1 – Intro., Bonding, Structure

http://www.engr.sjsu.edu/WofMatE/polymers.htm --
Even casual look shows PS&E consists of: Synthetic Chemistry; Kinetics, Reactor Design; Thermo.; Solid Mechanics; Rheology; Electrical, Optical Phenomena.

Note the scale in the SEM of PS – even though strands (not single chains), implies MW’s high, in millions (typical polymers up to 5x 10^6 range).

Good explanation of crossed polarizer operation (birefringence) at:

http://www.eng.ox.ac.uk/lc/introduction/nematics_1.html

OLEDs – what kind of groups?

Colloidal phenomena closely tied with polymer sci. – many polymers in solution adopt micellar structures shown – as conc. increases. more structure (hexagonal, cubic)

http://www.ch.ic.ac.uk/rzepa/mim/polymer/index.html --

PVC – note the rigidity of the molecule

natural rubber – shows importance of conformation to properties

SBR – shows advantages of copoly. in commercial products – poy(butadiene) too soft, PS not rubbery enough at low T’s.

Poly(carbonate) – the polymer usually made from CO(Cl)_2. They’re showing “green” alternative – note how certain groups lead to rigidity.
Poly(peptides) and poly(saccharides) – infinite variety – conformation makes all the difference.

http://www.pslc.ws/mactest/maindir.htm - skipping part 1, but the auto parts section (1) illustrates difference between “polymer” and commercial product (tires). Most of the tire isn’t “polymer” (as normally defined).

http://www.pslc.ws/mactest/level2.htm -

Aramids illustrate importance of conformation and configuration (positional isomers) in a big way, and show that ANY polymer will eventually be processed.

Classification of polymer physical states – Glass, Rubber, Thermoset (hard rubber), Crystalline, Solution, Melt.

Aramids – Typically only 2 states, but you can always make the glass if you want to (how?).

In Crystalline state, plastic deformation possible, but polymer is strong (high modulus), tough (high yield stress and energy to break), and chemically resistant (relative to similar amorphous material).

Why are aramids fire resistant? What properties of use here?

PP illustrates importance of conformation similarly – even the syndiotactic now produced. Atactic would melt at lower T (why?).

What is glass transition T (called $T_g$)? What would crosslinking do to $T_g$?
Note that (some) crosslinking can also duplicate the intermolec. forces needed to give strong fibers, but strong intermolecular forces better [e.g., nylon 6,6 a better fiber than PE, with $T_m = 265^\circ C$ vs. $137^\circ C$ for linear HDPE]

Typical sec. forces – (a) dipole-dipole; (b) induced dipole; (c) H-bonding (F, N, O, Cl)

Aside on poly. phase transitions ---

$$\Delta G_{x_{sition}} = \Delta H - T \Delta S$$

Will solid poly. melt??

$\Delta H$ - endo - strongly so for polar / networked polymers

$\Delta S$ - can be strongly (+) – When?

Why won’t poly. boil??

(Energy of separation) $>$ (Energy to rupture bonds)

NOTE: In poly. thermo., $E/V$ usually better correlating function. $E/N$ has little meaning, due to mol wt. distribution (MWD).
2 – Molecular Weights (M’s), Distributions (MWD)

Both M and MWD affect phys. properties, processing (e.g., M ↑, impact strength ↑).

http://web.umr.edu/~wlf/MW/definitions.html?molecular+weight+definitions
- definitions, example.  [or Ch3_MWD_PR.doc , from Dr. Russo]

\[ M_i = \text{mol. wt. of chains with } i \text{ units; } N_i = \text{number of chains with } i \text{ units; } W_i = \text{weight of chains with } i \text{ units.} \]

\[ N_i, \ W_i, N_iM_i^2 \text{ etc. are the “random variables” which are being averaged.} \]

Another way to think of these averages is as collections of “moments” in probability theory.  \( M_n \) based on first and zeroth moments etc.

The viscosity average is based on a specific measurement, the “intrinsic viscosity” measurement  
[ viscosity in an infinitely dilute solution – directly related to mol. wt. – why?]
http://web.umr.edu/~wlf/MW/Mark.html

A “theta” solvent is a bad solvent.  For “a” near 0.5, \( M_v \) roughly in between \( M_n, M_w \).

Note that DP (often written as \( X_n, X_w \) to denote based on number, weight etc.) is just an average weight divided by the monomer mol. wt.  For copolymers?
**The polymerization kinetics determine MWD.** Often these distributions are surprisingly simple. In some cases, the distribution will be close to Gaussian, although more often it is closer to a geometric distribution known in polymer science as the “Schultz-Flory” (or just Flory, or sometimes “most probable”) distribution.

e.g., - see [http://www.engin.umich.edu/~cre/07chap/frames.htm](http://www.engin.umich.edu/~cre/07chap/frames.htm) (section 7e, part g).

“M” here can refer to EITHER molecules (for addition poly.) or functional groups (for step poly.). So p is related to what common term in ChE?

Amazingly, some polymerizations produce Schultz-Flory distributions with “p” not related to this parameter at all.

Problem: For the geometric distribution:

prob. = $p^{j-1}$, calculus tells us that as $p \rightarrow 1$, $\sum p^{j-1} = (1-p)^{-1}$ (just divide!)

From this, determine the number average DP.

Nice e.g. on GPC in Ch3_MWD_PR.doc.