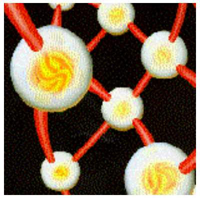


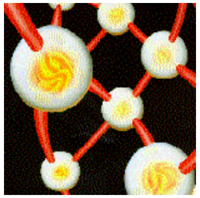
Polymers in Modified Asphalt

Robert Q. Kluttz

KRATON Polymers

Polymers in Modified Asphalt

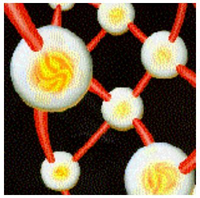
- Types of Polymers
- Compatibility of Polymers
- Effects of Polymers
- Analysis of polymers
- Recovery of PMA



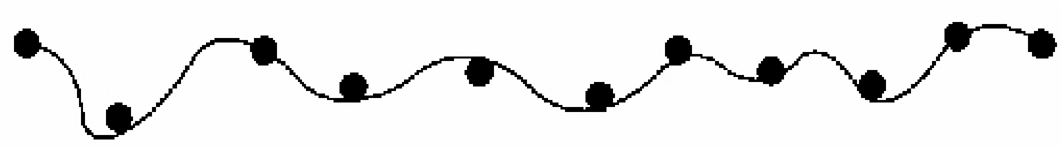
What Is a Polymer?
Some Examples

Polymers are everywhere… You eat them, You wear them, You work with them, You use them all the time!

- carbohydrates
- proteins
- nucleic acids
- wood
- cotton
- silk
- nylon
- polyester
- polystyrene
- PVC
- adhesives
- coatings
- fibers
- elastomers
- foams

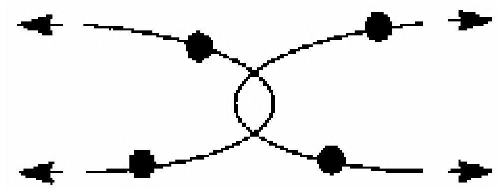


What Is a Polymer?



A polymer is a long string (or net) of small molecules connected together through chemical bonds.

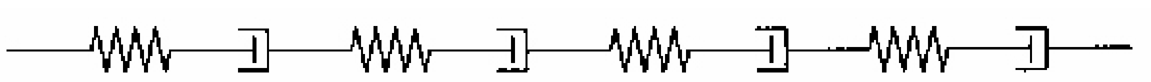
A **polymer** is made of distinct **monomer** units all connected together.



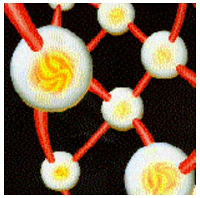
OK, but why is that important?

The chain connectivity of the polymer can give the chain great **strength**...and at the same time they can be very **flexible**.

It also make the polymer viscosity high in both the solution and melt state ... Now liquids behave elastically to some degree ... they are **viscoelastic**.



They are **easily moldable**, castable, soluble, spinnable, etc. ... and so many useful objects can be made from them.



Differing Monomers

(Repeat Units)

<u>Homopolymer</u> *AAAAAAAAAAAAAAAAAAAA*

<u>Copolymers</u>

Random B*A*B*A*BBB*AA*B*A*B*A*B*AA*BB*A*B

Alternating ABABABABABABABABABAB

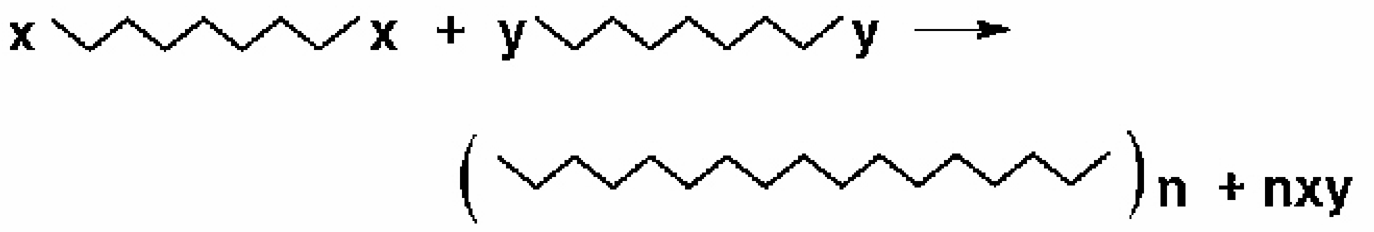
Block BBBBBB*AAAAAAAA*BBBBBB

Grafted

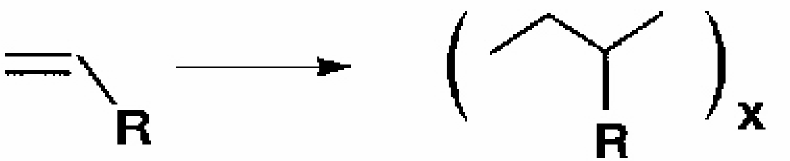
AA AAA AAA
BBBBBBBBBBBBBBBBBBBB
AAA AAA

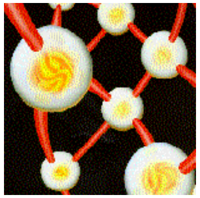
Polymer Synthesis

- Condensation Polymerization
  - Splits off a small molecule (usually water)
  - Requires at least di-functional monomers

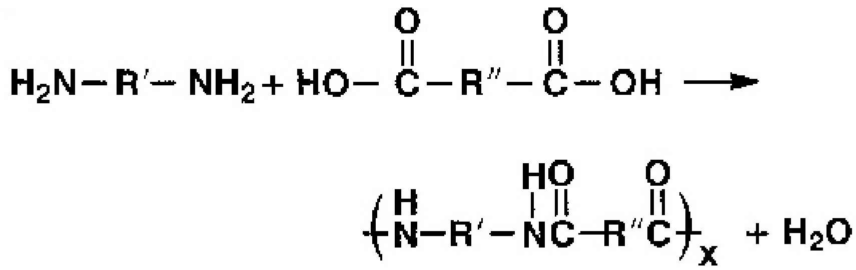


- Addition Polymerization
  - No molecule split off
  - Involves the opening of a double bond

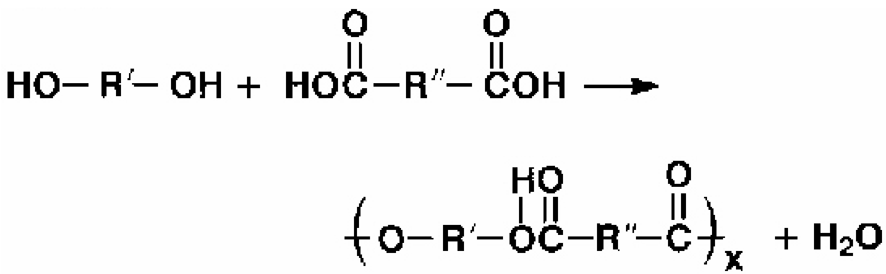




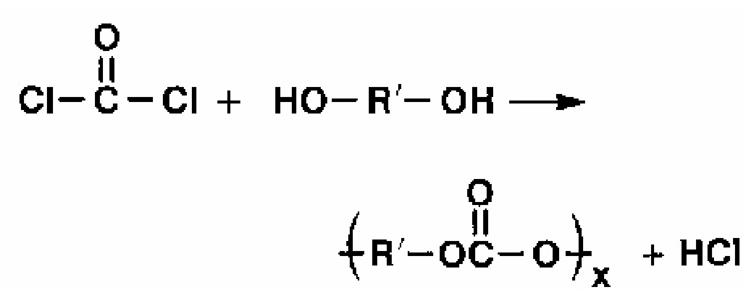
Condensation Polymers



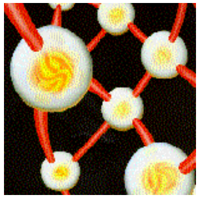
Polyamides



Polyesters



Polycarbonates



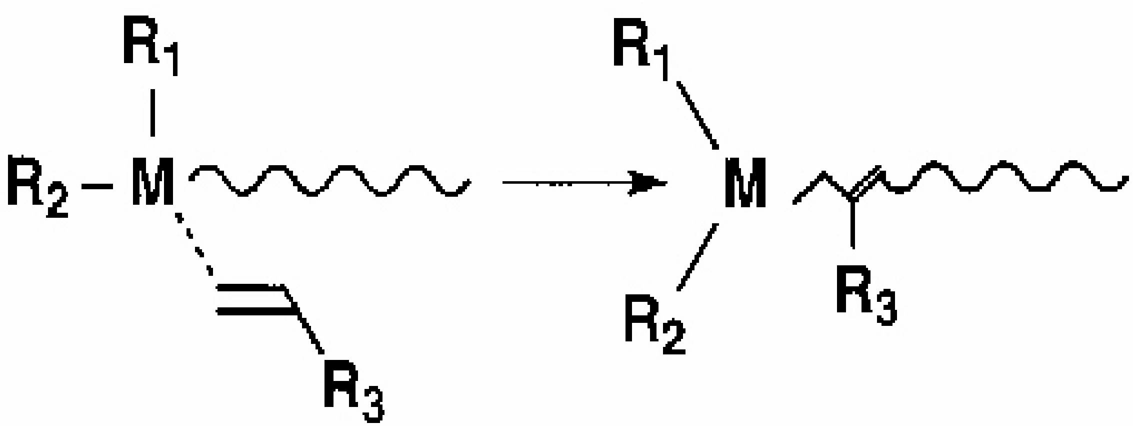
Addition Polymerization

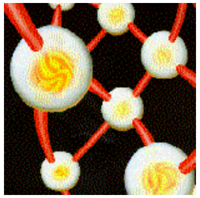
Cationic

$$R^{\oplus} + M \longrightarrow RM^{\ominus} \xrightarrow{M} RMMMM^{\ominus}$$

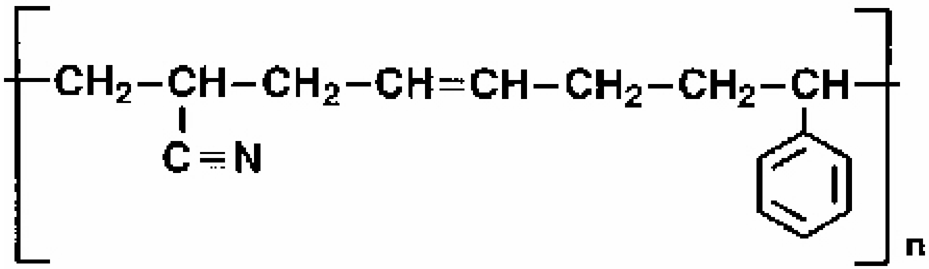
Coordination Polymerization

Ziegler Natta

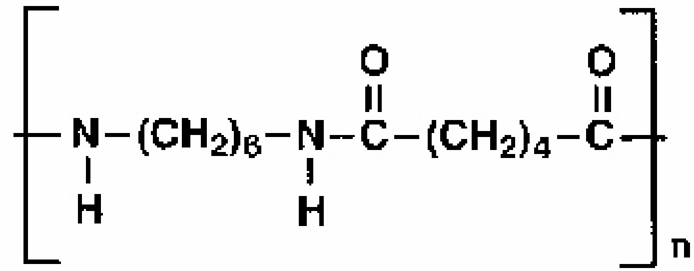




Structures of Common Polymers

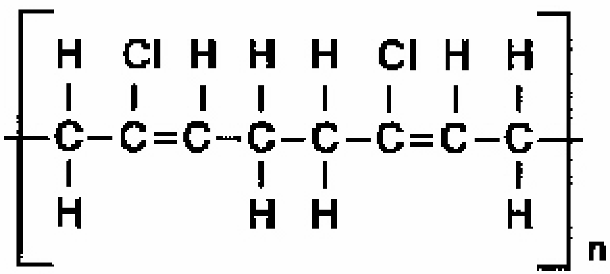


ABS T_g = 110° to 125°C

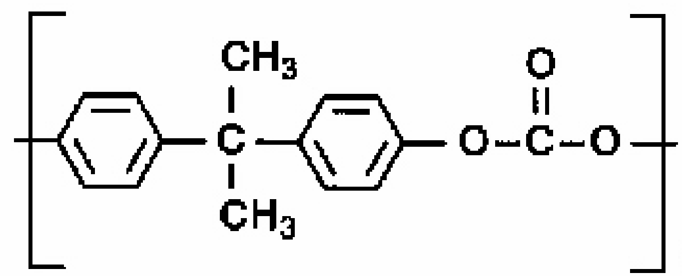


Nylon 6,6 MP = 240° to 265°C

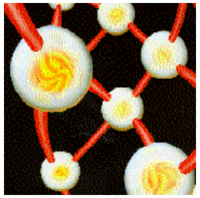
T_g = 50°C to 60°C



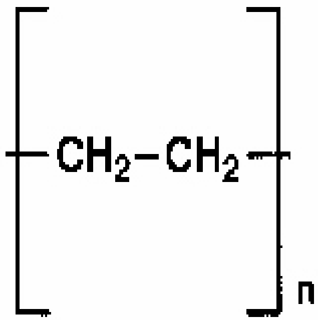
Neoprene $T_g \simeq$ −40° to −20°C



Polycarbonate T_g = +140° to +150°C

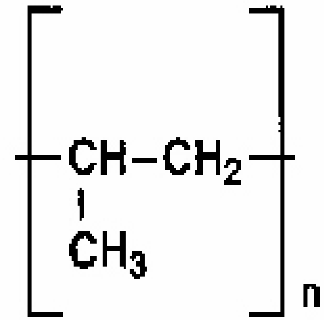


Structures of Common Polymers



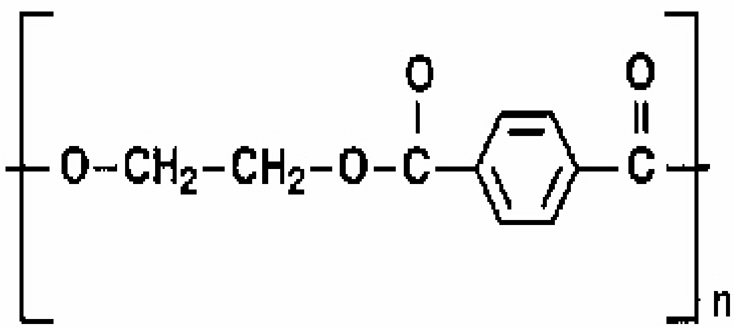
Polyethylene

Mp = 130° to 140°C
Tg = −125°C



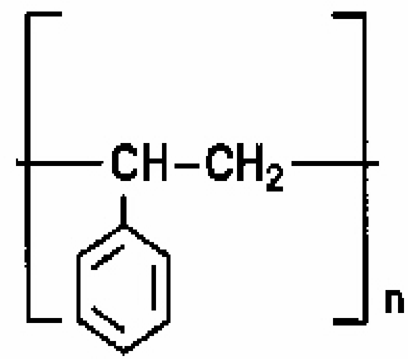
Polypropylene

MP = 165° to 175°C
T_g = −20°C to −5°C



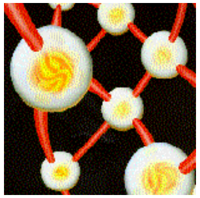
Polyethylene Terephthalate (PET)

Mp = 245° to 265°C
Tg = 70° to 80°C

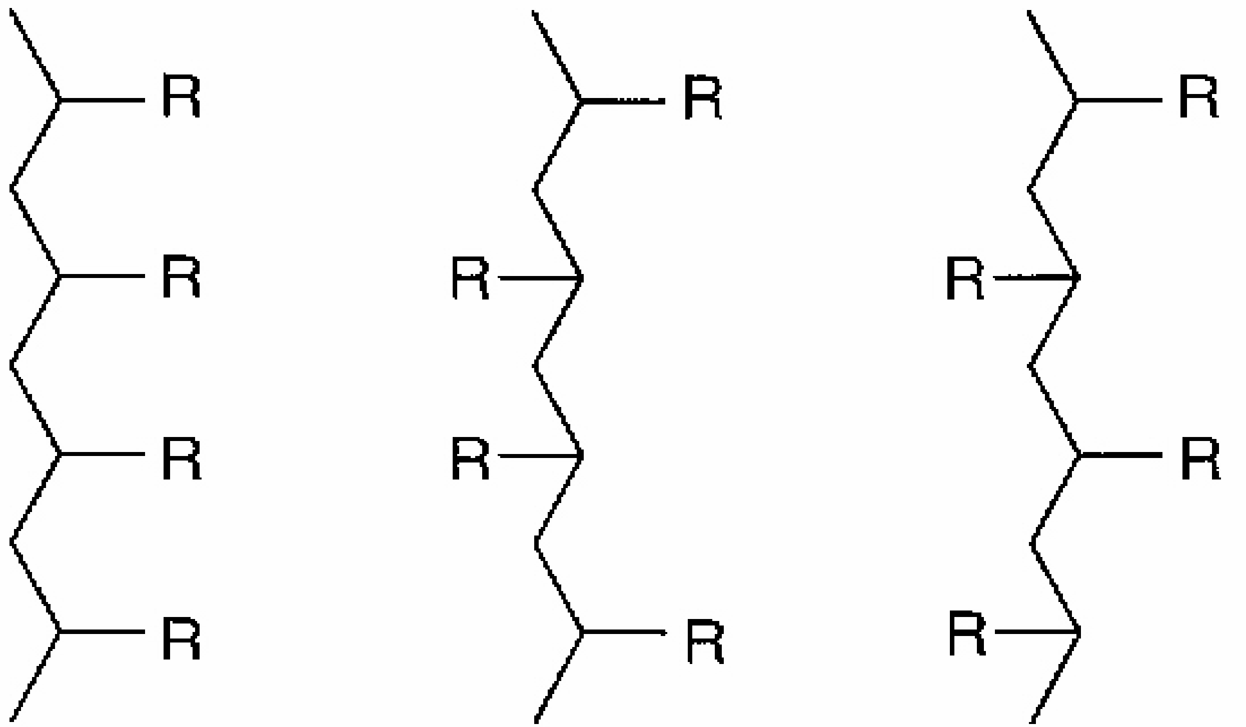


Polystyrene

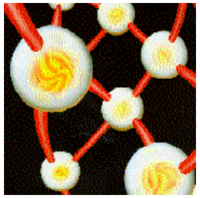
T_g = 90° to +110°C



Stereoisomerism

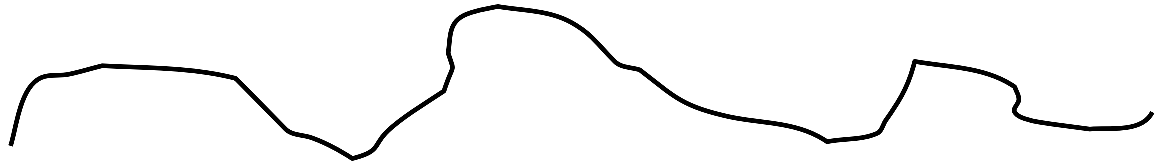


isotactic | atactic | syndiotactic

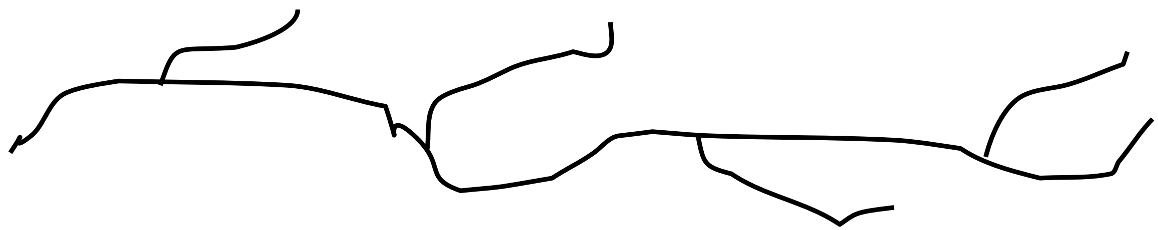


Polymer Structures

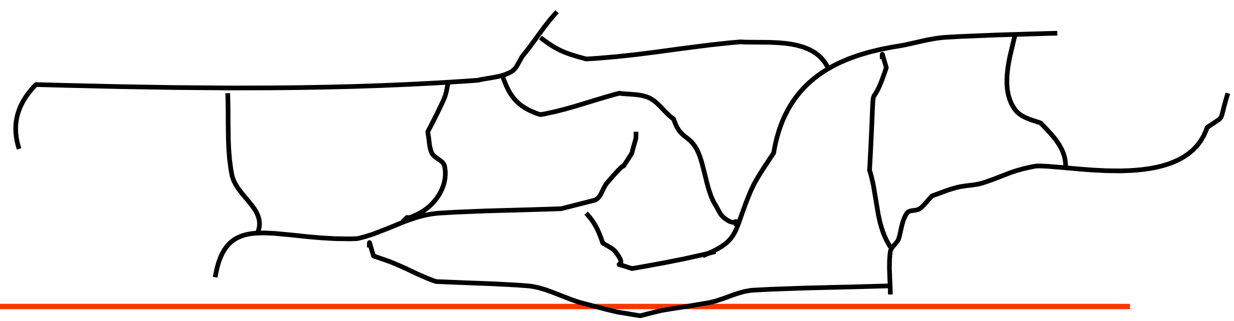
Linear



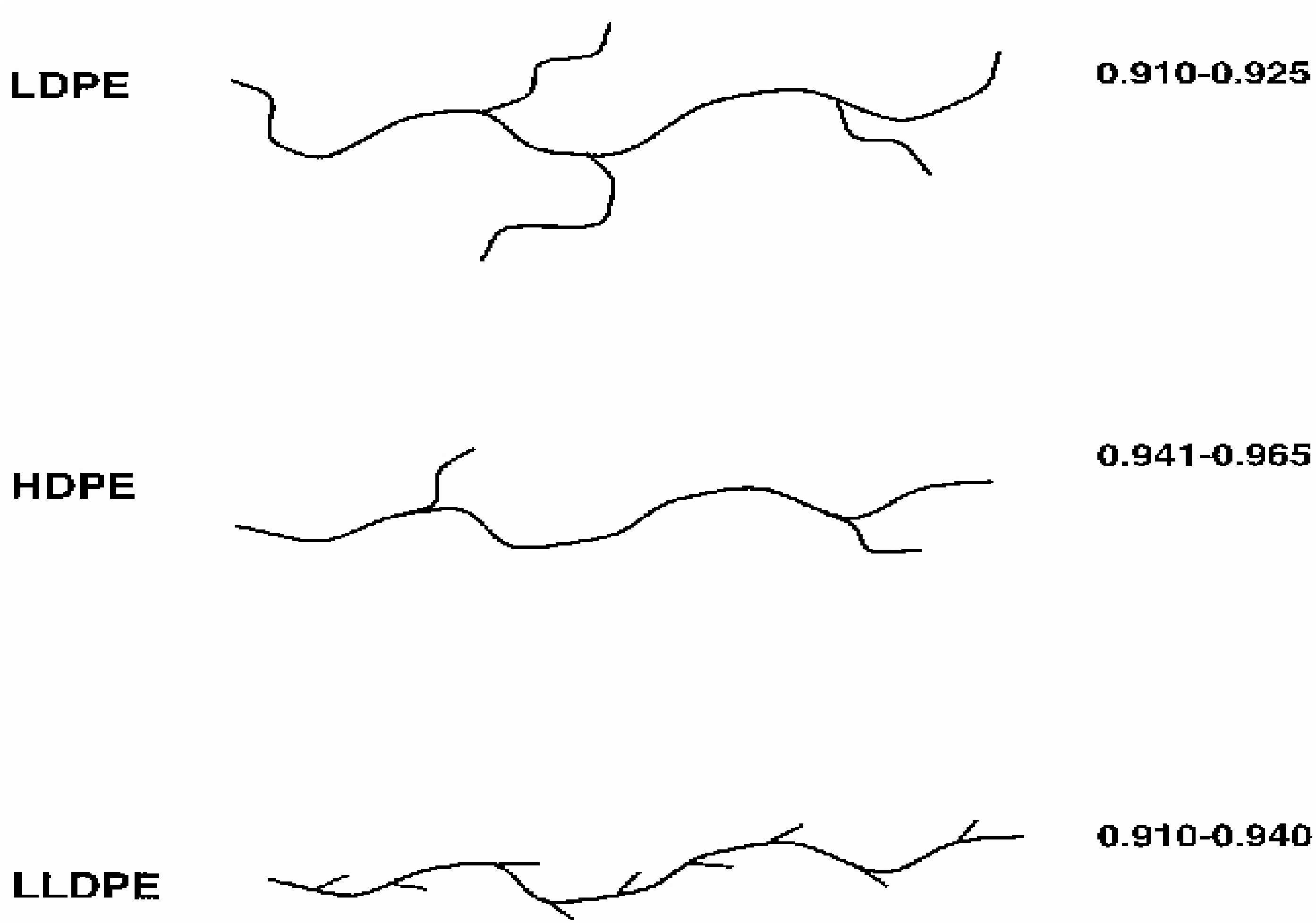
Branched



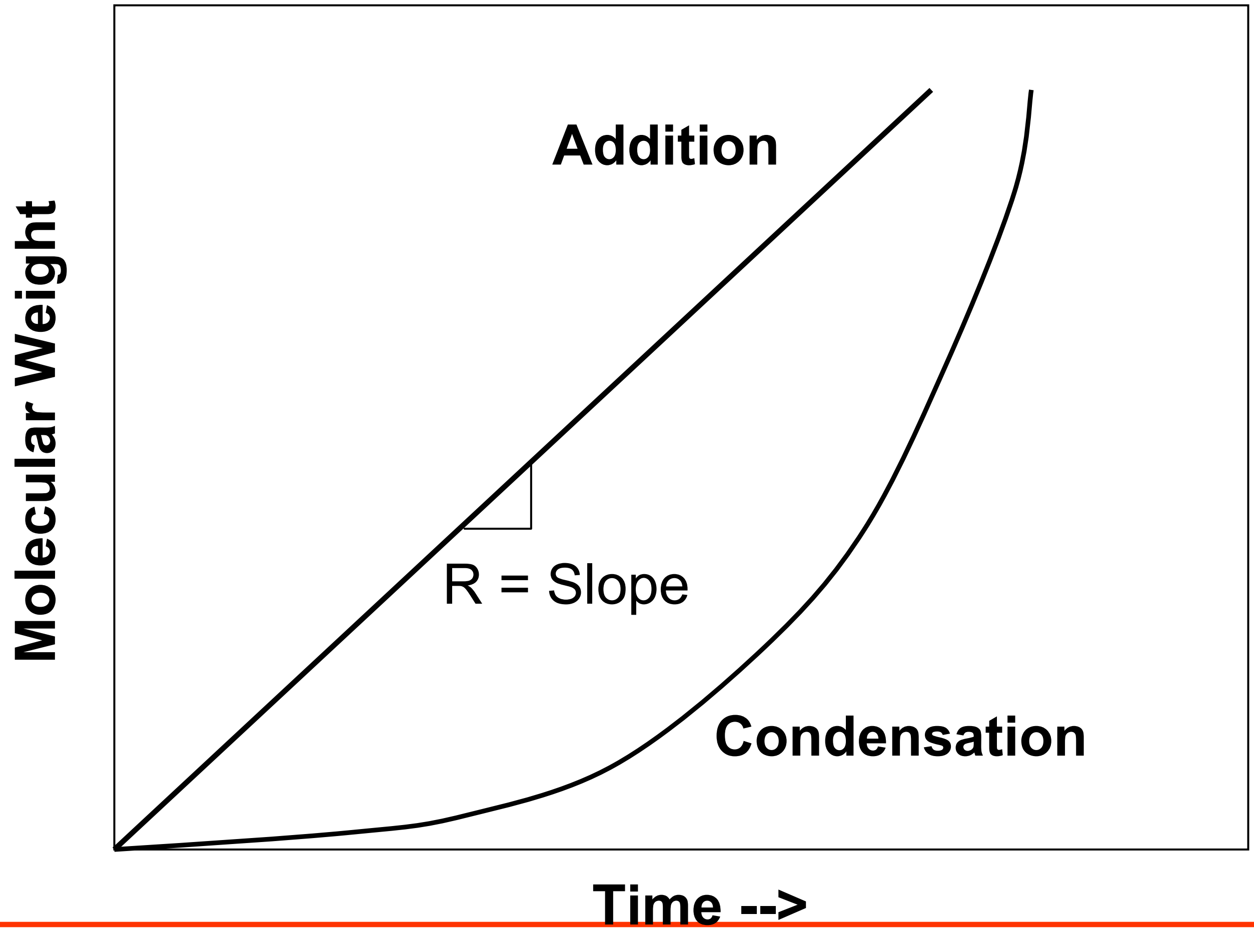
Cross-linked



Types of Branching

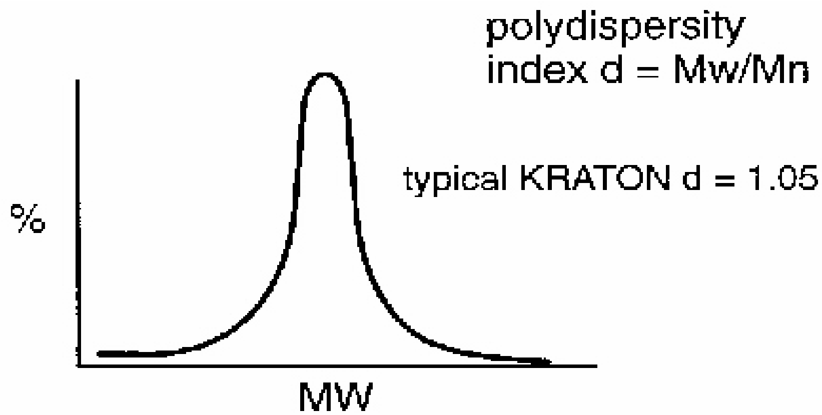


Molecular Weight Growth

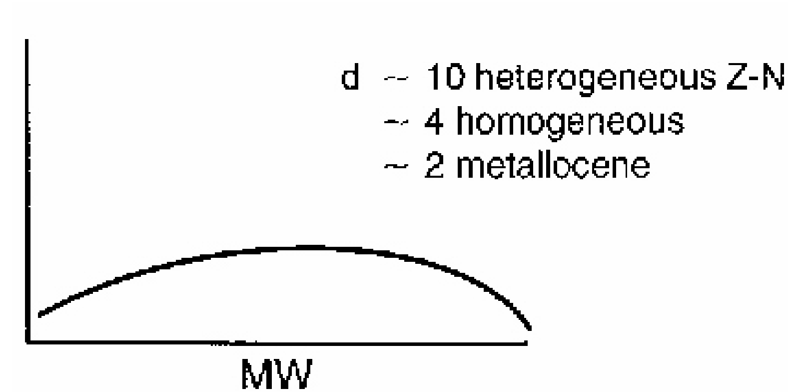


R = constant implies no termination

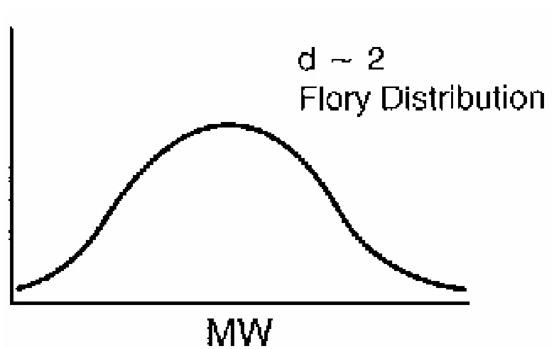
Molecular Weight Distributions



ANIONIC



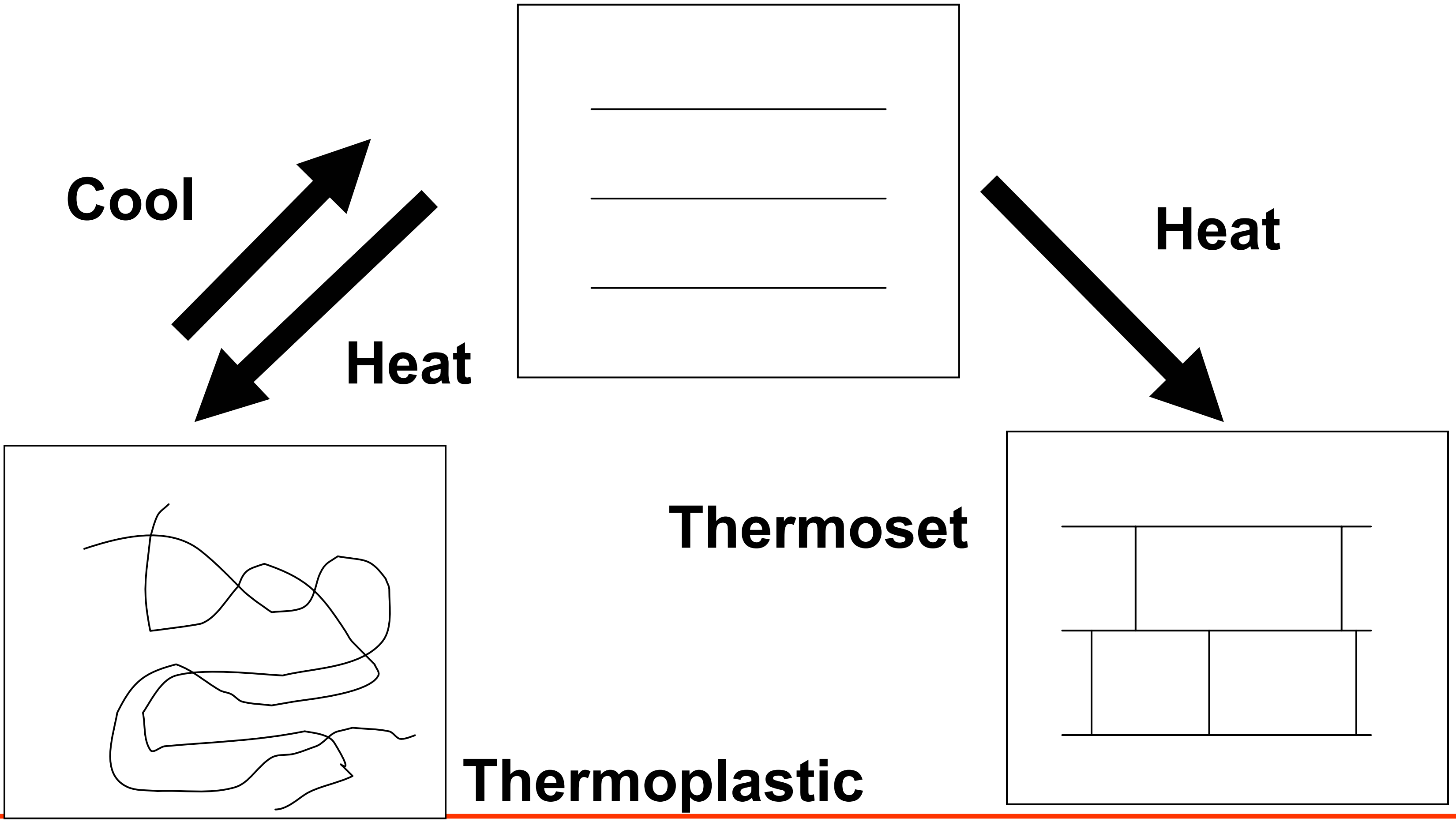
ZIEGLER-NATTA FREE RADICAL



CONDENSATION

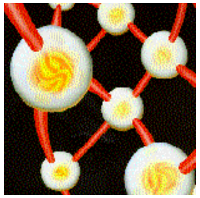
Type of reaction determines molecular weight distribution. Measured by GPC.

Thermoplastic vs. Thermoset



Physical States of Polymers

- **Amorphous**
  - Glass Transition Temperature (Tg)
- **Semi-crystalline**
  - Glass Transition Temperature <u>and</u> melting point (Tm)
  - Regular Structure
  - Hydrogen Bonding or Dipole Interactions



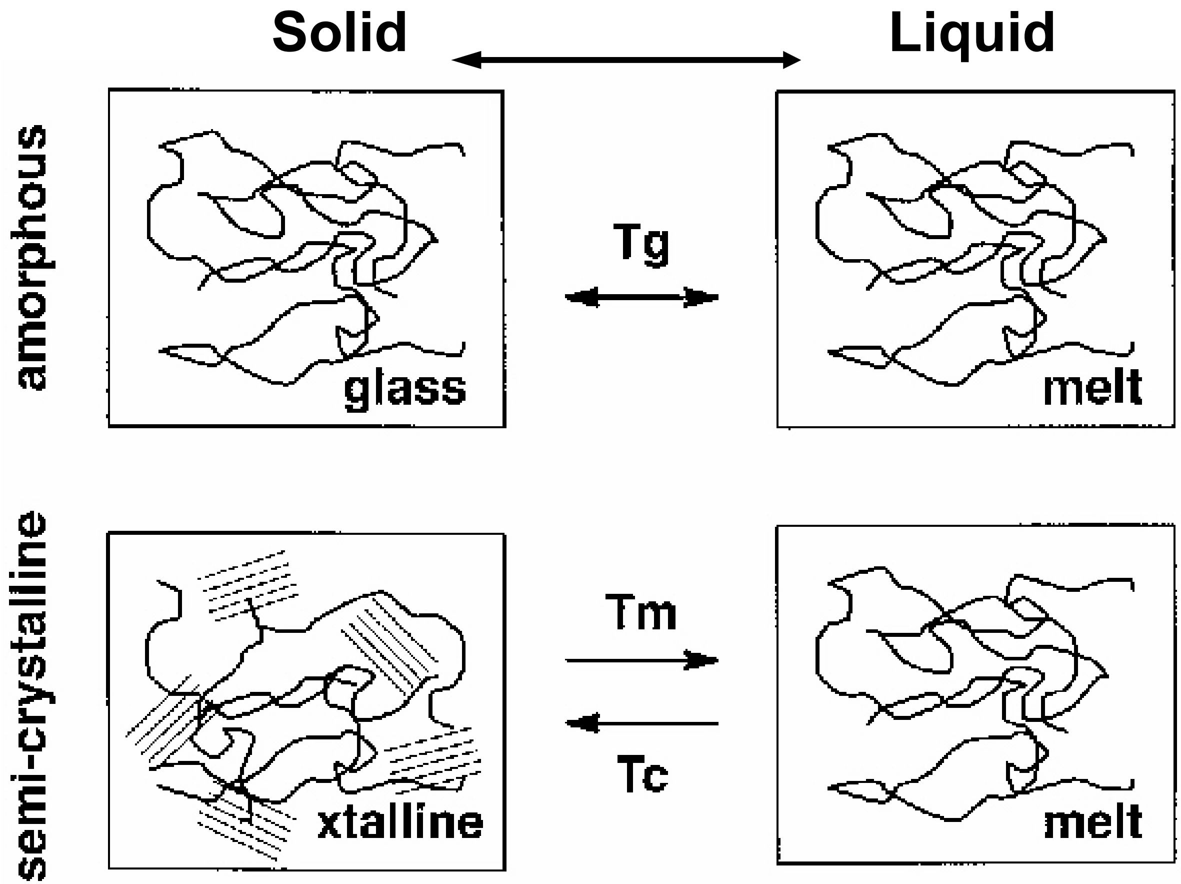
Physical States of Polymers

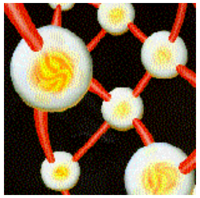
Glass:

Not ordered on a molecular scale, sometimes very brittle, easily penetrated by solvents/plasticizers

Crystal:

very strong local order, not easily penetrated by solvents, Tm can be relatively high



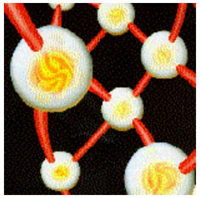


Separation

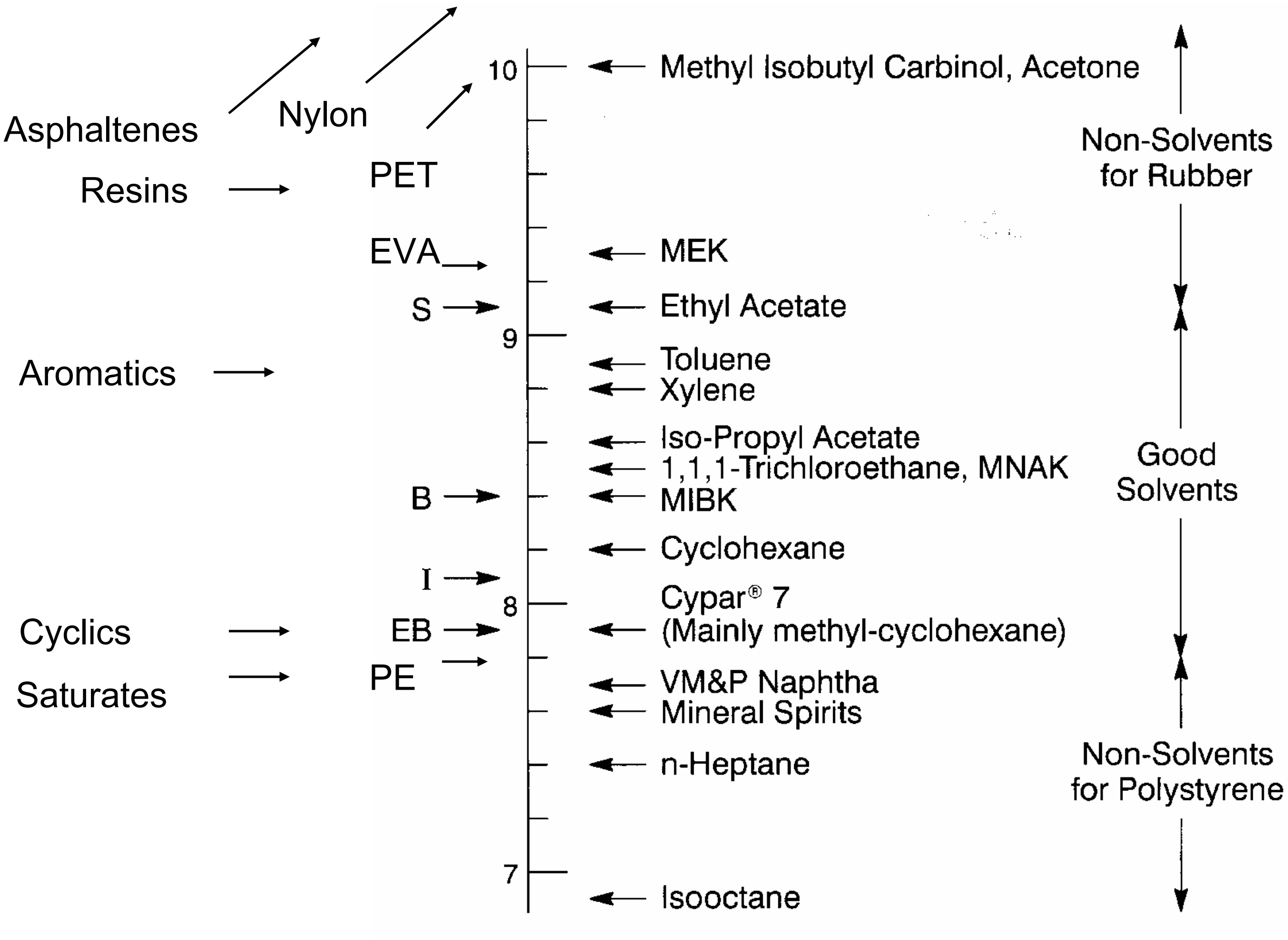
- **My asphalt has waxes, asphaltenes, metals, salts, etc., yet it stays together. Why do my polymers separate?**
- **Because Flory-Huggins says so!**

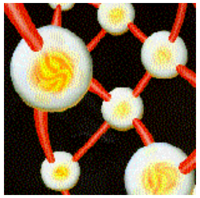
- $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$
- $\Delta G_{mix}/RT = (\varphi_A/X_A)\ln\varphi_A + (\varphi_B/X_B)\ln\varphi_B + \chi_{AB}\varphi_A\varphi_B$

- **where**
- $\chi_{AB} = (\delta A - \delta B)^2/RT$



Solubility Parameters





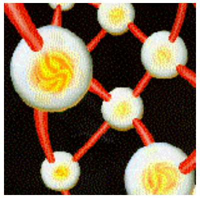
“Dispersion” in Asphalt

- What is the appropriate scale?
- Millimeter scale – visible particles
- Micrometer scale – HMAC film thickness
- Nanometer scale – molecular size

- Working Premise – to truly be considered a binder modifier, the modifier must disperse at approximately the scale of HMAC film thickness and behave more as a liquid than as a solid at mixing and compaction temperatures.

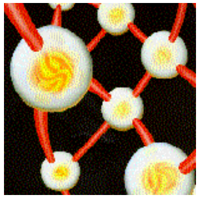
Polymer Requirements for Asphalt

- **Requirements for Dispersion in Asphalt**
  - Thermoplastic
  - Suitable Polarity
  - Minimal Ionic Interactions
  - Minimal Crystallinity
- **Requirements for Processing in Asphalt**
  - Suitable Molecular Weight
  - Suitable Stability
  - Suitable Dispersibility at Processing Temp



So What Does That Leave?

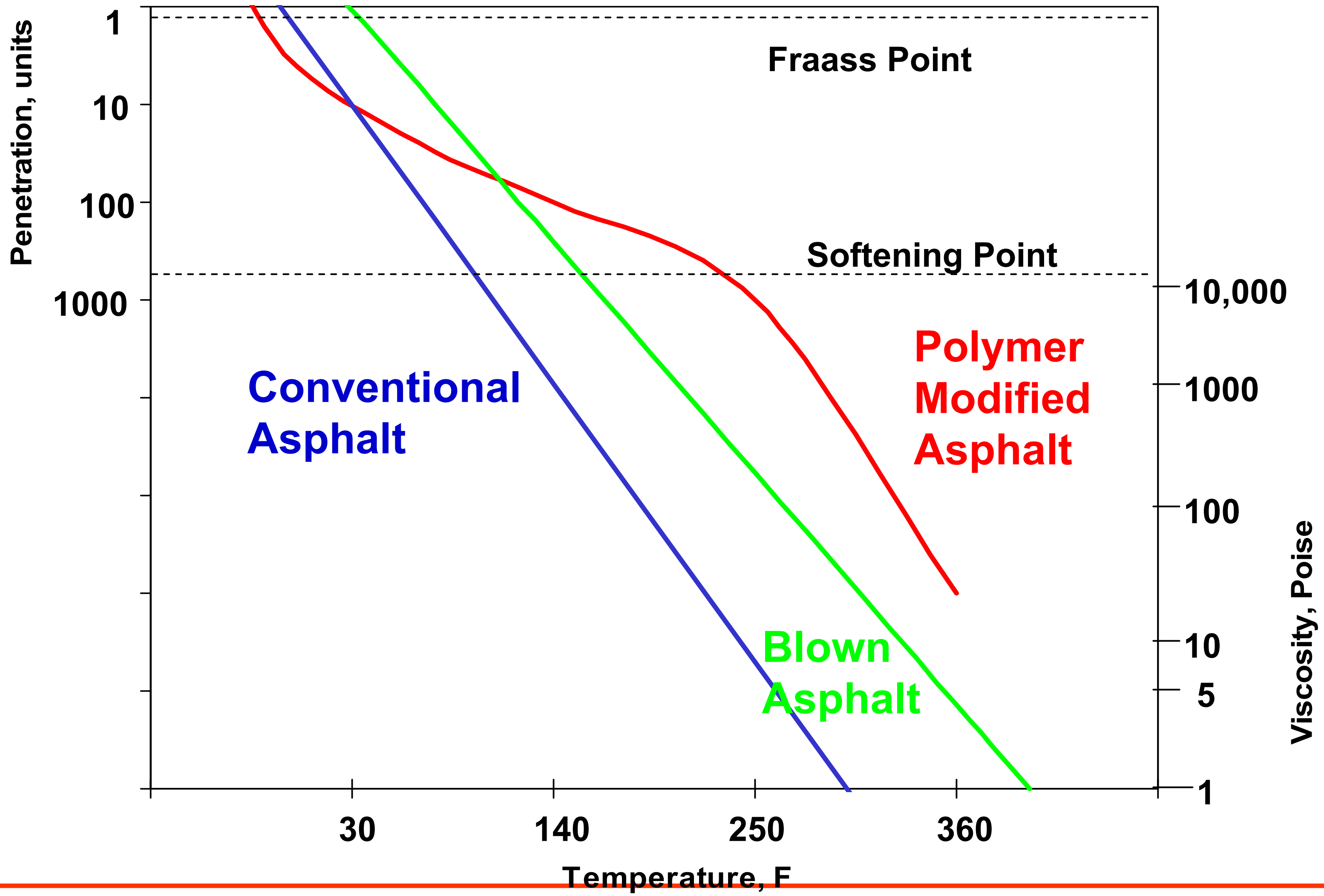
- **Low Crystallinity Polyolefins (LDPE, APP, etc.)**
- **Styrene Diene Polymers**
  - Styrenic Block Polymers (SBS)
  - Random Styrene Diene Polymers (SBR)
- **Olefin Vinyl Polymers (EVA, PVC)**
- **Olefin Acrylic Polymers (Ethylene Acrylates)**



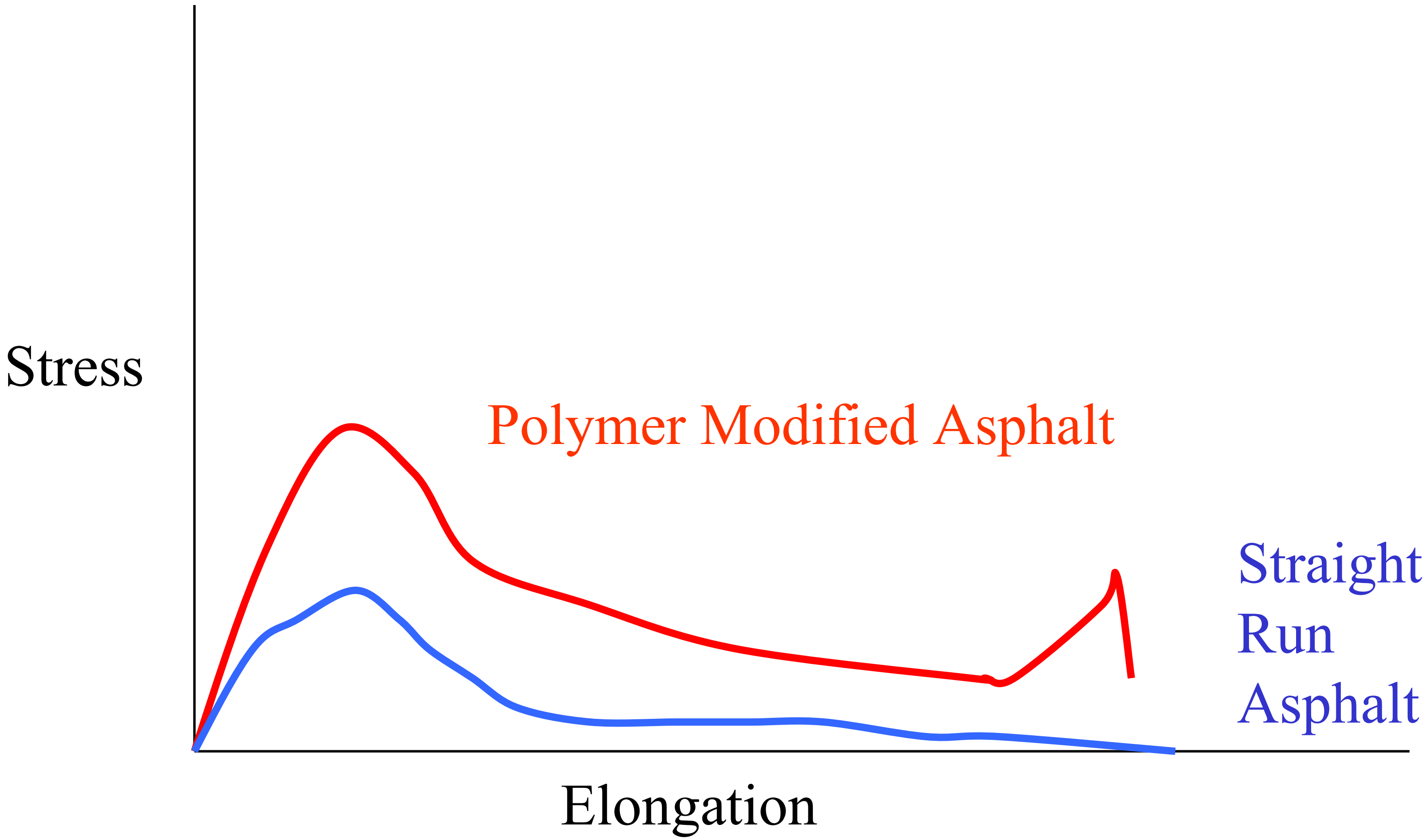
Physical Effects of Polymers in Asphalt

- Reduce Temperature Susceptibility
- Increase Tensile Strength
- Increase Elasticity

Temperature Susceptibility of Polymer Modified Asphalt

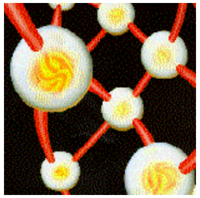


Tensile Properties



Analysis of Polymers in Asphalt

- Infrared Analysis
- NMR Analysis
- GPC Analysis
- Microscopy

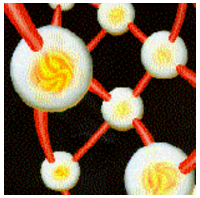


Recovery of PMA from Hot Mix

- Polymers may crosslink
- Polymers may adhere strongly to aggregate
- Polymers may be less soluble in the extraction medium than they are in hot asphalt
- **There is no guarantee that extracting 98+% of asphalt will also extract 98+% of the polymer modifier.**

Recovery of PMA from Hot Mix

- Asphalt and polymers age.
- The chemical changes may alter the thermodynamic minimum morphology.
- The semi-rigid matrix of PMA may not allow morphological changes to accommodate the change in thermodynamically favored morphology
- Dissolving, then reprecipitating, the PMA will most definitely allow morphological rearrangement.
- **Thus the morphology of extracted PMA, and thus the rheological properties of extracted PMA, may be different from those in in situ PMA in hot mix.**



Thank you for your kind attention!

Questions? Comments?