Chapter 3. Chemical Structure and Polymer Morphology

Chemical Structure ⟷ **Morphology**

Chemical Structure
- Chemical composition
- Stereochemistry

Morphology
- Structure
- Arrangement
- Physical form

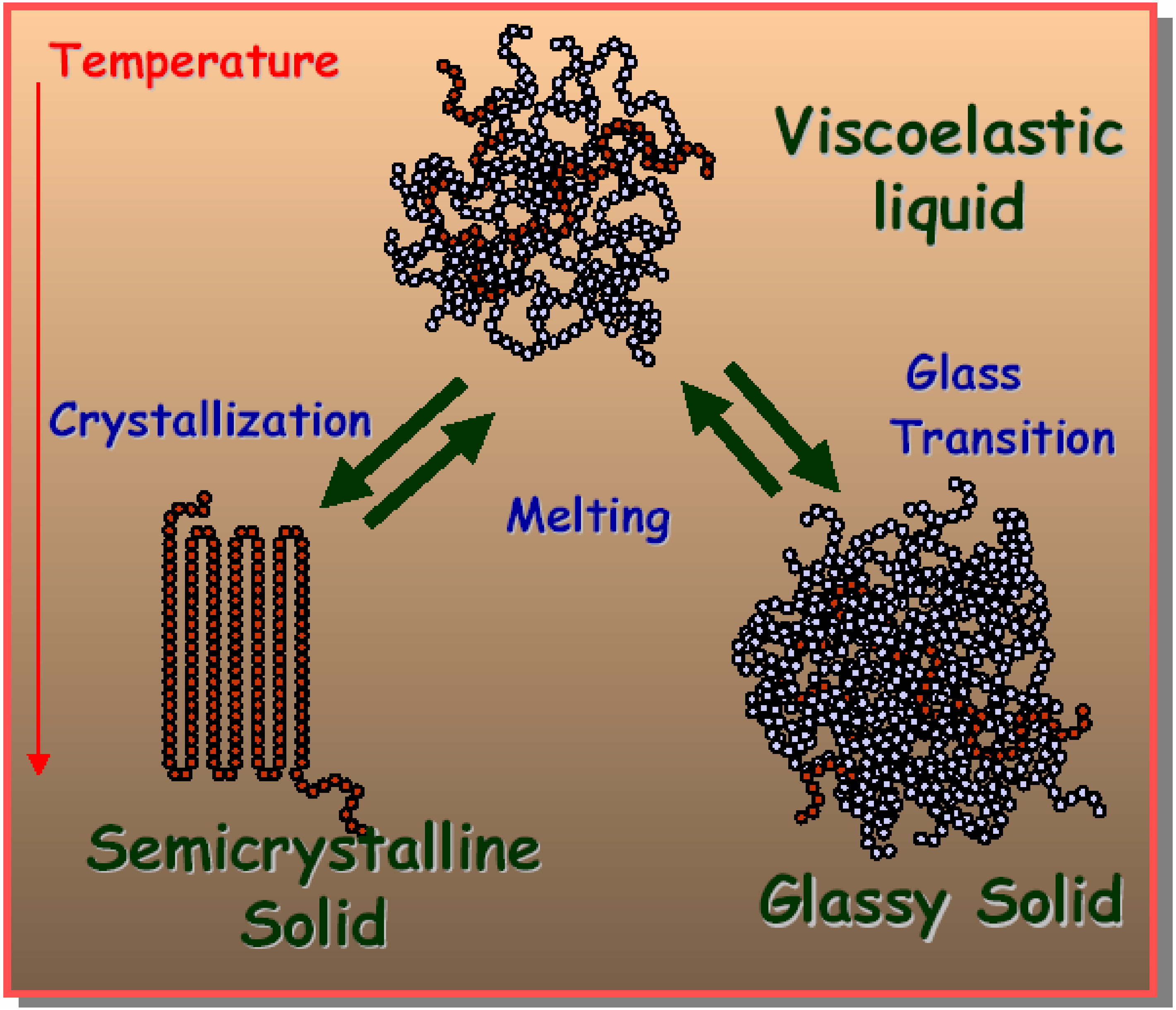
- Amorphous
- Crystalline
- (Semicrystalline)

Intermolecular and Intramolecular forces

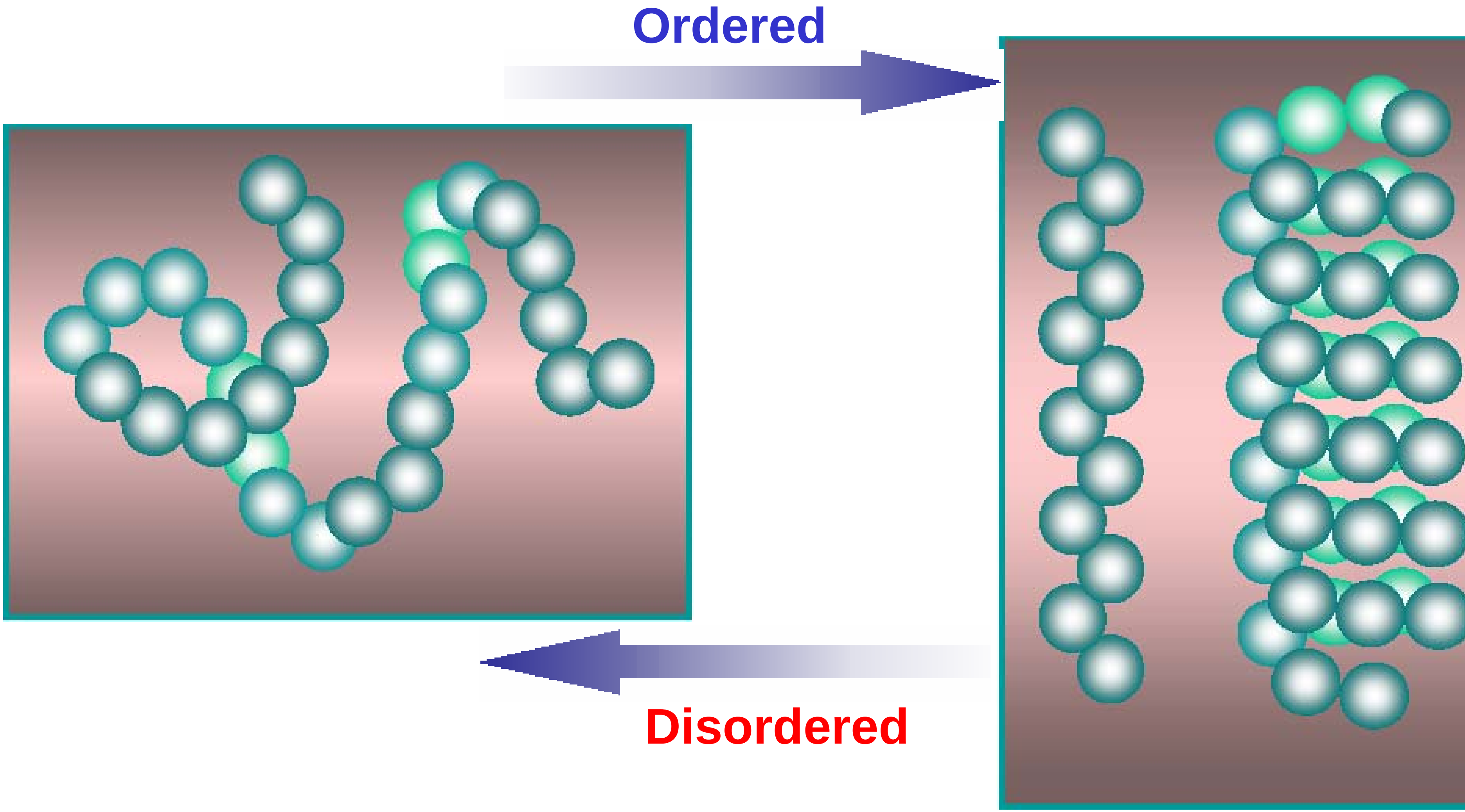
⇕

Mechanical and Thermal properties

Polymer Solid State

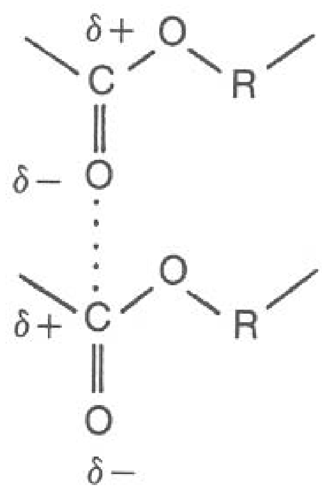


Conformations

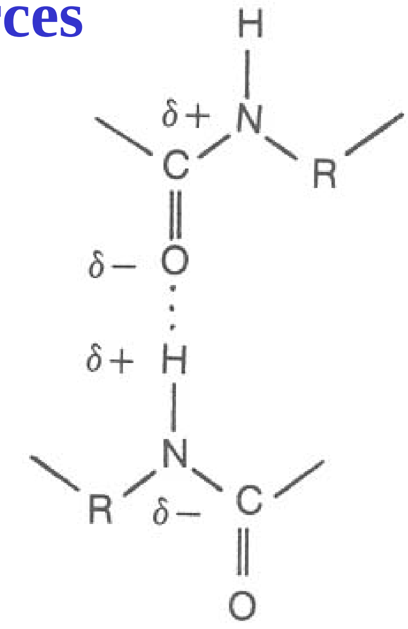


3.2 MW and Intermolecular Forces

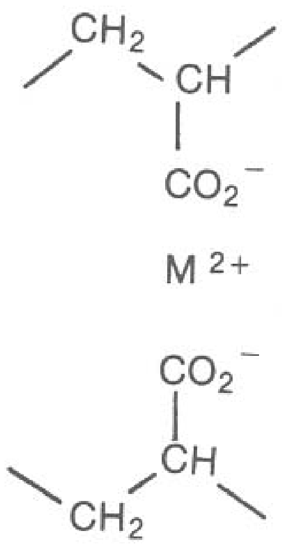
Van der waals
In nonpolar polymer



Dipole-dipole
In polyester



H bonding
In polyamide



Ionic
In carboxyl-containing polymer

Weak

Low MW

Amorphous

Intermolecular and intramolecular interaction →

Strong

High MW

Crystalline

∵ Shorter distance

- **Relationship of Polymer Properties to Order**

  A) **Intermolecular forces decrease very rapidly with distance**

  ∴ **They are much higher in crystalline materials than in amorphous ones.**

  B) **Example: Elastomer**

  1) Unstretched Elastomer:

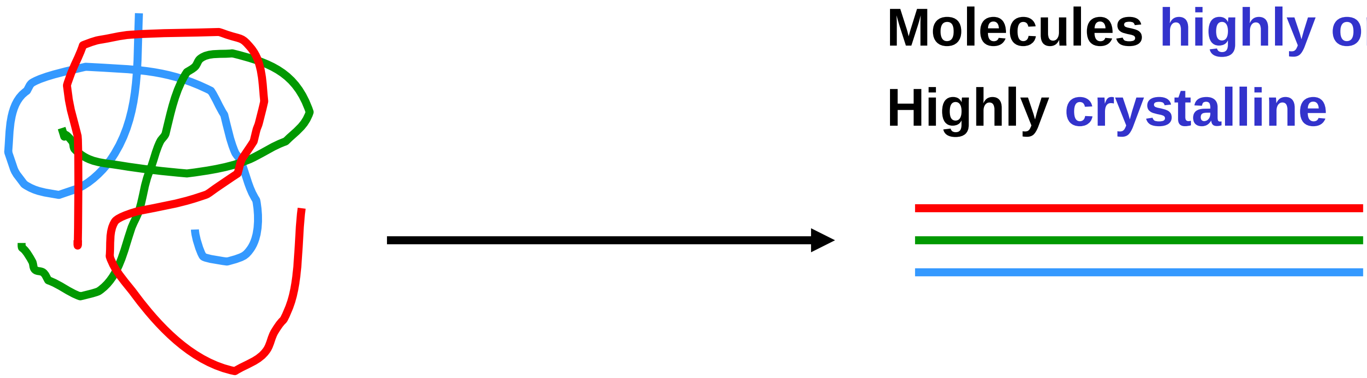
  Amorphous

  2) After Stretching:

  Up to 600% elongation

  Molecules highly ordered

  Highly crystalline



  3) Property changes

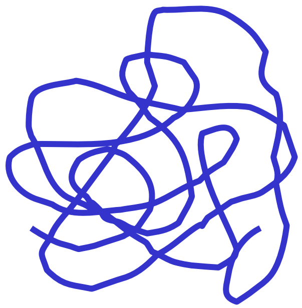
  Stiffness (Modulus increases 2,000 fold)

  Chemical resistance (cf. 1st stage in dissolution of polymers)

3.3 Amorphous State - Rheology

Rheology : science of deformation and flow

Relaxation :



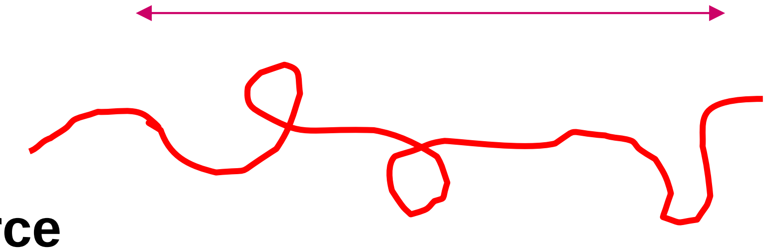
apply force

withdraw force

relaxation

"elastic"

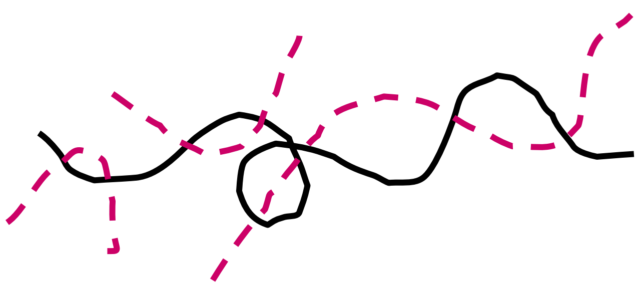
force



Undisturbed configuration

Thermodynamically favorable ← Large entropy

Small entropy



Flowing liquid: very viscous

∵ chain entanglement and frictional effects

∴ Polymer : viscoelastic material

Viscoelasticity

If we stretch a crystalline solid, the energy is stored in the chemical bonds

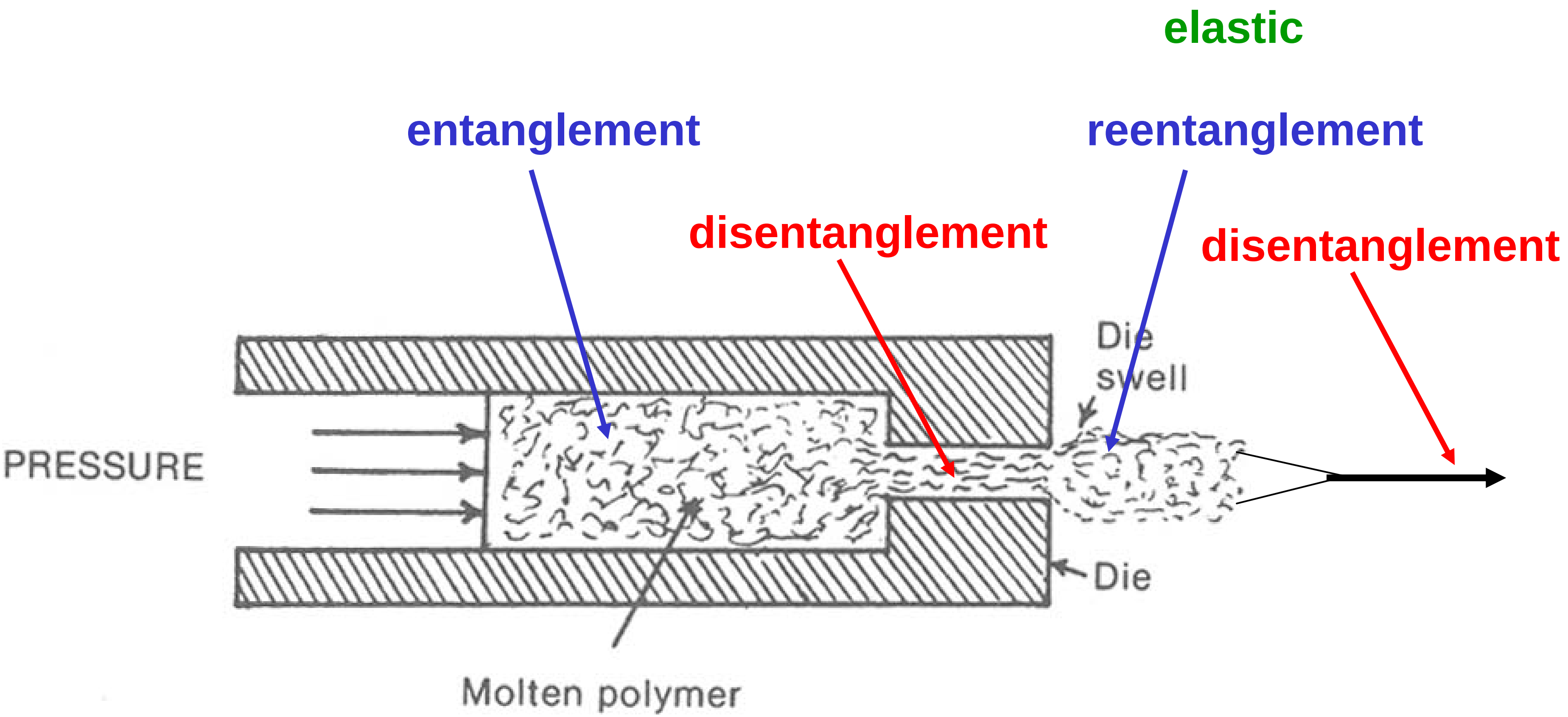
If we apply a shear stress to a fluid, energy is dissipated in flow

VISCOELASTIC

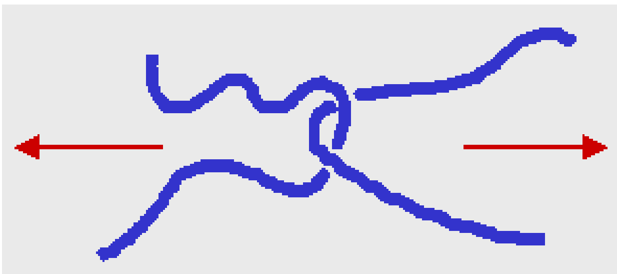
Ideally elastic behaviour

Ideally viscous behaviour

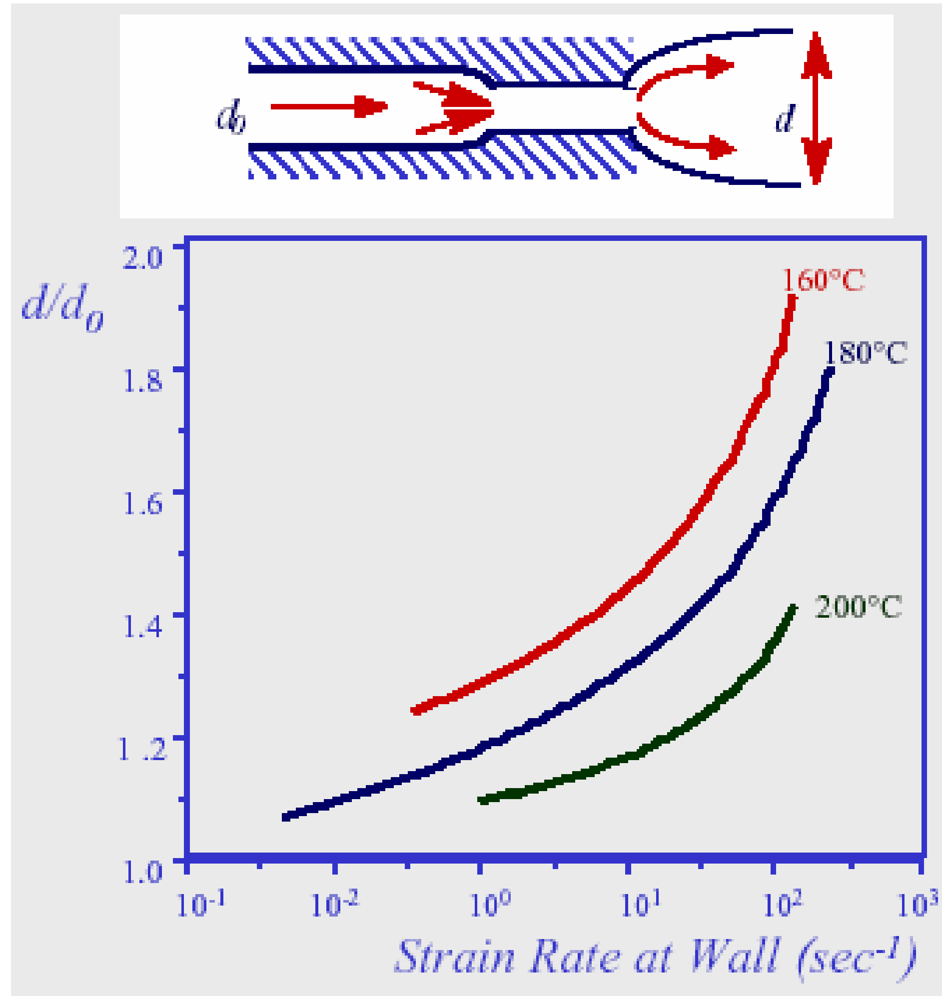
Fig 3.2 Polymer flow through a die orifice



Entanglements and the Elastic Properties of Polymer Melts



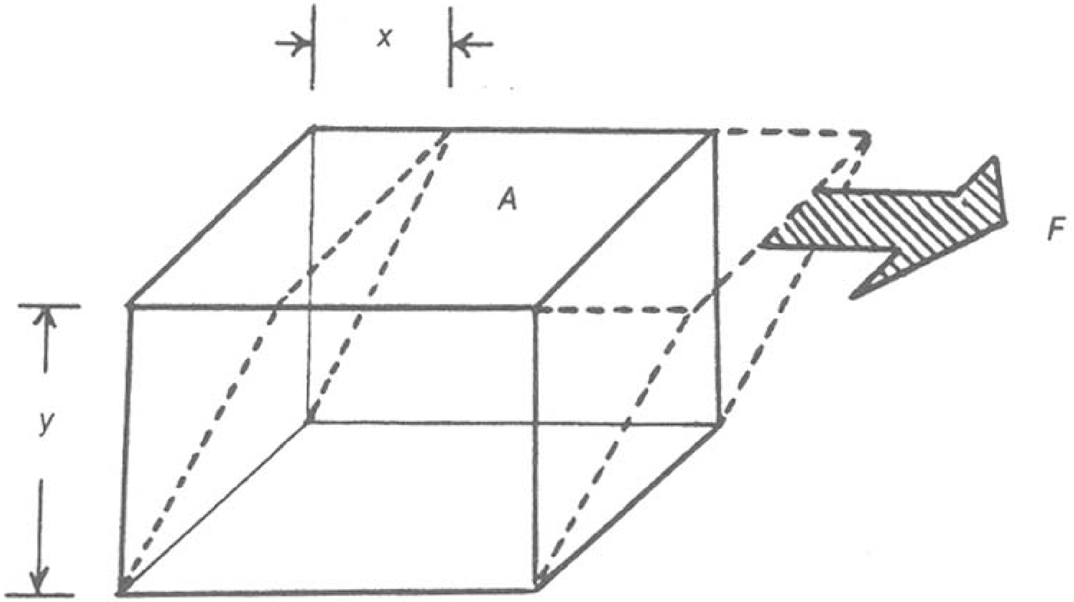
Depending upon the rate at which chains disentangle relative to the rate at which they stretch out, there is an elastic component to the behavior of polymer melts. There are various consequences as a result of this.



Jet Swelling

Fig 3.3 Shear (tangential stress):

Force applied to one side of a surface in a direction parallel to the surface



Shear

Shear stress (dyne/cm², N/m²): force per unit of surface area

$$\tau = \frac{F}{A}$$

Molecular flow in a function of

- **Temperature** (**Kinetic energy**)
- **Molecular weight** (**Entanglement**)
- **Molecular structure** (**Intermolecular forces**)

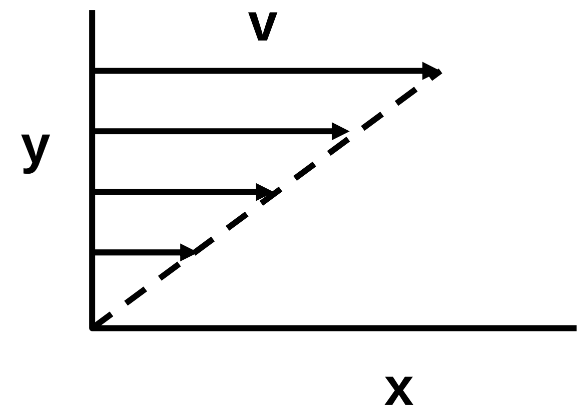
Viscosity = a measure of **resistance to flow**

Shear strain (γ) = amount of deformation of one plane w.r.t. another

$$\gamma = \frac{x}{y}$$

Shear modulus (G)

$$G = \frac{\tau}{\gamma}$$



Shear rate ($\dot{\gamma}$)
= velocity gradient

$$\dot{\gamma} = \frac{dv}{dy}$$

$$\dot{\gamma} = \frac{dv}{dy} = \frac{\frac{dx}{dt}}{dy} = \frac{\frac{dx}{dy}}{dt} = \frac{d\gamma}{dt}$$

Newton's law of viscosity

$$\tau = \eta \dot{\gamma}$$

where

η = viscosity

(poise = dyne•s/cm², pascal-seconds = Pa•s = N•s/m²)

Pa•s = 10 poise = 1000 centipoise

		η Pa•s	cP
air	=	10^{-5}	10^{-2}
water	=	10^{-3}	1
glycerine	=	1	10^{3}
molten polymer	=	10^{2} - 10^{6}	10^{5} - 10^{9}

Viscosity ⟺ Temp

$$\eta = Ae^{\frac{E_a}{RT}}$$

where

A = constant

E_a = activation energy for viscous flow

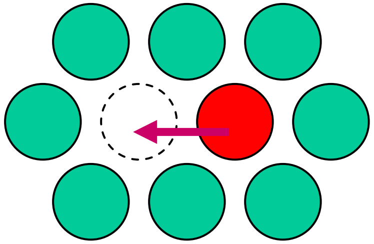
determined by localized segmental motion of polymer chains

relatively insensitive to MW

highly dependant on chain structure & branching

Viscous flow takes place by successive jumps of segments until the whole chain has shifted.

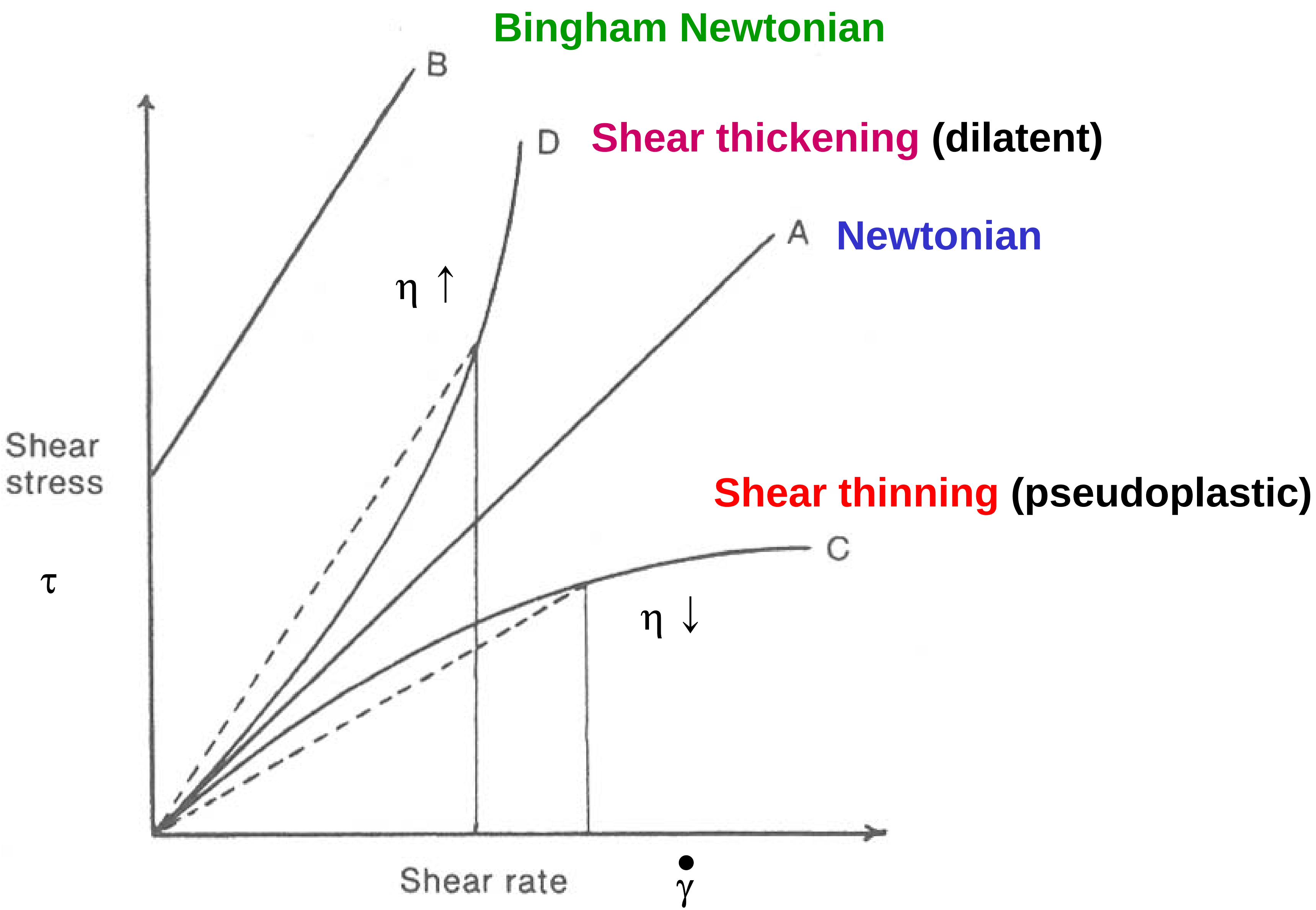
E_a ⟺ cohesive energy



The more bulky the chain branch or substituent, the higher the E_a.

The bulkier the group, the more sensitive the polymer viscosity to changes in temperature.

Fig 3.4 Types of shear flow



Bingham Newtonian fluid

$$\tau = \tau_c + \eta\dot{\gamma}$$

where

τ_c = critical shear stress = threshold stress

= initial resistance to flow

Structured arrangement of the molecules arising from conformational & secondary bonding forces that must be disrupted by the application of an initial stress (τ_c) before the molecules begin to flow.

Shear Thinning (Pseudoplastic) and Shear Thickening

Power low equation

$$\tau = A\dot{\gamma}^{B}$$

$$\log \tau = \log A + B \log \dot{\gamma}$$

where

- A = constant
- B = index of flow

For Newtonian fluid,
B = 1 and A = η

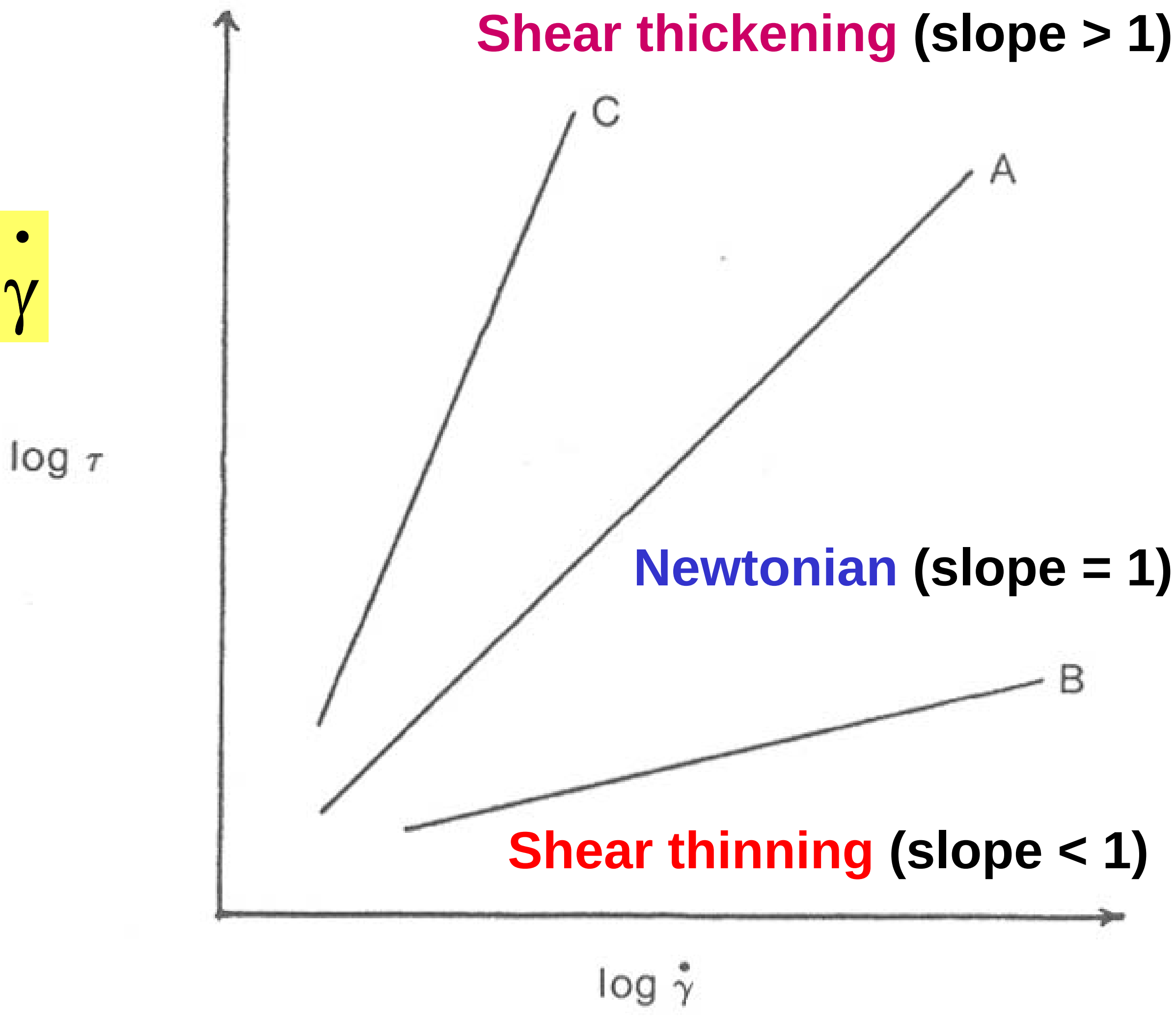
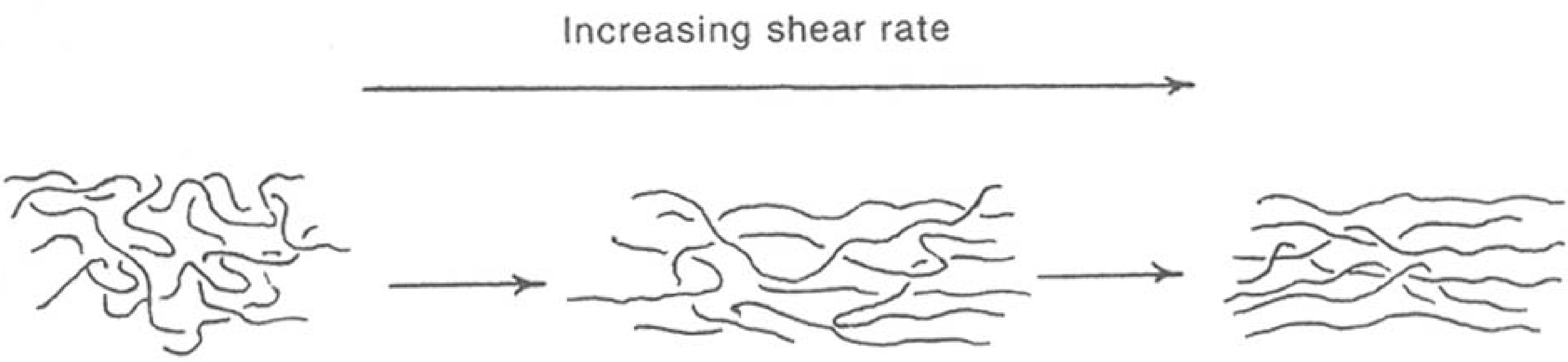


Fig 3.5 Power law plots

Fig 3.6 Shear Thinning from Disentanglement



Entanglement

Disentanglement

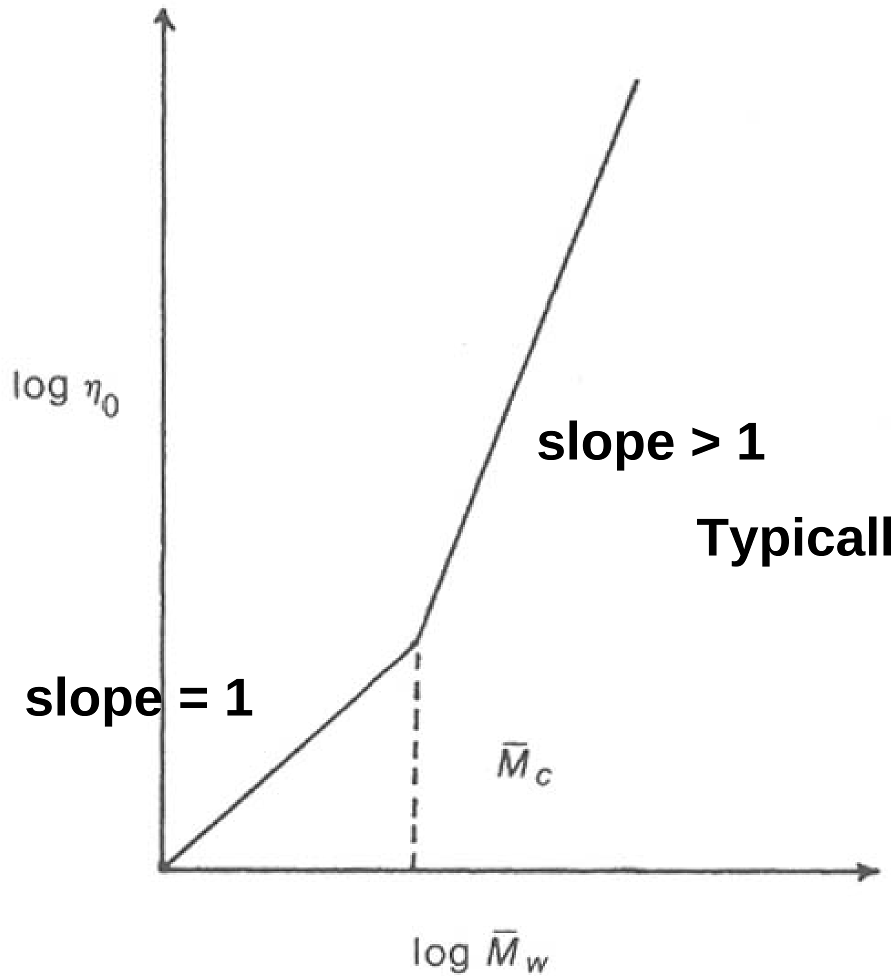
Shear thickening

Much less common

As $\dot{\gamma} \uparrow$, reasonably ordered arrangement of molecules become more disordered, hence entangled.

Entanglement$\uparrow$

Fig. 3.7 Effect of MW on viscosity



slope > 1

Typically slope = 3.4

slope = 1

where

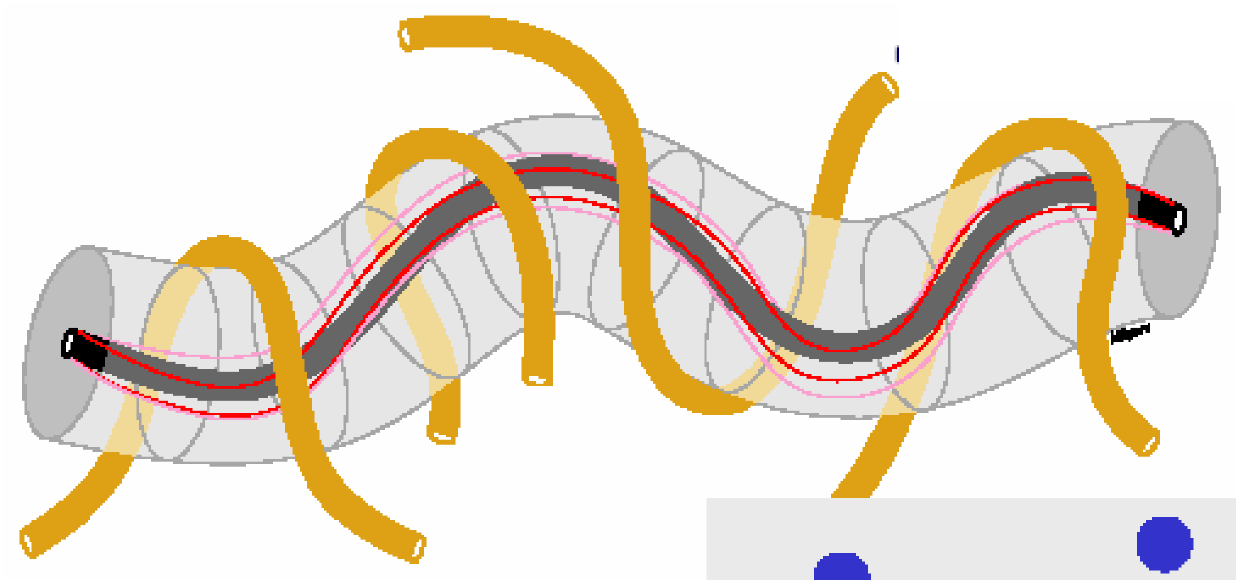
M_c= crtical MW for entanglement to begin

4,000 < M_c<15,000 for most common polymers

Critical DP ≈ 600

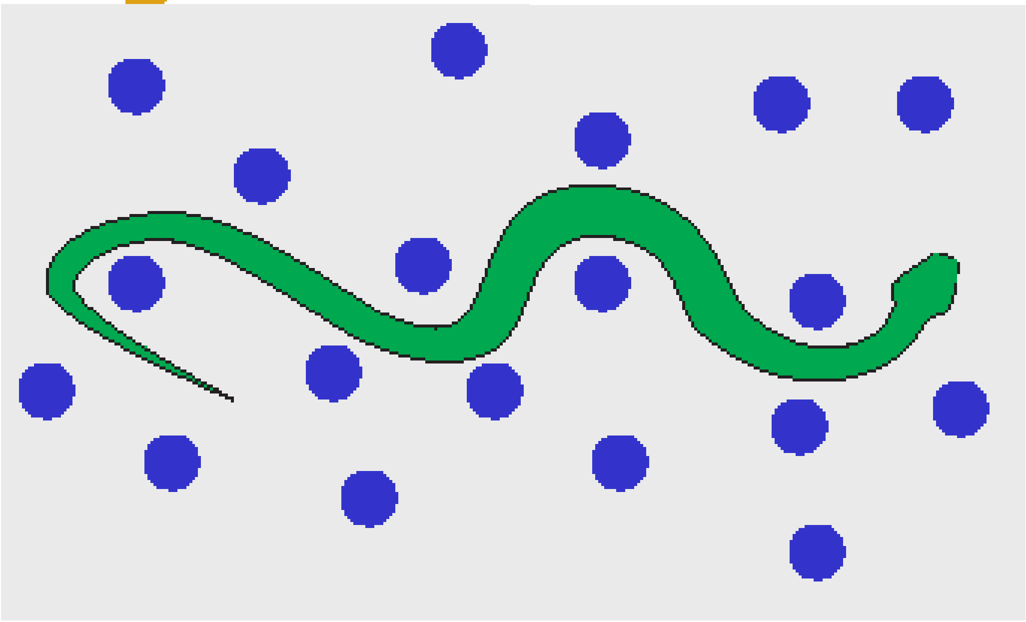
Critical chain length, rather than MW, is necessary for entanglement.

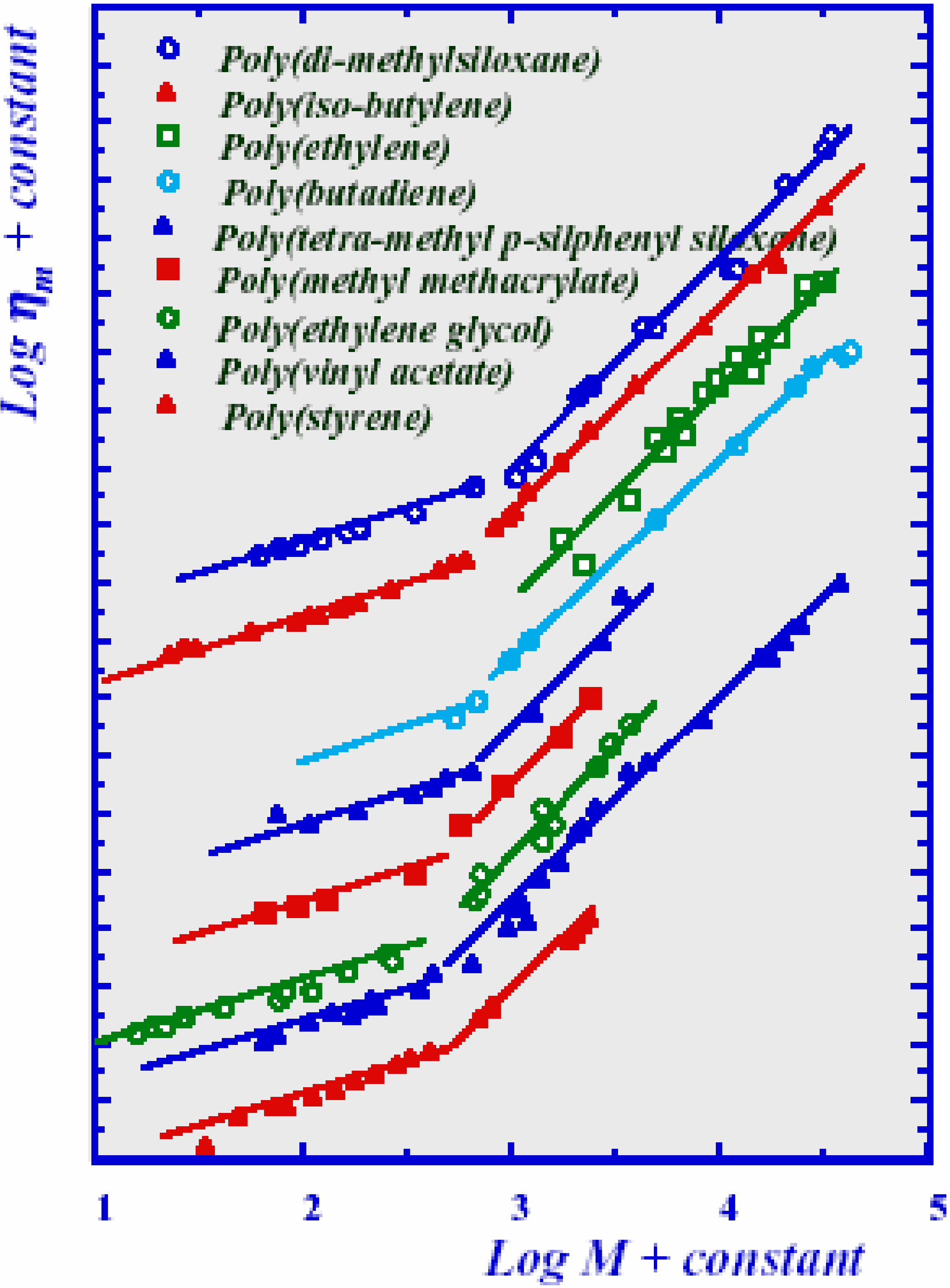
How Do Chains Move - Reptation



$$D \sim 1/M^2$$

$$\eta_0 \sim M^3$$





Variation of Melt Viscosity with Molecular Weight

$$\eta_m = K_L(DP)^{1.0}$$

$$\eta_m = K_H(DP)^{3.4}$$

Entanglements

Short chains don’t entangle but long ones do - think of the difference between a nice linguini and spaghettios, the little round things you can get out of a tin (we have some value judgements concerning the relative merits of these two forms of pasta, but on the advice of our lawyers we shall refrain from comment).

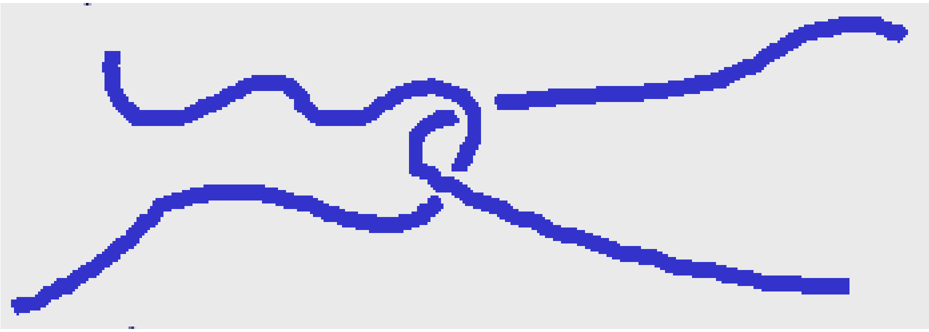
Entanglements

Viscosity - a measure of the frictional forces acting on a molecule

Small molecules - the viscosity varies directly with size

$$\eta_m = K_L(DP)^{1.0}$$

At a critical chain length chains start to become tangled up with one another, however



Then

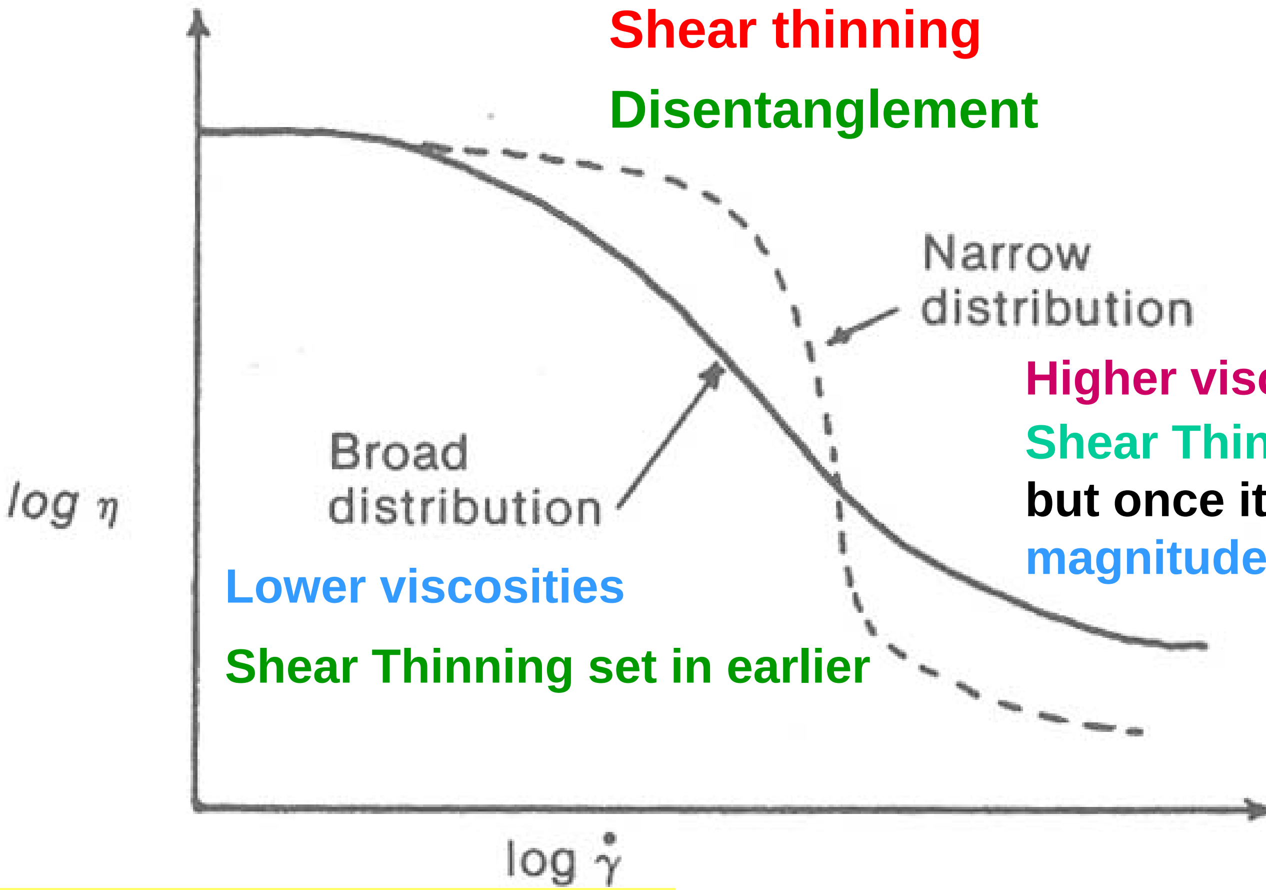
$$\eta_m = K_H(DP)^{3.4}$$

Fig 3.8 Effect of MWD on shear thinning

Newtonian region | Power low region | Newtonian region

Shear thinning

Disentanglement



Higher viscosities

Shear Thinning sets in later

but once it does set in its

magnitude is larger.

Lower viscosities

Shear Thinning set in earlier

$$\eta = \frac{\tau}{\dot{\gamma}} = \frac{A\dot{\gamma}^{B}}{\dot{\gamma}} = A\dot{\gamma}^{-(1-B)} = A\dot{\gamma}^{-p}$$

p = 0.85 for monodisperse polymers

p = 0.60 for highly polydisperse polymers

Viscosity ⟺ Branching

As Chain Branching ↑

Hydrodynamic volume ↓

Degree of entanglement ↓

η ↓

However

Secondary bonding forces ↓

∴ **Mechanical properties ↓**

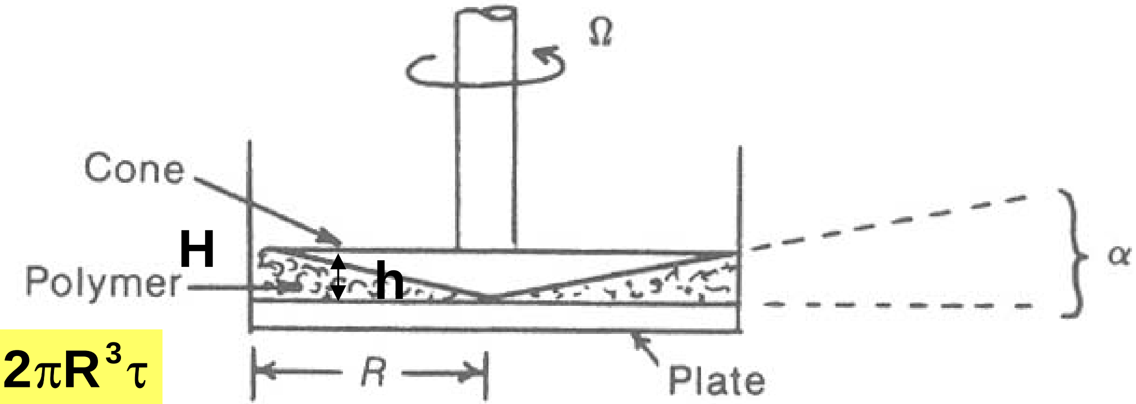
Dendrimers

Dendrimers take this effect to the extreme

Further, Dendrimers show a smaller dependence of viscosity on temperature.

∴ **Dendrimers make better lubricants in variable temperature applications.**

Fig 3.9 Cone - plate rotational viscometer

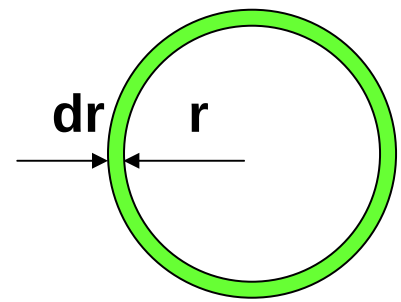


$$M = \int_0^R r \times F dr = \int_0^R 2\pi r^2 \tau dr = \frac{2\pi R^3 \tau}{3}$$

$$\therefore \quad \tau = \frac{3M}{2\pi R^3}$$

$$\dot{\gamma} = \frac{dv}{dh} = \frac{r\Omega}{h} = \frac{\Omega}{\alpha}$$

$$\eta = \frac{\tau}{\dot{\gamma}} = \frac{3\alpha M}{2\pi R^3 \Omega} = \frac{kM}{\Omega}$$



area = $2\pi r dr$

$$\tau = \frac{F}{A}$$

F = $2\pi r \tau dr$

where

M = torque (dyne/cm, N/m)

R = cone radius

Ω = angular velocity (degrees/s, rad/s)

α = cone angle (degrees, rad)

$$k = \frac{3\alpha}{2\pi R^3}$$

3.4 Glass Transition Temperature (T_g)

Amorphous Phase Changes

1) Heat an amorphous solid from low temp

a) Heating $\Rightarrow$ increased kinetic energy of molecules

b) Increased motion initially only short range, i.e., vibrations & rotations

2) The Glass Transition Temperature, T_g

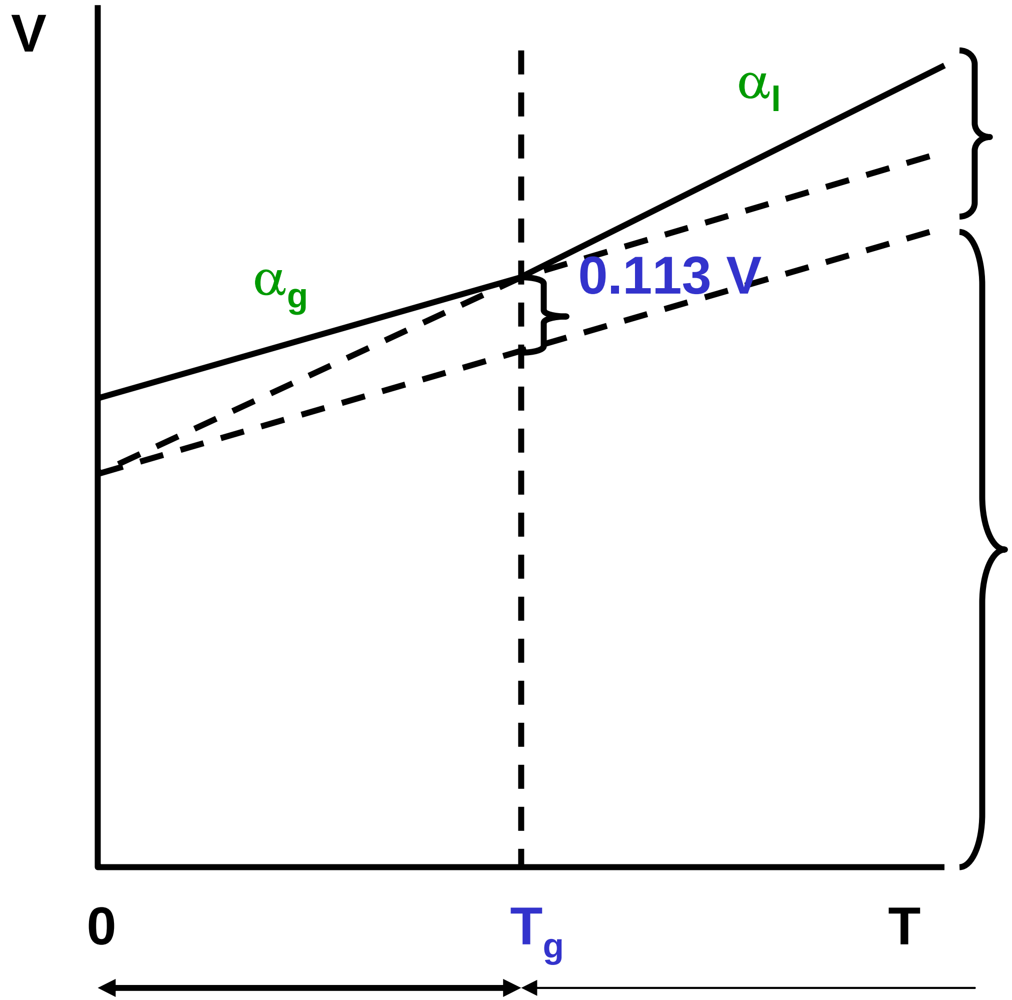
Fundamental change in properties from brittle crystalline to rubbery at some critical temperature

3) At higher temperature get melting, T_m

Lose elastomeric properties & the material starts to flow as a liquid

Glass Transition Temperature (T_g)

$V = V_o + V_f$



V_f Free volume

V_o Occupied volume

V_o ↑ linearly with T ↑

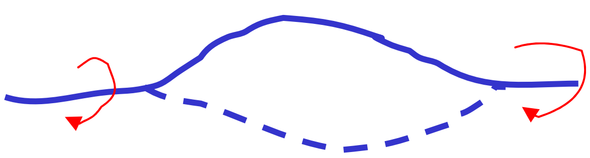
∵ Amplitude of thermal vibration ↑

V_f = constant

∵ Chains are frozen

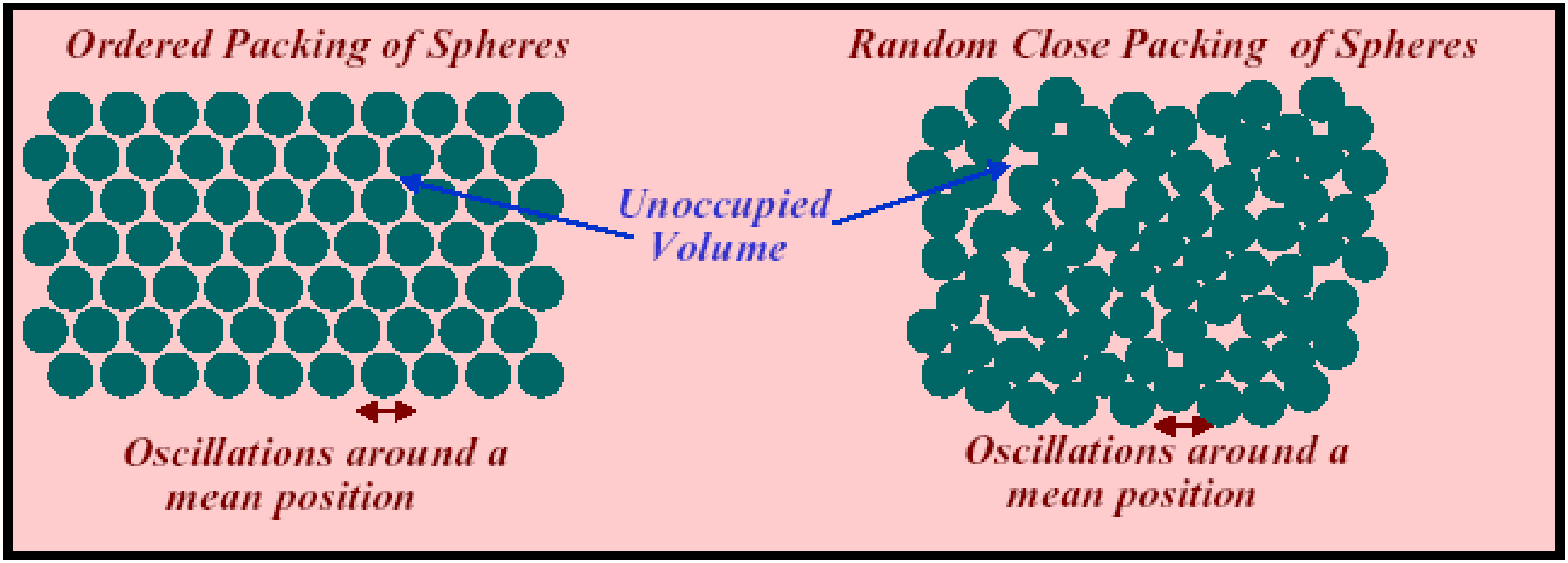
V_f ↑

∵ Molecular motion ↑



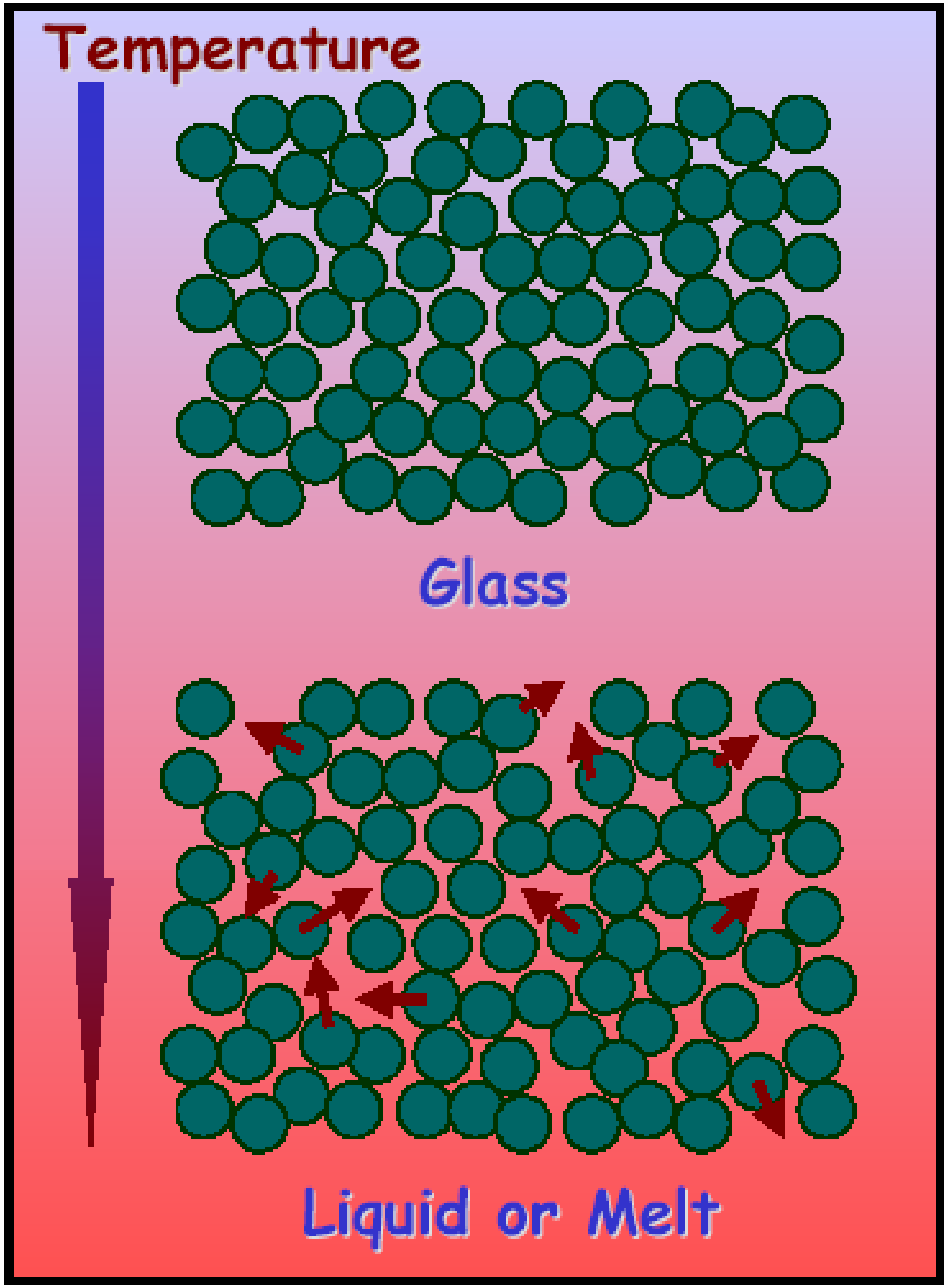
At T_g, 20 – 50 chain atoms are involved in the segmental movement.

Free Volume

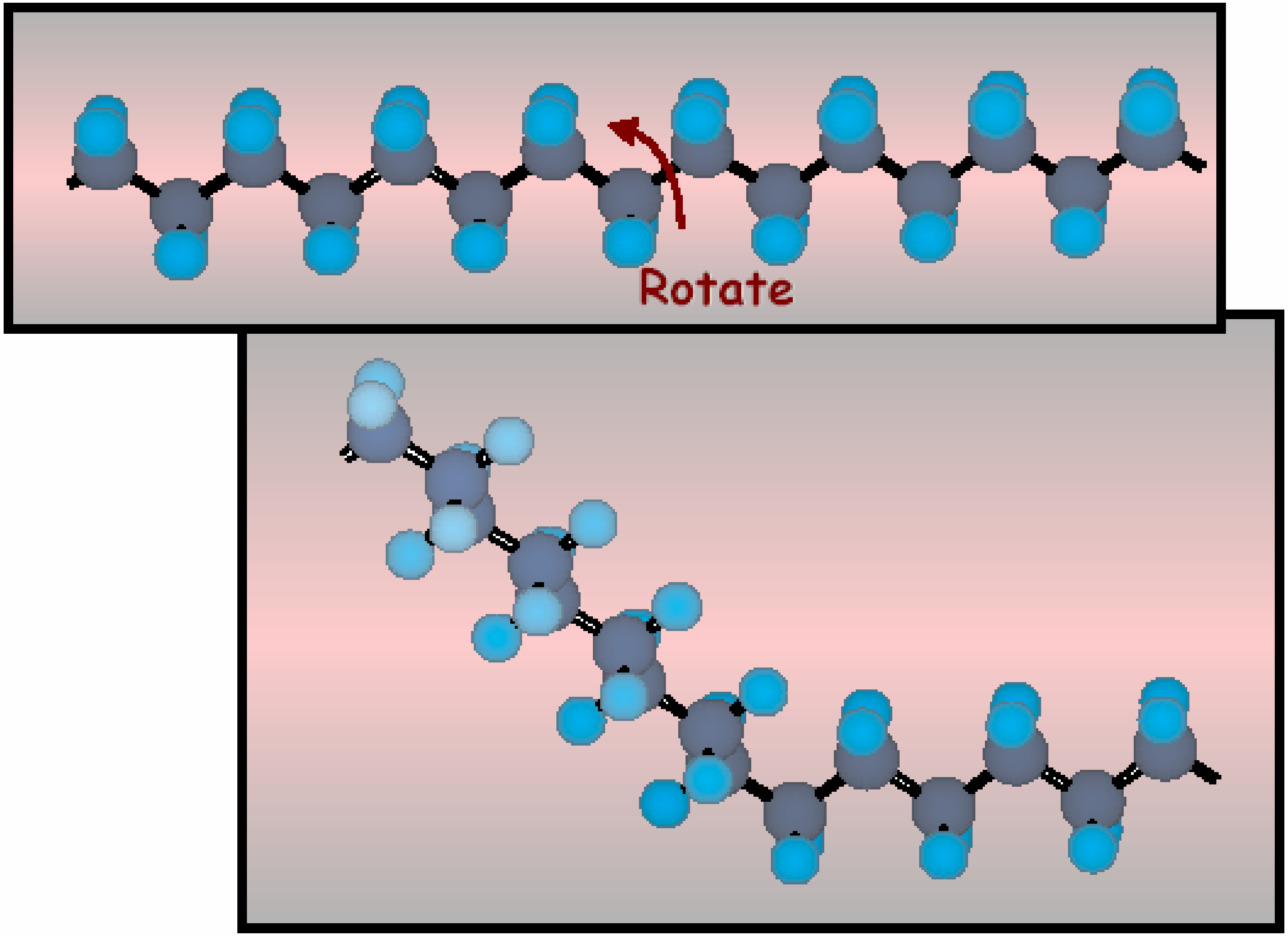


Ordered Packing of Spheres
Random Close Packing of Spheres
Unoccupied Volume
Oscillations around a mean position
Oscillations around a mean position

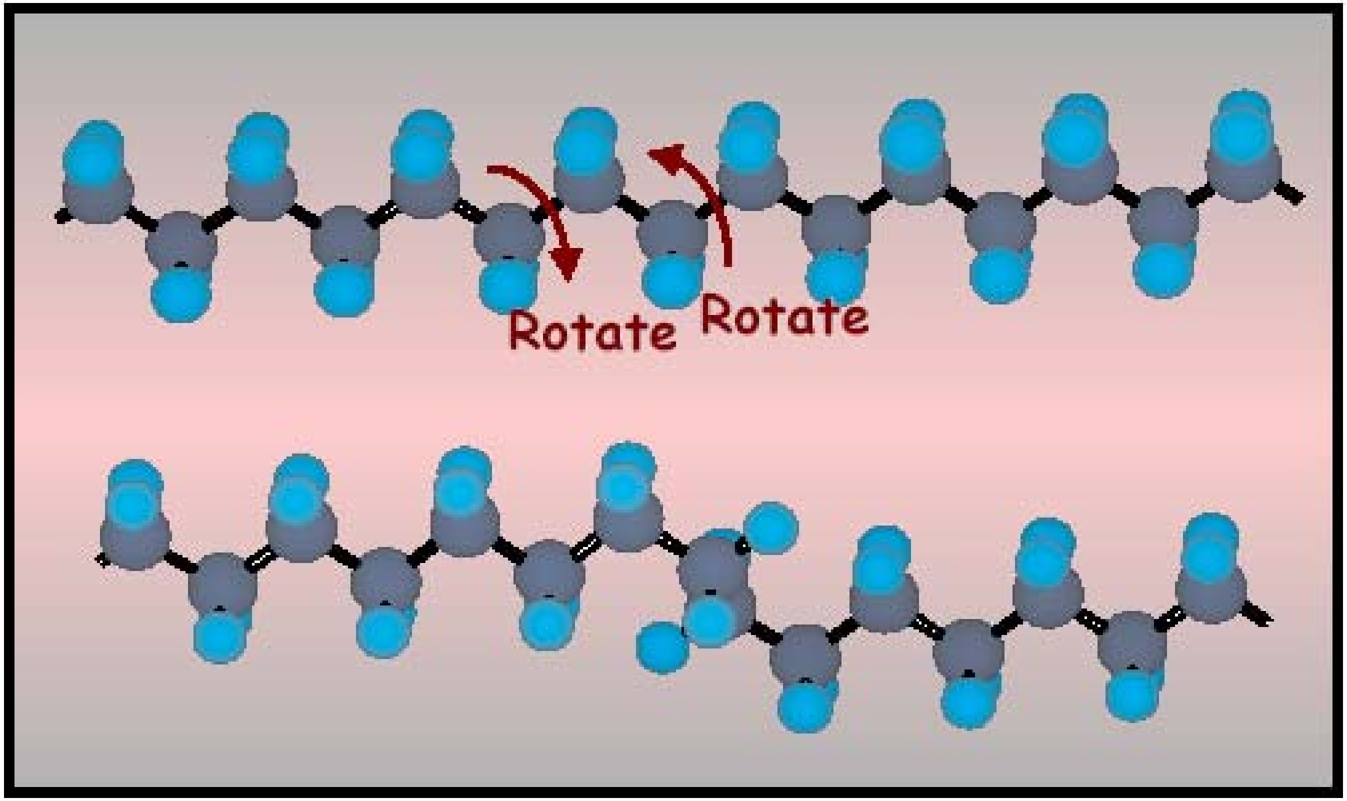
Free Volume



Motion in Polymers - The Dynamics of Polymer Chains



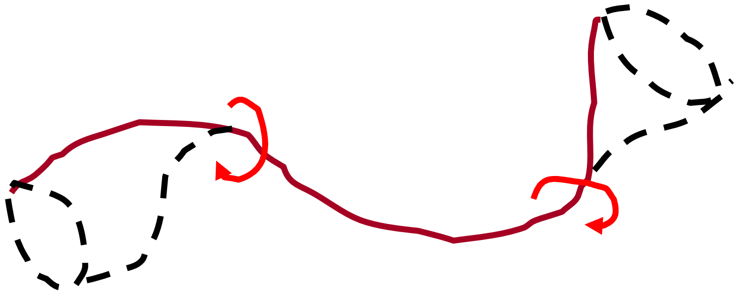
Motion in Polymers - The Dynamics of Polymer Chains



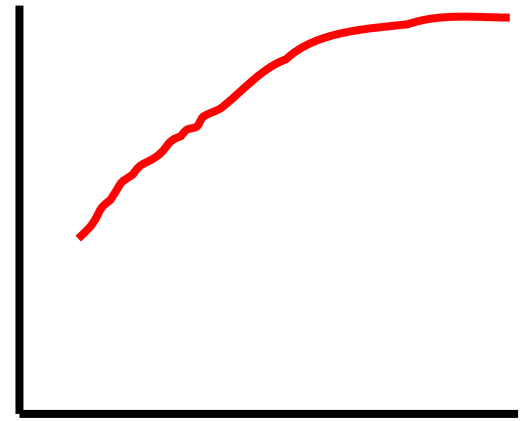
Factors affecting Tg

1) MW

MW ↑ ➡ # of chain ends ↓ ➡ V_f ↓ ➡ T_g ↑



$$T_g = T_g(\infty) - \frac{K}{M_n}$$

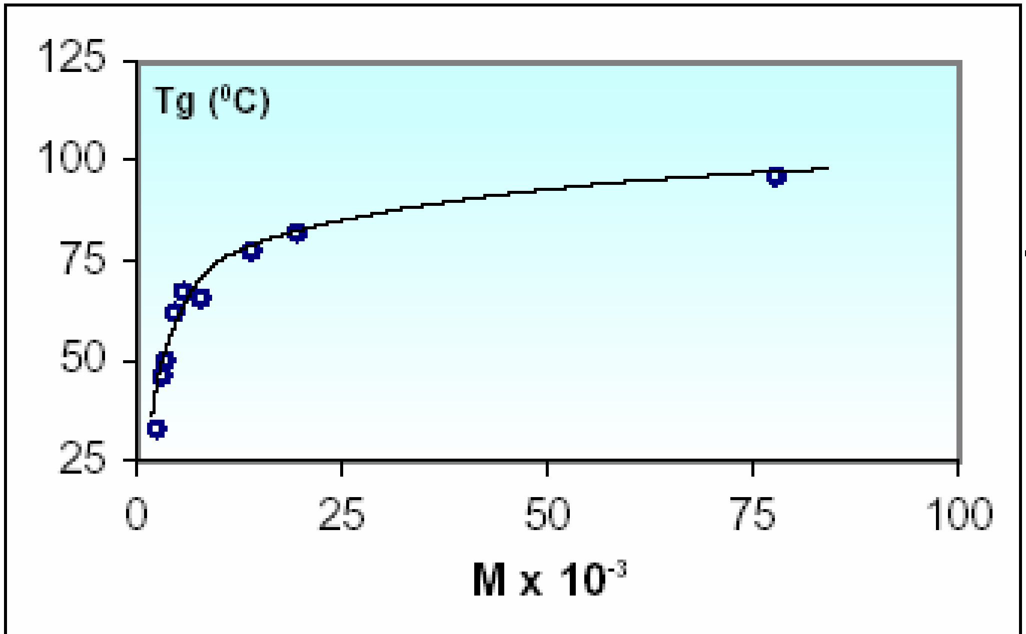


Ex) PS T_g = 40 ℃ M_n = 3,000

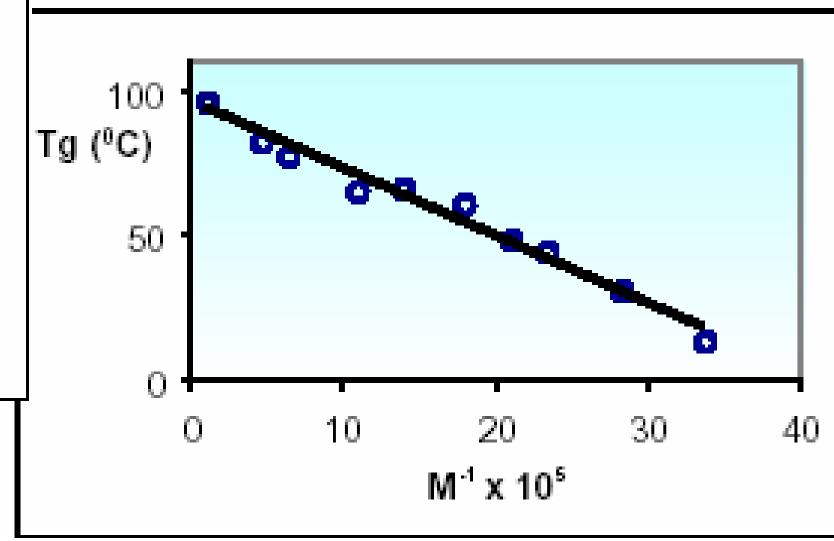
100 ℃ M_n = 300,000

Factors that Affect the Tg

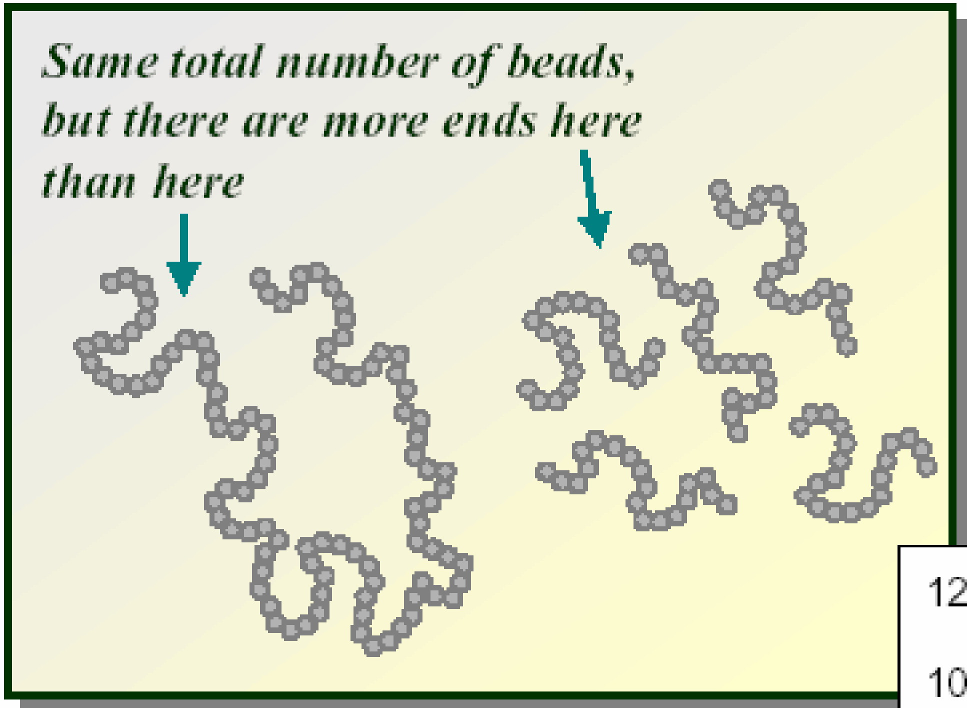
Molecular Weight

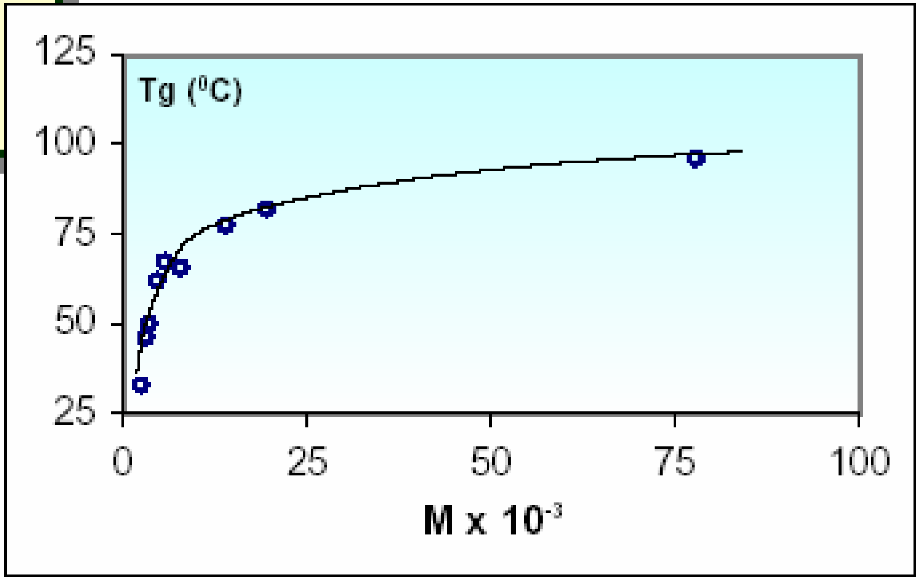


$$T_g = T_g^{\infty} - \frac{K}{\overline{\overline{M_n}}}$$



Factors that Affect the Tg
Molecular Weight

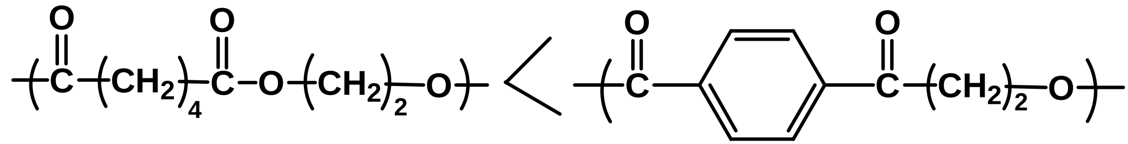




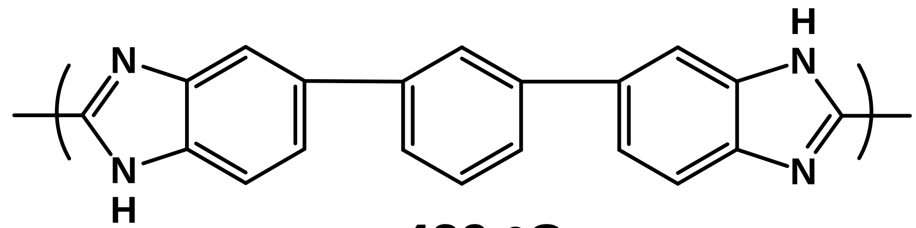
2) Chain flexibility

Flexible chain : low T_g

Rigid chain : high T_g



- 63 °C **69 °C**

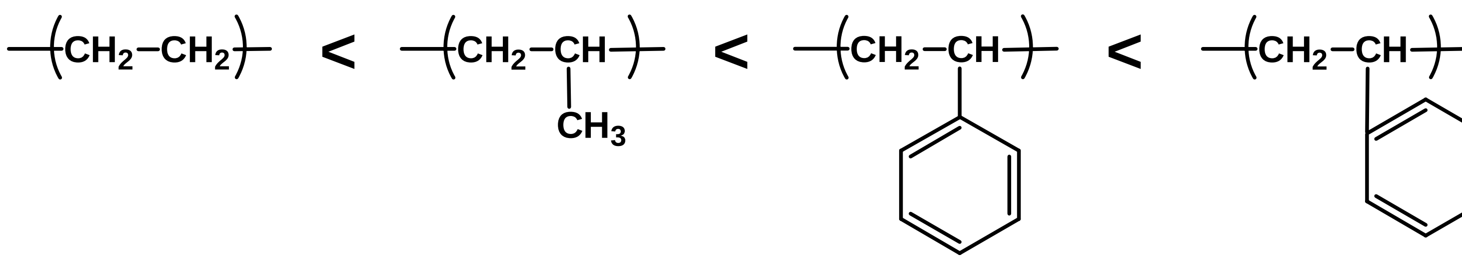


429 °C

3) Steric effect

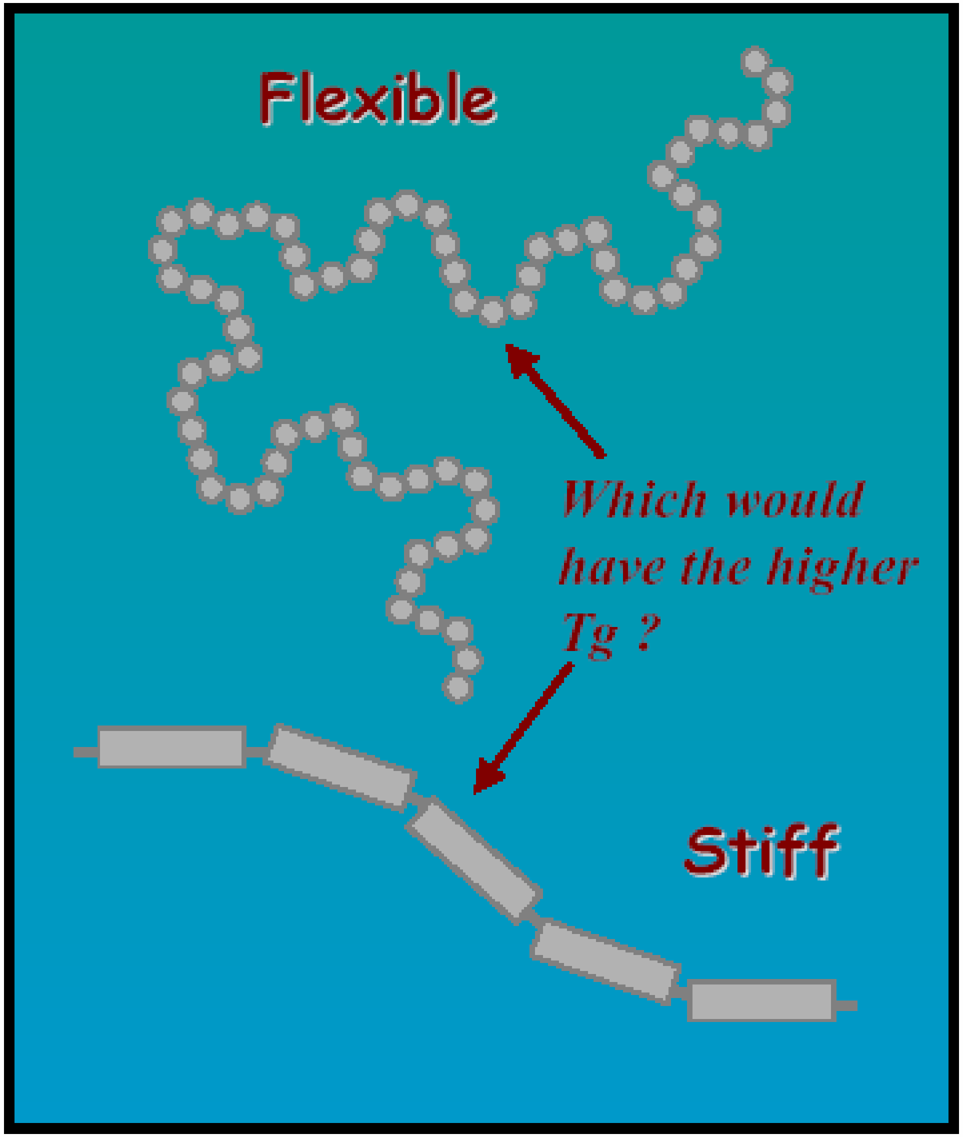
Bulkier substituent ⇨ Less rotational freedom ⇨ Higher T_g

a) T_g↑ with molar volume of pendant group↑



- 20 °C **5 °C** **100 °C** **151 °C**

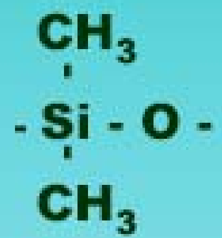
Factors that Affect the Tg
Chain Stiffness



Chain Stiffness

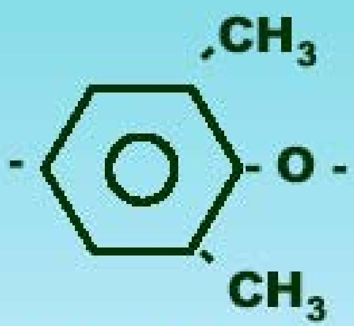
$-CH_2-CH_2-$ $\quad T_g \sim -80^0C$

Polyethylene



$T_g \sim -120^0C$

Poly (dimethyl siloxane)



$T_g \sim 200^0C$

Poly (phenylene oxide)

Factors that Affect the Tg
Chemical Structure

$-CH_2-CH(CH_3)-$

Atactic Polypropylene

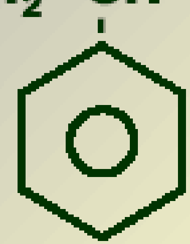
$T_g \sim ?$

$-CH_2-CH_2-$

Polyethylene

$T_g \sim ?$

$-CH_2-CH-$



Atactic Polystyrene

$T_g \sim ?$

Bulky Substituents

$-CH_2-CH_2-$

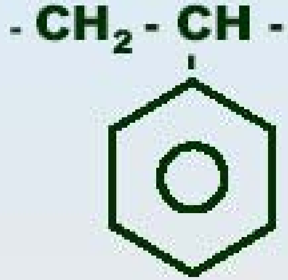
Polyethylene

$T_g \sim -80^0C$

$-CH_2-CH(CH_3)-$

Atactic Polypropylene

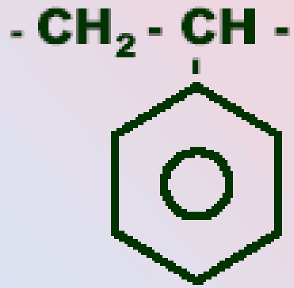
$T_g \sim -10^0C$



Atactic Polystyrene

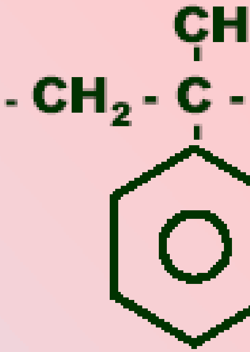
$T_g \sim 100^0C$

Bulky Substituents



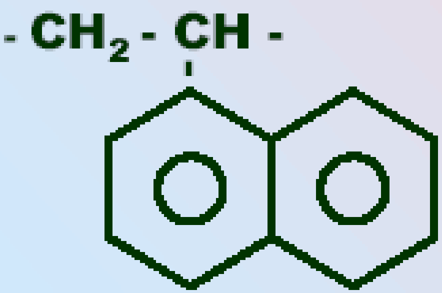
$T_g \sim 100^0C$

Atactic Polystyrene



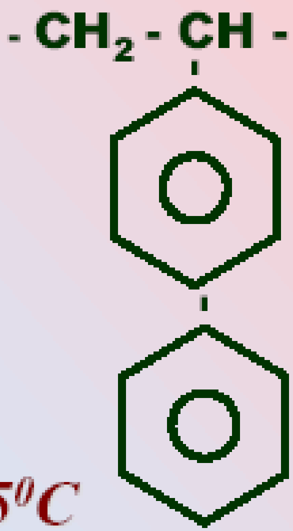
$T_g \sim 175^0C$

Atactic
Poly(α-methyl styrene)



$T_g \sim 135^0C$

Atactic
Poly(1-vinyl naphthalene)

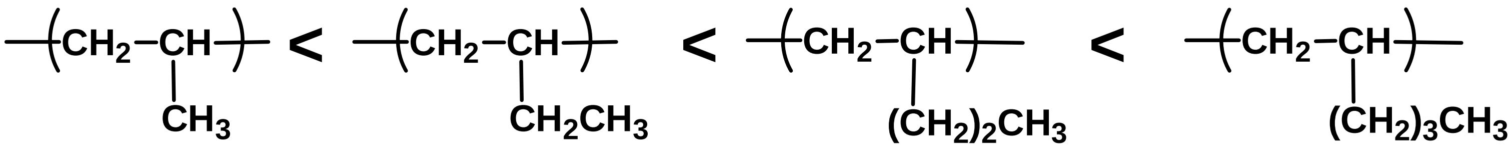


$T_g \sim 145^0C$

Atactic Poly(vinyl biphenyl)

b) T_g↓ with flexibility of pendant group↑

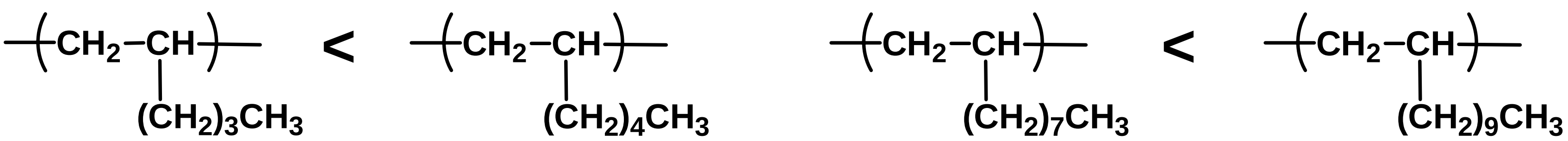
∵ Plasticizing effect



5 °C   - 24 °C   - 40 °C   - 50 °C

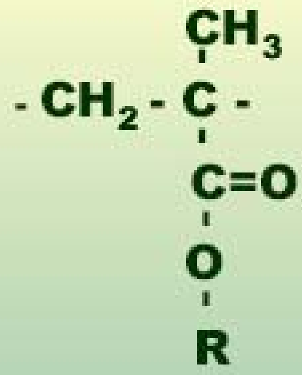
c) T_g↑ with chain length of pendant group↑

∵ Entanglement or side-chain crystallization



- 50 °C   - 31 °C   - 41 °C   - 6 °C

Flexible Substituents



R = Methyl $- CH_3$

R = Ethyl $- CH_2 - CH_3$

R = Propyl $- CH_2 - CH_2 - CH_3$

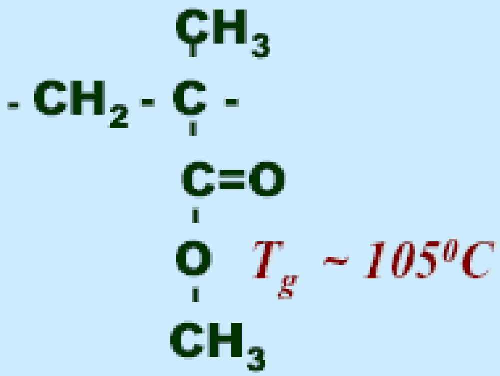
R = Butyl $- CH_2 - CH_2 - CH_2 - CH_3$

etc.

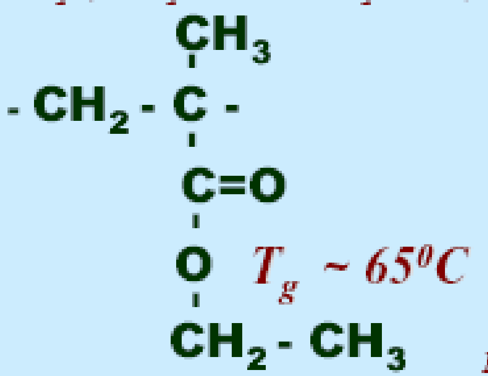
Flexible Substituents

Increase free volume

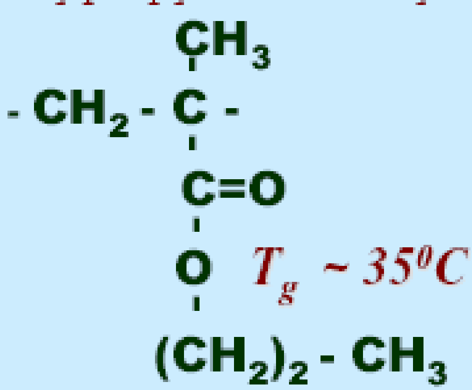
Poly(methyl methacrylate)



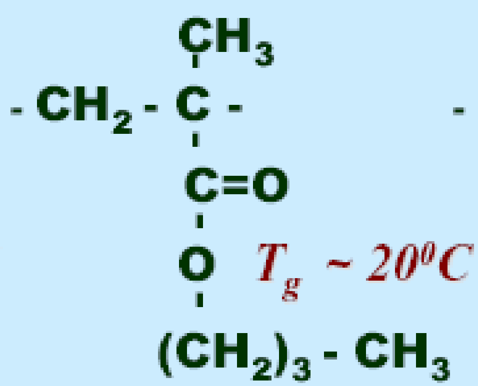
Poly(ethylmethacrylate)



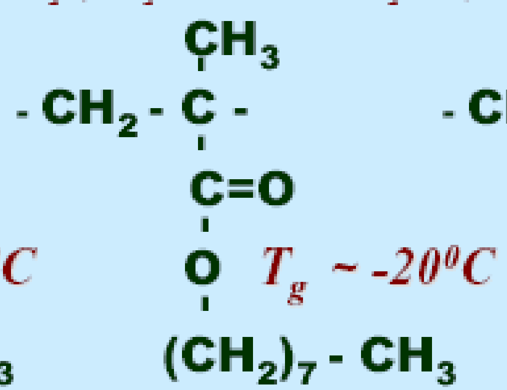
Poly(propyl methacrylate)



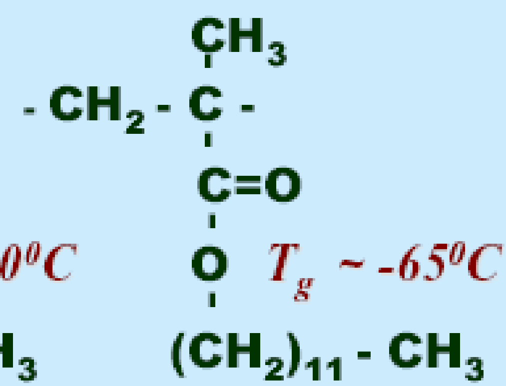
Poly(butyl methacrylate)



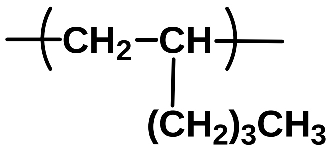
Poly(octyl methacrylate)



Poly(dodecyl methacrylate)



d) T_g↑ with branching of pendant group↑



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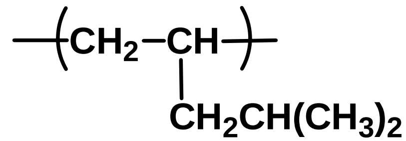

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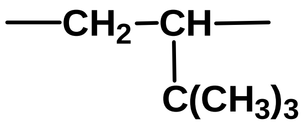
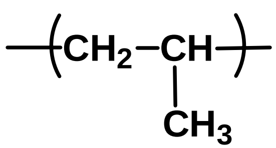


- 50 °C | 29 °C | 64 °C

e) T_g↑ with polarity of pendant group↑



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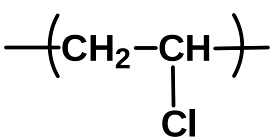

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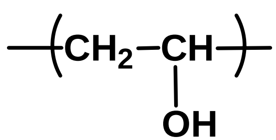
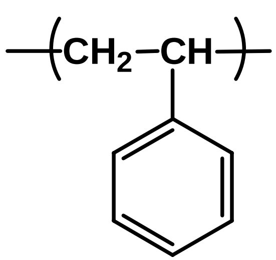


5 °C | 81 °C | 85 °C



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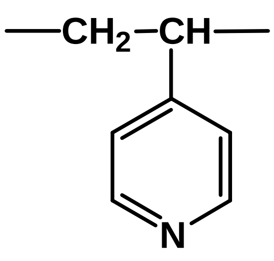


100 °C | 142 °C

The Effect of Intermolecular Interactions

$-CH_2-\underset{|}{C}H-$
$\quad CH_3$

Atactic Polypropylene

$T_g \sim -10^0C$

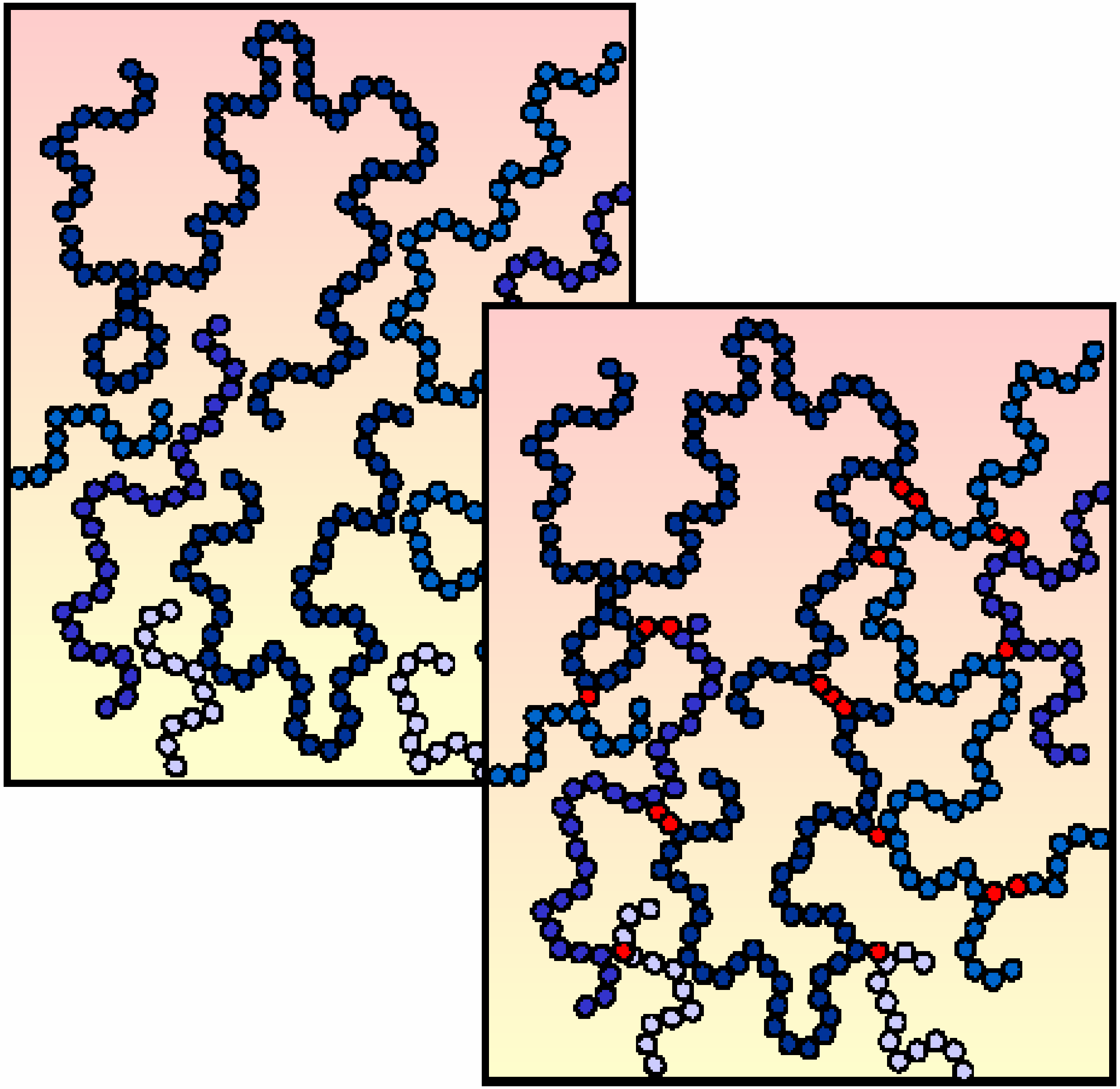
$-CH_2-\underset{|}{C}H-$
$\quad Cl$

PVC

$T_g \sim +87^0C$

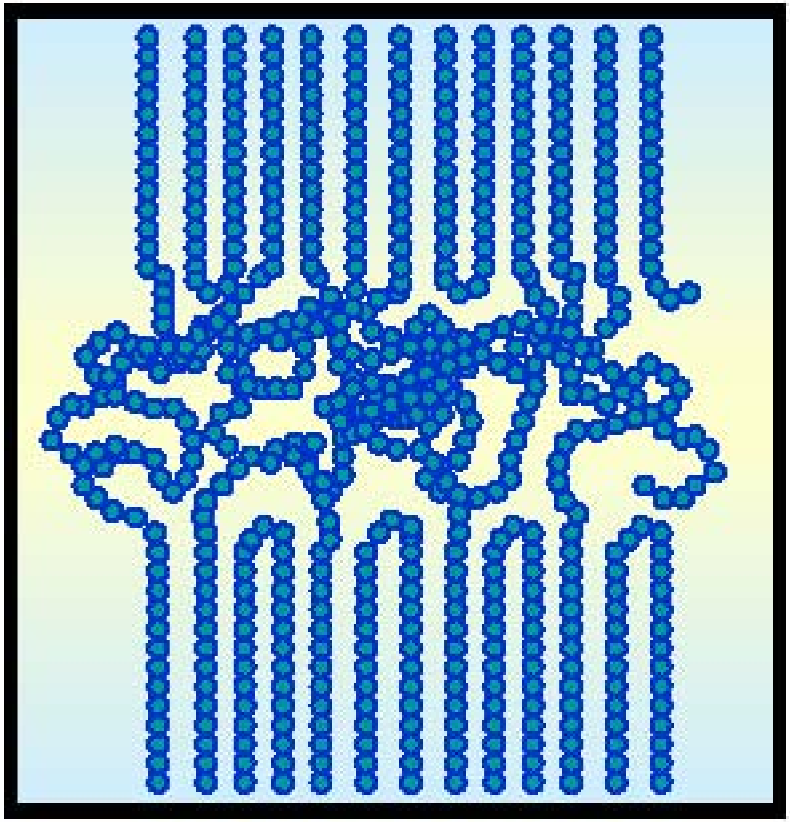
$T_g \uparrow$

The Effect of Cross - Linking



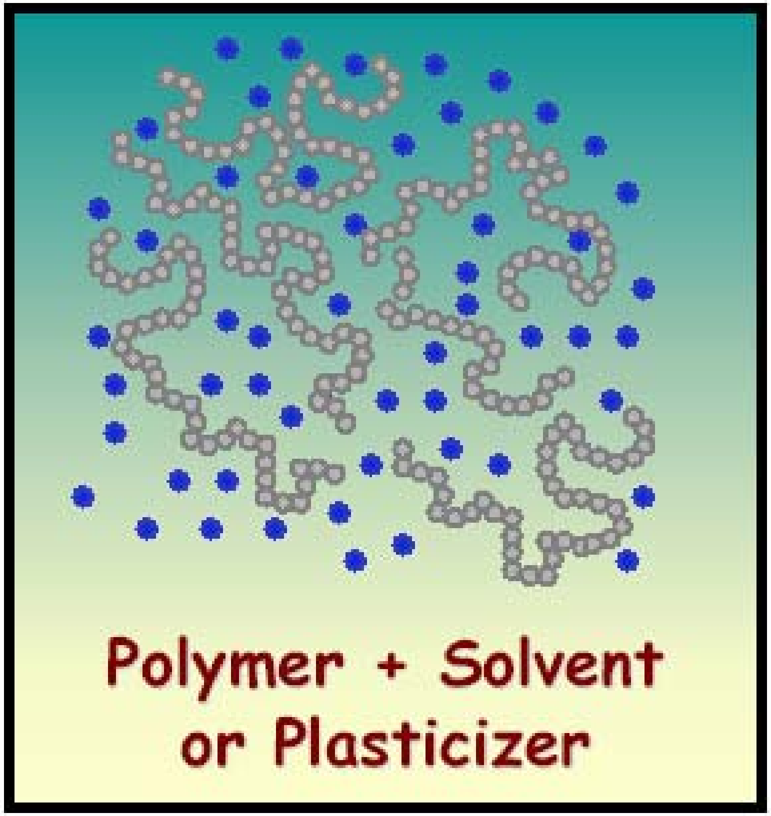
$T_g \uparrow$

The Effect of Crystallization



$T_g \uparrow$

The Effect of Diluents



$T_g \downarrow$

Plasticized PVC

Cable sheathing.

PVC "leather".

Cling wrap.

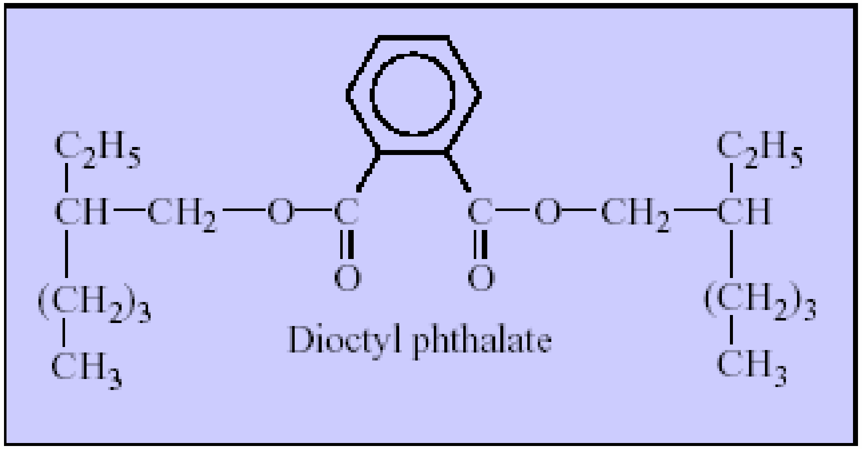
PVC bottles.

PVC apparel.

PVC apparel.

Plasticized PVC

Soft plasticized PVC toys



A water filled plasticized PVC teething ring.

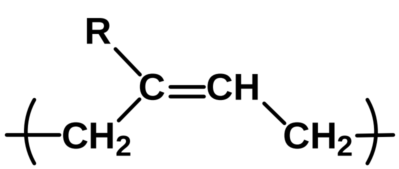
4) Stereochemistry

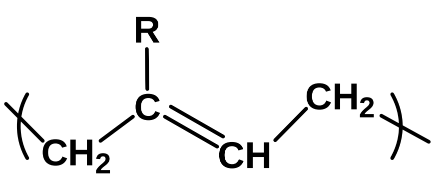
Table 3.3 T_g of Diene Polymers

Polymer	T_g (°C) cis	T_g (°C) trans
1,4-Polybutadiene	- 102	- 58
1,4-Polyisoprene	- 67	- 70
1,4-Polychloroprene	- 20	- 40

→ cis: lower T_g

→ trans: lower T_g





Isomerism in Polymers

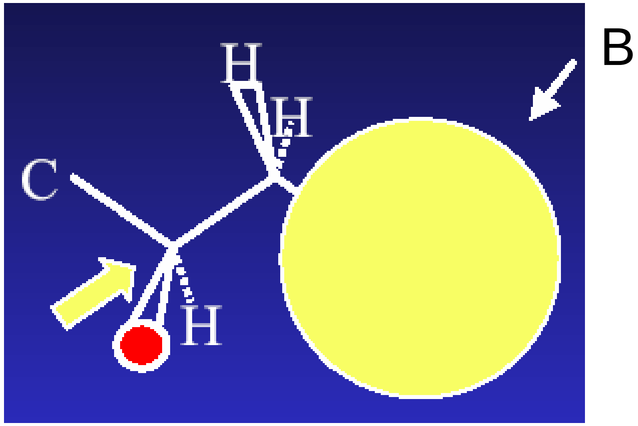
Two molecules are said to be isomers if they are made up of the same number and types of atoms, but differ in the arrangement of these atoms.

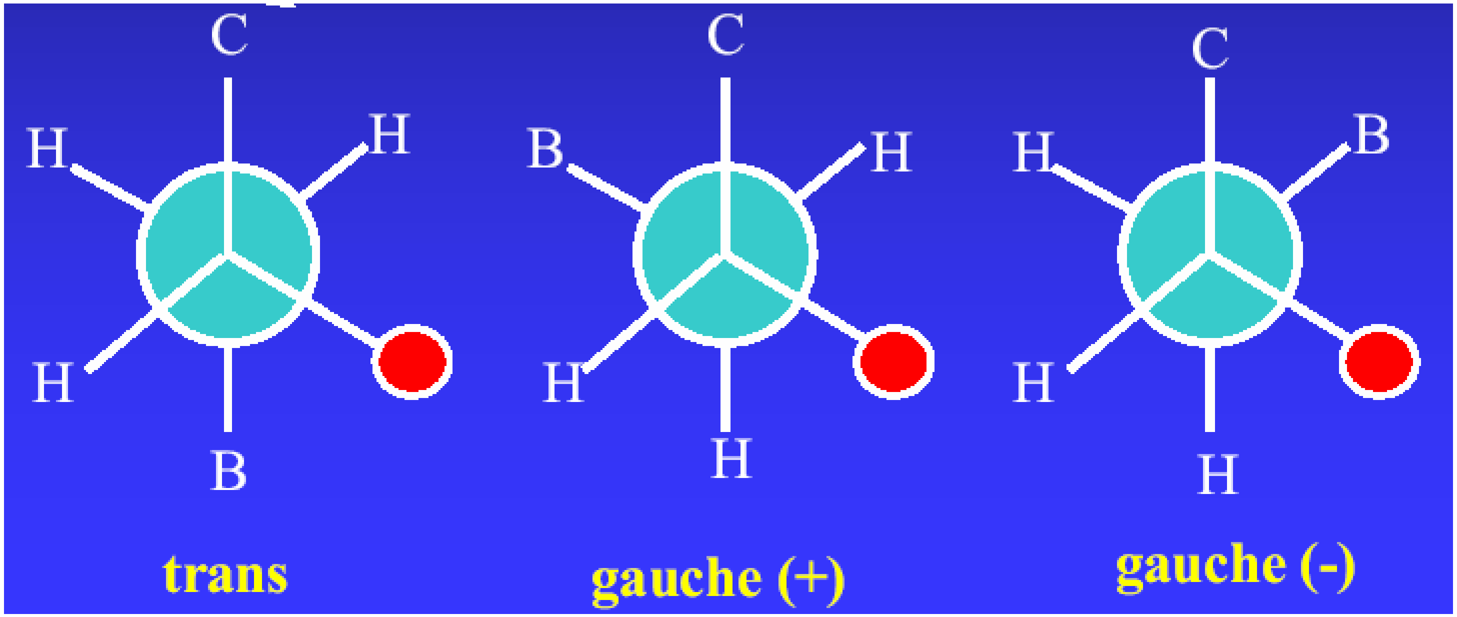
- **Sequence isomerism**
- **Stereoisomerism (in vinyl polymers)**
- **Structural isomerism (in diene polymers)**

Conformational Isomerism

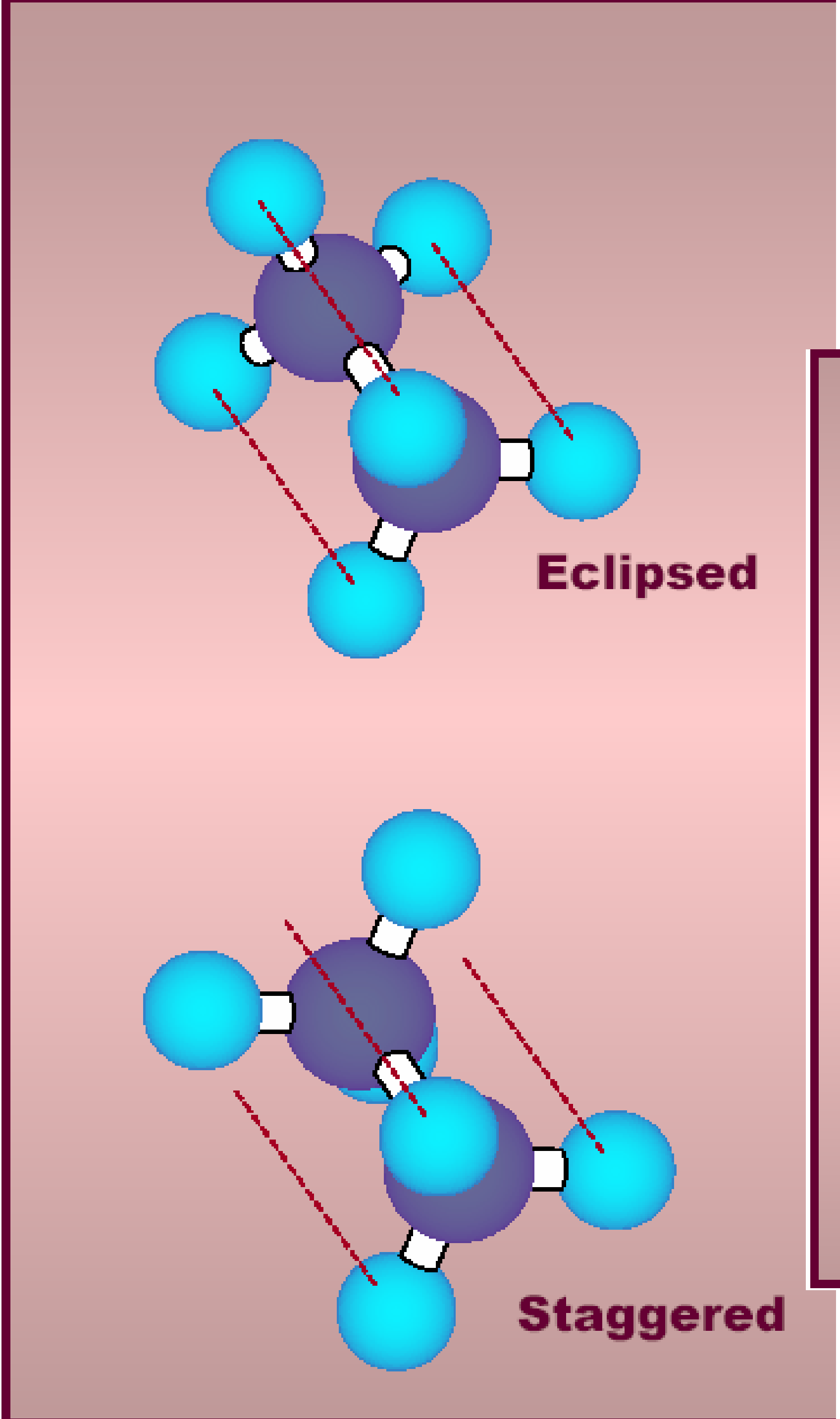
Consider Newman projections of an internal bond.

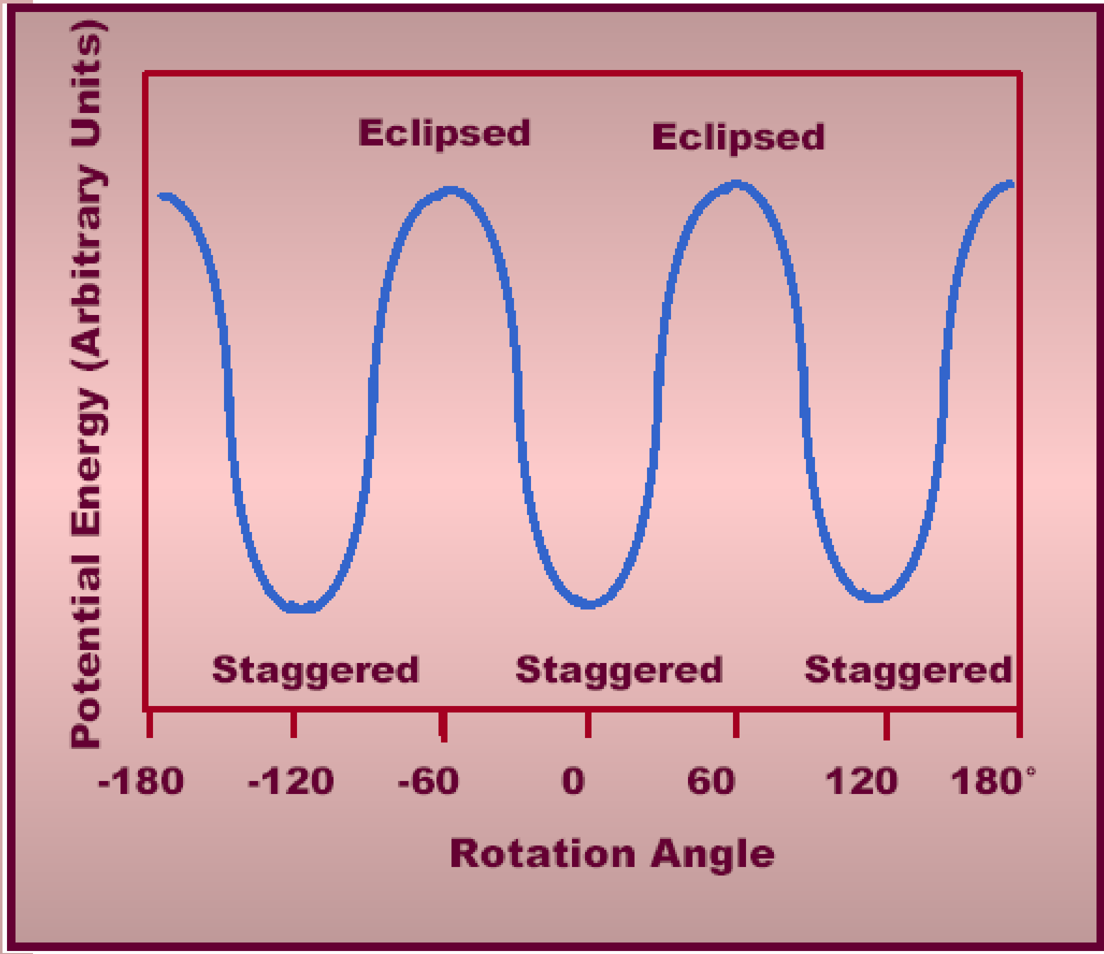
Look along the direction of the first internal bond in this meso dyad.





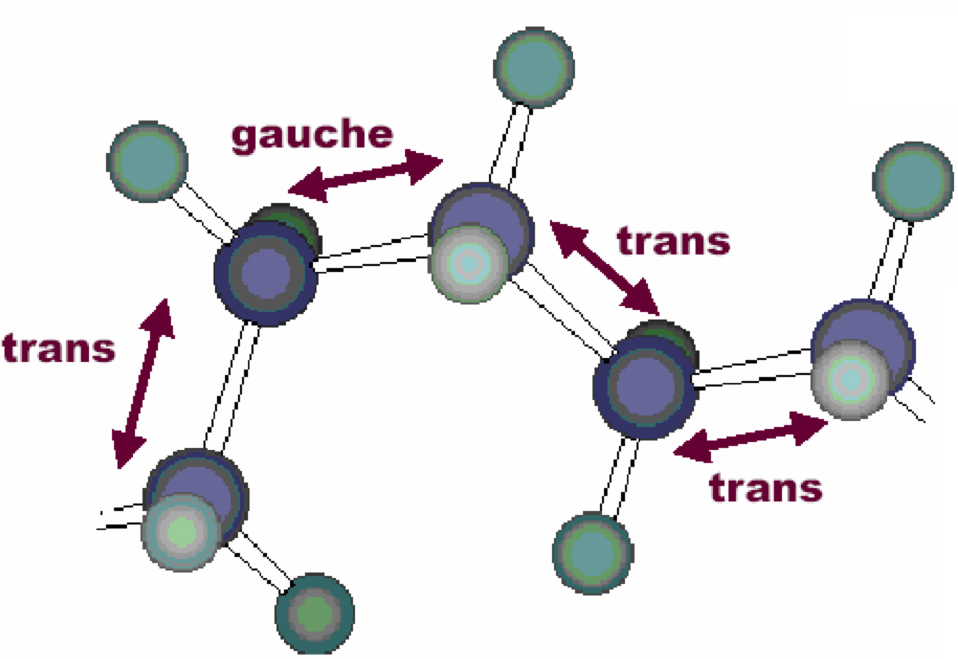
Conformations

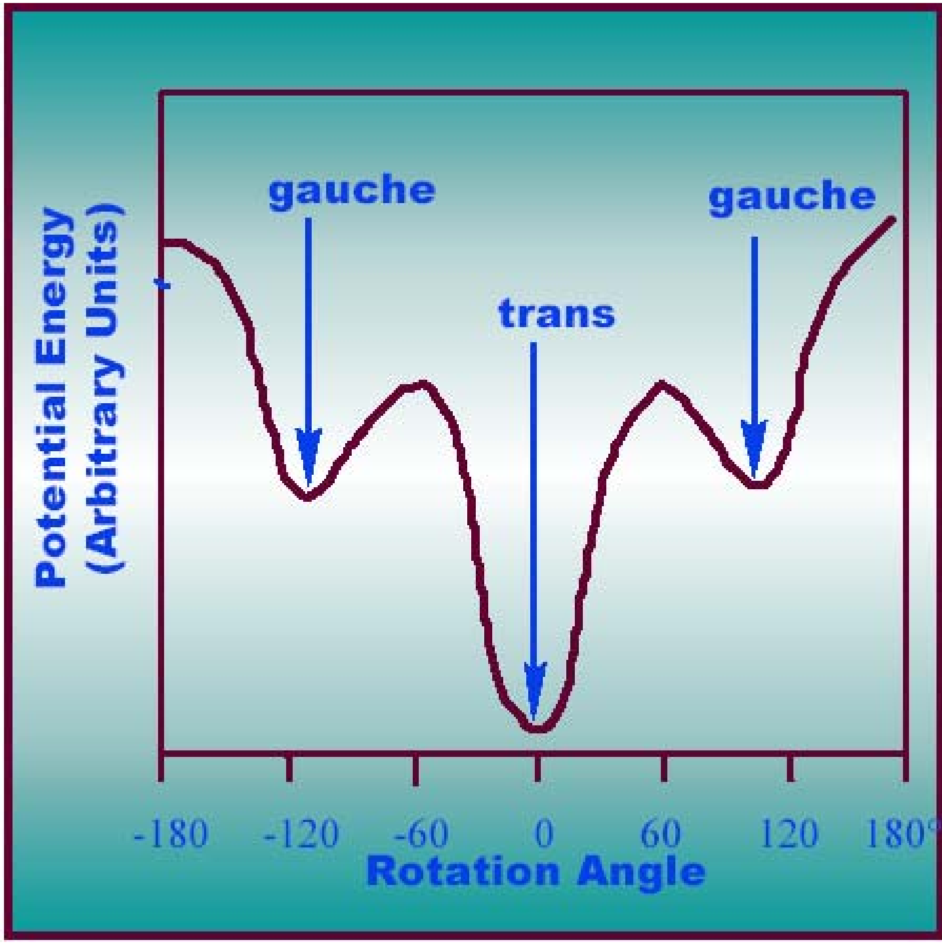




Conformations; or how do Chains Fold

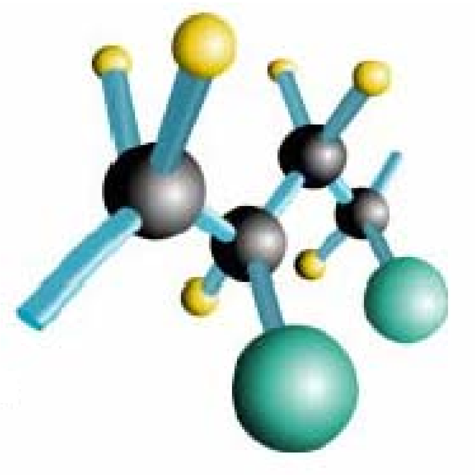
Polyethylene



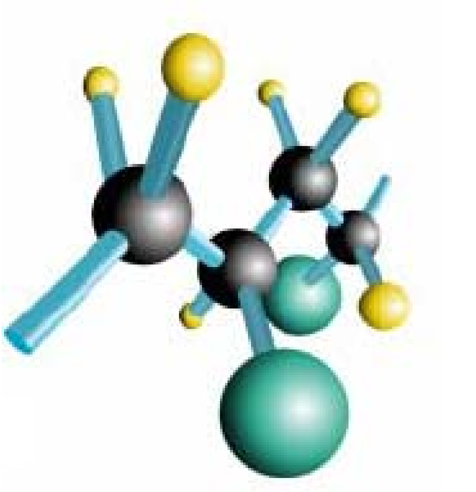


Stereoisomerism in Vinyl Polymers

Polymerization of a vinyl monomer, CH_2= CHX, where X may be a halogen, alkyl or other chemical group (anything except hydrogen!) leads to polymers with microstructures that are described in terms of tacticity.



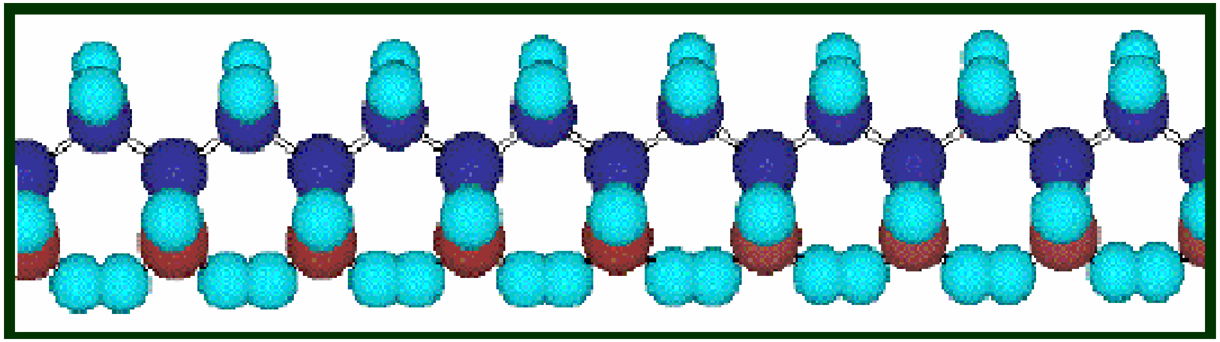
Meso Diad



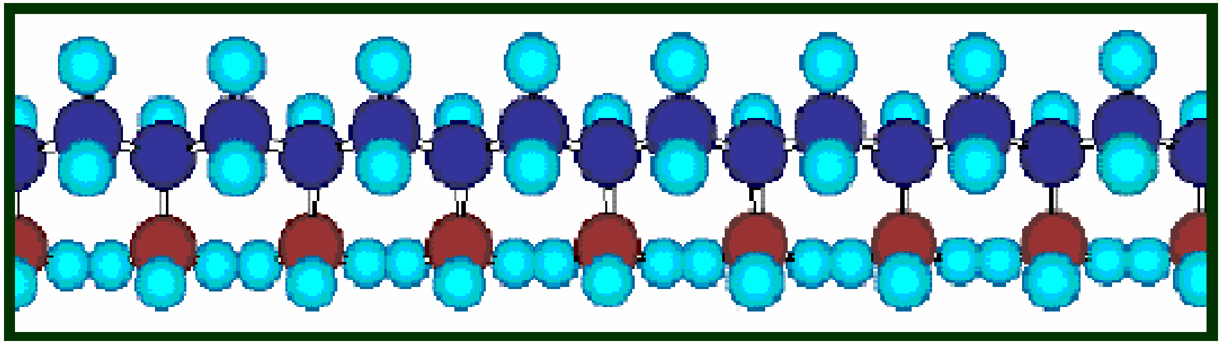
Racemic Diad

Isotactic Chains

Part of an isotactic polypropylene chain seen from the side



The same chain seen more from the top



100% meso dyads

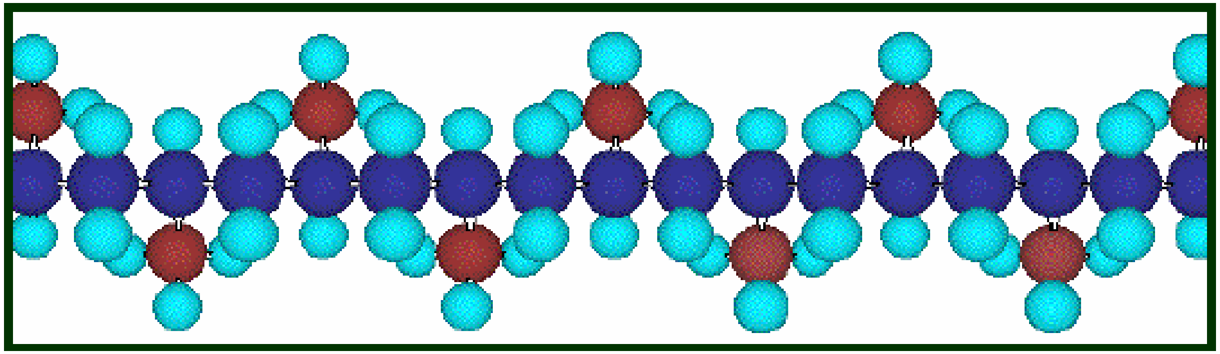
Syndiotactic Chains

Here are two more polypropylene chains, both shown as if we were looking down from "on top". One of these consists of units that are all racemic to one another and is called syndiotactic. The other has a random arrangement of units and we call such chains atactic. Which one is the atactic chain , A or B ?

100% racemic dyads

A

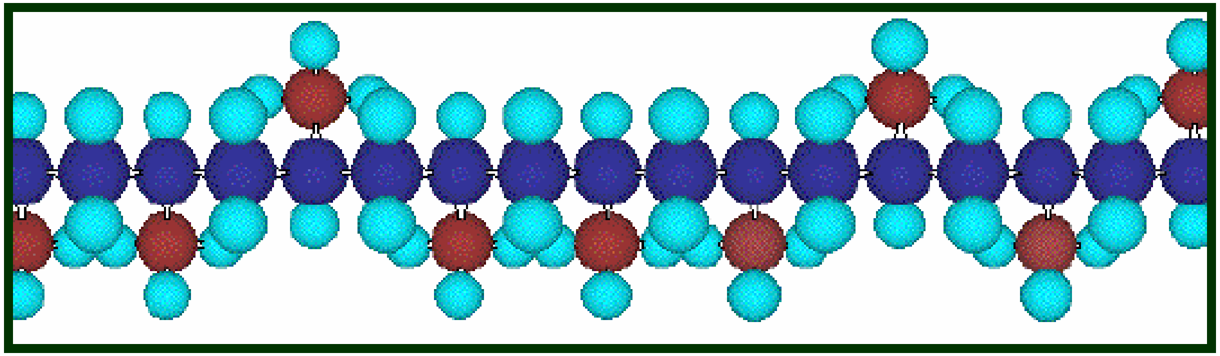
syndiotactic



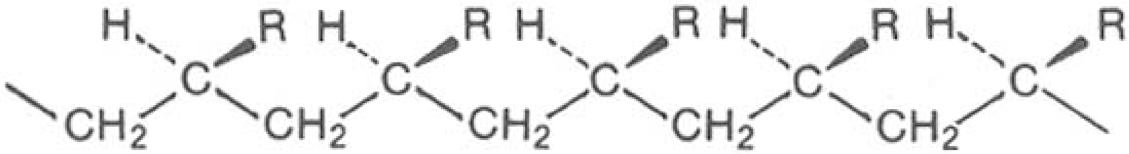
50% meso 50% racemic dyads

B

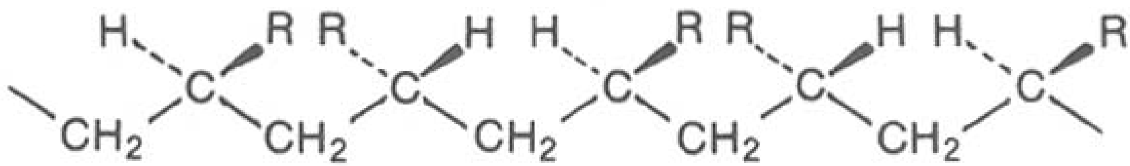
atactic



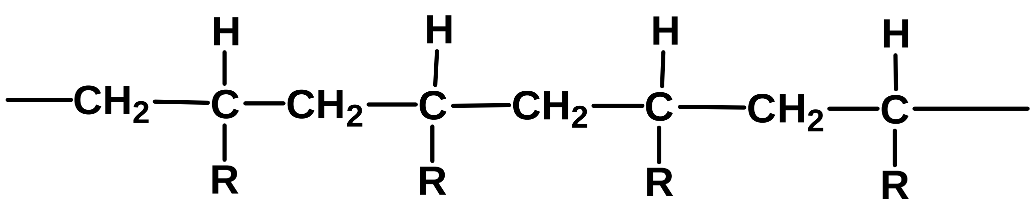
3.5 Stereochemistry



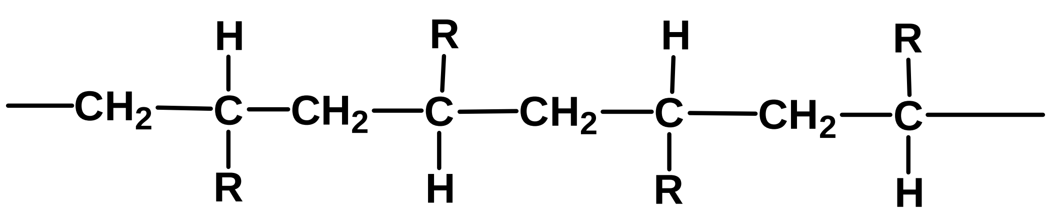
Isotactic



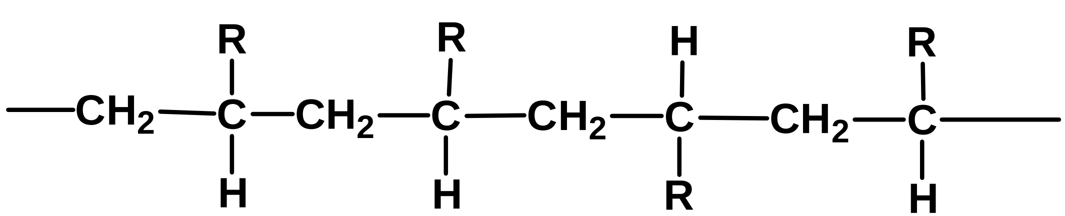
Syndiotactic



Isotactic



Syndiotactic

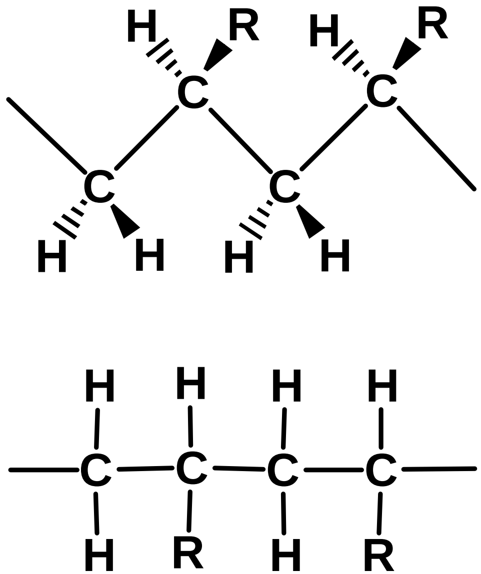


Atactic

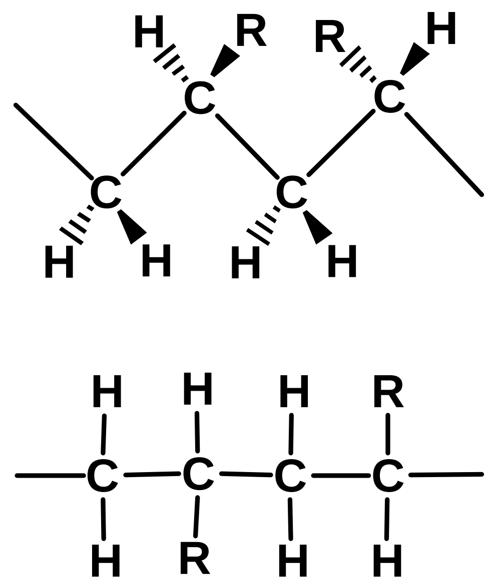
3.5 Stereochemistry

Stereoregular polymers derived from monomer $CH_2{=}CHR$

Dyad



meso (m)



racemic (r)

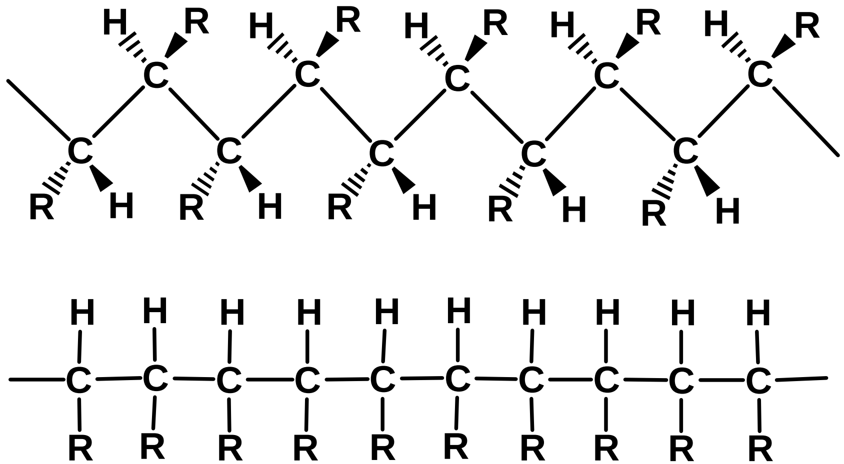
Triad

mm	mr (or rm)	rr
isotactic	heterotactic	syndiotactic

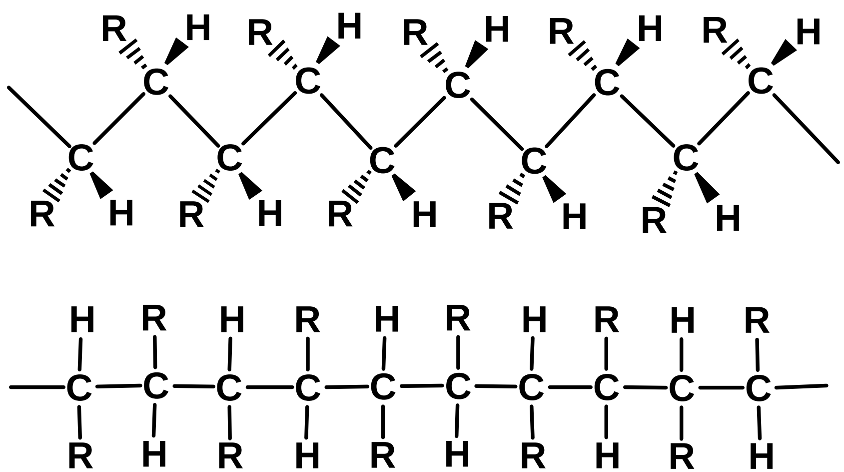
Tetrad

mmm **mmr (or rmm)** **mrm** **rmr** **rrm (or mrr)** **rrr**

Stereoregular polymers derived from monomer CHR=CHR

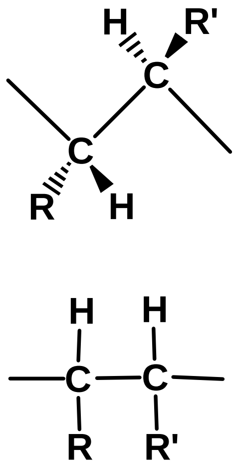


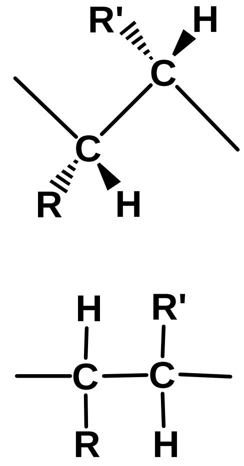
Isotactic



Syndiotactic

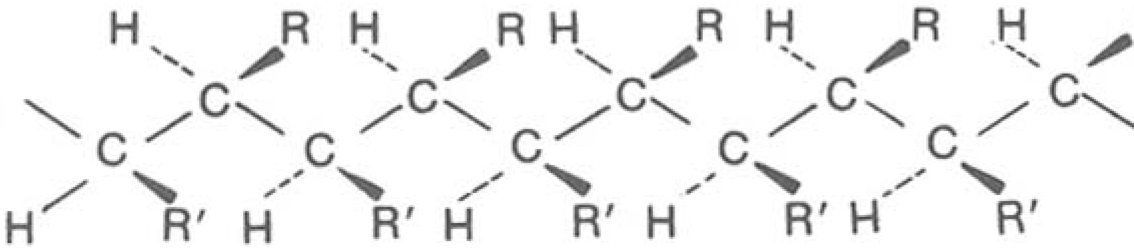
Stereoregular polymers derived from monomer RCH=CHR’



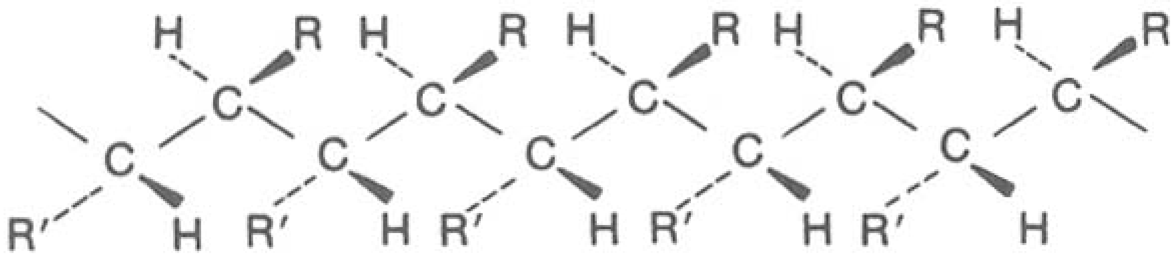


Erythro

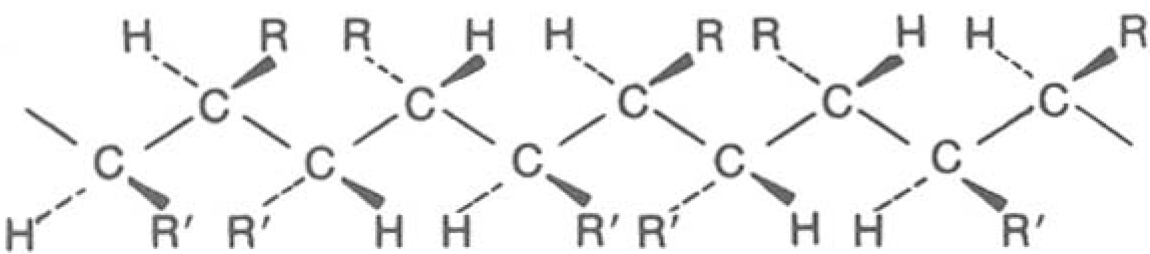
Threo



Threo-diisotactic

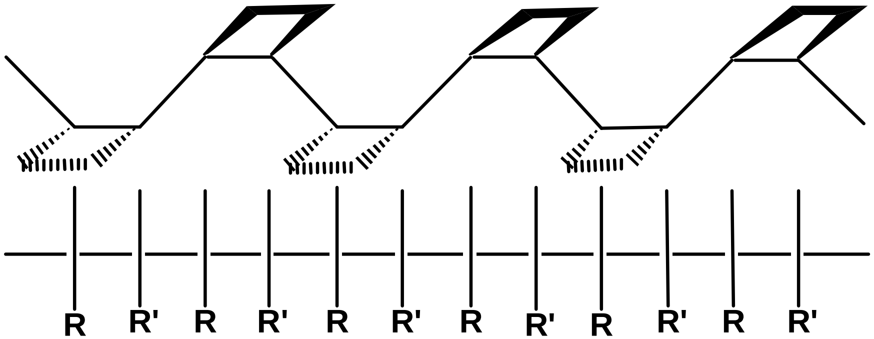


Erythro-diisotactic

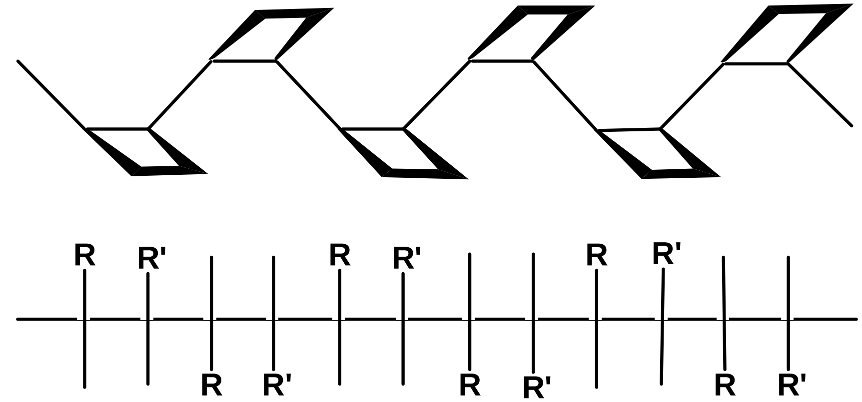


Disyndiotactic

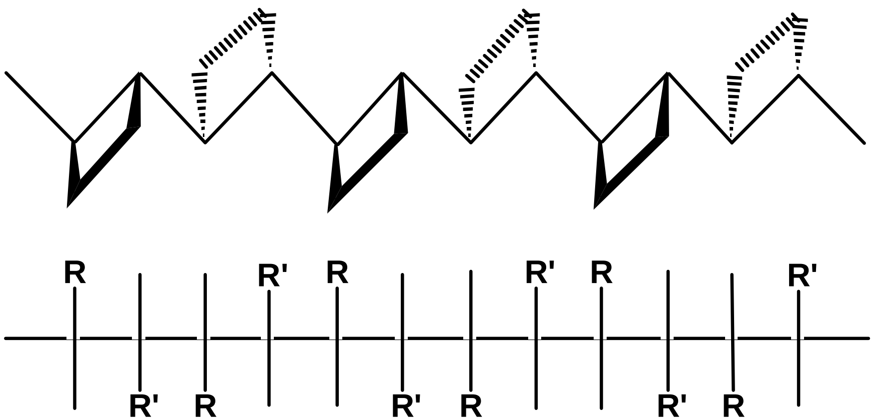
Stereoregular polymers derived from cyclobutene



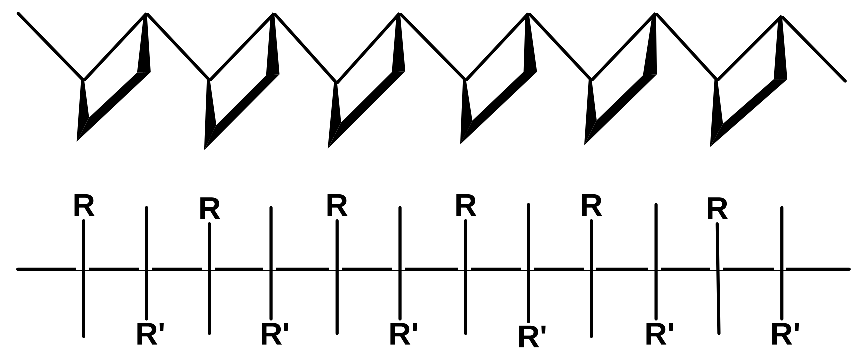
Erythro-diisotactic



Erythro-disyndiotactic

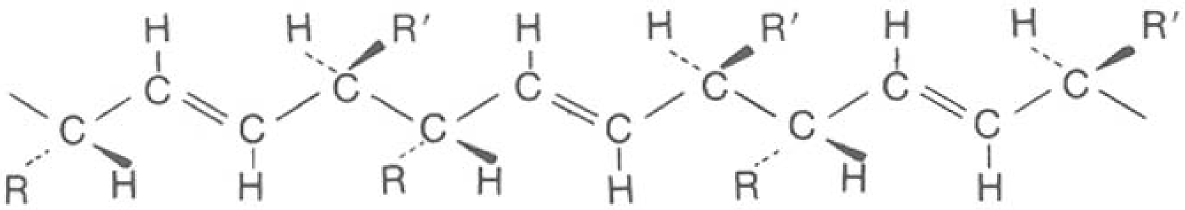


Threo-disyndiotactic

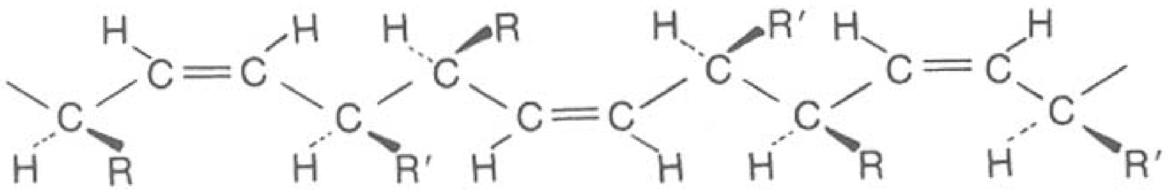


Threo-diisotactic

Stereoregular polymers derived from CHR=CH-CH=CHR’



Trans-erythro-diisotactic



Cis-threo-disyndiotactic

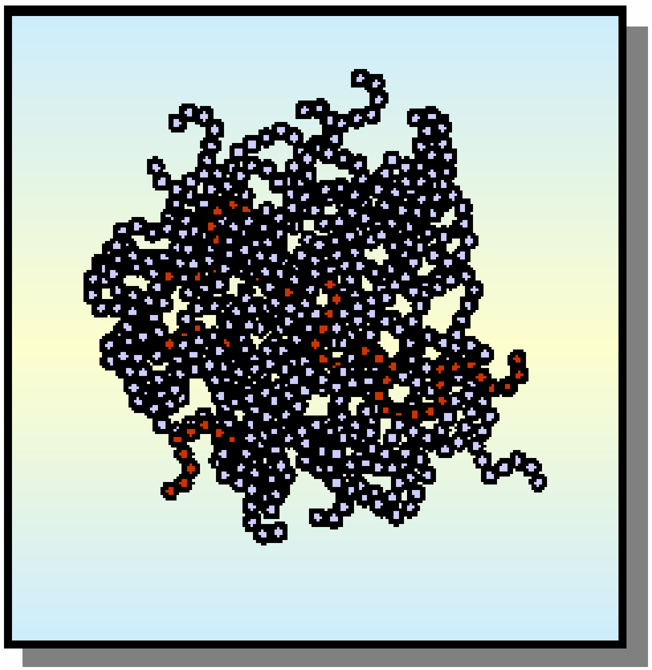
Table 3.4 T_g of Polymers of Varying Tacticity

	T_g (°C)		
Polymer	**Syndiotactic**	**Atactic**	**Isotactic**
PMMA	105	105	38
Poly(ethyl methacrylate)	65	65	12
Poly(t-butyl methacrylate)	114	118	7
PP	- 4	- 6	- 18
PS	100		99

T_g (syndiotactic) ≈ T_g (atactic) > T_g (isotactic)

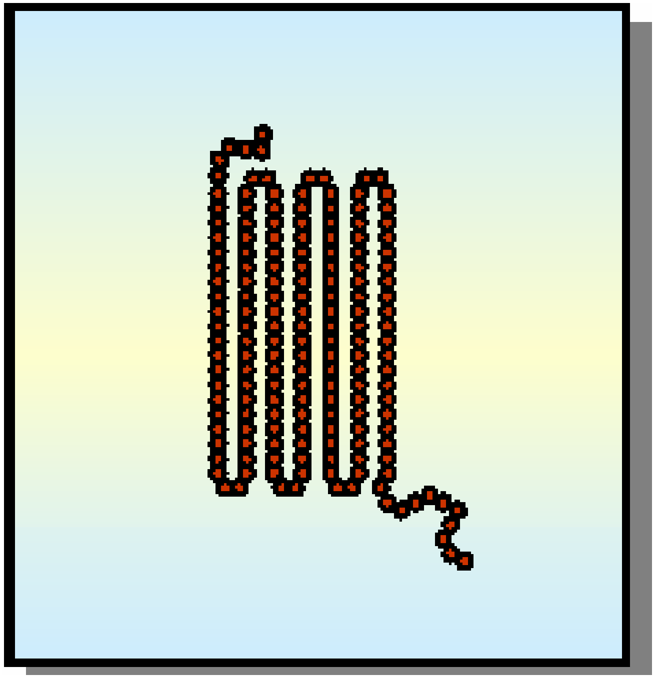
Crystallinity in Polymers

Let's establish a simple connection between structure and properties right from the beginning. We'll explore polymer morphology in more detail later, but simplistically we can get:



RANDOM COILS

Like "cooked spaghetti"

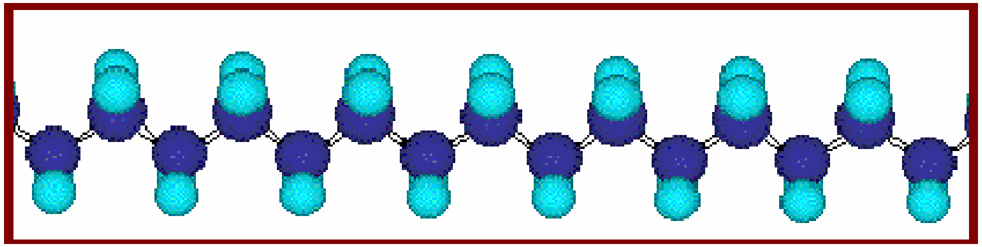


SEMICRYSTALLINE POLYMERS

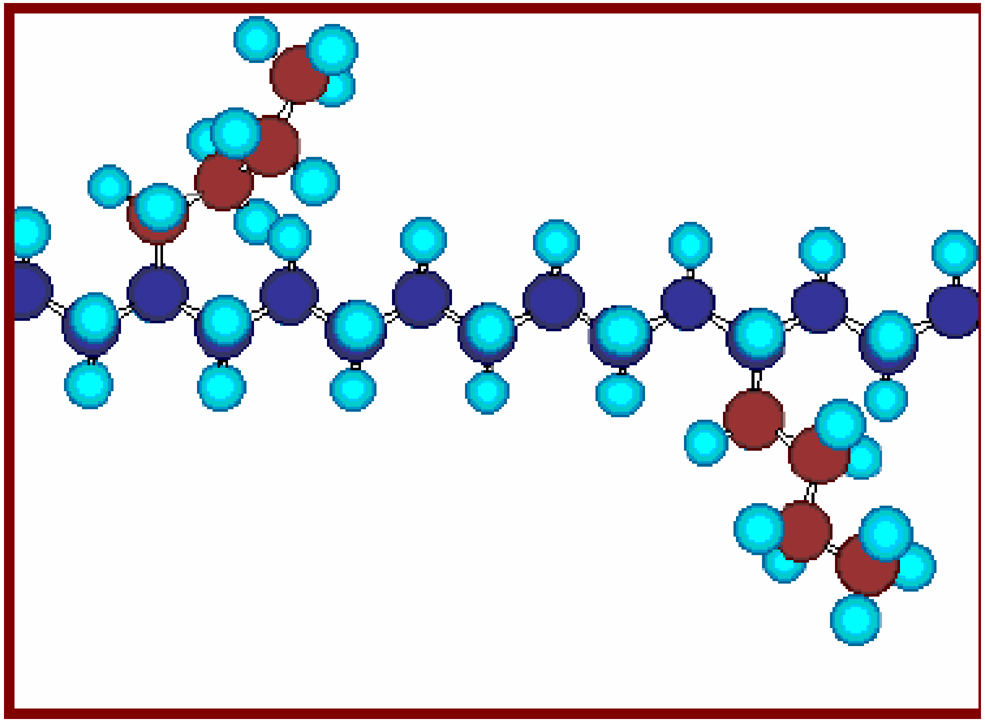
A bit like "uncooked spaghetti"

Linear and Branched Polyethylenes

Linear

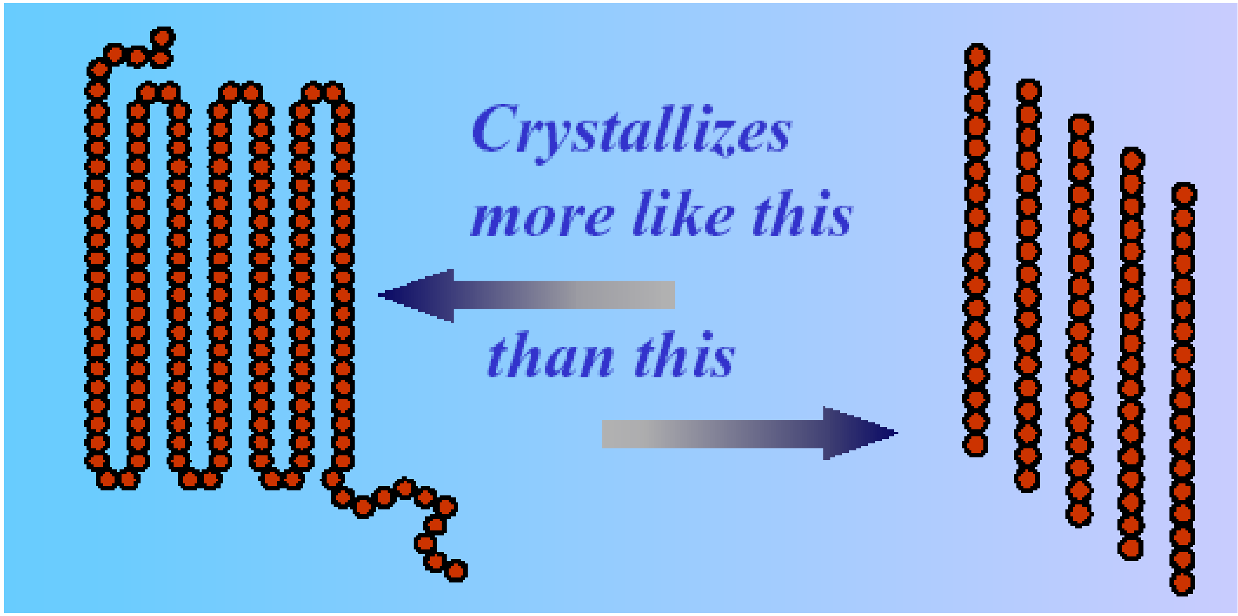


Branched



Which of these is more likely to crystallize?

The answer is linear!



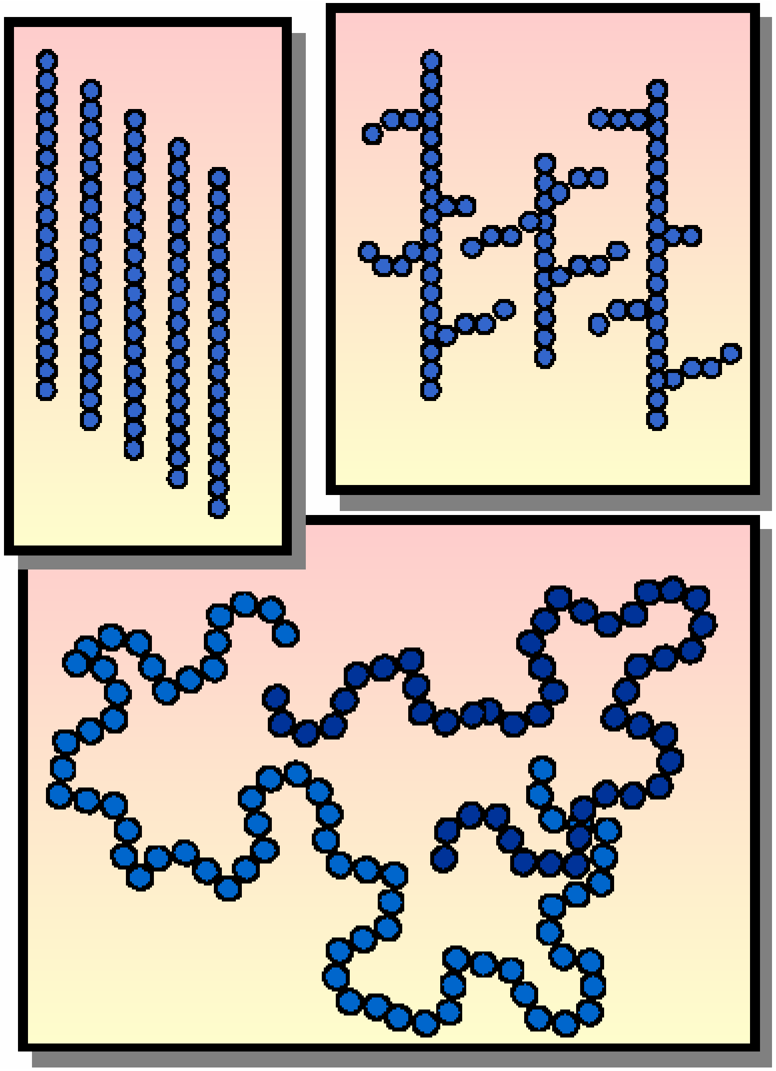
Various grades of polyethylene are produced commercially and are often referred to as "high density" or "low density". Which do you think is the high density polyethylene

A. The linear, more crystalline stuff ?

B. The (somewhat) branched less crystalline stuff ?

The answer is still linear!

Chains that cannot crystallize (e.g., highly branched ones), or even linear chains that are heated above their crystalline melting points, actually look something like cooked spaghetti or random coils.



They do not pack as closely together as in the crystalline state.

3.6 Crystallinity

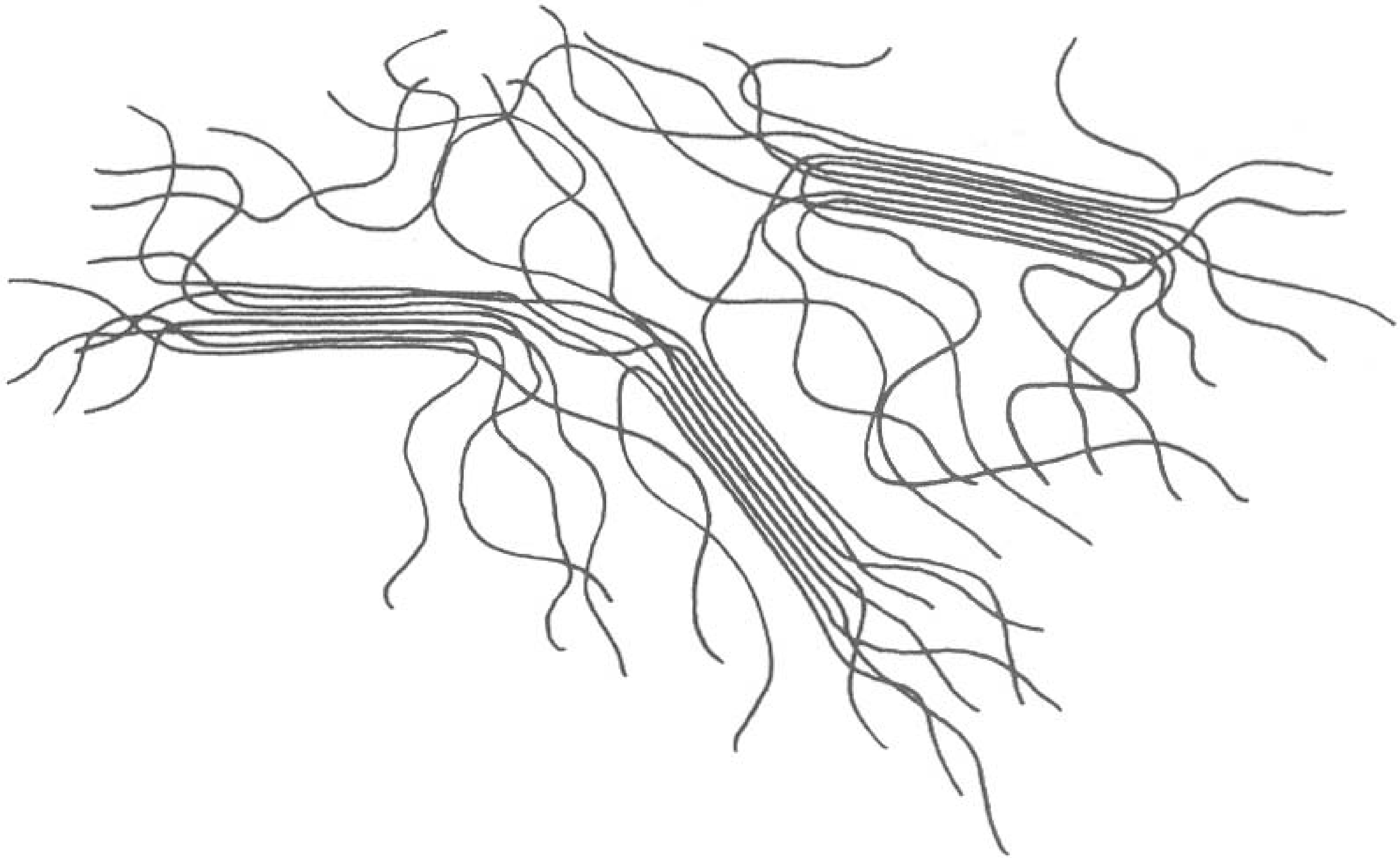
Requirements for Crystallinity

- Highly stereoregular structure with little or no chain branching
- Highly polar groups that give rise to very strong dipole-dipole interactions

Crystallization Methods

- Cooling of molten polymer
- Evaporation of polymer solutions
- Heating of a polymer under vacuum or in an inert atmosphere at a specified temperature ($T_g < T < T_m$) = Annealing
- Stretching a polymer sample above T_g = Drawing

Fig 3.15 Fringed micelle model



Any particular polymer chain may extend through a number of crystallites

Fringed Micelle Model

The First Really Useful Model

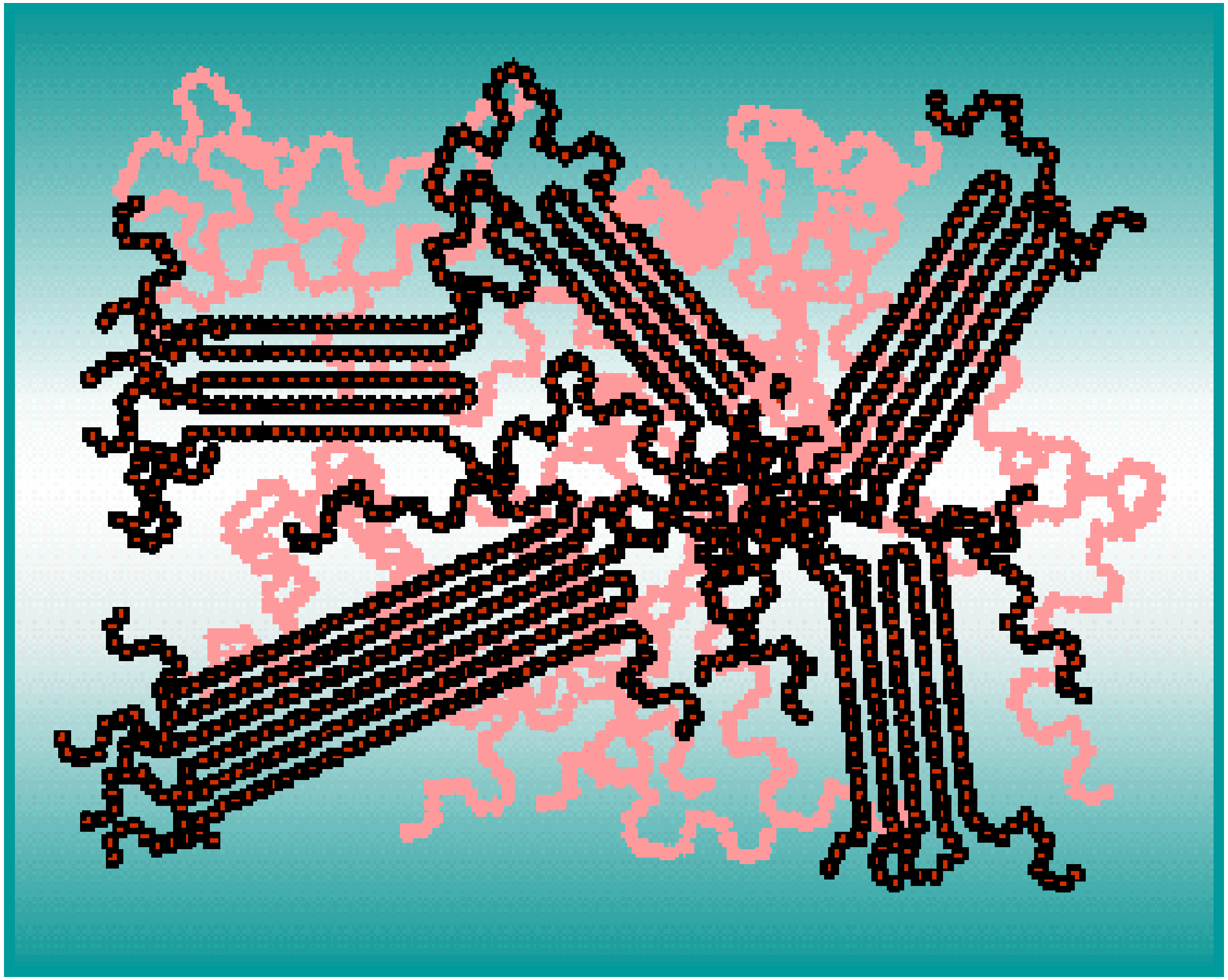
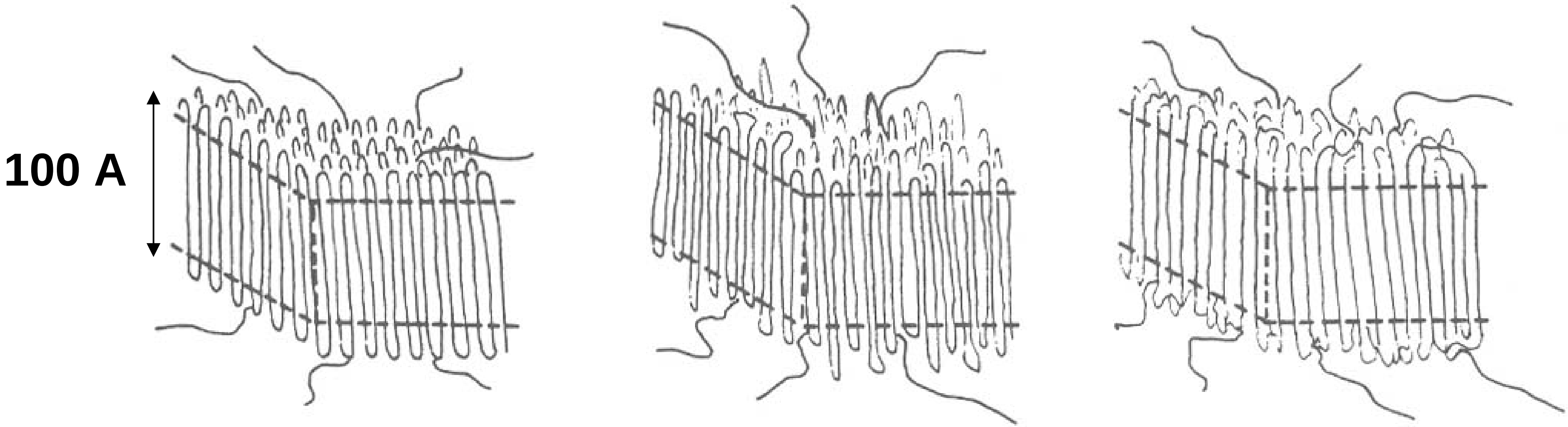


Fig 3.16 Folded-Chain Lamella Model



(a)
Regular Adjacent Folds

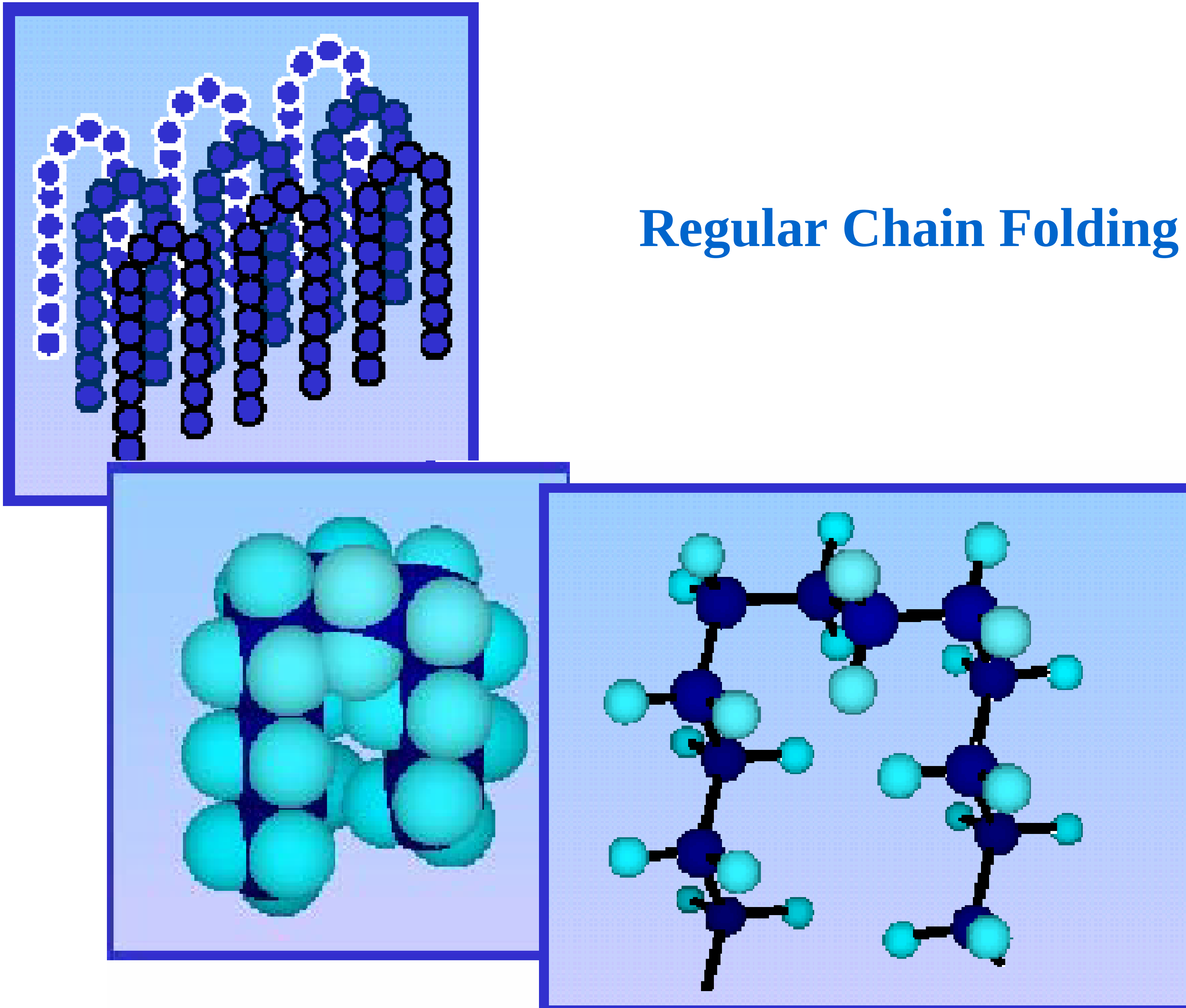
(b)
Irregular Adjacent Folds

(c)
Nonadjacent Switchback

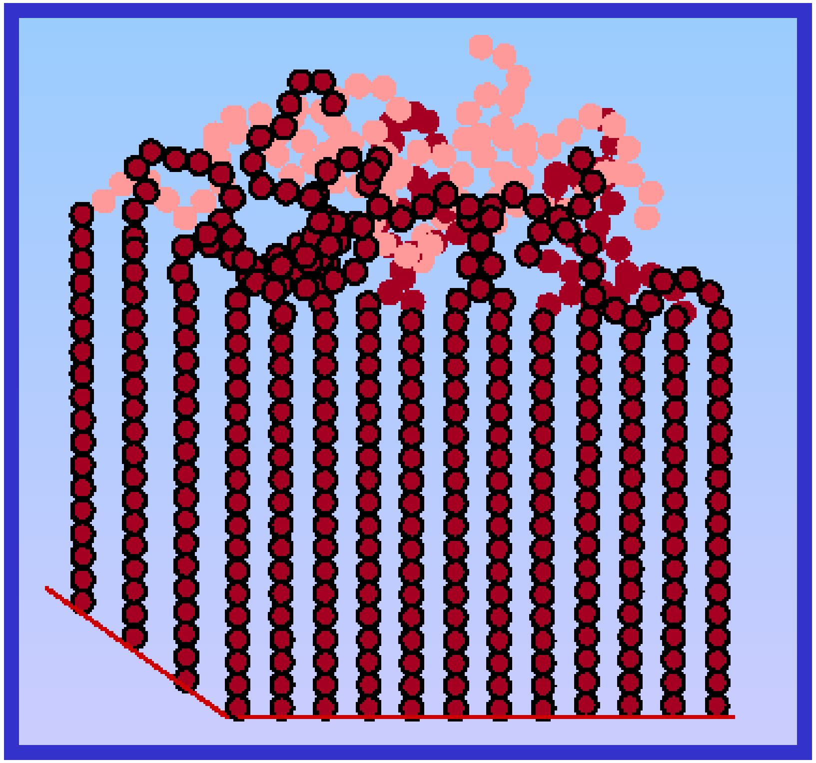
From Dilute Solution

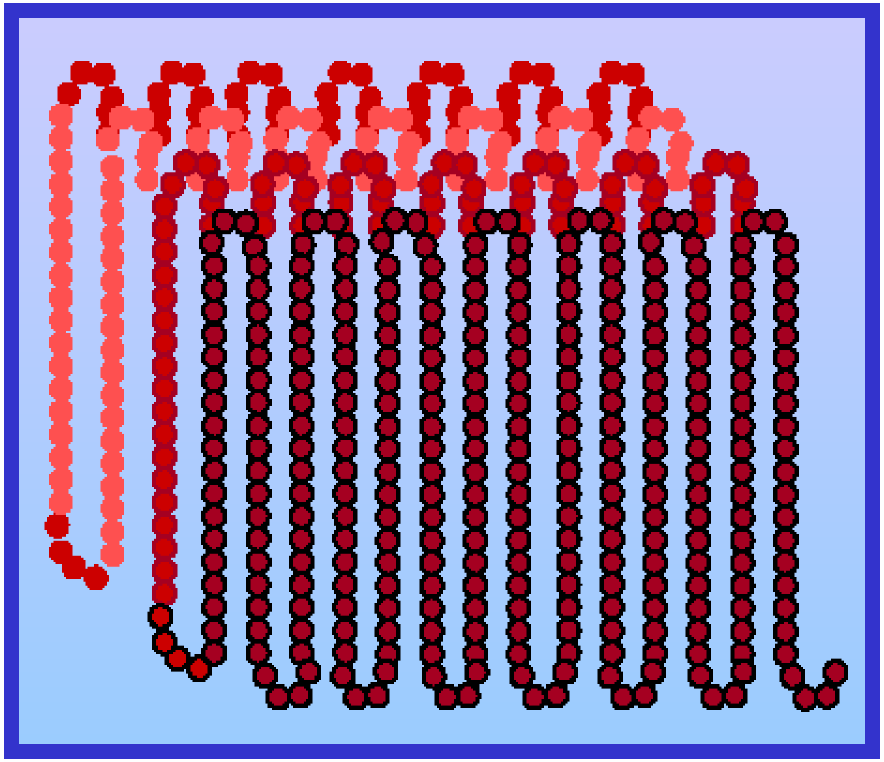
From Melt

Regular Chain Folding



Flory Switchboard Model





Irregular Chain Folding

(Random Re-entry)

From Melt

Spherulite

Regular Folding Chain

(Adjacent Re-entry)

From Dilute Solution

Single Crystal

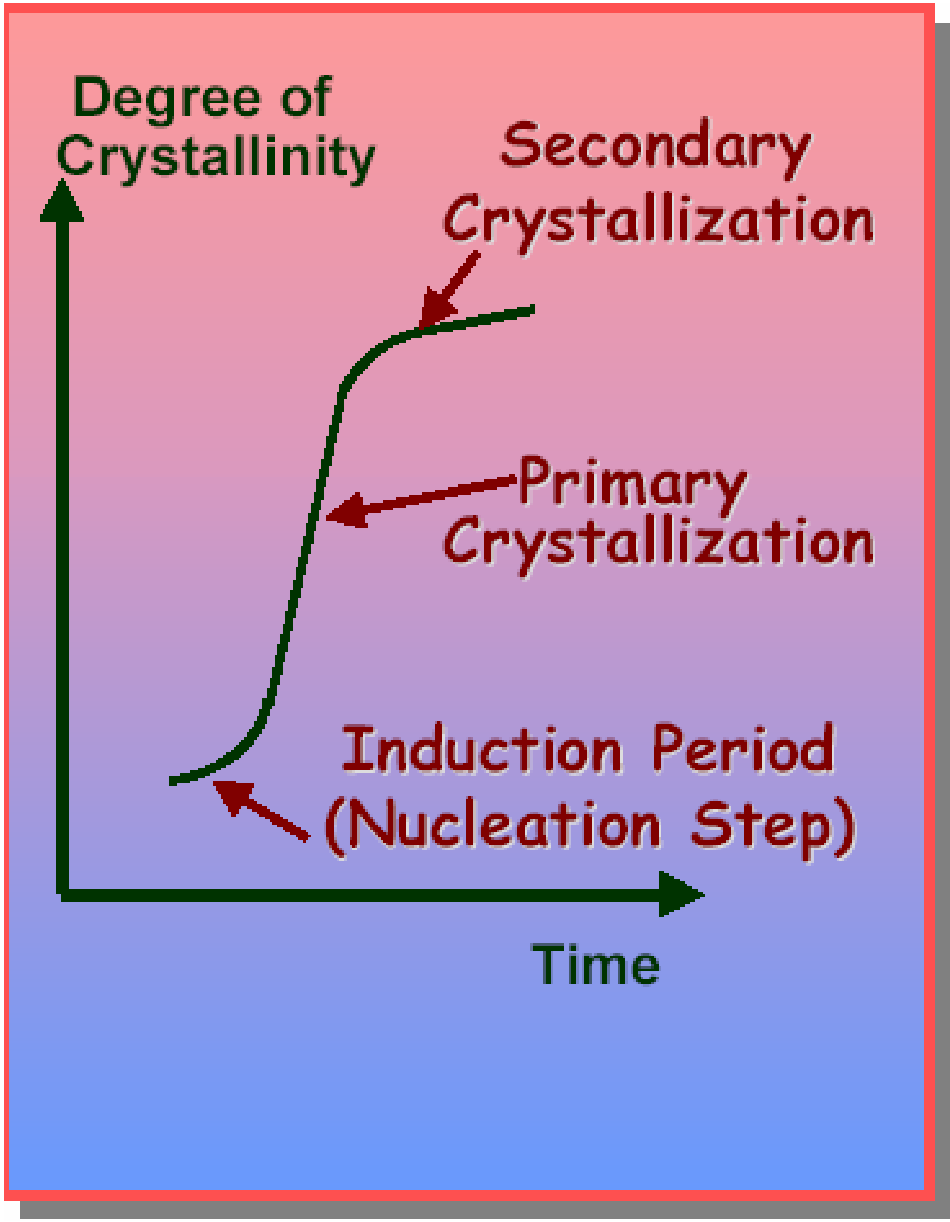
Nucleation : Onset of Crystallization

Homogeneous nucleation : Polymer molecules begin to align nucleation occurs randomly throughout the matrix

Heterogeneous nucleation : At the interface of a foreign impurity

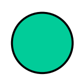
Crystallization Kinetics

General Features

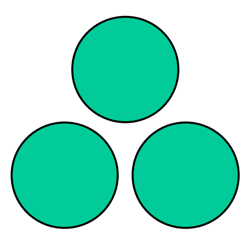


- Induction period - Formation of primary nuclei

- Primary crystallization - A period of fast spherulitic growth



- Secondary crystallization - A period of slower crystallization that occurs once the spherulites have impinged on one another



Primary Crystallization:

• Once a nucleus has been formed growth is predominantly in the lateral direction.

• There is a considerable increase in the fold period behind the lamellar front during crystallization from the Melt.

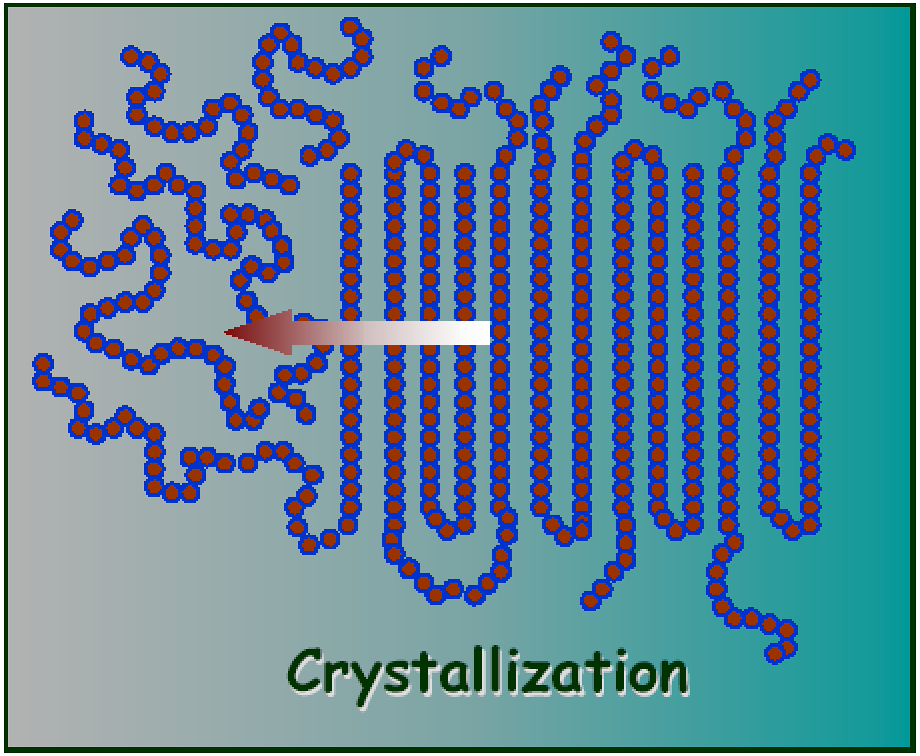
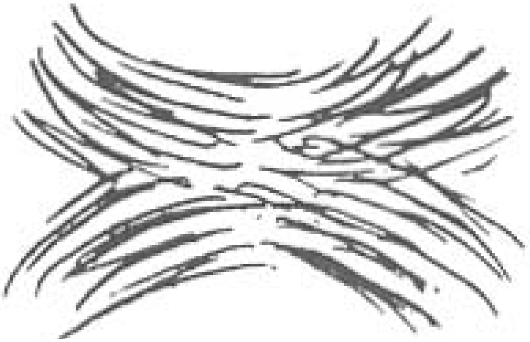


Fig 3.17 Crystalline Morphologies

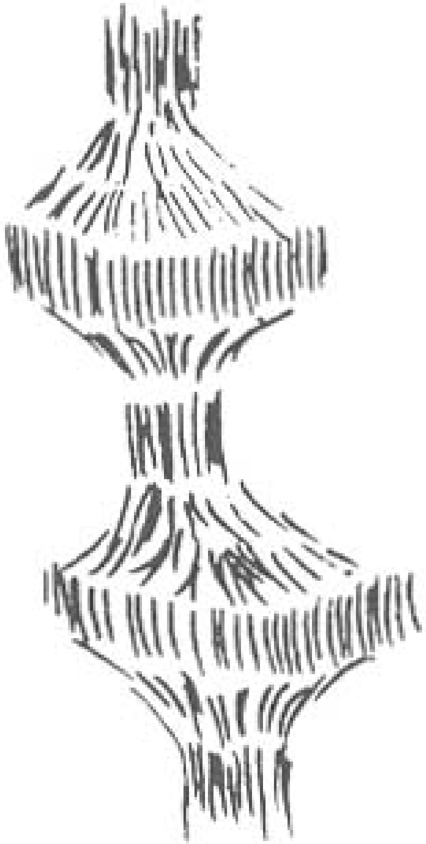


(a) Spherulites

Molten polymer or
Concentrated polymer solution

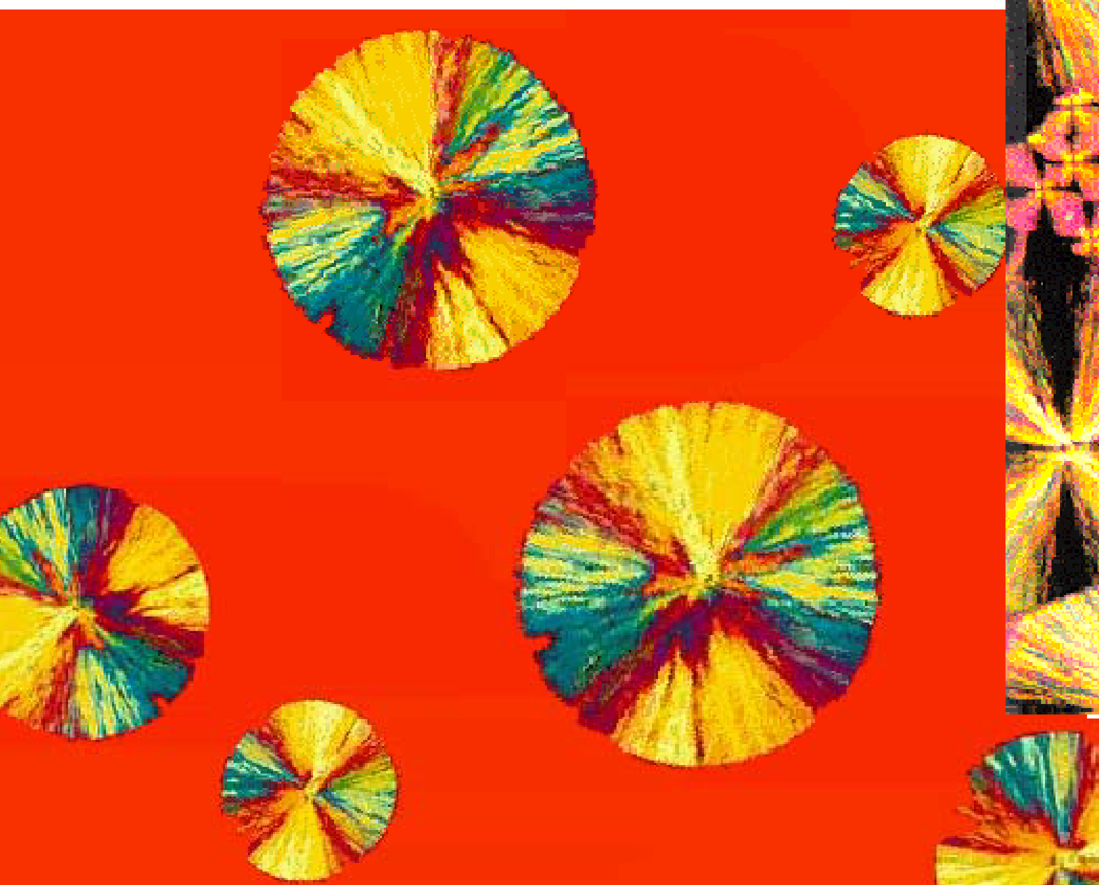
(b) Drawn Fibrillar

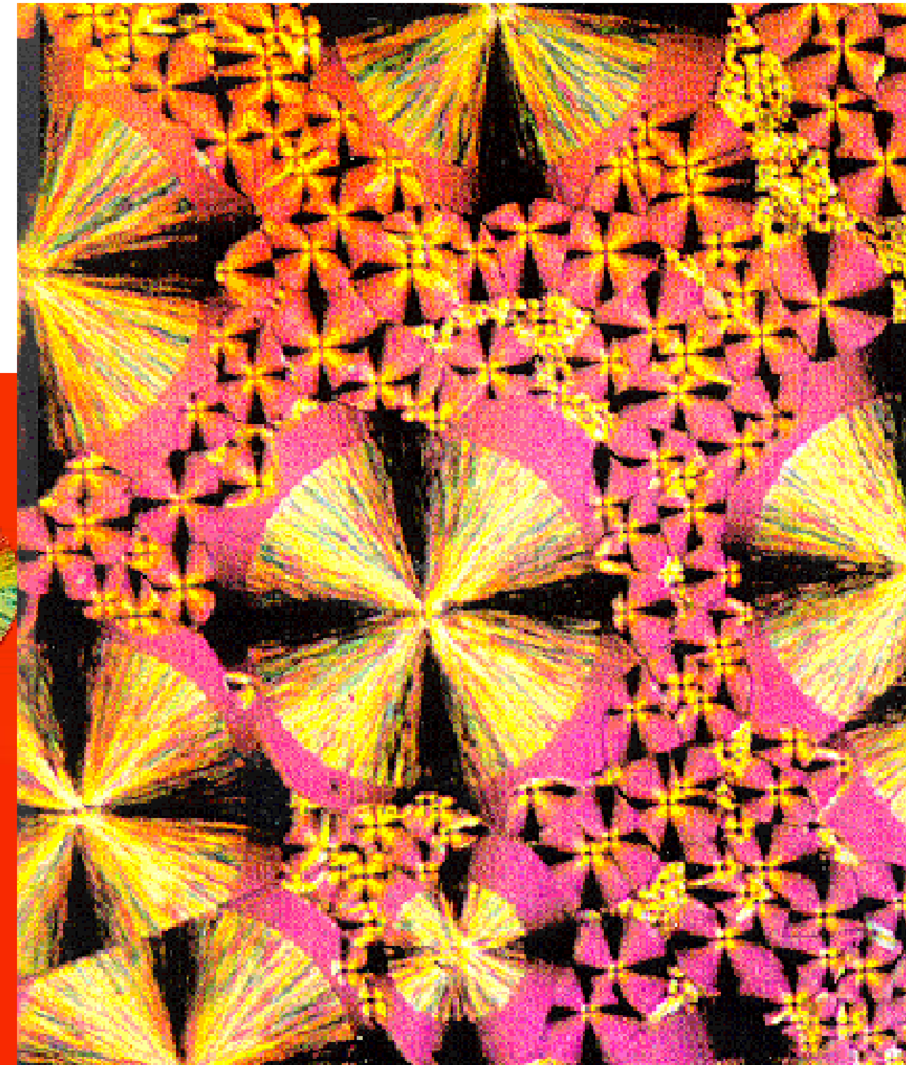
Crystallization in stirred solutions or melts
One crystalline growth on another
Lamella growth on long fibrils



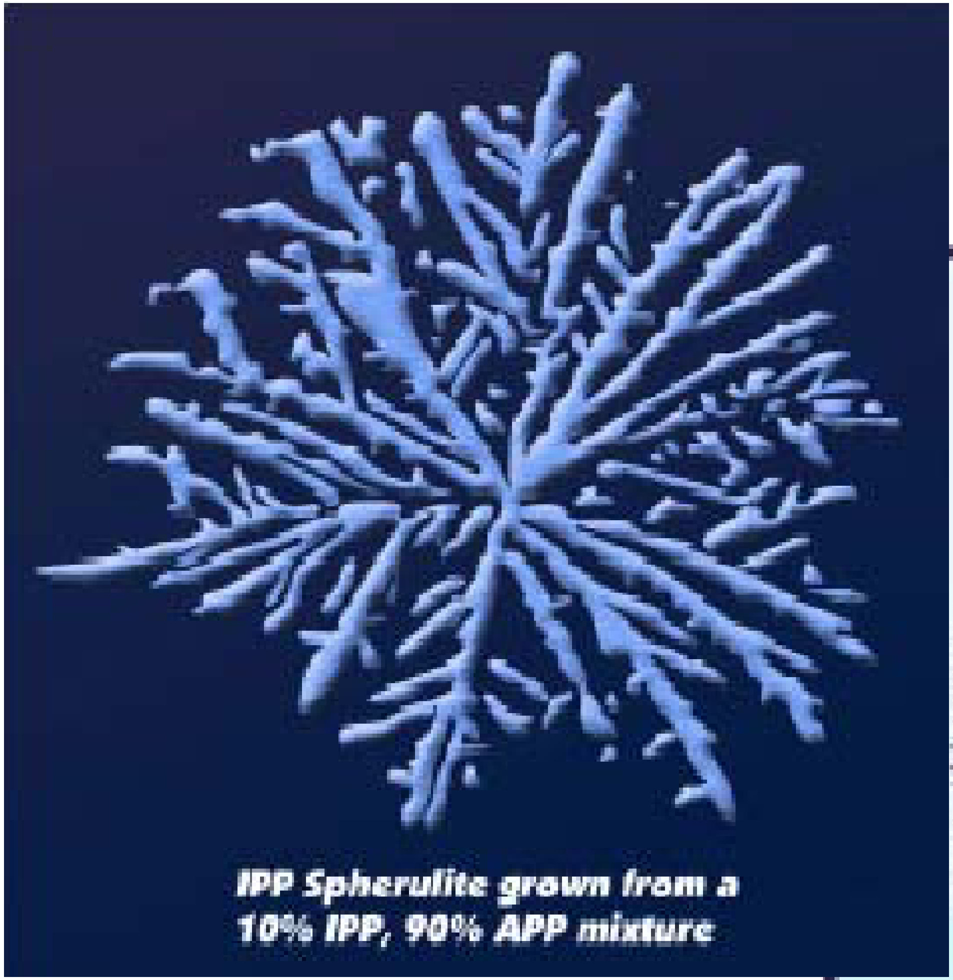
(c) Epitaxial (shish kebab)

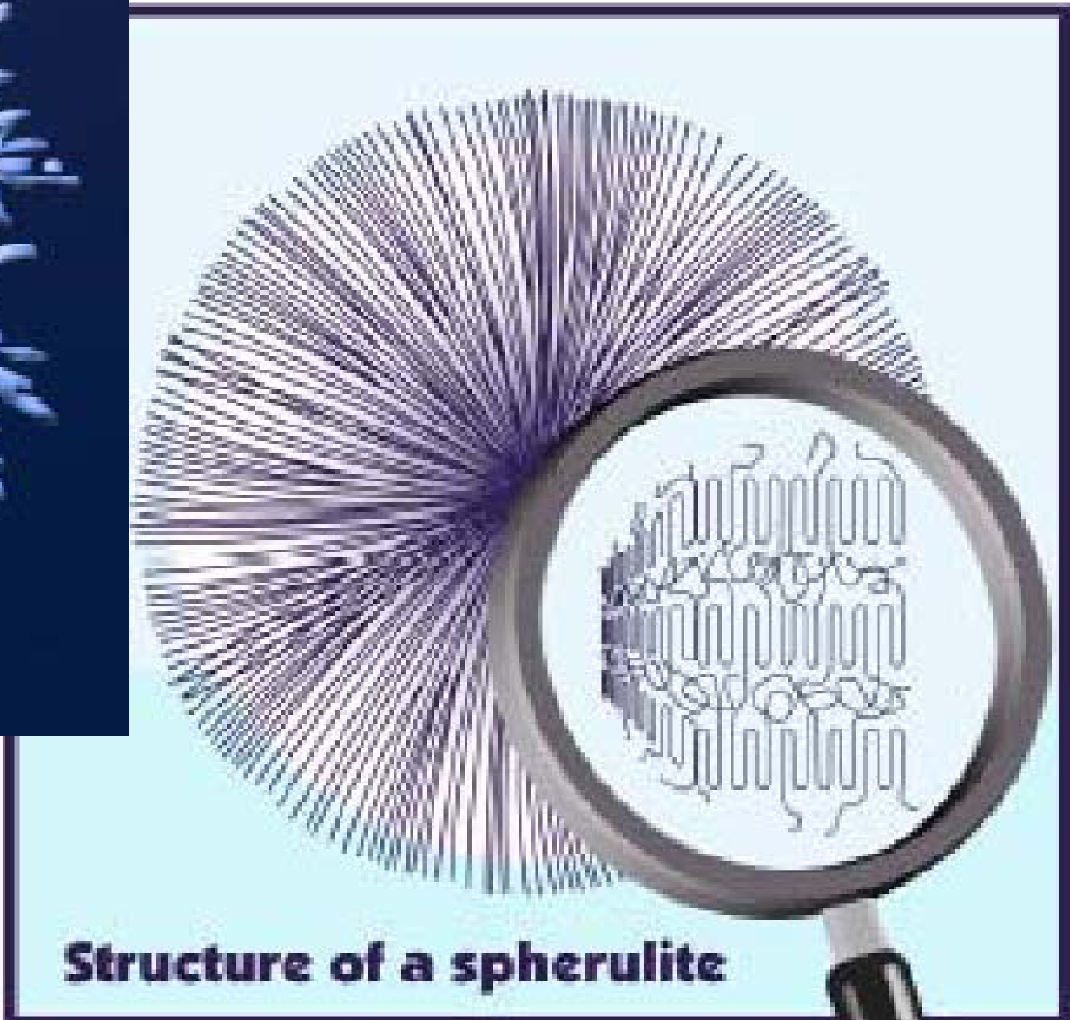
Spherulites





Spherulites





- **Effects of Crystallinity**

1) **Mechanical Property Improvements**

   a) **Stronger** b) **Stiffer**

   ∵ **Average interchain distance↓**

   ⇨ **More effective intermolecular secondary forces**

   ⇨ **Superior mechanical properties**

2) **More Opaque** ∵ **Scattering of light by the crystallites**

3) **Higher Density**

4) **More Solvent Resistant**

   c.f., Polymer dissolution model

   ∴ **Degree of non-dissolution is an approximate measure of degree of crystallinity.**

Effect of Crystallinity on Properties

The type of polyethylene that goes into milk jugs is stronger, stiffer, but more opaque (less optically clear) than the type of polyethylene that is used to make film wrap (greater optical clarity, more flexible, but less strong) . Can you figure out which type of polyethylene is used to make film wrap ?

A. High density

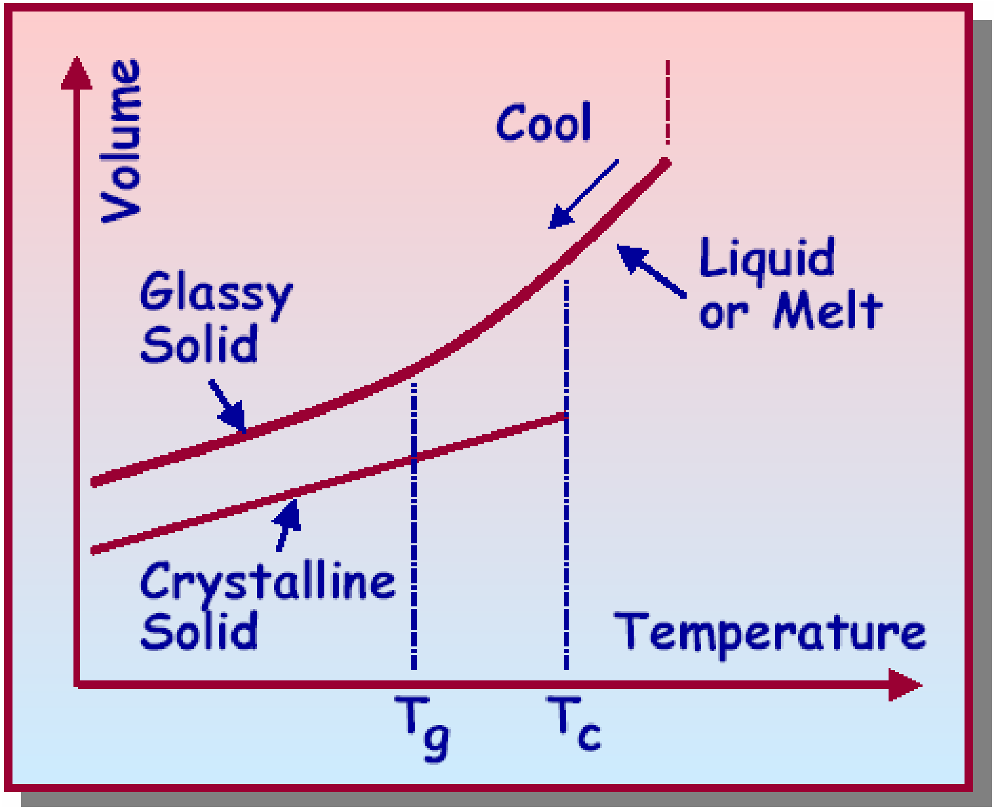
B. Low density

Property	Change with Increasing Degree of Crystallinity
Strength	Increases
Stiffness	Increases
Toughness	Decreases
Optical Clarity	Decreases Semi-crystalline polymers usually appear opaque because of the difference in refractive index of the amorphous and crystalline domains, which leads to scattering.
Barrier Properties	Increase Small molecules usually cannot penetrate or diffuse through the crystalline domains.
Solubility	Decreases Solvent molecules cannot penetrate the crystalline domains, which must be melted before the polymer will dissolve. Solvent resistance increases with degree of crystallinity

Glassy State

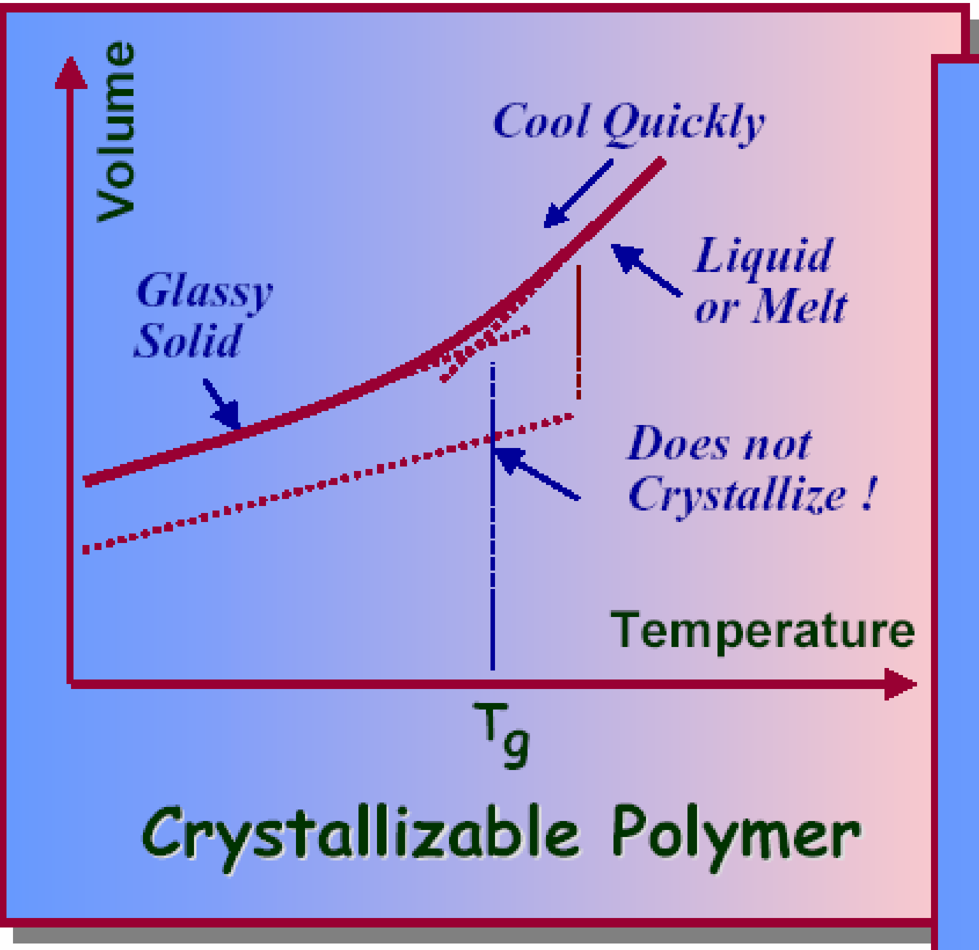
Observed Behavior depends on:

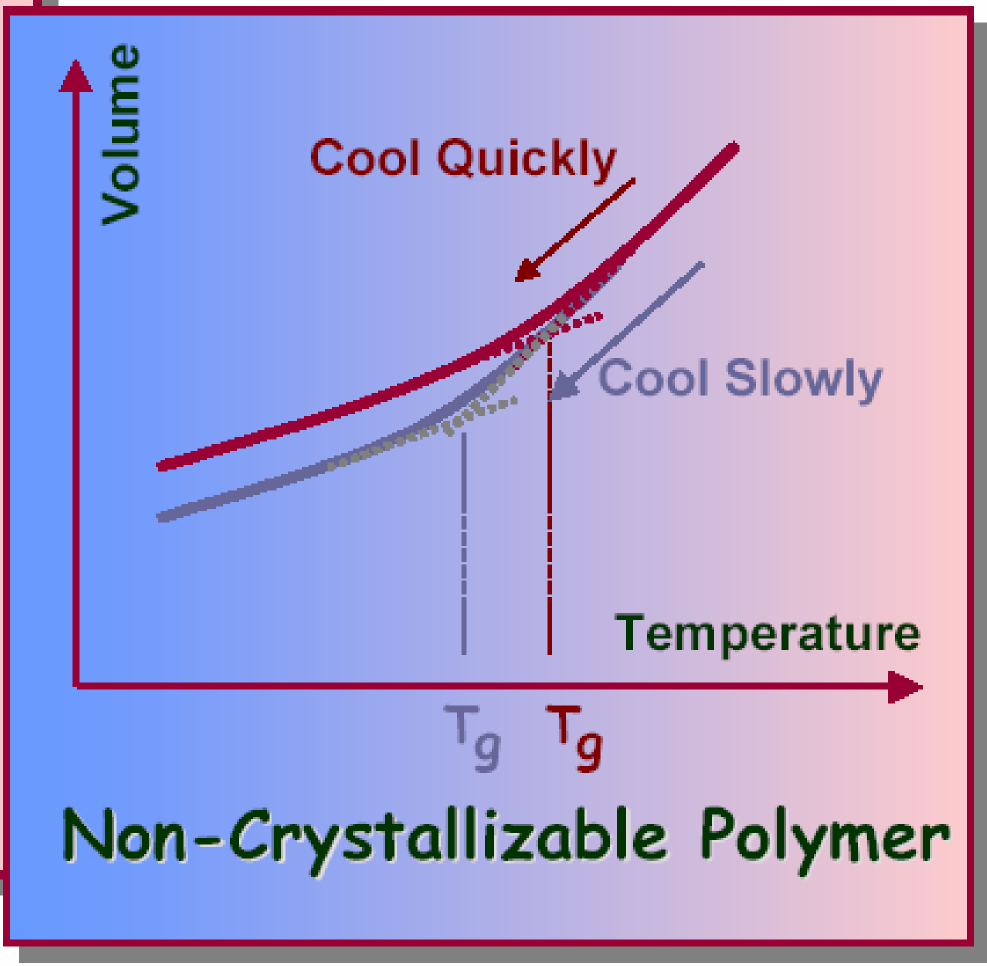
- **Structure**
- **Cooling Rate**
- **Crystallization Kinetics**



Crystallizable materials can form metastable glasses.
What about polymers like atactic polystyrene that cannot crystallize?

Kinetics, Crystallization and Glass Transition

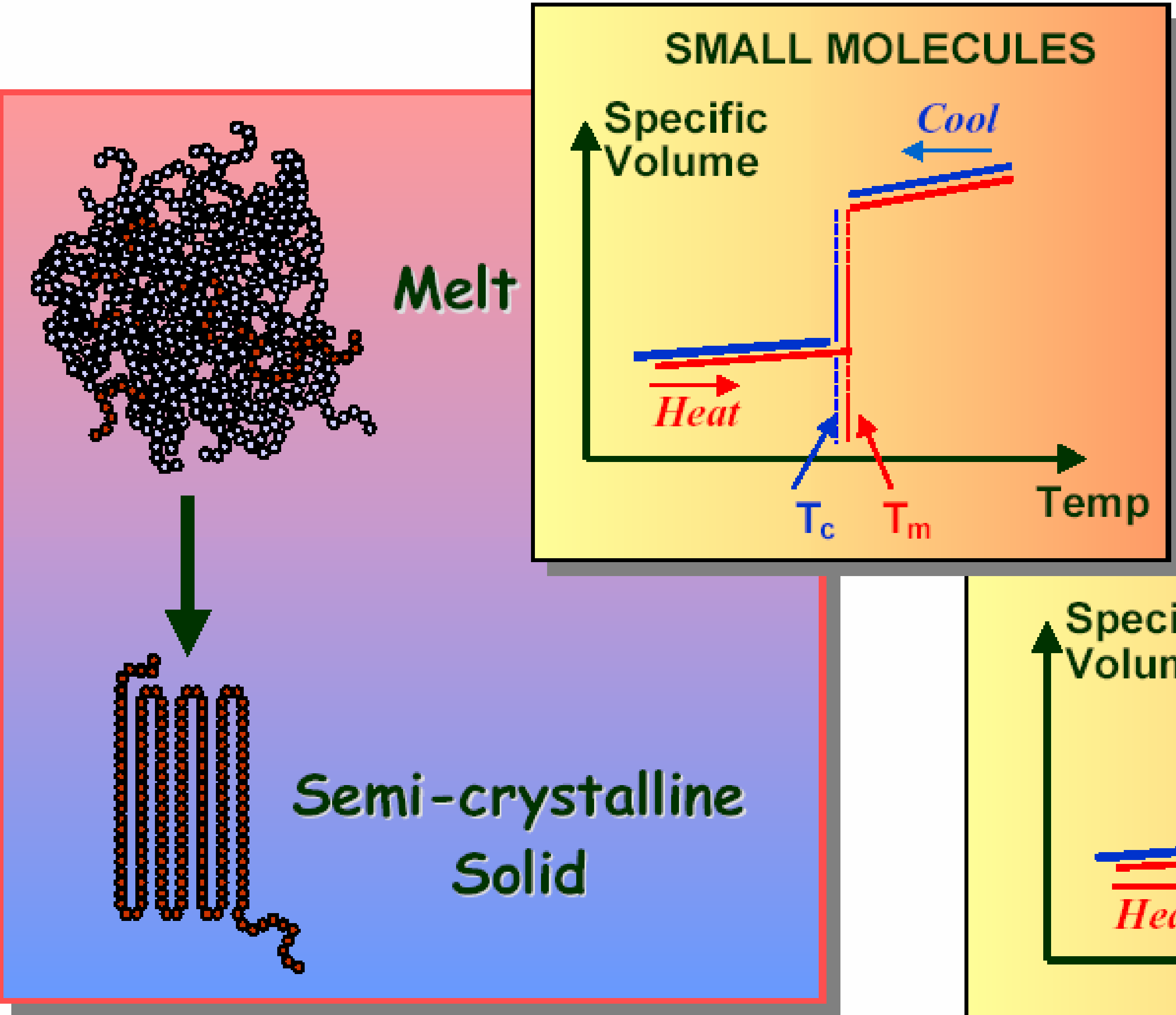




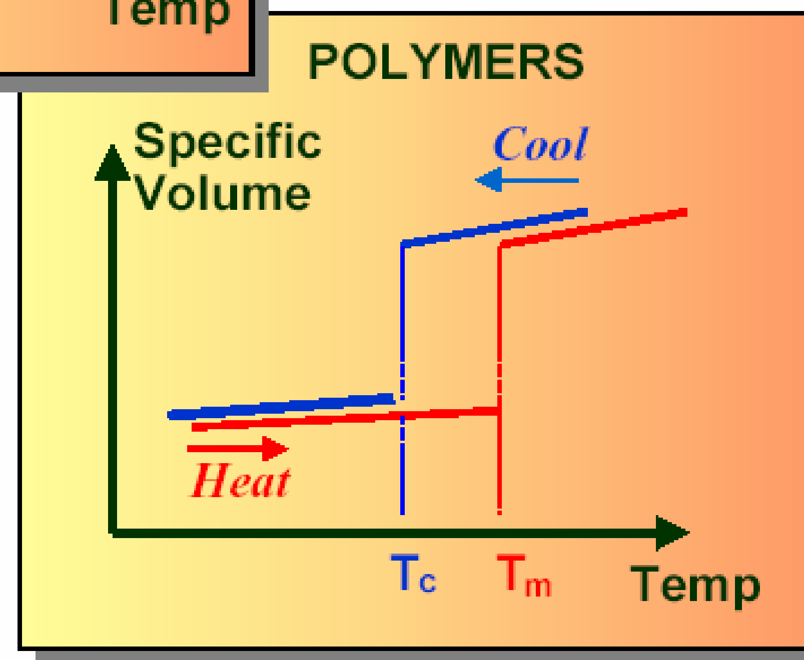
Quenching = quick cooling

Slower cooling ⇨ Lower V_f ⇨ Lower T_g

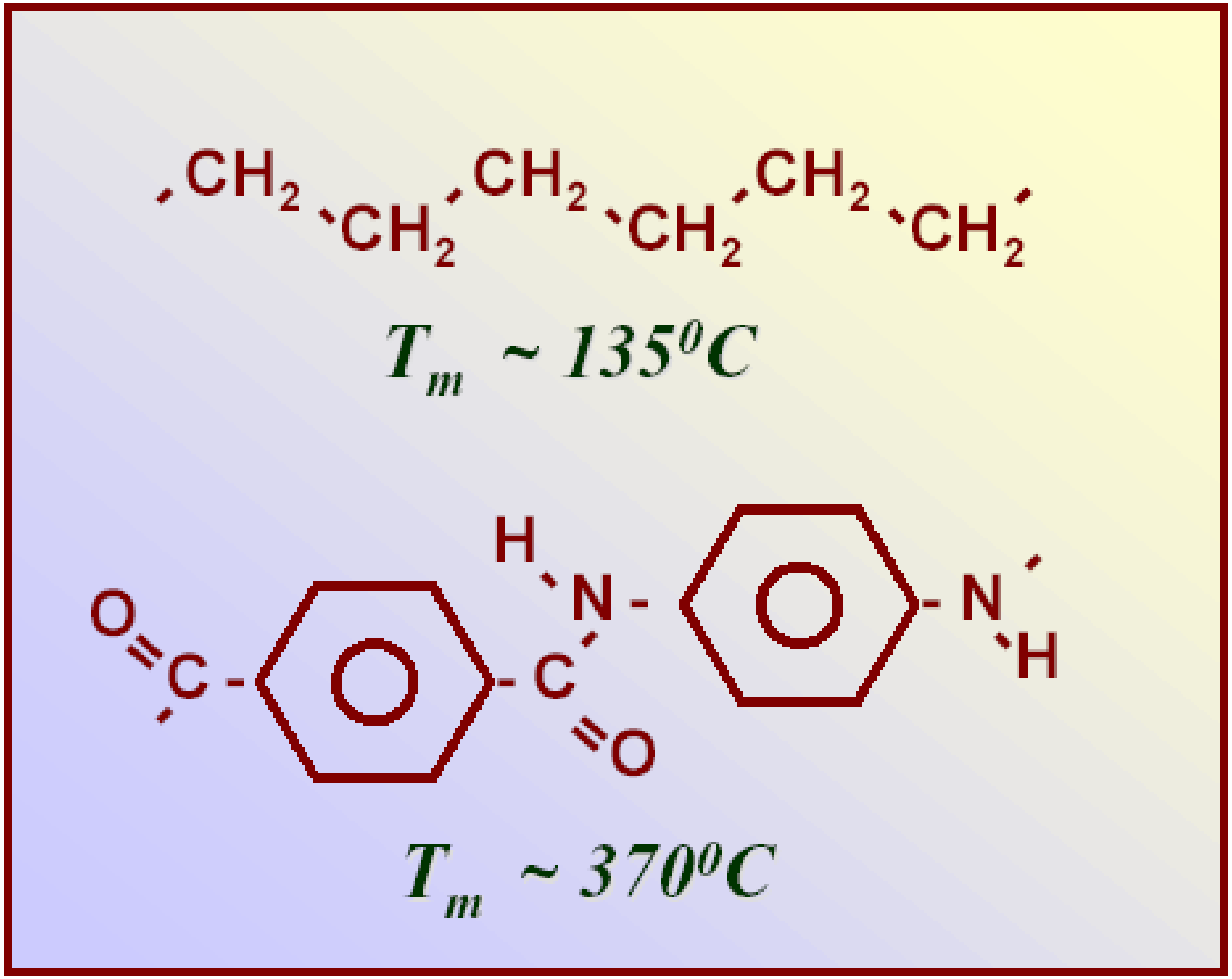
Polymer Crystallization



What is undercooling ?

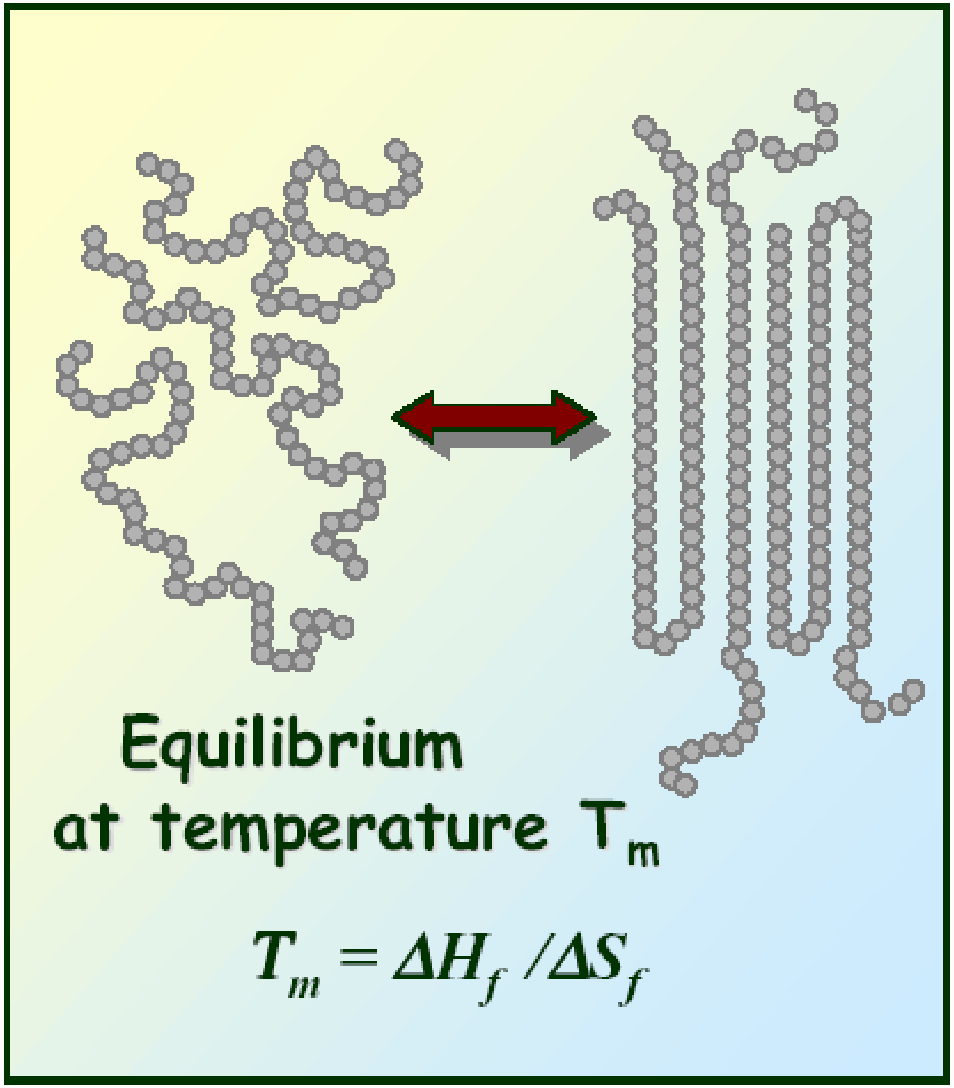


Factors that Affect the Melting Temperature of Polymer Crystals



Why?

Effect of Chemical Structure



$$\Delta G_f = \Delta H_f - T\Delta S_f$$

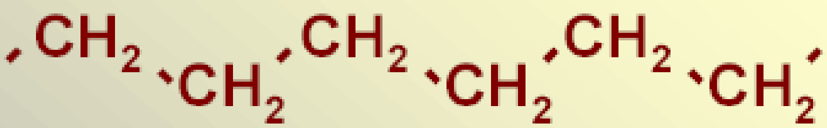
And at Equilibrium

$$\Delta G_f = 0$$

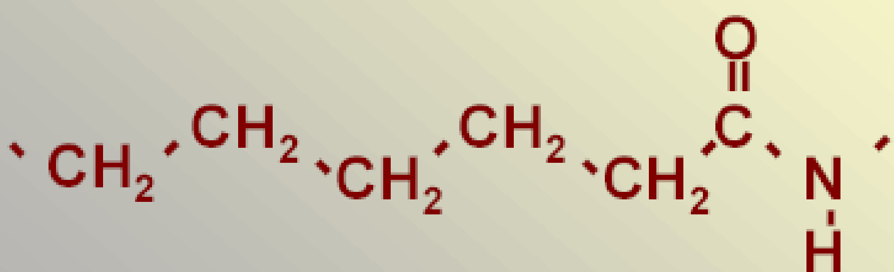
Hence $$T_m = \Delta H_f / \Delta S_f$$

The subscript "f" stands for fusion

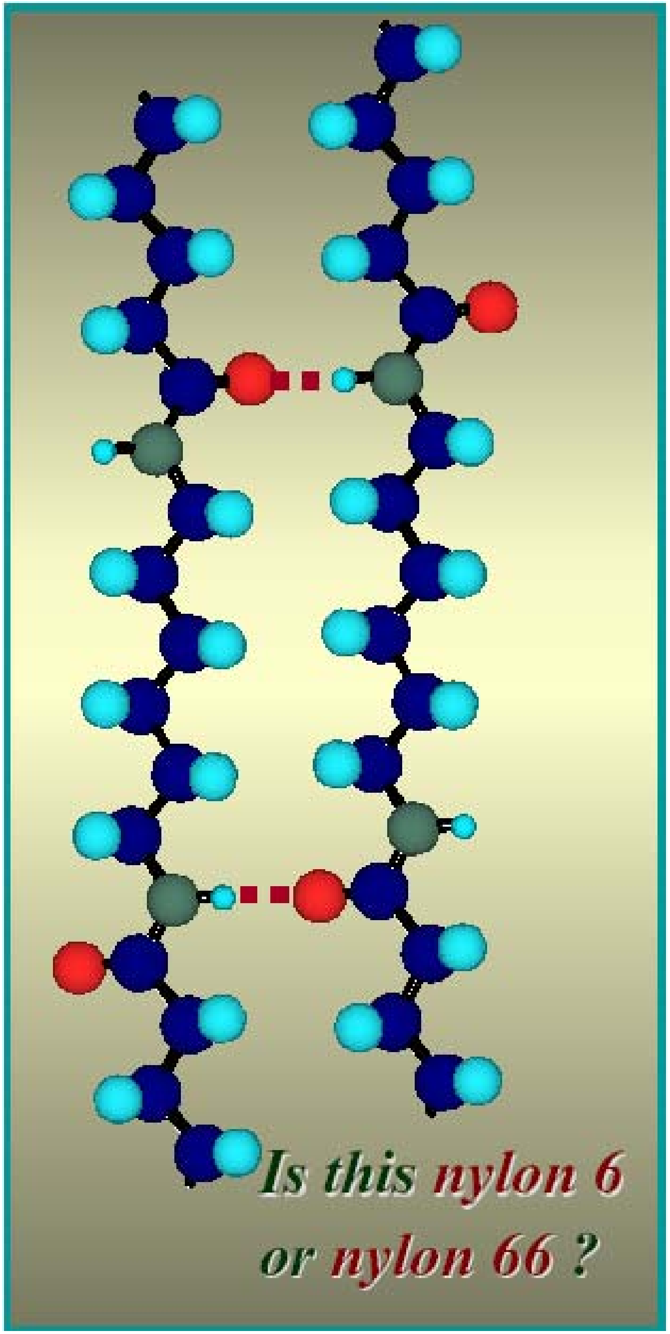
Intermolecular Interactions



$T_m \sim 135^0C$

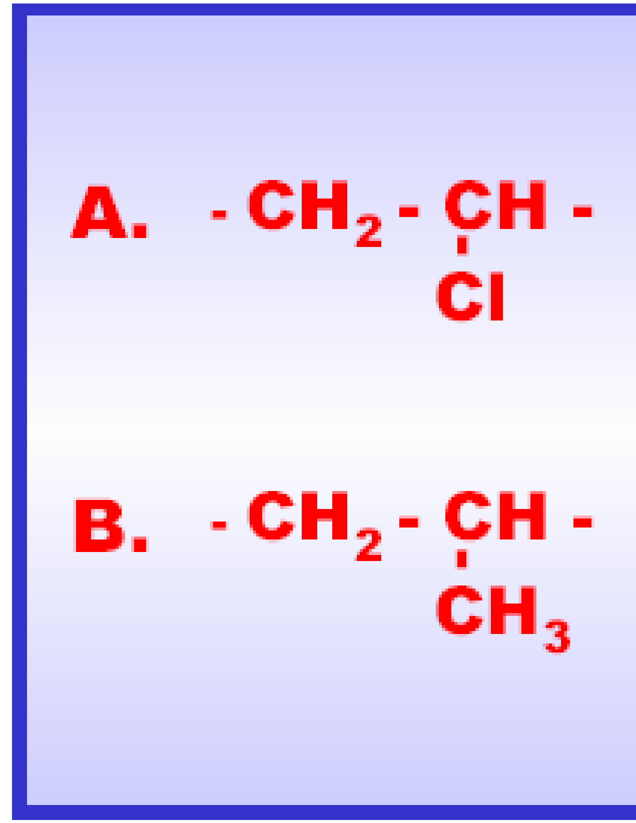


$T_m \sim 265^0C$



Effect of Intermolecular Interactions

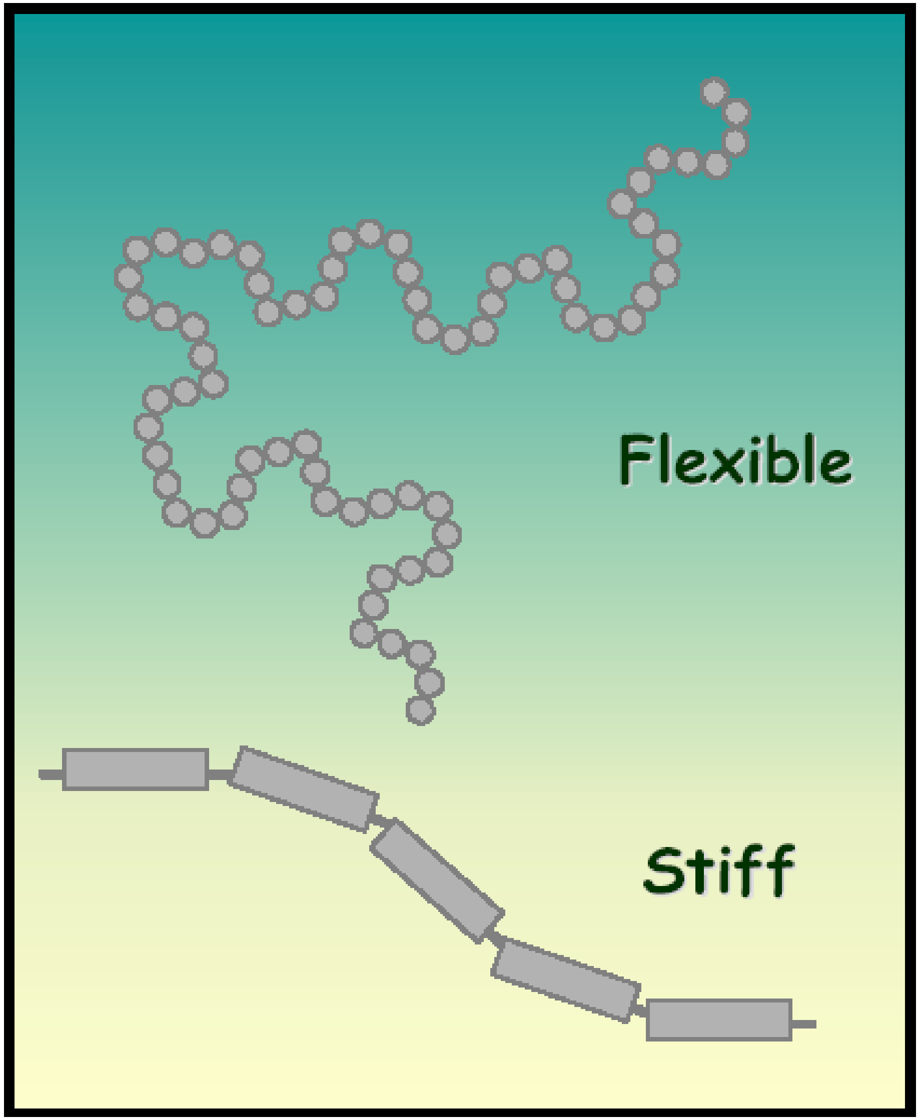
Would you expect
syndiotactic poly(propylene)
or
syndiotactic PVC
to have the higher melting point?



ΔH_f : Large

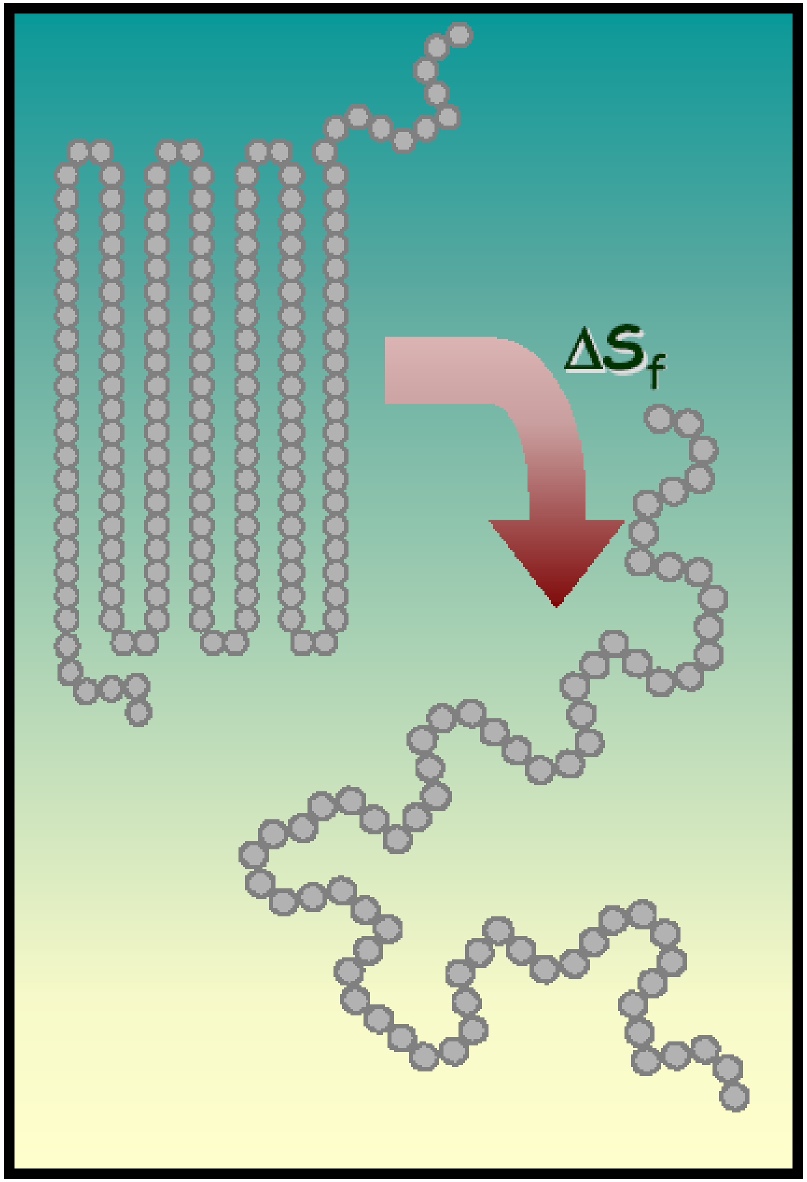
T_m : High

Entropy and Chain Flexibility



$$T_m = \Delta H_f / \Delta S_f$$

Entropy and Chain Flexibility



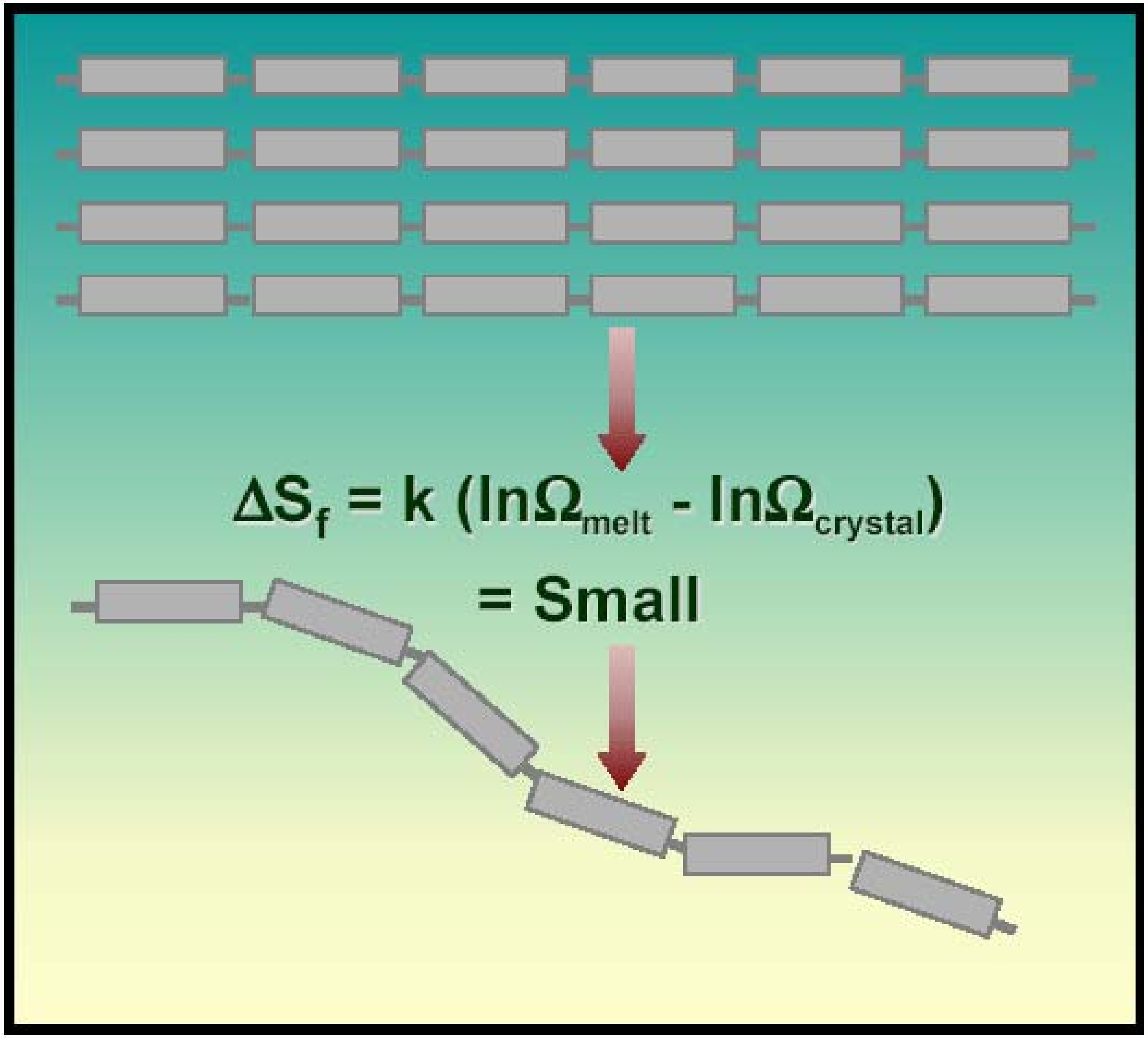
$$S = k \ln\Omega$$

$$\Delta S_f = k\,(\ln\Omega_{melt} - \ln\Omega_{crystal}) = Large$$

ΔS_f : Large

T_m : Low

Conformational Entropy and the Melting Point



$T_m = \Delta H_f / \Delta S_f$

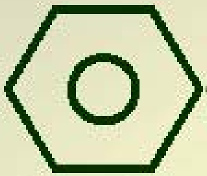
ΔS_f : Small

T_m : High

Entropy and the Melting Point

$-CH_2-CH_2-$
Polyethylene
$T_m \sim 135^0C$

$-CH_2-CH_2-O-$
Poly (ethylene oxide)
$T_m \sim 65^0C$

$-CH_2-CH_2-$  $-$
Poly (p-xylene)
$T_m \sim 400^0C$

ΔS_f : Small

T_m : High

Entropy and the Melting Point

- CH_2 - CH_2 -

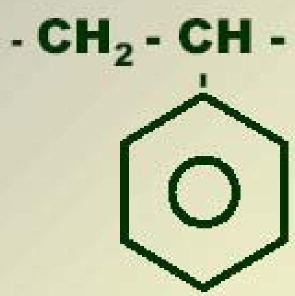
Polyethylene

$T_m \sim 135^0C$

- CH_2 - CH -
  |
  CH_3

Isotactic Polypropylene

$T_m \sim ?$

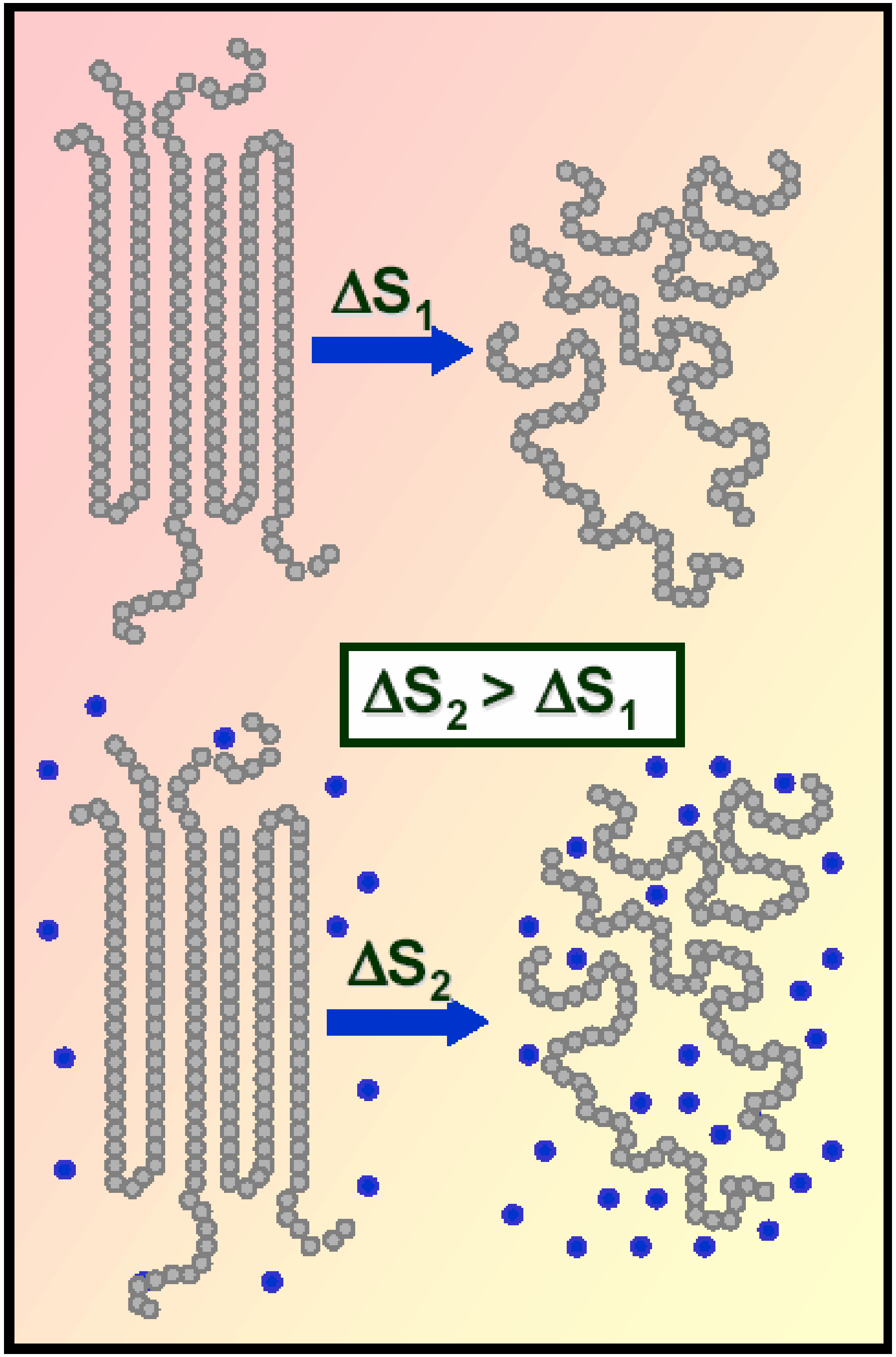


Isotactic Polystyrene

$T_m \sim ?$

ΔS_f : Small

T_m : High

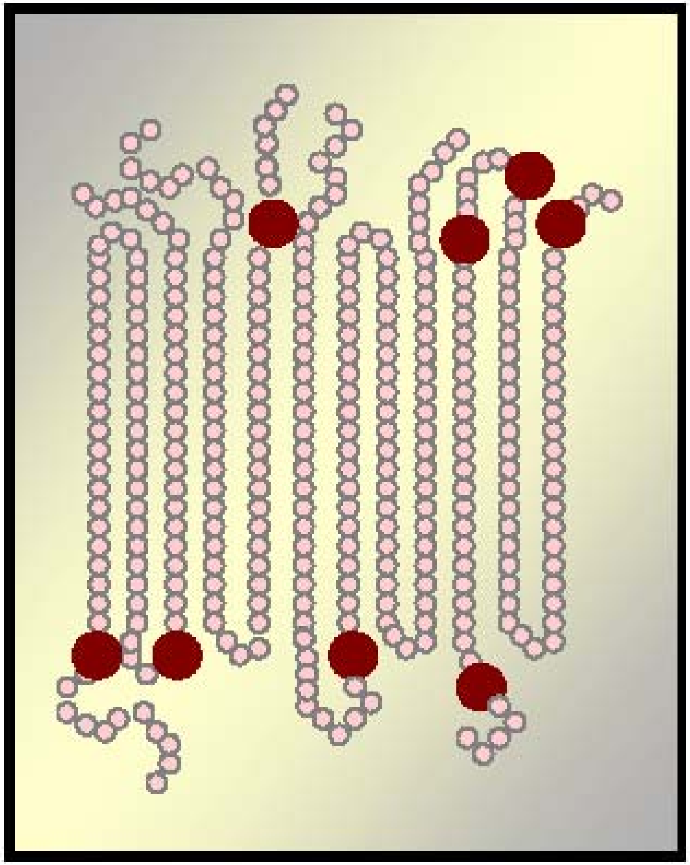


The Effect of Diluents

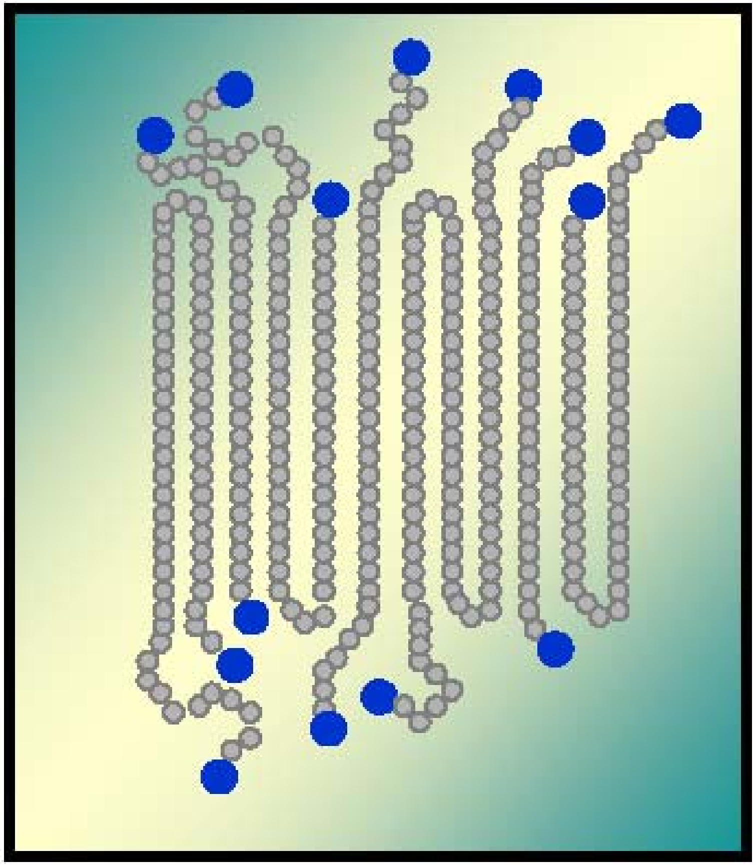
ΔS_f : Large

T_m : Low

The Effect of Copolymerization and Molecular Weight



High MW



Low MW

ΔS_f : Large

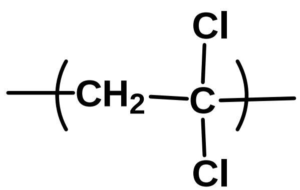
T_m : Low

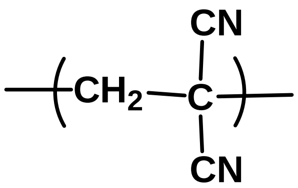
Table 3.5 T_g and T_m

Polymer	T_g (°C)	T_g (K)	T_m (°C)	T_m (K)
cis-1,4-Polyisoprene	- 73	200	26	299
trans-1,4-Polyisoprene	- 58	215	74	347
cis-1,4-Polychloroprene	- 20	253	70	343
trans-1,4-Polychloroprene	- 40	233	101	374
Poly(methyl vinyl ether)	- 31	242	144	417
Poly(vinyl chloride)	81	354	265	538
Polystyrene (isotactic)	100	373	242	515
Poly(ethylene adipate)	- 63	210	54	327
Poly(hexamethylene adipamide)	57	330	268	541
Poly(ethylene terephthalate)	69	342	268	541

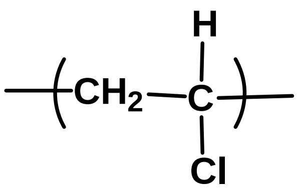
$$T_g = \frac{1}{2} \sim \frac{2}{3} \times T_m$$

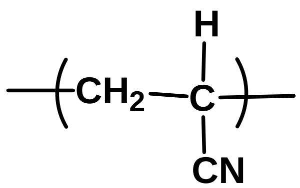
- **Stereoregularity**





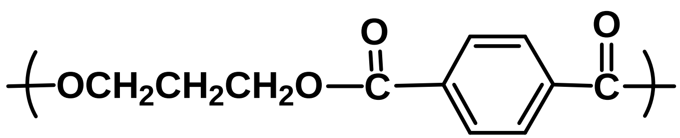
Highly crystalline



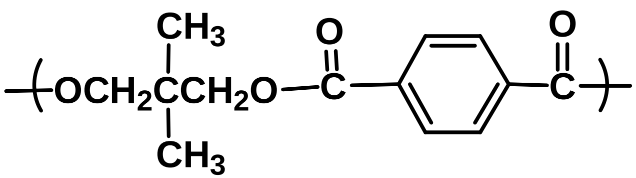


Atactic

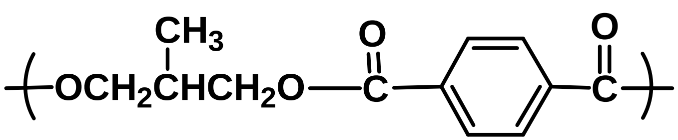
Very low degree of crystallinity



Crystalline m.p. 220 °C



Crystalline m.p. 140 °C



Noncrystalline

3.7 Liquid Crystallinity

Liquid Crystals: Fourth state of matter

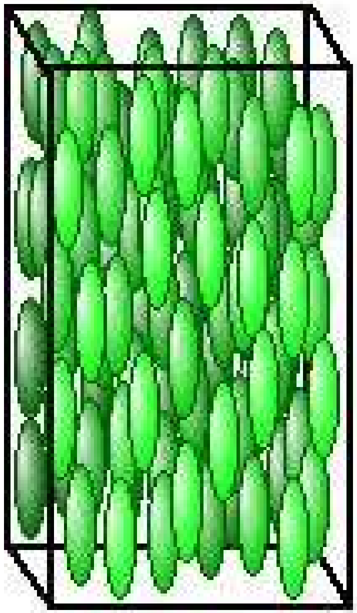
- **Liquid with Ordered Region**
  = Mesophase
- **Liquid with anisotropic behavior**
- **Occur between conventional m.p. and true isotropic solution**

Lliquid crystalline polymer (LCP)

- **Lyotopic LCP: form in solution** — **Above critical concentration**
- **Thermotropic LCP: form in the melt** — **Below critical temperature**

Liquid Crystal Phases

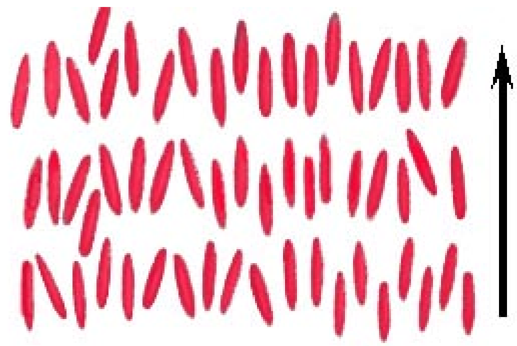
1) Nematic Phase



directional

2) Smectic A Phase

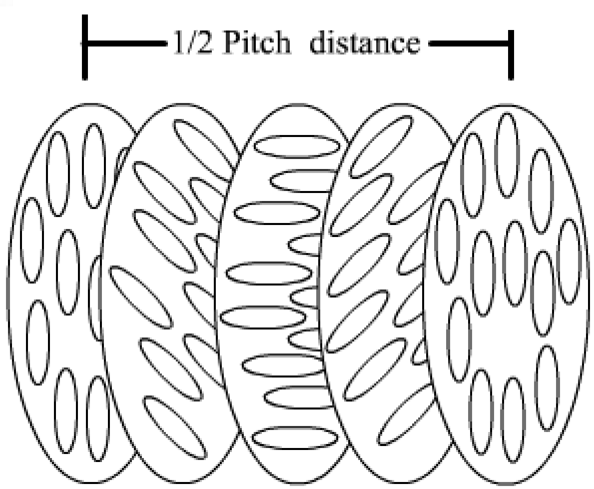
directional layer

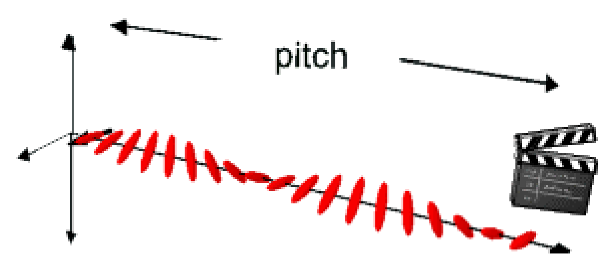


3) Smectic C Phase

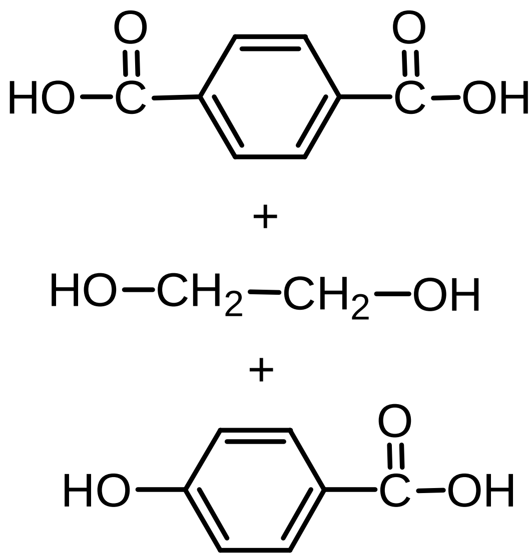
4) Cholesteric Phase

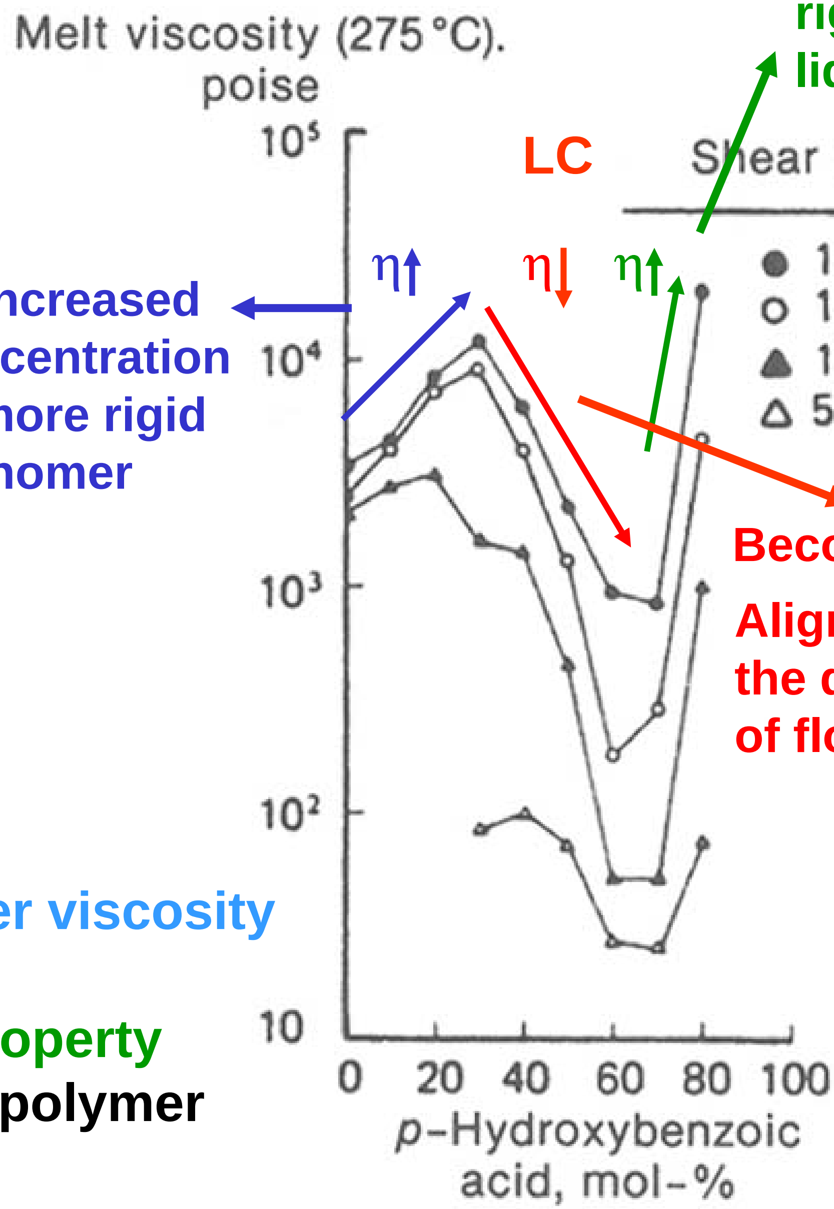
rotational (optically active)





Ex) Thermotropic LCP: Copolyester





∵ Increased concentration of more rigid monomer

∵ Too much rigidity to form liquid crystal

Becomes opaque

Alignment in the direction of flow

Advantage of LC

Easy processing ∵ Lower viscosity

Improved mechanical property ∵ ordered alignment of polymer molecules

- **Lyotropic LCP: Aromatic Polyamide**

Du Pont Kevlar

$$H_2SO_4 \text{ solution} \xrightarrow{\text{extrusion}} \text{Fiber}$$

Tensile strength of Kevlar > T.S. of steel

Density of Kevlar < Density of steel

Uses: Tire Cord, Bulletproof vest

- **Drawbacks LCP**

  Very high m.p.

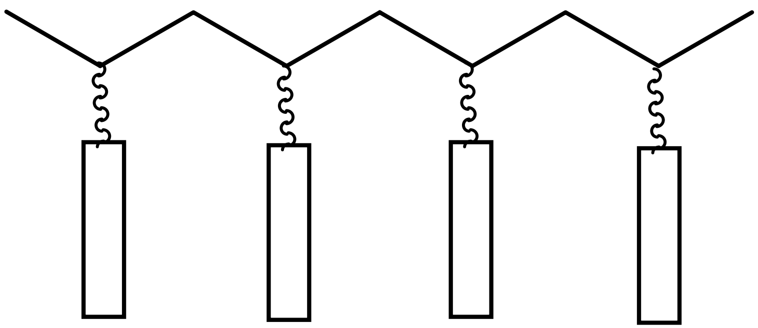
  Difficult to dissolve in the usual organic solvents

<Solution>

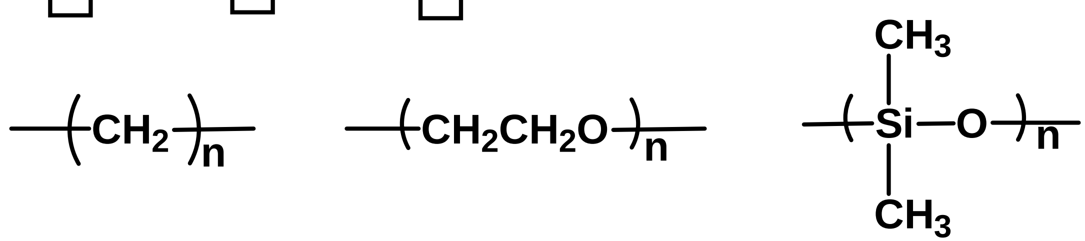
a) Separate mesogens with flexible spacers

Mesogen: rigid group responsible for the mesophases

b) Attach mesogens with flexible spacers to the backbone



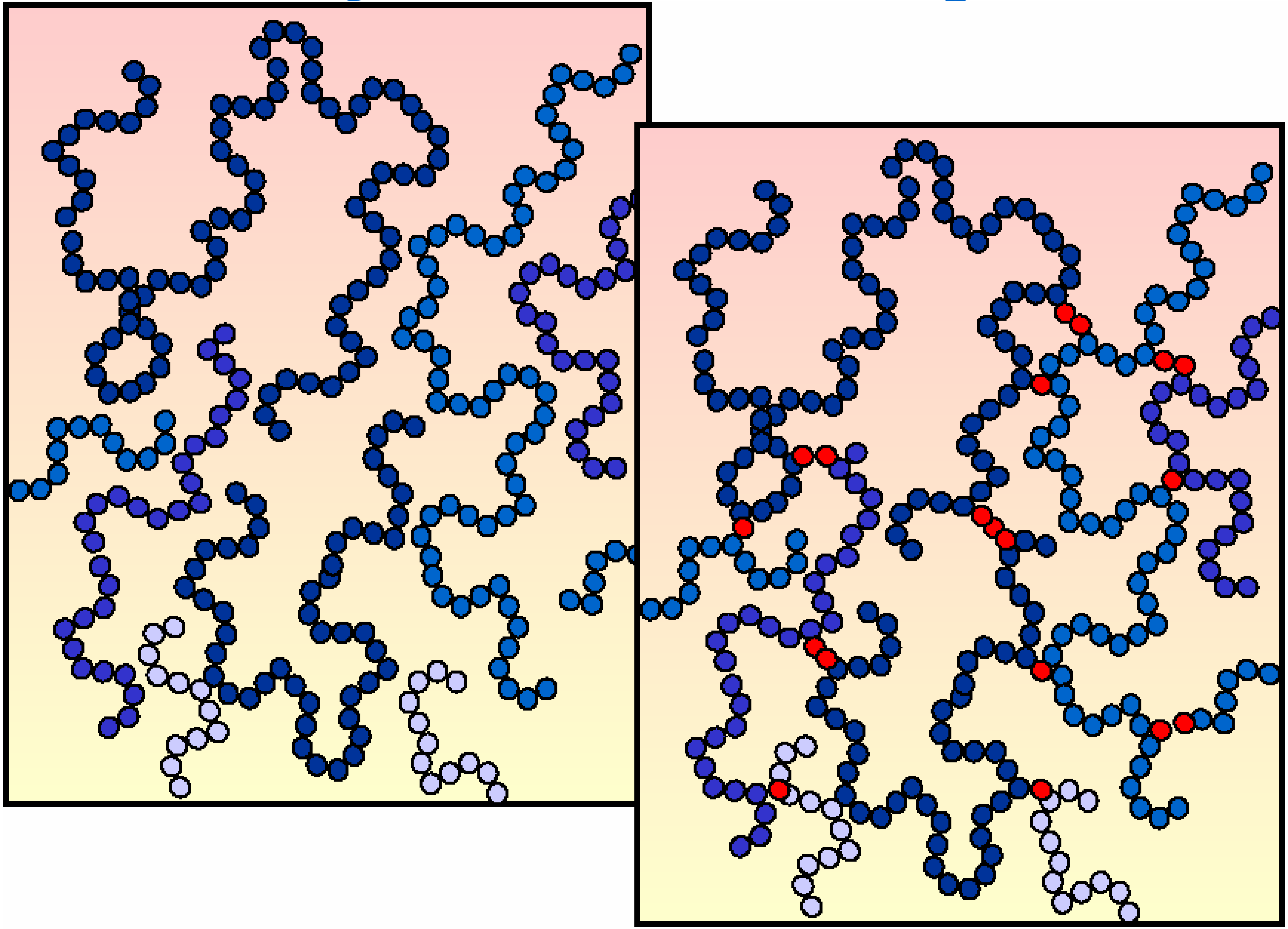
Flexible spacers



Use of flexible spacers

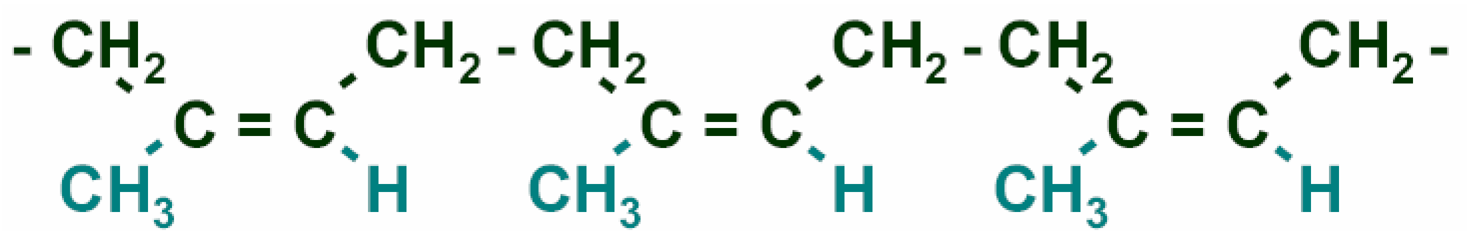
- More tractable
- But weaker mechanical properties

Importance of Cross-Linking



Network formation by cross-linking

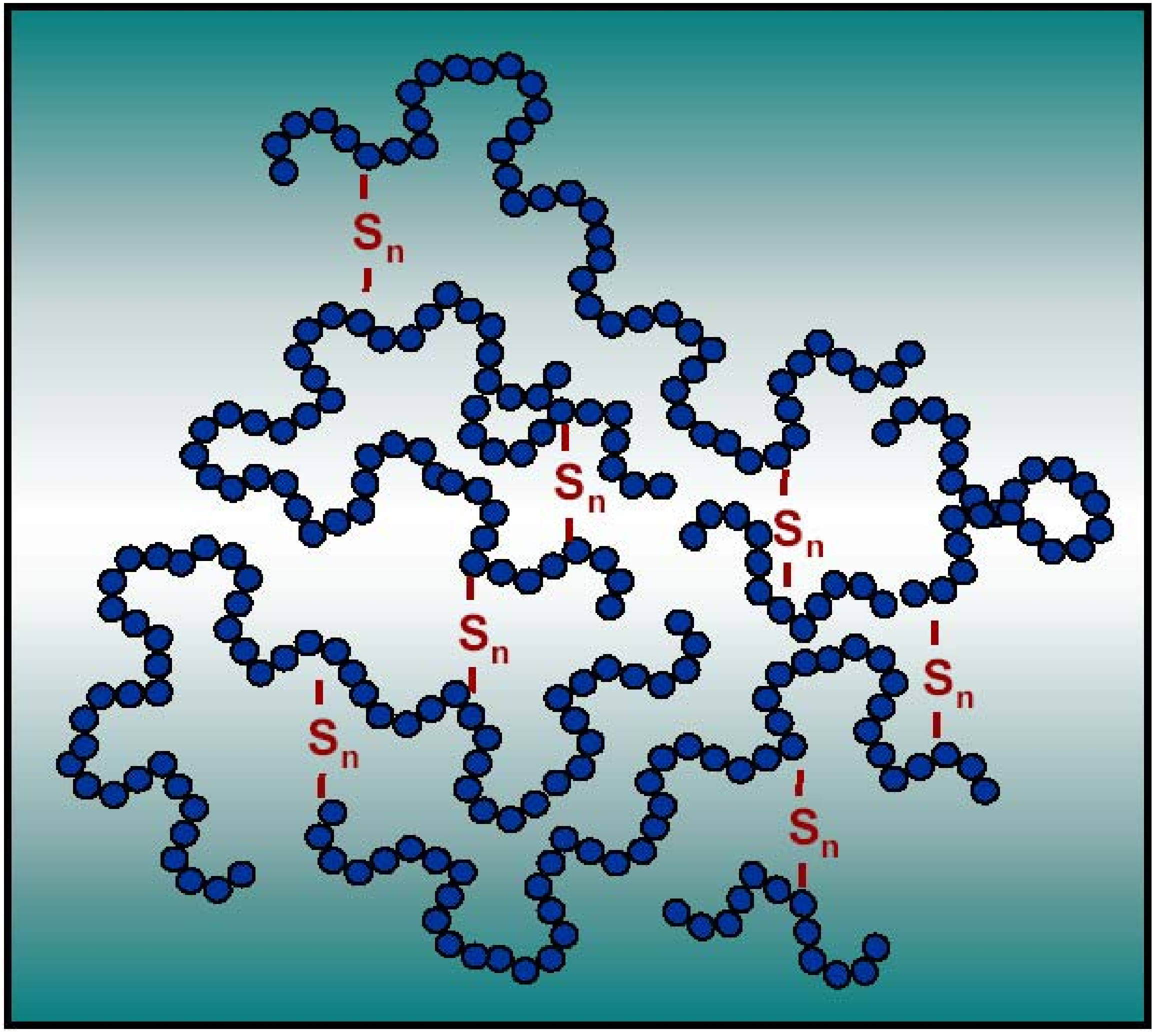
An example of cross-linking is the reaction of natural rubber or poly(isoprene) ;



with sulfur (or, as we prefer, sulphur) . The sulfur interconnects the chains by reacting with the double bonds.

Network formation by cross-linking

This is the process originally discovered by Charles Goodyear, (vulcanization).
Note that the linkages shown on the right actually consist of short chains of sulfur atoms.
Cross-linking is crucial in making elastomers with useful properties, as it prevents the chains from slipping past one another.



3.8 Chemical Crosslinking (curing)

Methods

1) Polymerization of polyfunctional monomers
2) Crosslinking after the linear polymer is formed

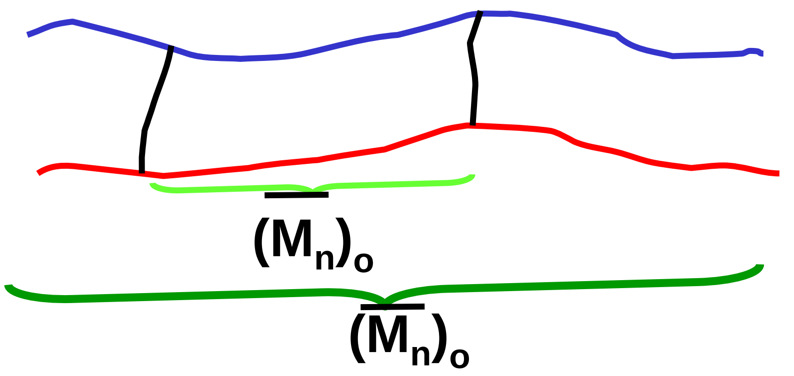
Gel: Solvent-swollen crosslinked polymer

Microgel: very small gel (300-1000 μm)

Crosslink density (Γ)

≡ # of crosslinked monomer units per main chain

$$\Gamma = \frac{(\overline{M}_n)_o}{(\overline{M}_n)_c}$$



where

$(\overline{M}_n)_o = \overline{M}_n$ of uncrosslinked polymer

$(\overline{M}_n)_o = \overline{M}_n$ of between crosslinks

Higher Γ : more rigid , more brittle, higher T_g

Elastomer : very low Γ, ~ crosslink per 100 monomer units

highly flexible main chain

3.9 Physical Crosslinking

A) Disadvantage of covalent crosslinking

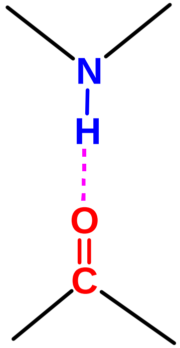
- cannot be dissolved or molded
- cannot be recycled

<Solution>

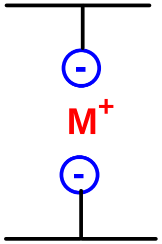
Thermally labile crosslinks : **Break apart** on heating; **Reform** on cooling

1) **H bond**

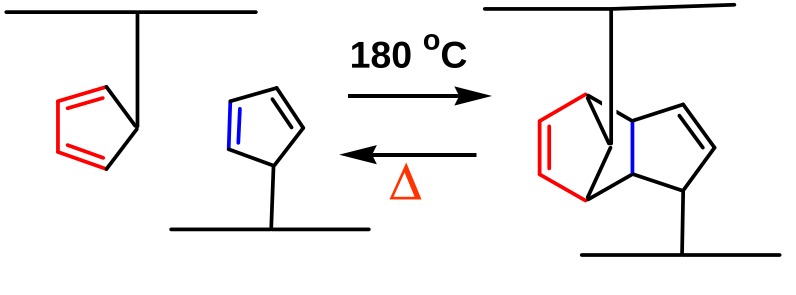
Gelatin



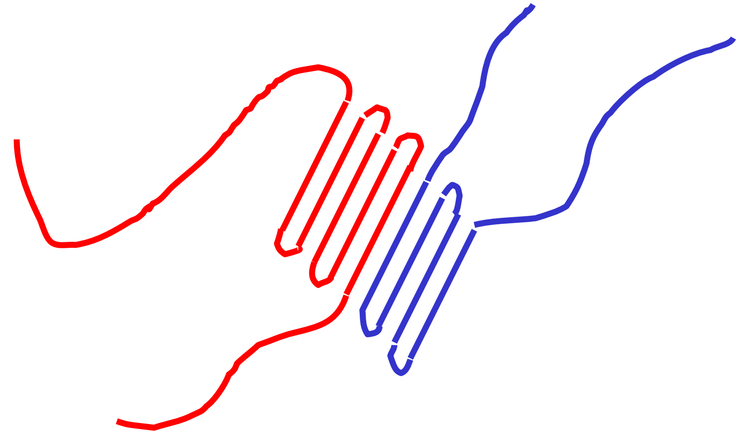
2) **Ionic** crosslink



3) Reversible **covalent** crosslink



4) Crystallite

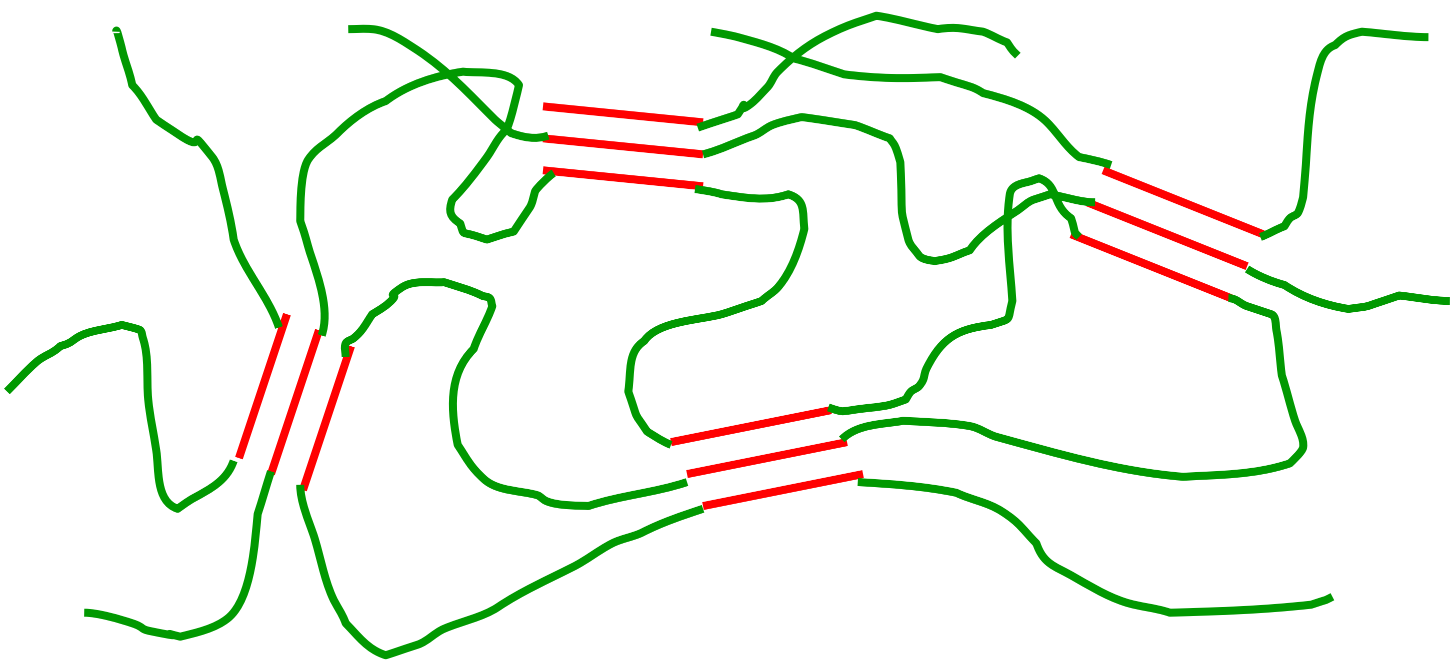


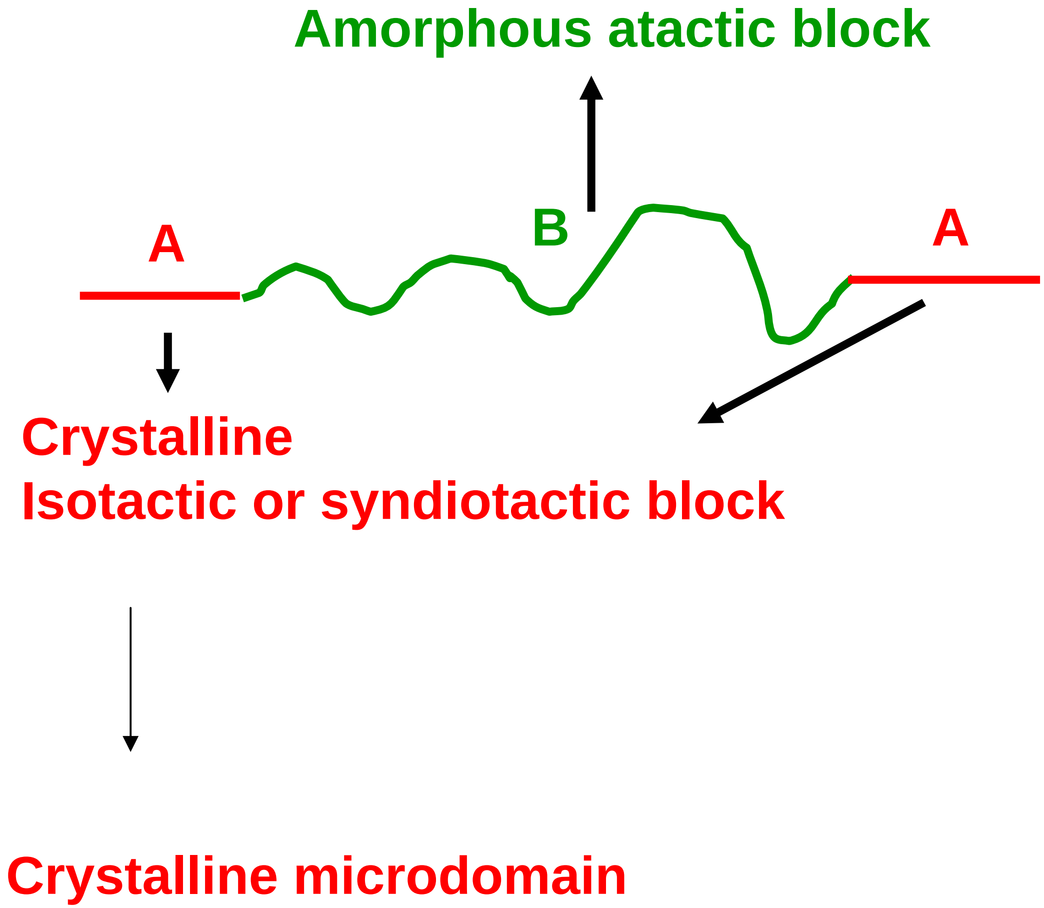
5) Block copolymer

ABA type

Short, rigid polystyrene long, flexible polybutadiene

Immiscible (incompatible) → microdomains within polymer matrix





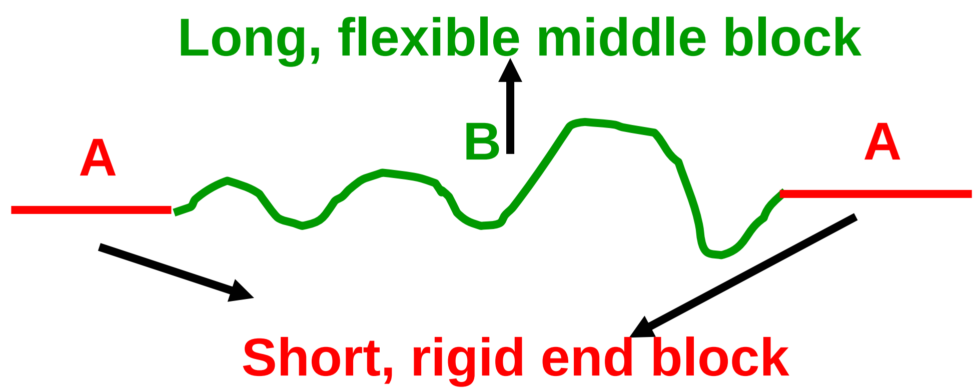
Amorphous atactic block
A
B
A
Crystalline
Isotactic or syndiotactic block
Crystalline microdomain

Table 3.6 Commercially Important Thermoplastic Elastomers

Type	End Blocks	Middle Block
Styrenic	Polystyrene	PolyBD or polyisoprene
Polyolefin	Isotactic PP	Ethylene-propylene copolymer
Polyurethane	Rigid polyurethane	Flexible polyester or polyether
Copolyester	Rigid polyester	Flexible polyester
Polyamide	Rigid polyamide	Flexible polyether

$T_g > RT$ (End Blocks)

$T_g < RT$ (Middle Block)



3.9 Polymer Blends

= Polyblends = Polymer Alloys

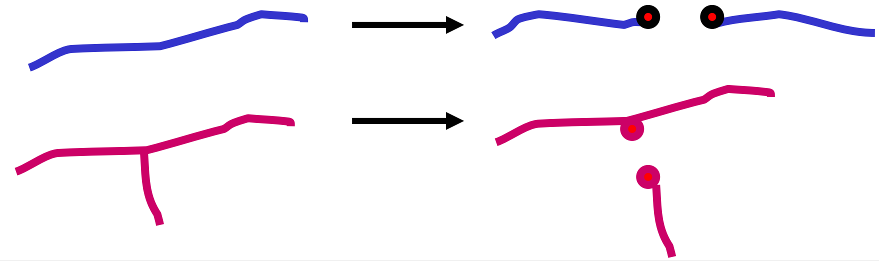
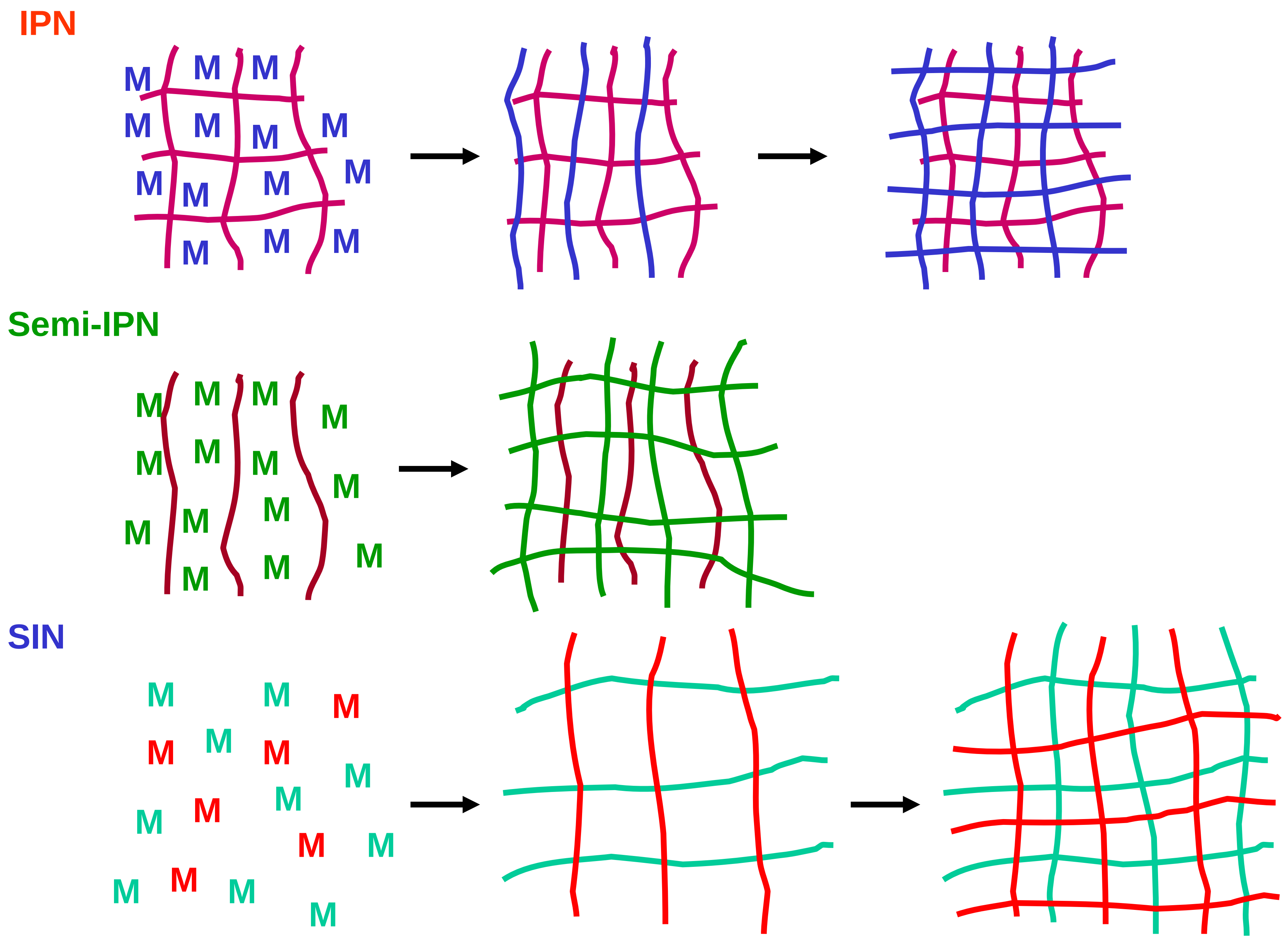


Table 3.7 Types of Polyblends

Types	Description
Mechanical blends	**Polymers are mixed at $T > T_g$ or T_m for amorphous and semicrystalline polymers, repectively**
Mechanochemical blends	**Polymers are mixed at shear rates high enough to cause degradation. Resultant free radicals combine to form complex mixtures including block and graft components**
Solution-cast blends	**Polymers are dissolved in common solvent and solvent is removed**
Latex blends	**Fine dispersions of polymers in water (latexes) are mixed, and the mixed polymers are coagulated**

Types	Description
Chemical blends	
Interpenetrating polymer networks (IPN)	Crosslinked polymer is swollen with different monomer, then monomer is polymerized and crosslinked
Semi-IPN	Polyfunctional monomer is mixed with thermoplastic polymer, then monomer is polymerized to network polymer (also called pseudo-IPN)
Simultaneous IPN (SIN)	Different monomers are mixed, then homopolymerized and crosslinked simultaneously, but by noninteracting mechanism
Interpenetrating elastomeric networks (IEN)	Latex polyblend is crosslinked after coagulation


IPN
M
Semi-IPN
M
SIN
M

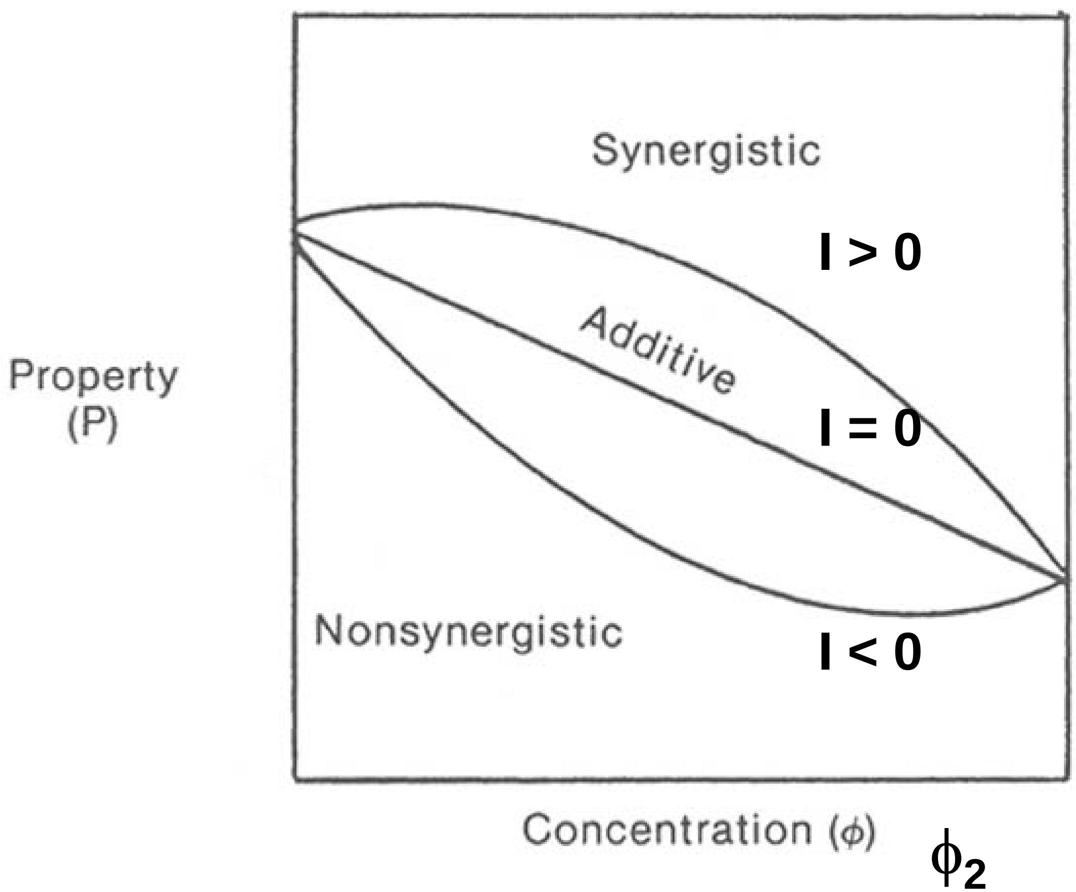
Miscible blends: clear, single T_g

Immiscible blends: opaque, separate T_g's

A) For a binary homogeneous blend

1) Property $P = P_1\phi_1 + P_2\phi_2 + I\phi_1\phi_2$ $\qquad T_g = w_1T_{g2} + w_2T_{g2}$

where { ϕ = volume fraction in the mix; I = interaction term } $\qquad$ w = weight fraction



{ Favorable intermolecular interaction

New types of interactions between chains

e.g. Dipole–dipole attraction between polymer components

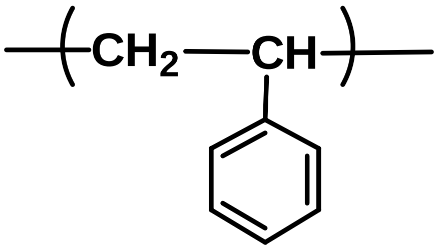
e.g., Ionic or hydrogen bonds occur or are strengthened }

{ Unfavorable intermolecular interaction

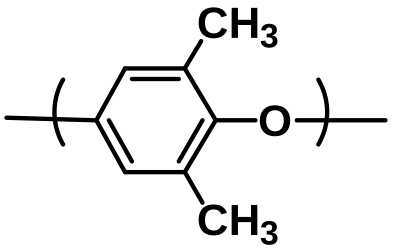
e.g., Prevention or disruption of crystallinity }

2) Miscible Polyblend

Noryl (GE) ⟸ PS + PPO



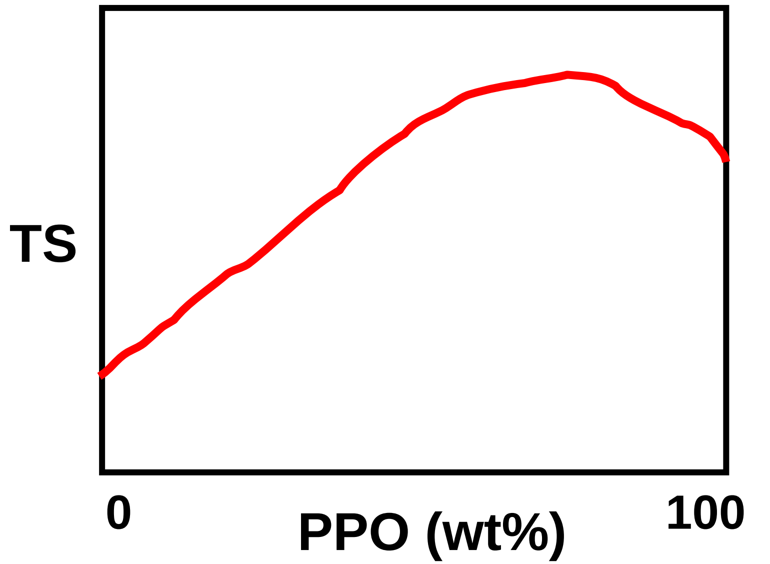
inexpensive



Relatively expensive

Properties of Noryl

- T_g: Additive
- Tensile strength (TS): Synergistic



LDPE + EPDM

TS: Synergistic if EDPM semicrystalline

Nonsynergistic if EDPM amorphous

∵ Crystallites in LDPE nucleate crystallization of ethylene segments in EDPM

B) Immiscible Polyblends

1) One polymer: continuous phase → determine properties

The other polymer : dispersed as a noncontinuous phase (in the form of fibrils, spheres, lamellae, and so on)

e.g. 50:50 blends of PS and PBD

PS ↙ Hard, glassy polymer

PBD ↘ Elastomer

{ Hard if PS continuous phase
Soft if PS dispersed phase

2) Problem with immiscible blends

Poor physical attraction at phase boundaries

→ Phase separation under stress

→ Poor mechanical properties

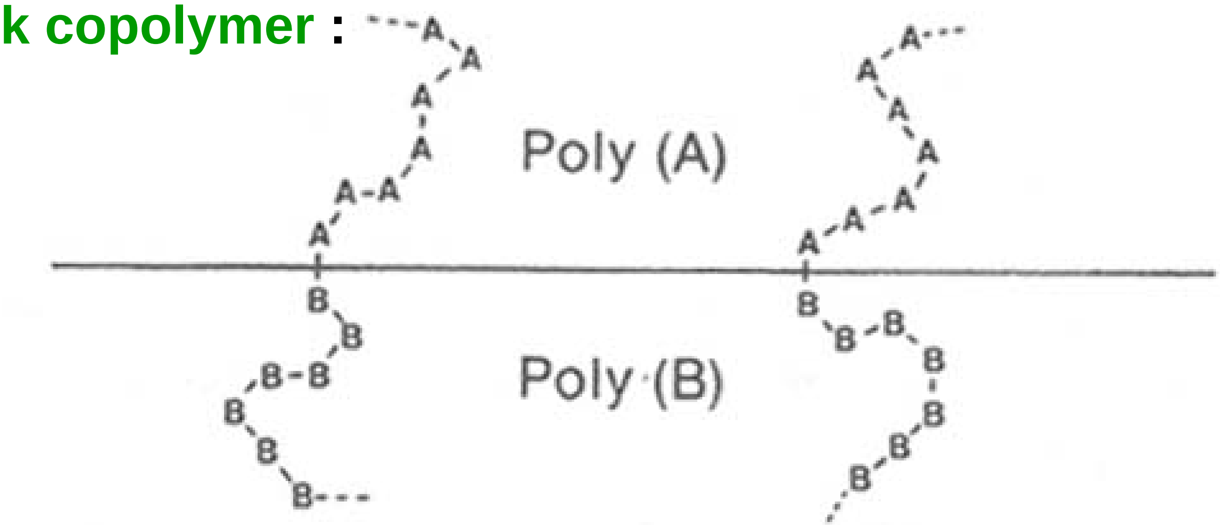
<Solution>

1) IPN: Physically “locked” together by interdisterbed 3-D network
   Still undergo phase separation into microdomains

2) Compatilizer:

   AB block copolymer: localize at the phase boundary and help “glue” the phases together
   Expensive, 1 wt% can significantly increase interfacial adhesion

Fig 3.22 AB block copolymer :



Immiscible blends without interfacial agent

High–impact PP: PP + ethylene-propylene copolymer

Natural affinity

3) In situ graft copolymeration

ABS: engineering plastic

St-BD copolymer dissolved in St and acrylonitrile (AN)

Copolymerization : chain-transfer reactions produce grafts

# of grafts in small, but is sufficient to provide the necessary interfacial adhesion