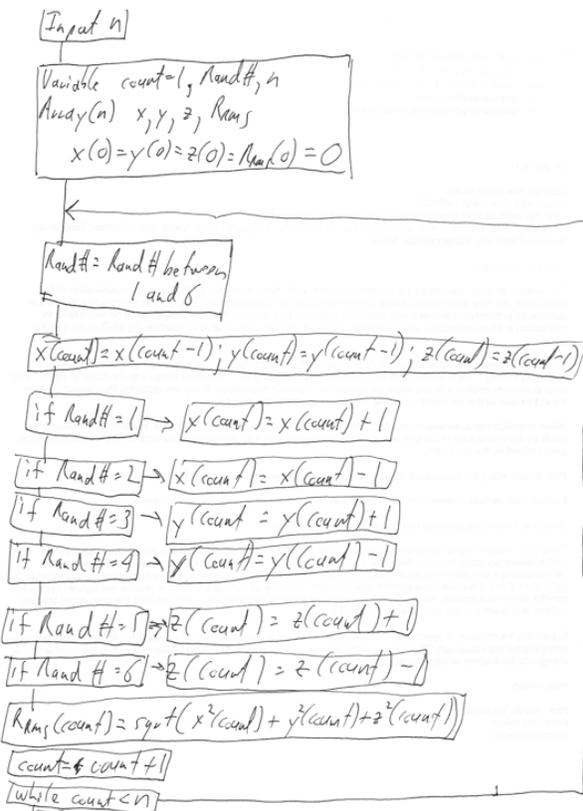


CME 300 Properties of Materials

Answers Homework 6 October 31, 2011

- 1) Outline a computer program to create a random walk structure similar to the program on the web site: <http://zeus.plmsc.psu.edu/~manias/MatSE443/Study/7.html> The input is n and the output are a series of n x , y and z positions for a random walk and the root mean square end-to-end distance. What do you expect to be the relationship between R and n from this program?



$R = n^{1/2}$ since l is 1.

- 2) Polymers in solution do not follow a random walk due to “excluded volume”.

- Give the scaling law followed by polymers in solution,
- comment on the average size difference for a chain of 100,000 units of step length 5\AA in solution and in the melt,
- explain what you think “excluded volume” means and
- propose why polymers in the melt or solid state follow a random configuration.

$$R \sim n^{3/5} l$$

The ratio of a self-avoiding walk to a random walk is $n^{3/5-1/2} = 3.2$. The random walk chain has $R = 1580\text{\AA}$ and the self-avoiding walk chain, $R = 5000\text{\AA}$.

Excluded volume means that a polymer chain cannot cross itself because it takes up space and excludes itself from the space that it occupies.

Polymers in the melt or solid state do not display excluded volume because chains screen the enthalpic interactions between other chains at high concentrations. This is like the inability to hear a conversation in a room with a lot of noise, the noise from other chains drowns out the binary interactions making the chains insensitive to the presence of other parts of the same chain.

- 3) *The ideal rubber law states that the retractive force on a stretched chain is proportional to the absolute temperature. Compare this functionality with the ideal gas law (using $P = F/A$). What is the connection between an ideal gas and an ideal rubber/polymer chain in terms of the thermal response? In what way is increasing the chain molecular weight similar to reducing the gas atom density (n/V)?*

In an ideal gas $PV = nkT$ or $F/A = \rho kT$ so $F = KT$ where $K = A\rho k$. This is the same functionality as an ideal rubber where $F = 3kTR/nl^2 = K'TR$ where $K' = 3k/nl^2$.

The ideal chain can be thought of as an ideal gas where the gas atoms have been connected by a wire like a bead necklace. It is the thermal motion of the beads that leads to the thermal retractive force, just as the pressure in an ideal gas is caused by the thermal motion of the gas atoms that collide with the walls of the container.

K in the ideal gas law is proportional to the density of gas atoms while K' in the ideal chain law is proportional to the inverse of the chain mass. Since chains are fractal objects, larger chains have a lower density of mer units.

- 4) *How can a disk be distinguished from a random-walk polymer chain using fractal scaling laws? Is a disk self-similar? ("Self-similarity" means that the object "looks the same" at different magnifications. Mass-fractal objects display self-similarity.)*

The mass-fractal dimension of a disk and a random-walk polymer chain are both 2. They can be distinguished by the connectivity dimension or by the minimum dimension. For a disk $c = 1$ and $d_{min} = 1$ and for a random walk chain $c = 1$ and $d_{min} = 2$.

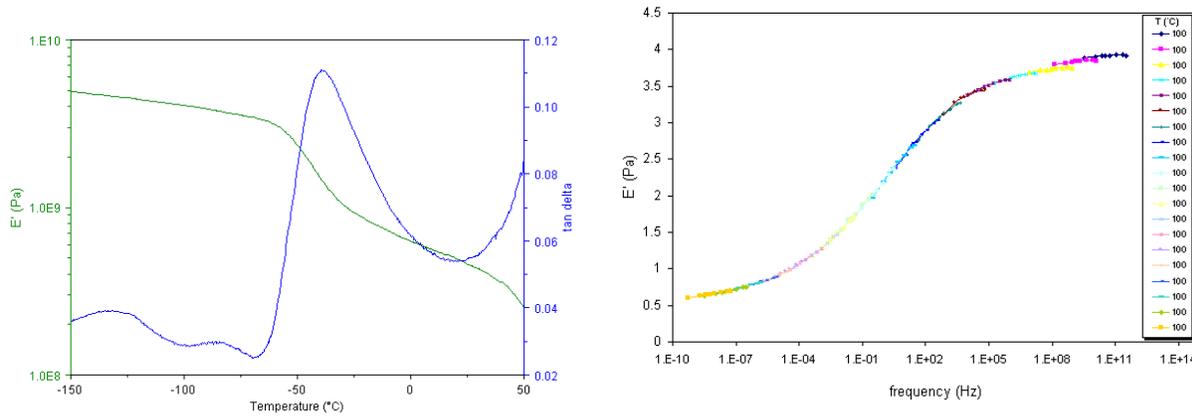
A disk is self similar if it is considered that increase of magnification for an infinitely thin disk results in a similar disk segment.

- 5) *How does the overlap concentration change for a chain of 10,000 units and a step length of 5\AA to a chain of 100,000 units with a similar step length if the chain is in a solution ($d_f = 5/3$)?*

The overlap concentration c^* is calculated from $c^* \sim n^{(1-3/d_f)}$ so the overlap concentration decreases by a factor of 6.3 in going from 10,000 to 100,000 units.

- 6) *The space shuttle Challenger exploded 73 seconds after takeoff in January 28, 1986. "Disintegration of the entire vehicle began after an O-ring seal in its right solid rocket booster (SRB) failed at liftoff. The O-ring failure caused a breach in the SRB joint it sealed, allowing pressurized hot gas from within the solid rocket motor to reach the outside and impinge upon the adjacent SRB attachment hardware and external fuel tank. This led to the separation of the right-hand SRB's aft attachment and the structural failure of the external tank. Aerodynamic forces promptly broke up the orbiter."*

The morning of take-off the temperature was close to freezing. Explain how this low temperature could effect a rubber o-ring to cause this disaster. Use a plot of elastic modulus versus temperature and a plot of elastic modulus versus frequency (rockets vibrate at high frequency) in your explanation.



Near the glass transition temperature (about -30°C in left plot) the material goes through a dramatic transition in properties from a hard, brittle glass at low temperature, to a leathery material at T_g to an elastomer at high temperature. Frequency can shift this transition temperature. In the right figure the glass transition at room temperature is observed at about 5 Hz. If the frequency increases the material becomes glassy. On the launch day the space shuttle was 30 to 40°F below it's safe operating temperature, so the rubber seals were brought closer to their glass transition temperature. Coupled with the extremely high frequency of vibration that occurs on liftoff, at least one of the seals shattered. This may have been a common occurrence and the rockets had two seals. The investigating commission indicated that an oxide generally filled the gap in the rocket engine but on the particular day extremely high winds at high altitude cause stress on the rockets that broke the oxide that had filled the hole caused by shatter of the o-rings. The tragedy was caused by a combination of events that began with T_g .

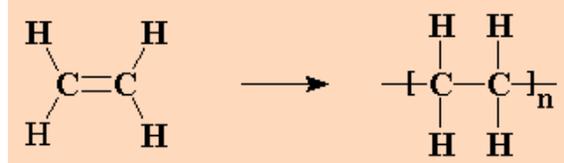
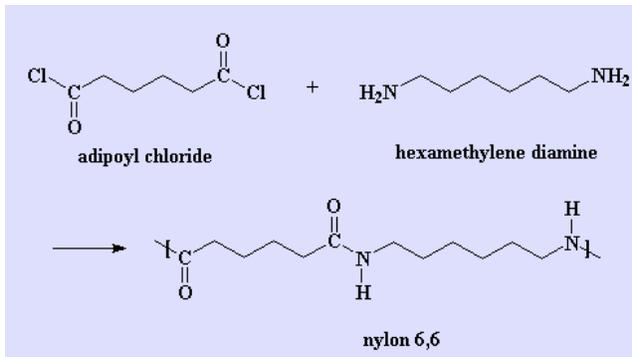
7) Sketch the storage modulus versus frequency and storage modulus versus temperature plots for a crosslinked and uncrosslinked polymer through the glass transition region. Explain the mechanical properties below the glass transition, at the glass transition and above the glass transition temperature.

This is answered in 6. For an uncrosslinked polymer the modulus goes to 0 slightly above the glass transition temperature. A rubbery plateau is seen where chain entanglements can serve as short lived crosslinks.

8) There are two main types of polymerization reactions used to produce synthetic polymers. Give one example of each of these and sketch out the reaction scheme for both.

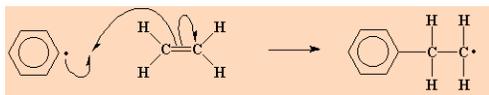
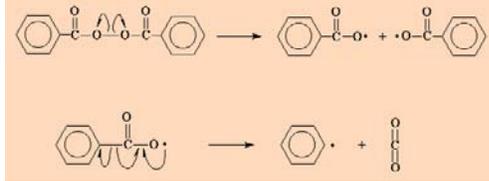
Polyethylene polymerization for chain growth polymerization

Nylon 6, 6 polymerization for step growth polymerization

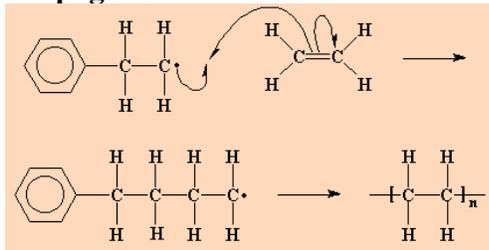


Initiation:

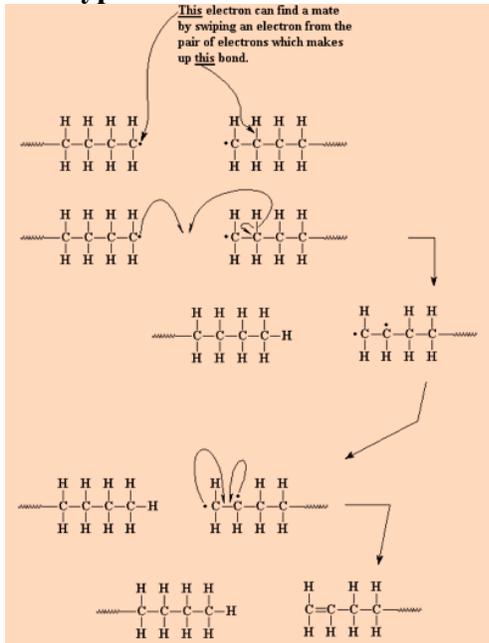
Free radical initiator benzoyl peroxide



Propagation:



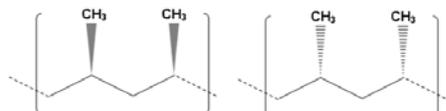
One type of Termination:



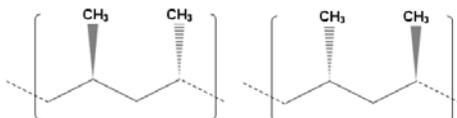
9) A commercial polyethylene has a $PDI = M_w/M_n$ of 16 and $M_w = 120$ kDa. $M_z/M_w = 2$. A similar polymer has the same PDI and M_w but $M_z/M_w = 3.5$. Do you expect dramatically different viscosity from the second polymer? Why or Why not? What feature in the molecular weight distribution could account for the difference between these two polymers?

A high value for M_z/M_w indicates a high molecular weight component in the molecular weight distribution. Since the melt viscosity goes with the molecular weight to the 3.4 power a small amount of high molecular weight species can have a large impact on the melt viscosity for the material. A higher melt viscosity is expected for the second polymer.

10) Triad tacticity is classified as isotactic, syndiotactic and heterotactic. Using polypropylene show Natta projections that show racemic and meso diads then explain how these are used to produce the three types of triads. In terms of r and m describe an atactic polymer. In terms of iso, syndio and hetero describe an atactic polymer. Would atactic polypropylene be of commercial use? Why?



Meso Diads

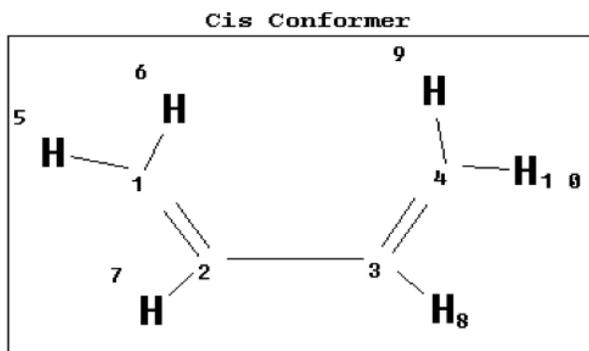
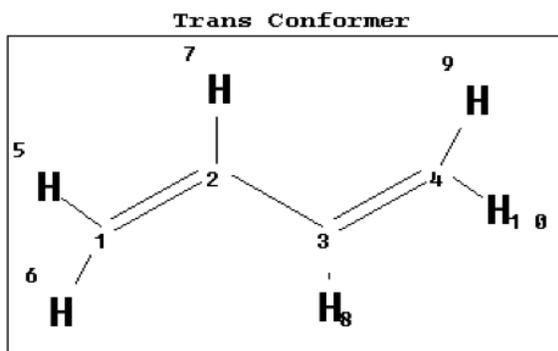


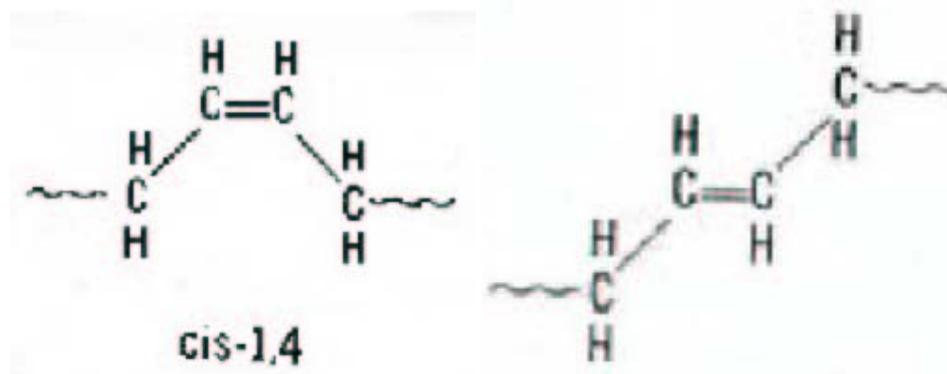
Racemic Diads

Isotactic Triad: mm; Syndiotactic Triad: rr; Heterotactic Triad: mr or rm

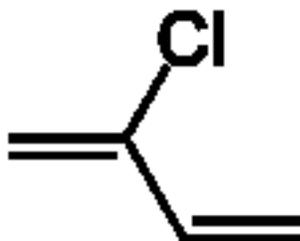
Atactic means random tacticity so for diads this means 50% r and 50% m, for triads this means 25% isotactic, 25% syndiotactic and 50% heterotactic since there are twice as many ways to make a heterotactic as an isotactic or syndiotactic triad.

14.12 Sketch cis and trans structures for (a) butadiene, and (b) chloroprene.

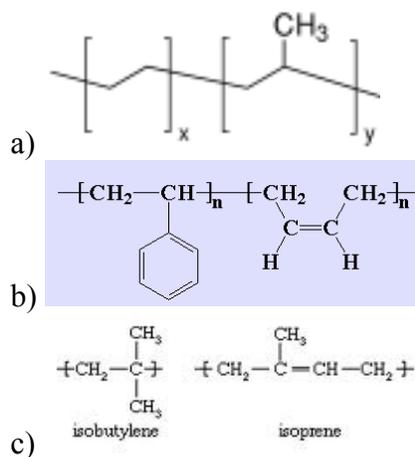




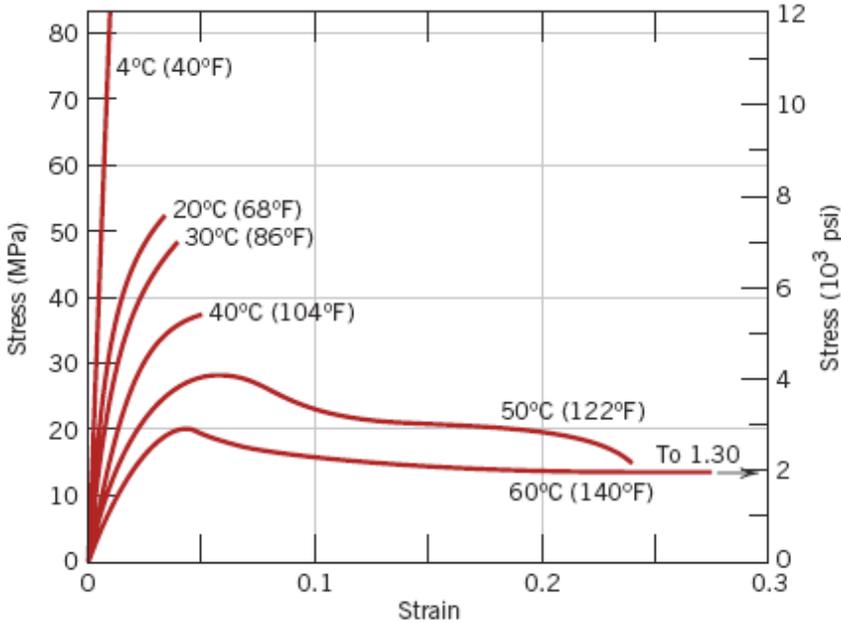
Trans Chloroprene



14.15 Sketch the repeat structure for each of the following alternating copolymers: (a) poly(ethylene-propylene), (b) poly(butadiene-styrene), and (c) poly(isobutylene-isoprene).



15.1 From the stress–strain data for poly(methyl methacrylate) shown in Figure 15.3, determine the modulus of elasticity and tensile strength at room temperature [20°C (68°F)], and compare these values with those given in Table 15.1.



The modulus is $30 \text{ MPa}/0.015 = 2000 \text{ MPa} = 2.0 \text{ GPa}$. The tensile strength is about 53 MPa.

Table 15.1 Room-Temperature Mechanical Characteristics of Some of the More Common Polymers

<i>Material</i>	<i>Specific Gravity</i>	<i>Tensile Modulus [GPa (ksi)]</i>	<i>Tensile Strength [MPa (ksi)]</i>	<i>Yield Strength [MPa (ksi)]</i>	<i>Elongation at Break (%)</i>
Poly(methyl methacrylate)	1.17–1.20	2.24–3.24 (325–470)	48.3–72.4 (7.0–10.5)	53.8–73.1 (7.8–10.6)	2.0–5.5

15.3 For some viscoelastic polymers that are subjected to stress relaxation tests, the stress decays with time according to

$$\sigma(t) = \sigma(0) \exp\left(-\frac{t}{\tau}\right) \quad (15.10)$$

where $\sigma(t)$ and $\sigma(0)$ represent the time-dependent and initial (i.e., time = 0) stresses, respectively, and t and τ denote elapsed time and the relaxation time; τ is a time-independent constant characteristic of the material. A specimen of some viscoelastic polymer with the stress relaxation that obeys Equation 15.10 was suddenly pulled in tension to a measured strain of 0.5; the stress necessary to maintain this constant strain was measured as a function of time. Determine $E_r(10)$ for this material if the initial stress level was 3.5 MPa (500 psi), which dropped to 0.5 MPa (70 psi) after 30 s.

$$\sigma(0s) = 3.5 \text{ MPa and } \sigma(30s) = 0.5 \text{ MPa}$$

$$\sigma(0s)/\sigma(30s) = \exp((30-0)/\tau) = 3.5/0.5 = 7$$

$$\tau = 30s/\ln(7) = 15.4 \text{ s}$$

$$\sigma(10s) = 3.5 \text{ MPa } \exp(-10\text{MPa}/15.4\text{MPa}) = 1.8 \text{ MPa}$$