light cross-linked rubbers swell,
- Unvulcanized materials would dissolve,
- Hard rubbers and thermosetting materials may not swell in any solvent.

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Many non-polar crystalline polymers do not dissolve, except at the temperature near their crystalline melting points.

Explanation:

Crystallinity decreases as the melting point is approached and the melting point is depressed by the presence of the solvent, thus solubility can often achieved at temperatures below melting point.

Examples:

Linear PE (T_m = 135 ℃), soluble in many liquids at 100 ℃.

PTFE (T_m = 325 ℃), soluble in few liquids at >300 ℃.

Nylon-66 (T_m = 265 ℃), soluble in liquids at RT.

For polymers, with the same chemical type and molecular weight, the branched species are more soluble than their linear species.

Theory of solubility $\longrightarrow$ thermodynamics of polymer solutions.

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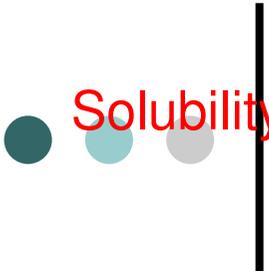
Solubility parameters

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

where: ΔG is the free energy of mixing (<0),

ΔH is the heat of mixing,

T is the temperature of mixing, and

ΔS is the entropy of mixing (>0).

For reasonably non-polar molecules and in the absence of hydrogen bonding, ΔH is positive.

$$\Delta H = \nu_1\,\nu_2\,(\delta_1 - \delta_2)^2$$

Where: ΔH is the heat of mixing/volume,

ν_1 , ν_2 are the fractions of solvent and polymer respectively,

δ^2 is the cohesive energy density or

the energy of vaporization/volume for small molecules or
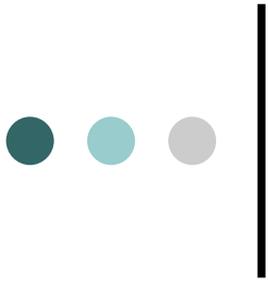
solubility parameter.

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Table 7.1. Page 153 Billmeyer

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In the absence of strong interactions such as hydrogen bonding, $(\delta_1 - \delta_2) < 3.5 - 4.0$.

The structure of a polymer determines δ_2

$$\delta_2 = \frac{\rho \sum E}{M}$$

where ρ is the density of polymer,
   E is the sum over the structural configuration of the repeating
      unit in the polymer chain,
   M is the repeat molecular weight.

Solvents with high solubility have usually small and compact molecules, these kinetically good solvents do not need thermodynamically good. Solvents of a kinetically good and a thermodynamically good liquid are often very powerful and rapid polymer solvents.
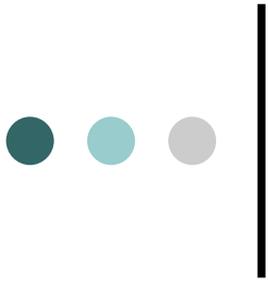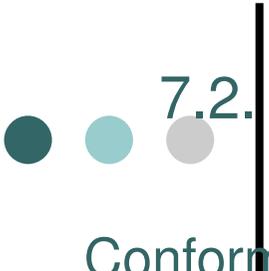
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Table 7.2. Page 154 Billmeyer

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7.2. Conformations of dissolved polymer chains

Conformations are the arrangements of polymer chain in term of rotations about single bonds.

A polymer molecule is a randomly coiling mass most of whose conformations occupy many times the volume of its segment.

The average density of segments within a dissolved polymer molecule is $\approx$ 10^{-4} – 10^{-5} g/cm^3.

The polymer-solvent interaction forces determine the size of the molecular coil.

A "good" solvent, where the polymer-solvent highly contact, the coils are relatively extended.

A "poor" solvent, where the polymer-solvent does not contact, the coils are contracted.

The random-coil nature of the dissolved, molten, amorphous, and glassy states of high polymers is important.

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The random coil arises from the relative freedom of rotation associated with the chain bonds of most polymers and the number of conformations accessible to the molecule.

Fig 7.2 Billmeyer

Example of a fully extended chain is all-trans planar zigzag carbon chain.

Some important terms:
• Contour length,
• Radius of gyration, $\left(\bar{r}^2\right)^{1/2}$: the root-mean-square distance between its ends,
• The root mean-square-root distance of the elements of the chain from its centre of gravity, $\left(\bar{s}^2\right)^{1/2}$

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Freely jointed chain

A simple model of a polymer chain consists of a series of x links of length l joined in a linear sequence without restrictions on the angles between successive bonds.

Classical random-flight method (Rayleigh, 1919)

$$\left(\bar{r}^2_{\ f}\right)^{1/2} = lx^{1/2}$$

where f is the random-flight end-to-end distance,

$$\left(\frac{\bar{r}^2_f}{M}\right)$$ is a characteristic property of the polymer chain structure and independent of molecular weight.
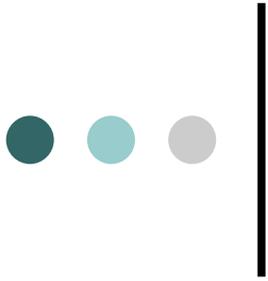
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Fig 7.3.

W is the probability to find such an array has a given end-to-end distance r.

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Short-range interactions

● The effect of short-range interactions on the dimensions of random-Coil polymers can be calculated from another model.

Modern polymer chemistry model (Flory, 1919)

Several effects are considered for this model.

•The restriction to fixed bond angle θ expands the chain by a factor of $[(1 - \cos \theta)/(1 + \cos \theta)]^{1/2}$ or it is equal to $\sqrt{2}$ for C-C bonds.

•Restricted rotation   steric hindrances, potential-energy barriers, resonance leading to rigid planar conformations increases dimensions.

•Conformations by 2 atoms close together along chain further expansion

•Pentane interference (interaction between 1st and 5th chain atoms in a sequence.

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The net results of all of these effects is called
- A characteristic ratio of the square of the actual chain dimensions in the absence of longitudinal interactions or unperturbed dimensions $\left(\overline{r_0}^2\right)$

- The square of the random-flight end-to-end distance, l^2x.

Fig 7.3.

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Long-range interactions and the excluded volume

Each segment of a real chain exists within a volume from which all other segments are excluded $\longrightarrow$ the excluded volume theory.

A statistical approach
The actual dimensions of the real chain:

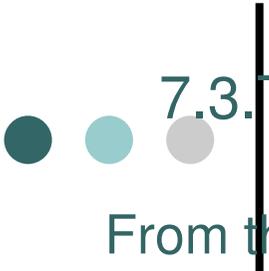$$\left(\overline{r^2}\right)^{1/2} = \alpha\left(\overline{r_0^{\,2}}\right)^{1/2}$$

where α is an expansion factor and depends on the nature of the
solvent and the temperature.

$\alpha >>> \longrightarrow$ "good" solvent and vice versa

When $\alpha = 1$, the chain attains its unperturbed dimensions.
At this condition, the temperature is called the Flory temperature, Θ.
A solvent used at $T = \Theta$ is called a Θ solvent.

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7.3. Thermodynamics of polymer solutions

From the study of solution properties, it is possible to obtain information about the size and the shape of polymer molecules.

Simple liquid mixture

The free energy of dilution of a solution in an equilibrium between 2 phases

$$\Delta G_A = kT \ln\left(\frac{P_A}{P_A^0}\right)$$ Colligative property of solution

where ΔG is the free energy of dilution resulting from the transfer of one molecule of liquid A, from the pure liquid state with vapour pressure P_A^0 to a large amount of solution with vapour pressure P_A.

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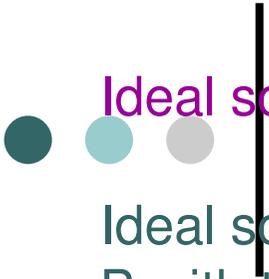
Ideal solution

Ideal solution is the simplest type of mixing between components A and B with the same size, shape, and force fields.

Raoult's law: the partial vapour pressure of each component in the mixture is proportional to its mole fraction.

The pressure of liquid A:

$$P_A = P_A^0 \frac{N_A}{N_A + N_B} = P_A^0 n_A$$

where n_A is the mole fraction of A.

$$\Delta G_A = kT \ln n_A$$

The total free energy of mixing:

$$\Delta G = N_A \Delta G_A + N_B \Delta G_B$$

$$\Delta G = kT(N_A \ln n_A + N_B \ln n_B)$$

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Types of mixing solutions:
• Ideal solutions, $\Delta H = 0$.
• Athermal solutions, $\Delta H = 0$, $\Delta S \neq \Delta S_{ideal}$
• Regular solutions, $\Delta S = \Delta S_{ideal}$, H is finite.
• Irregular solutions, both ΔH and ΔS deviate from the ideal values.

In an ideal mixing, the heat of mixing, $\Delta H = 0$.
The entropy of mixing:

$$\Delta S = k(N_A \ln n_A + N_B \ln n_B)$$

Many mixtures are regular solutions.
Polymer solutions deviate from ideal solutions. Even the mole fraction is replaced with the volume fraction $\longrightarrow$ bad correlation with experimental results.

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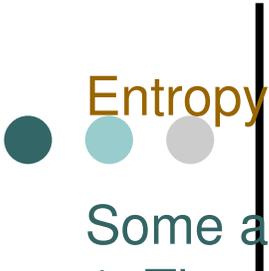
Entropy of mixing

Some assumptions are drawn for polymer solution:
1. The polymer molecules consist of a large number x of chain segments of equal length, flexibly joined together,
2. Each link occupies 1 lattice site,
3. The solution is concentrated so that the occupied lattice sites are distributed randomly.

Flory-Huggins theory of polymer solutions:

$$\Delta S = k(N_1 \ln v_1 + N_2 \ln v_2)$$

$$v_1 = \frac{N_1}{N_1 + xN_2} \qquad v_2 = \frac{xN_2}{N_1 + xN_2}$$

where υ_1 and υ_2 are the volume fractions of the solvent and the polymer, respectively,
x is the number of chain.

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Heat and free energy of mixing

$$\Delta H = \chi_1 kT N_1 \nu_2$$

$$\Delta G = kT(N_1 \ln \nu_1 + N_2 \ln \nu_2 + \chi_1 N_1 \nu_2)$$

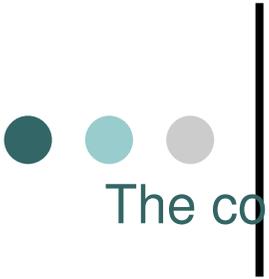where χ_1 is the interaction energy per solvent molecules / kT

Other thermodynamics quantities

The partial molar free energy of mixing:

$$\Delta \overline{G}_1 = kT[\ln(1 - \nu_2) + \left(1 - \frac{1}{x}\right)\nu_2 + \chi_1 \nu_2^2)$$

The osmotic pressure:

$$\pi = \frac{kT}{V_1}\left(\frac{\nu_2}{x} + (\frac{1}{2} - \chi_1)\nu_2^2 + ...\right)$$

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The coefficient of $\upsilon_2{}^2$ is known as the second virial coefficient A_2

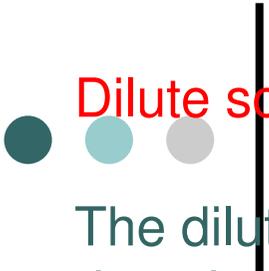$$A_2 \equiv \frac{\overline{v}_2^2}{N_0 V_1} \left(\frac{1}{2} - \chi_1\right)$$

The Flory-Huggins theories were compared with experimental data of rubber in benzene. It is found that the partial molar heat of dilution

$$\Delta H = \chi_1 k T v_2^2$$

was not observed.
The entropy of mixing was in fair agreement with the theory.
The other properties did not match with the theoretical values.

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Dilute solutions

The dilute polymer solution is discontinuous in structure and consists of domains or clusters of polymer chain segments separated on the average by regions of polymer-free solvent.

The partial molar heat: $\Delta \overline{\mathrm{H}}_1 = kT\kappa_1 v_2^2$

$$\kappa_1 - \psi_1 = \chi_1 - \frac{1}{2}$$

The partial molar entropy: $\Delta \overline{\mathrm{S}}_1 = k\psi_1 v_2^2$

The partial molar free energy: $\Delta \overline{\mathrm{G}}_1 = kT(\kappa_1 - \psi_1)v_2^2$

The Flory temperature: $\Theta = \dfrac{\kappa_1 T}{\psi_1}$

At $T = \Theta$, the partial molar free energy due to polymer-solvent interactions is zero and the deviations from ideal solution vanish.

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7.4. Phase equilibrium in polymer solutions

Polymer-solvent miscibility

Equilibrium between amorphous polymer and solvent(s).
When the temperature of a polymer solution $\uparrow$ or $\downarrow$ $\longrightarrow$
the solvent becomes thermodynamically poorer $\longrightarrow$
polymer and solvent are no longer miscible in all proportions
$\longrightarrow$ the mixture separates into 2 phases.
In this condition, χ_1 exceeds a critical value ($\chi_1 \cong \frac{1}{2}$)

The phase separation takes place in 2 temperatures:
• The upper critical solution temperature,
• The lower critical solution temperature $\longrightarrow$ 2 critical values of χ_1

$\downarrow$

2 values of Θ

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Binary polymer-solvent systems

In a binary system, the equilibrium between 2 phases occurs when the partial molar free energy for each component is equal in each phase. (The 1st and 2nd derivatives of ΔG_1 to $v_2 = 0$) *see slide 20*

The critical volume fraction:
$$v_{2c} = \frac{1}{1+x^{1/2}} \approx \frac{1}{X^{1/2}}$$

For a typical polymer, $x \cong 10_4$, $v_{2c} \cong 0.01$

The critical value of χ_1:
$$\chi_{1c} = \frac{(1+x^{1/2})^2}{2x} \cong \frac{1}{2} + \frac{1}{x^{1/2}}$$

The temperature at which phase separation begins:
$$\frac{1}{T_c} = \frac{1}{\Theta}\left[1 + \frac{1}{\psi_1}\left(\frac{1}{x^{1/2}} + \frac{1}{2x}\right)\right] = \frac{1}{\Theta}\left(1 + \frac{C}{M^{1/2}}\right)$$

where C is a constant of the polymer-solvent system
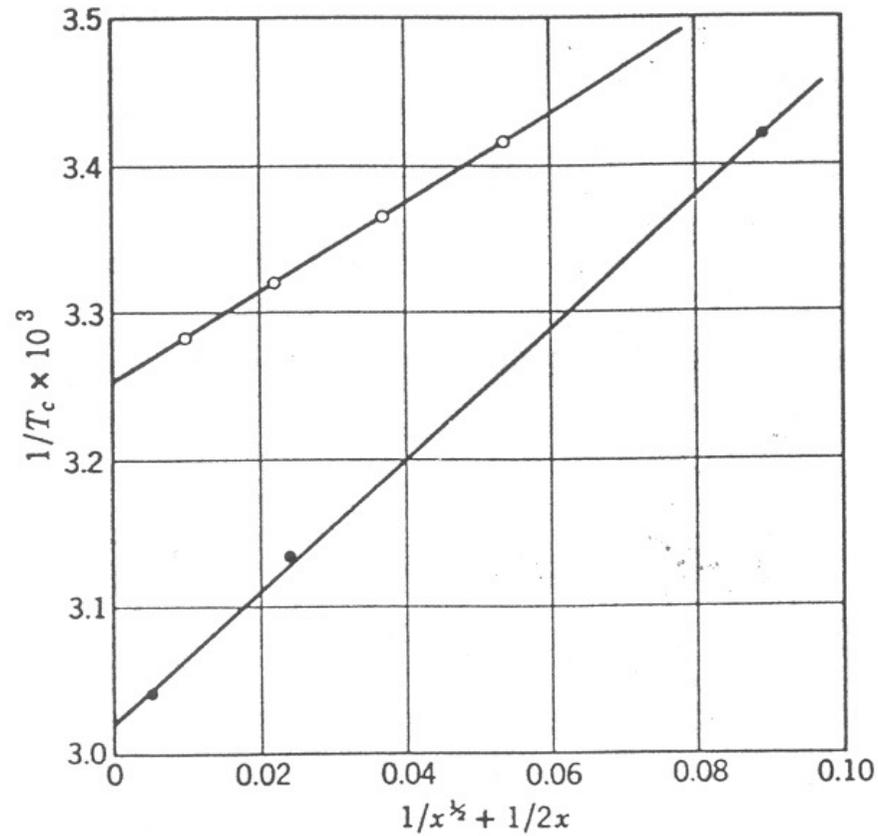
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FIG. 7-11. Dependence of critical temperature for phase separation on molecular weight for (○) polystyrene in cyclohexane, and (●) polyisobutylene in diisobutyl ketone (Shultz 1952).

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Multi component systems

This system consists of a heterogeneous polymer in a single solvent.
It is assumes that χ for all values of x are identical, only the size parameter x itself varies from one molecular species to another.

To make the calculation simple:

$$\ln\left(\frac{v'_x}{v_x}\right) = \sigma x$$

where σ is a parameter that relates precipitated and dilute phases,
v_x' and v_x are the concentrations of species x in the precipitated phase and the dilute phase, respectively.

So that:

$$\sigma = v_2\left(1 - \frac{1}{\overline{x}_n}\right) - v'_2\left(1 - \frac{1}{\overline{x}'_n}\right) + \chi_1\left[(1 - v_2)^2 - (1 - v'_2)^2\right]$$

where v_2' and v_2 are the total polymer concentrations in 2 phases,
x_n is the number average of x.

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Region II: semidilute region

Region I: dilute region

Region III: semidilute &
concentrated Θ region

Region I': Θ region

Region IV: negative
region of τ
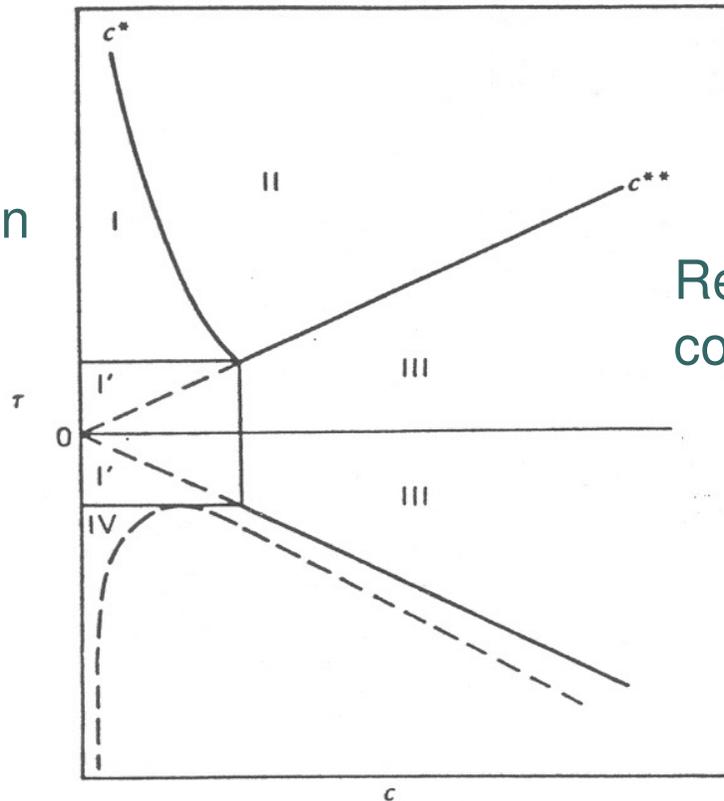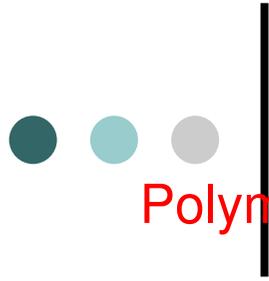
$$\tau = \frac{(T - \Theta)}{\Theta}$$

FIG. 7-15. Typical phase diagram of a polymer solution. See the text for explanation. (Reprinted with permission from Daoud 1976, Figure 3, page 974.)

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Polymer-polymer miscibility

The phase separation in polymer-polymer systems has been in interest because the interesting properties of compatible polymer blends has been increased.
In general, polymers mixed are totally immiscible.
However, some of them existed.
Some of the experimental data agree with the Flory-Huggins theory.

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7.5. Fractionation of polymers by solubility

Some techniques for fractionating polymers by solubility differences are existed.

7.5.1. Bulk fractionation by nonsolvent solubility technique

This method takes place by adding nonsolvent to a dilute solution of the polymer until a slight turbidity develops at the temperature of fractionation $\longrightarrow$ homogeneous mixture $\longrightarrow$
The precipitation phase settles to a coherent layer and the supernatant phase is removed $\longrightarrow$ precipitated phase is added.
This process is repeated until the polymer is isolated from the precipitated phase (10% polymer).

The selection of solvent and precipitant are important.
Some considerations are stability and volatility of the liquids and their ability to form a highly swollen, mobile gel phase.

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7.5.2. Column elution technique

The most important techniques & widely practiced for fractionating polymers are by solubility differences.

Solvent-gradient elution

Polymer is placed in contact with a series of liquids of gradually increasing solvent power. Species of lowest molecular weight (the highest solubility) dissolve in the 1st liquid and higher molecular-weight fractions in subsequent liquid.

To achieve a rapid equilibrium, the polymer is in a very thin film form.

This process takes place in a mixing vessel, obtained a continuous gradient of solvent-nonsolvent composition and eluted through a column.

Thermal-gradient elution

A small temperature gradient is added from one to the other of the column.

Each species experiences a series of solution and precipitation steps through temperature-gradient column.

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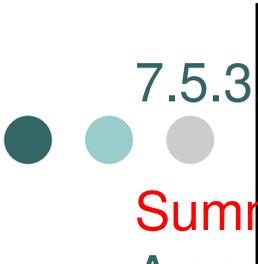
7.5.3. Analytical precipitation technique

Summative fractionation
A series of polymer solutions is used. In each solution, part of the polymer is precipitated and the point of fractionation being varied throughout the series.

Turbidimetric titration
A precipitant is added slowly to a polymer solution. The turbidity due to precipitated polymer is measured by the decrease in intensity of a beam of transmitted light or by the increase in intensity of scattered light.

7.5.4. Effect of polymer structure on solubility-based fractionation

Effect of chemical type
The solubility of polymers is primarily determined by their chemical compositions. So that fractionation is likely to occur as a result of these compositions.

Effect of chain branching
Branching increases the solubility of high polymers. Branched polymers being separated will consist of a mixture of species, some with low branching and low molecular weight, others with more branched but with higher molecular weight.

Effect of crystallinity
Fractionation by molecular weight can be done for precipitation of polymer to a crystalline phase, especially if crystalline melting point is a strong function of molecular weight.

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