Lecture 8

Polymers and Gels

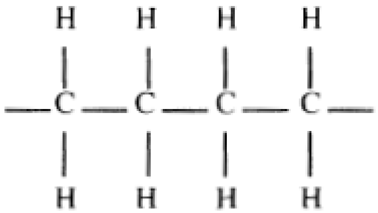
Variety of polymeric materials

- Polymer – molecule made by repeating of covalently joint units.
- “Living polymers” (not considered in this lecture) – long-chain objects connected by physical forces e.g. giant worm-like micelles, actin filaments etc.
- Many of physical properties of polymers have **universal** characteristic related to generic properties of long string-like molecules

Variety of polymeric materials

- Polymers are predominantly based on carbons though often contain other elements in the chain and sometimes don’t involve carbon at all.

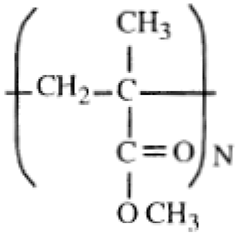
Polyethylene



or $(CH_2)_N$

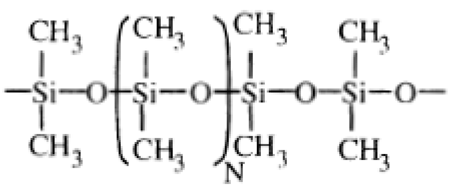
where N = degree of polymerisation

Polymethyl methacrylate



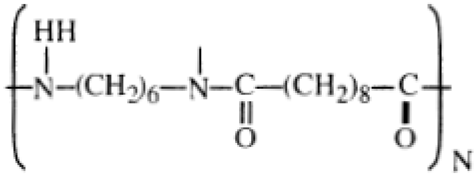
PMMA or Perspex (ICI trade name)

Polydimethyl siloxane

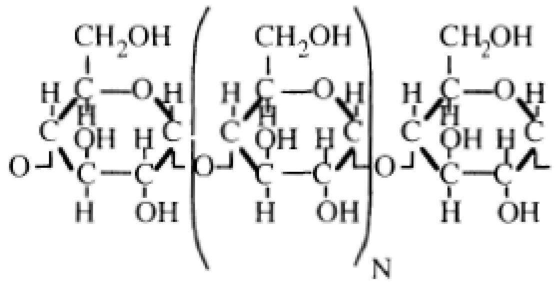


PDMS or silicone oil

Nylon 6-10

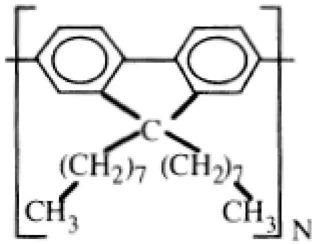


Amylose



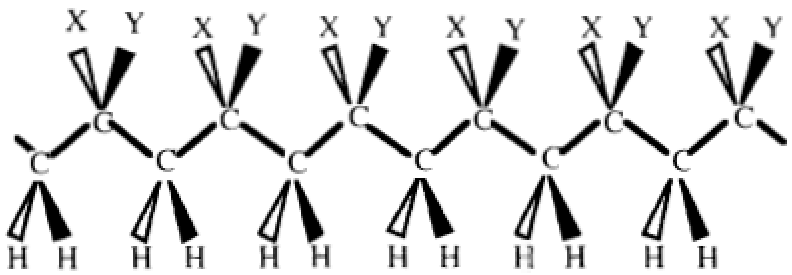
Starch

Poly(di-octyl fluorene)

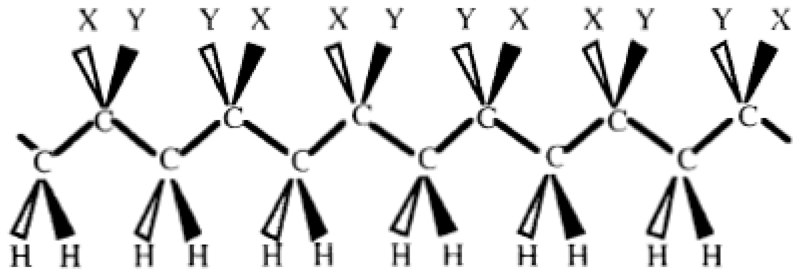


Stereochemistry of polymers

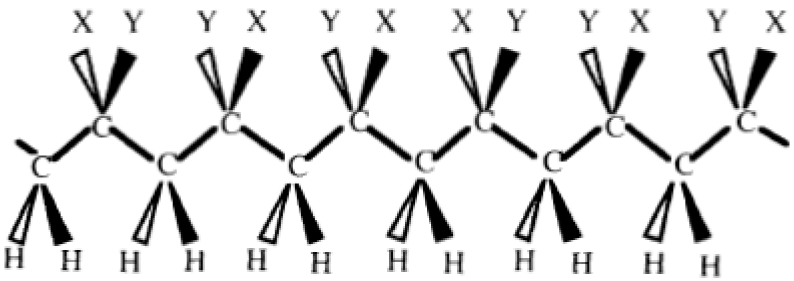
- If polymer has more than one type of side groups different arrangement are possible



Isotactic



Syndiotactic



Atactic

- **Atactic** arrangement involves **quenched disorder** and therefore prevents crystallization: polymer will form glass at low temperature

Architecture of polymers

quenched disorder

- **linear** or **branched**
- average number of units in the chain: **degree of polymerization N** or **molecular mass M**
- distribution of lengths: **polydispersity**
- formed of the same units: **homopolymers** or several types of units: **copolymers**

quenched disorder

strictly prescribed sequence leading to self-assembly

- copolymers: **random**, **sequenced** copolymers (DNA, proteins), **block copolymers** (units arranged in blocks)

microphase separation with complex morphologies

Block copolymers in nanotechnology

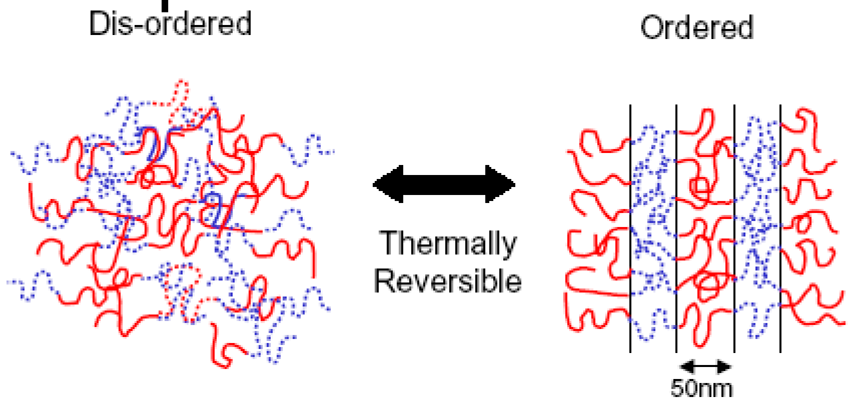
- polymers where repeat units come in blocks:
  - AB di-block copolymers

    A–A–A–A–A–A–A–A–B–B–B–B–B–B–B–B

  - ABA tri-block copolymers

    A–A–A–A–B–B–B–B–B–B–B–B–A–A–A–A

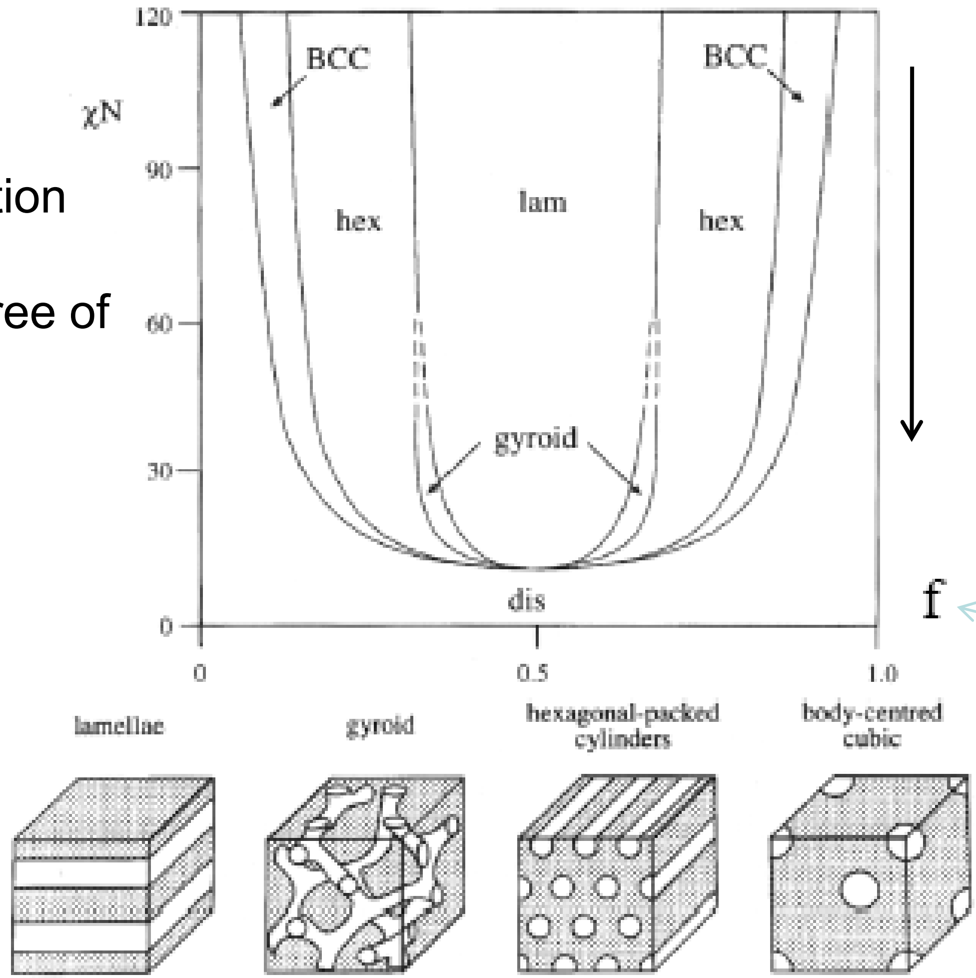
- can be combination of different polymers, e.g. amorphous (rubbery) and crystalline (hard)
- If units are very different chemically they will pahse separate. This microphase separation leads to a zoo of possible structures



Phase diagram of a block copolymer

- The structures formed depend on the relative length of blocks and compatibility of polymers

χ – Flory interaction parameter,
N – diblock degree of polymerization

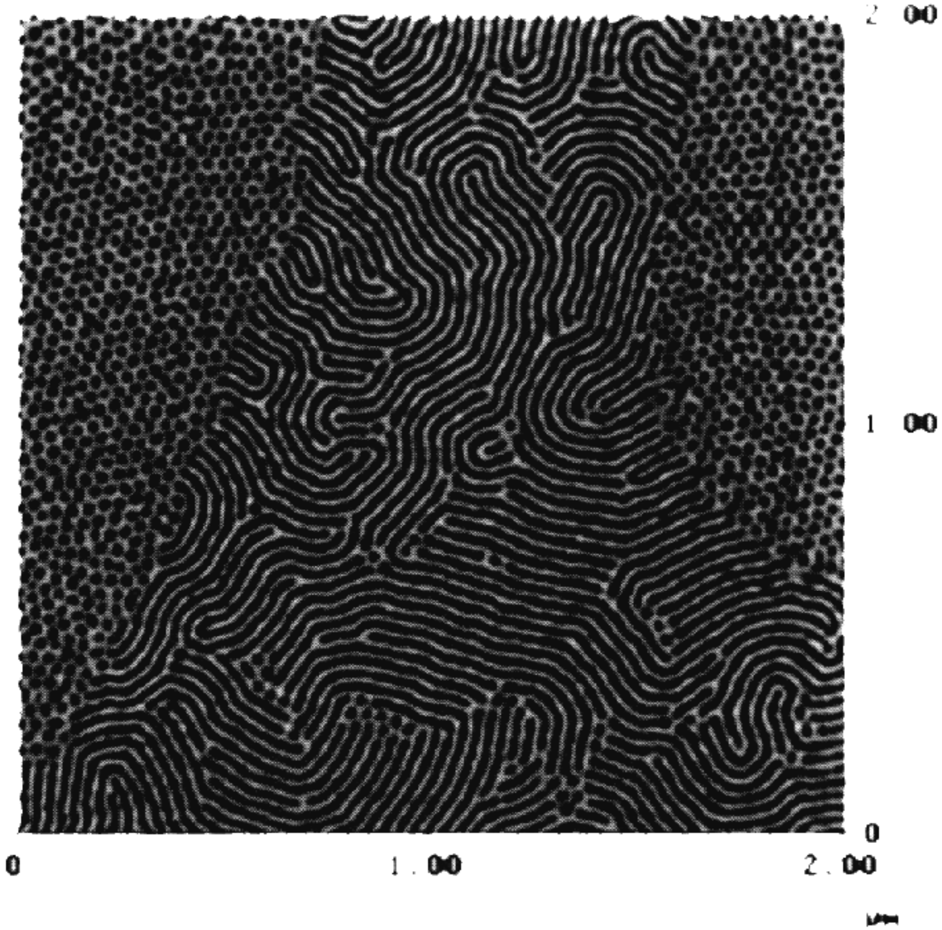


temperature increase

volume fraction of "A" block

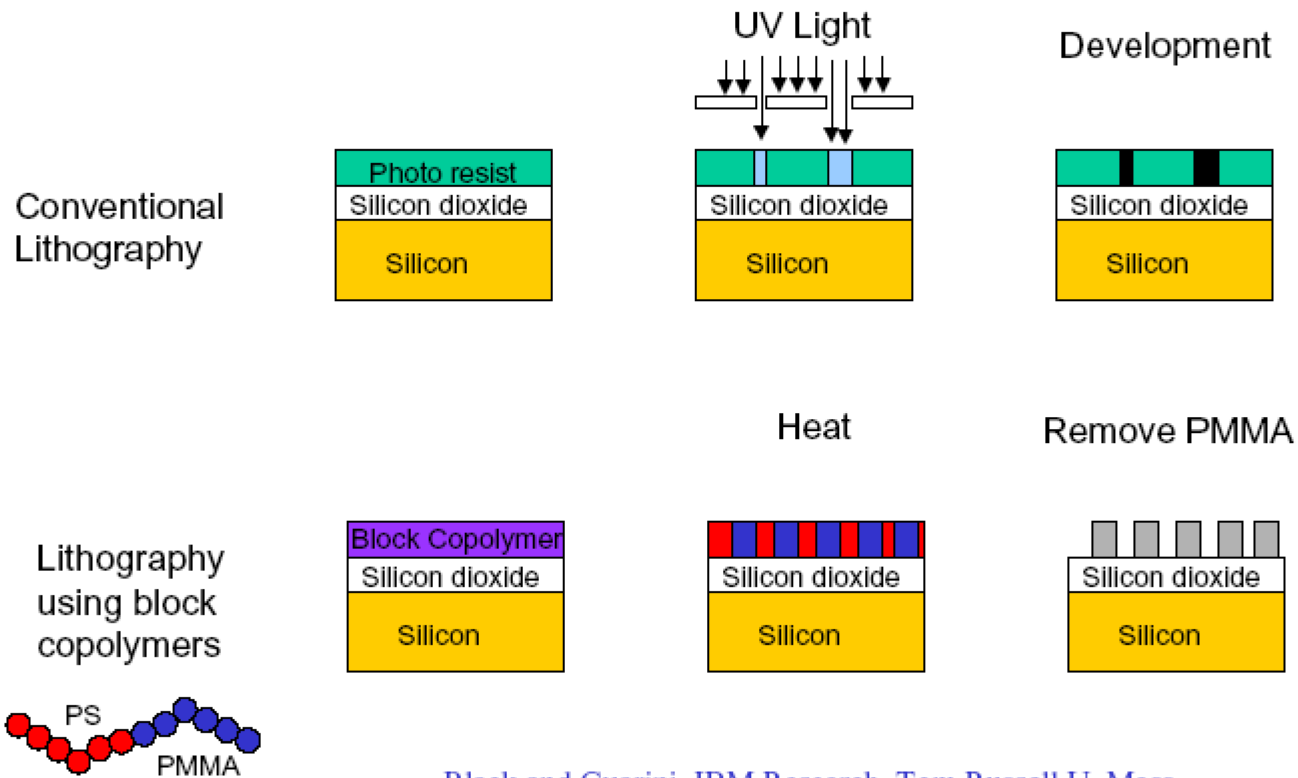
Structure of block copolymers

- AFM of a triblock copolymer Kraton D-1102 (van Dijk and van der Berg, 1996)



Nanopatterning with block copolymers

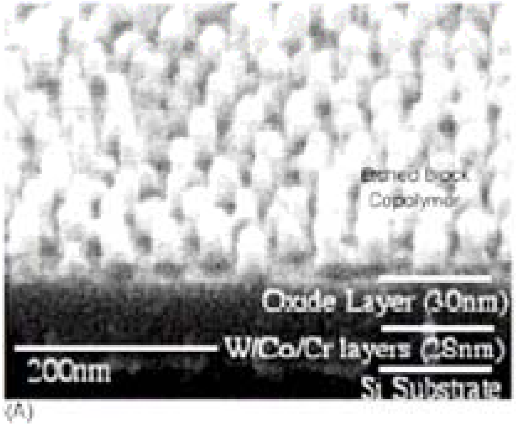
- provides cheap way to produce nanostructures, e.g. for magnetic storage



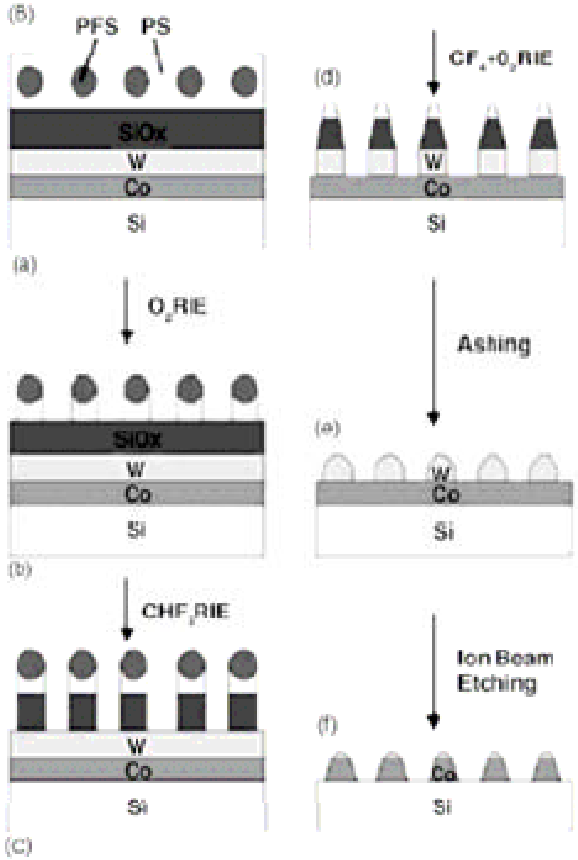
Black and Guarini, IBM Research. Tom Russell U. Mass.

Creating nanodots

poly(styrene-b-ferrocenylsilane) block copolymer



Structure applicable to hard drive manufacture

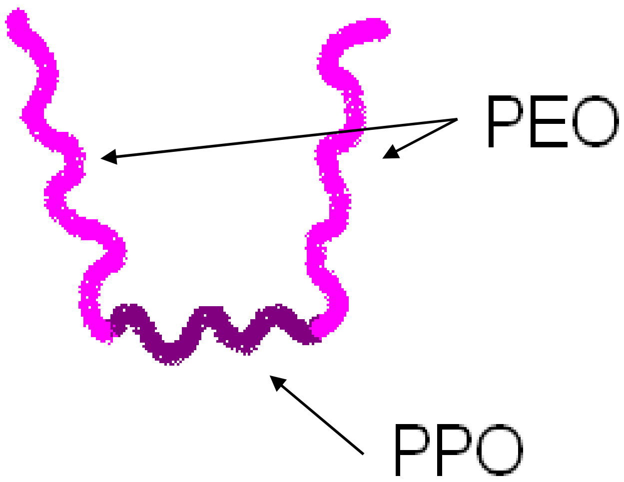


J.Y. Cheng, C.A. Ross, V.Z.H. Chan, E.L. Thomas, R.G.H. Lammertink, G.J. Vancso, Adv. Mater. 13, 1174–1178 (2001)

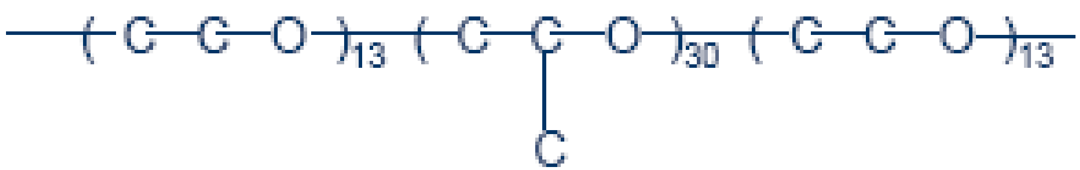
Pluronics™ copolymers for drug delivery

- Symmetrical hydrophobically associating triblock copolymers, Poly(propylene oxide) and poly(ethylene oxide)

$$HO—(CH_2\text{-}CH_2\text{-}0)_n—(\overset{\overset{\displaystyle CH_3}{|}}{C}H_2\text{-}CH_2\text{-}O)_m—(CH_2\text{-}CH_2\text{-}0)_n—H$$

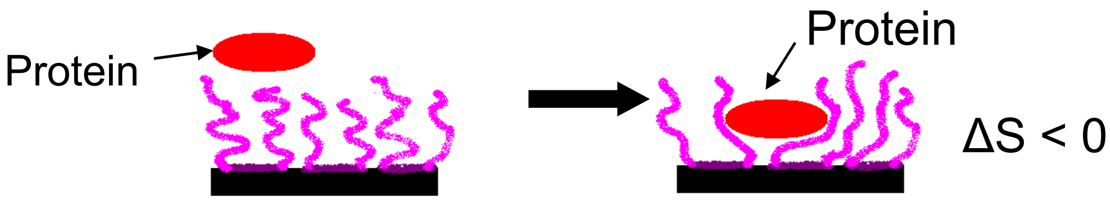


Pluronic L64™



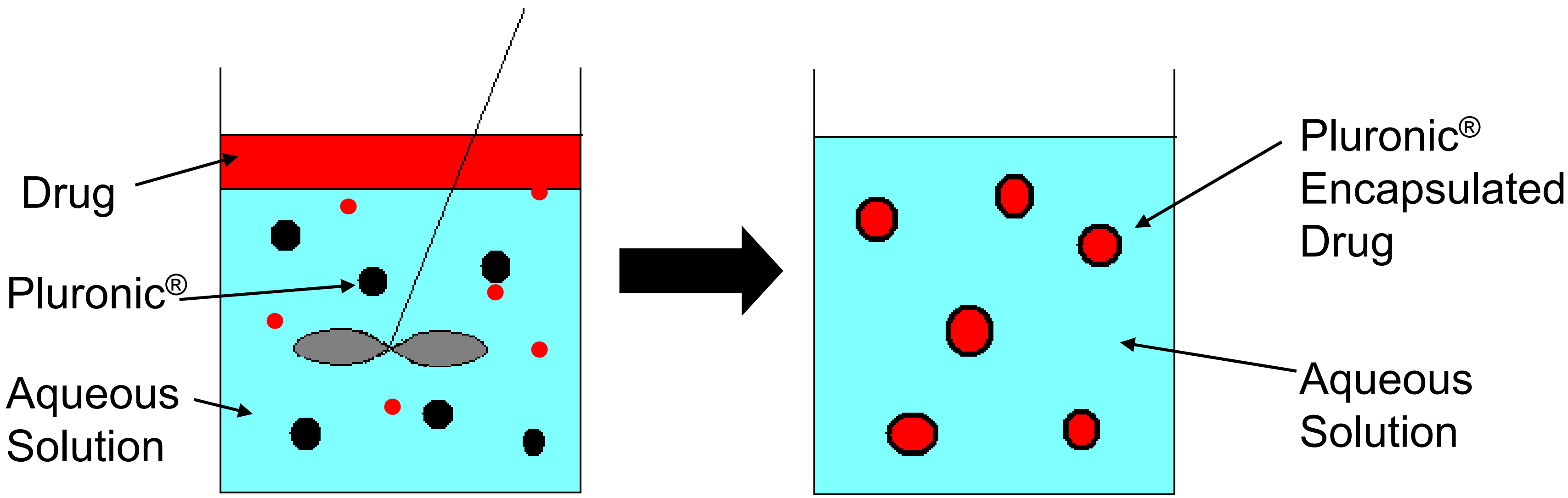
Pluronics copolymers

- Poly(propylen oxide)
  - Central hydrophobic core
  - Folds in aqueous solution
  - CH_3 groups interact by Van der Waals
  - Binds hydrophobic proteins
- Poly(ethylen oxide)
  - Hydrophilic
  - Soluble in water
    - Hydrogen bonding interaction
    - More PEO in Pluronic®, easier to dissolve
  - Moves freely in aqueous solution
  - High entropy → low protein adsorption



Drug encapsulation by Pluronics

- Form after passing critical micelle concentration (CMC) or critical micelle temperature (CMT)
- Suspensions can encapsulate drugs

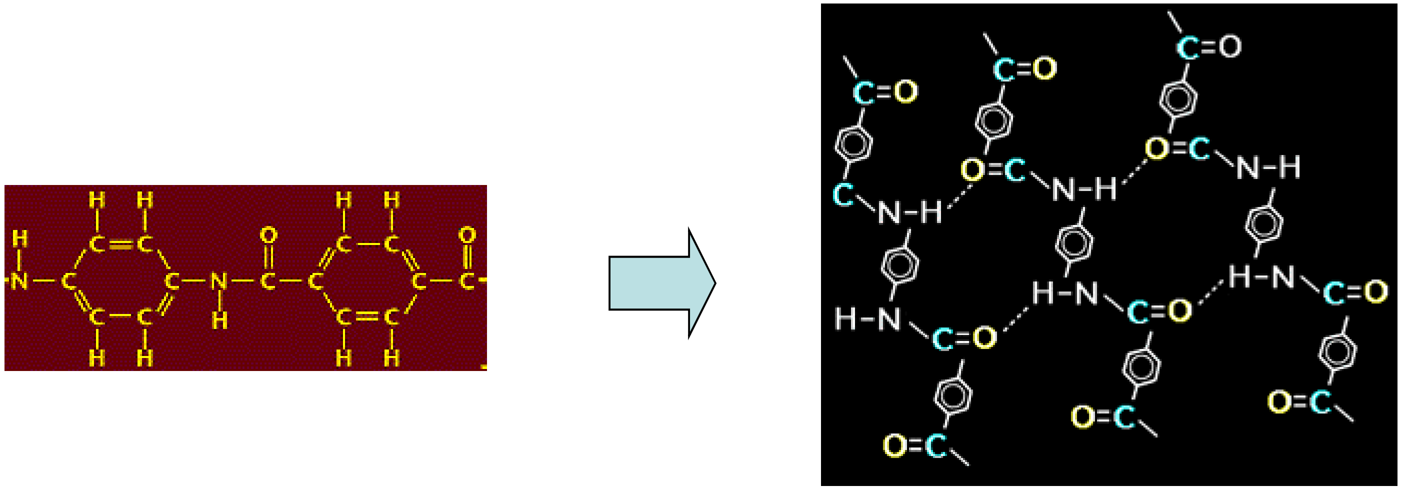


Physical state of polymers

- **Liquid:** often very viscous with particular viscoelastic properties
- **Glass:** very common due to quenched disorder
- **Crystalline:** often semi-crystalline: micro crystallites in amorphous matrix
- **Liquid crystalline:** can be formed in a case of rigid molecules, e.g. Kevlar

Kevlar

- Kevlar – aromatic polyamide
- chemically inert, mechanically strong, no degradation at low temperatures (down to -196 ºC)



Random walk and polymer chain

- **freely joint chain** polymer model – equivalent of random work
  - **end-to-end distance** $\vec{r} = \sum_{i=1}^{N} \overrightarrow{a_i}$
  - **mean square end-to-end distance**

$$\left\langle \vec{r} \cdot \vec{r} \right\rangle = \left\langle \left(\sum_{i=1}^{N} \overrightarrow{a_i} \right) \cdot \left(\sum_{j=1}^{N} \overrightarrow{a_j} \right) \right\rangle = \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \overrightarrow{a_i} \cdot \overrightarrow{a_j} \right\rangle$$

$$\left\langle \overrightarrow{r^2} \right\rangle = Na^2 + \left\langle \sum_{i \neq j}^{N} \overrightarrow{a_i} \cdot \overrightarrow{a_j} \right\rangle$$

0, as different links are **uncorrelated**

Entropy of a polymer chain

- Entropy of a macrostate is related to the number of available microstates (statistical weight):

$$S = k_B \ln \Omega$$

Entropy of a polymer chain

- In a case of 1D walk: $R_x = (N_+ - N_-)a_x; \quad \Omega_x = \frac{N!}{N_+!N_-!}$

$$\ln x! = x\ln x - x;\ \ \ln\Omega_x = -N\left[f\ln f + (1-f)\ln(1-f)\right],\ \ f = N_+/N$$

  - function has a maximum at f=1/2, let's make Taylor expansion around the maximum:

$$\ln\Omega_x = \ln\Omega_x(1/2) + (1/2 - f)\left(\frac{d\ln\Omega_x}{df}\right)_{f=1/2} + \frac{1}{2}(1/2-f)^2\left(\frac{d^2\ln\Omega_x}{df^2}\right)_{f=1/2} + \ldots$$

$$\ln\Omega_x \approx N\ln 2 - 2N\left(1/2 - f\right)^2;\ \ \ln\Omega_x \approx -\frac{R_x^{\ 2}}{2Na_x^{\ 2}}$$

  - in 3D: $\ln\Omega = \ln\Omega_x\Omega_y\Omega_z \approx -\frac{3R^2}{2Na^2}$

Entropy of a polymer chain

- Configurational entropy of a freely joint polymer chain:

$$S(r) \approx -\frac{3k_B R_x^{\,2}}{2Na_x^{\,2}} + const$$

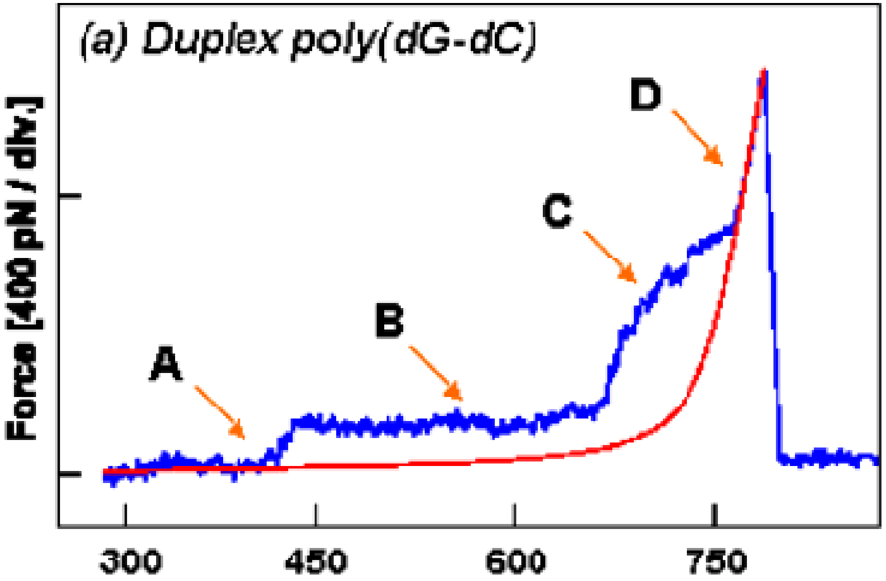
- Gibbs energy

$$\Delta G = -T\Delta S = \frac{3k_B T R_x^{\,2}}{2Na_x^{\,2}}$$

$$F = \frac{3k_B T}{Na_x^{\,2}} r$$

Entropic force, quite small

Stretching a DNA



- Dario Anselmetti et al, "Single Molecule DNA Biophysics with Atomic Force Microscopy", SingleMolecules, 2001

More realistic model: short range correlations

- realistically, correlation will not disappear for nearest neighbors due to e.g. bond angle

$$\left\langle \overrightarrow{a_i} \cdot \overrightarrow{a_{i-1}} \right\rangle = a^2 \cos\theta; \left\langle \overrightarrow{a_i} \cdot \overrightarrow{a_{i-m}} \right\rangle = a^2 (\cos\theta)^m$$

- the chain will behave as its subunits are effectively longer

$$\left\langle \vec{r}^{\,2} \right\rangle = \frac{N}{g} \left\langle c^2 \right\rangle = Nb^2$$

- correlations can be characterized by characteristic ratio

$$C_\infty = \frac{b^2}{a^2}$$

Excluded volume: Flory's approach

- Consider a molecule that occupies volume $\boldsymbol{r^3}$:
  - segment concentration: $$c \approx \frac{N}{r^3}$$
- This leads to reduction of entropy: $$\Delta G = \frac{k_B v N}{V} T = \frac{k_B v N^2}{2r^3} T$$
- Total energy including configurational energy:

$$\Delta G = \Delta G_{rep} + \Delta G_{el} = \frac{k_B T r^2}{N a^2} + \frac{k_B T v N^2}{2r^3}$$

- assuming excluded volume $\boldsymbol{v \sim a^3}$ and minimizing energy:

$$r \sim a N^{3/5}$$

Interaction between polymer segments

- Number of contacts for a polymer molecule:

$$N_{pp} = \frac{1}{2} zNvc; \;\; N_{ps} = zNv(1-c); \;\; N_{ss} = N_{ss}{}^{0} - \frac{1}{2} zNvc - zNv(1-c)$$

z – number of neighbors for any polymer segment or solvent molecule

- The interaction energy:

$$U_{\text{int}} = \frac{1}{2} zNvc(\varepsilon_{pp} + \varepsilon_{ss} - 2\varepsilon_{ps}) + zN(\varepsilon_{ps} + \varepsilon_{ss}) + N_{ss}{}^{0}\varepsilon_{ss}$$

$$U_{\text{int}} = k_B T \chi 2v \frac{N^2}{2r^3} + const; \;\; k_B T \chi = \frac{1}{2} z(\varepsilon_{pp} + \varepsilon_{ss} - 2\varepsilon_{ps})$$

- The total energy:

$$G_{rep} + U_{\text{int}} = k_B T v(1-2\chi) \frac{N^2}{2r^3} + const;$$

Interaction between polymer segments

- The total energy:

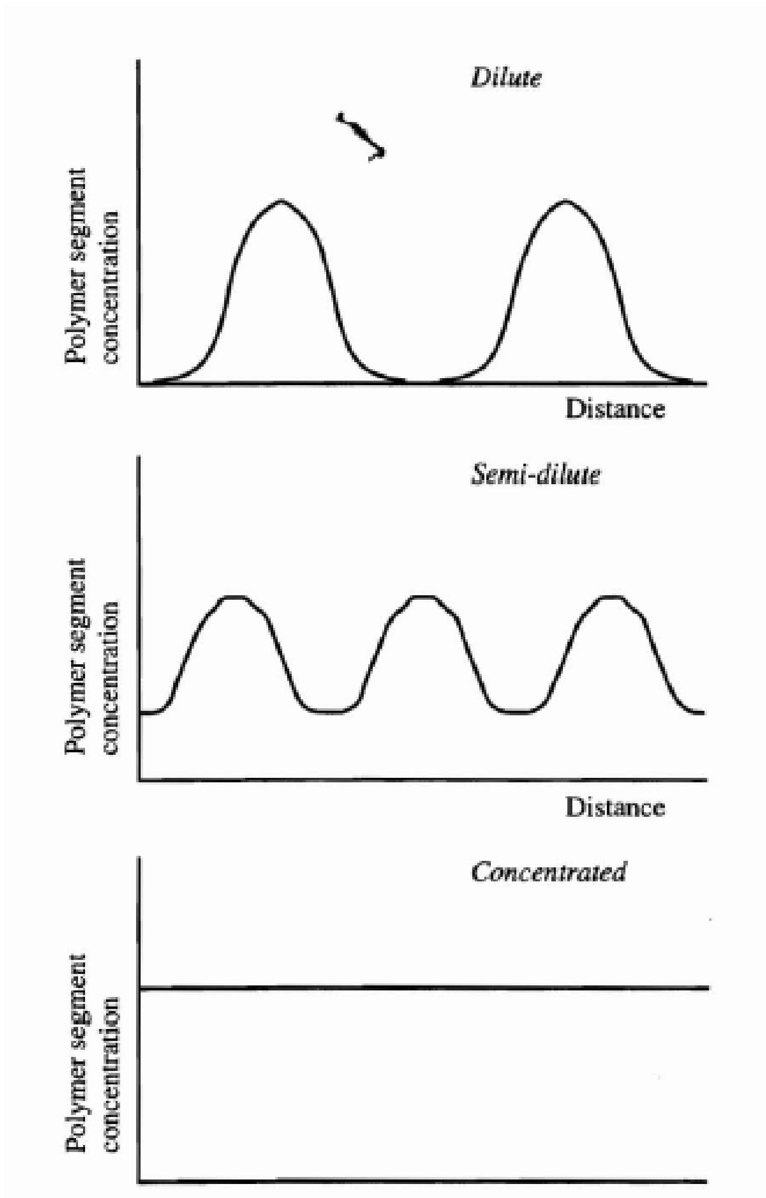
$$G_{rep} + U_{\text{int}} = k_B T v (1 - 2\chi) \frac{N^2}{2r^3} + const;$$

- We expect different behavior according to value ***χ:***
  1. χ ***<1/2*** polymer chain is expanded (swollen) – good solvent behavior
  2. χ ***=1/2*** repulsive effects are cancelled by attractive effects of polymer-solvent interaction. Polymer behaves as ideal random walk: theta condition
  3. χ ***>1/2*** attractive effect prevail, polymer forms a globule

- e.g. change in temperature could induce coil-globule transition

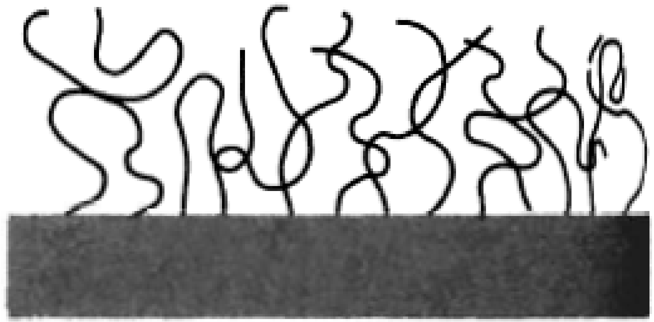
Flory theorem

- In the polymer melt, chains follow random walk statistics (in other words, upon increasing polymer concentration the effects related to excluded volume disappear).



Polymers grated on a surface

- The case of polymer densely grafted on the surface: "polymer brush" with the density of σ/a^2 chains per unit area and height h.



$$\Delta G_{el} = k_B T \frac{r^2}{Na^2} = k_B T \frac{h^2}{Na^2}$$

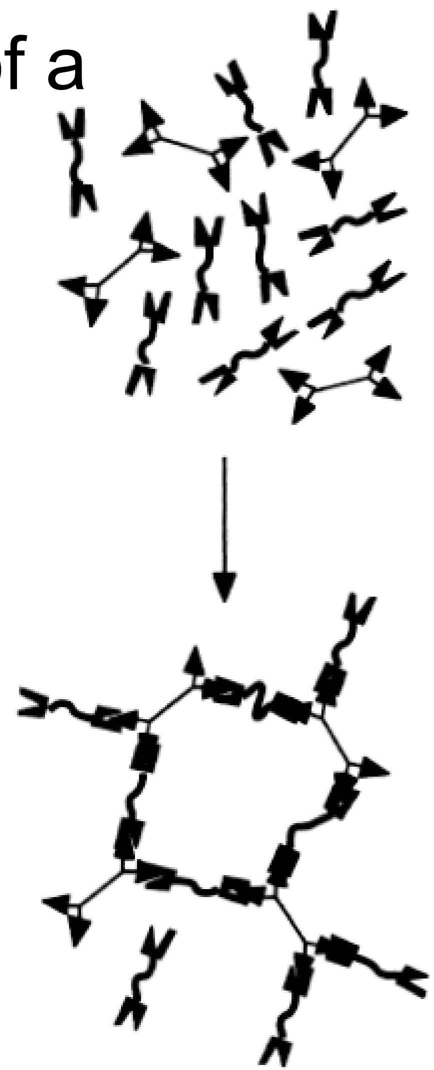
$$\Delta G_{rep} + \Delta U_{\mathrm{int}} = k_B T b(1-2\chi)\frac{\sigma N^2}{2ha^2}$$

minimizing total energy:

$$h \sim \left[\sigma b(1-2\chi)\right]^{1/3} N$$

Gels and gelation

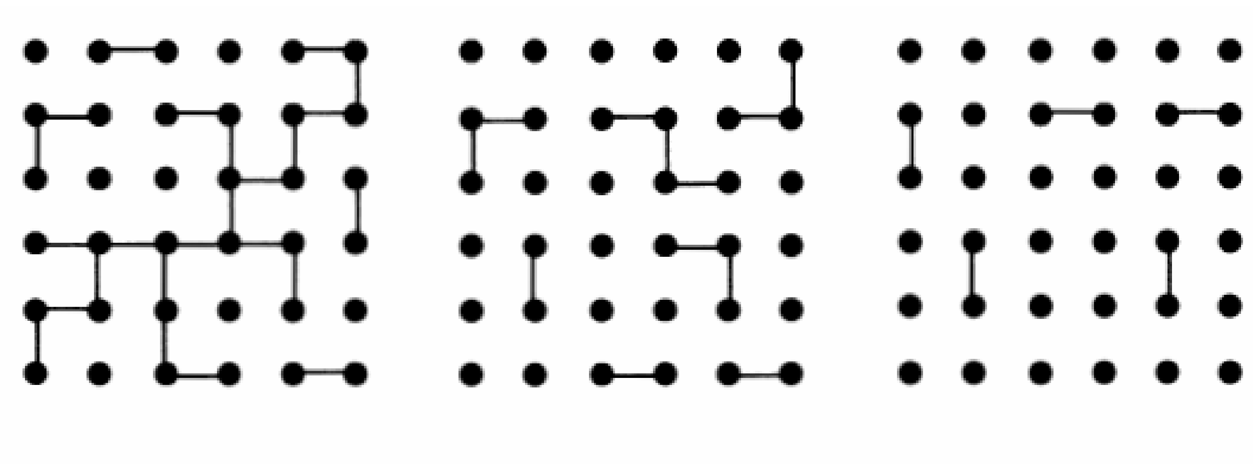
- Gel – material where subunits can bond to each other forming a network
- Gelation or sol-gel transition - formation of a material with non-zero shear modulus



- Gels
  - – chemical
    - termosetting resins (e.g. epoxy)
    - sol-gel glasses (silane polymerisation)
  - – physical
    - via microcrystalline regions
    - via microphase separation

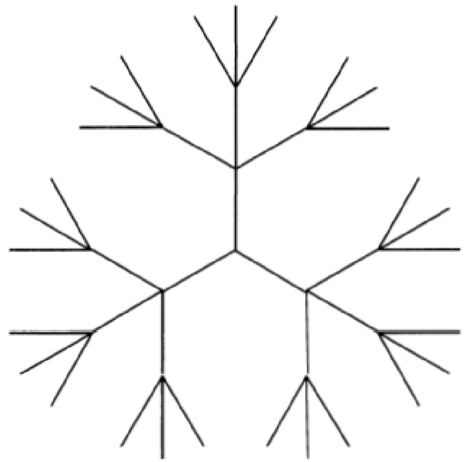
Theory of gelation

- Gelation occurs when an infinitely size cluster is formed



Gelation theory: Flory-Stockmayer model

- If the probability to form a bond is **f** and each point can connect to z other points, each monomer in n-th generation is linked to f(z-1) monomers in (n+1)th generation. The total number of bonds in n- generation:



$$N \sim \left[f(z-1) \right]^n$$

- So, there is critical probability f_c- **percolation threshold**:

$$f < f_c \quad N \xrightarrow{n\to\infty} 0$$

solution of finite clusters "sol"

$$f > f_c \quad N \xrightarrow{n\to\infty} \infty$$

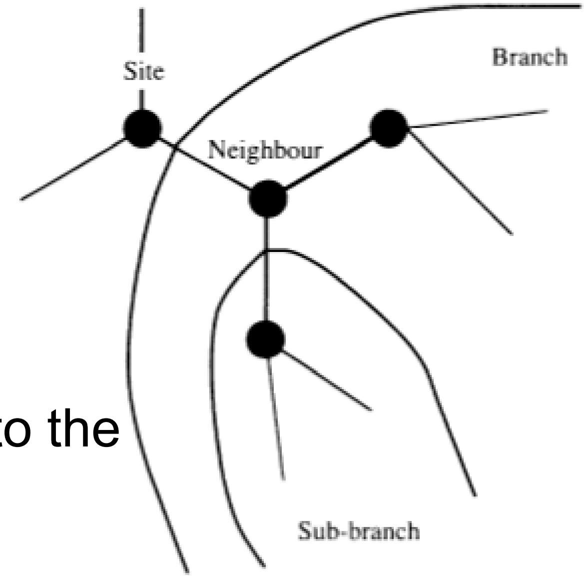
infinite cluster with non-zero shear module

$$f_c = \frac{1}{z-1}$$

near f_c, the mean cluster size will diverge

Gelation theory: Flory-Stockmayer model

- Now, we can calculate the number of bonds inside an infinite cluster ("gel fraction")
- Let's suppose that
  the probability for a site to be connected to infinite cluster is P.
  the probability that the site is not connected via particular branch is Q



- The probability that a neighbour is not connected to the infinite cluster is $Q^{(z-1)}$

$$Q = (1 - f) + fQ^{z-1}$$

$$Q = 1 \;\; or \;\; Q = \frac{1-f}{f}$$

- On the other hand,
  - the probability that a site is not connected to infinity is Q^z.
  - probability to be connected to a particular neighbour but not to infinity fQ^z.

$$f - P = fQ^z; \;\; \frac{P}{f} = 1 - \left(\frac{1-f}{f}\right)^3 \;\; \text{for } f > f_c \text{ or otherwise } \frac{P}{f} = 0$$

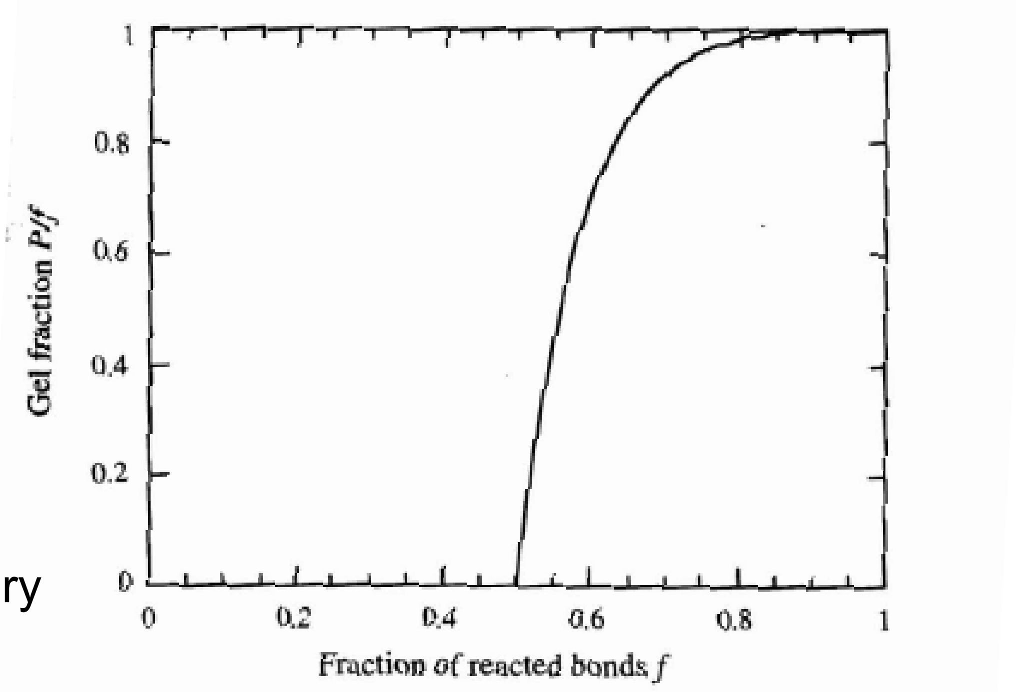
Gelation theory: Flory-Stockmayer model

- around the gelation point:

$$\frac{P}{f} = 3(f - f_c) + O(f - f_c)^2$$

- generally

$$\frac{P}{f} \sim (f - f_c)^{\beta}$$



β =1 in Flory-Stockmayer theory
β=0.41 from MC modelling