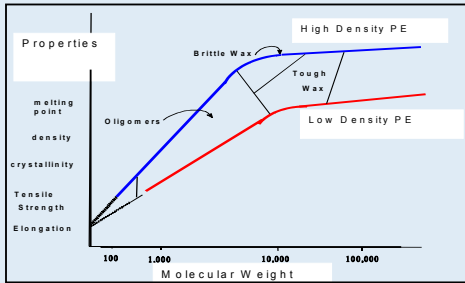


IMPACT OF MOLECULAR WEIGHT ON MATERIAL PROPERTIES

Increasing Degree of Polymerization, DP



Vinyl Monomers, $\text{CH}_2=\text{CH-X}$

X	Polymer	Abbreviation
H	Polyethylene	PE
CH ₃	Polypropylene	PP
Cl	Poly(vinyl chloride)	PVC
Phenyl	Polystyrene	PSt
CN	Polyacrylonitrile	PAN
COOCH ₃	Poly(methyl acrylate)	PMA
O-COCH ₃	Poly(vinyl acetate)	PVAc

Vinylidene Monomers, $\text{CH}_2=\text{C(X)Y}$

X	Y	Polymer	Abbreviation
CH ₃	CH ₃	Polyisobutylene	PIB
Cl	Cl	Poly(vinylidene chloride)	PVDC
F	F	Poly(vinylidene fluoride)	PVDF
Phenyl	CH ₃	Poly(α -methyl styrene)	
CH ₃	COOCH ₃	Poly(methyl methacrylate)	PMMA
CN	COOR	Poly(alkyl α -cyanoacrylate)	

Structural Complexity of Polymers

- **Homopolymers**
 - Head to Tail vs. Head to Head Adducts
 - 1,2- vs 1,4 Adducts
 - Tacticity of Enchainments
 - Branching

Tacticity

- **Isotactic**
 - All asymmetric carbons have same configuration
 - Methylene hydrogens are meso
 - Polymer forms helix to minimize substituent interaction
- **Syndiotactic**
 - Asymmetric carbons have alternate configuration
 - Methylene hydrogens are racemic
 - Polymer stays in planar zig-zag conformation
- **Heterotactic (Atactic)**
 - Asymmetric carbons have statistical variation of configuration

Structural Complexity of Polymers

- **Copolymers**
 - Identity and Number of Comonomers
 - Ratio and Distribution of Comonomers
 - Statistical Alternating
 - Gradient
 - Blocks Grafts

Structural Complexity of Polymers

- **Molecular Weight**
 - Molecular Weight Distribution, MWD
 - Polydispersity Index, PDI
- Mn, Mw, Mz, Mv Averages
- Crosslinking Density
- - Length of Crosslinks

Structural Complexity of Polymers

- Time Dependent Changes
- **Chemical Reactions**
 - Hydrolysis
 - Dehydrohalogenation
 - - Photodegradation
 - Oxidation

Structural Complexity of Polymers

- **Thermal Degradation**
 - Processing
 - Aging
- **Crystallization**
 - Changes in Polymorphism
- Weathering-- Combination of Above
- Plasticizer Loss -- Imbrittlement

Microscopic Properties (Intermolecular Interactions)

- Chain entanglement –amorphous
- Chain ordering--liquid crystalline
- Crystallinity
- Phase separations (microdomains)
- **Morphology**

Types of Intermolecular Forces

Type of Force	Relative Strength	Low Molecular Analog	Polymer
• Dispersion or • Van der Waals	Weak	Methane Hexane	Polyethylene Polypropylene
• Dipole-Dipole	Medium	CH ₃ Cl CH ₃ CO ₂ CH ₃	PVC PMMA
Hydrogen bonding	Strong	H ₂ O CH ₃ CONH ₂	Cellulose Proteins
Electrostatic	Very Strong	CH₃CO₂Na⁺	Ionomers

Macroscopic Properties (Physical Behavior)

- **Tensile and/or Compressive Strength**
- **Elasticity**
- **Toughness**
- **Thermal Stability**
- **Flammability and Flame Resistance**
- **Degradability**
- **Solvent Resistance**
- **Permeability**
- **Ductility (Melt Flow)**

GLASS TRANSITION, T_g

- Definition: The onset of segmental motion of segments with 40-50 carbon atoms
- Physical Change Expansion of volume
- Free volume required to allow segmental motion
- **T_g is an approximation**
 - Depends upon measurement technique
 - Depends upon molecular weight
 - Polystyrene MW = 4000 T_g = 40°C
 - = 300,000 = 100°

GLASS TRANSITION, T_g

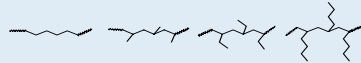
- Properties Affected
 - Specific Volume / Density
 - Specific Heat, C_p
 - Refractive Index
 - Modulus
 - Dielectric Constant
 - Permeability

FACTORS INFLUENCING T_g

- T_g is proportional to Rotational Freedom
- For symmetrical polymers T_g / T_m in °K $\cong 1/2$
- unsymmetrical polymers $\cong 2/3$
- **1. Chain flexibility**
- Silicone > Ether > Hydrocarbon > Cyclic HC > Aromatics

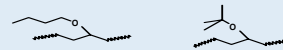
FACTORS INFLUENCING T_g

2. Steric Bulk of Substituents



T_g = -120°C 5°C -24°C -50°C

• Long side chains may act as plasticizers (C < 6)



- T_g = -55°C 88°C

FACTORS INFLUENCING T_g

- **3. Molecular Symmetry**
 - Asymmetry increases chain stiffness.
- **4. Polar Interactions increase T_g**
 - Hydrogen bonding
- **5. Molecular Weight up to Critical Limit**
- **6. Crosslinking**
 - Reduces Segment Mobility

FACTORS INFLUENCING T_m

- **1. Chain flexibility**
 - Silicone > Ether > Hydrocarbon > Cyclic HC > Aromatics
- **2. Substituents Producing Lateral Dipoles**
 - Hydrogen bonding
- **3. Molecular Symmetry**
 - Symmetry allows close packing

FACTORS INFLUENCING T_m

- 4. No Bulky Substituents to Disrupt Lattice if placement is Random
- 5. Structural Regularity
 - monomer placement
 - head to tail
 - 1,2- vs 1,4-
 - 1,2- vs 1,3- vs 1,4- aromatic substitution
 - geometric isomers of enchainments
 - cis or trans -C=C-; cyclic ring
 - tacticity

FACTORS REQUIRED TO PROMOTE CRYSTALLIZATION

- **Thermodynamic**
 1. Symmetrical chains which allow regular close packing in crystallite
 2. Functional groups which encourage strong intermolecular attraction to stabilize ordered alignment.

FACTORS REQUIRED TO PROMOTE CRYSTALLIZATION

- **Kinetic**
 1. Sufficient mobility to allow chain disentanglement and ultimate alignment
 - Optimum range for mobility
 - $T_m - 10^\circ \rightarrow T_g + 30^\circ$
 - at T_m segmental motion too high
 - at T_g viscosity too high
 2. Concentration of nuclei
 - concentration of nucleating agents
 - thermal history of sample

