3.012 Fund of Mat Sci: Structure – Lecture 23

GLASSES

Image removed for copyright reasons.

A photonic fiber made from polymeric and chalcogenide glasses (Prof. Fink)

Homework for Fri Dec 2

- Study: Chapter 2 of Allen-Thomas (2.5 excluded)

Last time:

1. Pair correlation functions
2. Bernal’s model of hard spheres, Voronoi polyhedra
3. Polymers: homo and co-polymers, tacticity, glass transition, termoplastics-elastomers-thermosets, addition or condensation polymerization, chain or step growth

Glass transition temperature

Free volume, V_F – extra space beyond that is needed to provide an ordered crystalline packing.

$$V_F(T) \equiv V(T) - V_0(T)$$

- V_0 is occupied specific volume of atoms or molecules in the xline state *and* the spaces between them: V_{XL}.
- V_F increases as T increases due to the difference in the thermal expansion coefficients (α_g vs α_l).
- $V_0(T) \approx V_{XL}(T) \quad \leftrightarrow \quad$ take $\alpha_g \approx \alpha_{XL}$
- $V_F(T) = V_F(T_g) + (T-T_g)\frac{dV_F}{dT} \quad T > T_g$
- define <u>fractional free volume, f_F</u>:

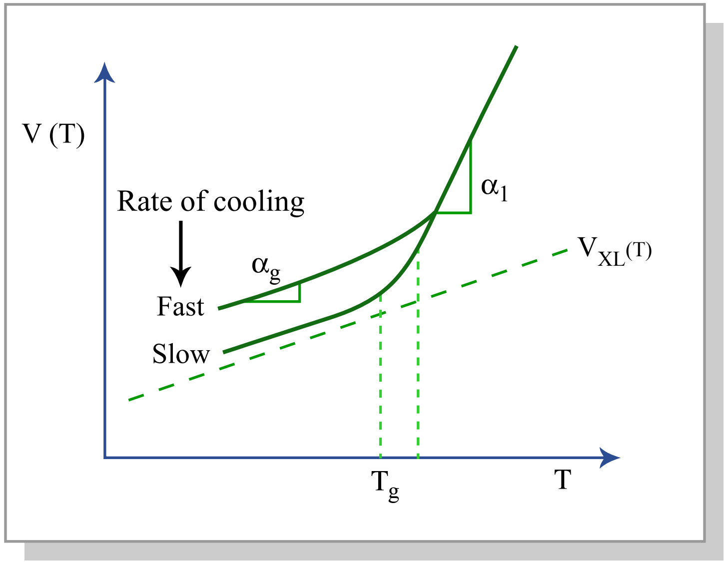


Figure by MIT OCW.

$$f_F(T) = f_F(T_g) + (T-T_g)\alpha_f \qquad \alpha_f = \alpha_l - \alpha_g$$

Viewpoint: T_g occurs when available free volume drops below critical threshold for structural rearrangement [VITRIFICATION POINT], *structure "jams up"*.

Glass transition temperature

Table removed for copyright reasons.

See page 39, Table 2.2 in in Allen, S. M., and E.L. Thomas. *The Structure of Materials*. New York, NY: J. Wiley & Sons, 1999.

Classification: mechanical

- Thermoplastics: (linear, or at most contain branches). Melting temperature, and a glass temperature. Recyclables.

- Elastomers: low degree of cross-linking (rubbers)

- Thermosets: high-degree of cross-linking, structural rigidity

Classification: structure

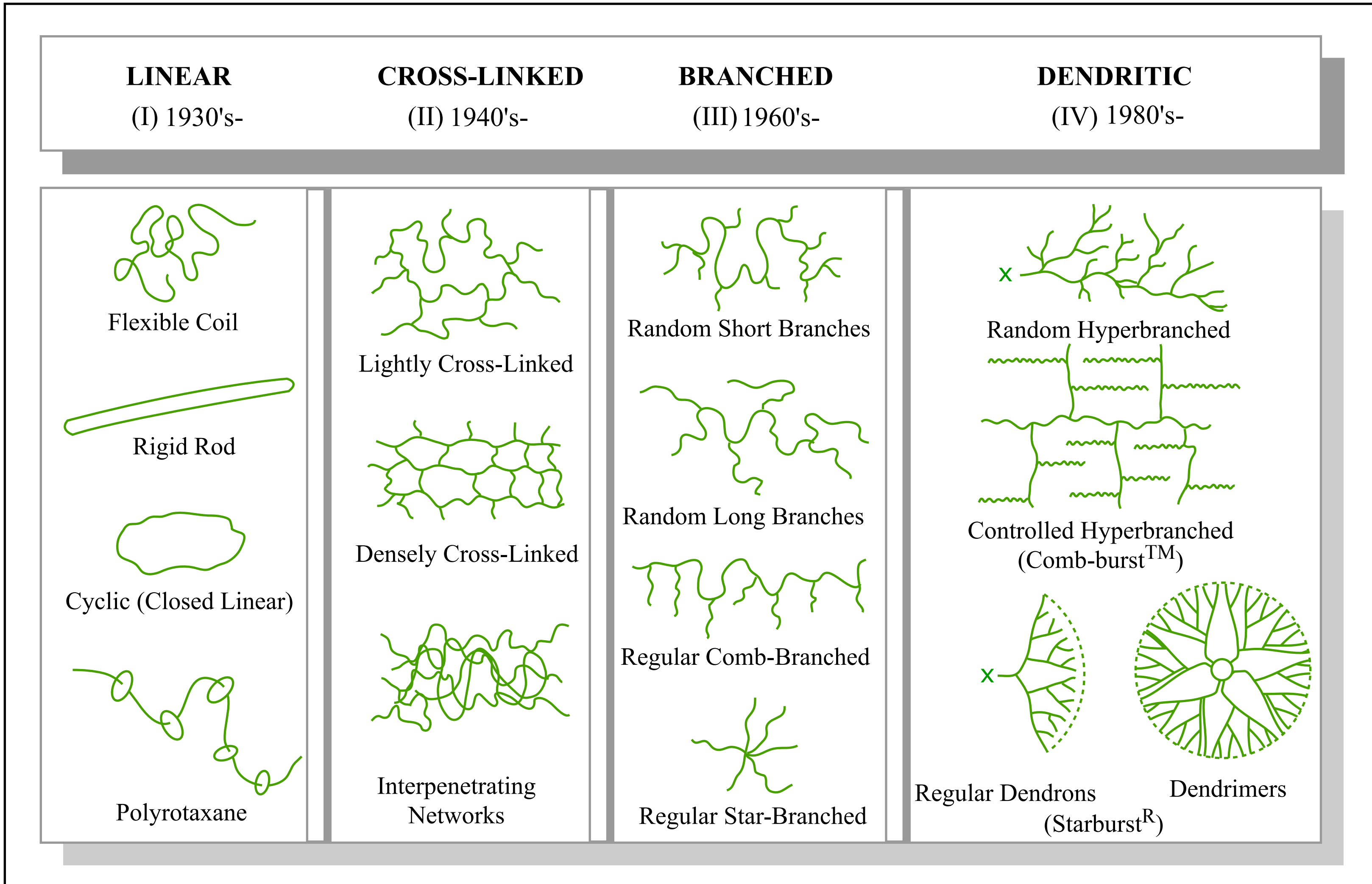
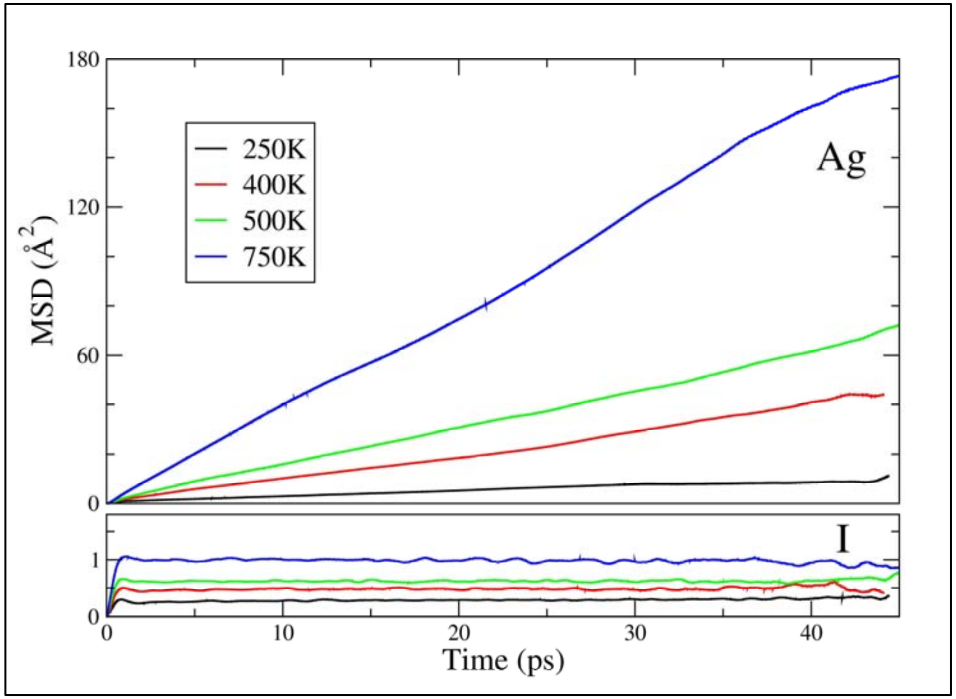


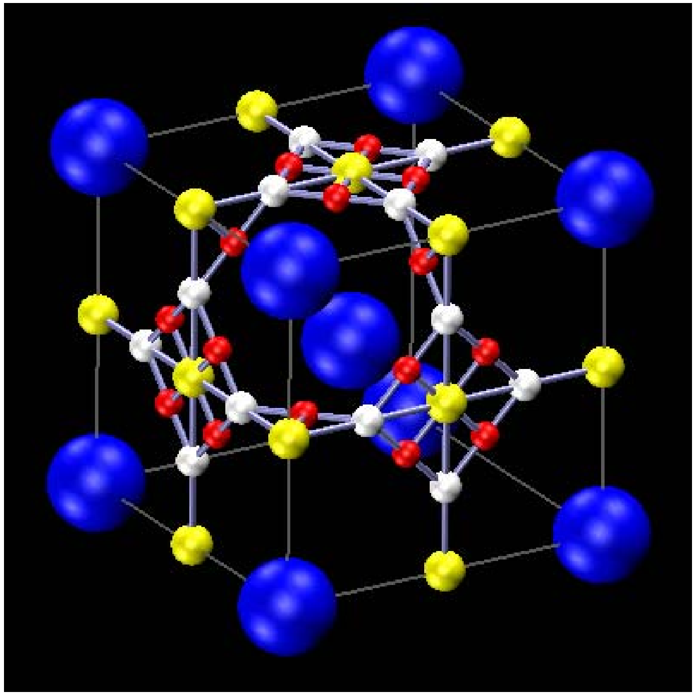
Figure by MIT OCW.

Random walks: size of polymers

Mean Square Displacements

Mean Square Displacements





Packing Fraction in Polymeric Glasses

Solvent quality factor

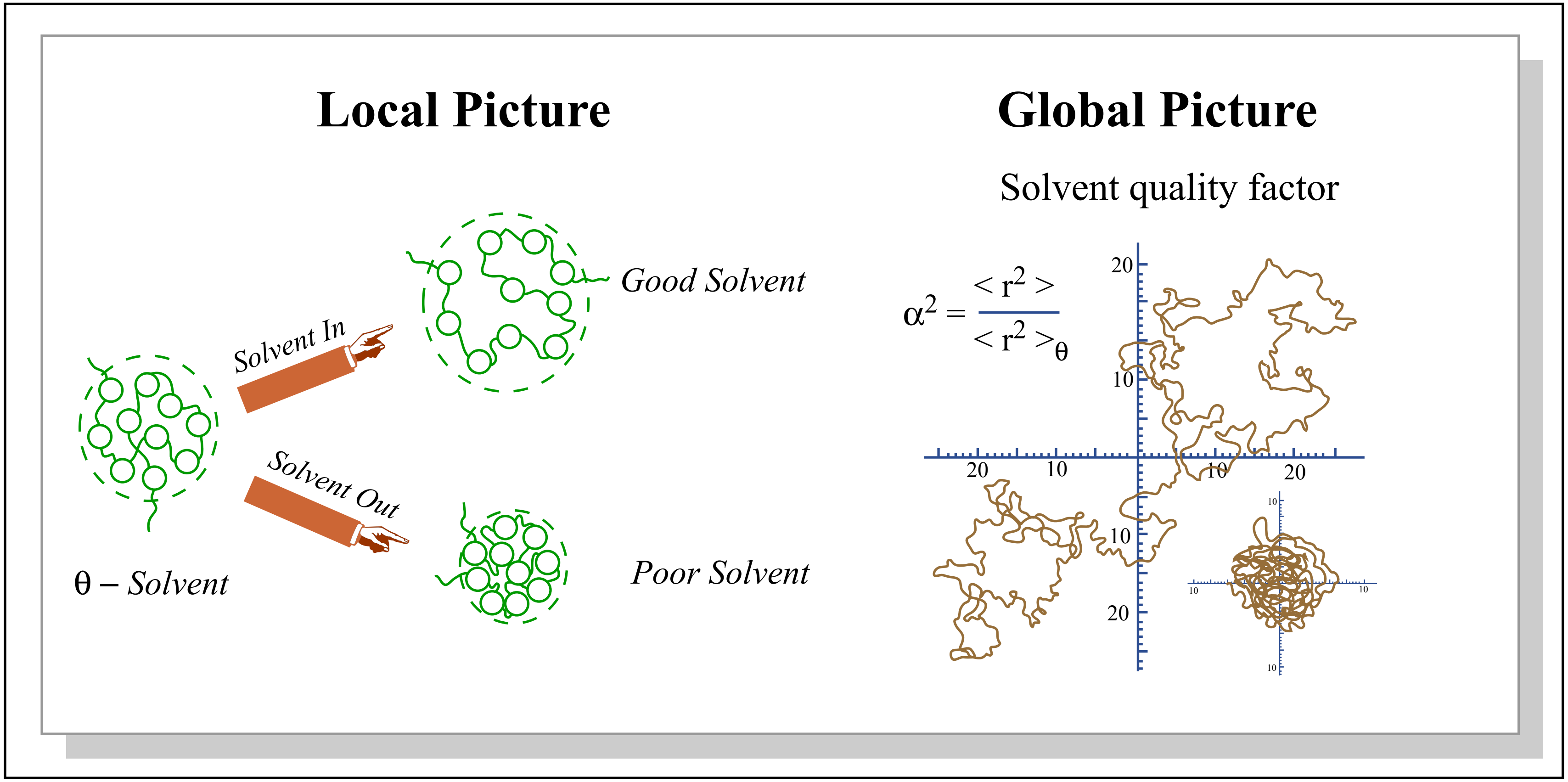


Figure by MIT OCW.

Theta condition

- In a good solvent the chain will expand – interaction between the polymer and the solvent is favored, and solvent-monomer contacts are maximized (and monomer-monomer contacts are minimized).
- In a poor solvent the chain will contract, to reduce interactions with the solvent. In practice, difficult to study (polymer will precipitate away).
- At the theta condition $\alpha=1$

Self-avoiding random walk

Figure by MIT OCW.

$\alpha = 1$, theta solvent

Θ condition: almost poor solvent

$$\langle r^2 \rangle_\theta \sim n l^2$$

$\alpha > 1$, good solvent

Self Avoiding Random Walk (SARW)

$$\langle r^2 \rangle \sim n^{\frac{6}{5}} l^2$$

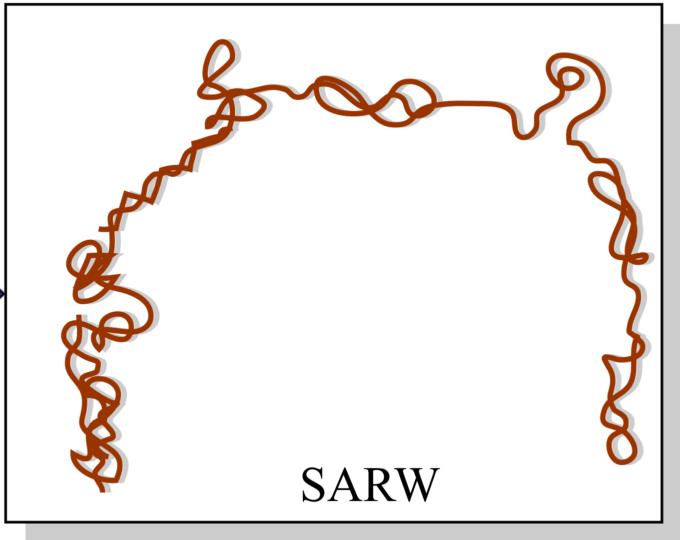


Figure by MIT OCW.

Diffusion: Rouse chain

- Low molecular weight linear polymers:

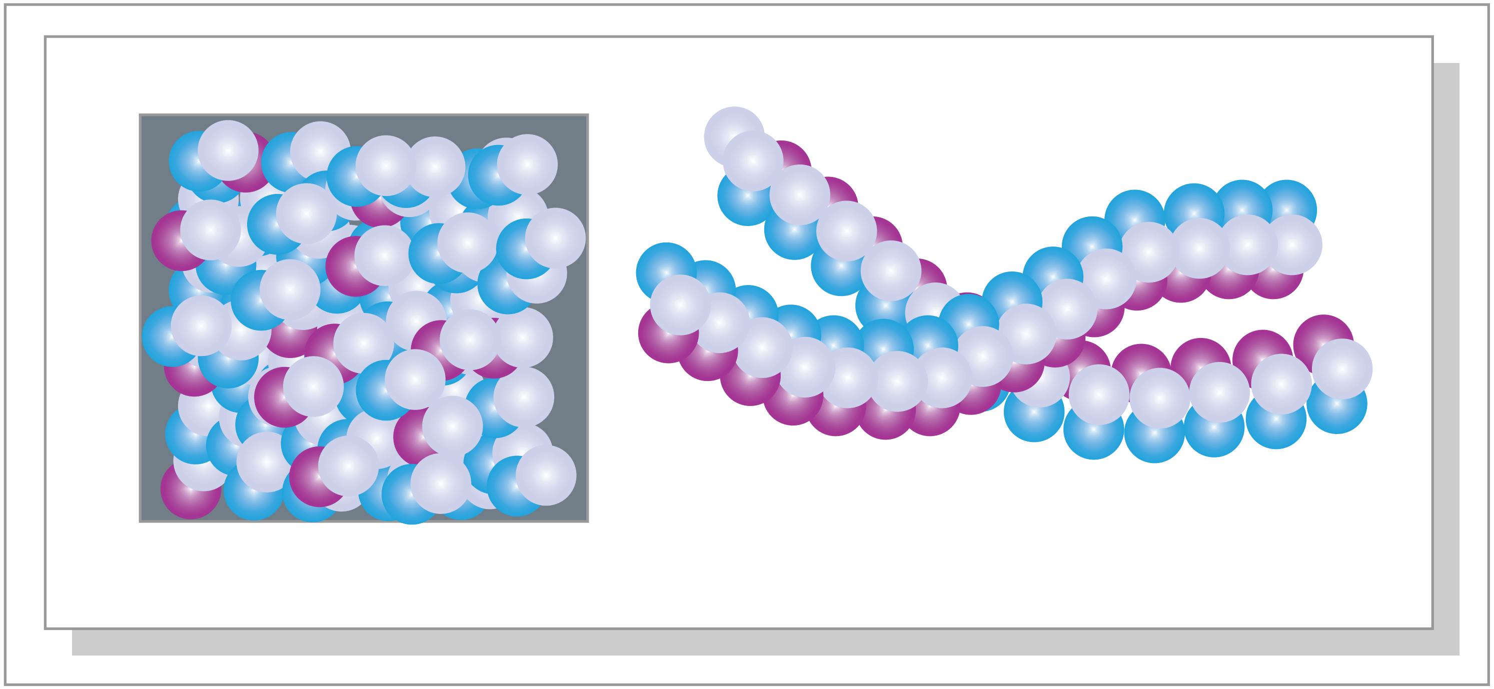
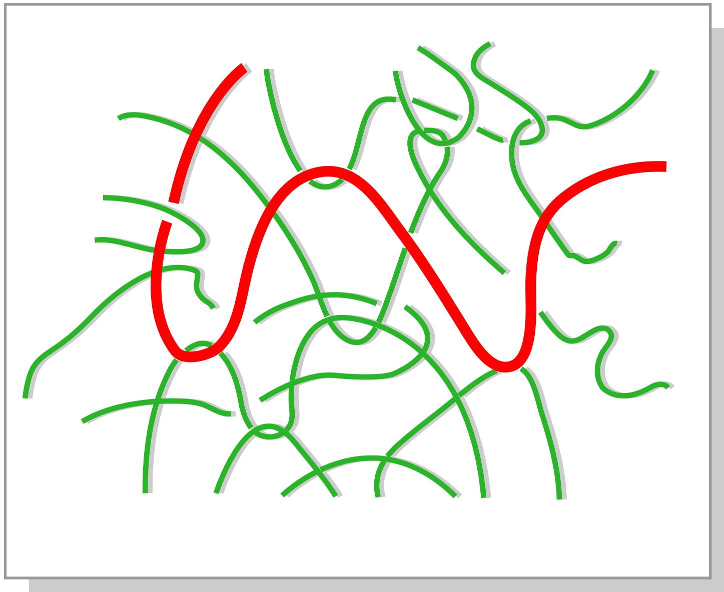


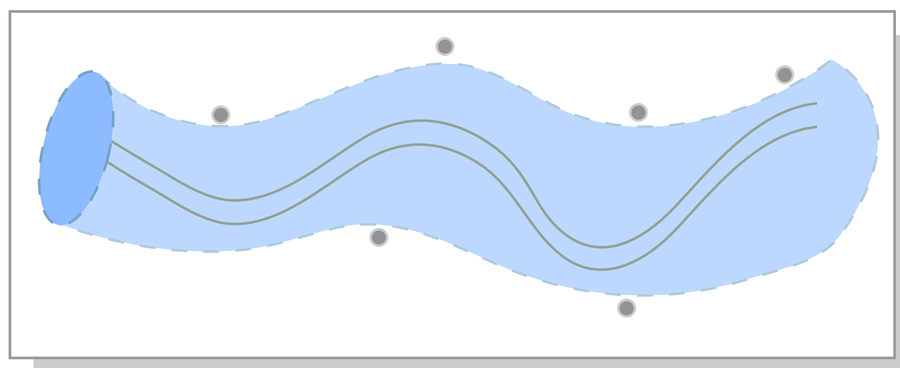
Figure by MIT OCW.

- An elastic string of Brownian particles in a viscous medium: diffusion=1/N

Large molecular weight: Reptation



Reptating chain, entangled



Portion of an effective constraining tube, defined by entanglements ● about a given chain.

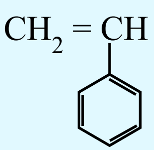
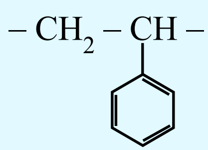
Monomer	Repeating Unit	Polymer Name	Uses
$CH_2 = CH_2$	$-CH_2-CH_2-$	Polyethylene	Film, toys, bottles, plastic bags
$CH_2 = CH$ (with Cl on CH)	$-CH_2-CH-$ (with Cl on CH)	Poly(vinyl chloride)	"squeeze" bottles, pipe, siding, flooring
$CH_2 = CH - CH_3$	$-CH_2-CH-$ (with CH_3 on CH)	Polypropylene	Molded caps, margarine tubs, indoor/outdoor carpeting, upholstery
		Polystyrene	Packaging, toys, clear cups, egg cartons, hot drink cups
$CF_2 = CF_2$	$-CF_2-CF_2-$	Poly(tetrafluoroethylene) Teflon®	Nonsticking surfaces, liners, cable insulation
$CH_2 = CH$ (with $C \equiv N$ on CH)	$-CH_2-CH-$ (with $C \equiv N$ on CH)	Poly(acrylonitrile) Orlon®, Acrilan®	Rugs, blankets, yarn, apparel, simulated fur
$CH_2 = C - CH_3$ (with $COCH_3$, $=O$, on C)	$-CH_2-C-$ (with CH_3 and $COCH_3$, $=O$, on C)	Poly(methyl methacrylate) Plexiglas®, Lucite®	Lighting fixtures, signs, solar panels, skylights
$CH_2 = CH$ (with $OCCH_3$, $=O$, on CH)	$-CH_2-CH-$ (with $OCCH_3$, $=O$, on CH)	Poly(vinyl acetate)	Latex paints, adhesives

Figure by MIT OCW.

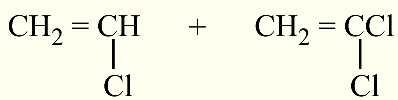
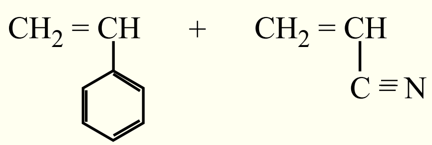
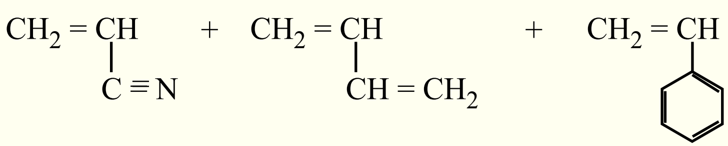
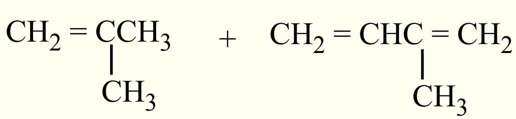
Monomer	Copolymer Name	Uses
 Vinyl chloride, Vinylidene chloride	Saran	Film for wrapping food.
 Styrene, Acrylonitrile	SAN	Dishwasher-safe objects, vaccum cleaner parts.
 Acrylonitrile, 1, 3-butadiene, Styrene	ABS	Bumpers, crash helmets, telephones, luggage.
 Isobutylene, Isoprene	Butyl rubber	Inner tubes, balls, inflatable sporting goods.

Figure by MIT OCW.

Network models: Continuous random network

- Monofunctional (dimers), bifunctional (linear chains), trifunctional or more (networks)

Images removed for copyright reasons.
See page 65, Figure 2.20 in Allen, S. M., and E.L. Thomas. *The Structure of Materials*. New York, NY: J. Wiley & Sons, 1999.

Oxide glasses

- Zachariasen constraints:
  - Each oxygen linked to not more than 2 cations
  - Functionality of central cation small
  - Oxygen polyhedra share corners
  - At least three corners of each polyhedron shared

Quartz and silica

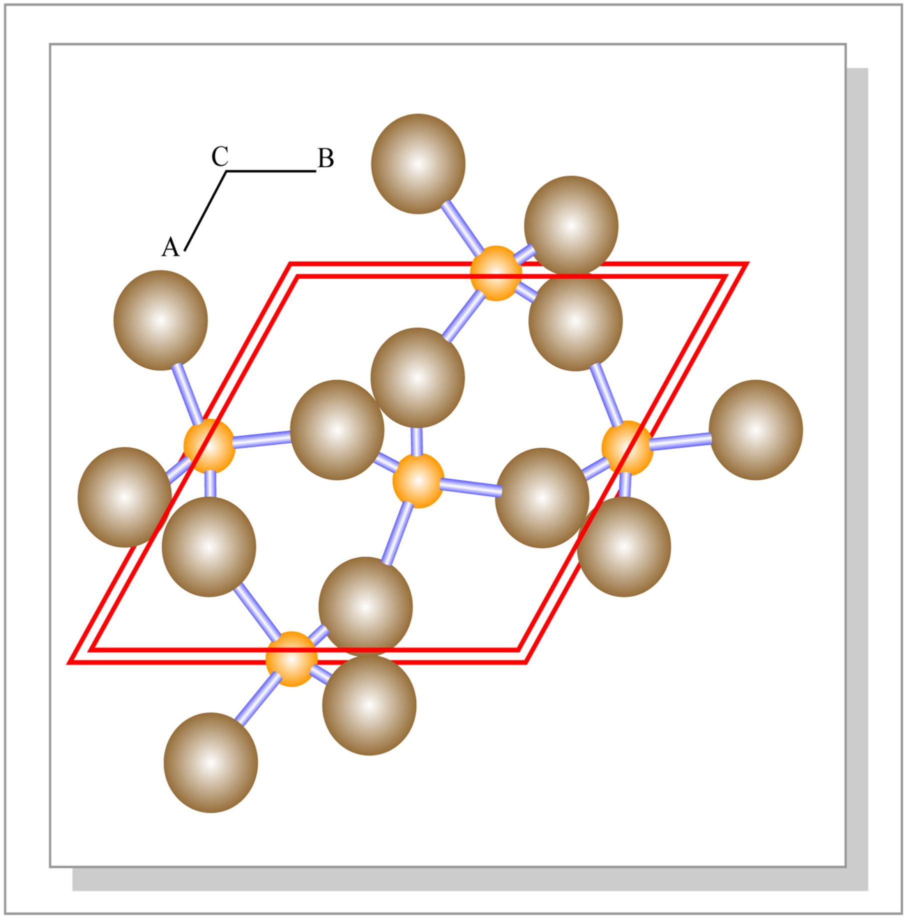


Figure by MIT OCW.

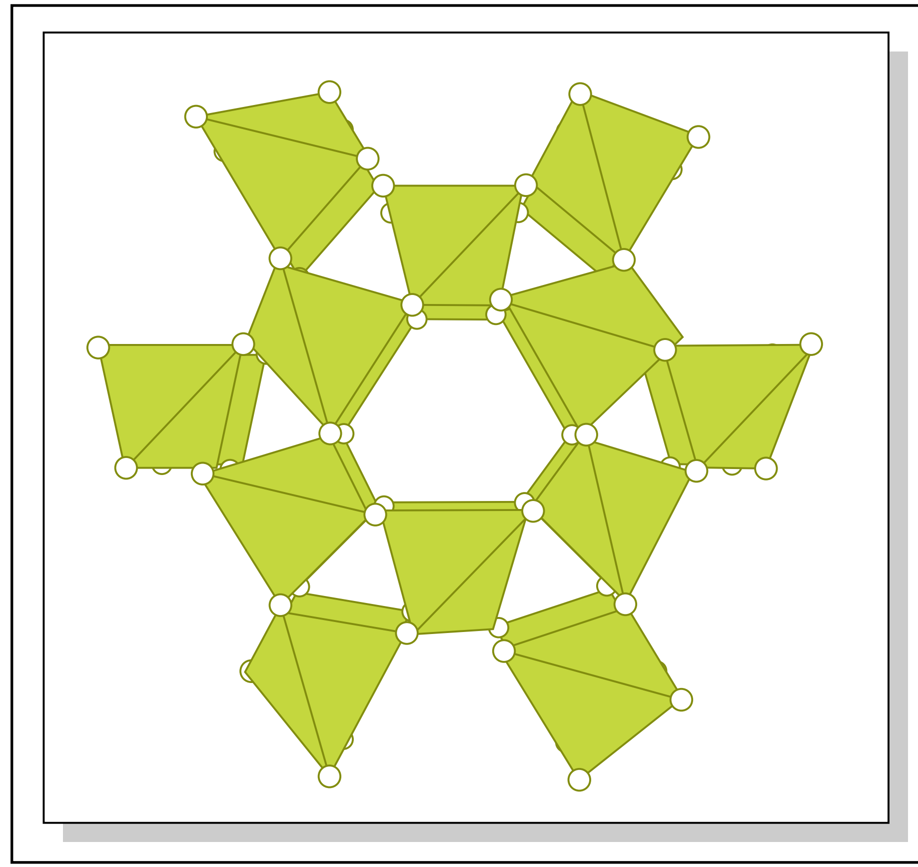


Figure by MIT OCW.

Network modifiers

Diagram of the effect of the lead-to-phosophorus ratio on phosphate glass removed for copyright reasons.
See page 71, Figure 2.25 in Allen, S. M., and E. L. Thomas. *The Structure of Materials*. New York, NY: J. Wiley & Sons, 1999.

Chalcogenide glasses

Diagram of the schematic bonding pattern of a chalcogenide network glass removed for copyright reasons.
See page 72, Figure 2.27 in Allen, S. M., and E. L. Thomas. *The Structure of Materials*. New York, NY: J. Wiley & Sons, 1999.