Leibniz-Institut
für Polymerforschung
Dresden

Polymers in Solution

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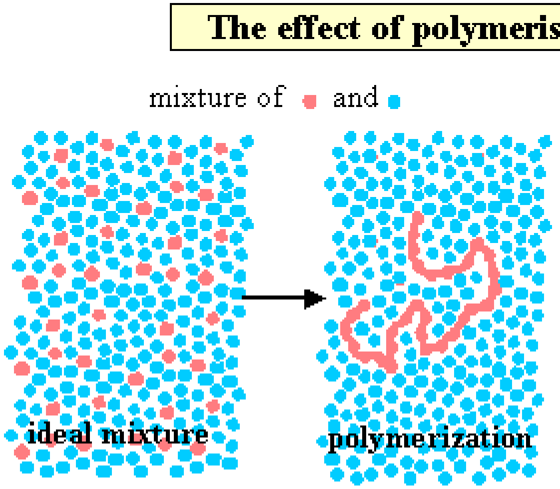
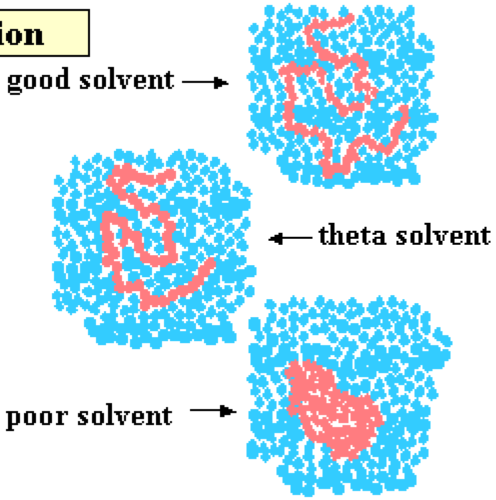
3. Thermodynamics of polymer solution and blends

1. Thermodynamic Classification of Solutions





Thermodynamic properties of the polymer solution depend on how "good" the solvent is for the polymer as well as on the polymer itself. The interaction between the solvent and the polymer and the degree of polymerization dictate the properties.

Second law of thermodynamics

$$\Delta G = \Delta H - \Delta(TS) = \Delta U + \Delta(pV) - \Delta(TS) = \Delta A + \Delta(pV)$$

G = Gibbs energy; H = enthalpy; U = internal energy; A= Helmholtz energy, free energy; S = entropy, p = pressure, V = volume and T = thermodynamic temperature

Mixing of two components : ideal + excess

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} = \Delta H_{mix} - T\Delta S_{mix,id} - T\Delta S_{mix,ex}$$

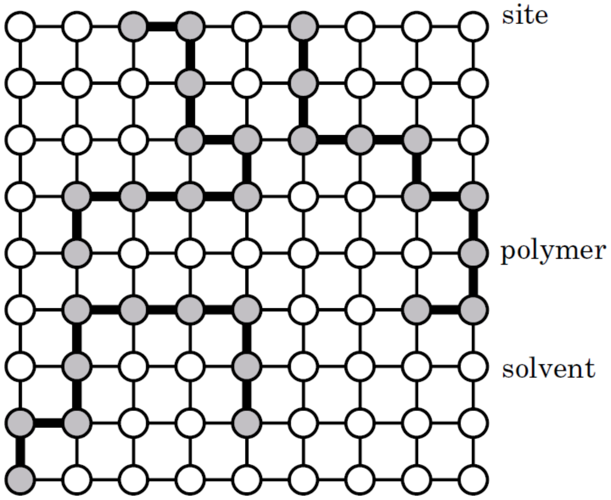
According to the various contributions, the solutions can be classified :

Type	ΔG_{mix}	ΔH_{mix}	$\Delta s_{mix,\ exc}$	Miscibility
Ideal	$-T\Delta S_{mix,id}$	0	0	At all T
Athermal	negative	0	positive	At all T
Regular	negative	negative	0	At all T
Irregular	negative	negative	positive	At all T
Pseudo-ideal (theta)	$-T\Delta S_{mix,id}$ ~0	$-\theta\Delta S_{mix,exc}$	$\Delta H_{mix}/\theta$	At θ

polymer coils

2. FLORY–HUGGINS MEAN-FIELD THEORY (1930)

Lattice Chain Model



The system consists of n$_{site}$ sites. Each site can be occupied by either a monomer of the polymer or a solvent molecule. Polymer chains consisting of N monomers are laid onto empty sites one by one until there are a total nP chains. Then, the unoccupied sites are filled with solvent molecules.

	Volume Fraction	Number of Molecules
Polymer	ϕ	$n_P = n_{site}\phi/N$
Solvent	$1-\phi$	$n_S = n_{site}(1-\phi)$

Entropy Mixing

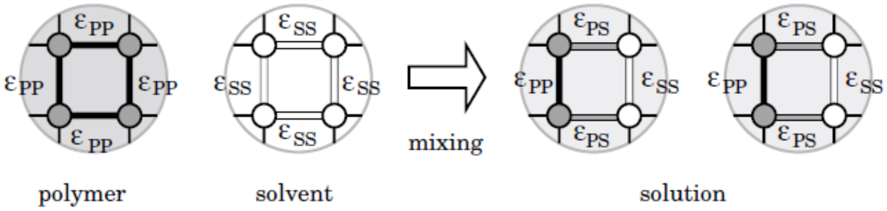
$$-\Delta S_{mix}/(k_B n_{site}) = \frac{\phi}{N}\ln\phi + (1-\phi)\ln(1-\phi) \qquad \text{Flory–Huggins}$$

ΔS_{mix} is greater than the entropy of mixing for an ideal solution. Greater number of conformations a polymer chain.

Flory's χ parameter or Flory–Huggins χ parameter- INTERACTION PARAMETER

Enthalpy of Mixing

$$\Delta G_{mix} = \Delta U_{mix} - T\,\Delta S_{mix}$$



$$\chi = \Delta U_{mix} / (kT\, N_s\, \phi_p)$$

Interaction Change Upon Mixing

$$\Delta U_{mix}/(n_{site} k_B T) = \chi\phi(1-\phi) \qquad \text{Flory–Huggins}$$

ΔU_{mix} depends on the interaction through χ. A system with the same χ has the same ΔU_{mix}.

A solution with $\chi = 0$ is called **an athermal solution.**

3. Free Energy, Chemical Potentials, and Osmotic Pressure

Helmholtz free energy of mixing

$$\Delta A_{\mathrm{mix}} = \Delta U_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}}$$

$$\boxed{\frac{\Delta A_{\mathrm{mix}}}{n_{\mathrm{site}} k_{\mathrm{B}} T} = \frac{\phi}{N}\ln\phi + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi) \quad \text{Flory–Huggins}}$$

Chemical Potentials

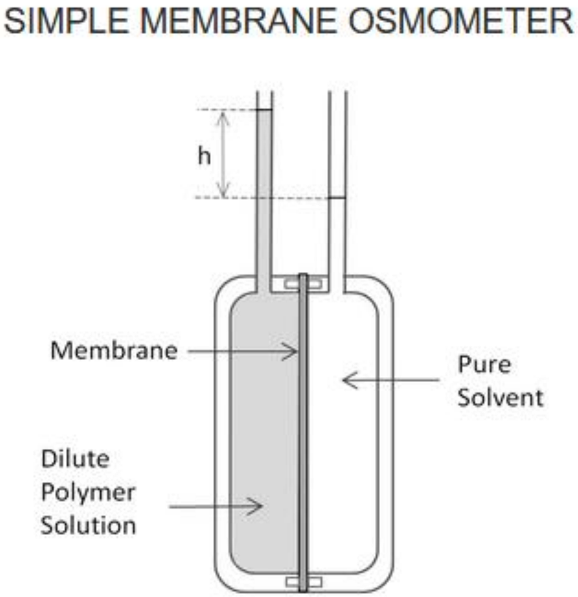
$$\frac{\Delta\mu_{\mathrm{S}}}{k_{\mathrm{B}}T} = \left(\frac{\partial}{\partial n_{\mathrm{S}}}\frac{\Delta G_{\mathrm{mix}}}{k_{\mathrm{B}}T}\right)_{T,p,n\mathrm{P}} = \ln(1-\phi) + \left(1-\frac{1}{N}\right)\phi + \chi\phi^2$$

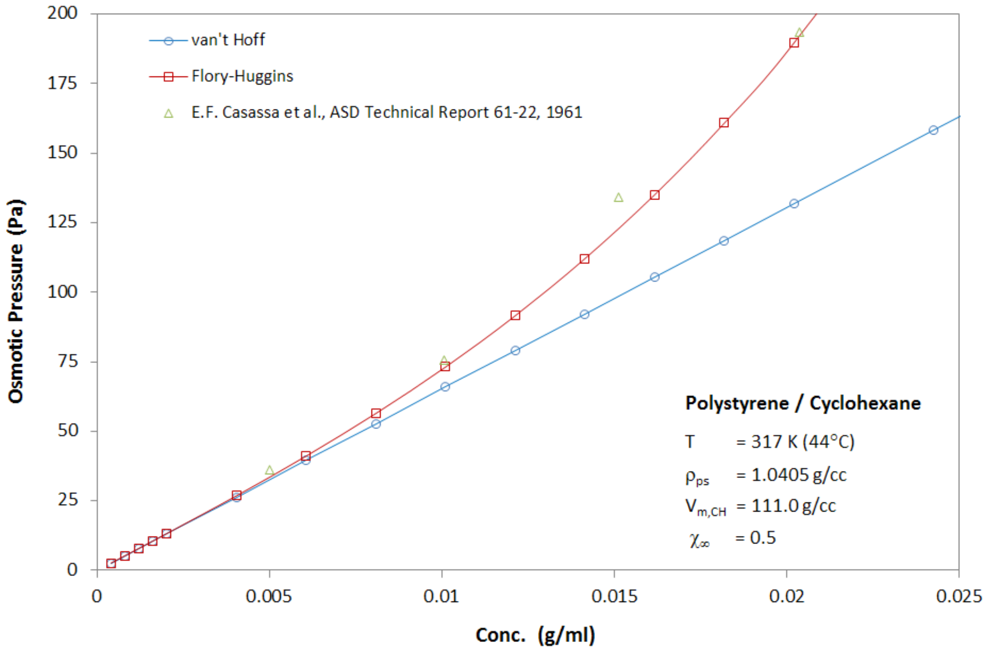
Osmotic Pressure

$$\boxed{\frac{\Pi v_{\mathrm{site}}}{k_{\mathrm{B}}T} = \frac{\Pi V}{n_{\mathrm{site}} k_{\mathrm{B}} T} = \frac{\phi}{N} - \ln(1-\phi) - \phi - \chi\phi^2 \quad \text{Flory–Huggins}}$$

3. Free Energy, Chemical Potentials, and Osmotic Pressure

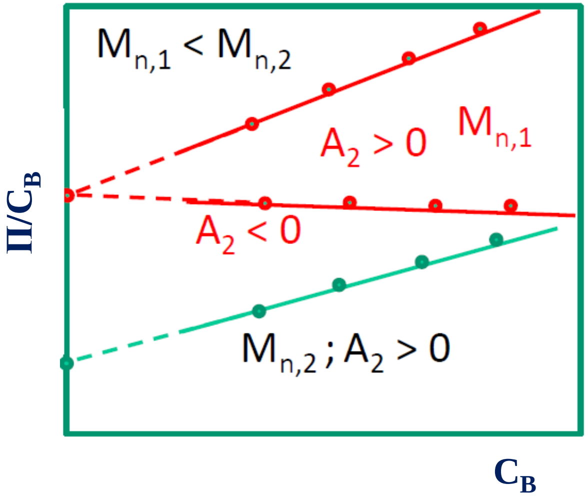
Osmotic Pressure of Polymer Systems





$$\frac{\pi}{c_B} = RT\left(\frac{1}{M_n} + A_2 c_B\right)$$

Determination of M_n and A_2



2. FLORY–HUGGINS MEAN-FIELD THEORY (1930)

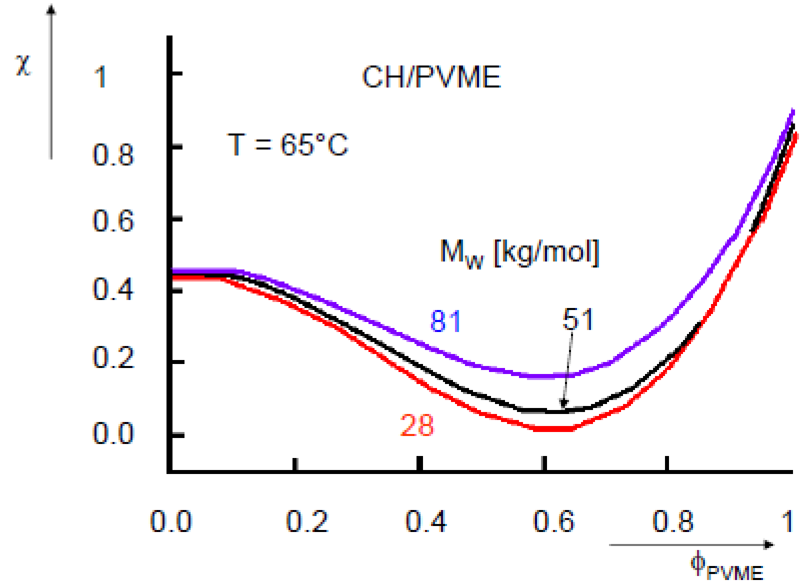
$\chi(T) = A + B / T$

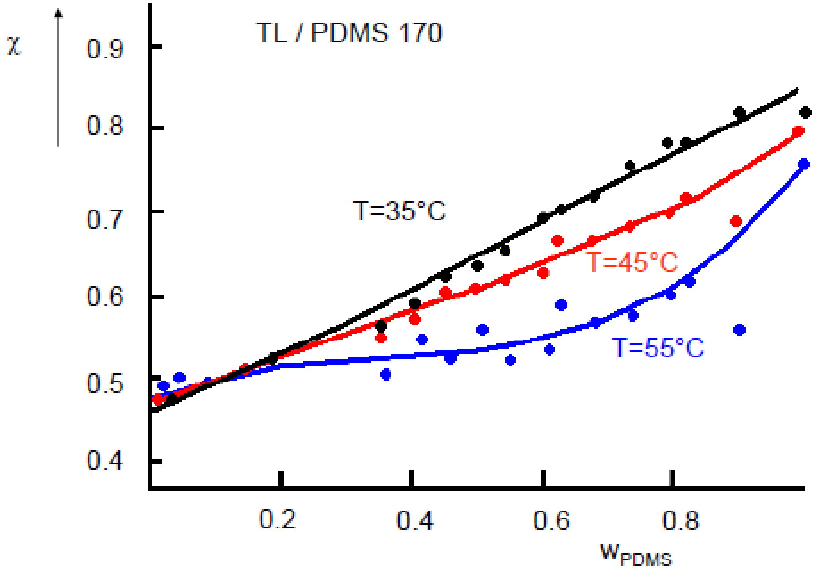
The temperature independent term A is the so-called "entropic part" of of χ, while B / T is called the "enthalpic part".

The parameter A and B have been tabulated for many polymer-solvent and polymer-polymer systems.

Flory-Huggins parameter for polymer + solvent - systems

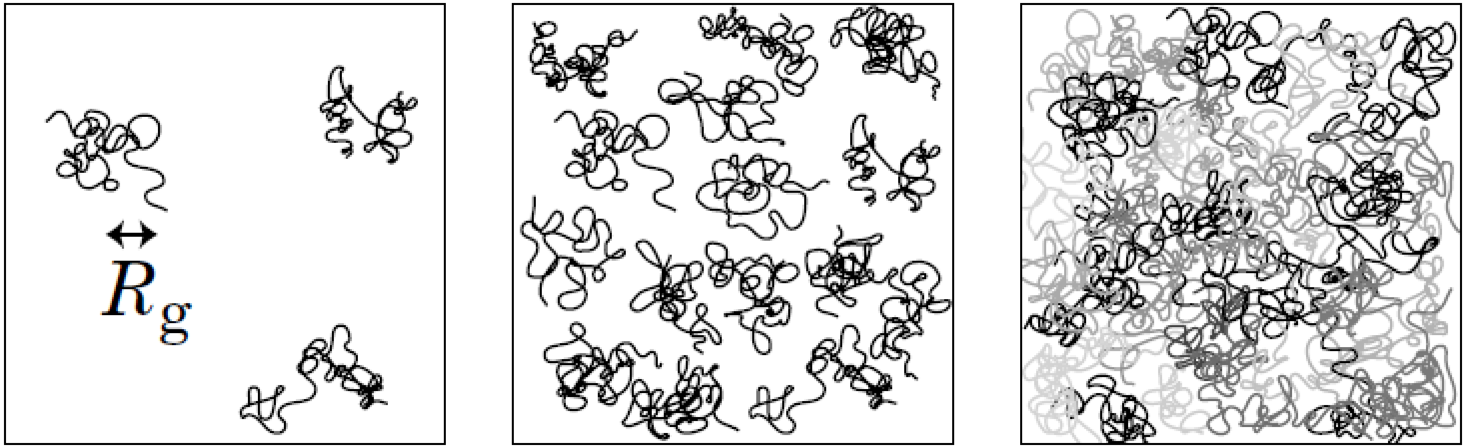
system	T [°C]	χ
cellulose nitrate + acetone	25	0.27
polyisobutylene + benzene	25	0.5
polystyrene + toluene	25	0.44
PVC + THF	26	0.15
rubber + CCl_4	20	0.28
rubber + benzene	25	0.44
rubber + acetone	25	1.37





2. FLORY–HUGGINS MEAN-FIELD THEORY (1930). Diluted conditions

Concentration Regimes for Linear Flexible Polymers



$$c \ll c^*$$

Dilute

The polymer chain interacts primarily with the solvent molecules. The solution is close to an ideal solution.

$$c \cong c^*$$

Semidilute

The thermodynamic properties of the semidilute solutions are greatly different from those of an ideal solution extrapolated to the same concentration. The existence of the semidilute regime is characteristic of the polymer solutions.

$$\boxed{c_*[\eta] = 1}$$

$$c \gg c^*$$

Chains are overlapped and entangled. Their mobility is greatly reduced compared with the chains in dilute solutions.

2. FLORY–HUGGINS MEAN-FIELD THEORY (1930). Diluted conditions

Concentration Regimes for Linear Flexible Polymers

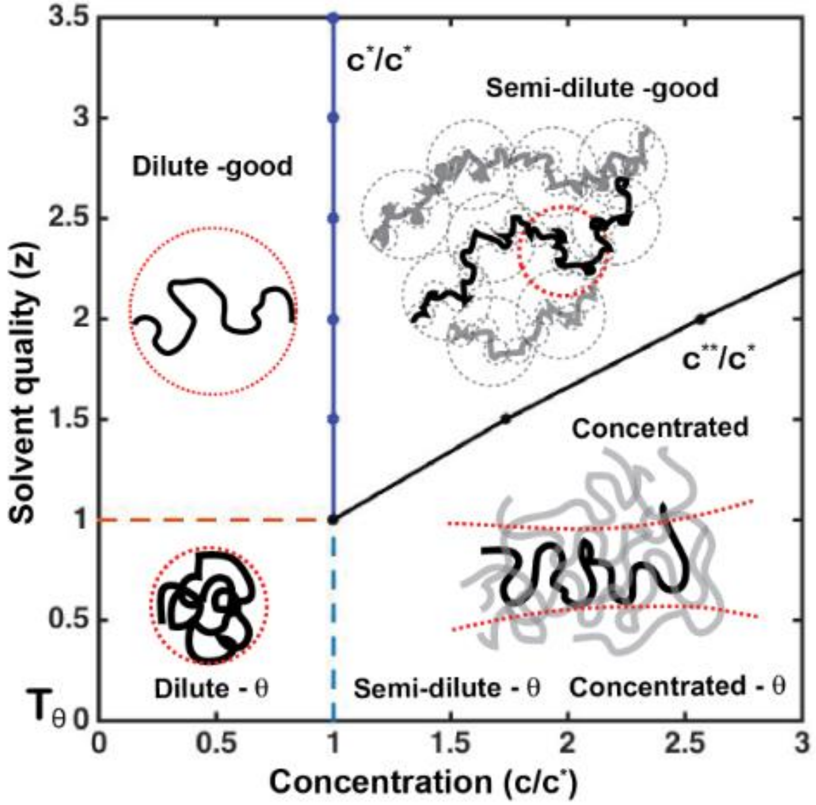
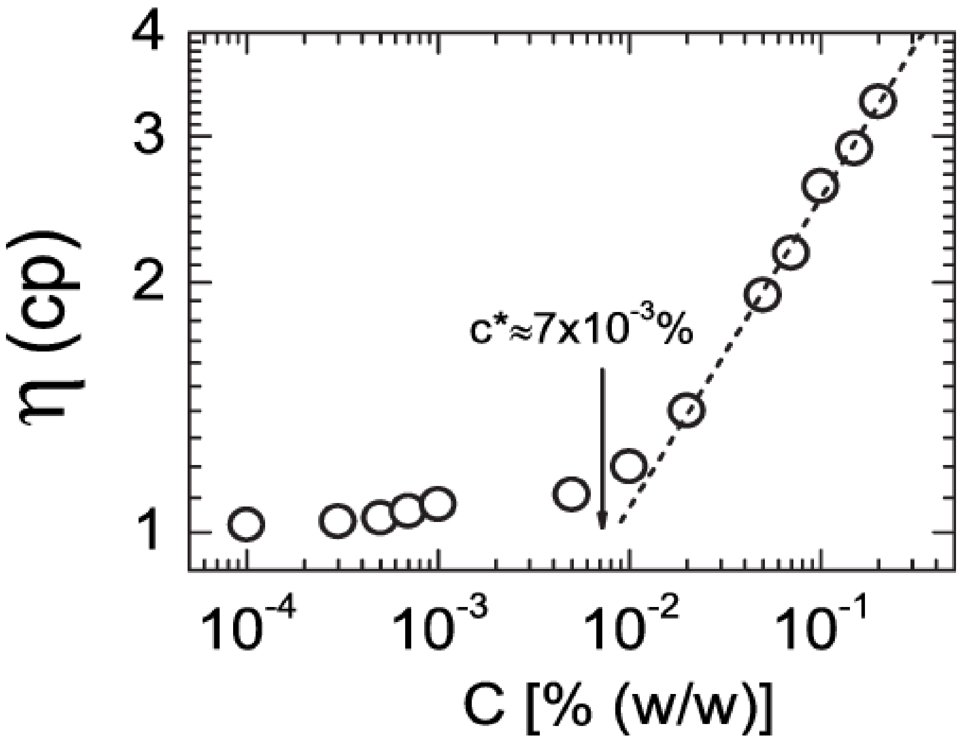


FIG. 1. Phase diagram for polymer solutions as a function of relative concentration c/c^* and solvent quality z (see Section II for details). For display purposes, we chose monomer size $b = 1$ and an excluded volume exponent $\nu = 0.56$ based on experimental results.

2. FLORY–HUGGINS MEAN-FIELD THEORY (1930). Diluted conditions

Concentration Regimes for Linear Flexible Polymers

$$c_*[\eta] = 1$$



The critical polymer concentration c * is determined as the concentration at the onset of the power law behavior of the viscosity as a function of polymer concentration c.

2. FLORY–HUGGINS MEAN-FIELD THEORY (1930). Diluted conditions

Osmotic compressibility (Π/Π_{ideal})

$$\frac{\Pi V}{n_{\mathrm{site}} k_{\mathrm{B}} T} = \frac{\phi}{N} + \left(\frac{1}{2} - \chi\right)\phi^2 + \frac{1}{3}\phi^3 + \cdots \quad \text{Flory–Huggins, dilute solution}$$

$$\Pi_{\mathrm{ideal}} = \frac{n_{\mathrm{site}}\phi}{NV} k_{\mathrm{B}} T$$

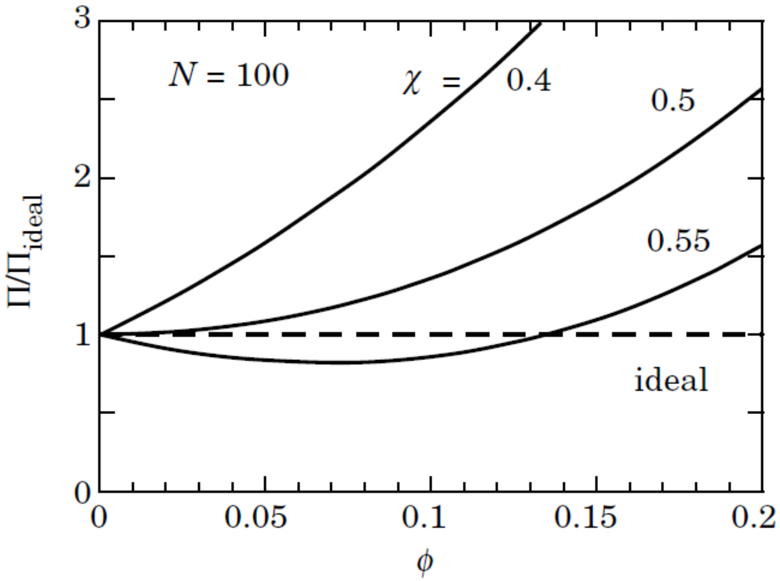


Figure 2.7. Osmotic compressibility (Π/Π_{ideal}) plotted as a function of ϕ for the ideal solution (dashed line) and nonideal solutions with $N = 100$ and $\chi = 0.4$, 0.5, and 0.55 (solid lines).

2. FLORY–HUGGINS MEAN-FIELD THEORY (1930). Diluted conditions

Virial Expansion

$$\boxed{\frac{\Pi}{N_A k_B T} = \frac{c}{M} + A_2 c^2 + A_3 c^3 + \cdots \qquad \text{virial expansion}}$$

$$c = \frac{M}{N_A N}\frac{\phi}{v_{\text{site}}}$$

$$\boxed{A_2 = \left(\tfrac{1}{2} - \chi\right) N_A v_{\text{site}} (N/M)^2}$$

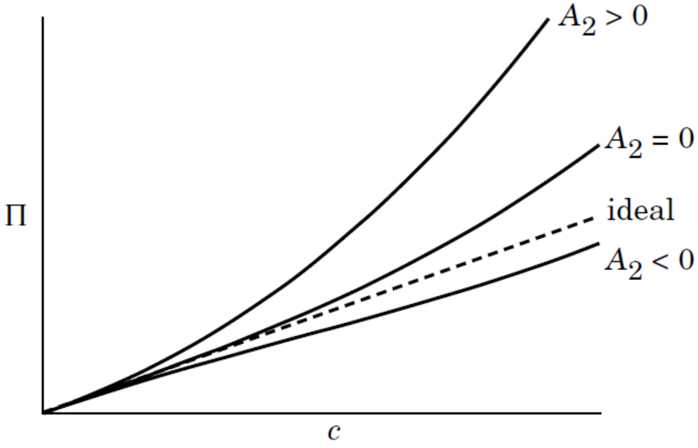
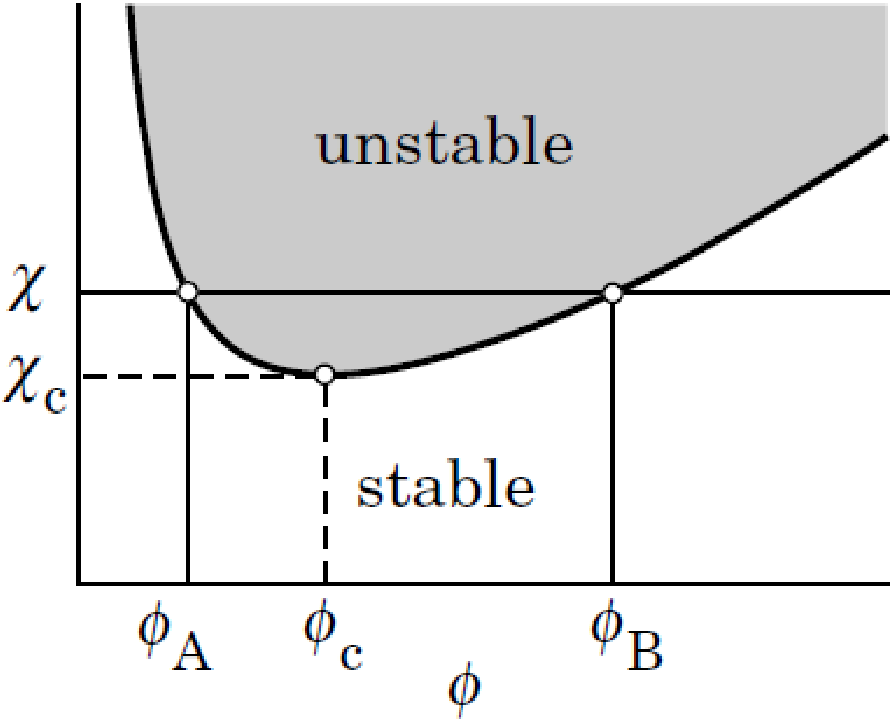


TABLE 2.4 Relationship Between A_2 and χ

A_2	Π	χ
+	$>\Pi_{\text{ideal}}$	$<1/2$
0	$\cong\Pi_{\text{ideal}}$	$=1/2$
−	$<\Pi_{\text{ideal}}$	$>1/2$

2. FLORY–HUGGINS MEAN-FIELD THEORY (1930). Diluted conditions

Coexistence Curve and Stability



The instability condition is given as

$$\frac{1}{\phi} + \frac{N}{1-\phi} < 2\chi N$$

The line that separates the stable region from the unstable region is called the **spinodal line**.

2. FLORY–HUGGINS MEAN-FIELD THEORY (1930). Diluted conditions

PHASE DIAGRAM AND THETA SOLUTIONS

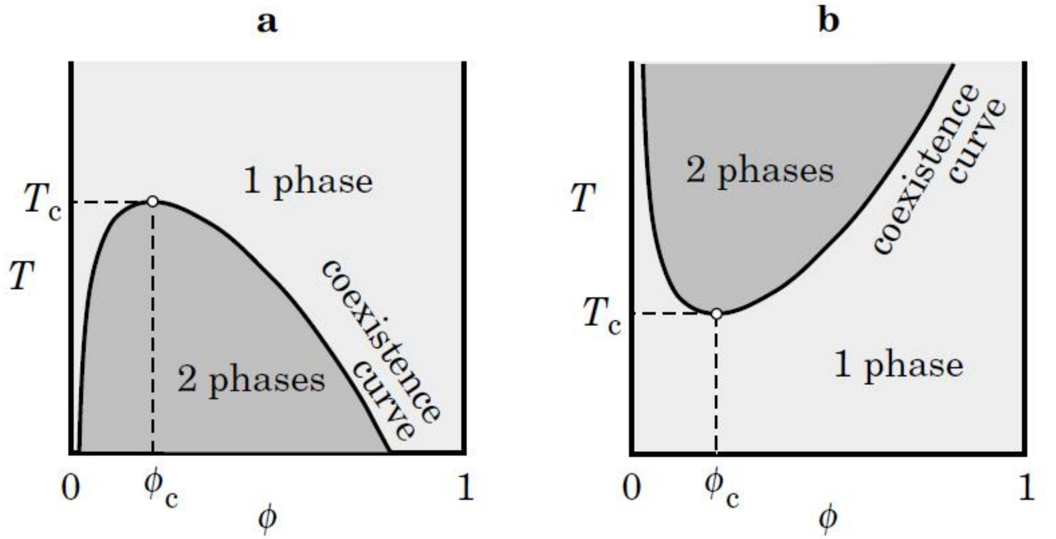


Figure 2.19. Phase diagram of polymer solution on temperature–composition plane. a: UCST-type phase diagram. b: LCST-type phase diagram. The critical point is at the apex of the coexistence curve and is specified by the critical temperature T_c and the critical composition ϕ_c.

The temperature at the critical condition is called the **critical temperature**.

The phase diagram has the critical temperature (*T*c) at the highest point on the coexistence curve- **upper critical solution temperature** (**UCST**).

The phase diagram has the critical temperature (*T*c) at the lowest point on the coexistence curve- **lower critical solution temperature** (**LCST**).

2. FLORY–HUGGINS MEAN-FIELD THEORY (1930). Diluted conditions

PHASE DIAGRAM AND THETA SOLUTIONS

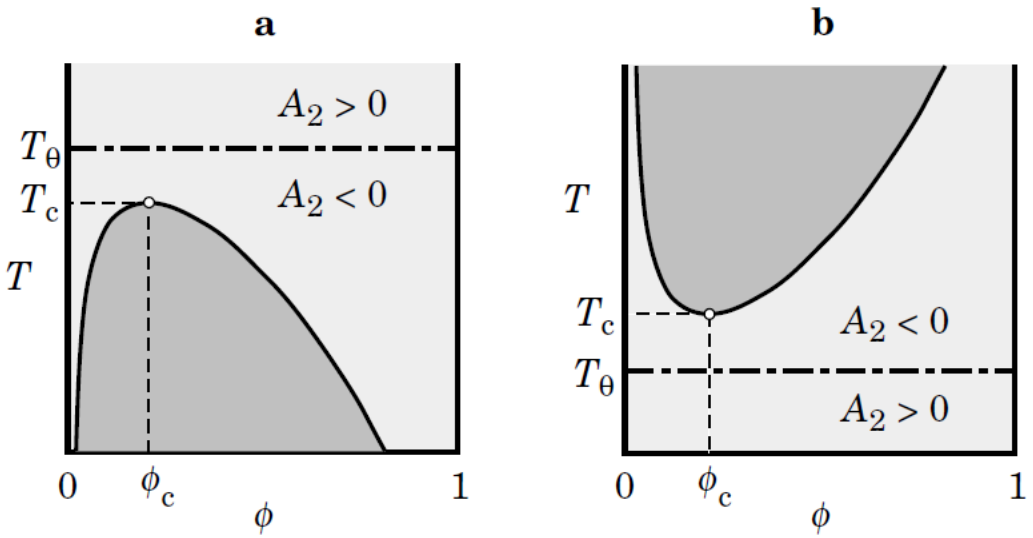


Figure 2.23. Relationship between the theta temperature T_θ with the critical temperature T_c. a: UCST-type phase diagram. b: LCST-type phase diagram. The second virial coefficient A_2 changes its sign at $T = T_\theta$.

The Theta-temperature ($A_2 = 0$) is the temperature for the particular theta-solvent which minimizes interactions between the polymer segments and the solvent. The theta temperature is different for each combination of polymer and solvent.

There is a slight molecular weight dependence of the temperature that renders $A_2 = 0$ when the molecular weight is not sufficiently high. The dependence is much smaller compared with the dependence of *Tc* on the molecular weight.

2. FLORY–HUGGINS MEAN-FIELD THEORY (1930). Diluted conditions

Solubility Parameter

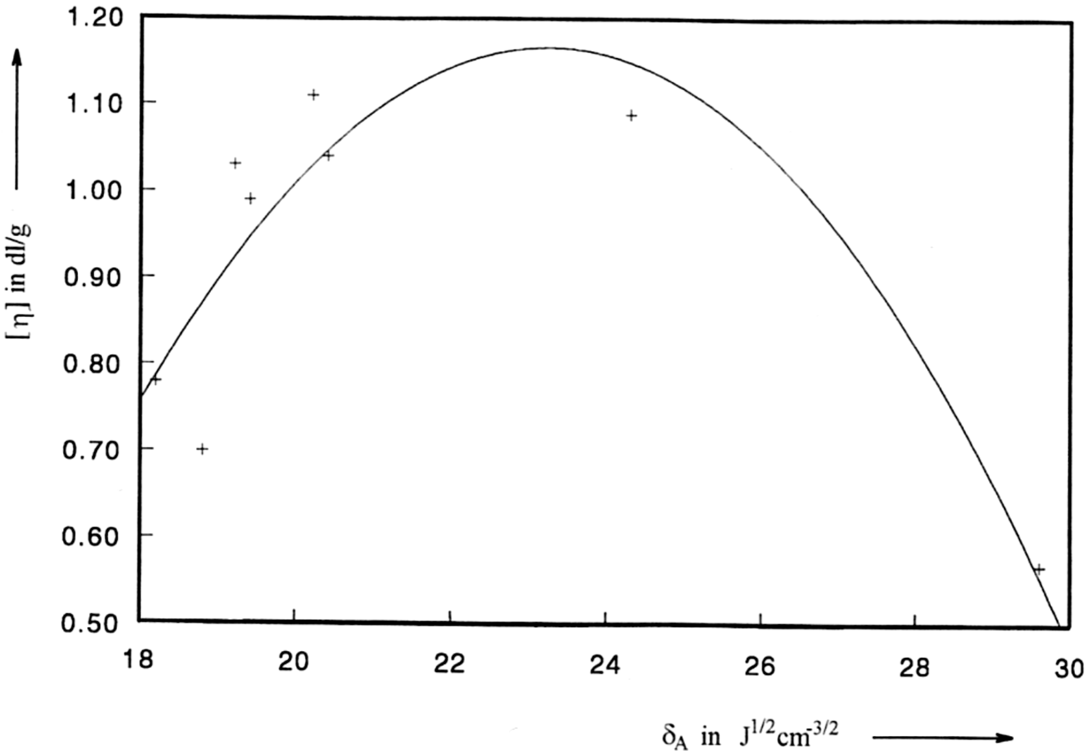
$$\chi = \frac{V_S}{N_A k_B T}(\delta_S - \delta_P)^2 + 0.34$$

$$\Delta H_m = n v_A \varphi_B (\delta_A - \delta_B)^2$$

$$\delta = \sqrt{\frac{\Delta H_v - RT}{V}}$$

Experimental determination of δ:

At $\Delta H_m = 0$, $\delta_A = \delta_B$ **having maximum intrinsic viscosity [η], which means maximum coil expansion**



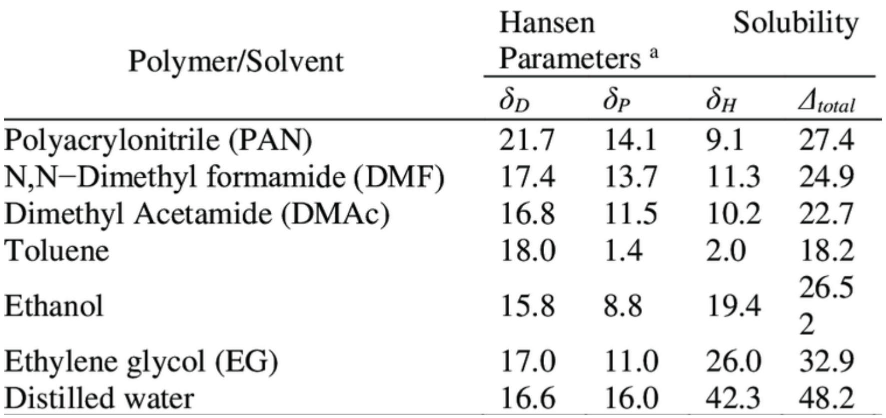
2. FLORY–HUGGINS MEAN-FIELD THEORY (1930). Diluted conditions

Solubility Parameter

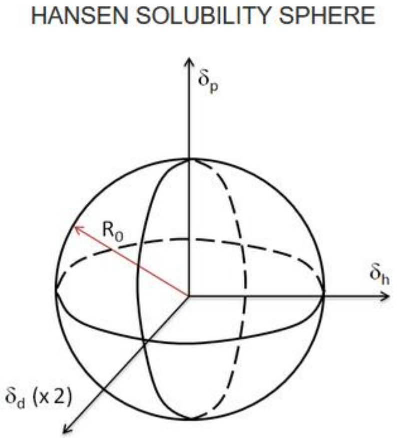
Hansen´s Three-dimensional solubility Parameter

$$\delta^2 = \delta_d^{\,2}\ \textit{(dispersion forces)} + \delta_p^{\,2}\ \textit{(polar forces)} + \delta_H^{\,2}\ \textit{(hydrogen bonding)}$$

The method is based on the idea that *like dissolves like*. This is the case when the solvent and the solute have similar Hansen Solubility Parameters.



Polymer/Solvent	Hansen Parameters [a]			Solubility
	δ_D	δ_P	δ_H	Δ_{total}
Polyacrylonitrile (PAN)	21.7	14.1	9.1	27.4
N,N–Dimethyl formamide (DMF)	17.4	13.7	11.3	24.9
Dimethyl Acetamide (DMAc)	16.8	11.5	10.2	22.7
Toluene	18.0	1.4	2.0	18.2
Ethanol	15.8	8.8	19.4	26.52
Ethylene glycol (EG)	17.0	11.0	26.0	32.9
Distilled water	16.6	16.0	42.3	48.2



$$R_a^{\,2} = 4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{h2} - \delta_{h1})^2$$

The distance R_a in the equation above can be compared with the solubility radius of the polymer, $\boldsymbol{R_0}$.

The radius of the solubility sphere is often called the ***interaction radius* and the ratio R_a / R_0 the *relative energy difference* (RED) of the system.**

$R_a / R_0 > 1$ → the compound is a non-solvent

$R_a / R_0 < 1$ → the compound is a solvent

$R_a / R_0 = 0$ → the compound may cause swelling

3. Thermodynamics of Polymer Blends

If **two polymers are mixed**, the most frequent result is a system that exhibits **a complete phase separation due to the repulsive interaction between the components.** Complete miscibility in a mixture of two polymers requires that the following condition is fulfilled:

$\mathbf{\Delta G_m = \Delta H_m - T\Delta S_m < 0}$

a) The value of $T\Delta S_m$ is always positive ➔ there is an increase in the entropy on mixing.

$$\Delta G_m < 0 \, , \left(\frac{\partial^2 \Delta Gm}{\partial \phi^2} \right)_{p,T} > 0$$

b) The sign of ΔG_m always depends on the value of the enthalpy of mixing ΔH_m $\mathbf{\Delta H_m < T\Delta S_m}$

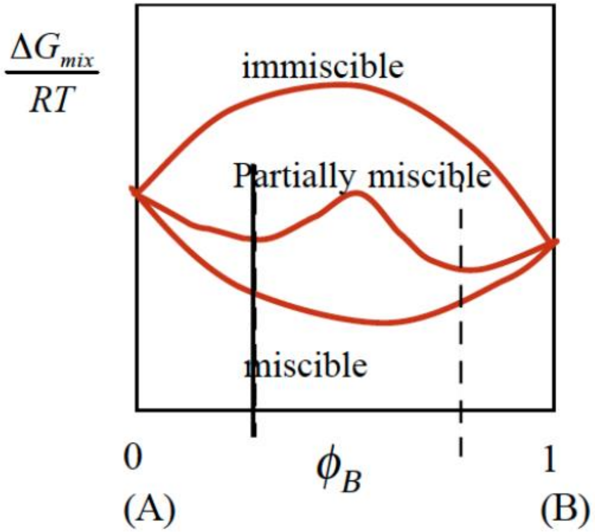
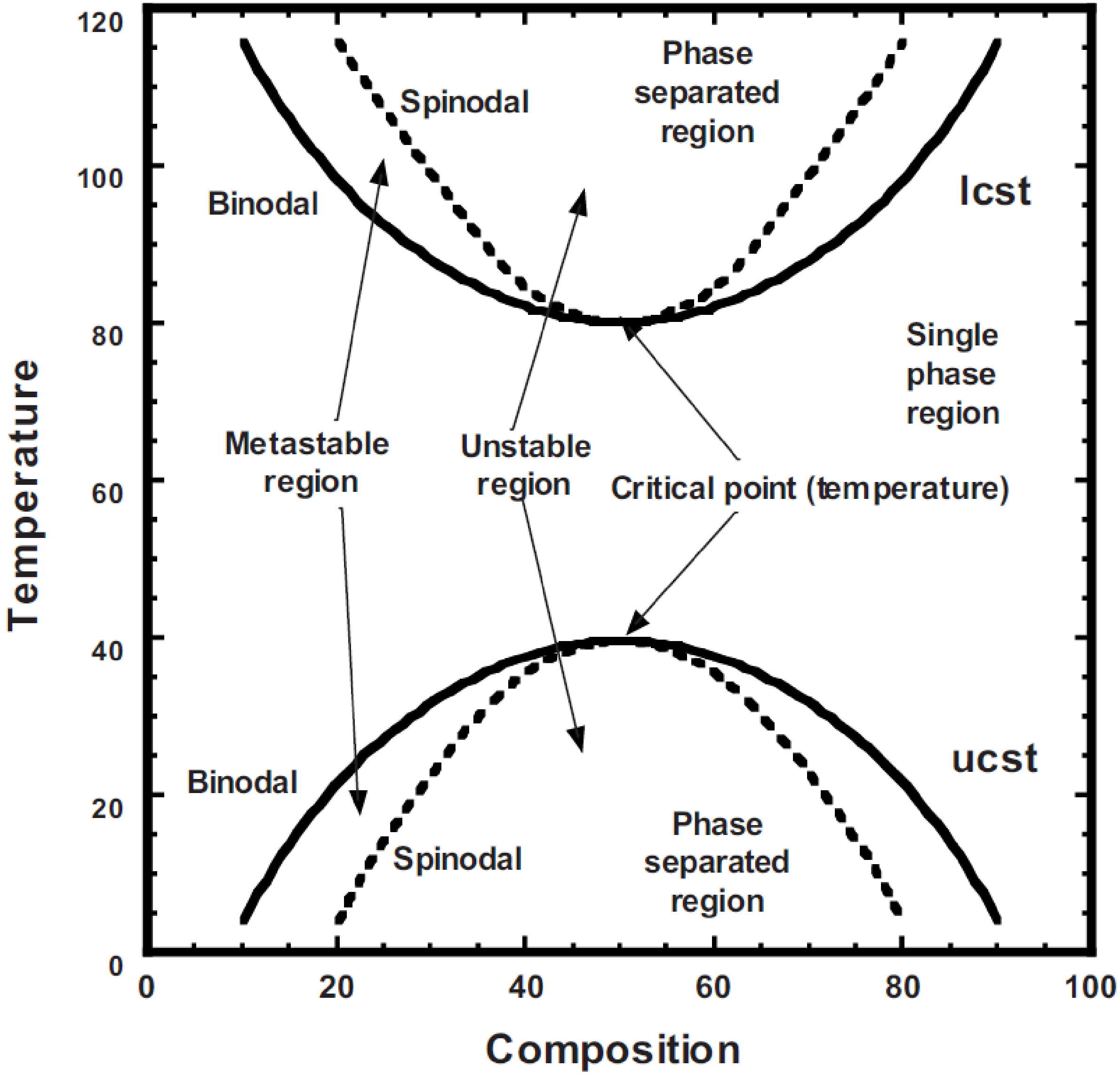


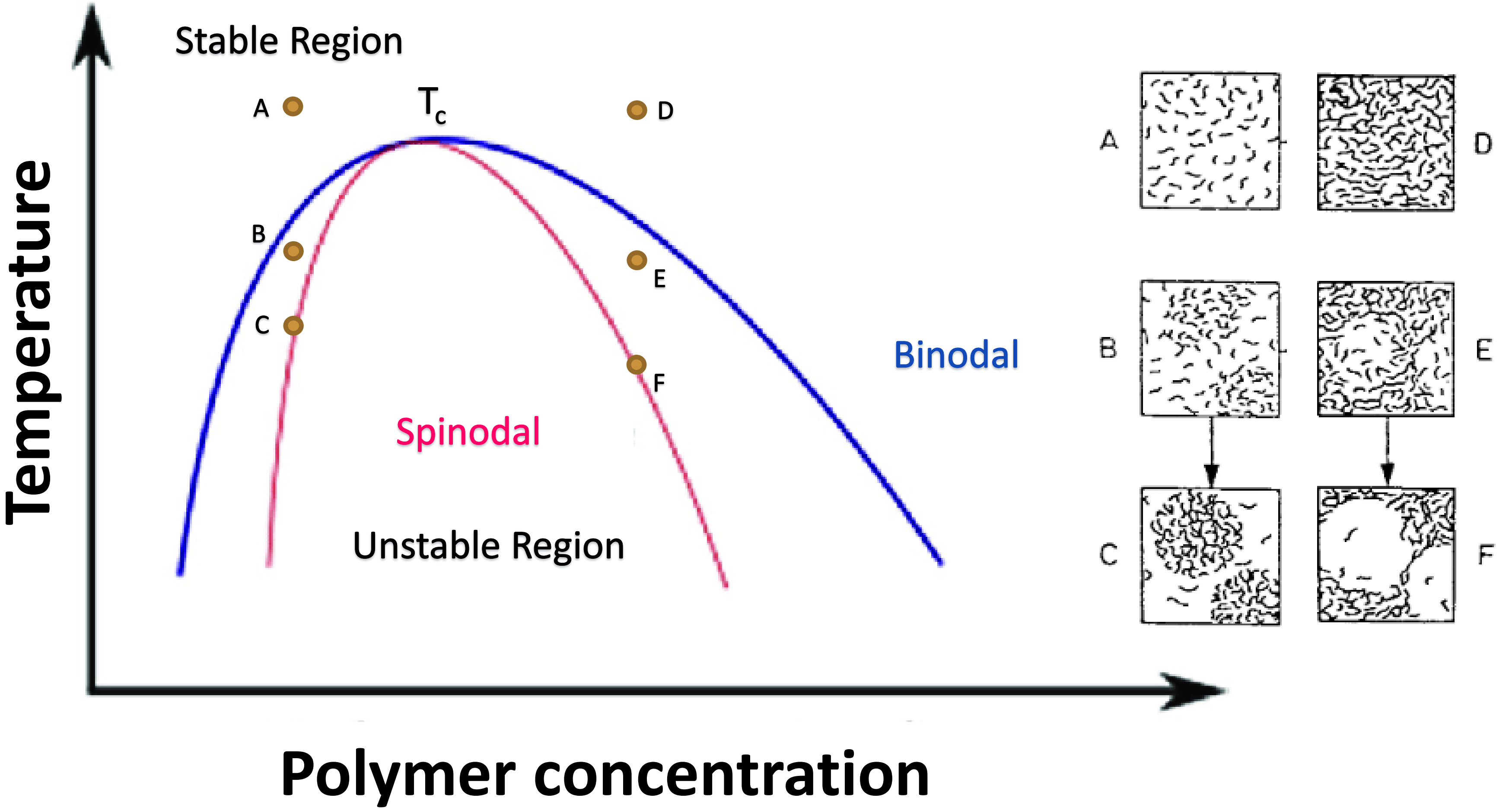
Figure 2. Gibbs free energy for miscible and immiscible polymer combinations

3. Thermodynamics of Polymer Blends

$$\left(\frac{\partial^2 \Delta Gm}{\partial \phi^2}\right)_{p,T} = 0$$ Spinodal



3. Thermodynamics of Polymer Blends



Binodal: Nucleation and growth separation in small spherical regions of the 2nd phase, which grow over time.

Spinodal: Phase separation as small overlapping worm structures (interconnected phase domains). After spinodal decomposition, coarsening of the structures in spheroidal domains.

3. Thermodynamics of Polymer Blends

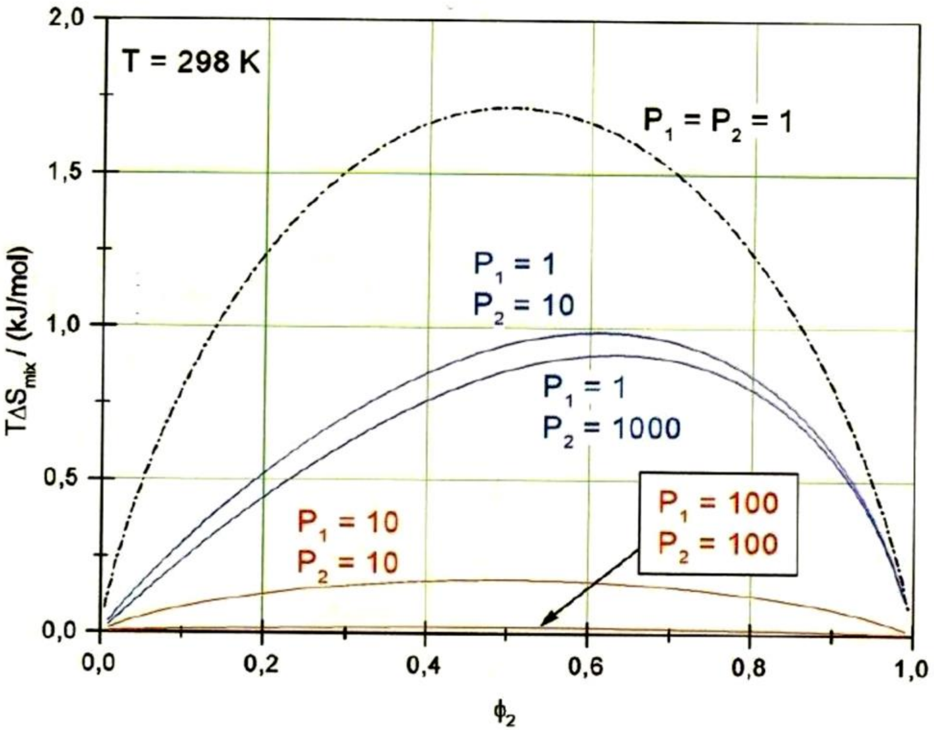
Entropy of mixing for polymer blends

$$\Delta S_m = -R\left(\frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2\right)$$

A large entropy of mixing for small molecule solutions!

Enormous differences in the entropy of mixing for polymer solutions versus regular solutions versus polymer blends!

ΔS_m, polymer-polymer < ΔS_m, polymer-small molecule< ΔS_m, small molecules



3. Thermodynamics of Polymer Blends

Enthalpy of Mixing

$$\Delta G_m = RT\left(\frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2 + \chi\Phi_1\Phi_2\right)$$

$$\Delta H_m = RT\chi\Phi_1\Phi_2$$

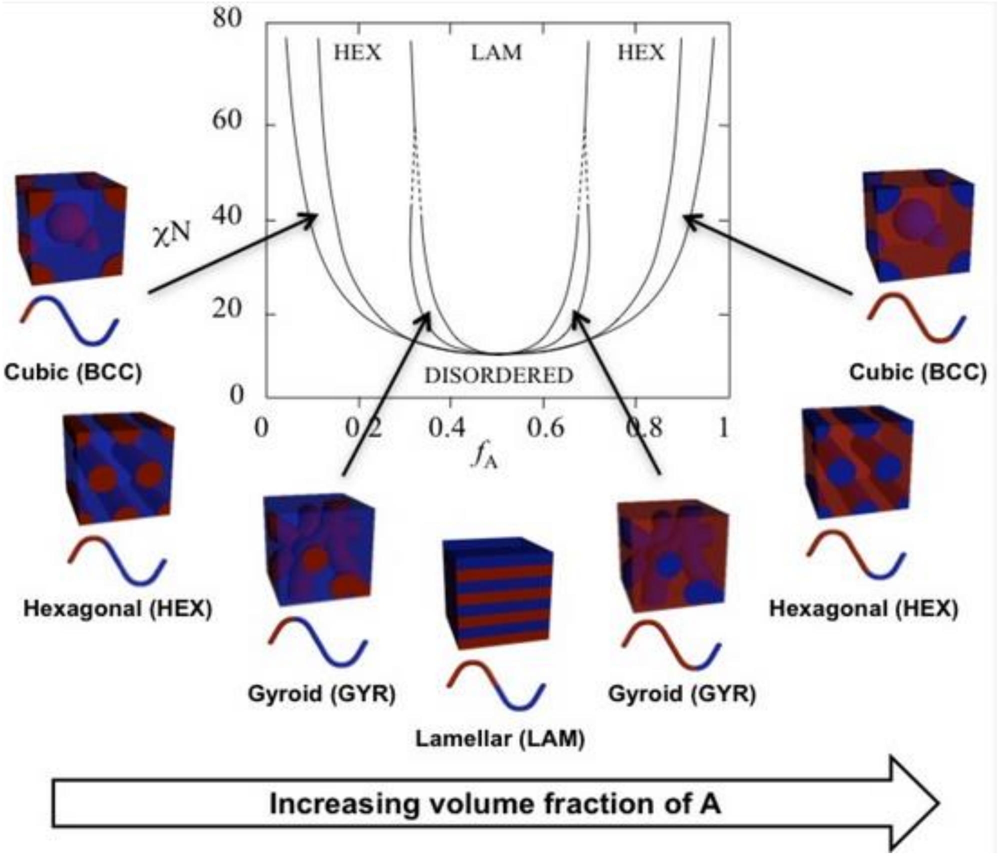
$$\chi_{cr} = 1/2\left(\frac{1}{\sqrt{r_1}} + \frac{1}{\sqrt{r_2}}\right)$$

- Most pairs of high molar mass polymers are immiscible. The positive mixing enthalpy together with negligible entropy contribute to the free energy of mixing.

- The enthalpy of mixing is primarily dependent on the energy change associated with changes during mixing. It is much less dependent on chain lengths. In the enthalpy of polymers mixing ΔH < 0, the interaction energy between heterogeneous molecules is higher than between homogeneous ones. **Enthalpy contributions often dominate the free energy of mixing in polymeric systems.**

- The **introduction of interacting groups by chemical modification of a polymer** or by copolymerization leads to negative contributions to the enthalpy of mixing. **This has been shown to lead to improved miscibility of an otherwise incompatible polymer pair.**

4. Microphase Separation in block copolymers



The **particular structure** adopted by a block copolymer depends on the following **controllable parameters;**

(i) the *Flory-Huggins interaction parameter* χ

(ii) the overall **degree of polymerisation N**

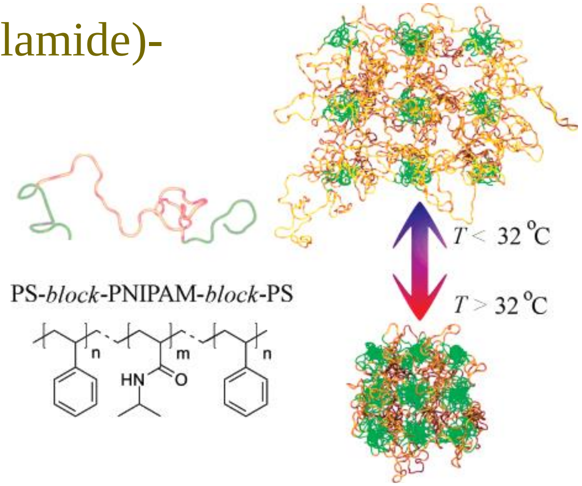
(iii) the **volume fraction** of the component blocks, f,

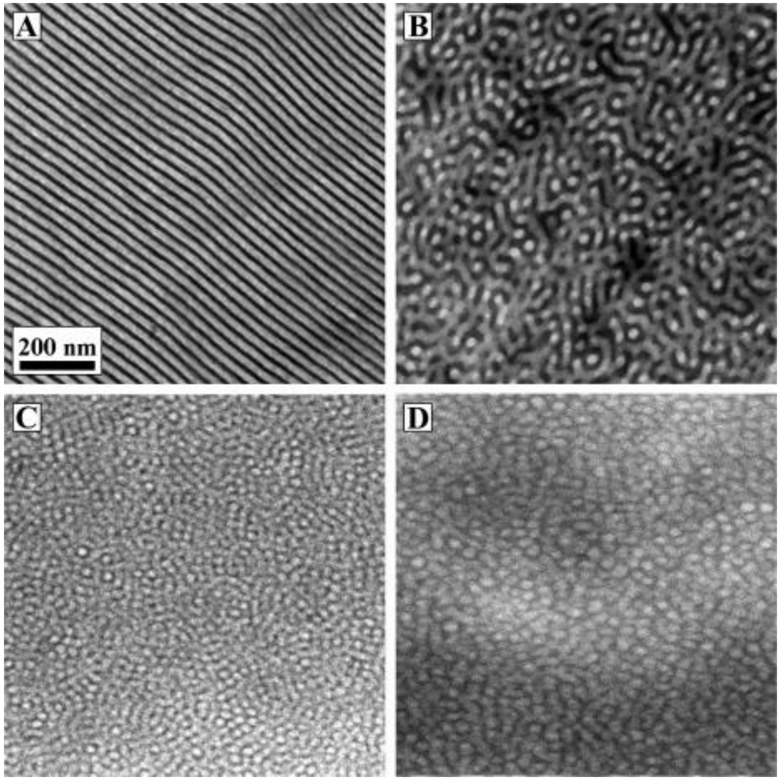
(iv) the particular **polymer architecture**

$$\chi = \frac{A}{T} + B$$

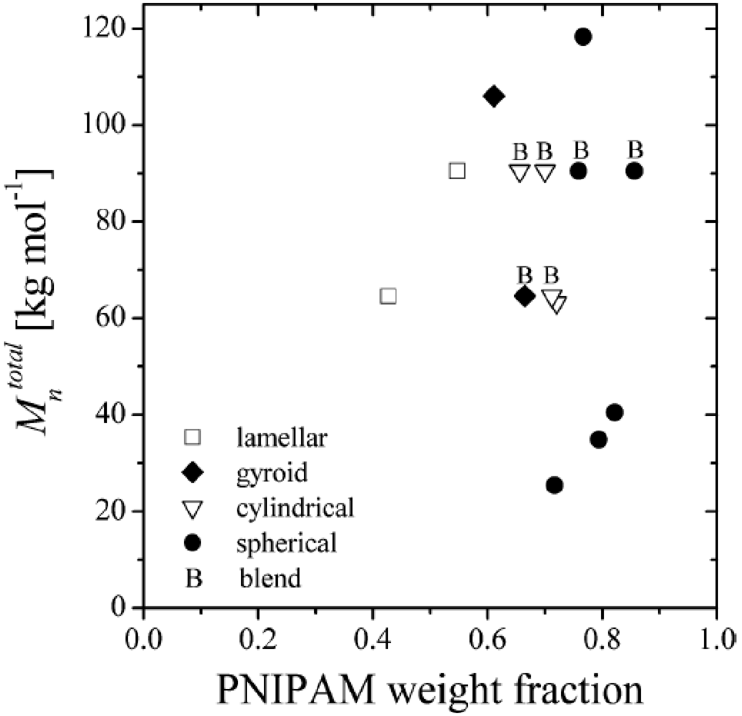
4. Microphase Separation in block copolymers. Examples

Phase Behavior and Temperature-Responsive Molecular Filters Based on Self-Assembly of Polystyrene-*block*-poly(*N*-isopropylacrylamide)-*block*-polystyrene





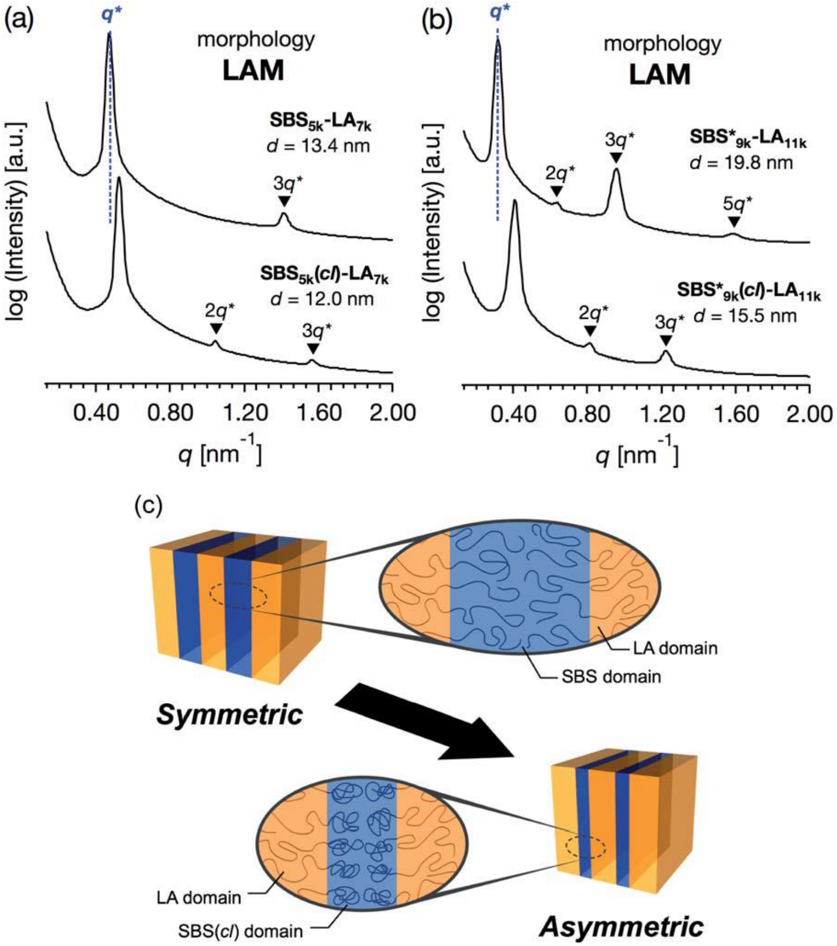
Representative TEM micrographs of pure PS-*b*-PNIPAM*b*-PS triblock copolymers in bulk: (A) PN43.65K (43 wt % PNIPAM) is **lamellar**, (B) PN61.106K (61 wt % PNIPAM) is **gyroid**, (C) PN72.63K (72 wt % PNIPAM) is **cylindrical/wormlike**, and (D)PN77.118K is **spherical**.

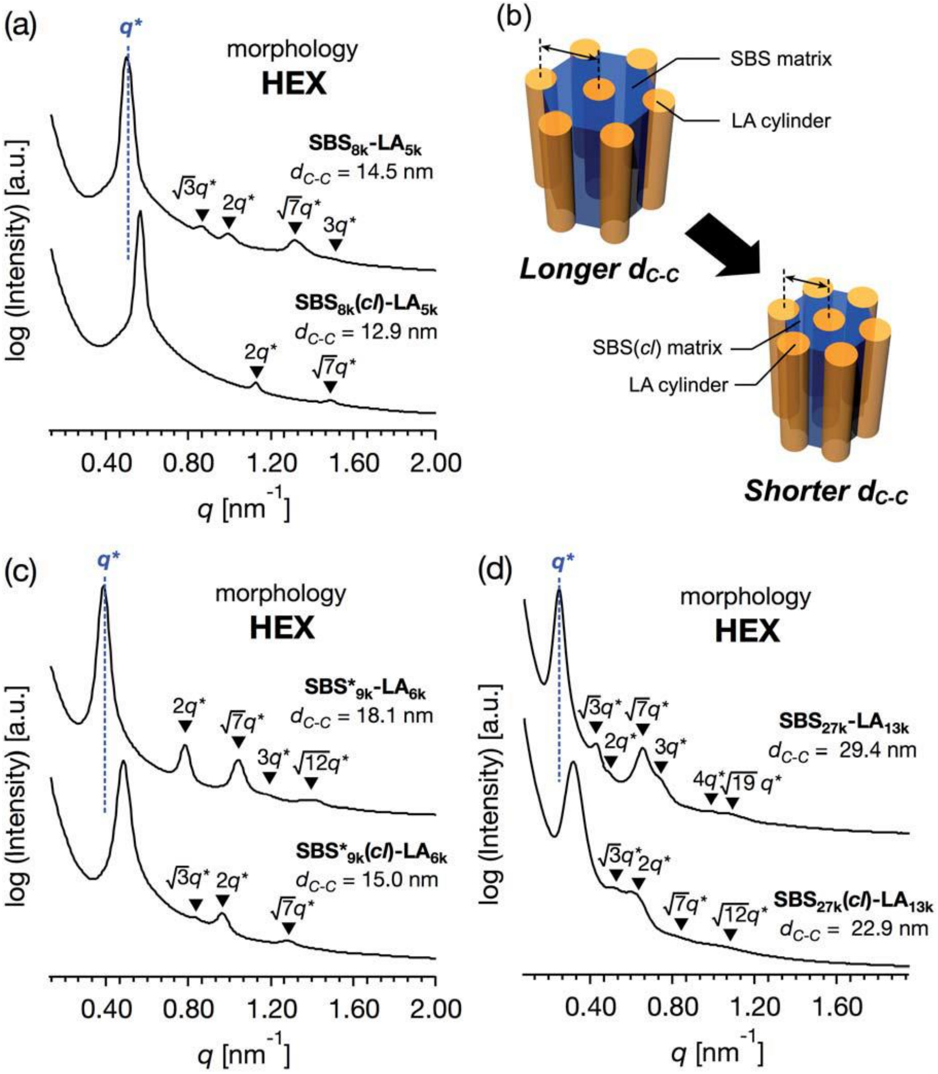


Macromolecules **2007,** *40,* 5827-5834

4. Microphase Separation in block copolymers. Examples

Downsizing feature of microphase-separated structures via intramolecular crosslinking of block copolymers





Chem. Sci., **2019**,10, 3330

Example questions

(1) How can you determine the overlap concentration c* experimentally? Why should experiments be performed in dilute solutions in order to obtain molecular parameter?

(2) Define theta-temperature

(3) How can you experimentally determine HUGGINS-interaction parameter χ?

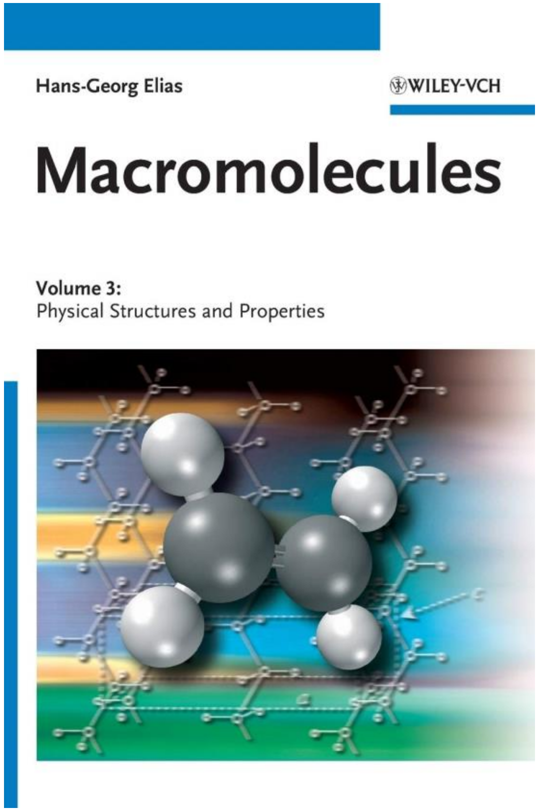
(4) What can you say about the solubility of a polymer and its conformation if you know that it is monodisperse with $\chi > 0.5$ in the corresponding solvent.

(5) How is the intrinsic viscosity changing in case that the solubility of a monodisperse polymer is improved.

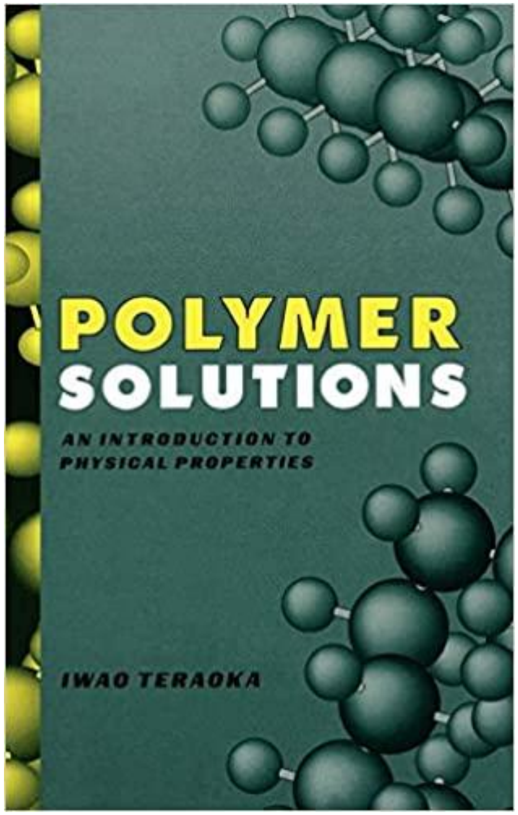
(6) Which parameters are defining phase separation in binary mixtures. What are the differences between polymer solutions and polymer blends?

Recommended Books

Macromolecules
Volume 3: Physical Structures and Properties
Hans-Georg Elias
Wiley-VCH GmbH & Co. KGaA, Weihnheim 2008


Hans-Georg Elias
WILEY-VCH
Macromolecules
Volume 3:
Physical Structures and Properties

Polymer Solutions
An introduction to physical properties
Iwao Teraoka
Wiley-Interscience 2002


POLYMER SOLUTIONS
AN INTRODUCTION TO PHYSICAL PROPERTIES
IWAO TERAOKA