Polymers

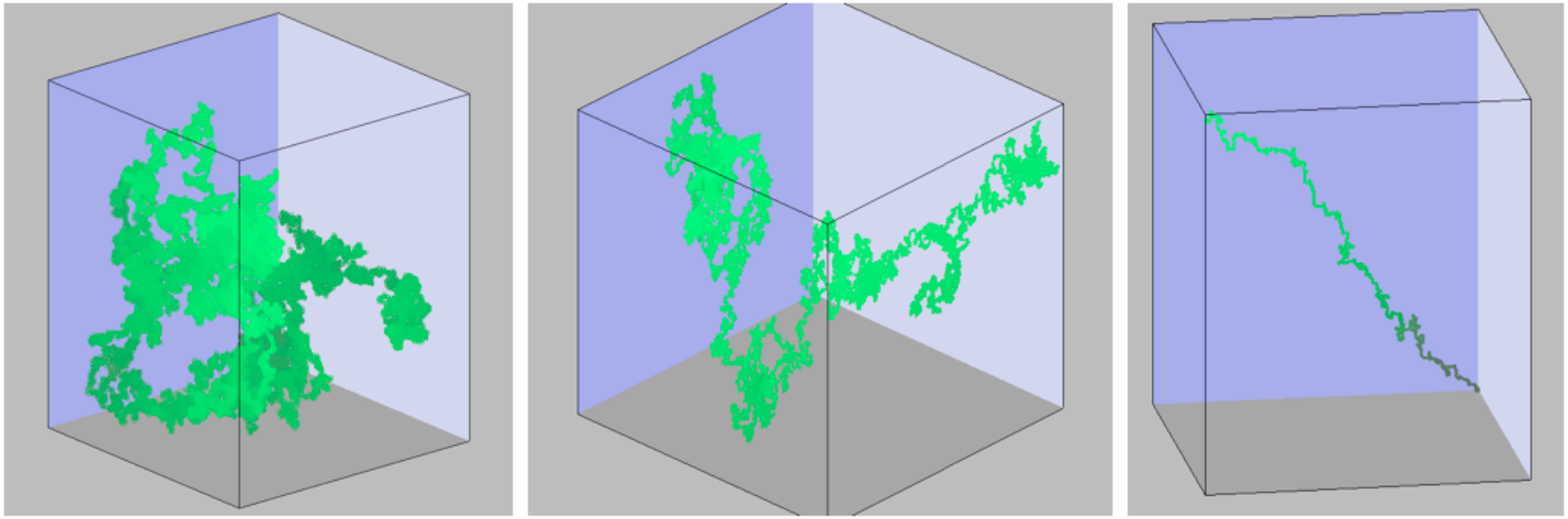


Figure 1. 50,000 setp Gaussian (left), 50,000 step SAW/SRI 1 cell (middle), 50,000 step SAW with 3 cell avoidance and 1 cell SRI (right). 50,000^3/5 = 660 and 50,000^0.5 = 224. End-to-end distance for the Gaussian is 71, for the SAW (1 step avoidance) is 397 and for 3 step avoidance is about 5000.

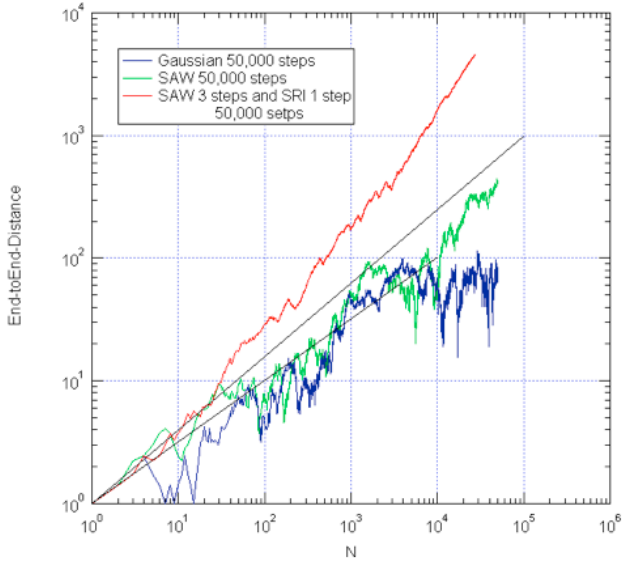


Figure 2. R end-to-end distance versus N in a log-log plot showing lines for 1/2 and 5/3 slope.

Polymers

$$\log\left\langle R^2\right\rangle^{1/2} \sim Slope\ \log(N)$$

$$\left\langle R^2\right\rangle^{1/2} \sim N^{Slope}$$

Steep Slope = 3/5 : Self-Avoiding Walk
(Polymer Solution)
Shallow Slope = 1/2 : Gaussian Random Walk
(Polymer Melt)

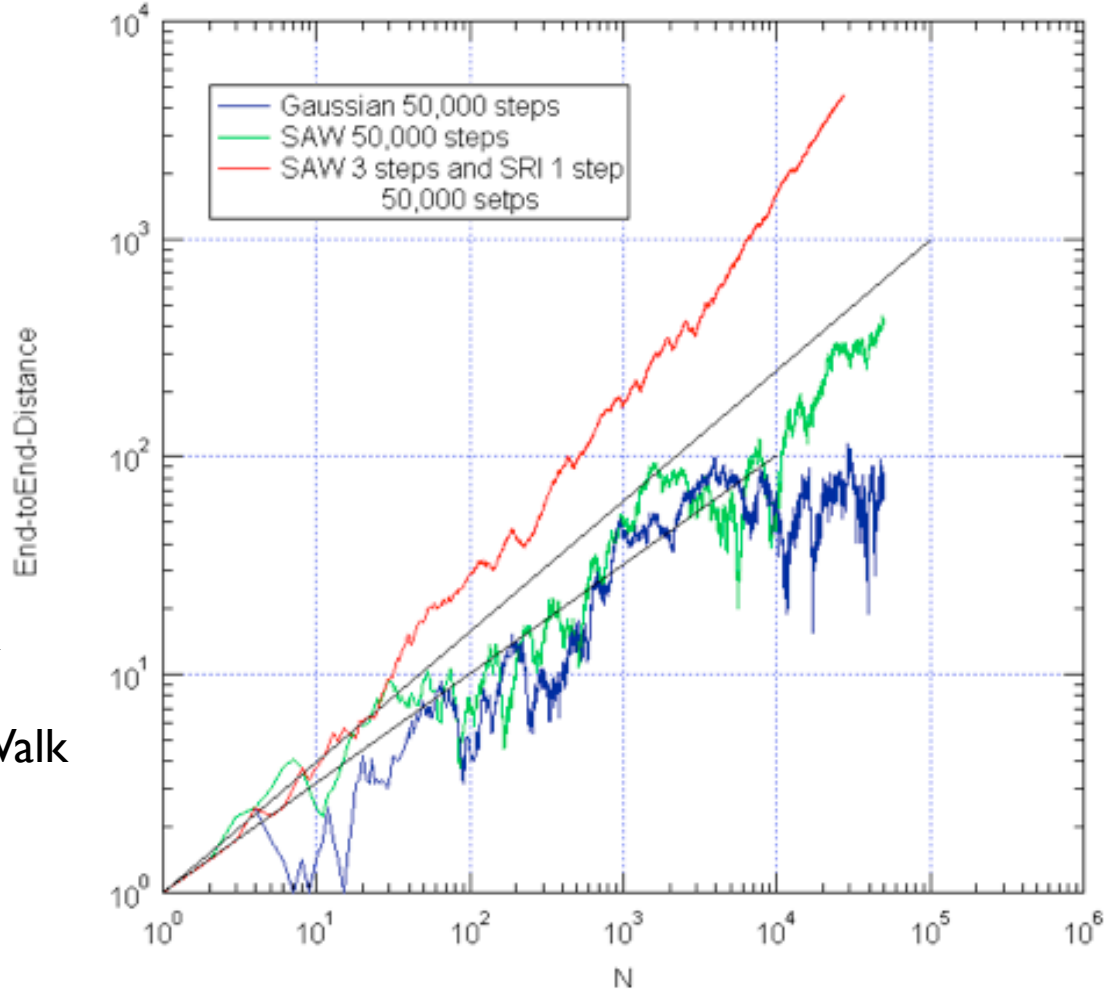
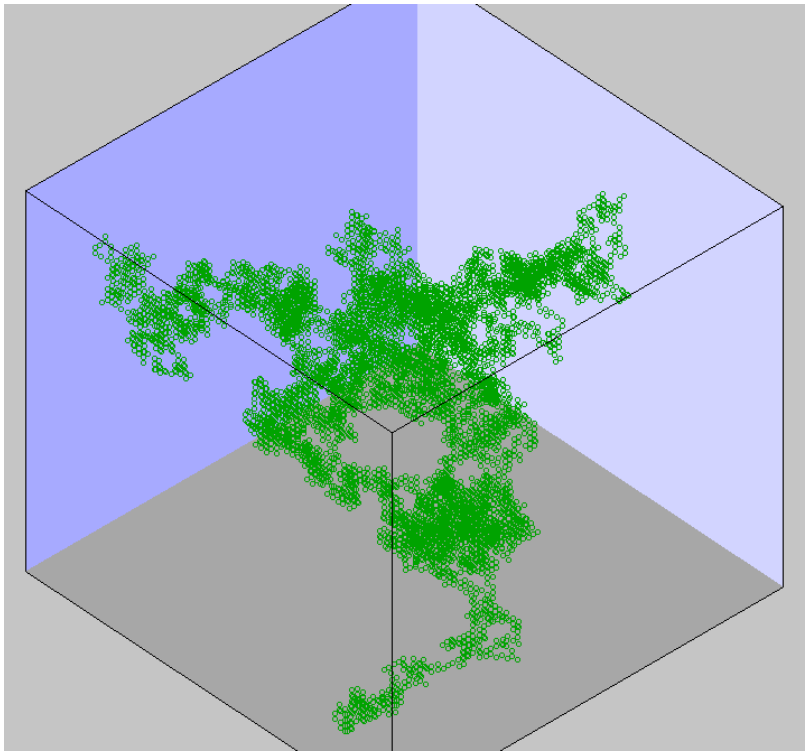


Figure 2. R end-to-end distance versus N in a log-log plot showing lines for 1/2 and 5/3 slope.



If we consider a series of chains

<R> = 0

$$\left\langle R^2 \right\rangle = \sum_{i=1}^{n}\sum_{j=1}^{n}\left\langle r_i \bullet r_j \right\rangle = nr^2$$

$$r_i \bullet r_j = 0$$

Except when i = j, and there are "n" of these

$$r_i \bullet r_i = 1$$

$R_{RMS} = n^{1/2}\,\ell$

Similar to diffusion $R \sim Dt^{1/2}$

The distribution of chain lengths, R, follows almost a Gaussian Distribution:

$$P_G(x,\mu,\sigma) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2\right] \qquad \text{1-d Gaussian}$$

$$P_G(R,n) = \frac{1}{\sqrt{2\pi n b^2}} \exp\left[-\frac{1}{2}\left(\frac{R}{b\sqrt{n}}\right)^2\right] \qquad \text{1-d Gaussian Walk of "n" steps}$$

Boltzman Equation

$$P(R) = \exp\left(\frac{-E(R)}{kT}\right)$$

By Comparison

$$E(R) = \frac{3kTR^2}{2nl^2}$$

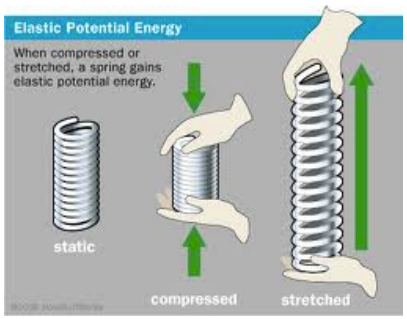
The energy of an ideal chain as a function of R

Energy of an Ideal Chain

$$E(R) = \frac{3kTR^2}{2nl^2}$$

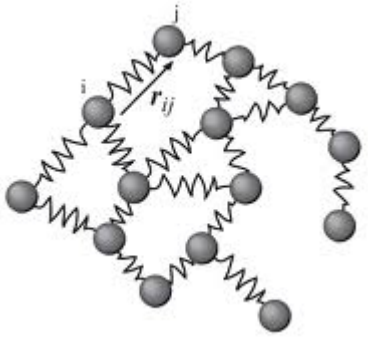
$$F = \frac{dE(R)}{dR} = \frac{3kT}{nl^2}R = k_{spr}R$$

(Change in energy is force times the change in distance)



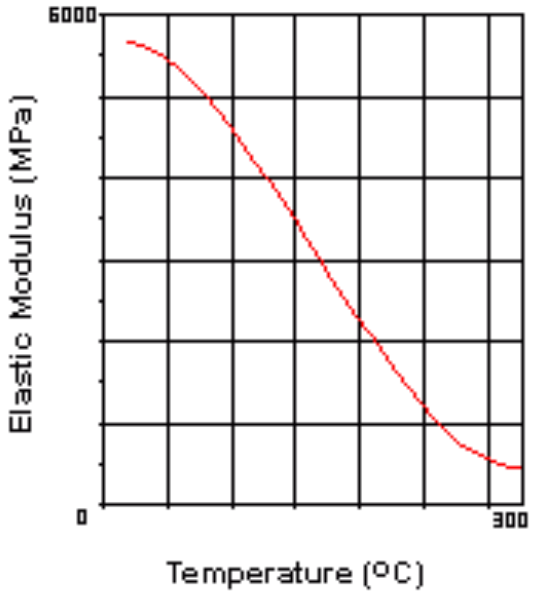
The ideal chain acts like a spring

The modulus of rubber is proportional to temperature and inversely proportional to the molecular weight between crosslinks.

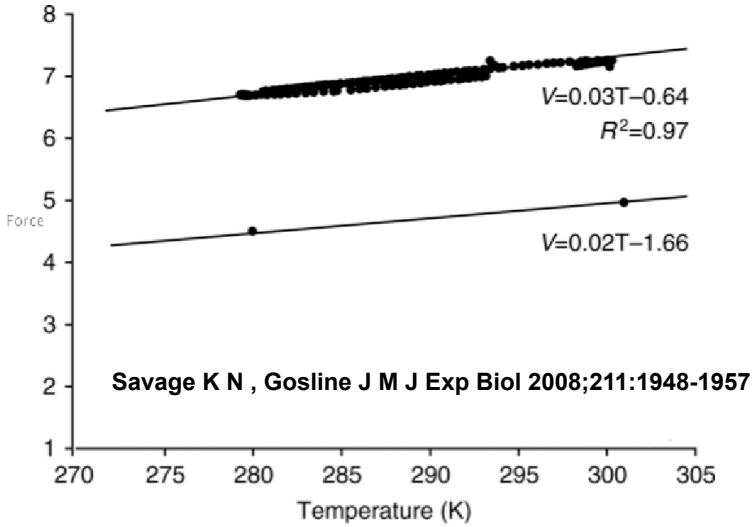


Generally Modulus **decreases** with temperature

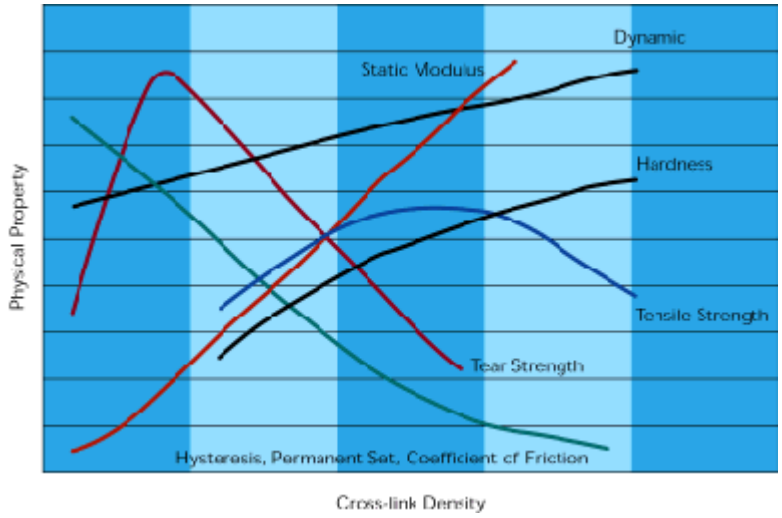
Metal



For an ideal elastomer it increase with T



Savage K N , Gosline J M J Exp Biol 2008;211:1948-1957



http://www.allsealsinc.com/allseals/Orings/or13.htm

This is due to the entropic nature of polymers

$$F = \frac{dE(R)}{dR} = \frac{3kT}{nl^2} R = k_{spr} R$$

Polymer Chains are Mass-Fractals

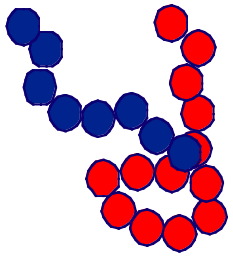
$R_{RMS} = n^{1/2}\, l$	Mass ~ Size^2
3-d object	Mass ~ Size^3
2-d object	Mass ~ Size^2
1-d object	Mass ~ Size^1
d_f-object	Mass ~ Size^{df}

This leads to odd properties:

density $$\rho = \frac{Mass}{Volume} = \frac{Mass}{Size^3} = \frac{Size^{d_f}}{Size^3} \sim Size^{d_f - 3}$$

For a 3-d object density doesn't depend on size,
For a 2-d object density drops with Size
Larger polymers are less dense

Mass Fractal dimension, d_f

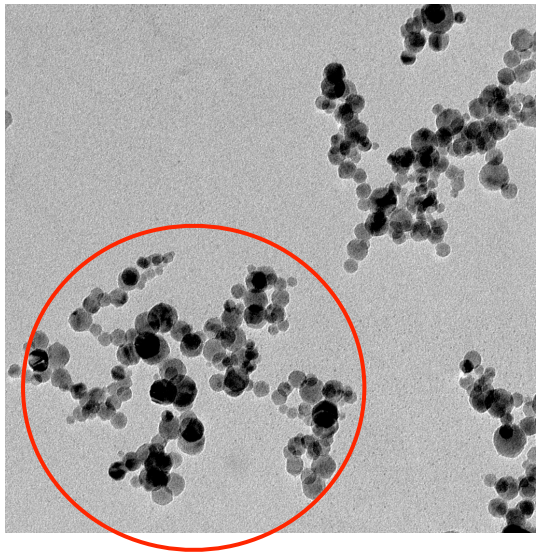


$$mass = z \sim \left(\frac{R}{d_p} \right)^{d_f}$$

z is mass/DOA
d_p is bead size
R is coil size

Random Aggregation (right) $d_f \sim 1.8$
Randomly Branched Gaussian $d_f \sim 2.3$
Self-Avoiding Walk $d_f = 5/3$

Problem:
Disk $d_f = 2$
Gaussian Walk $d_f = 2$



Nano-titania from Spray Flame

$R/d_p = 10$, $z \sim 220$
$d_f = \ln(220)/\ln(10) = 2.3$

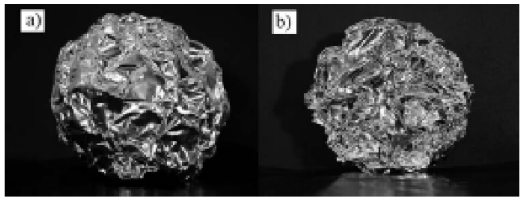
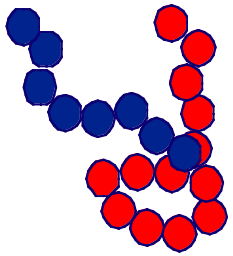


FIG. 1. Images of (a) balls folded from an aluminum sheet of thickness h=0.06 mm and edge size L=60 cm and (b) the cut through this ball. Balankin et al. (*Phys. Rev. E* **75** 051117

Mass Fractal dimension, d_f



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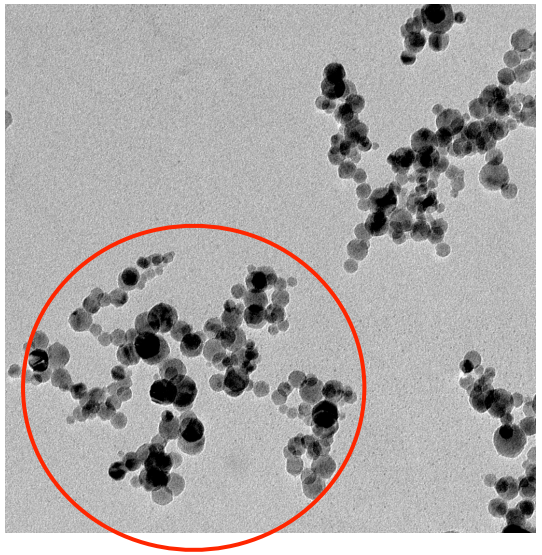
R is coil size



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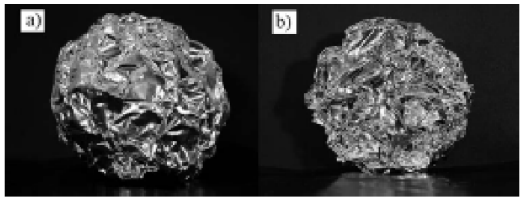
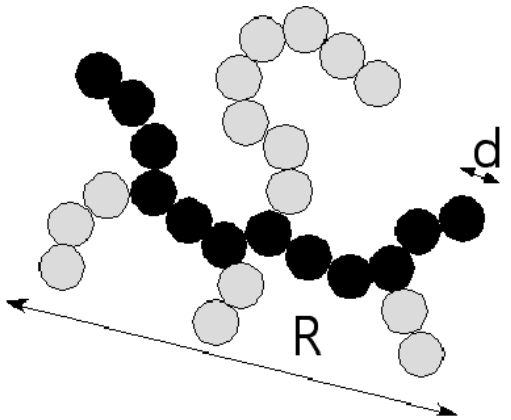


FIG. 1. Images of (a) balls folded from an aluminum sheet of thickness h=0.06 mm and edge size L=60 cm and (b) the cut through this ball. Balankin et al. (*Phys. Rev. E* **75** 051117

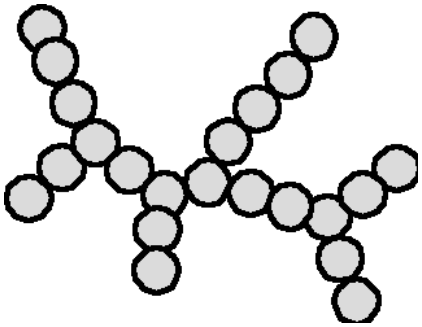
A measure of topology is not given by d_f.
Disk and coil are topologically different.
Foil and disk are topologically similar.

How Complex Mass Fractal Structures Can be Decomposed



Tortuosity

Connectivity



$$z \sim \left(\frac{R}{d}\right)^{d_f} \sim p^c \sim s^{d_{\min}}$$

$$p \sim \left(\frac{R}{d}\right)^{d_{\min}}$$

$$s \sim \left(\frac{R}{d}\right)^{c}$$

$$d_f = d_{\min} c$$

z	d_f	p	d_{min}	s	c	R/d
27	1.36	12	1.03	22	1.28	11.2

Consider a Crumpled Sheet

A 2-d Sheet has $c = 2$
d_{min} depends on the extent of crumpling

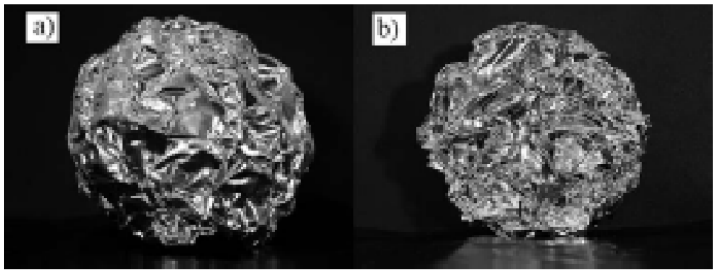
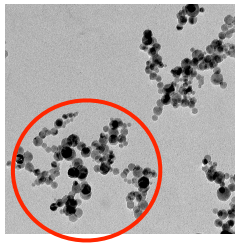


FIG. 1. Images of (a) balls folded from an aluminum sheet of thickness h=0.06 mm and edge size L=60 cm and (b) the cut through this ball.

$$d_f = 2.3$$
$$d_{\min} = 1.15$$
$$c = 2$$



$$d_f = 2.3$$
$$d_{\min} = 1.47$$
$$c = 1.56$$

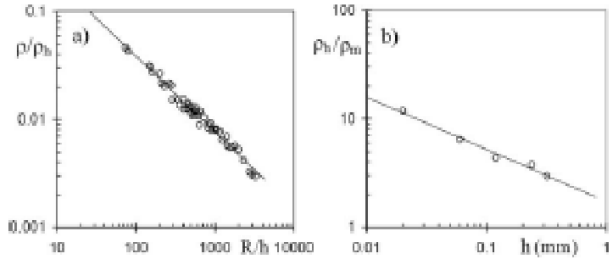


FIG. 3. (a) Data collapse for ρ/ρ_h versus R/h (the slope of the fitting line is $3-D=0.7009$, $R^2=0.98$); and (b) log-log plot of ρ_h/ρ_m versus h (straight line is given by $y=1.728x^{-0.4816}$, $R^2=0.98$).
Balankin et al. (*Phys. Rev. E* **75** 051117 (2007))

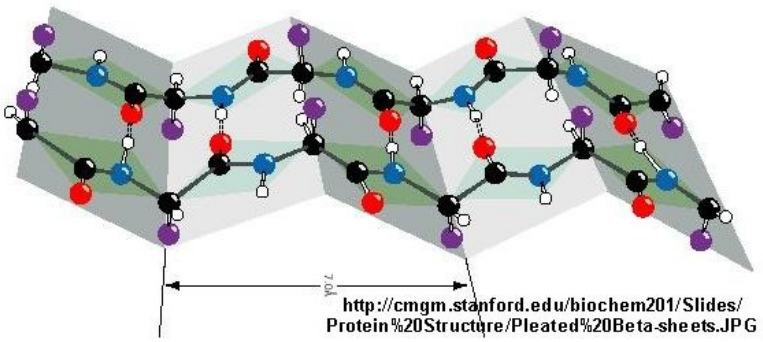
Disk

$$d_f = 2$$

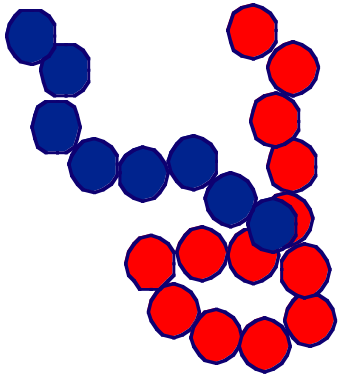
$$d_{\min} = 1$$

$$c = 2$$

Extended β-sheet
(misfolded protein)



Random Coil

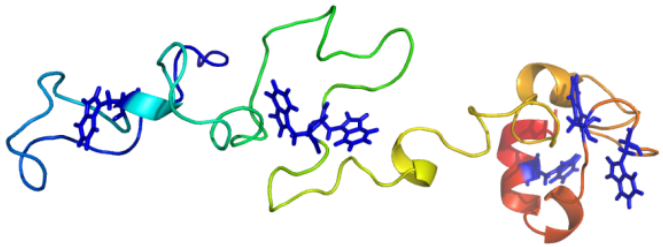


$$d_f = 2$$

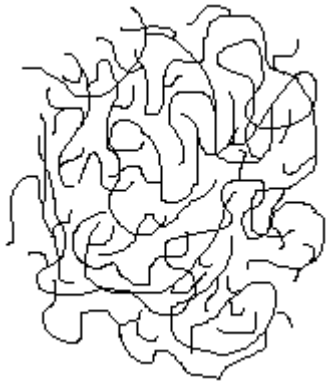
$$d_{\min} = 2$$

$$c = 1$$

Unfolded Gaussian chain



For a polymer in solution there is an inherent concentration to the chain since the chain contains some solvent

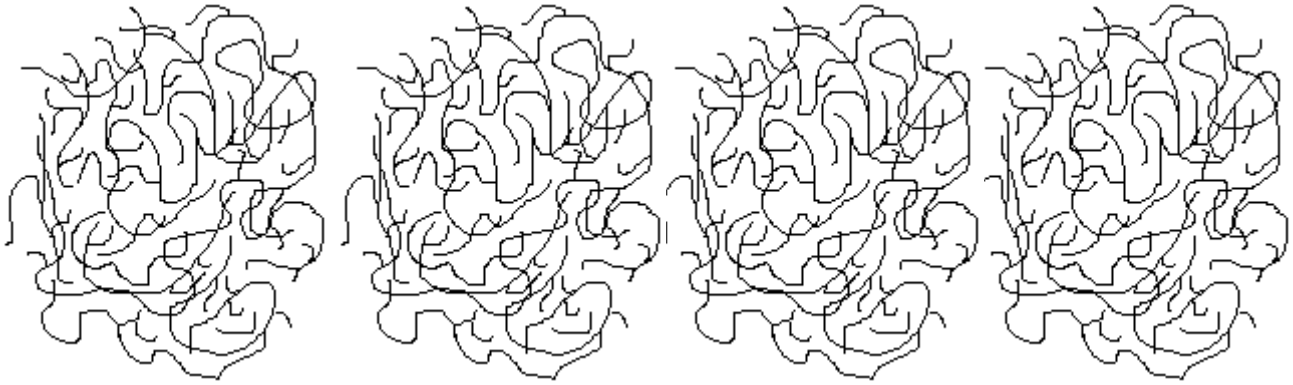


The polymer concentration is Mass/Volume, within a chain

$$c^* = \frac{Mass}{Volume} = \frac{Mass}{Size^3} = \frac{Size^{d_f}}{Size^3} \sim Size^{d_f - 3}$$

$$c^* \sim n^{\left(1 - 3/d_f\right)}$$

When the solution concentration matches c* the chains "overlap"
Then an individual chain is can not be resolved and the chains entangle
This is called a concentrated solution, the regime near c* is called semi-dilute
and the regime below c* is called dilute



In concentrated solutions with chain overlap chain entanglements lead to a higher solution viscosity

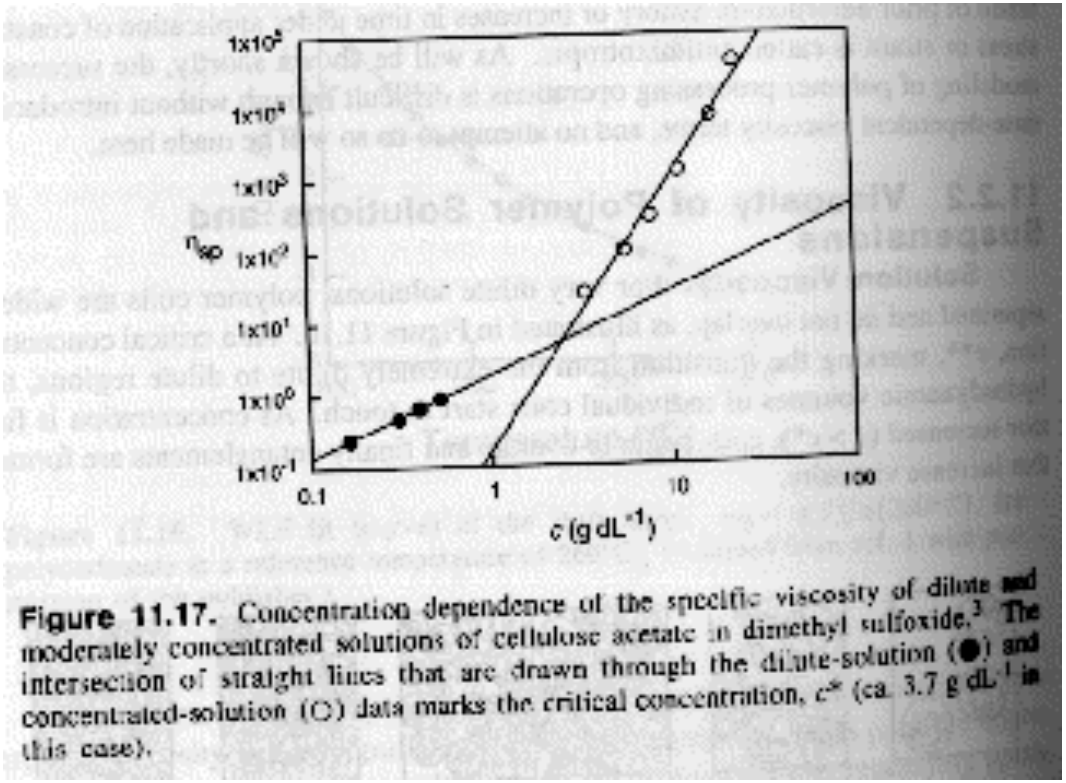


Figure 11.17. Concentration dependence of the specific viscosity of dilute and moderately concentrated solutions of cellulose acetate in dimethyl sulfoxide.[3] The intersection of straight lines that are drawn through the dilute-solution (●) and concentrated-solution (○) data marks the critical concentration, c^* (ca. 3.7 g dL^{-1} in this case).

J.R. Fried Introduction to Polymer Science

$$\eta \sim c^P$$

$$P = 1 \text{ for c} < \text{c*}$$

There is a similar behavior in Melt Viscosity as a function of Molecular Weight

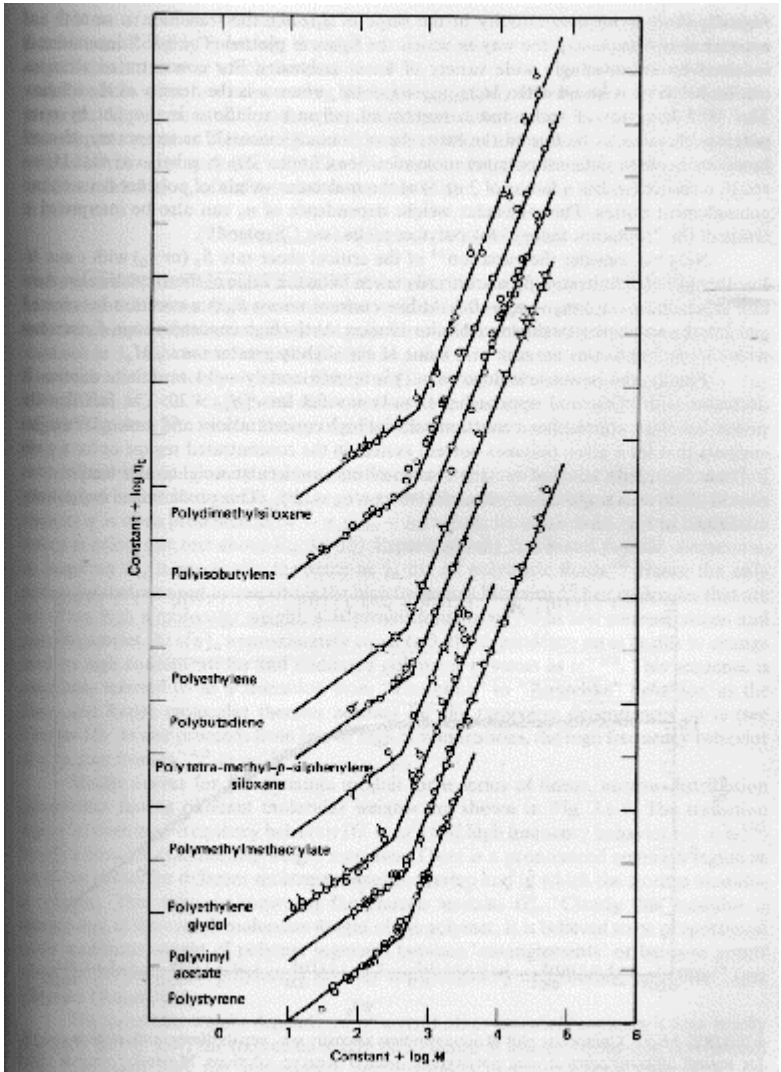
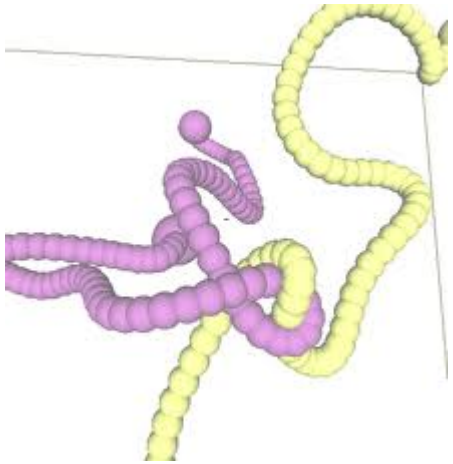


FIGURE 3.6-4. Plots of constant + log η_c vs. constant + log M for nine different polymers. The two constants are different for each of the polymers, and the one appearing in the abscissa is proportional to concentration, which is constant for a given undiluted polymer. For each polymer the slopes of the left and right straight line regions are 1.0 and 3.4, respectively. [G. C. Berry and T. G. Fox, *Adv. Polym. Sci.*, **5**, 261–357 (1968).]

$$\eta_0 \sim M^1 \quad \text{for M} < \text{M}_e$$

$$\eta_0 \sim M^{3.4} \quad \text{for M} > \text{M}_e$$



M_e is the entanglement molecular weight about 10,000 g/mole (10 kDa)

Many Macromolecular Properties Change at M_e

Onset of Shear Thinning Behavior in Rheology

Onset of Chain Folding Crystallization

Onset of Robust Mechanical Properties (Organic Powder versus Solid Plastic)

Onset of the ability to draw a fiber (melt strength)

Below the entanglement molecular weight we have an oligomer
above we have a polymer or a plastic material

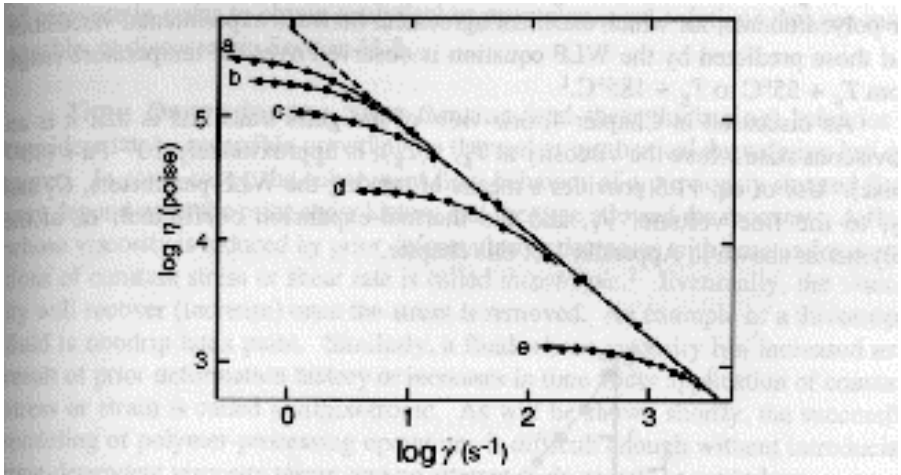


Figure 11.14. Effect of increasing molecular weight on the dependence of polymer viscosity on $\dot{\gamma}$ for polystyrene (M_c = 31,200) at 183°C. Molecular weights are (a) 242,000; (b) 217,000; (c) 179,000; (d) 117,000; and (e) 48,500. [Adapted from R. A. Stratton, *J. Colloid Interface Sci.*, **22**, 517 (1966), with permission of the publisher.]

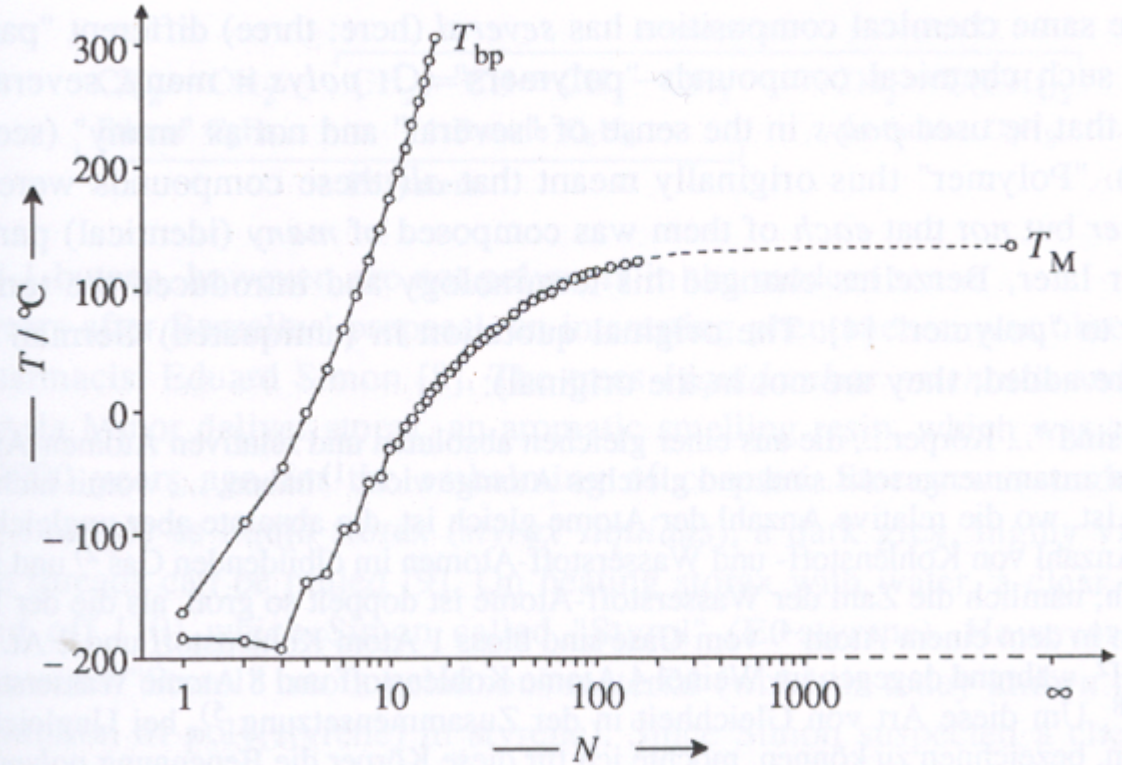
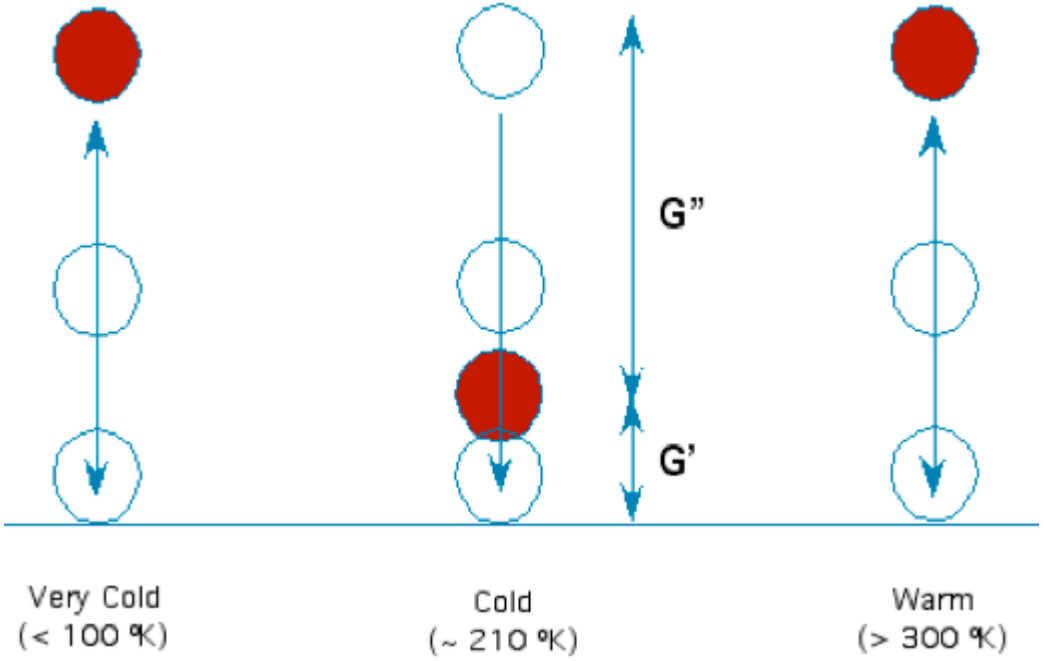
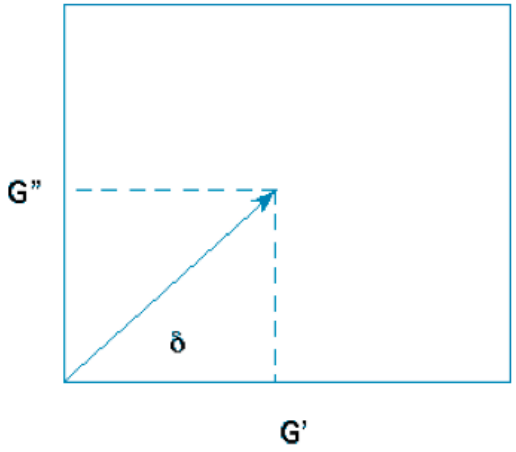


Fig. 1-1 Dependence of melting temperatures, T_M, and boiling temperatures, T_{bp}, of alkanes and poly(methylene)s, $H(CH_2)_NH$, on the number N of methylene groups per molecule [1, 2].

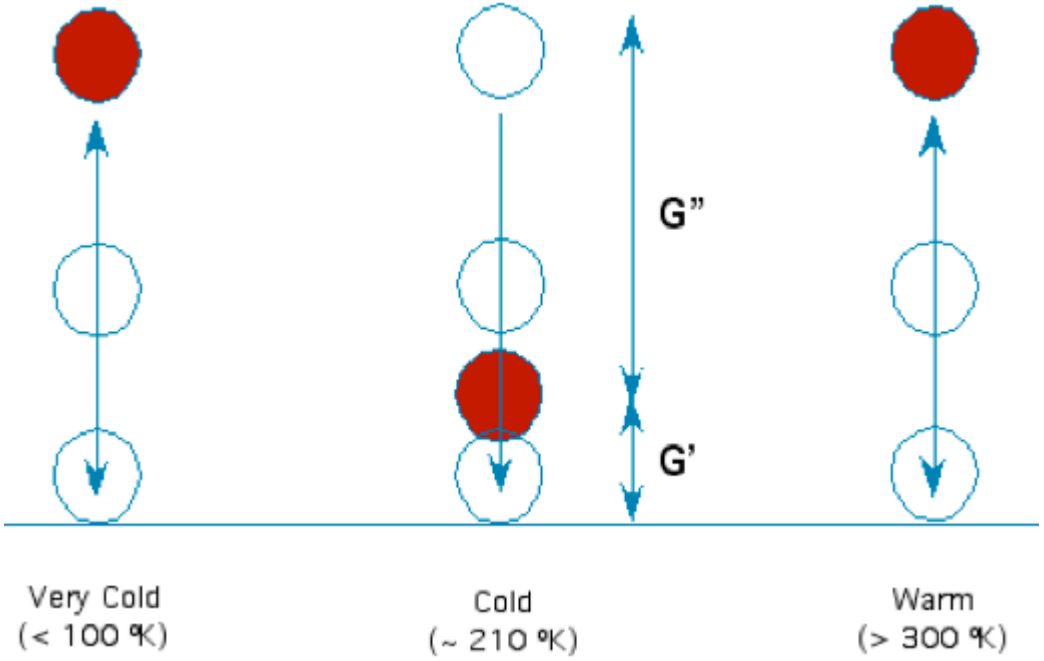
From Hans-Georg Elias, *Macromolecules* 2005 ([2] = B. Wunderlich *Macromolecular Physics* vol. 3 1980)

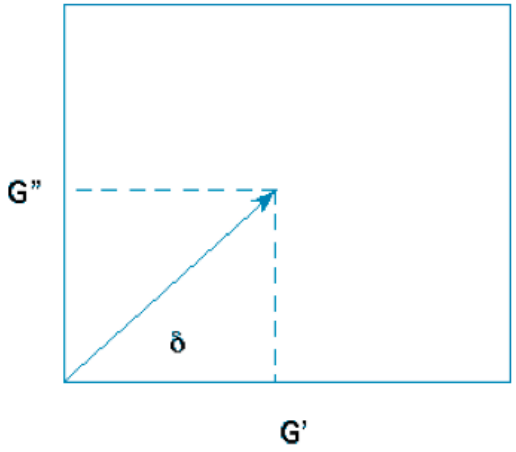
Viscoelasticity





Viscoelasticity

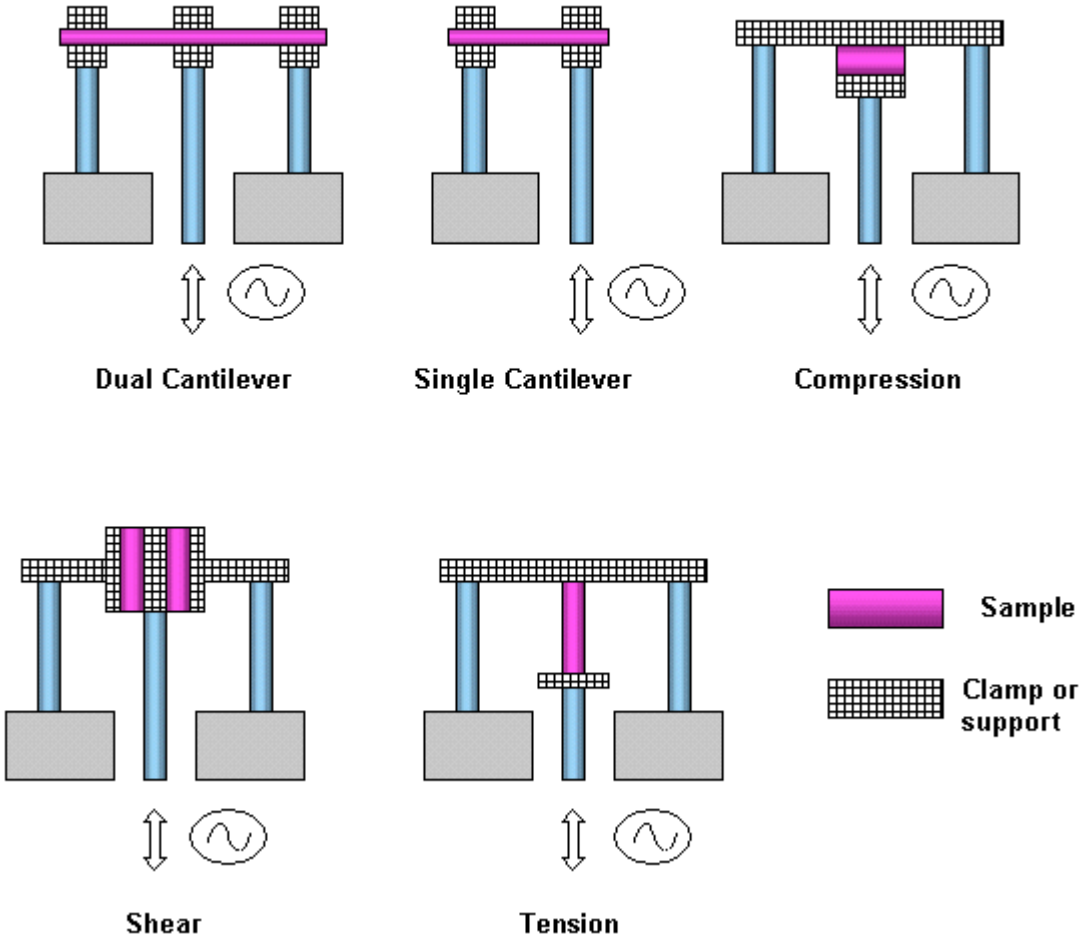


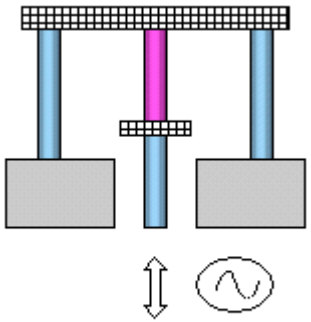


δ is the phase angle or phase lag
it is 0 for Hookean elastic behavior
and 90° (π/2) for Newtonian viscous behavoir
We usually talk about tan δ that varies from 0 to ∞

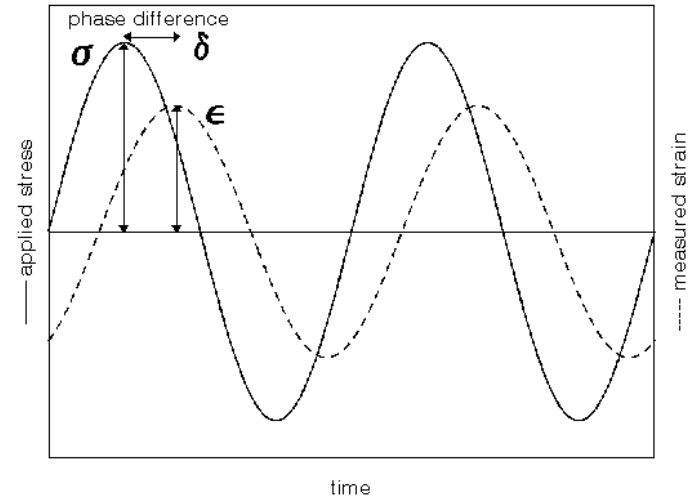
Dynamic Mechanical Testing

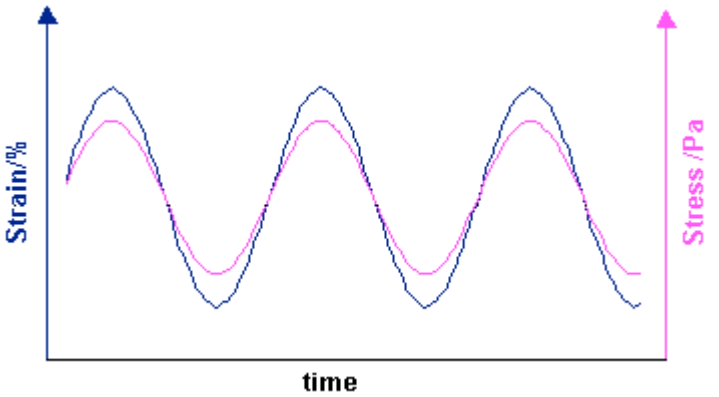
A typical instrument for performing DMA can deform the sample in a number of different w

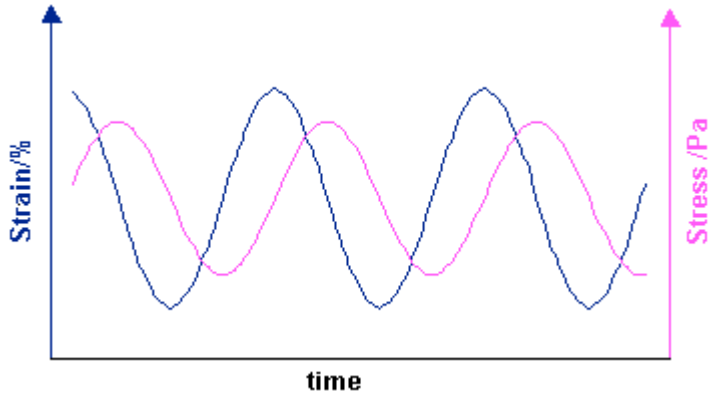


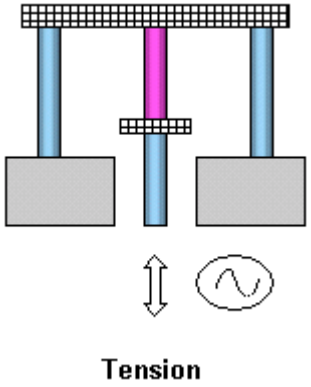


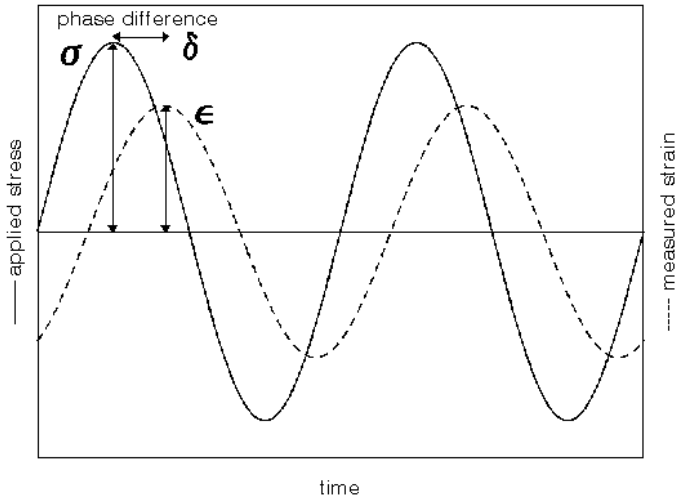
Tension

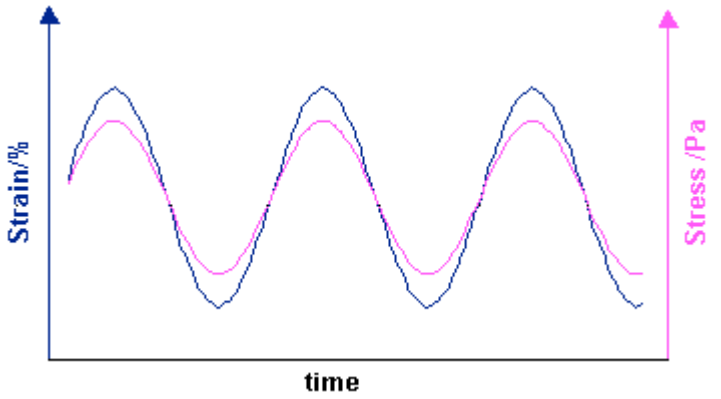

phase difference
σ
δ
ϵ
—— applied stress
---- measured strain
time


Strain/%
Stress /Pa
time

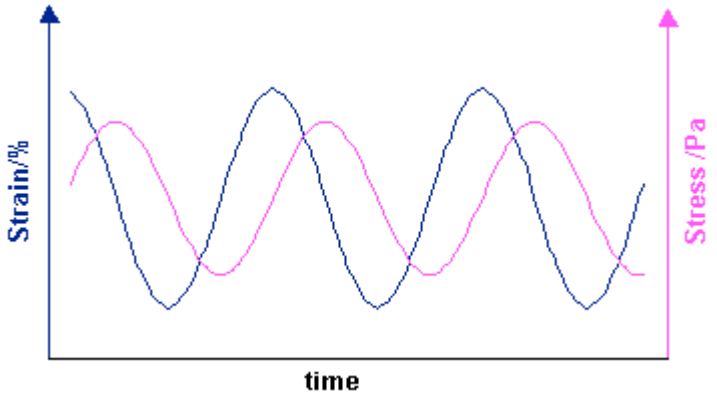

Strain/%
Stress /Pa
time



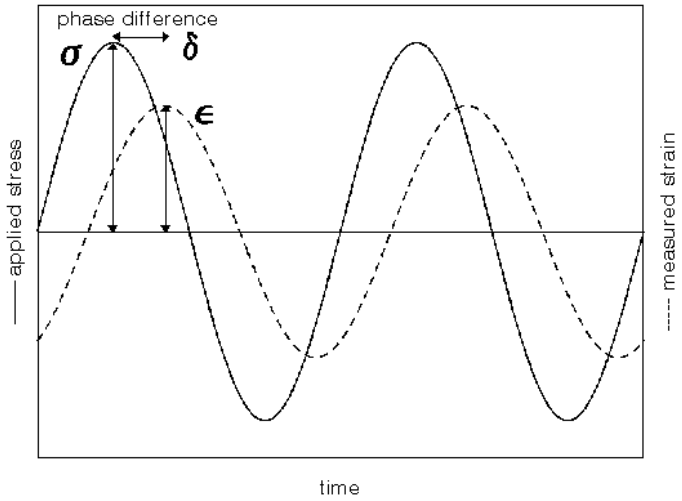


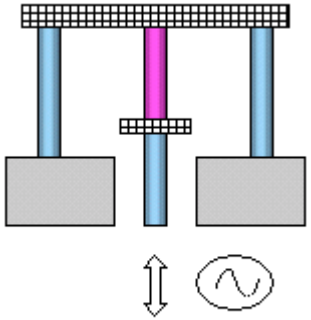


Hookean Elastic

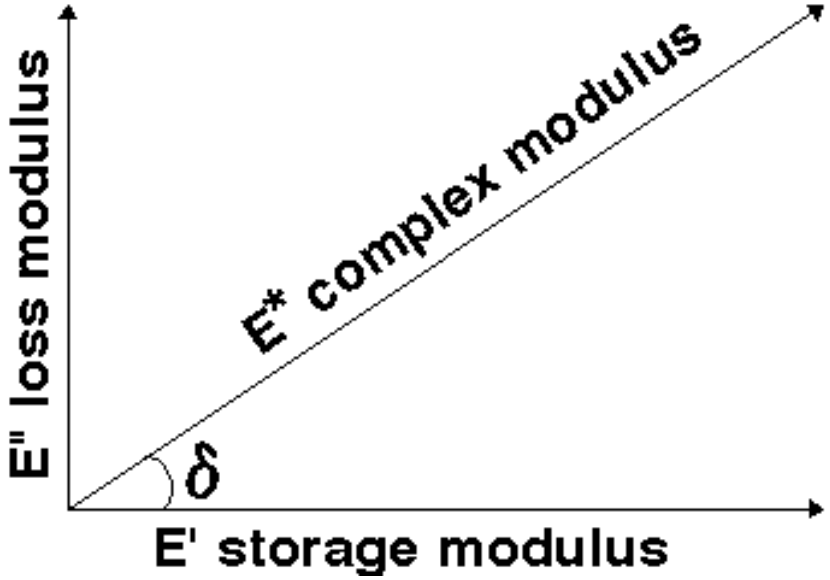


Viscoelastic





Tension

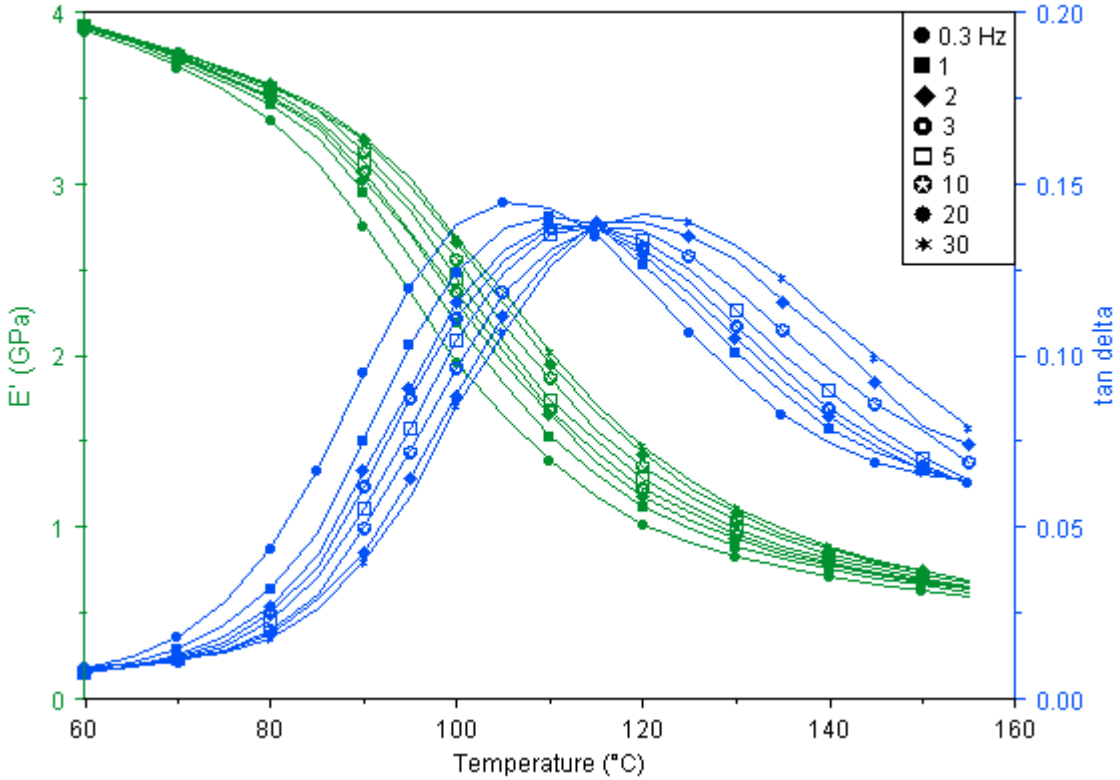


$$E^* = \frac{\epsilon_{max}}{\sigma_{max}}$$

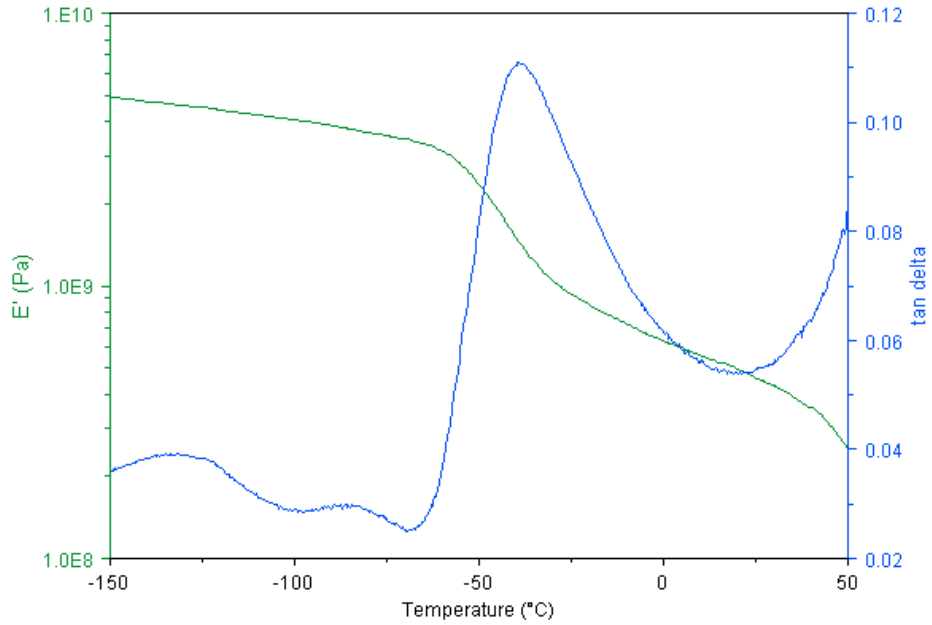
$$E' = E^* \cos\delta$$

$$E'' = E^* \sin\delta$$

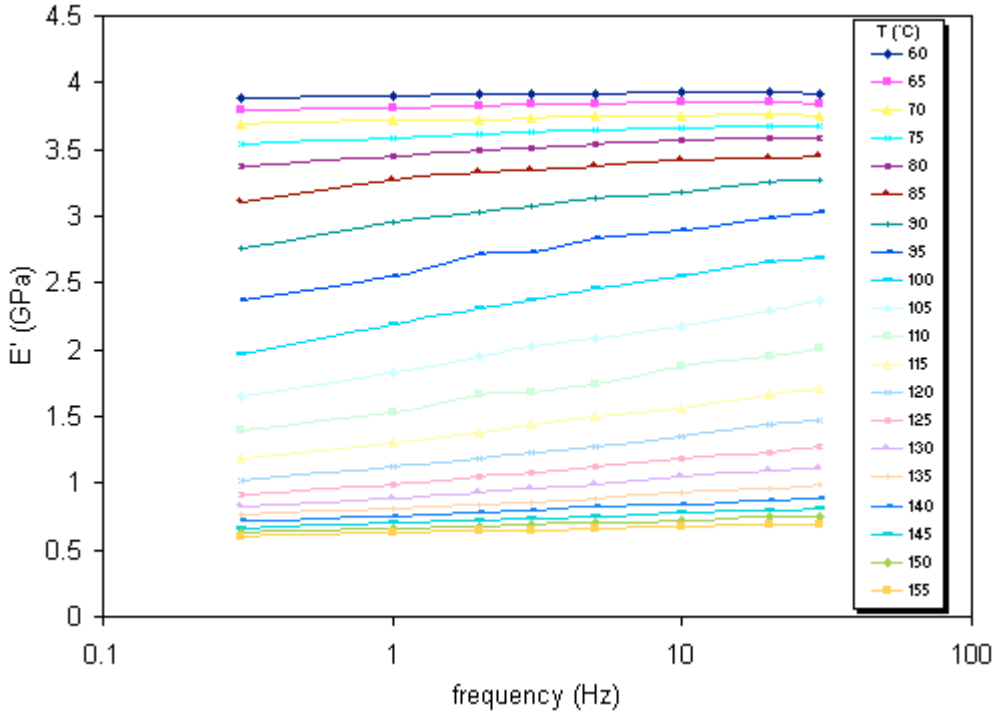
$$\tan\delta = \frac{E''}{E'}$$



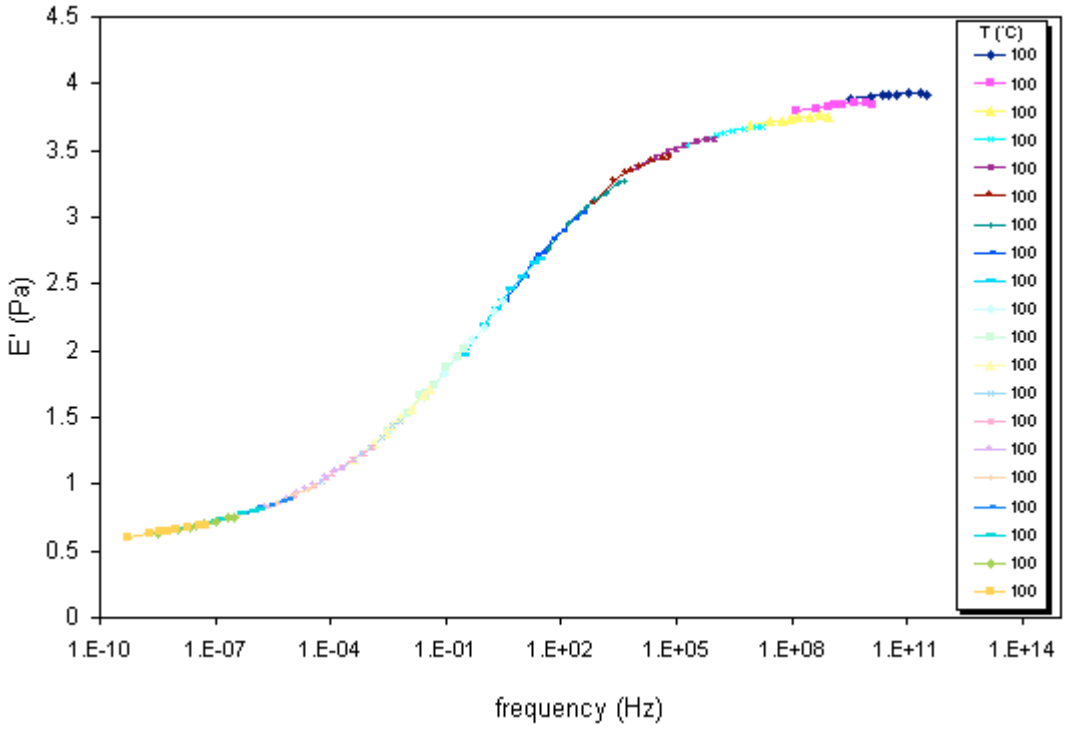
Measure at different frequencies



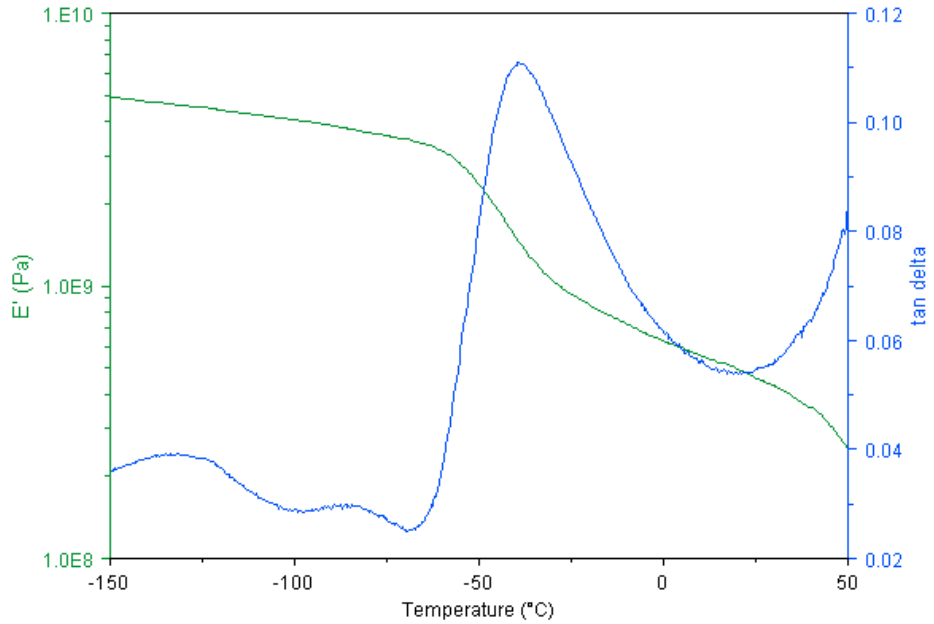
Combine to make a master curve
(Semi-Crystalline Polymer is Shown)



Can also combine frequencies for different temperatures

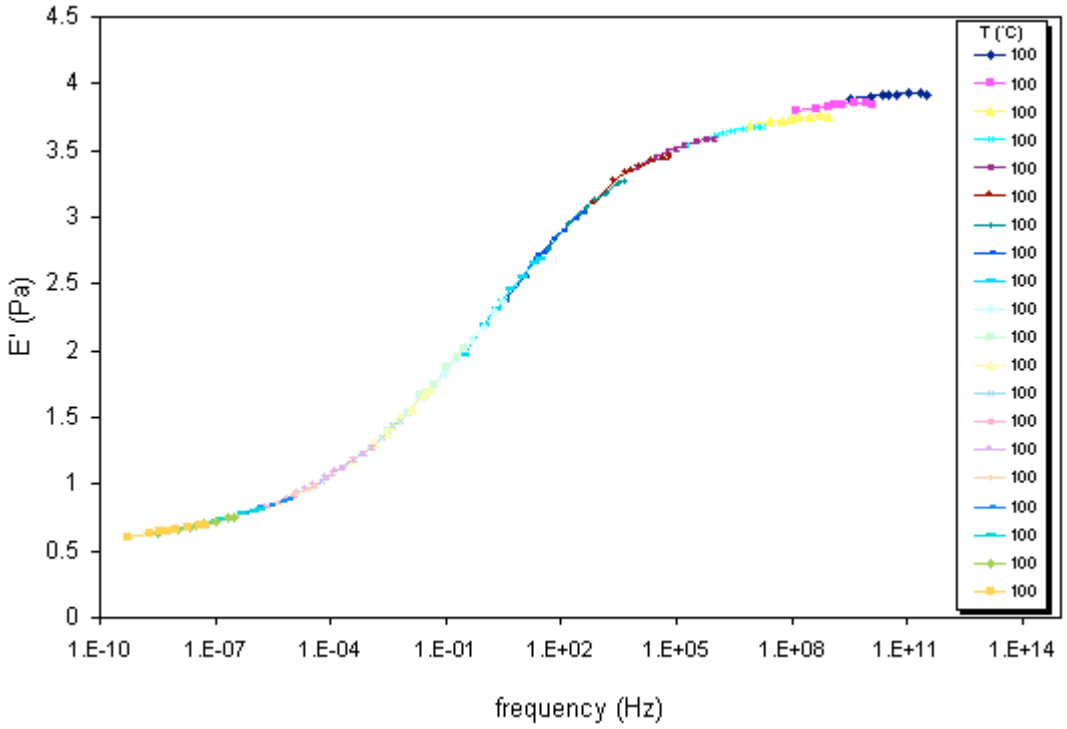


To yield a master curve in frequency

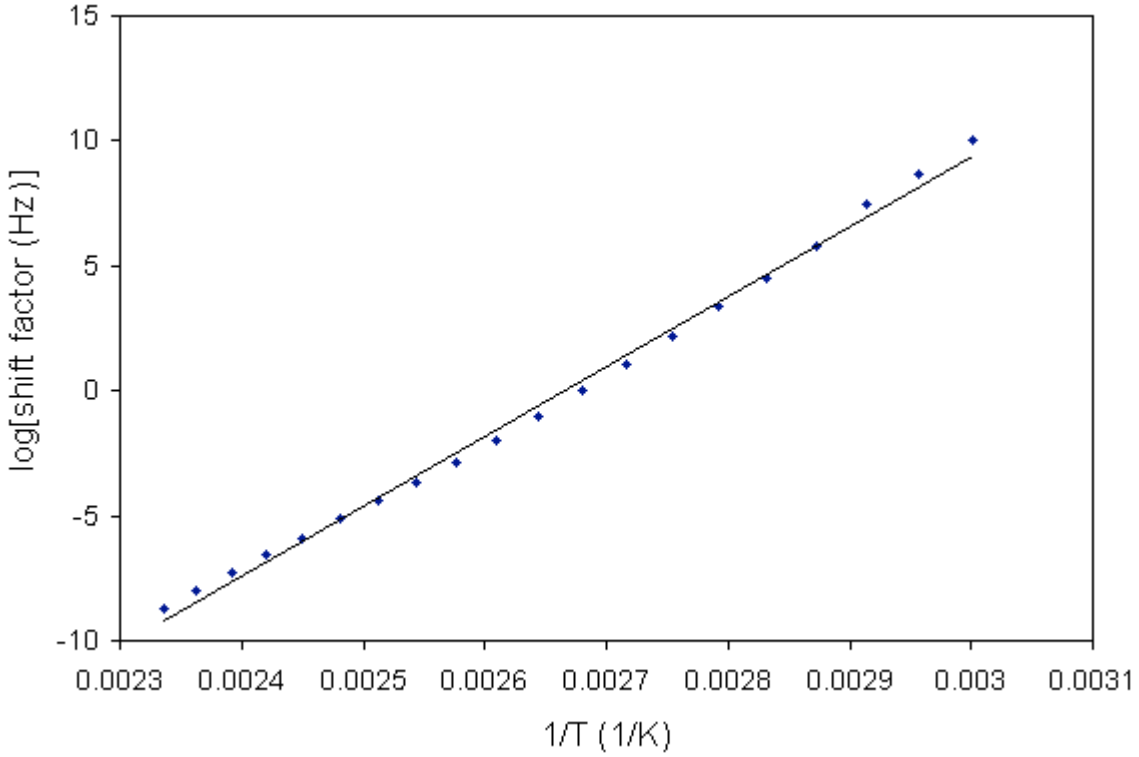


Time-Temperature Superposition

Temperature and Frequency
Plots are directly related
High Frequency => Low Temperature
Low Frequency => High Temperature



Williams-Landel-Ferry Shift Factor, a_T



$$\log[a_T] = C_1(T-T_{ref})/(C_2 + T - T_{ref})$$

What is T dependence of shift factor?

Define: $a_T = t(T)/t_r(T_r)$ where t and t_r can be thought of as relaxation times

$\log a_T = \log t(T) - t_r(T_r)$ such that $\log a_T$? as T?

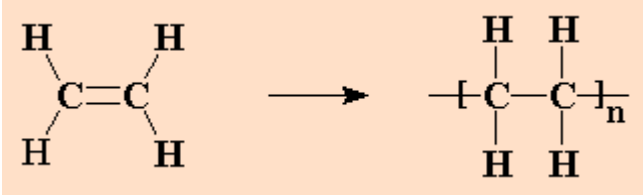
Synthesis of Polymers

Polymers are generally produced by organic reactions similar to the organic chemistry you have studied except that the synthesis either involves a **Chain Reaction** generally with 3 stages

Initiation: You start the chain reaction

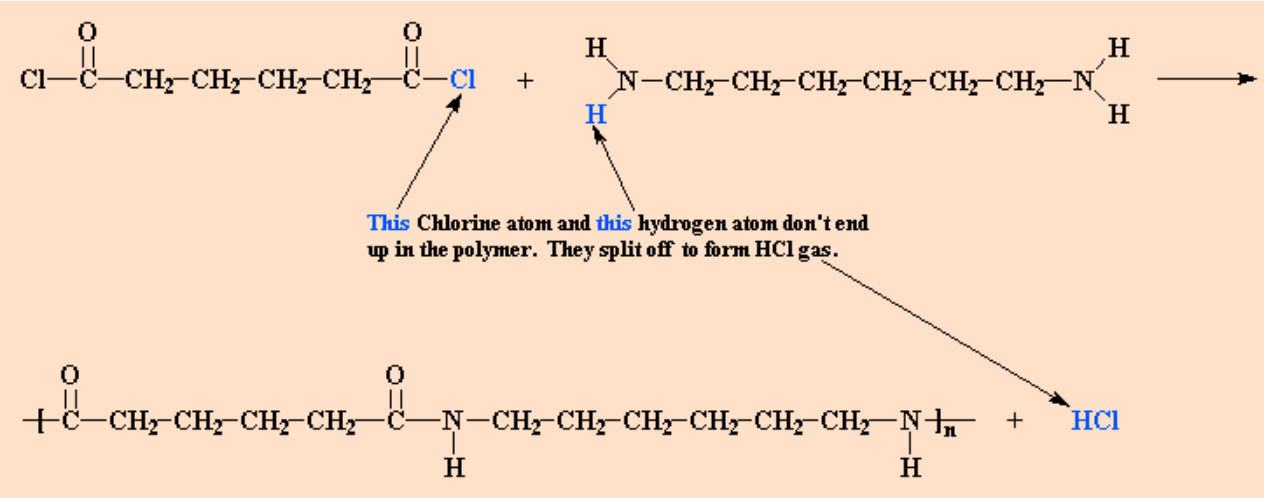
Propagation: You conduct the chain reaction

Termination: You end the chain reaction

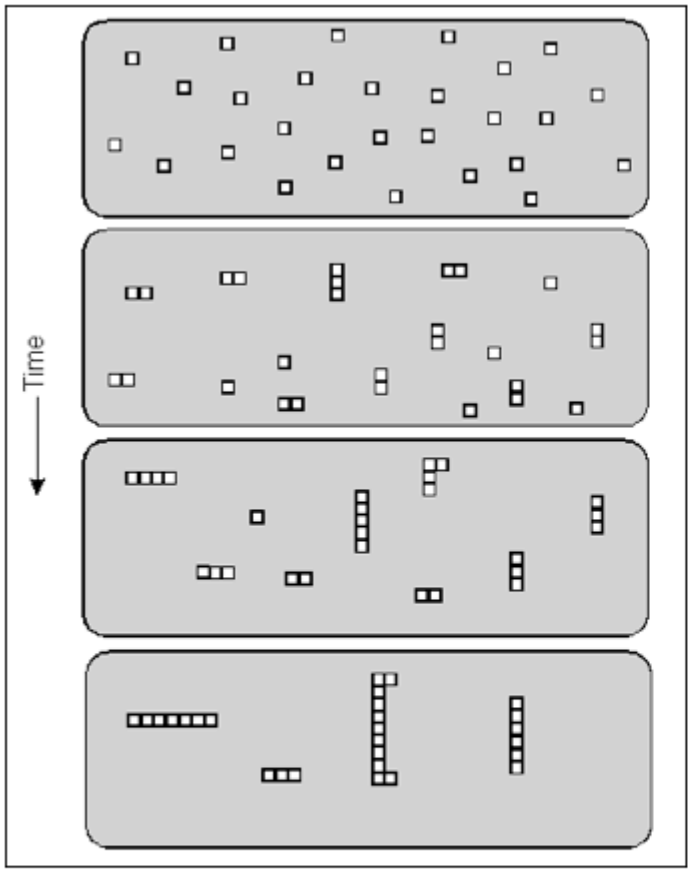


Or it involves a **Step-Growth Reaction** where a simple reaction occurs at two (or more) ends of a growing chain molecule. This type of reaction involves di-functional (or higher functional) reactants. The reaction proceeds until you run out of reactants or the system becomes too viscous for transport of reacting species to the reacting chain ends.

Condensation Reaction to Make Nylon

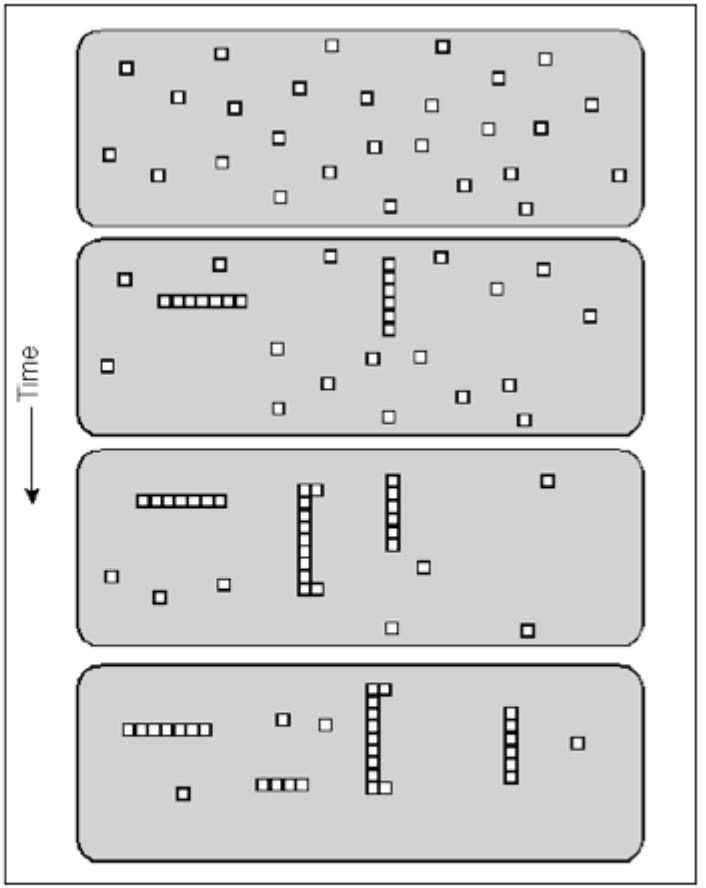


Step Polymerization



- Any two molecular species can react.
- Monomer disappears early.
- Polymer MW rises throughout.
- Growth of chains is usually slow (minutes to days).
- Long reaction times increase MW, but yield of polymer hardly changes.
- All molecular species are present throughout.
- Usually (but not always) polymer repeat unit has fewer atoms than had the monomer.

Chain Polymerization



- Growth occurs *only* by addition of monomer to active chain end.
- Monomer is present throughout, but its concentration decreases.
- Polymer begins to form immediately.
- Chain growth is usually very rapid (second to microseconds).
- MW and yield depend on mechanism details.
- Only monomer and polymer are present during reaction.
- Usually (but not always) polymer repeat unit has the same atoms as had the monomer

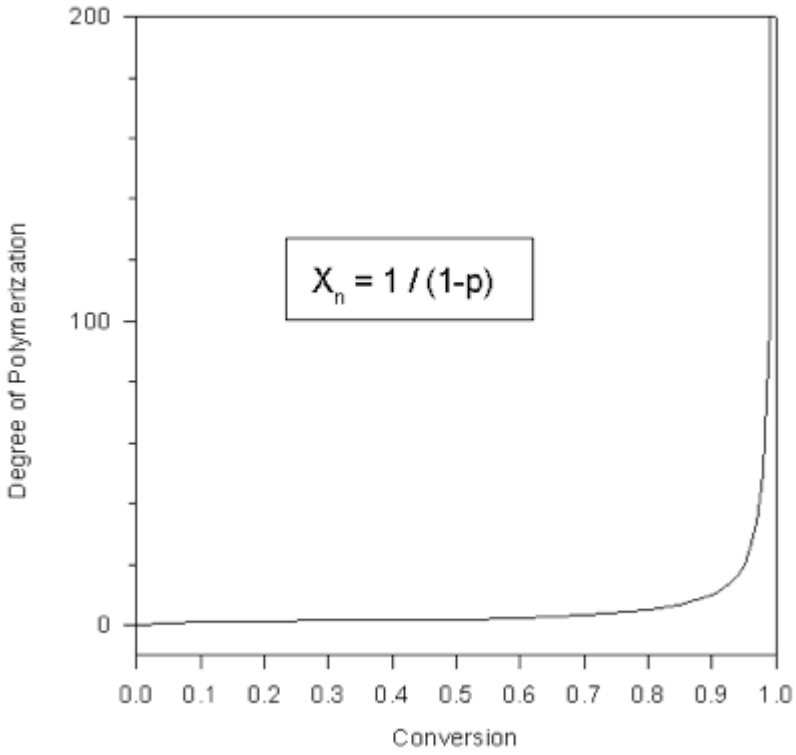
Carothers' Equations
For Step Growth Polymerization

$$\bar{x}_n = \frac{1}{(1-p)} \qquad \bar{M}_n = \frac{M_0}{(1-p)}$$

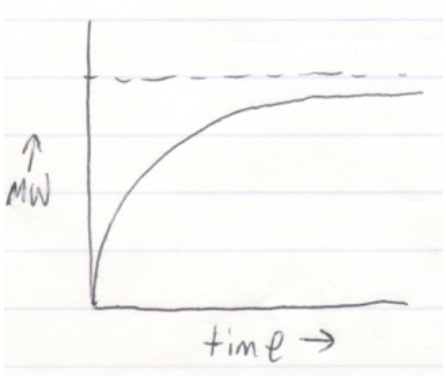
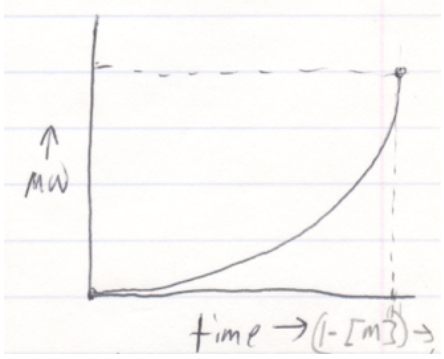
$$\bar{x}_w = \frac{(1+p)}{(1-p)} \qquad \bar{M}_w = \frac{M_0(1+p)}{(1-p)}$$

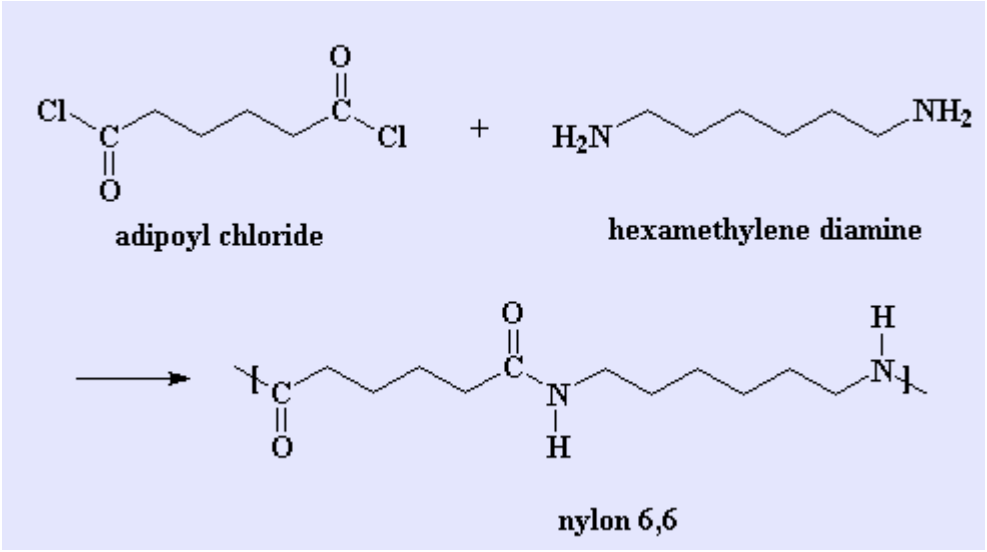
p = extent of reaction

M_0 = MW of monomer



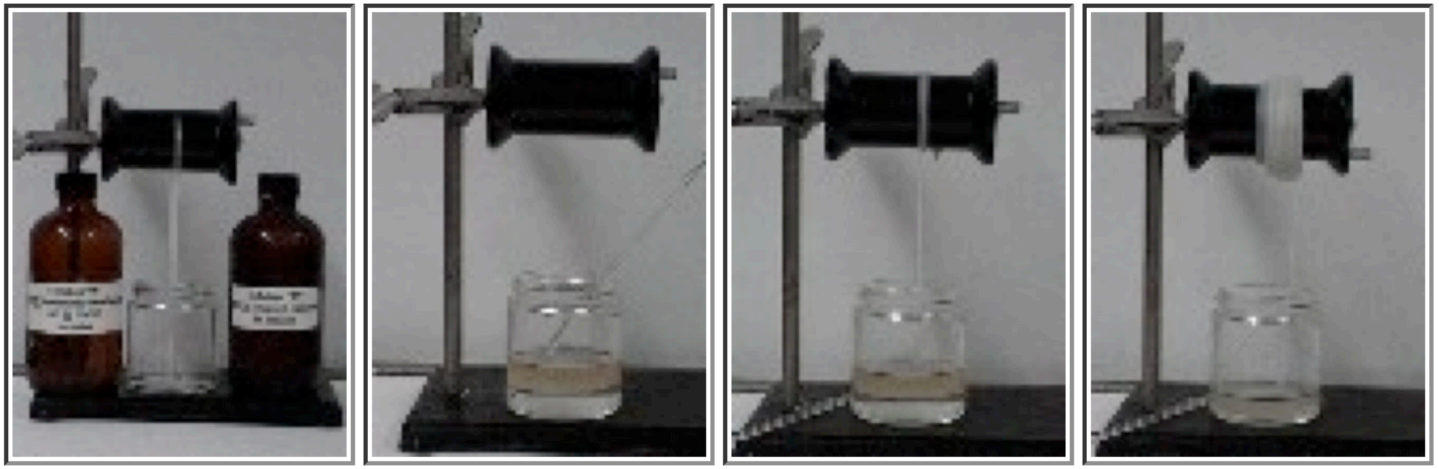
Chain Vs. Step Growth Polymerization

	Chain Growth	Step Growth
A. Mechanism	Distinct and Different -Initiation Step -Propagation Steps -Termination Step(s)	Distinct and Different Initiation, Propagation and termination are all the same step "Termination" is the last reaction that takes place
B. Monomer Concentration	Monomer is present throughout the reaction, even at the end	-Early in the reaction the monomer is depleted -Many dimers and trimers are produced early in the reaction. The monomer is consumed at early stages of the reaction
C. Polymer Molecular Weight		 Reaction must be driven to 99.9% complete to get a polymer



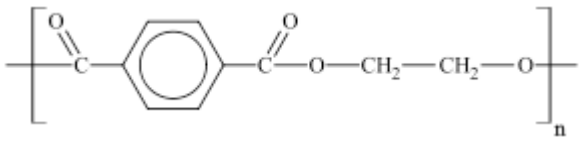
Solution "A" (0.5 M hexamethylenediamine ($H_2N(CH_2)_6NH_2$, also called 1,6-diaminohexane) and 0.5 M sodium hydroxide in water),
Solution "B" (0.2 M sebacoyl chloride ($ClOC(CH_2)_8COCl$) in hexane).

Nyon 6,10 by interfacial polymerization



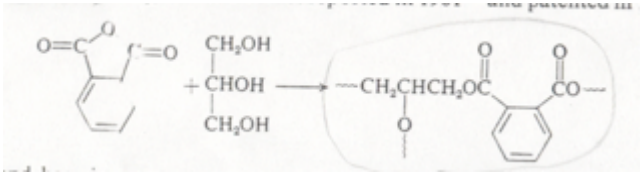
Polyesters

Poly ethylene terephthalate (PET or PETE)



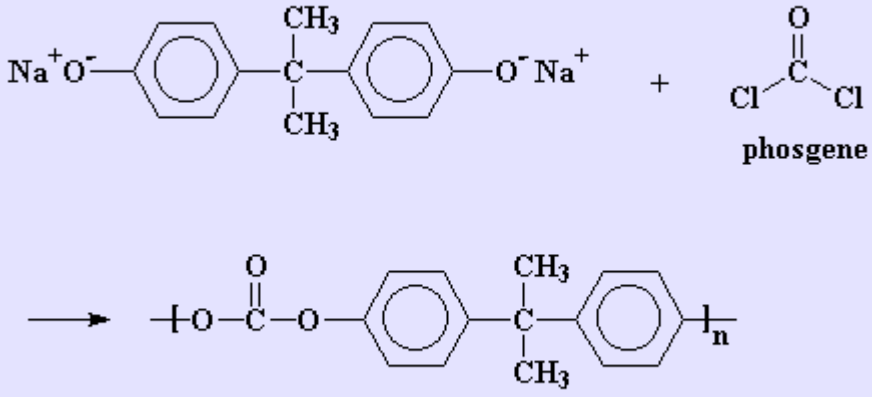
Terephthalic Acid and Ethylene glycol

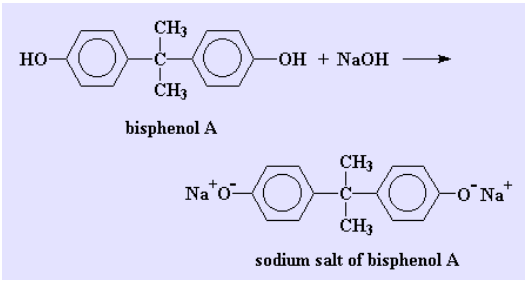
Glyptal Synthesis



Pthalic Anhydride
Glycerol (or Ethylene glycol)

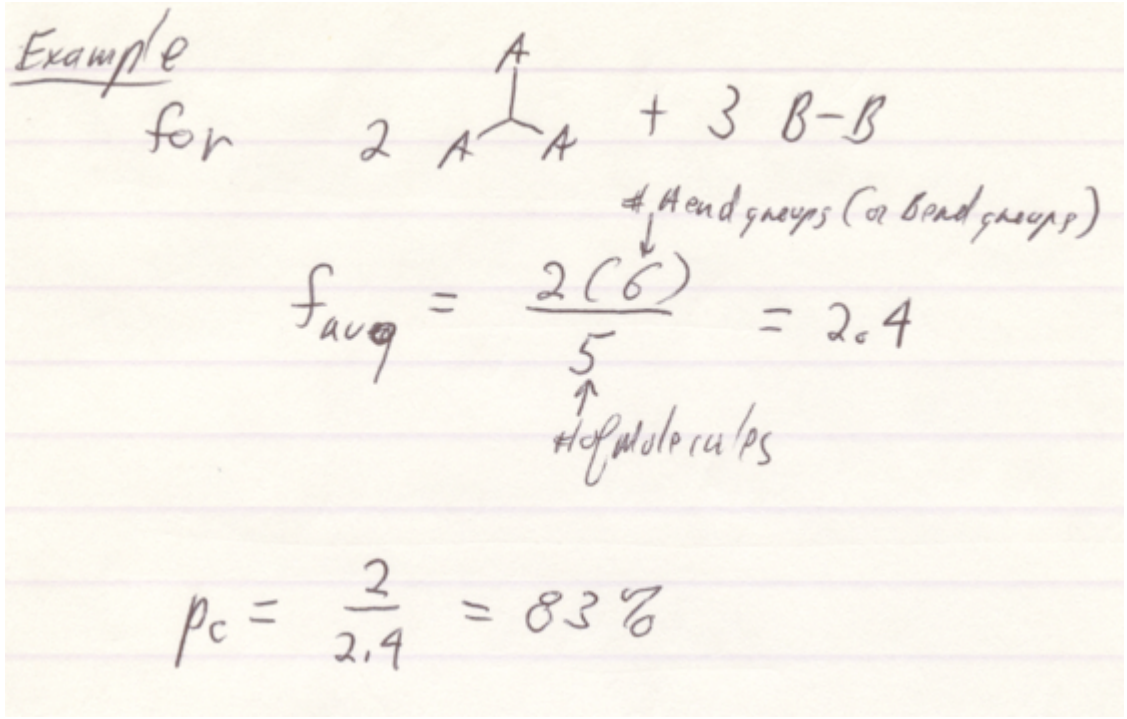
Polycarbonate (CD's)
bisphenol-A and phosgene

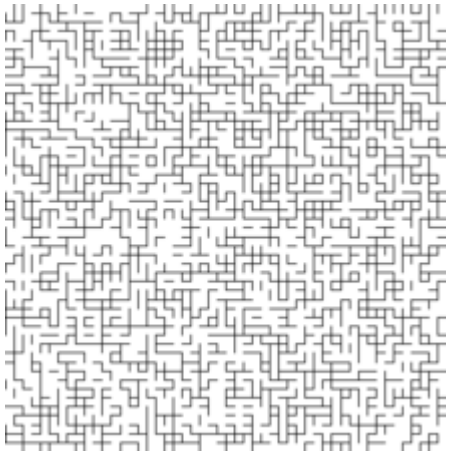




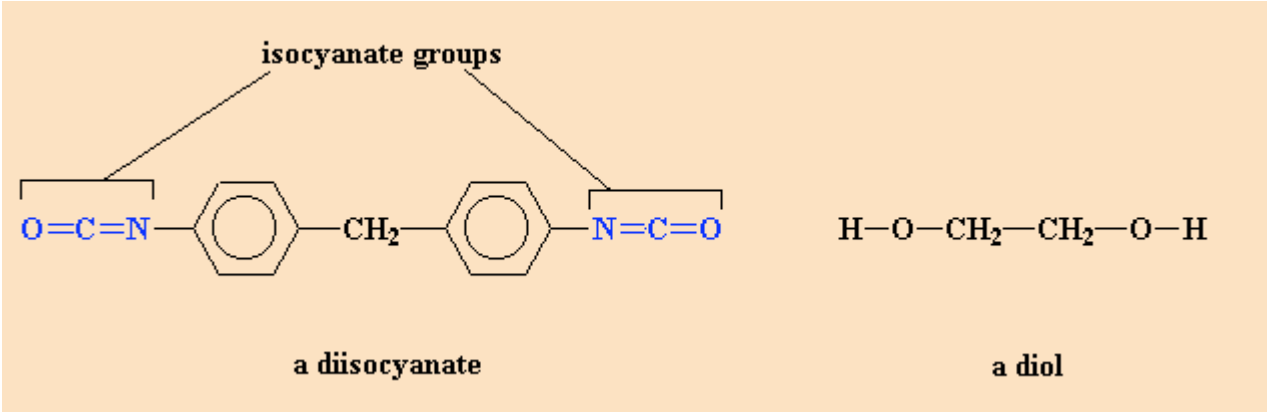
Gellation/Percolation

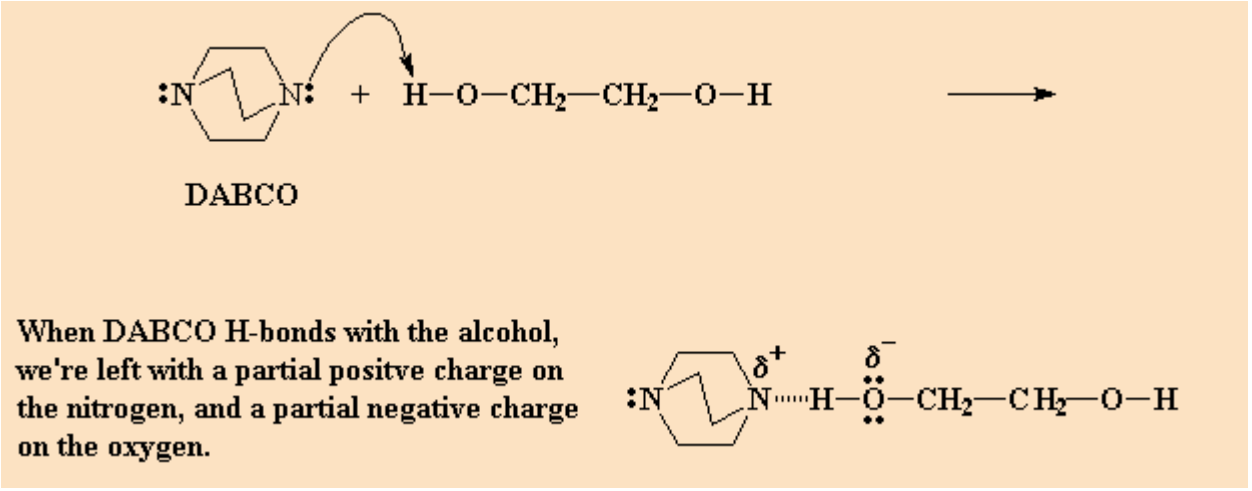
Carother's Method: Percolation occurs when $p=2/f_{avg}$



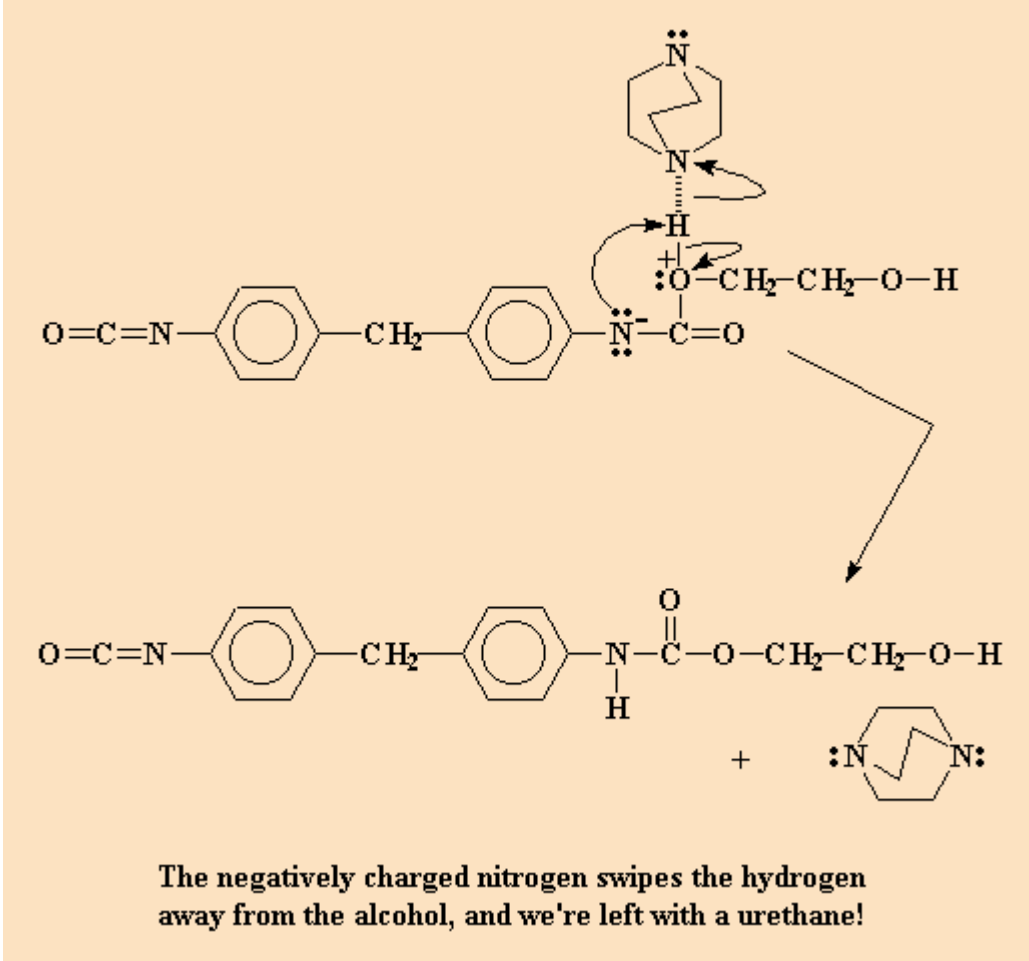


Polyurethane

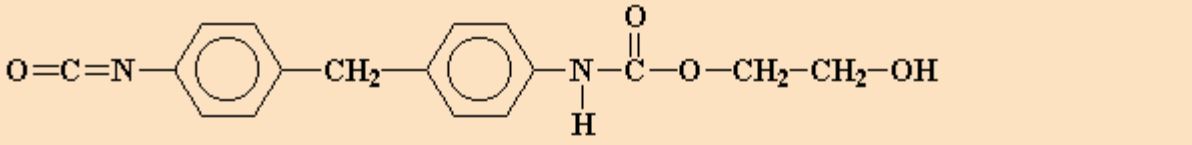




Polyurethane



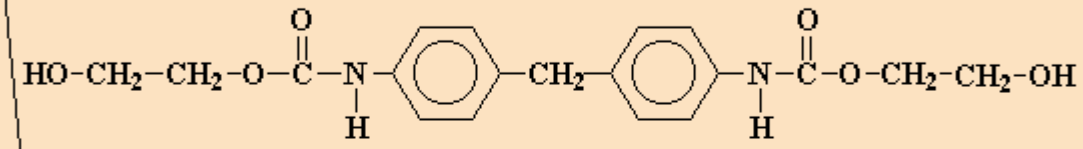
Polyurethane



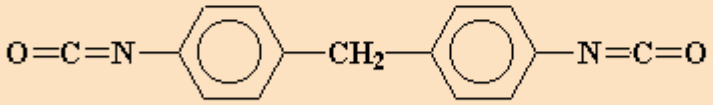
urethane dimer

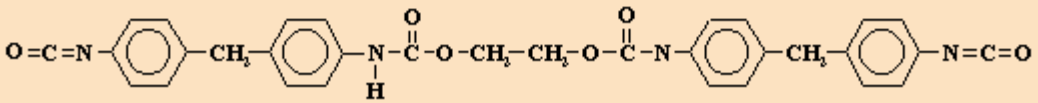
The urethane dimer can react with either a diol or a diisocyanate to form a trimer. It can even react with other dimers, trimers and higher oligomers.

HO–CH$_2$–CH$_2$–OH



a urethane trimer



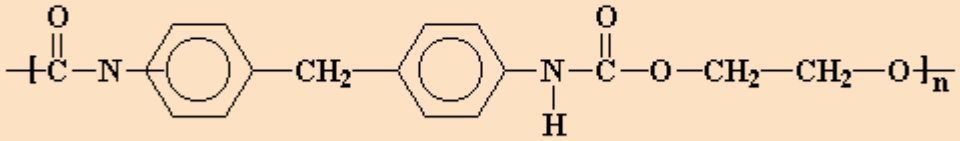


another urethane trimer

A step-reaction but **not** a condensation reaction.

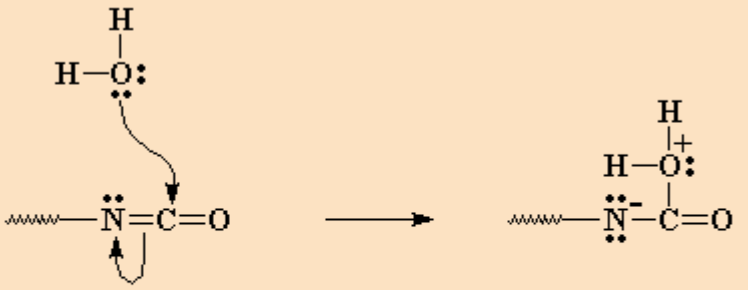
There is no byproduct so this is a useful reaction for coatings and other systems where you do not want droplets of condensate.

Eventually these oligomers will merge and merge until we get high molecular weight polymer.

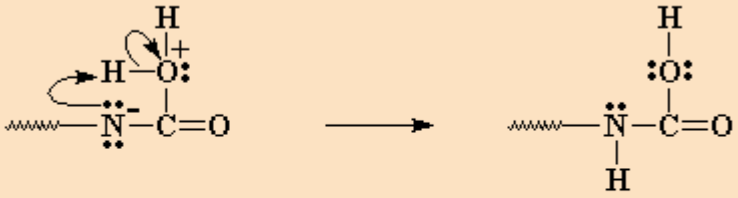


Finally, polyurethane

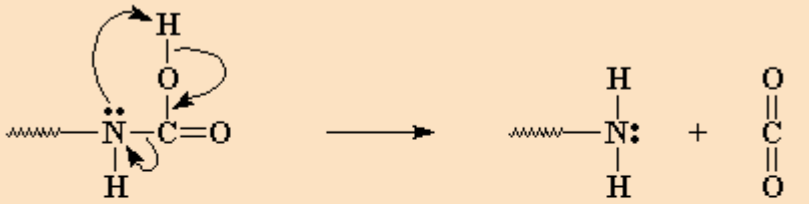
Polyurethane Foam



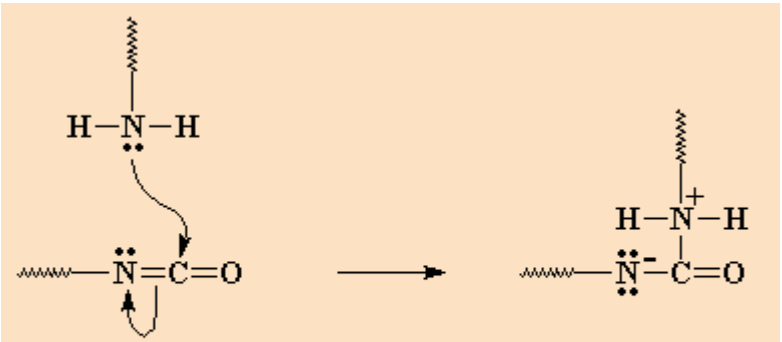
Step 1: A water molecule attacks the isocyanate carbon, giving us an ionic species.



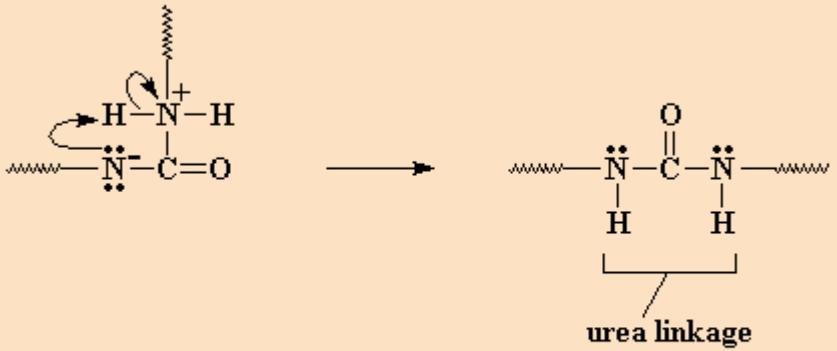
Step 2: The isocyanate nitrogen swipes a hydrogen from the water.



Step 3: The nitrogen swipes *another* hydrogen, making an amine and carbon dioxide.

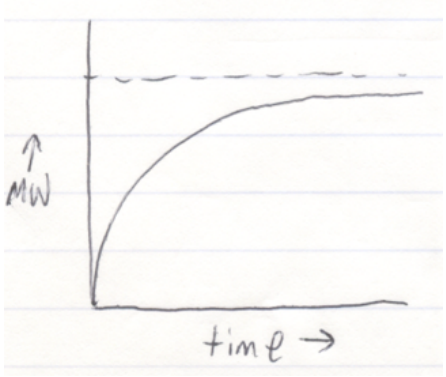
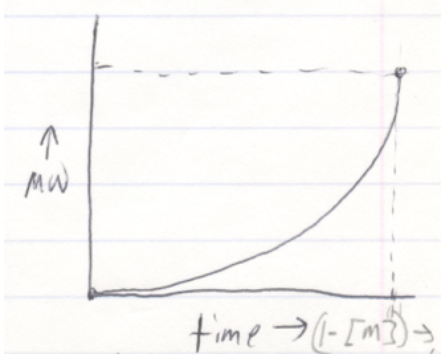


Step 4: The new amine attacks another isocyanate, just like the water attacked the old isocyanate.

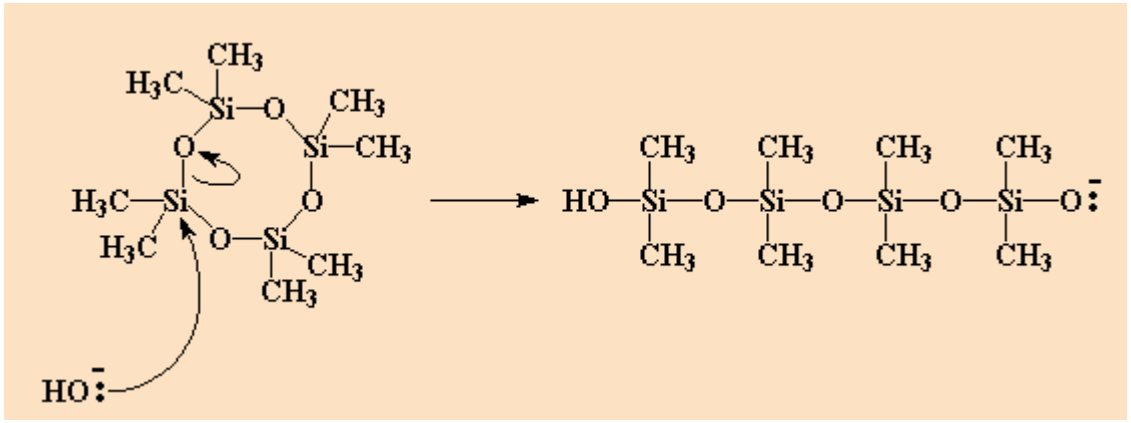


Step 5: The nitrogen swipes a hydrogen from the amine, creating a urea linkage in the polymer.

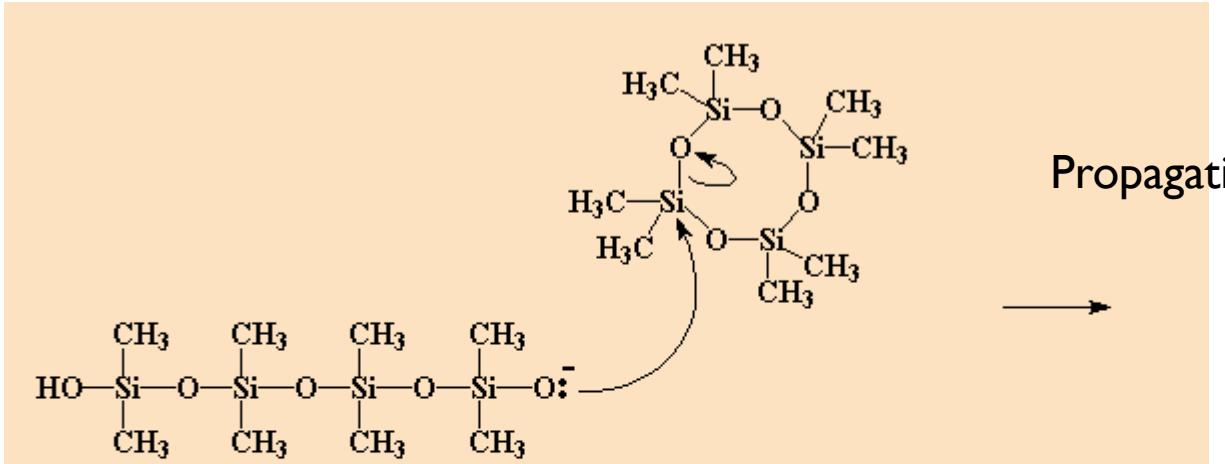
Chain Vs. Step Growth Polymerization

	Chain Growth	Step Growth
A. Mechanism	Distinct and Different -Initiation Step -Propagation Steps -Termination Step(s)	Distinct and Different Initiation, Propagation and termination are all the same step "Termination" is the last reaction that takes place
B. Monomer Concentration	Monomer is present throughout the reaction, even at the end	-Early in the reaction the monomer is depleted -Many dimers and trimers are produced early in the reaction. The monomer is consumed at early stages of the reaction
C. Polymer Molecular Weight		 Reaction must be driven to 99.9% complete to get a polymer

Chain Growth of Poly dimethyl siloxane (PDMS, Silicone)

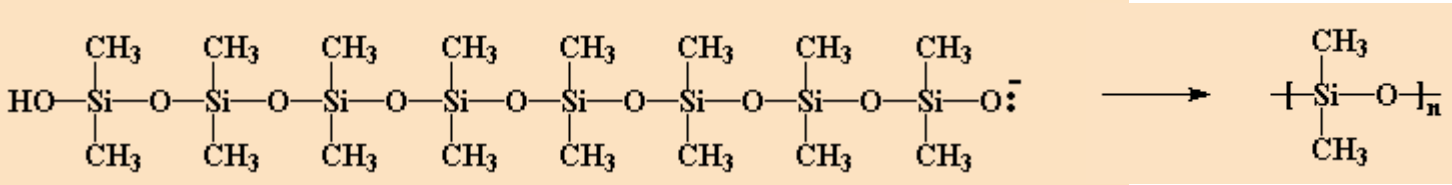


Initiation by Base

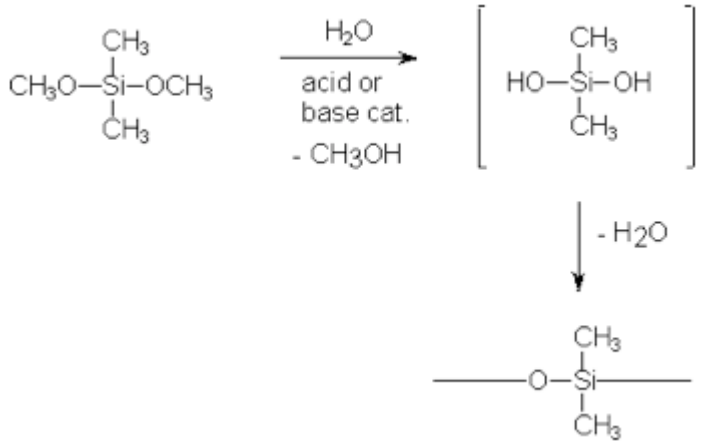


Propagation

Termination by Acid



Sol-Gel Crosslinking



TMOS

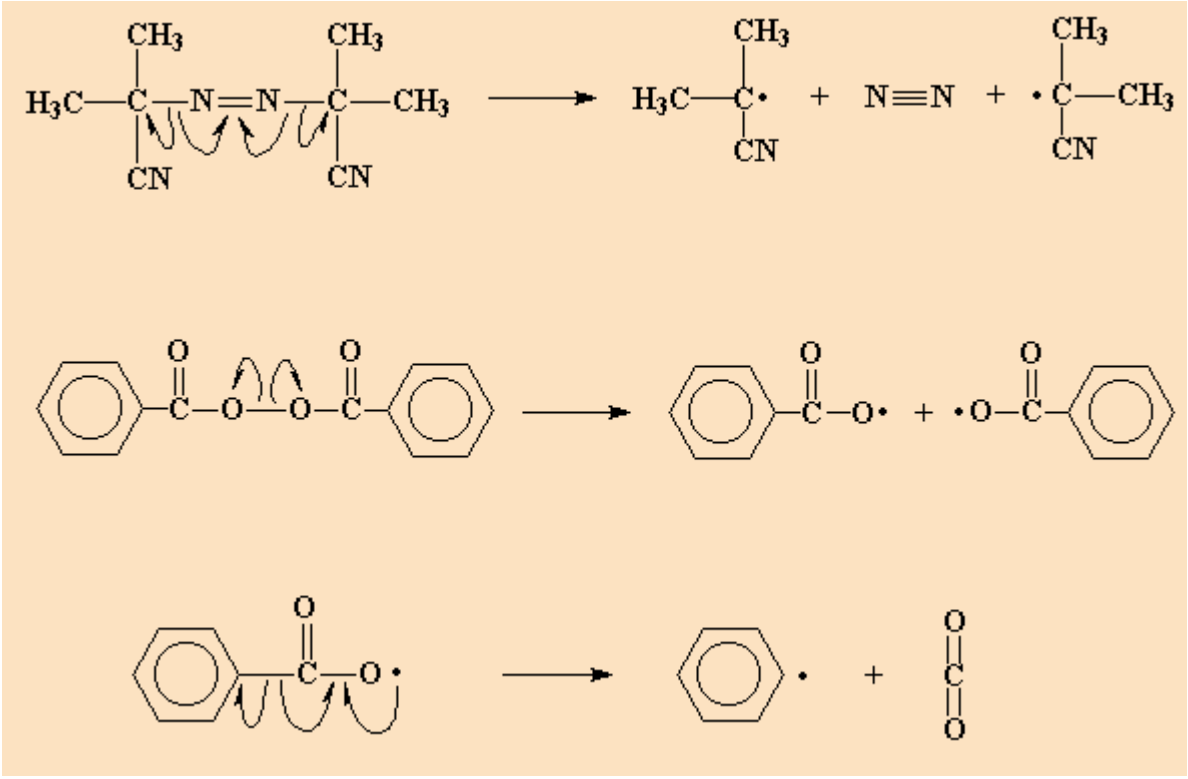
Ethoxy is TEOS

"SiO_2"

Sol-gel glass

Free Radical Chain Growth

Two Free Radical Initiators

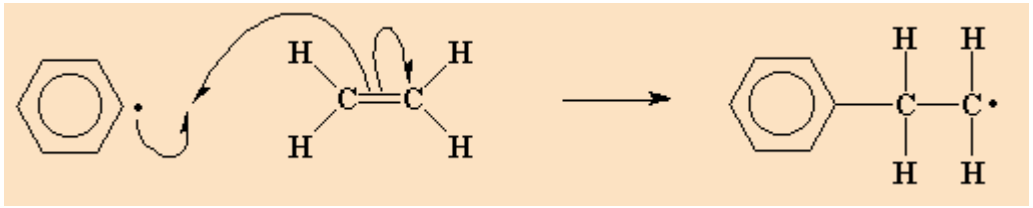


AIBN

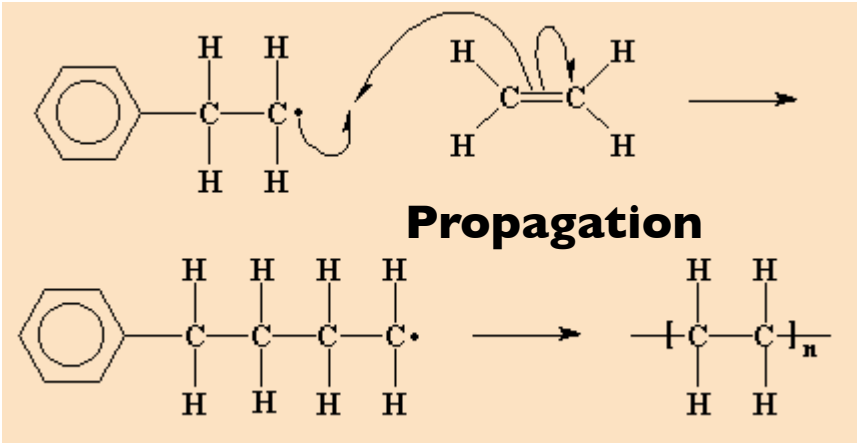
Benzoyl Peroxide

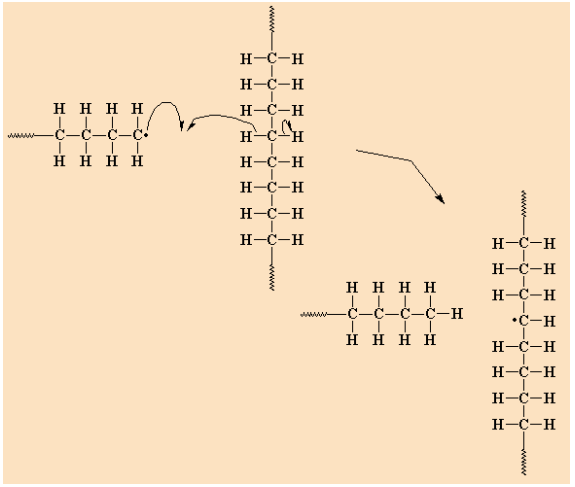
Both are dissociated by heat
AIBN is soluble in organic solvents
BP in water or organic solvents
(BP is explosive)

Initiation



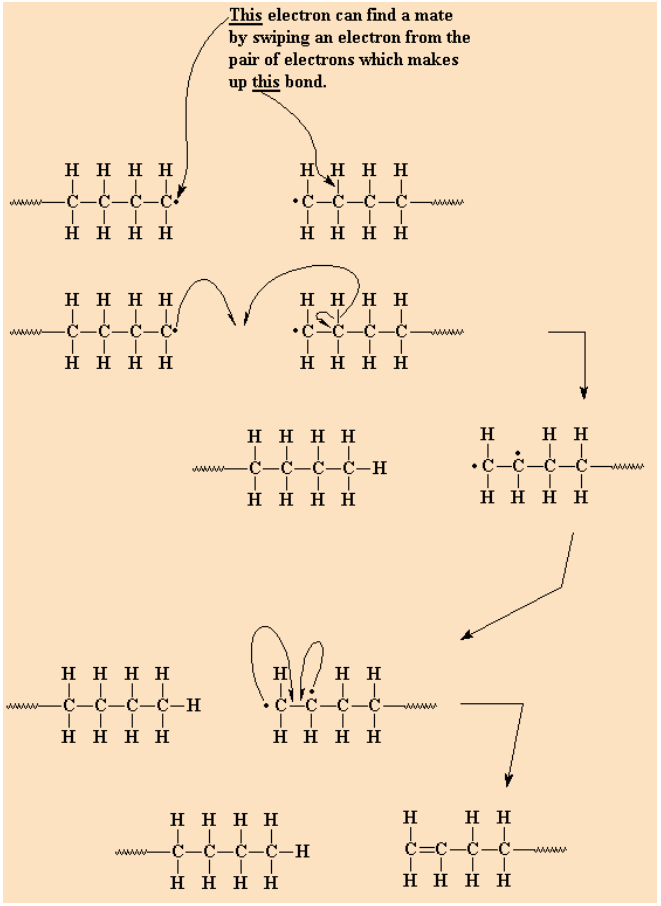
Propagation



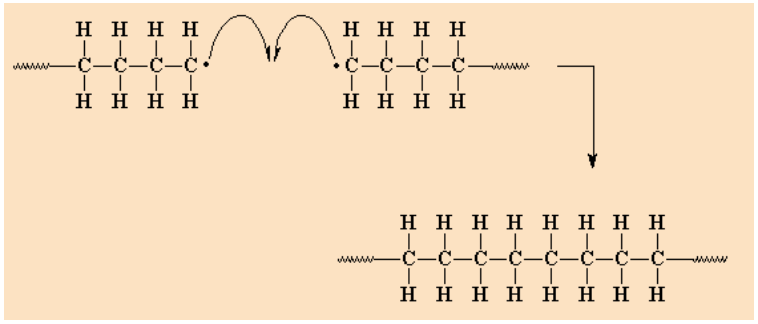


Hydrogen Abstraction

Termination

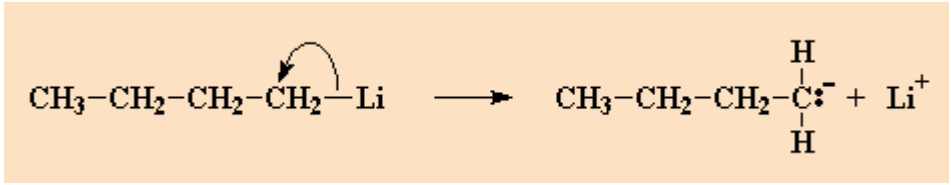


Disproportionation

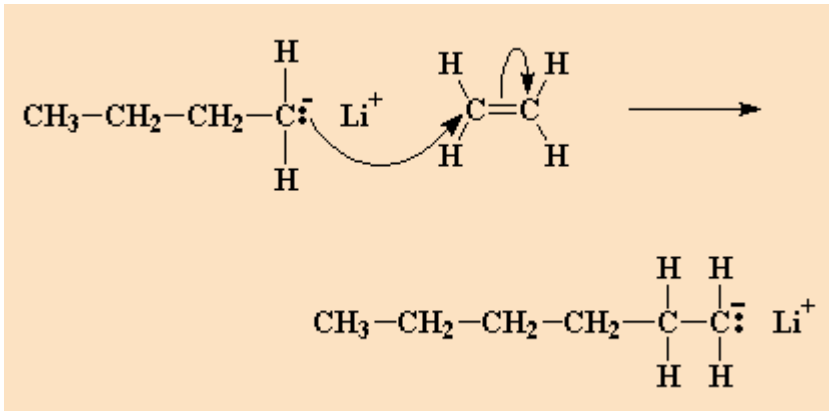


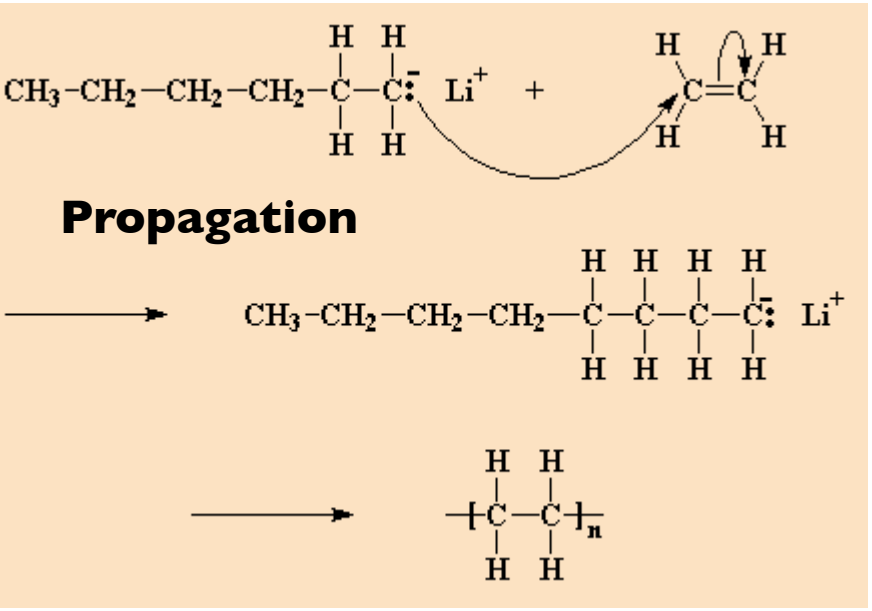
Coupling

Anionic Chain Growth

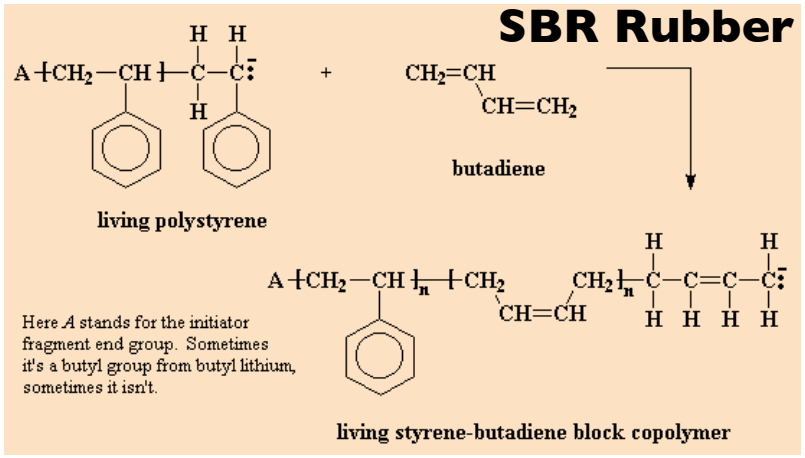


Initiation



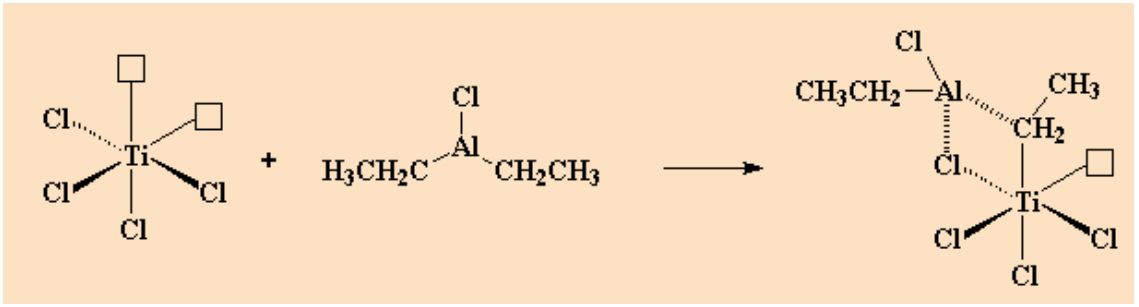


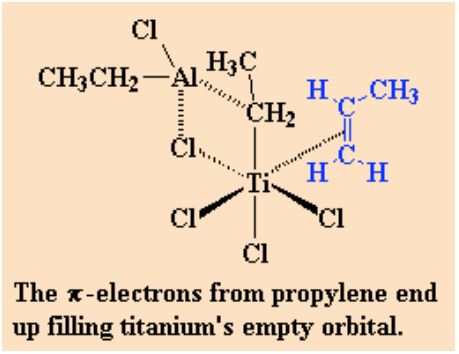
Propagation

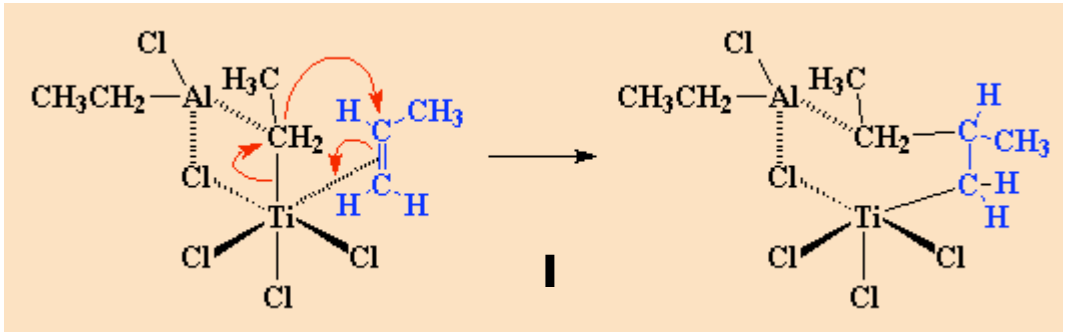


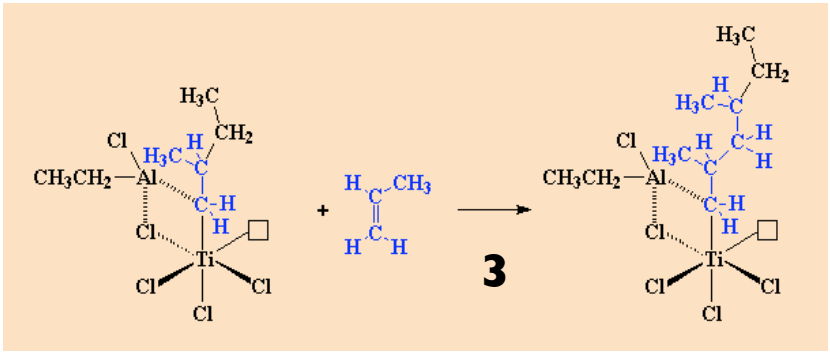
There is No Termination for Anionic

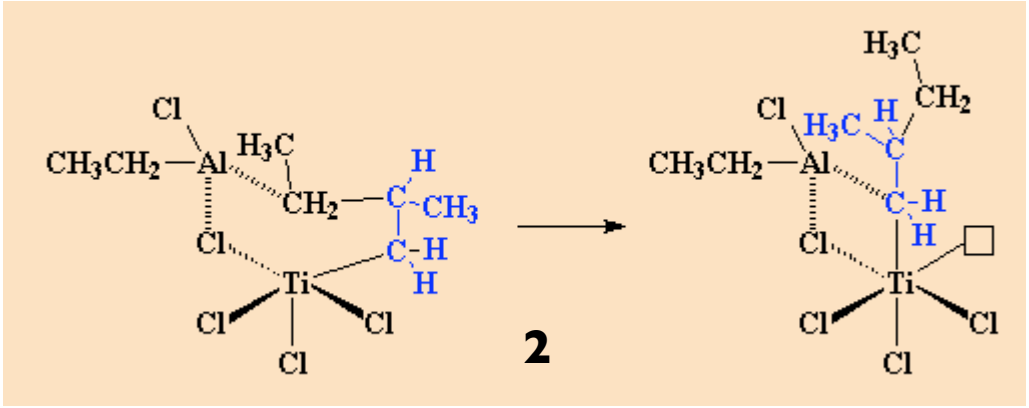
Ziegler-Natta Catalysts (Heterogeneous Catalysts)



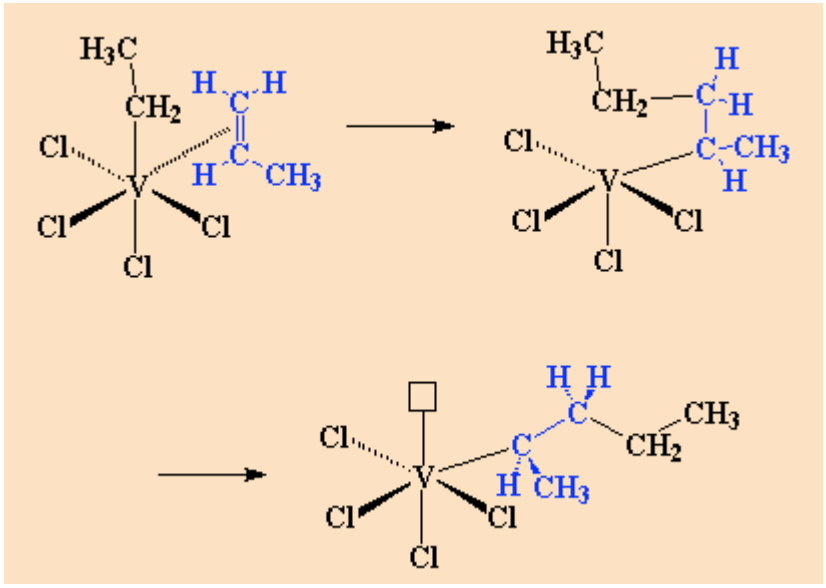


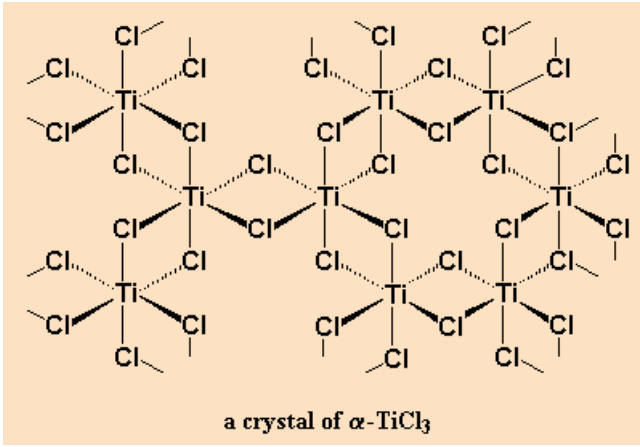


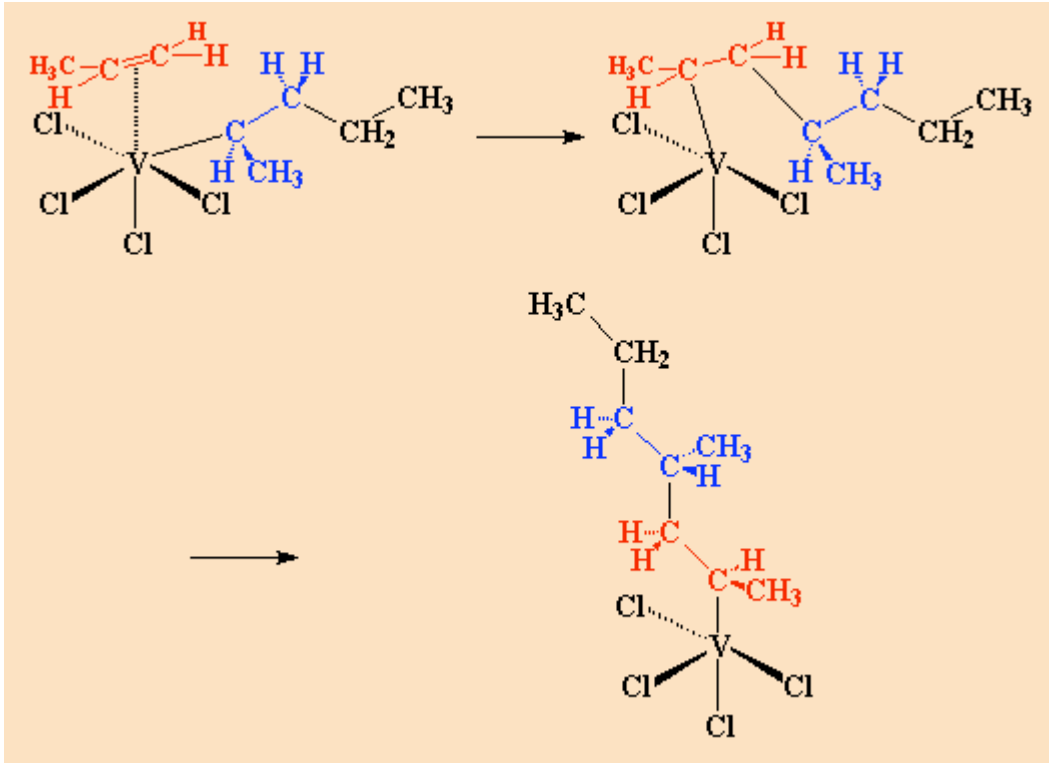


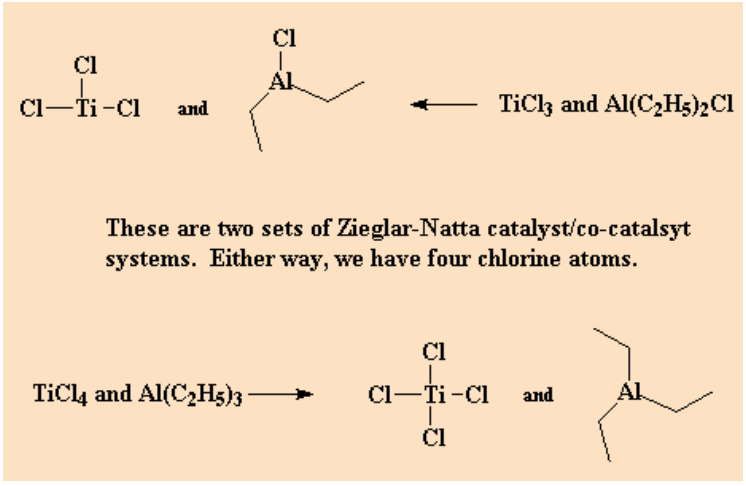


Isotactic Polypropylene by ZN Polymerization









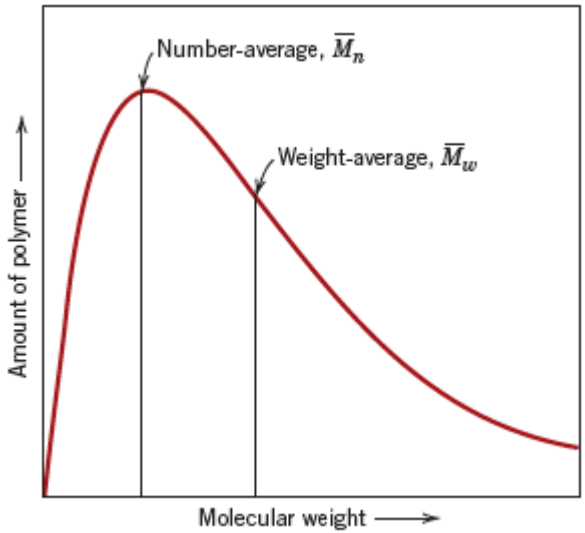
Polymers have a Dispersion in All Properties

Molecular Weight (Molar Mass)

Stereochemistry

Block Copolymer Composition

Branch Structure



Polymers have a Dispersion in All Properties

Molecular Weight (Molar Mass)

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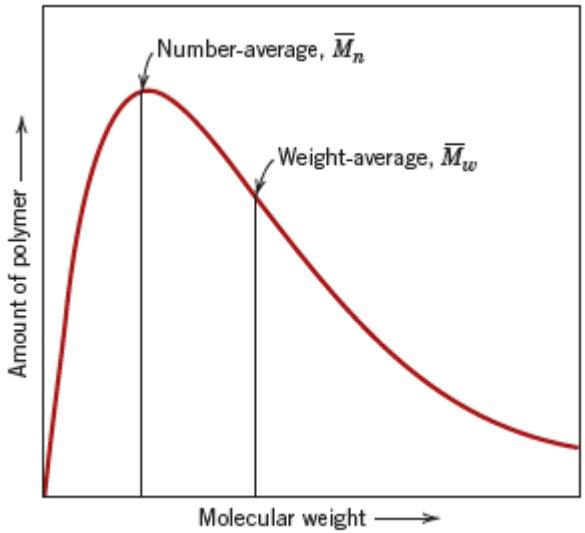
Block Copolymer Composition

Branch Structure



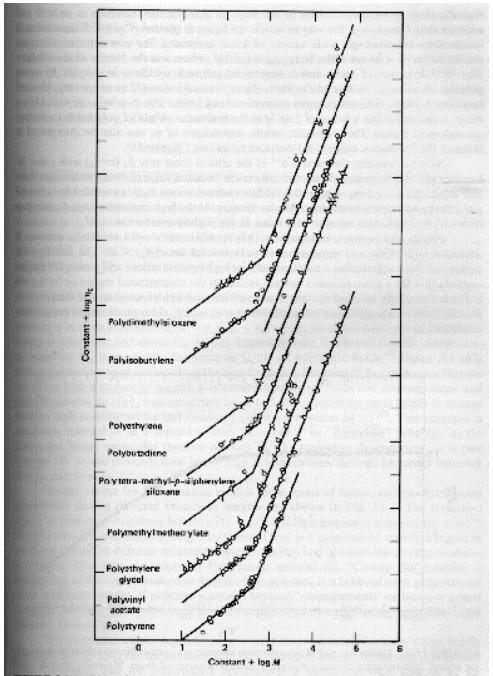
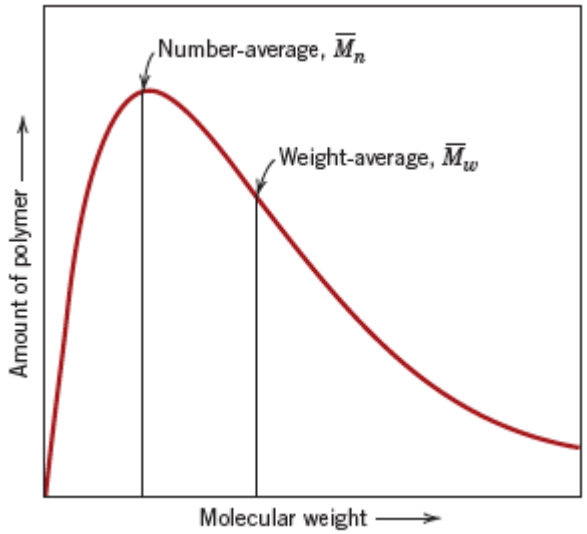


FIGURE 3.6-4. Plots of constant + log η_c vs. constant + log M for nine different polymers. The two constants are different for each of the polymers, and the one appearing in the abscissa is proportional to concentration, which is constant for a given undiluted polymer. For each polymer the slopes of the left and right straight line regions are 1.0 and 3.4, respectively. [G. C. Berry and T. G. Fox, *Adv. Polym. Sci.*, 5, 261–357 (1968).]

Molecular Weight Distribution



$$\overline{M}_n = \Sigma x_i M_i$$

$$DP = \frac{\overline{M}_n}{m}$$

$$\overline{M}_w = \Sigma w_i M_i$$

PDI = M_w/M_n

$$M_w = \sum_i x_i^2 M_i$$

$$M_z = \sum_i x_i^3 M_i$$

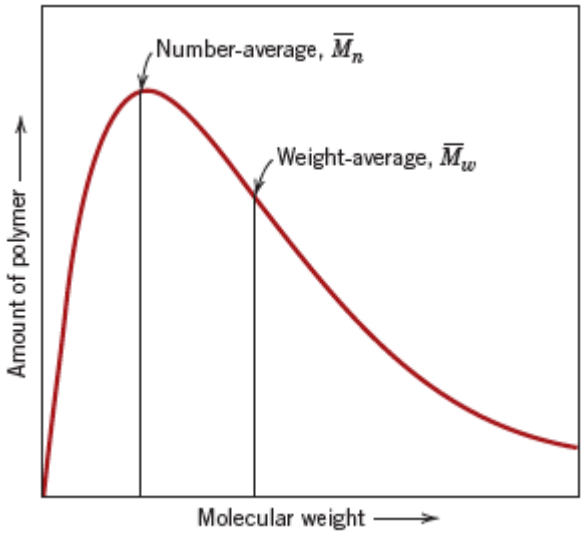
This can be directly related to the Gaussian Distribution

$$n_p = \frac{\int_{n=0}^{\infty} n^p P(n)dn}{\int_{n=0}^{\infty} P(n)dn}$$

$$n_1 = \frac{\int_{n=0}^{\infty} nP(n)dn}{\int_{n=0}^{\infty} P(n)dn}$$

$$n_w = \frac{\int_{n=0}^{\infty} n^2 P(n)dn}{\int_{n=0}^{\infty} nP(n)dn} = \frac{n_2}{n_1}$$

Molecular Weight Distribution



$$n_p = \frac{\int_{n=0}^{\infty} n^p P(n)dn}{\int_{n=0}^{\infty} P(n)dn}$$

$$n_1 = \frac{\int_{n=0}^{\infty} nP(n)dn}{\int_{n=0}^{\infty} P(n)dn}$$

$$n_w = \frac{\int_{n=0}^{\infty} n^2 P(n)dn}{\int_{n=0}^{\infty} nP(n)dn} = \frac{n_2}{n_1}$$

$$PDI = \frac{n_w}{n_1} = \frac{n_2}{(n_1)^2}$$

$$\sigma^2 = \frac{\int_{0}^{\infty} P(n)[n - n_1]^2 \, dn}{\int_{0}^{\infty} P(n)dn}$$

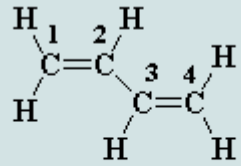
$$\sigma = n_1 [PDI - 1]^{1/2}$$

z-average

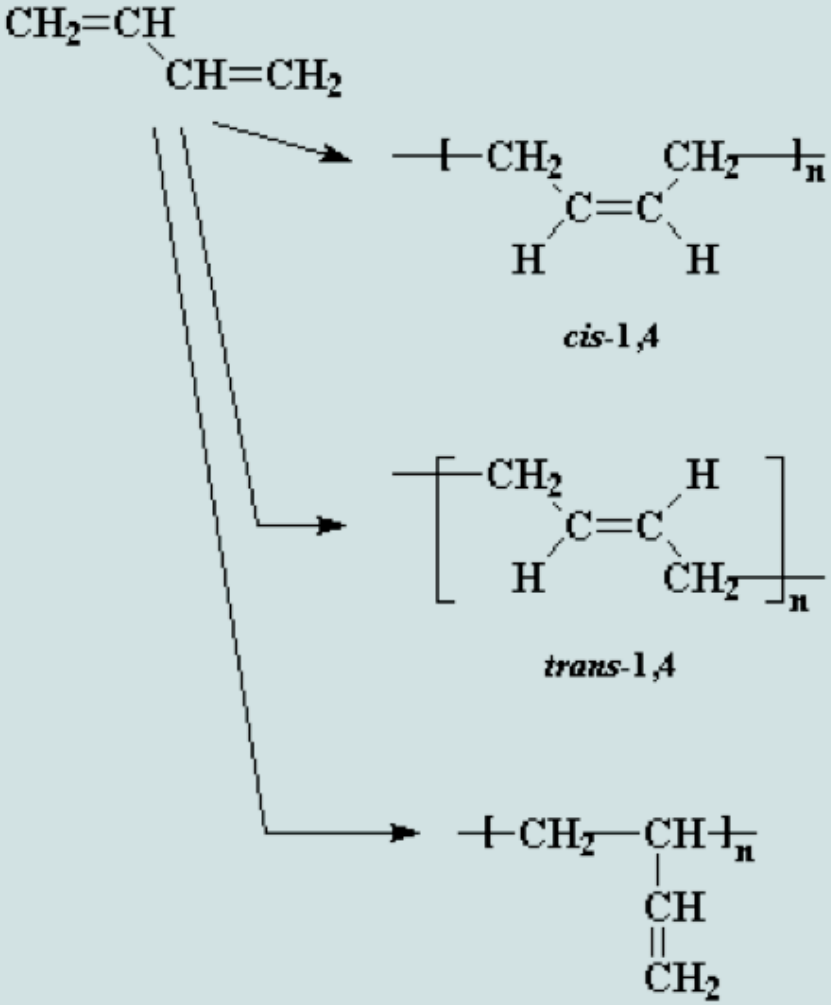
$$n_z = \frac{\int_{n=0}^{\infty} n^3 P(n) dn}{\int_{n=0}^{\infty} n^2 P(n) dn} = \frac{n_3}{n_2}$$

Viscosity Average

$$n_\nu = \left(\frac{\int_{n=0}^{\infty} n^{1+a} P(n) dn}{\int_{n=0}^{\infty} n P(n) dn} \right)^{1/a} \qquad 0.5 \leq \mathrm{a} \leq 0.8$$



Butadiene has two carbon-carbon double bonds, in the 1 and 3 positions, that is, starting at the carbon atoms numbered 1 and 3.

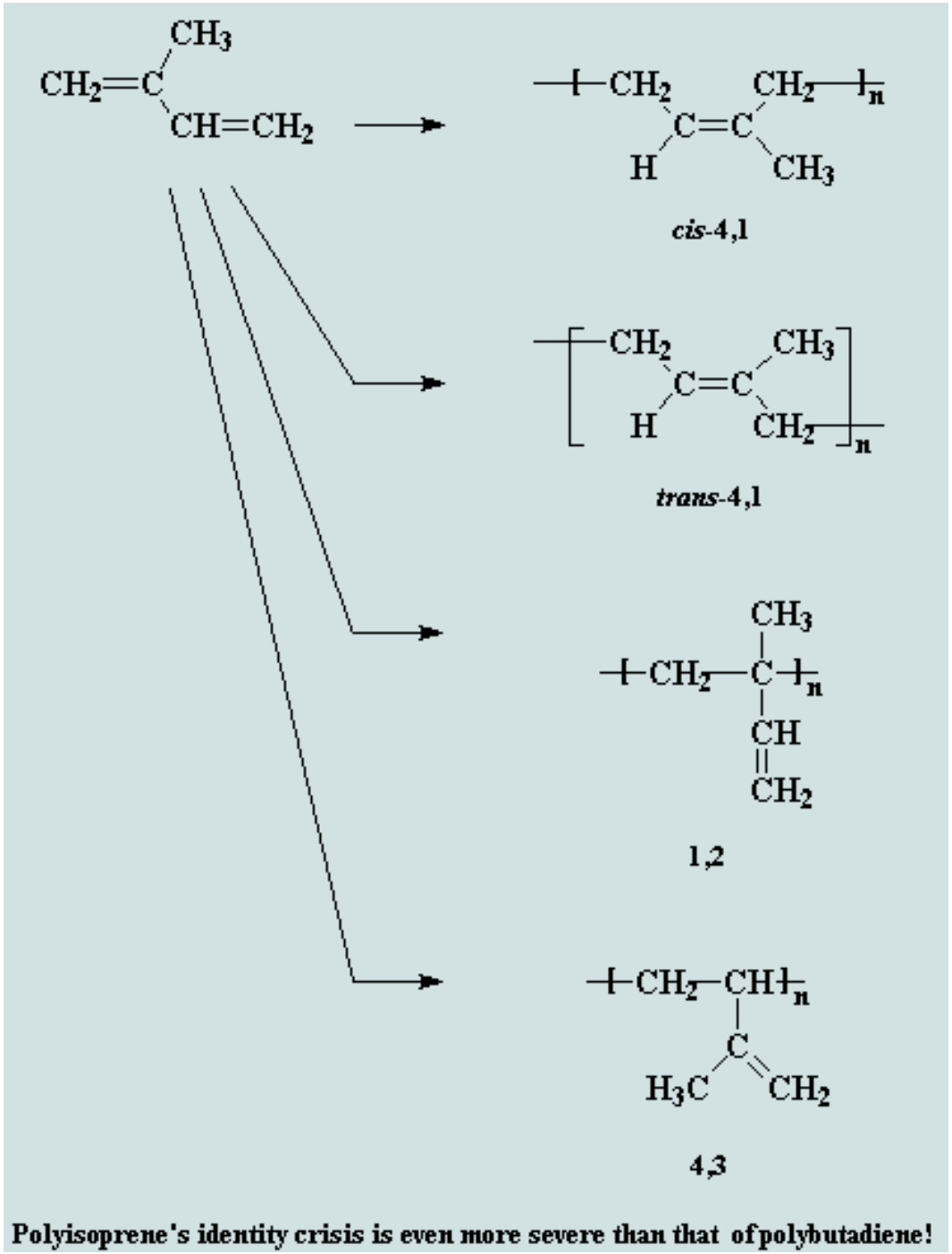


Note: *Cis* is Latin, and means "on this side". *Trans* is also Latin and means "on the other side". You may have seen them in place names like *Gallia Cisalpina*, meaning "land of the Celts on this side of the Alps", or *Transylvania*, meaning "land on the other side of the forest".

The top repeat unit is called "*cis*-1,4" because the carbon atoms of the carbon-carbon double bond are both bonded to the backbone chain on the *same side* of the double bond, and because the monomer is linked into the chain through carbon atoms 1 and 4.

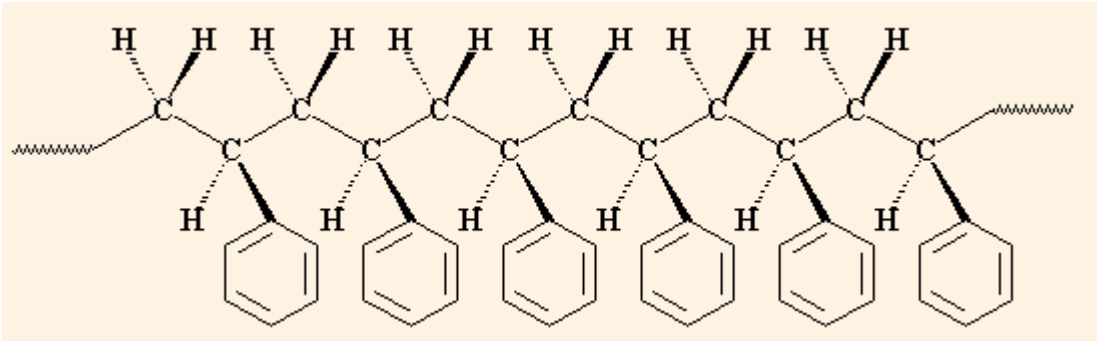
The second repeat unit is called "*trans*-1,4" because the carbon atoms of the carbon-carbon double bond, are bonded to the backbone chain on *opposite* sides of the double bond, and again the monomer is linked into the chain through carbon atoms 1 and 4.

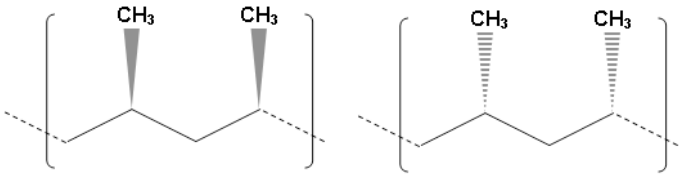
The bottom repeat unit is called "1,2" because the monomer is linked into the chain through carbon atoms 1 and 2. It is called "side vinyl" because the vinyl group, that is the carbon-carbon double bond is hanging off chain as a side group, rather than as part of the backbone chain.



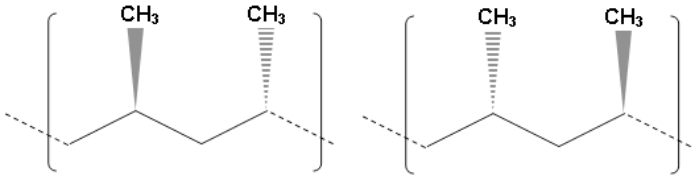
Polyisoprene's identity crisis is even more severe than that of polybutadiene!

Tacticity

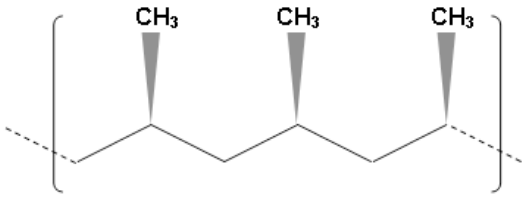




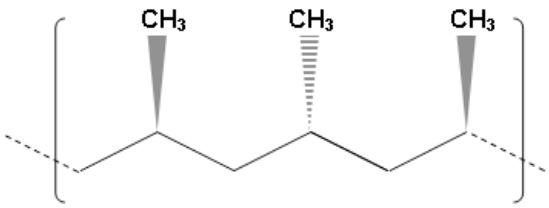
Meso Diad
(Meso) **m**



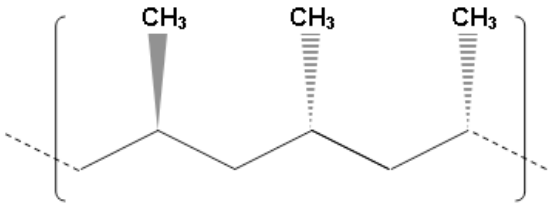
Racemo Diad
(Racemic) **r**



Isotactic Triad **mm**



Syndiotactic Triad **rr**



Heterotactic Triad **mr**
rm

Atactic Polmer

Has no tacticity

For a random distribution of tacticity: 50% r and 50% m or
25% isotactic, 25% syndiotactic, 50% heterotactic

Higher order groupings are important to crystallinity,
Pentads, Heptads, etc.
But there are limits to our ability to resolve tacticity using NMR

Polymer Processing

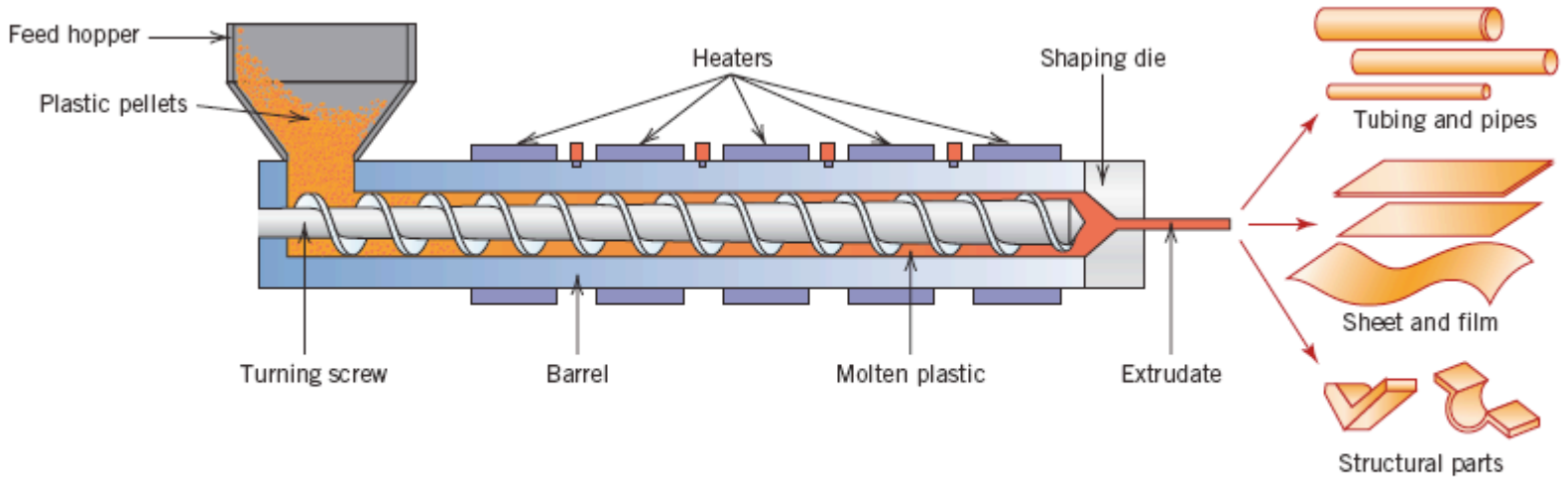


Figure 15.25 Schematic diagram of an extruder. (Reprinted with permission from *Encyclopædia Britannica*, © 1997 by Encyclopædia Britannica, Inc.)

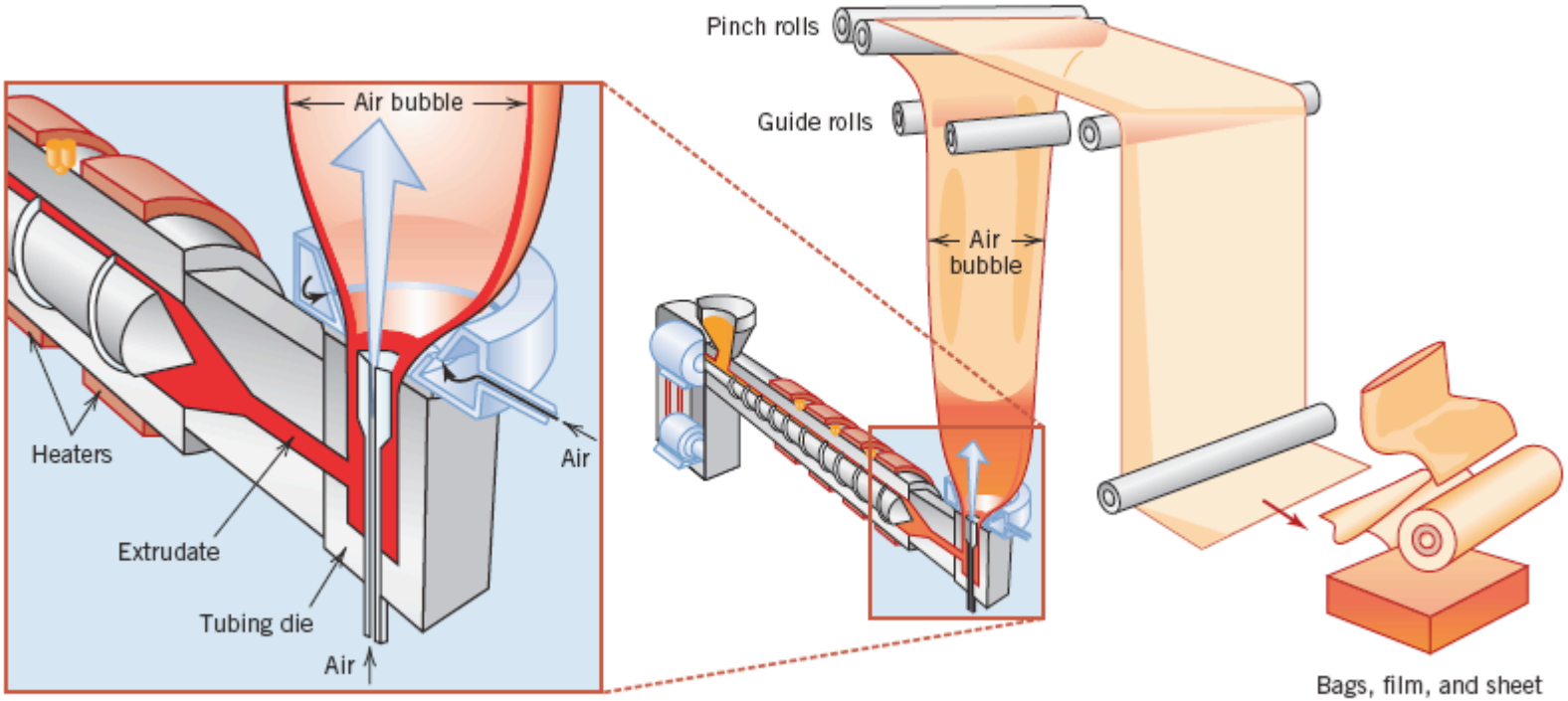


Figure 15.26 Schematic diagram of an apparatus that is used to form thin polymer films. (Reprinted with permission from *Encyclopædia Britannica*, © 1997 by Encyclopædia Britannica, Inc.)

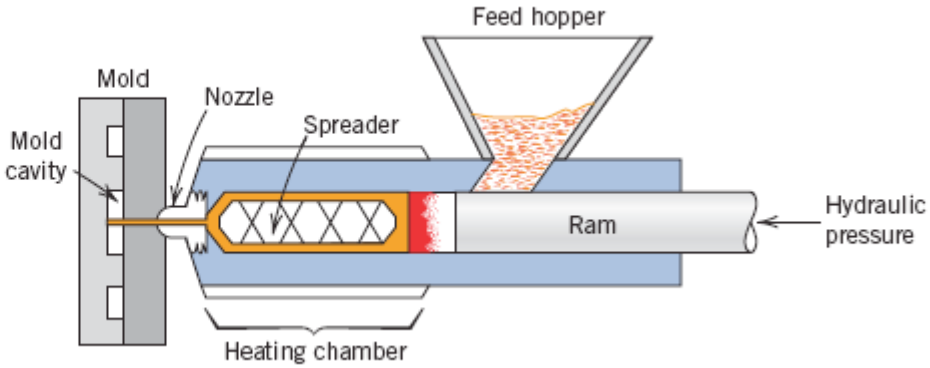


Figure 15.24 Schematic diagram of an injection molding apparatus. (Adapted from F. W. Billmeyer, Jr., *Textbook of Polymer Science,* 2nd edition. Copyright © 1971 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)