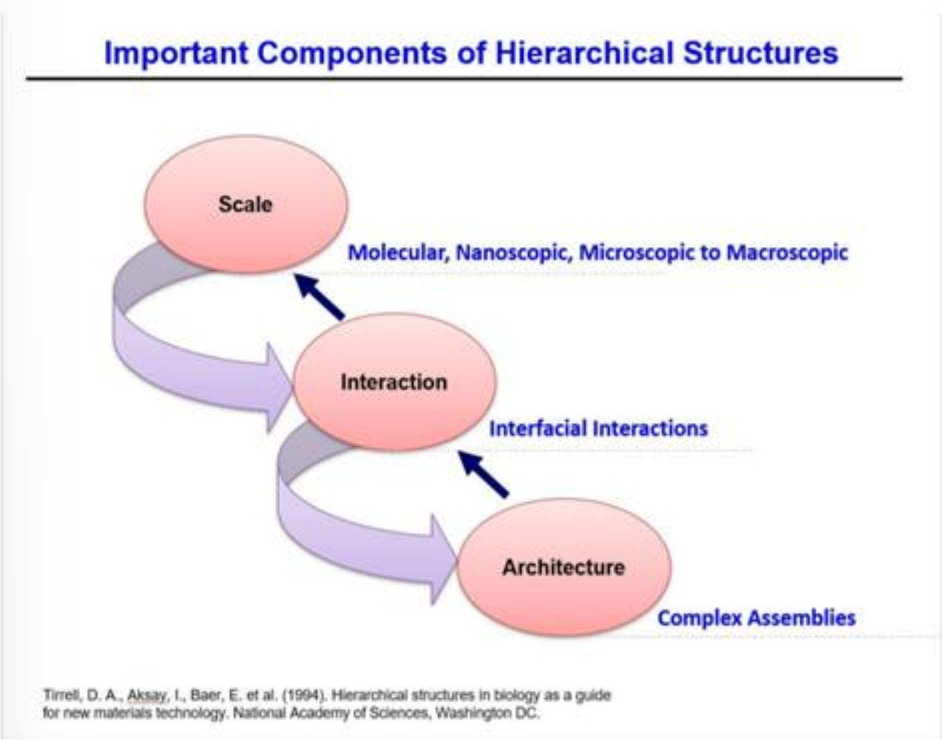
EMAC 276 Midterm Review

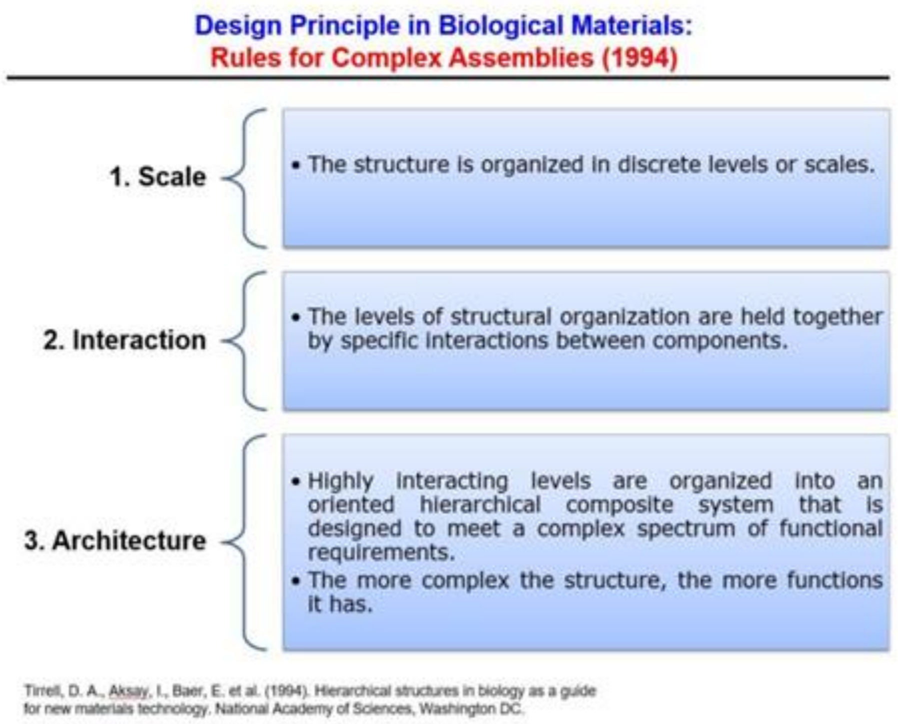
Midterm Exam on 3/7/25

Midterm Exam Format

- In class exam, taken on Canvas
- 50 questions
    - Multiple choice and T/F questions
- 50 minutes
- Open note

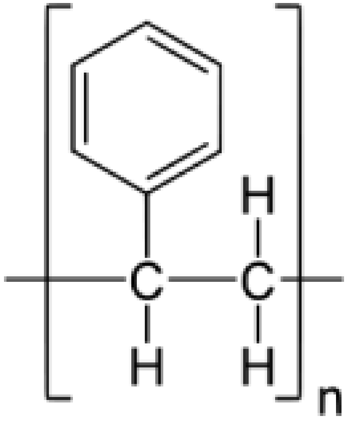
Hierarchical Structures





Polystyrene

- Free radical polymerization
  - Free radical is any molecular species capable of independent existence that contains an unpaired electron in an atomic orbital (unstable and highly reactive)
  - BPO or AIBN can be initiators
- Monomer can be formed from acetylene
- Amorphous
- Unmodified PS is very stiff and brittle
- Tg is a function of MW
- Extruded vs Expanded PS
- Reactivity Ratios



Reactivity Ratios for Free Radical Polymerization

The reactivity ratios r_1 and r_2 are defined as:

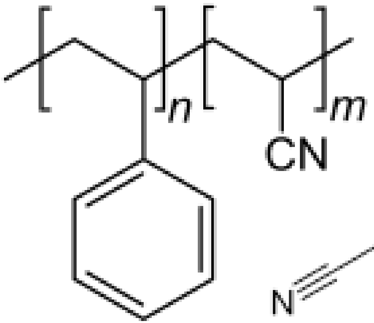
$r_1 = \frac{k_{11}}{k_{12}}$ The ratio of reactivity of monomer 1 (A) toward itself to the reactivity of monomer 1 toward monomer 2 (B).

$r_2 = \frac{k_{22}}{k_{21}}$

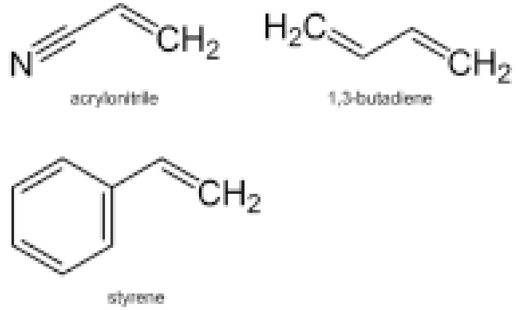
If the product of r_1 and r_2 is:

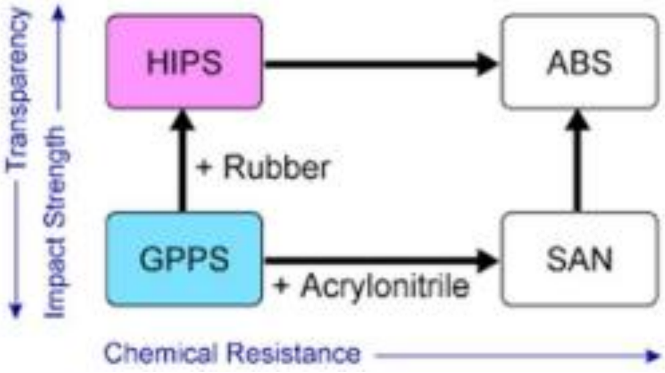
a) $r_1 * r_2 \sim 1$ – Random Copolymer – A A B B B A A A B A B A A A A
b) $r_1 * r_2 < 1$ – Alternating Copolymer – A B A B A B A B A B A B A B
c) $r_1 * r_2 >> 1$ – Block Copolymer – A A A A A A A A B B B B B B B

Styrene Copolymers (SAN, ABS)



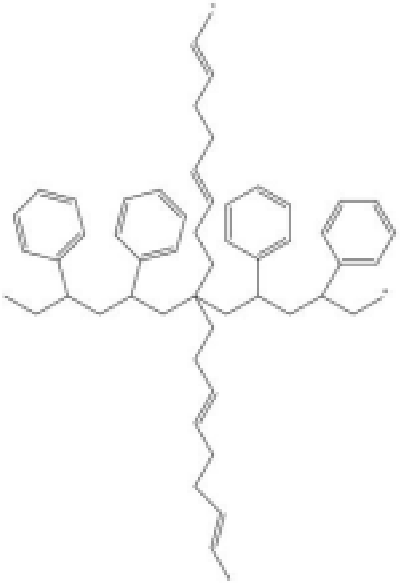
- Improve performance with derivatives
- SAN - Styrene Acrylonitrile Copolymer (70% styrene, 30% acrylonitrile)
  - Good stiffness, chemical resistance, flexural strength, thermal resistance
- ABS - Acrylonitrile Butadiene Styrene Copolymer
  - Good Impact resistance, used in 3D printing, Legos!

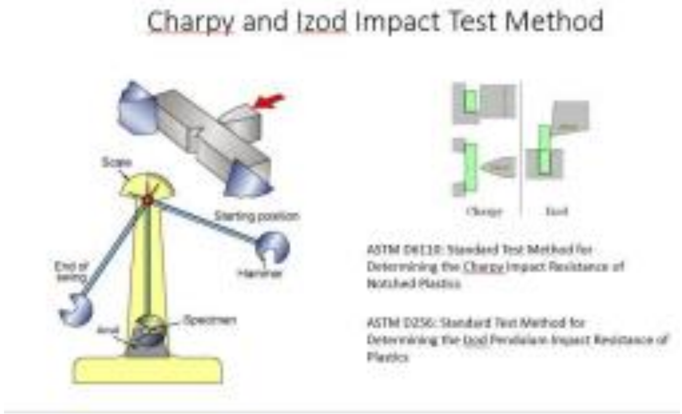


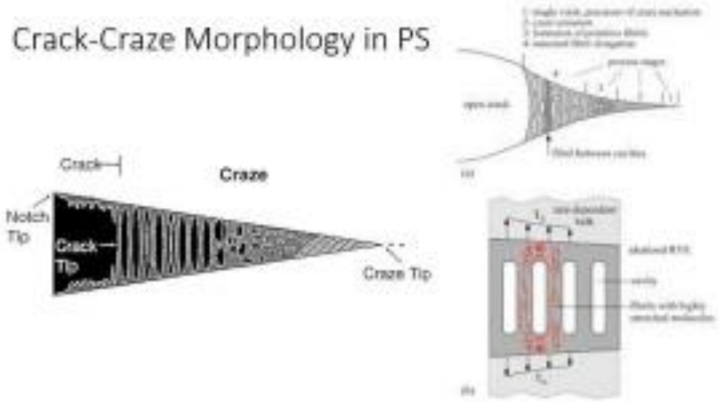


Styrene Copolymers (ABS, HIPS)

- Crack-Craze Morphology
  - Craze is in front of Crack
- Energy dissipation in rubber modified styrenics
- HIPS - High-Impact Polystyrene
  - Styrene + polybutadiene
  - Excellent impact resistance
- Charpy and Izod Impact Test for Impact Resistance

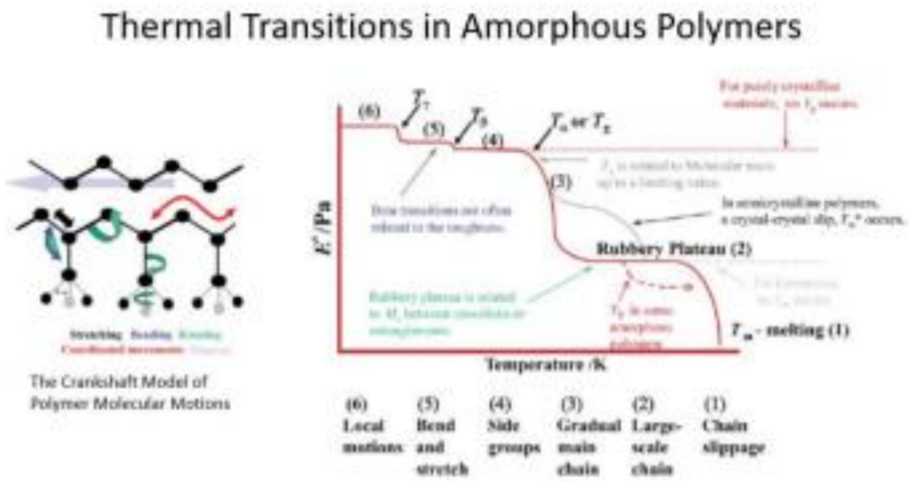


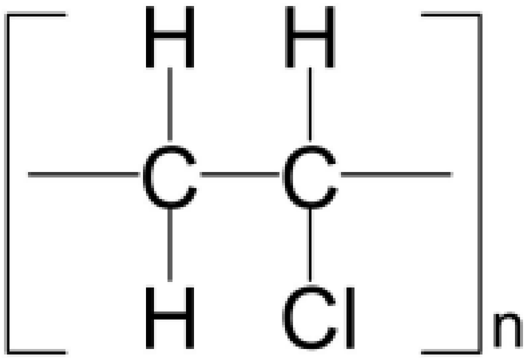




Vinyl Chlorides

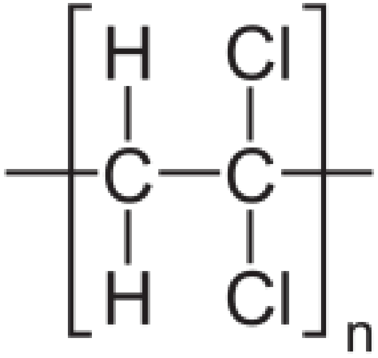
- Thermal Transitions
- Plasticizers reduce Tg, impacts tensile modulus and tensile strength
- PVC- Poly(vinyl chloride)
    - Highly sensitive to thermal degradation
- Organo-Tin Stabilizers in PVC
    - Prevents conjugation
    - Consumes HCl
    - Implement some plasticizing in PVC

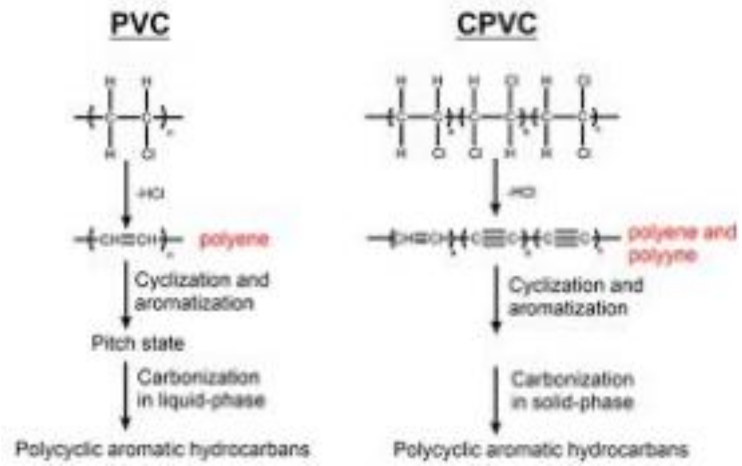




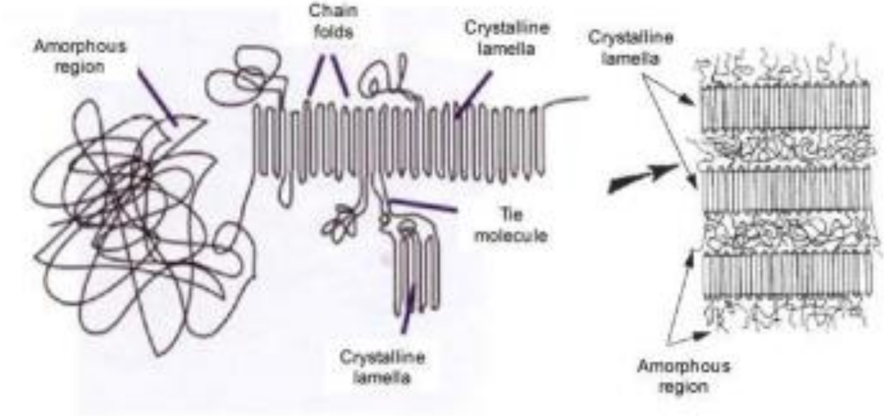
Vinyl Chlorides

- CPVC-Chlorinated PVC
  - Chlorination % increases Tg
- Polyvinylidene chloride - poly (1,1-dichloroethylene)
  - Discovered by accident
  - More sensitive to thermal degradation than PVC
  - Unstable, undergoes thermal decomposition at modest temps
- PVDC- Poly(1,2-dichloroethylene)
  - Chlorination of poly(acetylene)
  - Leading barrier polymer for high performance packaging films



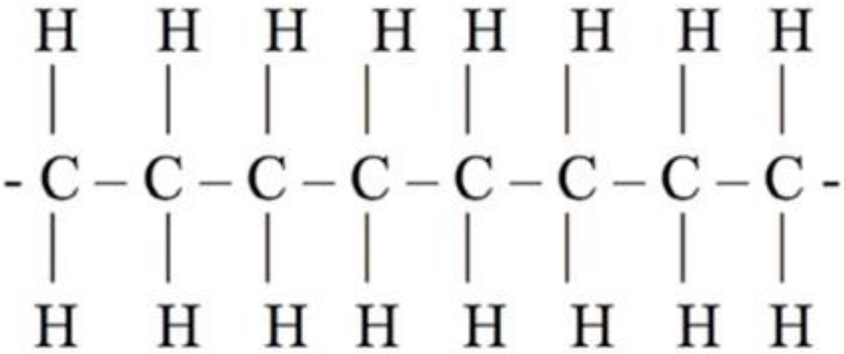


Polyolefins - PE



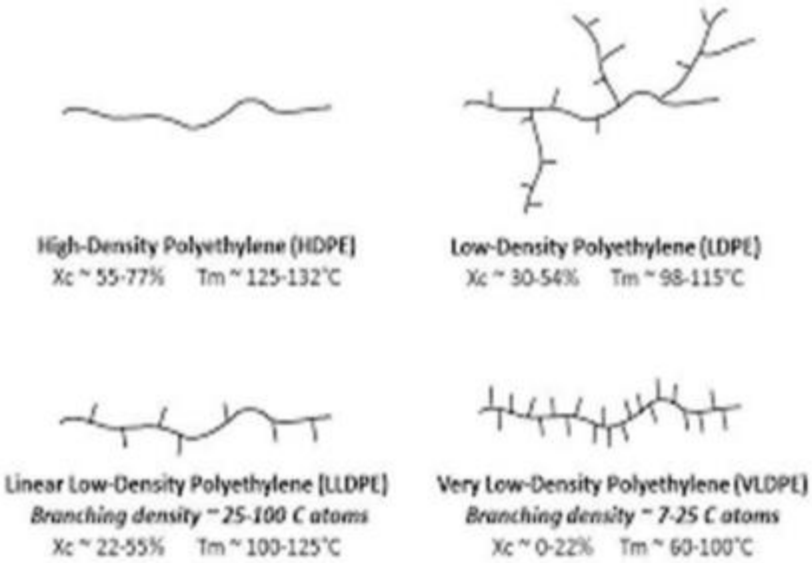
- Olefin polymer - polymers made from vinyl monomers produced from alkenes having a CnH2n structure
- Diversity of products
- PE - Polyethylene
  - Semi-crystalline
  - Classifications by density

Resin family	*Lower density limit g/cc*	*Higher density limit g/cc*
High Density Polyethylene (HDPE)	0.941	0.975
Medium Density Polyethylene (MDP)	0.928	0.941
Linear Low Density Polyethyl-ene(LLDPE/LDPE)	0.915	0.928
Very Low Density Polyethylene (VLDPE)	0.900	0.915
Elastomers/Plastomers	0.865	0.900



Polyolefins (LDPE and HDPE)

- Variance in branching between PE types
- LDPE - Low Density Polyethylene
  - Free Radical Polymerization
  - Long chain branching
  - Moderate chemical resistance, low cost, good processability, high impact strength, excellent insulator
  - ESC, high flammability, poor UV resistance
- HDPE - High Density Polyethylene
  - Coordination polymerization
  - Ziegler-Natta Polymerization
  - Greater resistance, better properties than LDPE, good stiffness, good insulator, low water absorption



Polyolefins - Polyethylene Copolymers

- Branching, co-monomer structure/content, and MW lead to diversity in structure
- Co-monomers
  - Propylene, butylene, hexene, octene
  - Tie chains
  - Ethylene-octene copolymers
- Plastomers - material which combines properties of plastics and elastomers

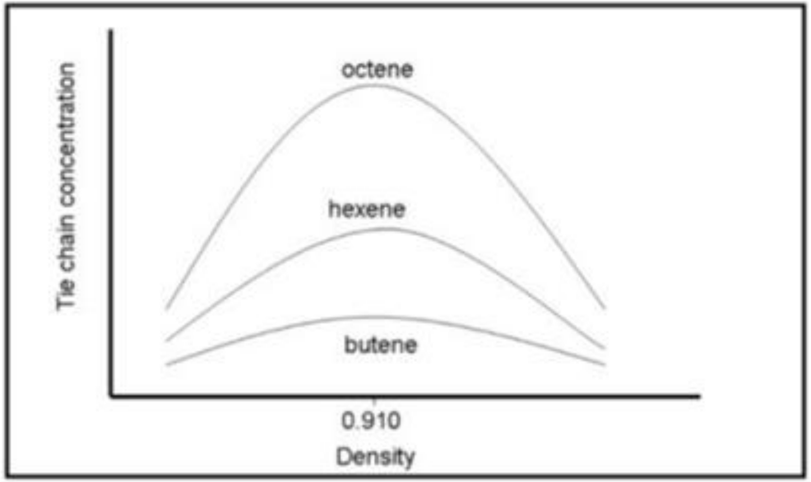
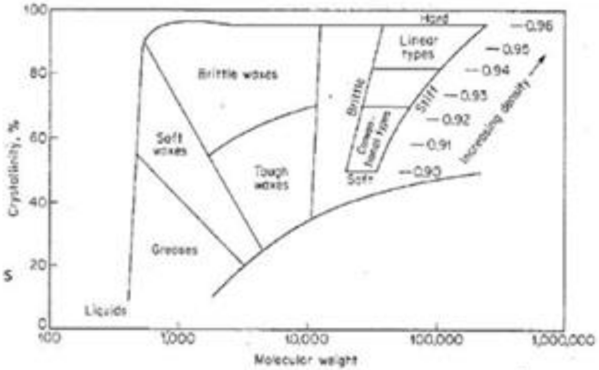
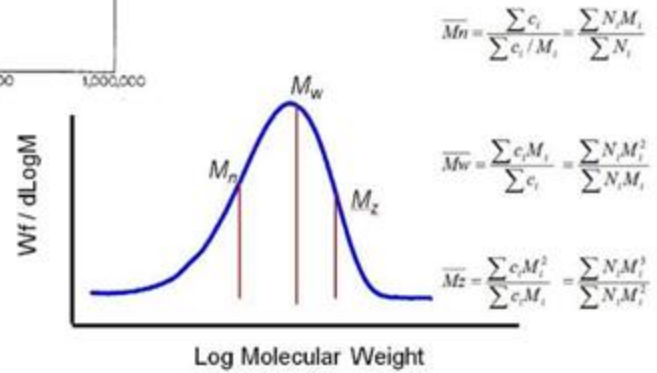


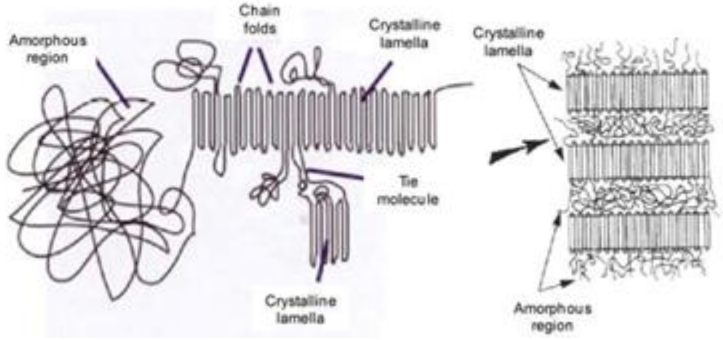
Figure 2. Tie chain concentration vs. density for common alpha olefin comonomers.

Polyolefins - ULMWPE and UHMWPE

- MW dependence on properties
- Molecular weight distributions
  - Mn < Mw < Mz (usually found with SEC)
  - Mv (found with viscometer)
- Ultra low molecular weight PE
  - PE wax
- Ultra high molecular weight PE
  - Ziegler-Natta polymerization
  - Downside: increased melt viscosity (difficult to process)
- PENT Test - measure the amount of time for a pre-notched crack to propagate through a PE specimen of a specific dimension
- Modal PE
  - Extends the ductile to brittle transition time
  - Bimodal PE
  - Multimodal PE

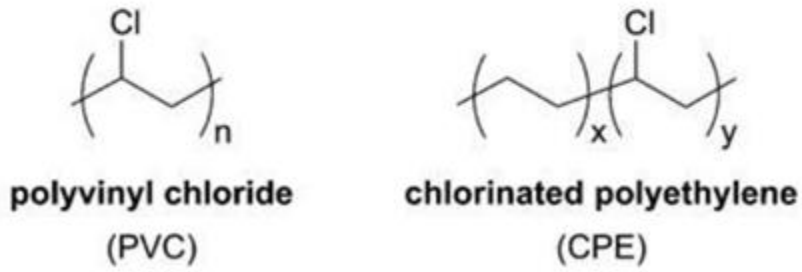






Polyolefins - CPE and PEX

- PE can undergo secondary reactions (modifications)
- CPE - Chlorinated polyethylene (different from PVC)
  - Good chemical properties, oil resistance, flame retardant properties, non-toxic, high filling performance
- PEX - Crosslinked polyethylene
  - Crosslinking methods: peroxide, radiation, silanes, UV with agent, E-beam
  - Increased density and stiffness

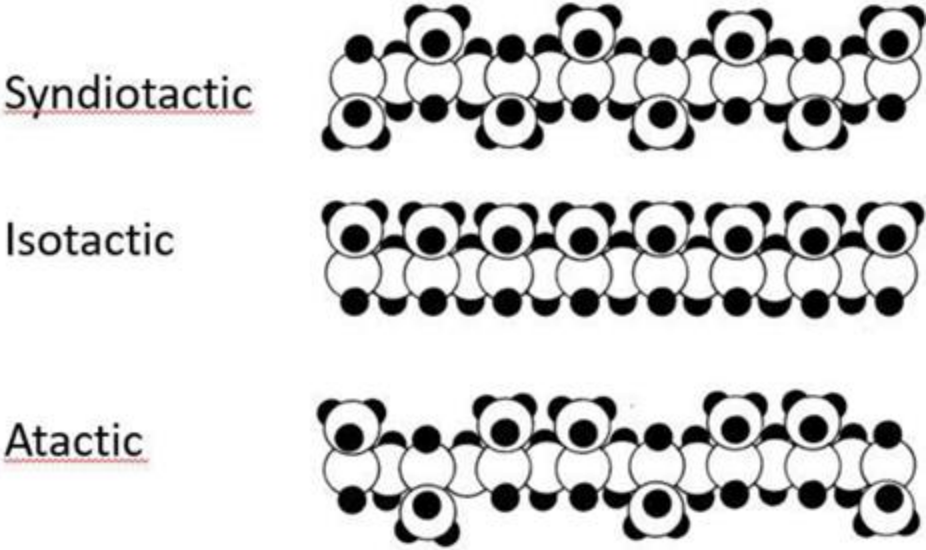


Comparison to PVC (57% Chlorine)
CPE (33 – 44% Chlorine)

Method \ Aspect	Silane	Peroxide	Radiation
Process flexibility	Very good	Small	Very good
Operation	Easy	Difficult	Difficult
Extruder	Standard	Special	Standard
Production rate	High as for PE	Low	High as for PE
Cost of post treatment	Low	-	High
Capital investment	Low	High	High
Diameter	No limit, thickness limited by speed of cross-linking	Difficult to achieve big diameters because of output	Limited by penetration depth of electron
Scrap rates	Low	High scrap	
Raw material costs	Slightly high	Low	Low
Levels of attainable cross-link density		High	Probability of variation
Other	Wider scope for formulation through broad processing window, recyclability	Energy intensive	Clean (pipe) because of fewer additives

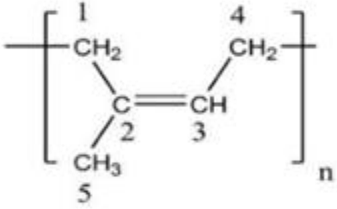
Polyolefins - PP and PB

- Polypropylene
  - Ziegler-Natta or Metallocene polymerization
  - Tacticity
  - Copolymers
  - Good processability, impact resistance, stiffness
  - Difficult to bond, flammable, UV degradable, poor chemical resistance (aromatics and chlorinated solvents)
- Polybutylene
  - Ethyl sidegroups
  - 11/3 and 3/1 crystal forms

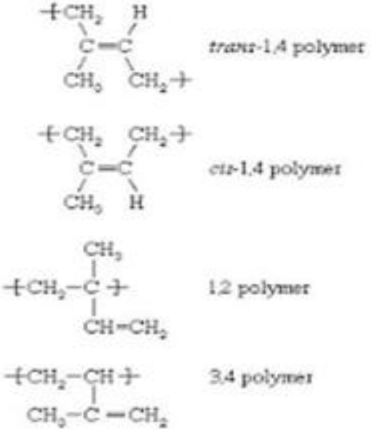


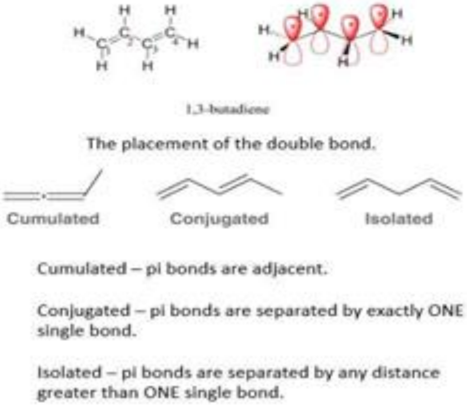
Polydienes - Natural Rubber

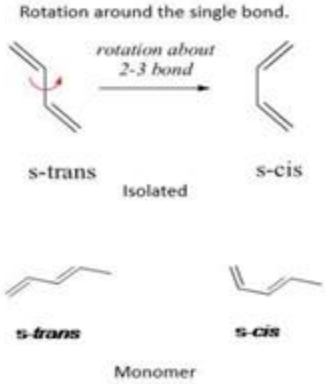
- Dienes: unsaturated hydrocarbons containing two double bonds
- Polyisoprene - natural rubber
  - Elastic properties
  - Five different configurations
  - Vulcanization (sulfur crosslinking)

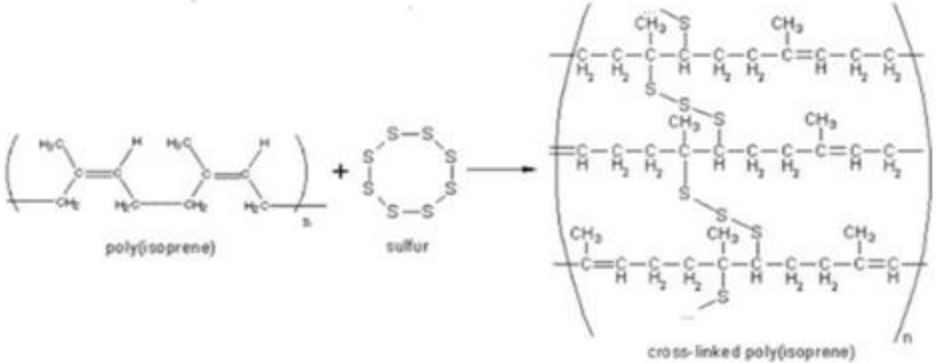


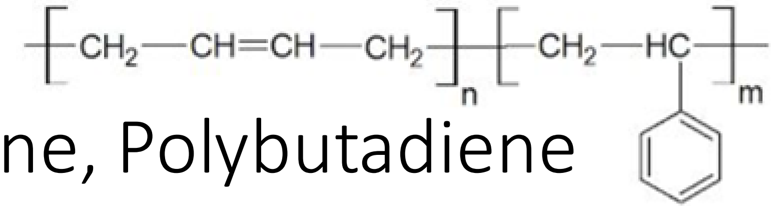
cis-1,4-polyisoprene





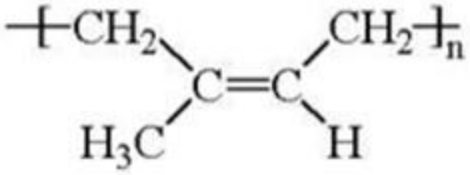


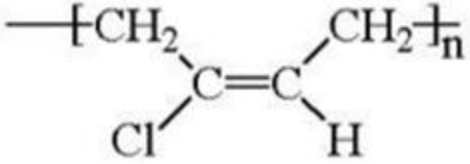


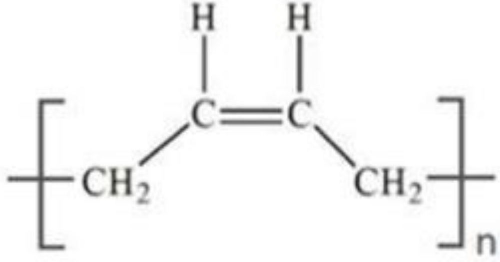


Polydienes - SBS rubber, Neoprene, Polybutadiene

- Neoprene - polychloroprene
  - Resists degradation more than natural rubber
  - Inert
  - Resists burning better than hydrocarbon based rubbers
  - Can be used as a foam
- Polybutadiene
  - Polymerization there are cis- and trans- bonds
- SBS/SBR Rubber - styrene butadiene styrene rubber
  - Anionic polymerization (many methods)
  - Block copolymer - phase dependent mechanical properties
  - TPE - thermoplastic elastomer

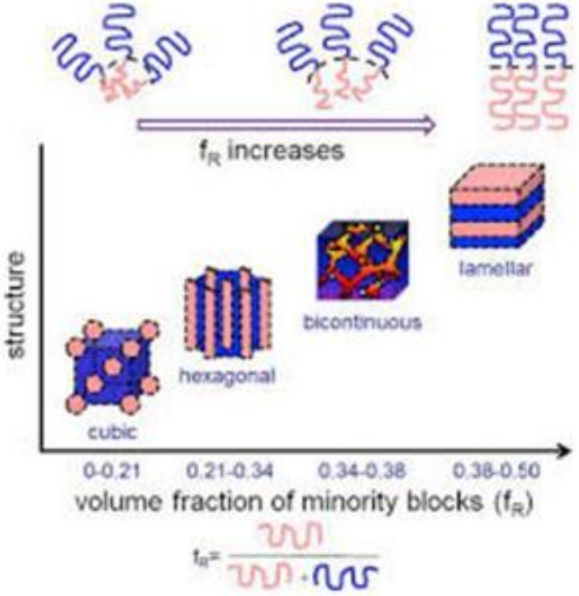


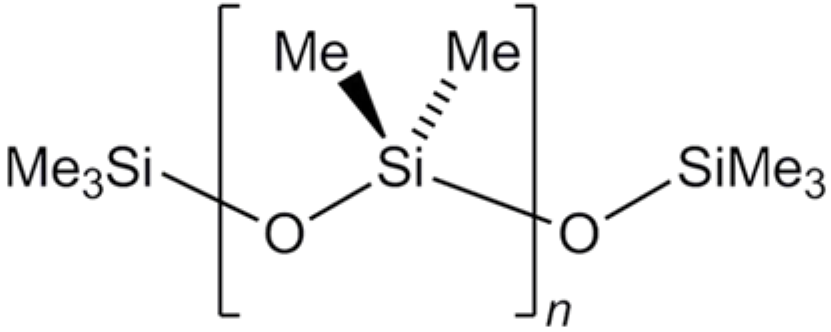


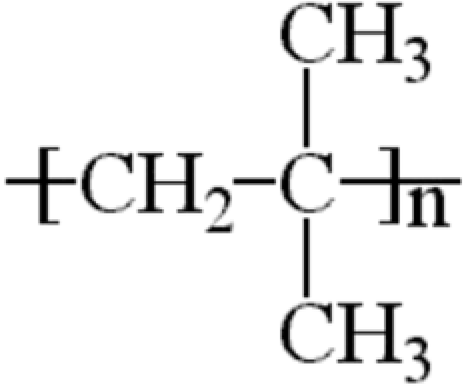


Elastomers

- Domain formation in block copolymers
- PIB - Polyisobutylene
  - Chewing gum
  - Oil derivatives
- PDMS (silicone) - polydimethylsiloxane
  - Crosslinking forms an elastomer







Study Tips

- Identify important details about each polymer:
  - How is it made?
  - What are its properties?
    - Do they change with outside influences
  - Can it be modified? If so, how?
    - How does the modification relate to the original polymer?
    - What new properties arise from the modification?
    - Is there a specific analytical test I can use to measure the properties?
  - How is it processed?
    - Can the processing technique be modified?
  - What products are made from this polymer?

- Remember polymer basics (EMAC270)
- Structure-property relationships are key
- Material covered by Dr. Zhu will not be tested – will be tested in Final Exam