Polymers in Modified Asphalt

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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!

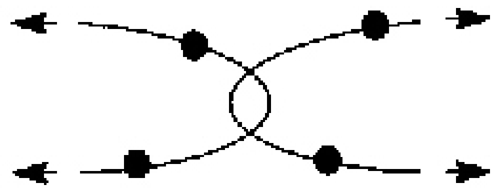
- carbohydrates
- proteins
- nucleic acids
- wood
- cotton
- silk
- nylon
- polyester

- polystyrene
- PVC
- adhesives
- coatings
- fibers
- elastomers
- foams

What Is a Polymer?

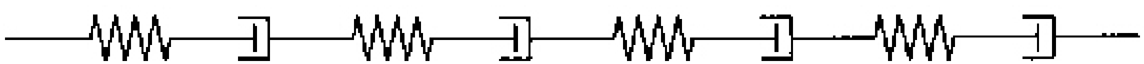
A polymer is a long string (or net) of small molecules connected together through chemical bonds.

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)

Homopolymer *AAAAAAAAAAAAAAAAAAAA*

Copolymers

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

Alternating ABABABABABABABABABAB

Block BBBBBB*AAAAAAAA*BBBBBB

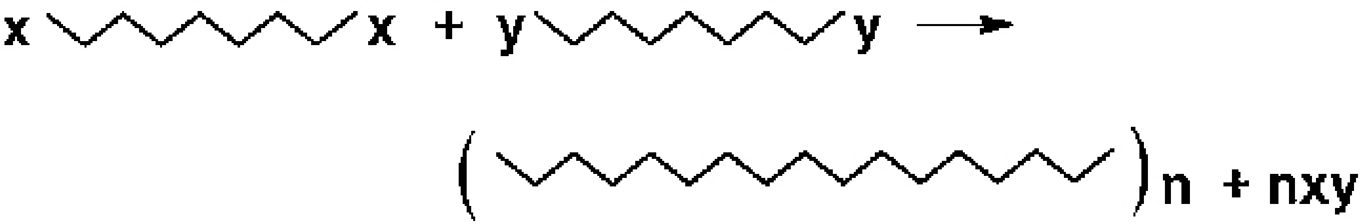
Grafted

A A A A A A A A

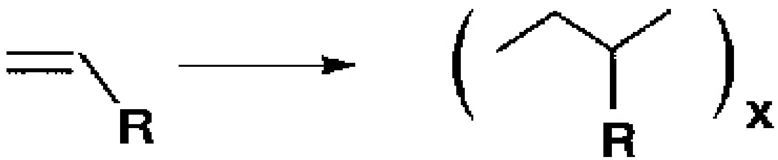
BBBBBBBBBBBBBBBBBBBB

A A A A A A

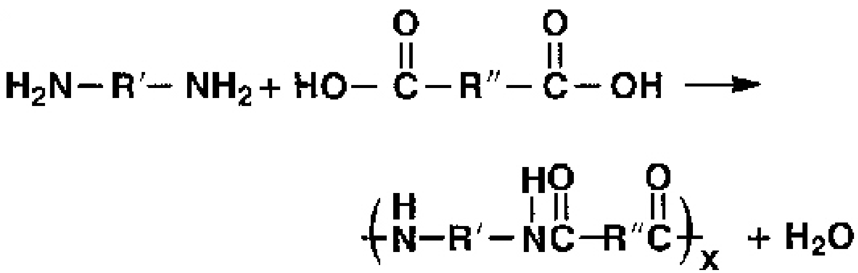
- Condensation Polymerization
  - Splits off a small molecule (usually water)
  - Requires at least di-functional monomers



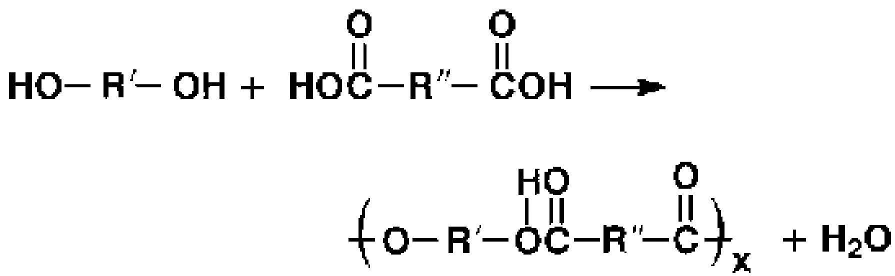
- Addition Polymerization
  - No molecule split off
  - Involves the opening of a double bond



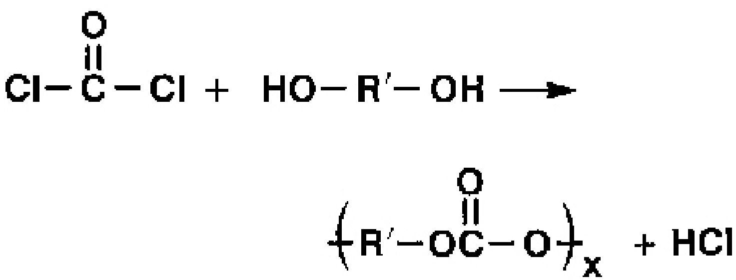
Condensation Polymers



Polyamides



Polyesters



Polycarbonates

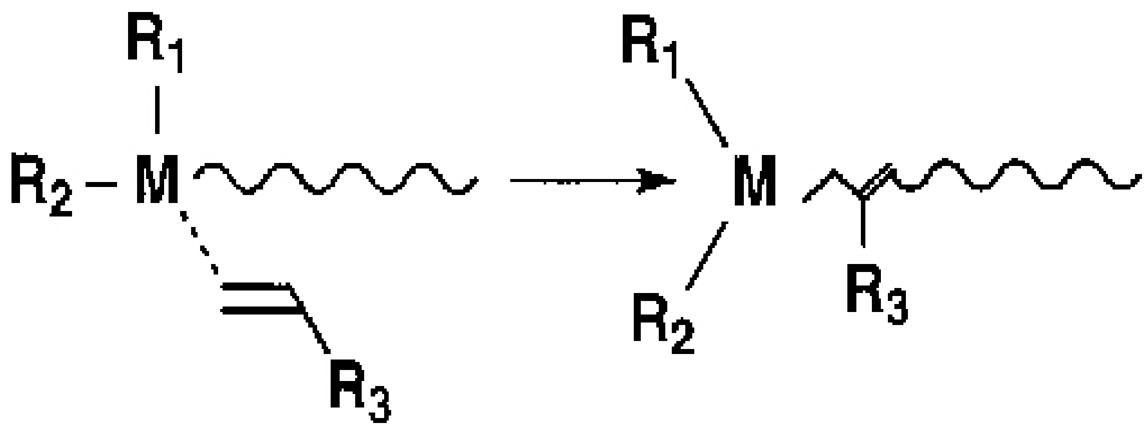
Addition Polymerization

Cationic

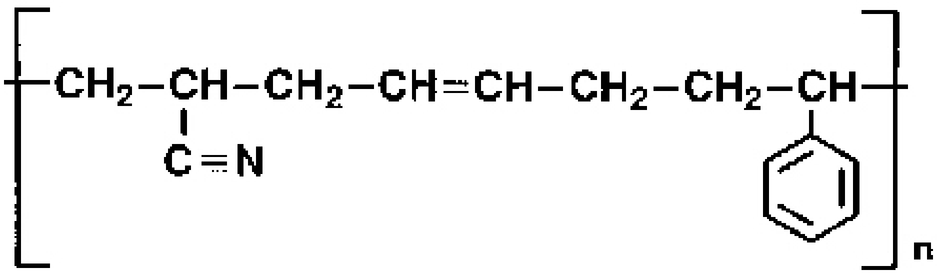
$$RI^{\circ} + M \longrightarrow RMI^{\ominus} \xrightarrow{M} RMMMMI^{\ominus}$$

Coordination Polymerization

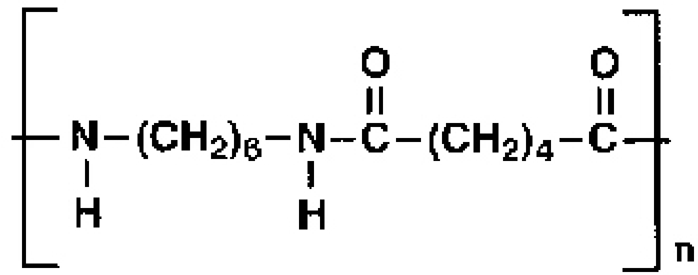
Ziegler Natta



Structures of Common Polymers

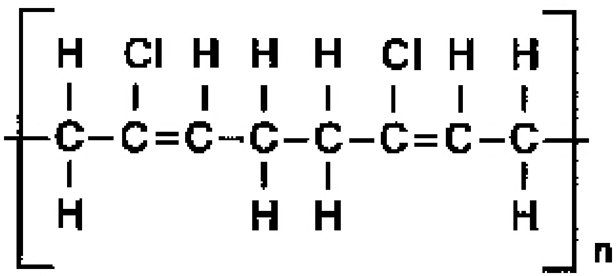


ABS $T_g = 110°$ to $125°C$

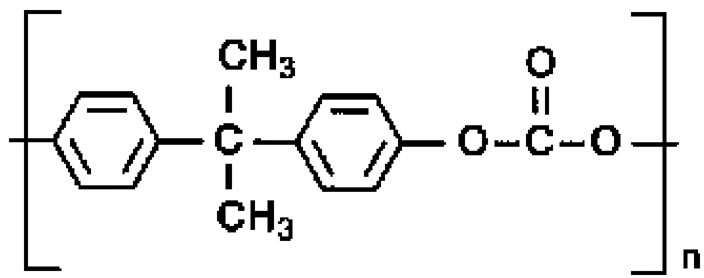


Nylon 6,6 $MP = 240°$ to $265°C$

$T_g = 50°C$ to $60°C$

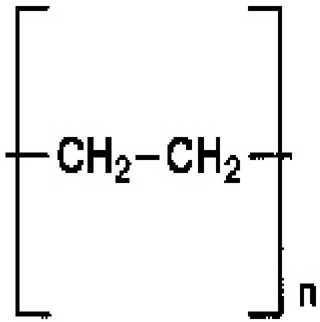


Neoprene $T_g \simeq -40°$ to $-20°C$

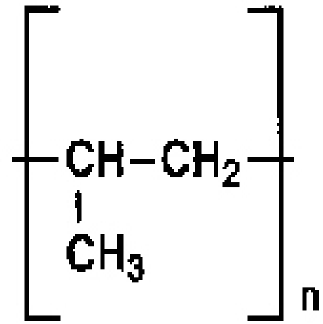


Polycarbonate $T_g = +140°$ to $+150°C$

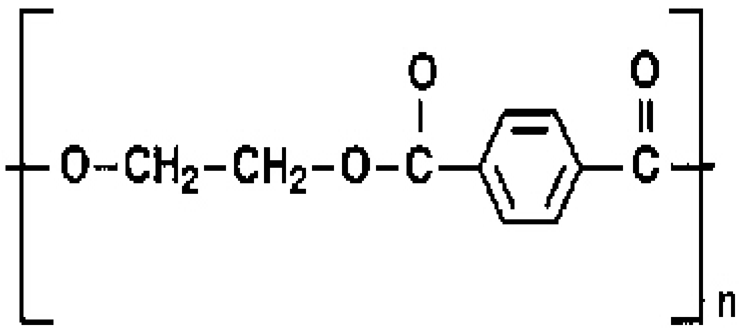
Structures of Common Polymers



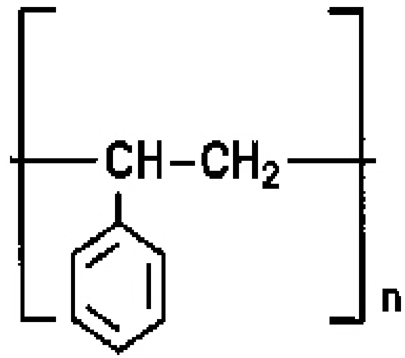
Polyethylene Mp = 130° to 140°C
Tg = −125°C



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

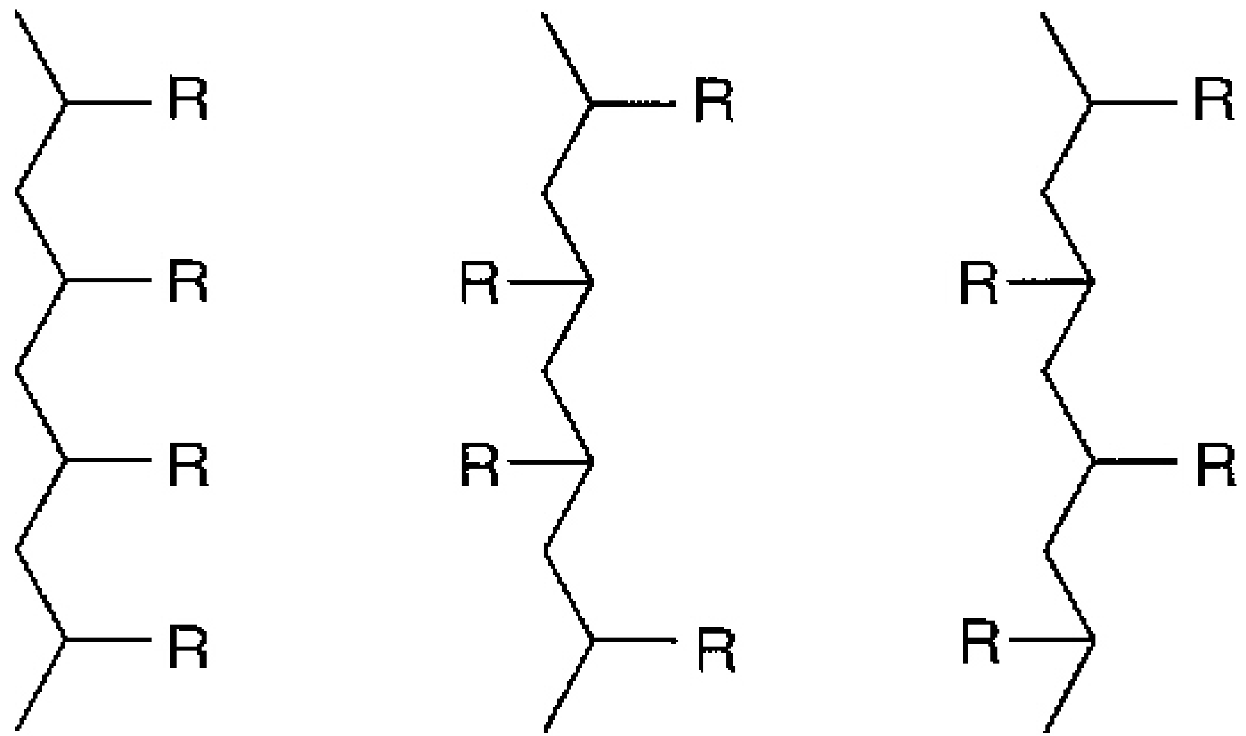


Polyethylene Terephthalate (PET) Mp = 245° to 265°C
Tg = 70° to 80°C



Polystyrene T_g = 90° to +110°C

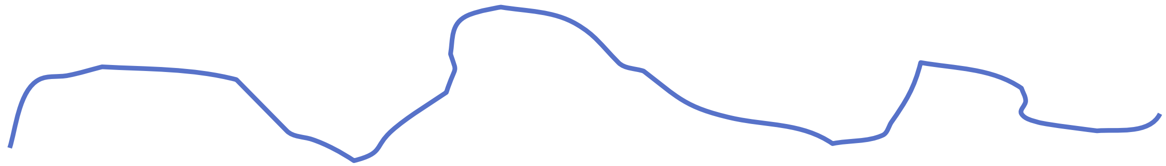
Stereoisomerism



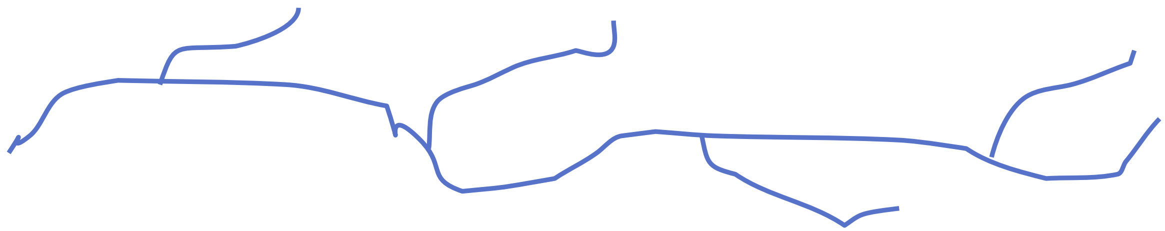
isotactic atactic syndiotactic

Polymer Structures

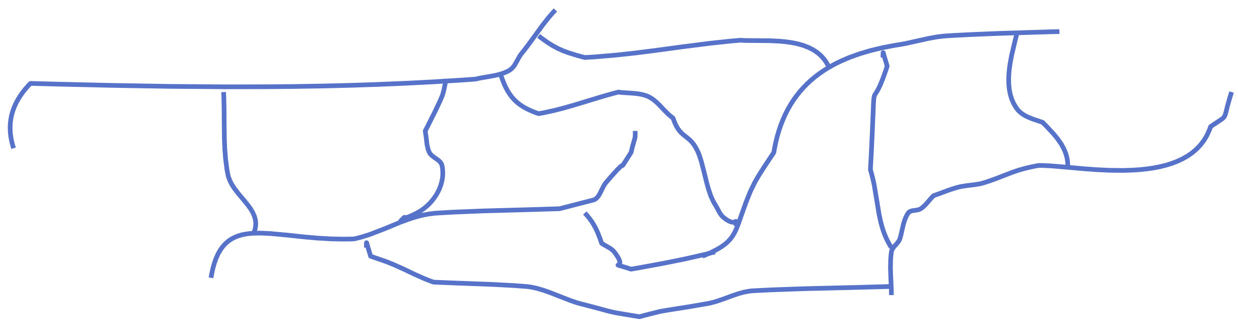
Linear



Branched

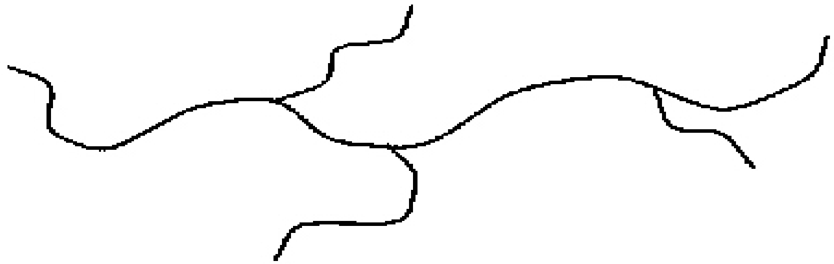


Cross-linked



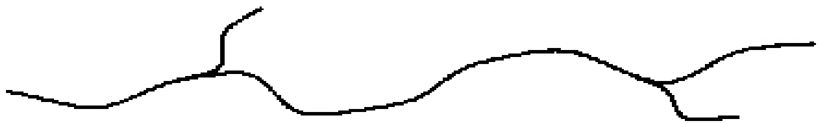
Types of Branching

LDPE



0.910-0.925

HDPE

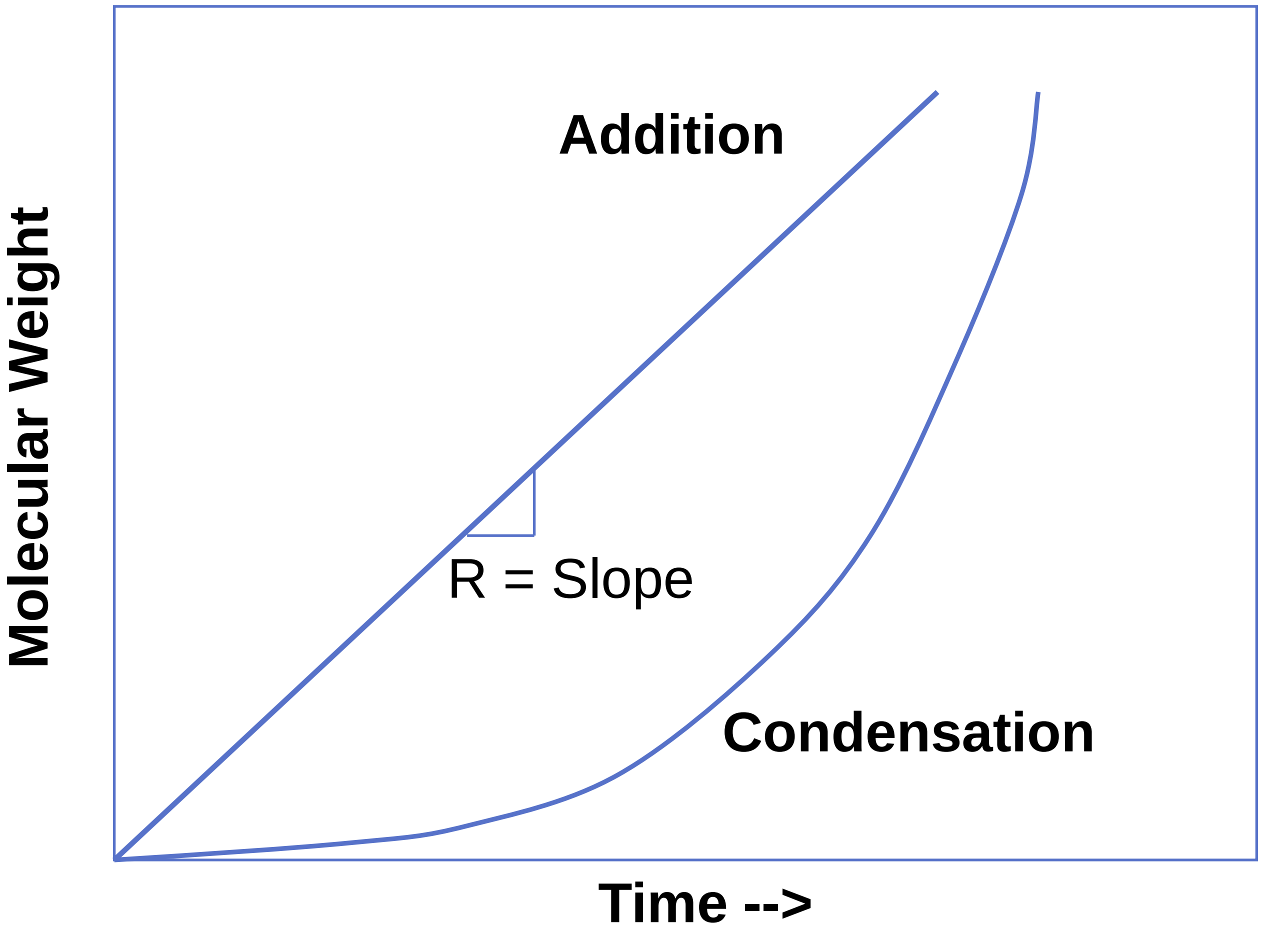


0.941-0.965

LLDPE

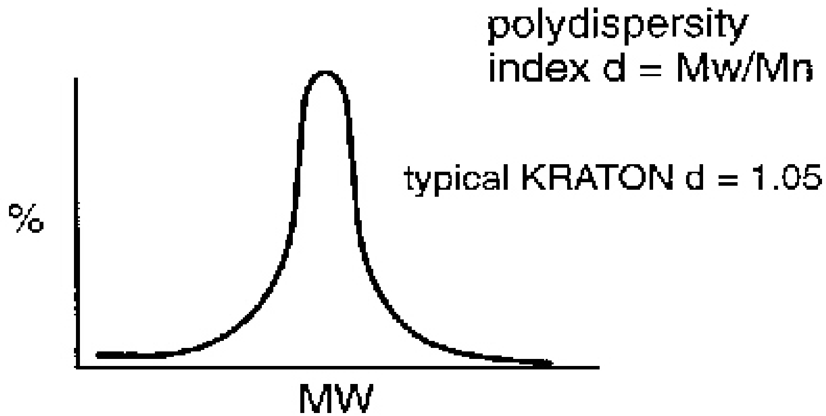
0.910-0.940

Molecular Weight Growth

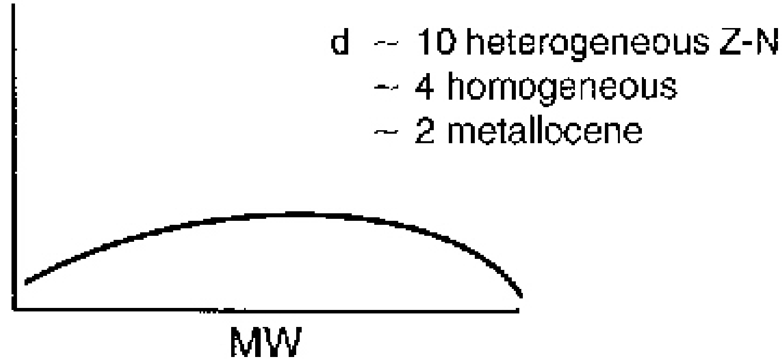


R = constant implies no termination

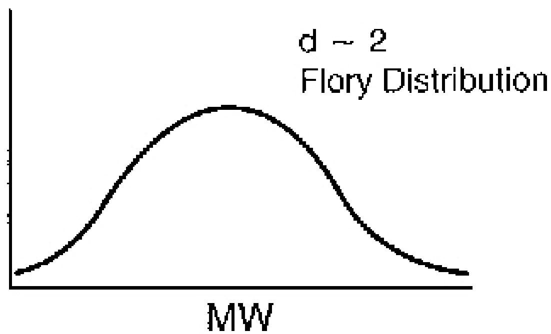
Molecular Weight Distributions



ANIONIC



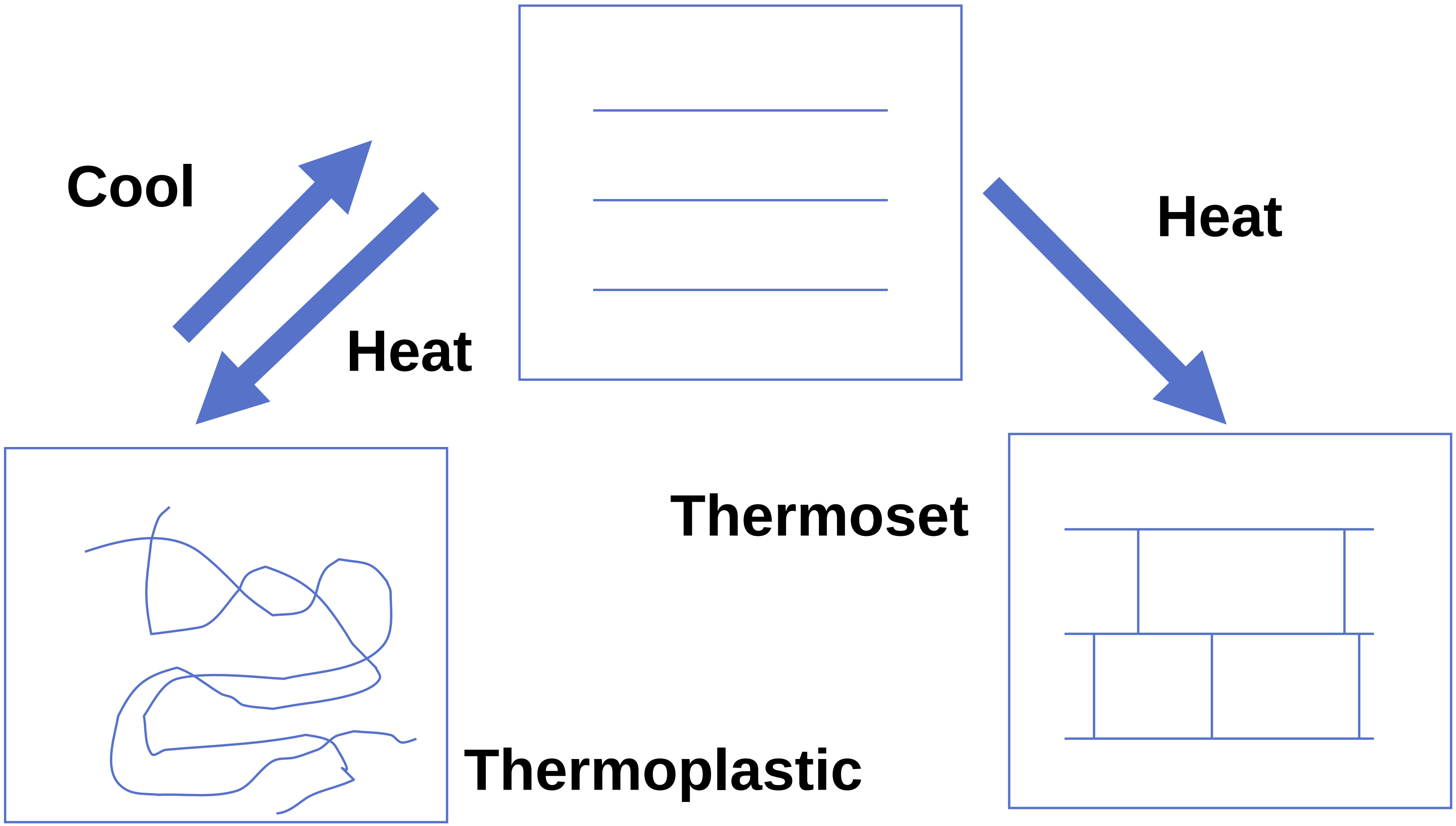
ZIEGLER-NATTA FREE RADICAL



CONDENSATION

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

Thermoplastic vs. Thermoset



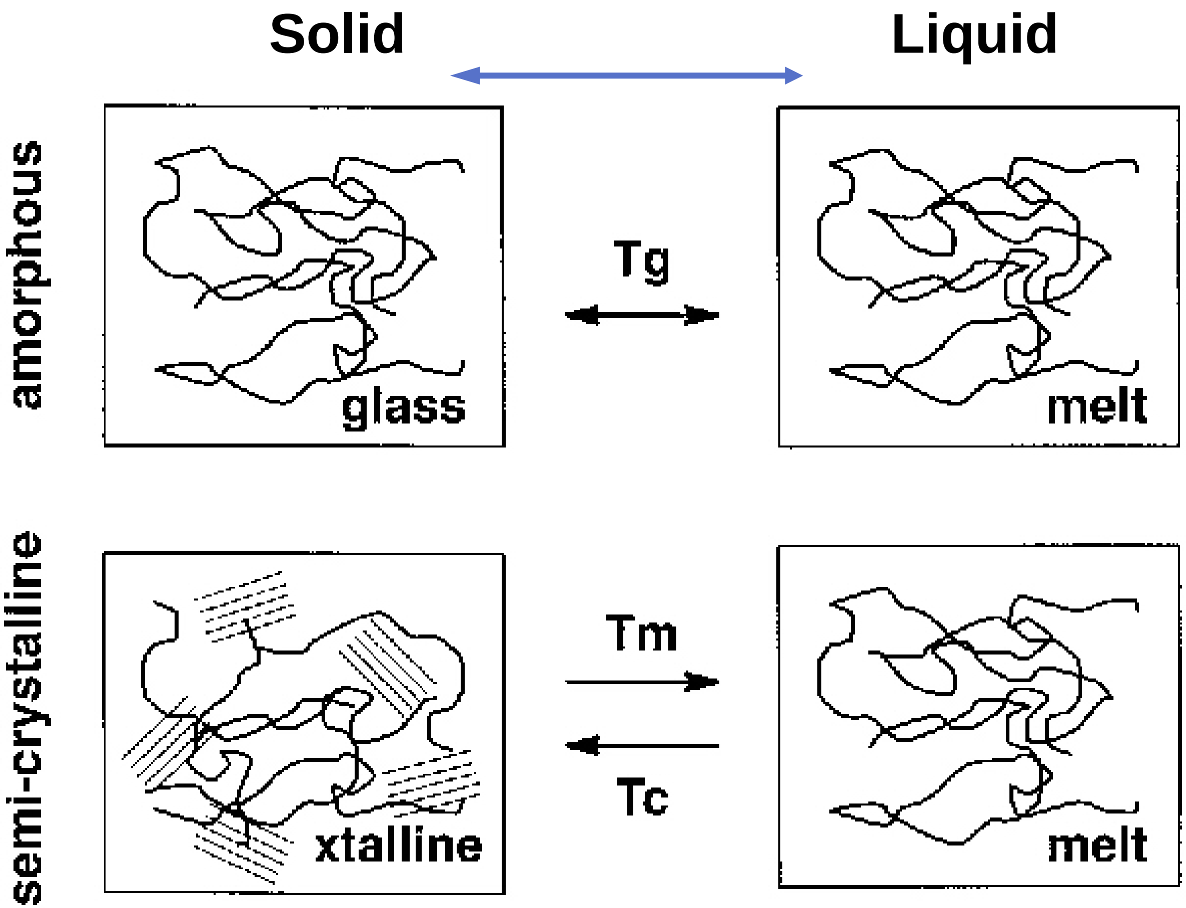
Physical States of Polymers

- Amorphous
  - Glass Transition Temperature (T_g)
- Semi-crystalline
  - Glass Transition Temperature and melting point (T_m)
  - 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

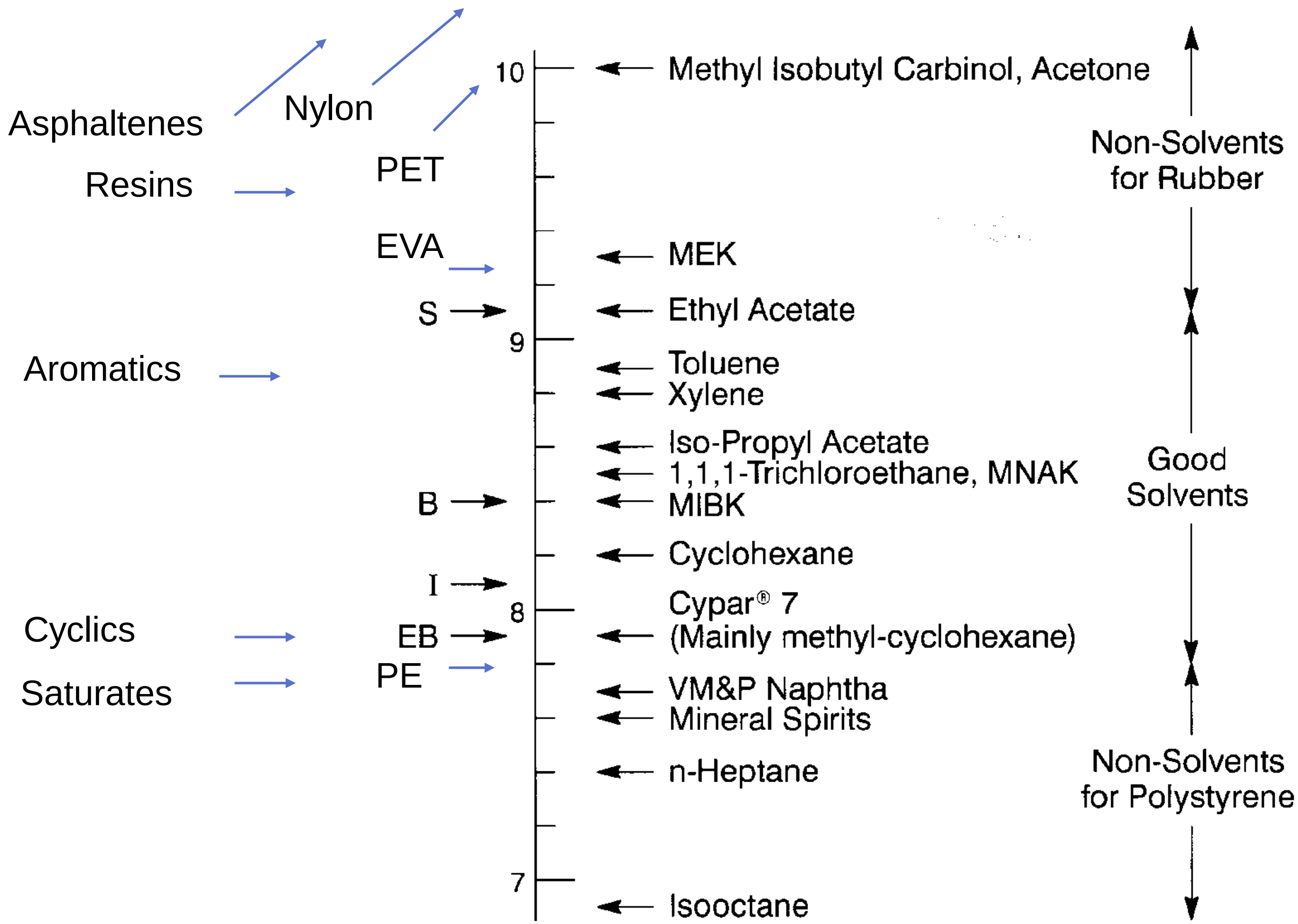
- My asphalt has waxes, asphaltenes, metals, salts, etc., yet it stays together. Why do my polymers separate?
- Because Flory-Huggins says so!

- $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

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

- 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.

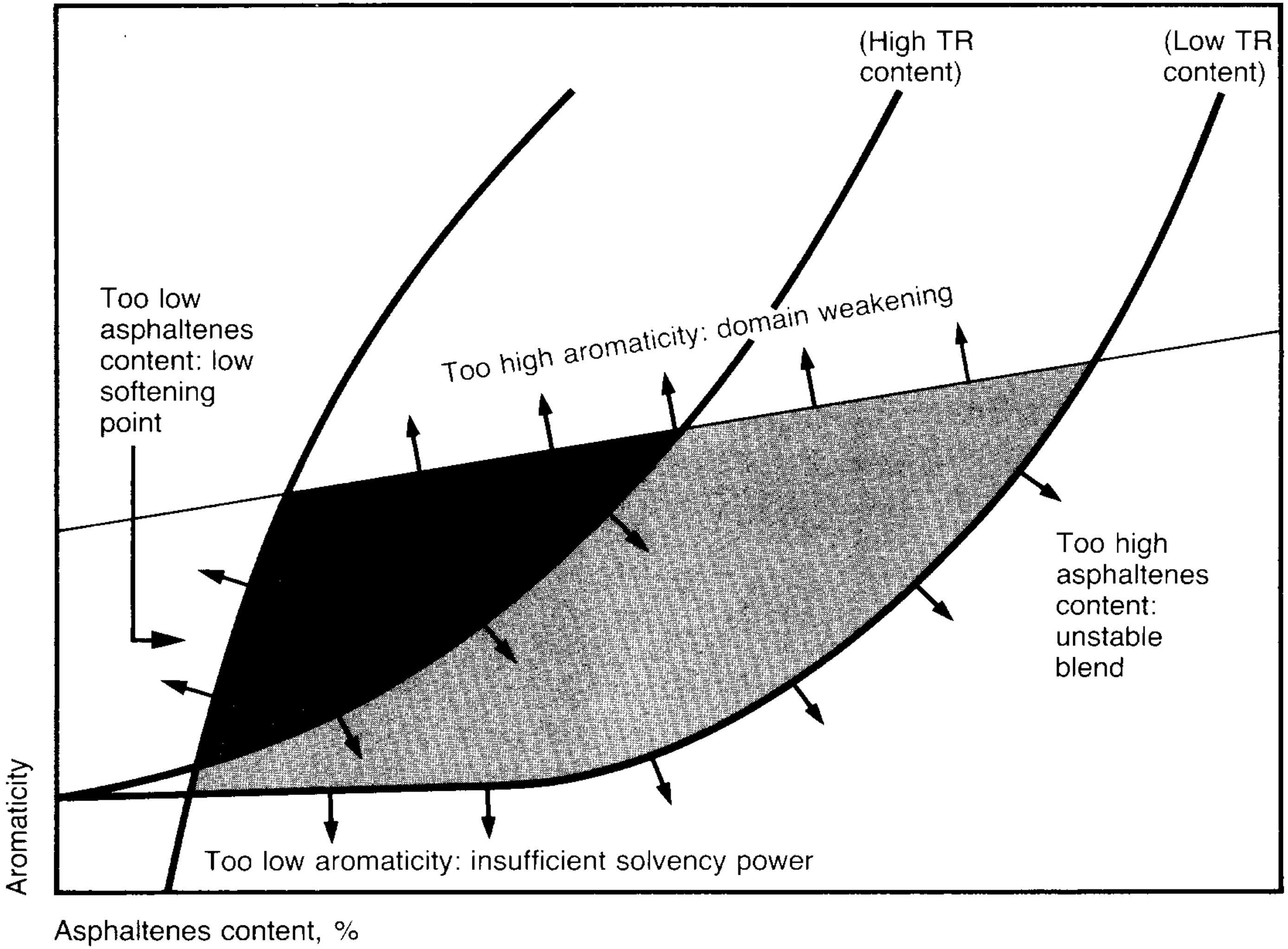
Polymer Requirements for Asphalt

- 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)

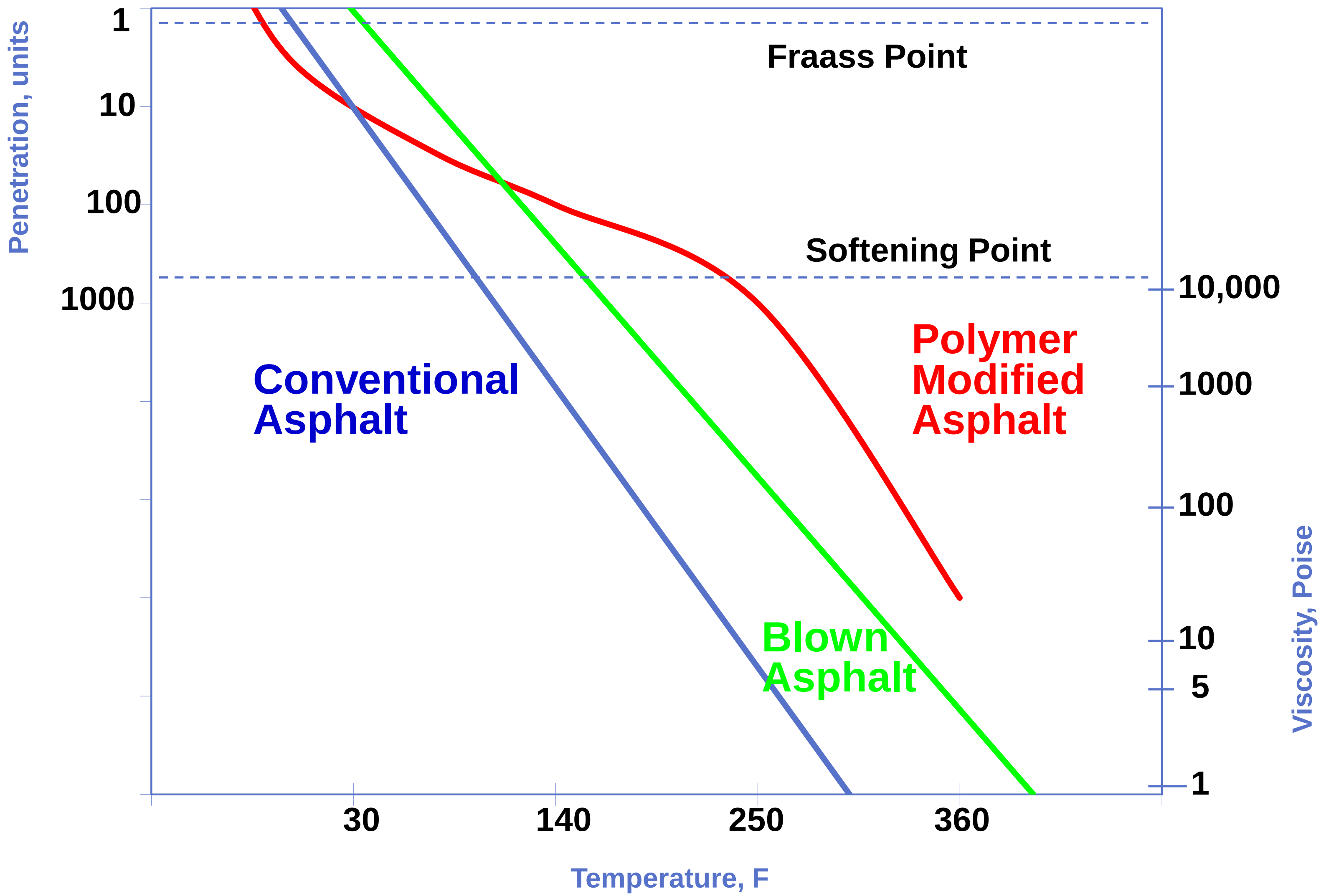
Asphalt Compatibility – SBS Example



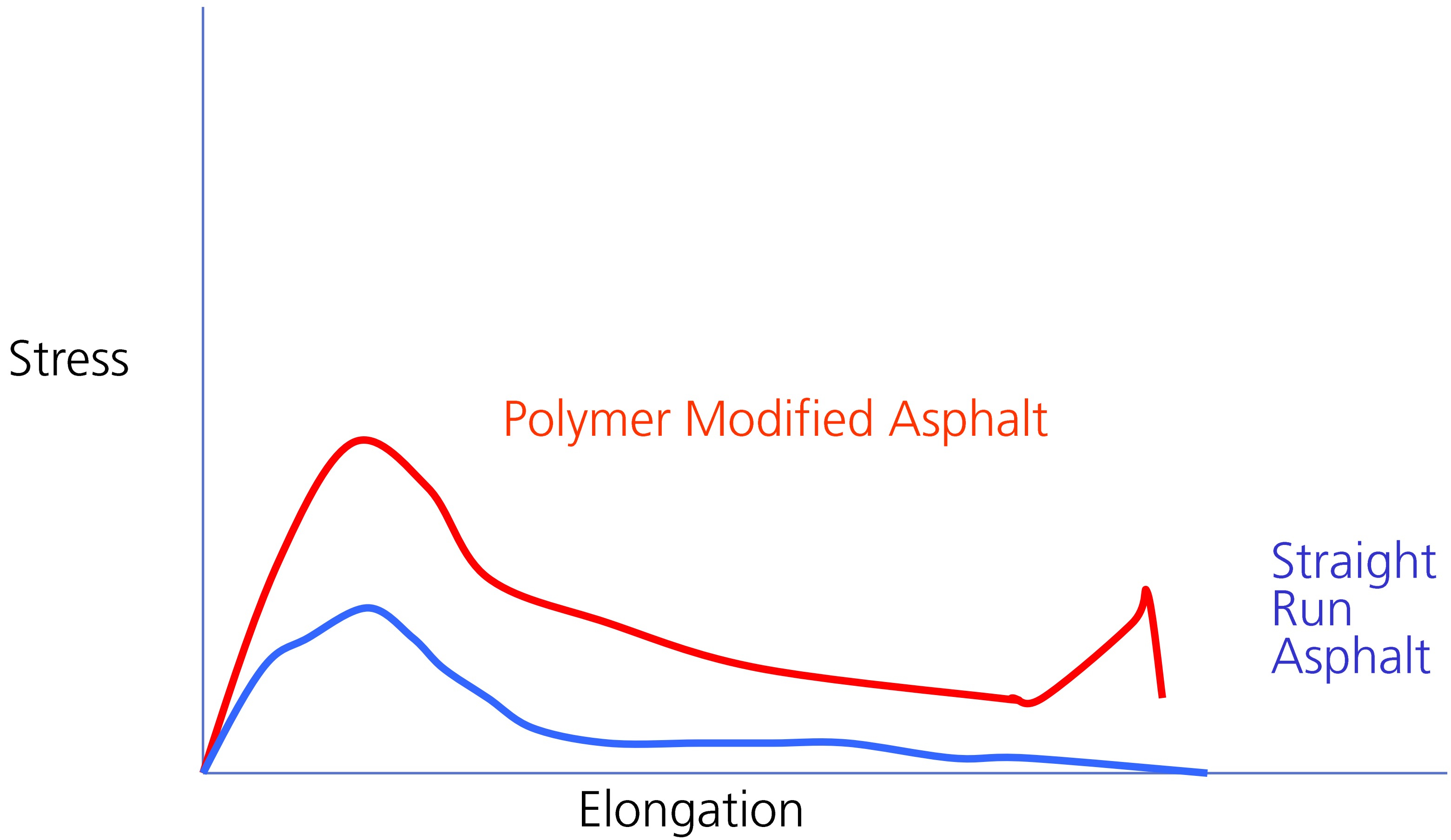
Physical Effects of Polymers in Asphalt

- Reduce Temperature Susceptibility
- Increase Tensile Strength
- Increase Elasticity

Temperature Susceptibility of Polymer Modified Asphalt



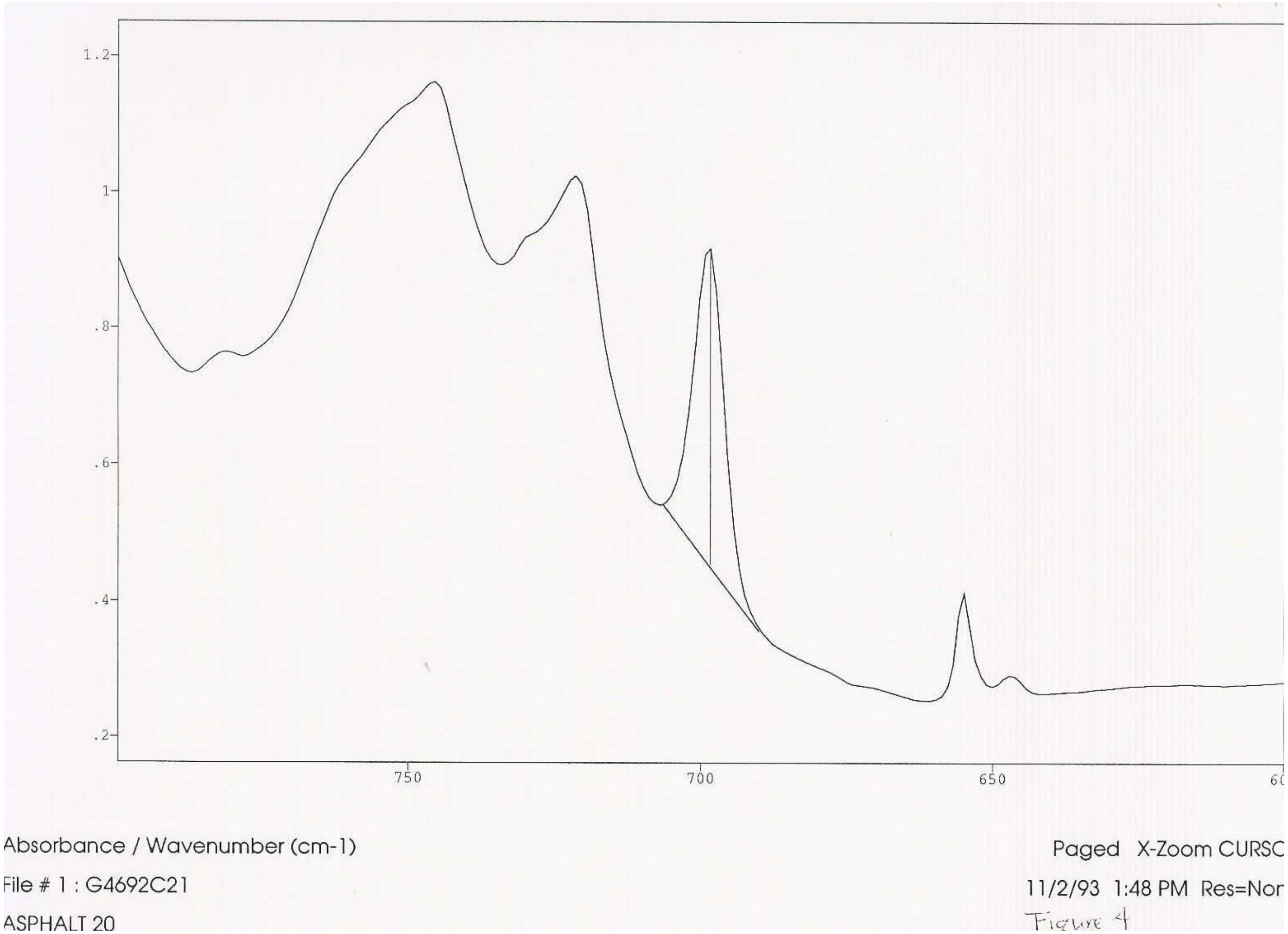
Tensile Properties



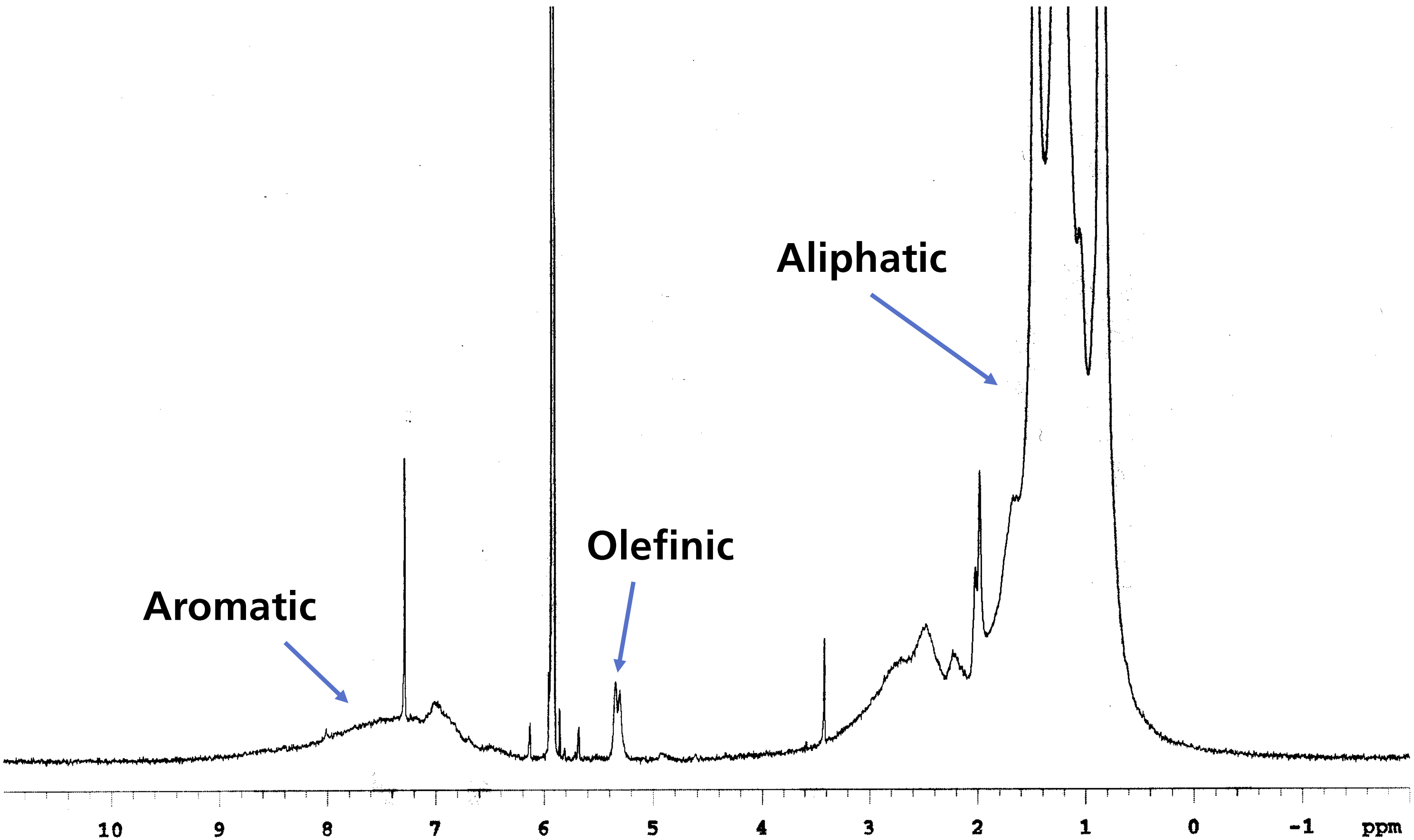
Analysis of Polymers in Asphalt

- Infrared Analysis
- NMR Analysis
- GPC Analysis
- Microscopy

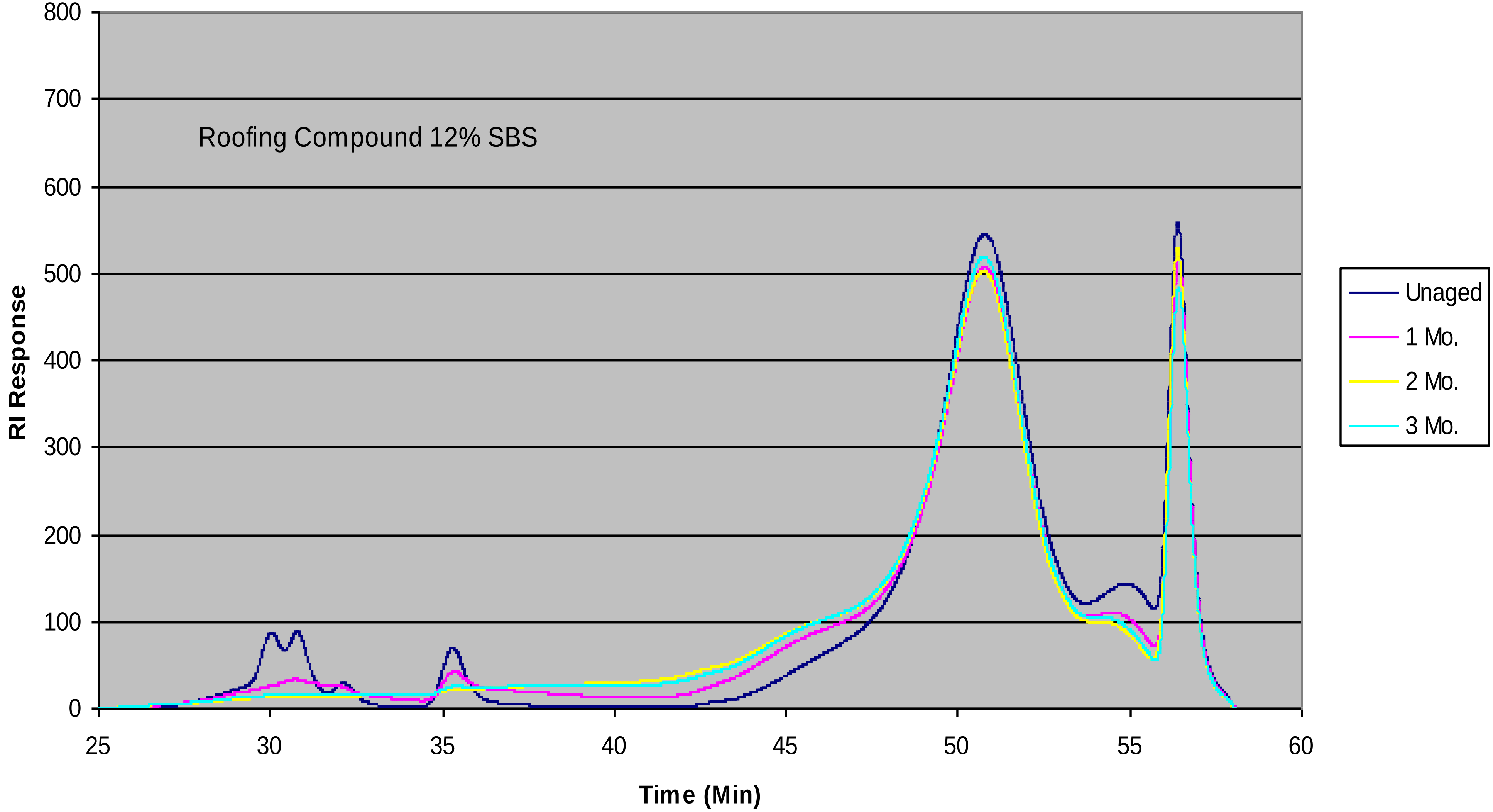
IR Analysis of Polymer in Asphalt



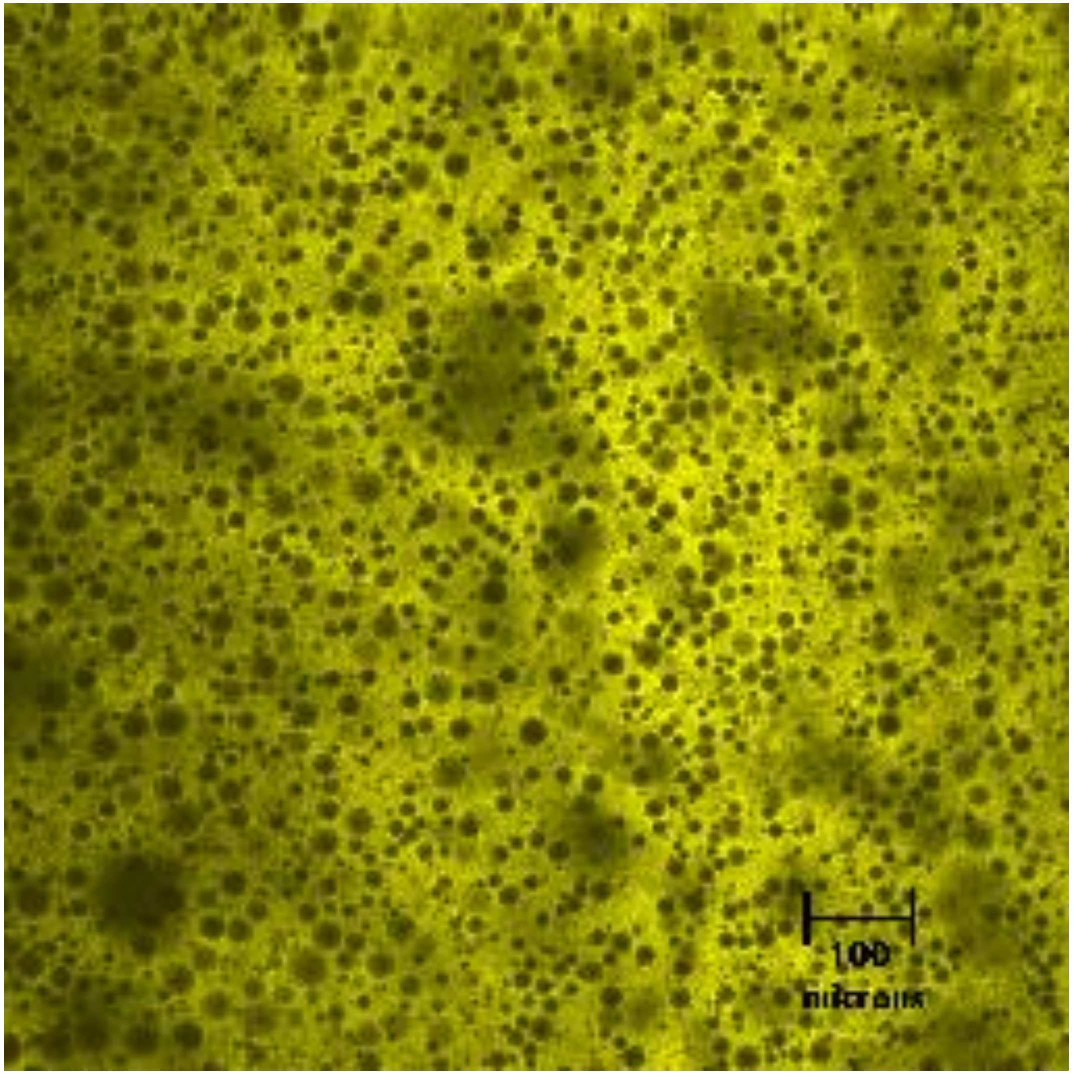
^{1}H NMR of Polymer in Asphalt



GPC of Polymer in Asphalt



Micrograph of SBS Polymer in Asphalt



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?

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