STRUCTURE

Chapter 7
Fundamentals of Polymer Science

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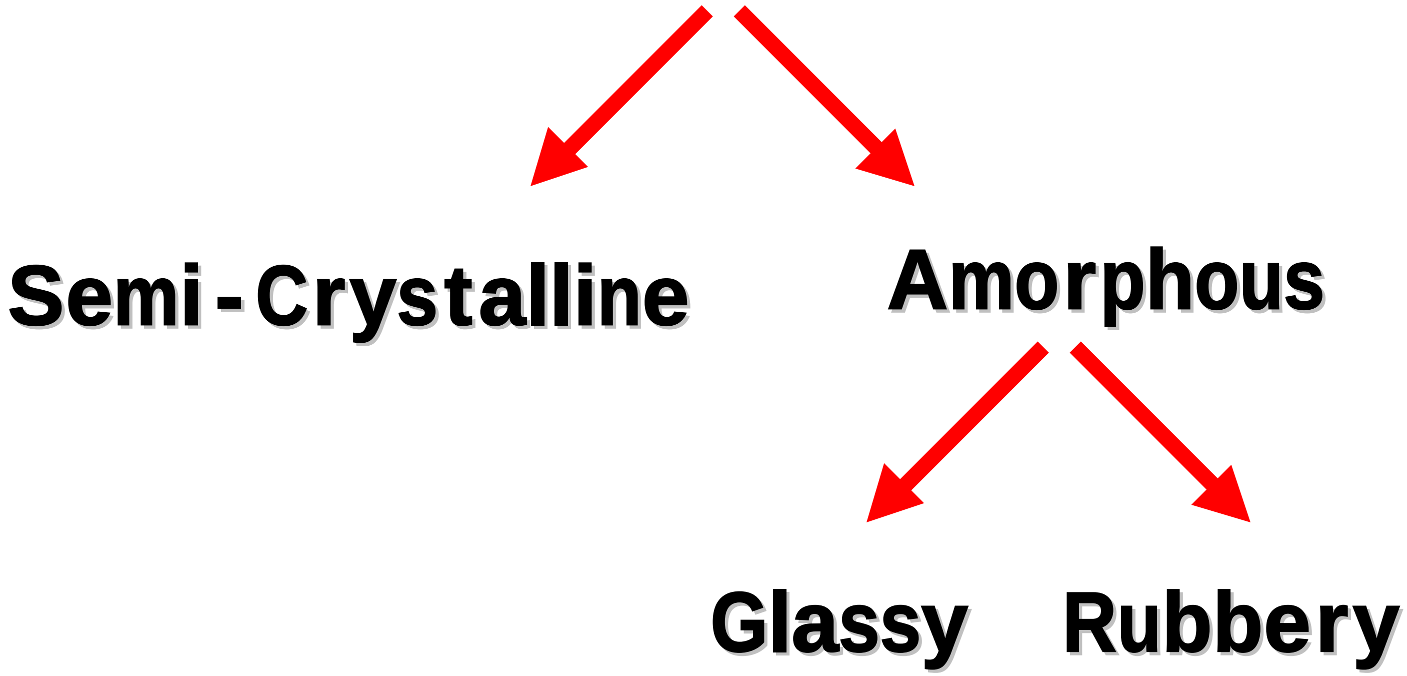
Partial support for this work was provided by the National Science Foundation's Advanced Technological Education Program."

Polymer "Solid" State



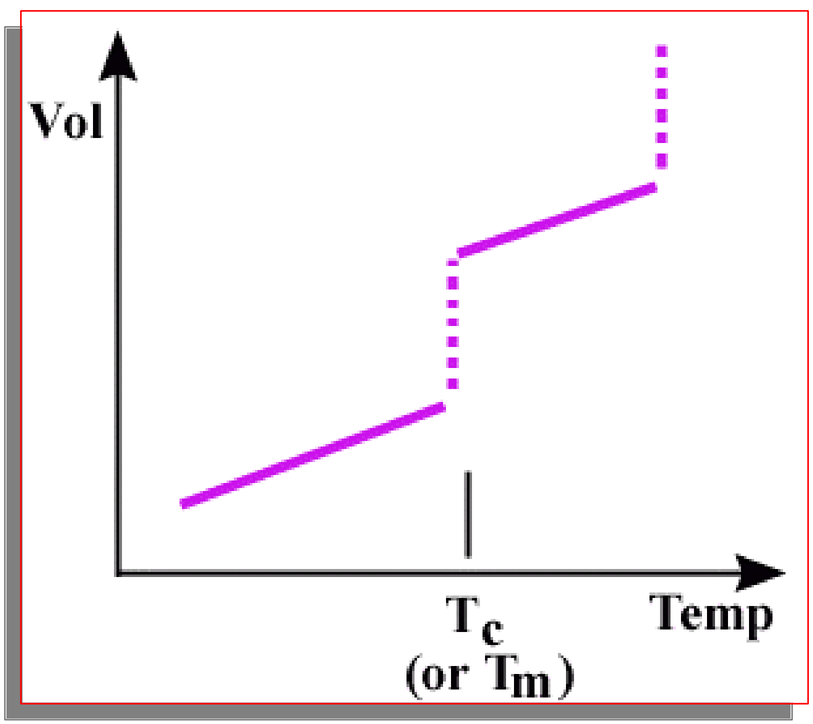
Q: Relationship to Microstructure

Q: Relationship of Structure to Properties

States of Matter

Small Molecules → **Gas**

"1st-Order" Transitions → **Liquid** ↓ **Solid (Crystalline)**



Gas

↓

Liquid

↓

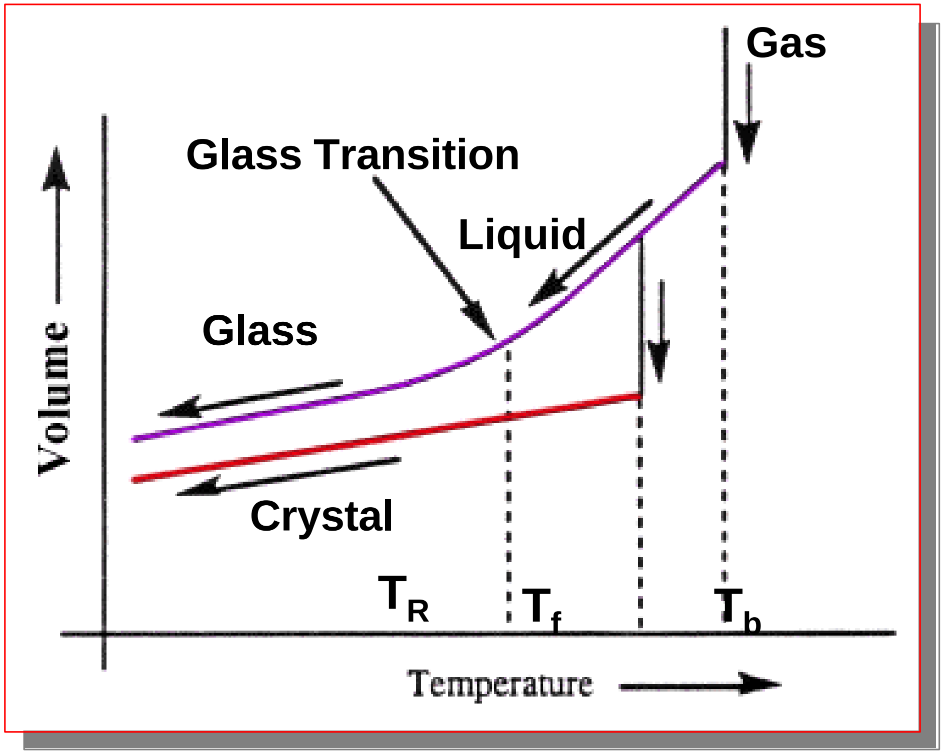
Solid

(Crystalline)

The Glassy State

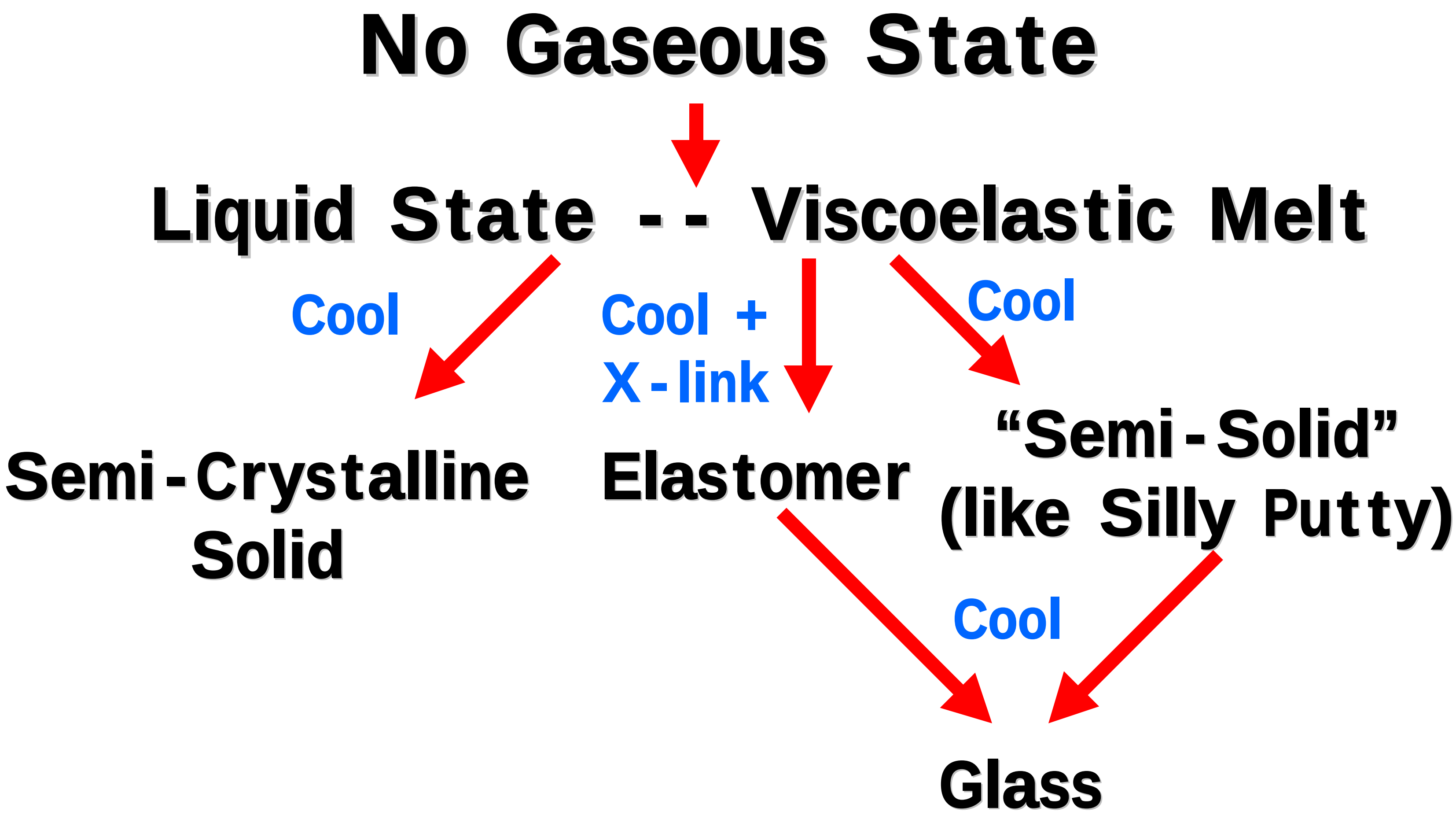
Two Possibilities; Observed Behavior depends on:

- *Structure*
- *Cooling Rate*
- *Crystallization Kinetics*



Many Materials form metastable glasses - what about polymers like PET, atactic polystyrene?

States of Matter



Also: **x-linked rubber + solvent (gel)**
liquid crystalline polymers, etc.

History of Rubber

~ 1500 Columbus Stumbles Across Haiti

~ 1600 Missionaries Observe Indians Making Crude Rubber Shoes (Caoutchouc)

1700 Joseph Priestly Invents a Name

1820 1st Rubber Shoes

1832 Mackintosh

1833 Goodyear Starts Work on Rubber

1844 Vulcanization

1875 Henry Wickham -- Pirate or Con-Man?

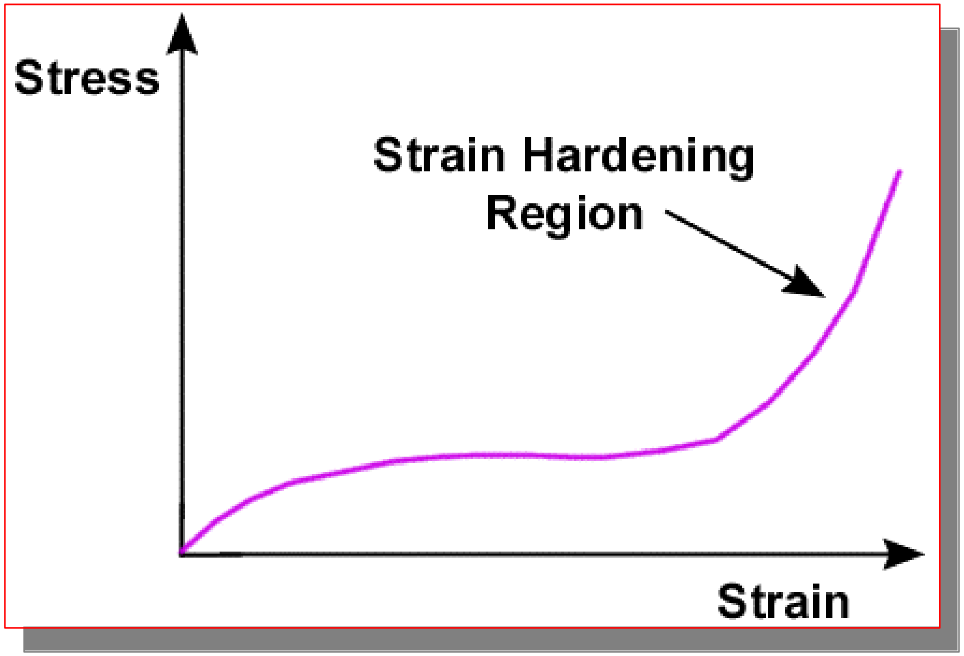
1922 Stevenson Plan

1942 Synthetic Rubber Project

1988 Penn State Rubber Project

Harrison Experiment

- Material Derived from Trojan-Enz
- Samples Cut Out With a Dog Bone Cutter
- Test -- Tensile Elongation (1 cm per minute)
- Uniaxial Deformation
  ~ 1,000 %
- Biaxial Deformation
  ~ 300 %
- Estimated Burst Pressure ~ 57 psi
  ~ 4 atm.



Polymer Structure

The Issues

- **Bonding & the Forces between Chains**
- **Conformations**
  - **Ordered**
  - **Disordered**
- **Stacking or Arrangement of Chains in Crystalline Domains**
- **Morphology of Polymer Crystals (and Things like Block Copolymers)**

Interactions

Interaction Energy Depends Upon the Balance Between Attractive and Repulsive Forces

Attractive Forces

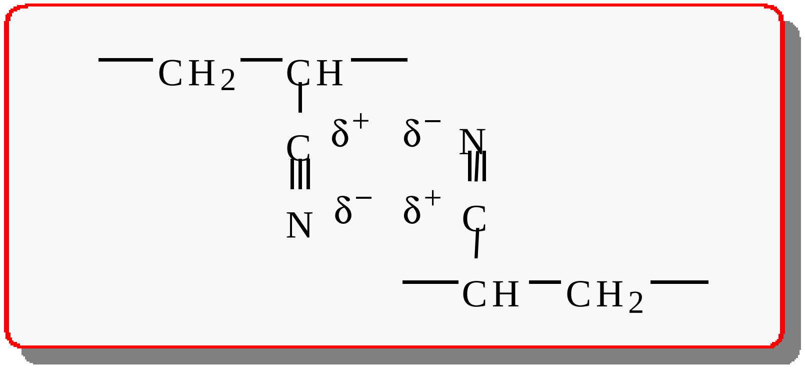
Type of Interaction	**Characteristics**	**Approximate Strength**
Dispersion Forces	Short Range	~0.2 to 2 kcal./mole
Dipole / dipole (Freely Rotating)	Varies as $1/r^6$	
Strong Polar Forces & Hydrogen Bonds	Complex Form, but Short Range	~ 1 to 10 kcal. / mole
Coulombic, as Found in Ionomers	Long Range, Varies 1/r	~ 10 to 20 kcal/ mole (?)

Dispersion Forces

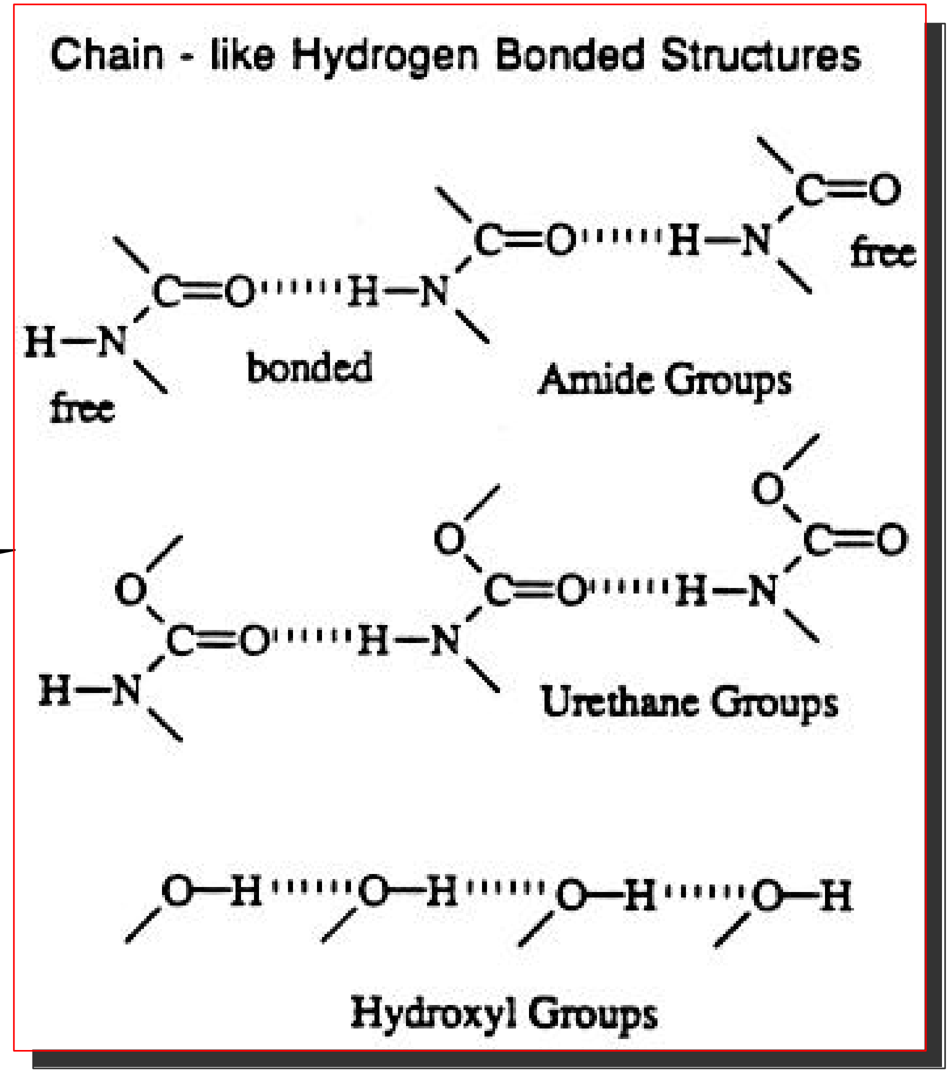
Interaction between fluctuating dipoles whose average value is zero (!)

eg: simple hydrocarbons

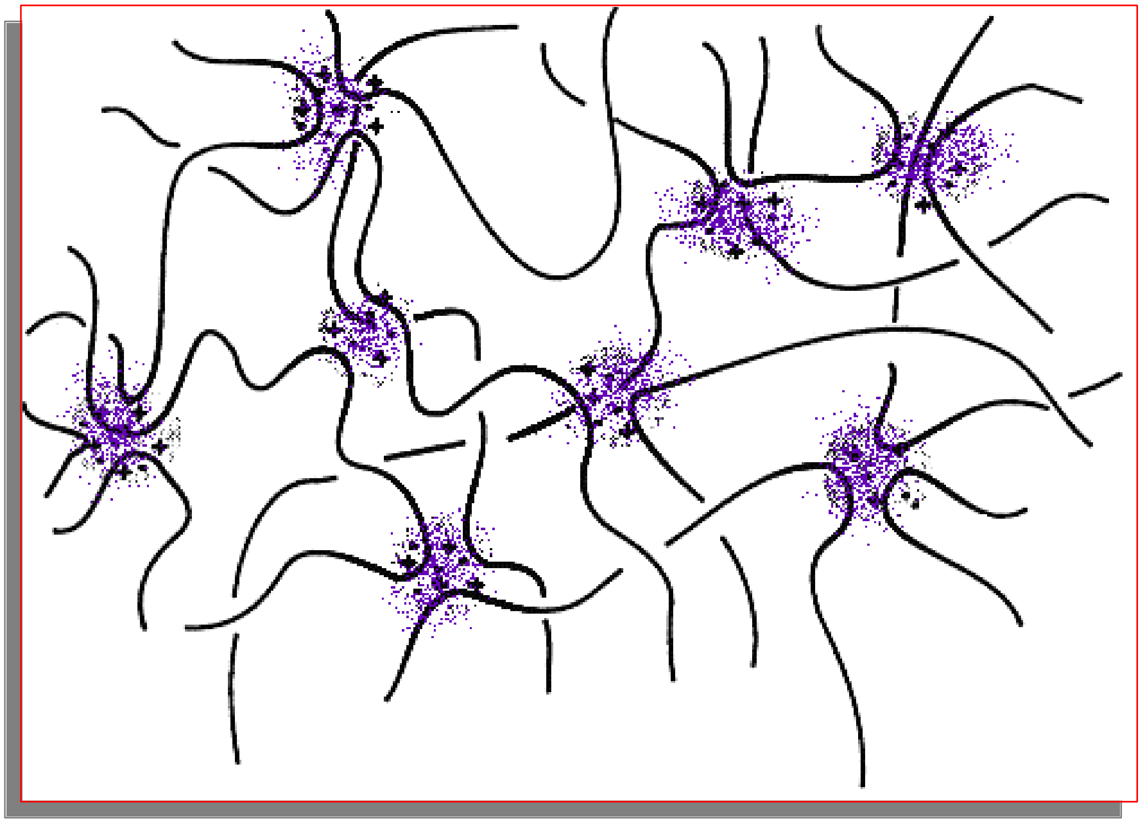
Polar Forces



Hydrogen Bonds



Ionomers



Schematic Diagram of Clusters in an Ionomer.

Interactions

- Hydrocarbons -- PE, IPP, PS, etc.
  - Weak Dispersion Forces
- Polar Polymers -- PVC, PAN, etc.
  - Eg: Those Containing Heteroatoms (O, N, Cl, F) -- Dipole/dipole Interactions
- Hydrogen Bonding Polymers
  - Eg: Nylons, Polyurethanes, etc.
- Ionomers
  - Eg: Surlyn

Increasing Interaction Strength