Chemical Structure & Polymer Morphology (Part I - Chapter 3 in Stevens)[1]

I   Introduction to Polymer Structure and Morphology

A) Desirable Polymer Properties

1) Plastic

   a) Toughness

   b) Durability

   c) Chemical Resistance (air, water, solvents)

   d) Light Stability

   e) Thermal Stability

   f) Flammability

   g) Transparency

   h) ….

2) Fiber

   a) Tensile Strength

   b) Spinnability

   c) Dyeability

   d) …

3) Elastomer (Rubber)

   a) Resilience

   b) …

4) Properties determined by chemical structure

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[1] The graphics in these notes indicated by "Figure/Table/Equation/Etc., x.x in Stevens" are taken from our lecture text: "Polymer Chemistry: An Introduction - 3rd Edition" Malcolm P. Stevens (Oxford University Press, New York,

a) ∴ Can be understood/predicted from Chemical Intuition

B) <u>Polymer Morphology ←→ Chemical Structure</u>

1) Polymer Morphology

    a) The structure, arrangement, and physical form of polymer molecules

    b) Closely related to

        i) Chemical Structure of Repeating Units (and End Groups)

        ii) Polymer Structure (e.g., linear, branched, …, monodisperse, …)

        iii) Topology, Higher Order Intrachain & Interchain Organization, Morphology

2) Common Polymer Morphologies

    a) Amorphous

        i) Almost no order (certainly over long ranges)

    b) Crystalline

        i) Long range order ⇒ regular arrays of molecules and/or molecular fragments

            ➢ Have both positional and orientational order

            ➢ For polymers can only be prepared by polymerization of a single crystal of the monomer

        ii) Semicrystalline

            ➢ For polymers this is a more realistic descriptor since there is very very seldom 100% order

1999).

> ➤ Typically, crystallinity is between 0% and 100%

c) Liquid Crystallinity

    i) Meaning

> ➤ Amorphous phase: Neither orientational nor positional order (isotropic)

> ➤ Crystalline phase: Both orientational and positional order

> ➤ Liquid Crystalline phase: Either orientational or positional order (or full order of one type but only partial order of the other)

    ii) "Walking the tightrope" between truly isotropic & crystalline materials

d) Crosslinking

    i) Chemical or Physical bonds between chains

    ii) Prevents independent motion of chains

e) Polymer Blends

    i) A way to get new properties in a product without developing a new polymer

II   Molecular Weight and Intermolecular Forces

A) Minimum (& Maximum) Molecular Weight

  1) Minimum required to get useful mechanical properties

    a) The actual value depends primarily on chemical structure

      i) stronger intermolecular forces $\rightarrow$ lower MW

    b) Secondary dependence on molecular topology

      i) e.g., linear, branched, star, dendrimeric, cyclic

  2) Maximum typically set by processability considerations

3) Interchain Forces

    a) Types

        i)   Covalent

        ii)   Ionic

        iii)   Hydrogen Bonding

        iv)   Dipole-Dipole

        v)   Dipole-Induced Dipole

        vi)   Van der Waals (London)

            ➢ proportional to surface areas of molecules in contact

            ➢ Recent study of Gecko feet using Van der Waals forces to stick to walls

    b) Characteristic Features

        i)   Strength

        ii)   Directionality

        iii)   If broken, nature of subsequent process

    c) Example:

        i)   Polyethylene of MW = 10,000 is a waxy solid but polyamides are hard brittle solids at MW down to 1,000

        ii)   Figure 3.1 in Stevens

        iii)   Polyamides, Polyesters, and Polyolefins make useful fibers at optimum MW in low tens of thousands, high tens to low
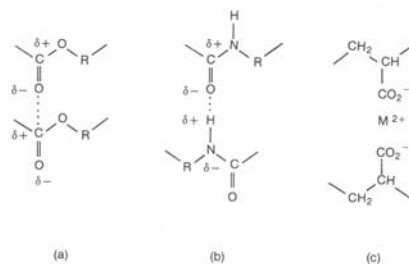

FIGURE 3.1. Intermolecular forces in polar polymers: (a) dipole–dipole in a polyester; (b) hydrogen bonding in a polyamide; and (c) ionic in a carboxyl-containing polymer.

hundreds of thousands, and high hundreds of thousands to millions of MW, respectively

4) Relationship of polymer properties to order

a) Intermolecular forces decrease very rapidly with distance

i) $\therefore$ they are much higher in crystalline materials than in amorphous ones

b) Example: Elastomer

i)   unstretched Elastomer:

➢ $\approx$ amorphous

ii)   after stretching:

➢ up to 600% elongation

➢ molecules highly ordered

➢ $\approx$ highly crystalline

iii)   Property changes

➢ Stiffness (modulus increases 2,000 fold)

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

III   Rheology and the Amorphous State

A) Definitions

1) Rheology is the study of flow

2) Amorphous state is characterized by no tendency to crystallinity in the solid state (a good definition?)

a) characteristic of all polymers above their melting points (except for liquid crystals and there it applies above their last transition temperature)

3) Vitrification occurs if amorphous state remains in sample on cooling to a solid (as opposed to crystallization)

    a) Example: Poly(ethylene terephthalate), PET

        i) In pop bottles is in vitrified (amorphous) state

        ii) In fibers is in semicrystalline state

B) Spaghetti Model

    1) Solid & Liquid Amorphous states differ in degree of molecular motion allowed

        a) local rotations, vibrations, translations vs.

        b) long range (segmental) motion

    2) liquid amorphous state resembles a bowl of worms or snakes

C) Deformation (Flow)

    1) With enough "freedom" for molecules the sample will initially be deformable and then will flow

    2) Applied force required

        a) direct mechanical pressure *vs.* gravitational pressure in deformation & flow, respectively

    3) In practice, detailed knowledge is primarily the realm of the engineer or physicist while Chemists need basics to help design materials

D) Relaxation, Elasticity, & Irreversible Flow

   1) Relaxation: If a force is applied and you get motion then (quickly) the force is withdrawn and the sample returns to original state

      a) Limited for each sample *wrt.*

         i)   speed of deformation

         ii)   duration sample held in deformed state

         iii)   degree of deformation

      b) Of course, determined by polymer structure & morphology in a complex fashion (but entanglement dominates, see later)

      c) This is the essence of elasticity

   2) Examples

      a) Silly Putty

         i)   polymeric & entangled

      b) Metals

         i)   delocalized bonding facilitates easy rearrangement (ductility)

      c) Ceramics

         i)   highly localized ionic & covalent bonding $\Rightarrow$ brittleness upon deformation

   3) Irreversible Flow

      a) Irreversible Flow: will occur if forces applied slowly, held to long, or deformed to far, the sample will not return to its original state

   4) Viscoelastic Behavior

      a) When flow characteristics are highly time dependent

      b) A very characteristic feature of polymers

E) Die Swell and Shrinkage

1) Figure 3.2 in Stevens

FIGURE 3.2. Schematic representation of polymer flow through a die orifice.

    a) polymer flow through an orifice

2) Die Swell

    a) e.g., an Amorphous polymer in an extruder

    b) Due to ordering in the die followed by relaxation after extrusion

3) Die Shrinkage

    a) Due to <u>dis</u>ordering in the die followed by relaxation <u>to a more ordered state</u> after extrusion e with a Liquid Crystalline polymer
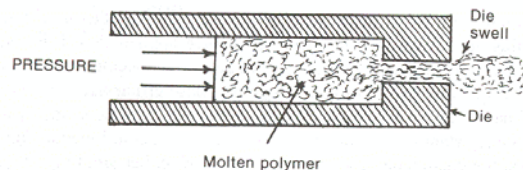
F) Shear (Tangential Stress)

1) Figure 3.3 in Stevens

FIGURE 3.3. Representation of shear (tangential stress).

    a) Application of force to one side of a rectangular block $\Rightarrow$ parallelogram

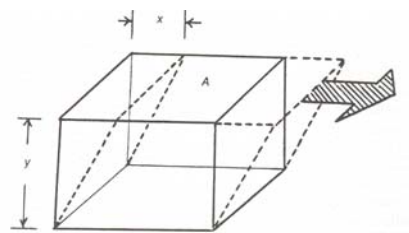**2) Shear Stress (τ) is the Applied Tangential Force to the sample**

    a) Higher τ means higher applied force

    b) $\tau \equiv F/A$

    c) F = Applied Force

    d) A = Surface Area of sample in contact with table

    e) This causes significant motion if molecules can flow past one another, e.g.:

        i)   Glass, Metal Block, & Covalent/Ionic Solids

            ➢ high $\tau \Rightarrow$ low motion

> ➤ Isotropic or anisotropic

    ii)   Graphite

> ➤ highly anisotropic

> ➤ τ low in graphite planes $\Rightarrow$ irreversible motion

> ➤ τ very high perpendicular to graphite planes $\Rightarrow$ irreversible motion

    iii)   Amorphous polymer

> ➤ $\tau \Rightarrow$ reversible motion and then irreversible motion

> ➤ due to flow of molecules past one another

3) **Shear Strain (γ)**, is the resultant tangential motion of top of sample *wrt.* the sample

base (which doesn't move)

   a) Higher γ mean more motion of the top of the block

   b) $\gamma \equiv X/Y$

   c) X = the motion of the block at its top

   d) Y = the height of the block

4) **Shear Modulus (*G*)** is a measure of the Stiffness of the Sample

   a) Higher *G* means a stiffer material

   b) $G \equiv \tau/\gamma$

   c) *G* = Shear Stress/Shear Strain

   d) *G* = Applied Force/Resultant Motion

5) **Shear Rate (γ dot)**, Velocity Gradient, is a measure of the rate of flow

   a) γ dot $\equiv d\gamma/dt$

   b) Shear Rate = the first derivative of Shear Strain as a function of Time

G) Types of Shear Flow

1) Figure 3.4 in Stevens

FIGURE 3.4. Types of shear flow: (A) Newtonian; (B) Bingham Newtonian; (C) shear thinning (pseudoplastic); and (D) shear thickening (dilatant).

2) Newtonian

    a) Shear Stress (Applied Force) $\propto$ Shear Rate (resultant motion in a tangential direction)

    b) Shear Stress = Viscosity x Shear Rate

    c) $\tau = \eta(\dot\gamma)$

    d) Since Viscosity increases rapidly with molecular rate, so will Applied Force (Shear Stress)

        i) M_V bar $= \Sigma N_i M_i^{(1.x)} / \Sigma\ N_i M_i^{0.x}$

        ii)   Where x is typically close to 1 and $\therefore$ 1.x is typically close to 2 &

        iii) $\therefore$ M_V bar $= \Sigma N_i M_i^{(1.9)} / \Sigma\ N_i M_i^{0.9}$ in a typical case

3) Bingham Newtonian

    a) Shear Stress (Applied Force) $\propto$ Critical Applied Force + Shear Rate (resultant motion in a tangential direction)

    b) Shear Stress = Critical Shear Stress + Viscosity x Shear Rate
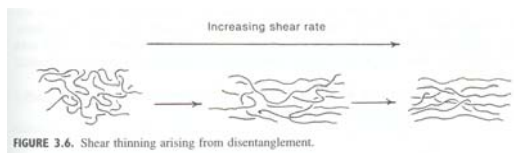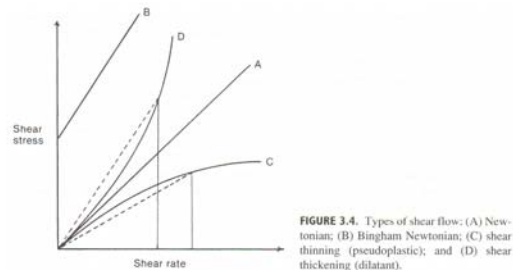
    c) $\tau = \tau_c + \eta(\dot\gamma)$

4) Shear Thinning (Pseudoplastic Deformation)

    a) As motion starts, viscosity **de**creases which **de**creases the Shear Stress that needs to be applied

    b) Figure 3.6 in Stevens

FIGURE 3.6. Shear thinning arising from disentanglement.

    c) Due to progressive detangling of polymer chains

        i)   cf. hair brushing

       ii)   cf. poring spaghetti

   d) At high enough Shear Rates, chains start to break and $\therefore$ viscosity drops rapidly

5) Shear Thickening (Dilatant Deformation)

   a) As motion starts, viscosity **in**creases which **in**creases the Shear Stress that needs to be applied

   b) Due to progressive tangling of polymer chains (e.g., liquid crystalline polymer)

6) Real World

   **a)** Combinations and Higher Order Behaviors

H) Power Law Expression for Flow

FIGURE 3.5. Power law plots: (A) Newtonian (slope = 1); (B) shear thinning (slope <1); and (C) shear thickening (slope >1).

   1) Figure 3.5 in Stevens

   2) Shear Stress = Constant (Shear Rate)^{Constant}

   **3)** $\tau = A(\gamma \; dot)^{B}$

      a) A related to viscosity of sample

      b) B related to how viscosity changes when motion starts

   4) Newtonian and Bingham Newtonian

      a) $\Rightarrow B = 1$

   5) Shear Thinning

      a) $\Rightarrow B < 1$

      b) Again, due to increasing disentanglement

   6) Shear Thickening

      a) $\Rightarrow B > 1$

      b) Again, due to increasing entanglement
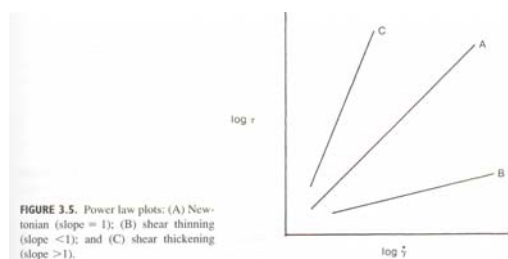
I) <u>**Critical Molecular Weights for Entanglements**</u>

FIGURE 3.7. Effect of molecular weight on Newtonian viscosity.

1) <mark>Figure 3.7 in Stevens</mark>

    a) Initially, viscosity increases relatively slowly with increasing MW, at the Critical MW all of a sudden the viscosity increases much more rapidly
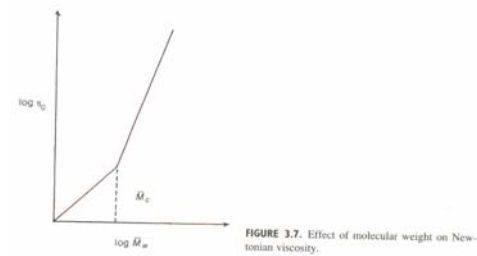
    b) Plot log of intrinsic viscosity as a function of log of M_w bar

    c) Below M_c bar, slope is 1

    d) Above M_c bar, slope is > 1

2) Typical range of M_c bar

    a) Typically 4,000 to 15,000 (depending on polymer structure) for a random coil polymer

    b) Corresponds to a degree of polymerization of about 600 (i.e., DP bar = 600) irrespective of polymer structure

        i) $\therefore$ This change in viscosity is a function of topology/entanglement and not chemical interactions

        ii) This can be considered the "Magic Point" between materials that behave like small/discrete molecules and polymers/plastics

J) <u>**Relationship of MW & Polymer Structure to Viscosity & $\therefore$ Flow**</u>

1) Since viscosity increases as some power of MW, it will increase extremely rapidly at higher MW

    a) $\therefore$ Keep MW as low as possible for the application
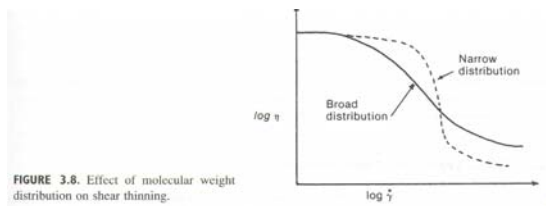
2) Viscosity & MW Distribution

   a) <mark>Figure 3.8 in Stevens</mark>

FIGURE 3.8. Effect of molecular weight distribution on shear thinning.

   b) Narrow MW distributions have highest viscosities

      i)   Also, Shear Thinning sets in later but once it does set in its magnitude is larger

   c) Broad MW distributions have lower viscosities

      i)   Also, Shear Thinning set in earlier

3) Viscosity & Branching

   a) More branching

      i) $\Rightarrow$ Lower Apparent Hydrodynamic Volume

        ➢ $\therefore$ lower viscosity

        ➢ However, one also lowers secondary intermolecular forces with branching (due to poorer packing)

        ➢ and hence can weaken mechanical properties

   b) Dendrimers

      i)   Dendrimers take this effect to the extreme

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

        ➢ $\therefore$ Dendrimers make better lubricants in variable temperature applications

4) Influence of Shape & Rigid Rod Polymer

   a) Mark-Houwink-Sakurada Equation

      i) $[\eta] = K \, (\bar{M_v})^a$

ii) $a \approx 0.5$ for random coils

iii) $a \approx 1.0$ (1.5) for rigid rods

b) $\therefore$ Rigid-rod polymers are substantially more viscous at same MW

K) Viscosity Determinations in Polymer Melts

1) Rotating objects in melt and measure torque $\Rightarrow$ viscosity
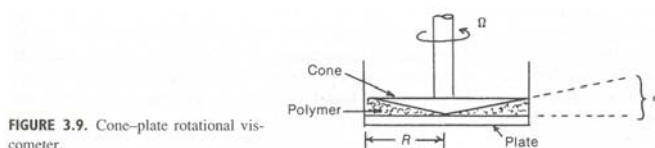
2) Rotating Cone-Plate Viscometer

a) Figure 3.9 in Stevens

3) Rotating Cone Viscometer

FIGURE 3.9. Cone–plate rotational vis-
cometer.

4) Rotating Rod Viscometer

5) Empirical Methods

a) Pore time or velocity

b) Back pressure/torque on pumps

IV   Glass Transition Temperature

A) 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

a) Fundamental change in properties from brittle crystalline to rubbery at some

    critical temperature

3) At higher temperature get melting, mp

a) lose elastomeric properties & the material starts to flow as a liquid

B) Molecular Level Changes at T_g

1) Increase in long-range motion

a) segmental motion begins

i) coordinated motion of large sections of chain at T_g

ii) 20-50 atoms in polymer backbone move cooperatively at T_g

2) Segmental motion requires increase Free Volume around chain segments

a) ∴ the total volume of the sample must increase at T_g

b) This change is measurable at T_g

C) Other Changes at T_g

1) Enthalpy change

a) can be measured by calorimetry

b) essentially a change in the materials heat capacity (density & mobility)

2) Modulus (stiffness) decreases

a) measurable by mechanical methods (DMA, TMA, etc.)

3) Refractive Index changes

a) primarily as a function of density

4) Thermal Conductivity changes

a) due to both changes in mechanical structure and density changes

D) <u>Factors Determining Tg</u>

   **1)** Tg is an approximate number at best

        a) 30 °C discrepancies in literature not uncommon

        b) thermal, mechanical, optical methods can give values that differ by several degrees

        c) difficulties in getting reproducible samples

        d) sample history effects

        e) "aging" by light, aerial oxidation, etc.

    2) Chemical structure effects (more later)

    3) Molecular Weight effects

        a) lower molecular weights correspond to higher free volumes (i.e., from the ends) and the fact that ends of chains are intrinsically more mobile than the middle of strands

        b) For PS

            i) M_n bar of 3,000 has T_g of 40 °C

            ii) M_n bar of 300,000 has T_g of 100 °C

E) <u>Influence of Chemical Structure on T_g</u>

    1) T_g is a function of rotational freedom

        a) $\therefore$ Anything that reduces rotational freedom will increase T_g

        b) steric or electronic impediments to free rotation increase T_g

        c) Examples

            i)   torsional rotation about C-C backbones in polyolefins

> ➢ torsional barrier to rotation in ethane is ≈ 3 kcal/mole

> ➢ c.f., expected steric effects with ethane, butane, "di-*tert*-butylethane"

> ➢ typically ∴ bulkier side chains result in increased T_g

    ii) torsional rotation about Si-O backbones in silicones

> ➢ lower torsional barriers ⇒ lower T_g

> ➢ -[-SiMe$_2$-O-]$_n$- *vs*. -[-CH$_2$-CH$_2$-]$_n$-

2) T_g is a function of free volume

    a) ∴ Anything that reduces free volume will increase T_g

    b) at some point, bulky side chains increase free volume and hence decrease T_g

3) Other influences on T_g

    a) plasticizing effect of flexible side chains

    b) entanglements of longer side chains

    c) polarity, H-bonding, etc., of side chains

4) Vinyl Polymer trends in T_g

    a) Table 3.1 in Stevens

    b) trends for linear side chains (**4-11**)

    c) side chain size for **5**, **21**, **22**

    d) branching (**12-16**, **17** & **18**)

        i) branching increases T_g via increased steric barriers to rotation

    e) interchain forces

TABLE 3.1. Glass Transition Temperature (T_g) of Representative Vinyl Polymers[a]

Polymer $\left[\text{CH}_2\text{CH} \atop R \right]$

Number		R	T_g (°C)
4	Polyethylene	H	−20
5	Polypropylene	CH$_3$	5
6	Poly(1-butene)	CH$_3$CH$_2$	−24
7	Poly(1-pentene)	n-C$_3$H$_7$	−40
8	Poly(1-hexene)	n-C$_4$H$_9$	−50
9	Poly(1-heptene)	n-C$_5$H$_{11}$	−31
10	Poly(1-decene)	n-C$_8$H$_{17}$	−41
11	Poly(1-dodecene)	n-C$_{10}$H$_{21}$	−6
12	Poly(3-methyl-1-butene)	CH(CH$_3$)$_2$	50
13	Poly(4-methyl-1-pentene)	CH$_2$CH(CH$_3$)$_2$	29
14	Poly(3,3-dimethyl-1-butene)	C(CH$_3$)$_3$	64
15	Poly(5-methyl-1-hexene)	CH$_2$CH$_2$CH(CH$_3$)$_2$	−14
16	Poly(4,4-dimethyl-1-pentene)	CH$_2$C(CH$_3$)$_3$	59
17	Poly(vinyl n-butyl ether)	O-C$_4$H$_9$-n	−55
18	Poly(vinyl t-butyl ether)	O-C$_4$H$_9$-t	88
19	Poly(vinyl chloride)	Cl	81
20	Poly(vinyl alcohol)	OH	85
21	Polystyrene	C$_6$H$_5$	100
22	Poly(2-vinylnaphthalene)		151
23	Poly(4-vinylpyridine)		142

[a]Data from Peyser.[14a]

      i)   e.g., CH_3, Cl, OH of comparable size yet, **5**, **19**, & **20** have vary different

          T_g values due to differences in interchain forces

      ii)   e.g., phenyl to pyridyl side chains in **21** & **23**

5) Non-Vinyl Polymer trends in T_g

    a) Table 3.2 in Stevens

    b) Hydrogen-Bonding

      i)   e.g., polyesters *vs.* polyamides for **25** & **29**

          ➤ (also effects of bond order of backbones!)

    c) chain stiffening effect

      i)   **24** *vs.* **26**, **25** *vs.* **27**

      ii)   Bisphenol A (a polycarbonate), compound **34** and polymer **28**

      iii)   extreme stiffening in semibenzimidazole **33**

6) Stereochemical Effects on T_g

    a) Table 3.3 in Stevens for polybutadienes

    b) effects of side chains clear for R = H, Me, Cl

    c) *cis vs. trans* effects hard to predict

      i)   due to confounding effects of backbone stiffness & free volume

7) Utility considerations

    a) for a polymer to be a useful thermoplastic, T_g must be higher than intended working temperatures (but not too high for processing)

TABLE 3.2. Glass Transition Temperature (T_g) of Representative Nonvinyl Polymers[a]

Number	Polymer	T_g (°C)
24	—C(CH₂)₄CO(CH₂)₂O—	−63
25	—C(CH₂)₄CO(CH₂)₄O—	−118
26	—C⟨◯⟩CO(CH₂)₂O—	69
27	—C⟨◯⟩CO(CH₂)₄O—	80
28	—O⟨◯⟩C(CH₃)₂⟨◯⟩OC—	149
29	—C(CH₂)₄CNH(CH₂)₆NH—	57
30	—C(CH₂)₄CNH(CH₂)₁₀NH—	50
31	—NH(CH₂)₅C—	77
32	—NH(CH₂)₁₀C—	46
33	(semibenzimidazole structure)	429

[a]Data from Peyser.[14a]

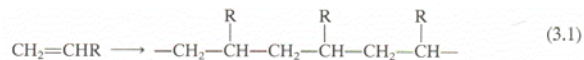(structure of compound **34**:) HO—⟨◯⟩—C(CH₃)₂—⟨◯⟩—OH, **34**
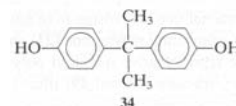
TABLE 3.3. Glass Transition Temperature (T_g) of Diene Polymers

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

[a]Data from Peyser.[14a]
[b]Data from Burfield and Lim.[15]

b) for elastomers, T_g must be below working temperatures

F) Stereochemistry (stereoregularity) & Tacticity

1) Heads & Tails

a) Stevens Equations 3.1 & 3.2

$$CH_2=CHR \longrightarrow -CH_2-CH-CH_2-CH-CH_2-CH- \quad (3.1)$$
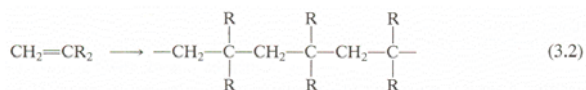
b) **head-to-tail** polymerization

$$CH_2=CR_2 \longrightarrow -CH_2-C-CH_2-C-CH_2-C- \quad (3.2)$$

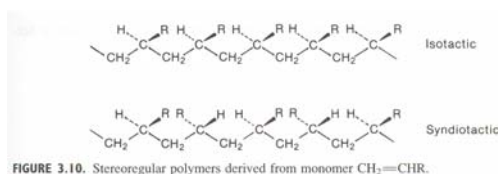typically preferred in polymerization mechanisms

c) **head-to-head** & **tail-to-tail** polymerization do occur but are typically infrequent

2) Relative stereochemistry at adjacent centers

a) terminology from Natta (of Ziegler Natta fame (1963 Nobel Prize))

FIGURE 3.10. Stereoregular polymers derived from monomer CH₂=CHR.

b) Figure 3.10 in Stevens

c) Isotactic

   i) each chiral center has same configuration (on same side)

d) Syndiotactic

   i) chiral centers alternate their configurations (on opposite sides)
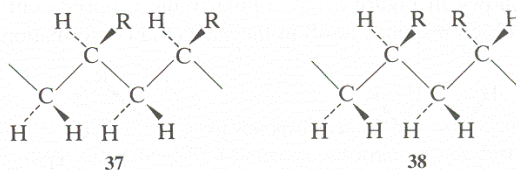
e) Atactic/Heterotactic

   i) random configurations

f) Stereoblock polymers
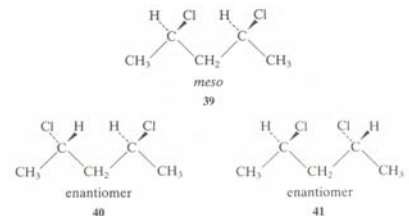
   i) blocks in polymer have different stereochemistry

3) Tactic Dyads

a) Molecules 37 & 38 in Stevens

b) Isotactic Dyad $\longleftrightarrow$ Meso Like

37   38
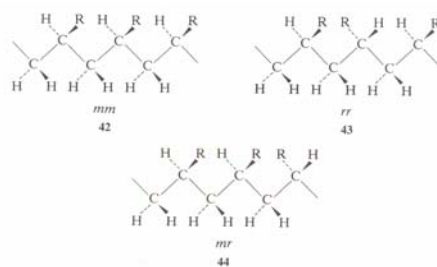
        i)   Meso Dyads designated as m

    c) Syndiotactic Dyad $\longleftrightarrow$ Racemic Like (chiral)

        i)   Racemic Dyads designated as r

    d) Small Molecules analogues or m & r dyads

        i)   Molecules 39-41 in Stevens

        ii)   39 is meso, m

        iii)   40 & 41 are racemic, r

4) Tactic Triads

    a) Three possible forms

        i)   Molecules 42-44 in Stevens

        ii)   42 is mm

        iii)   43 is rr

        iv)   44 is mr (or rm)

    b)

5) Tactic Tetrads

    a) six possible forms

    b) rrr, rrm (or mrr), rmr, mrm, mmr (or rmm), & mmm

6) Evaluate the tacticity problems

    a) graphical determination from pictures

    b) experimental determination from NMR (later)

7) Other types of polymeric tacticity not discussed

    a) 1,2 and 1,1' disubstituted monomers

    b) from cyclic monomers

   c) from dienes

8) Dependence to T_g on Tacticity

   a) <mark>Table 3.4 in Stevens</mark>

   b) Syndiotactic T_g typically > Isotactic T_g

   c) Atactic T_g is typically similar to Syndiotactic T_g

TABLE 3.4. Glass Transition Temperature (T_g) of Polymers of Varying Tacticity[a]

Polymer	T_g (°C)		
	Syndiotactic	Atactic	Isotactic
Poly(methyl methacrylate)	105	105	38
Poly(ethyl methacrylate)	65	65	12
Poly(t-butyl methacrylate)	114	118	7
Polypropylene[b]	−4	−6	−18
Polystyrene	100[c]		99[c]

[a] Data from Peyser[14] unless otherwise noted.
[b] Data from Burfield and Doi.[23]
[c] Data from Ishihara, Kuramoto, and Uoi, *Macromolecules*, **21**, 3356 (1988).

9) Dependency of crystallinity on Tacticity

   a) Increasing regularity in stereochemistry $\Rightarrow$ increased crystallinity

V   <u>**Crystallinity**</u>

A) <u>Polymer Crystallinity</u>

1) Factors promoting crystallinity

   a) highly stereoregular polymers

   b) little or no branching

   c) highly polar groups

2) Structures of Crystallites in polymers

   a) <mark>Stevens Figure 3.15</mark>

   b) Fringed Micelle model

FIGURE 3.15. Schematic representation of a polymer matrix showing crystalline regions (fringed micelle model).

B) <u>Induction of Crystallinity</u>

1) Annealing

   a) holding a polymer at an elevated temperature below its melting point

   b) the extra thermal energy (and hence segmental motion) allow crystallization

2) Drawing

    a) stretching a polymer fiber above its T_g

    b) stretching a polymer film above its T_g

    c) both cases often result in loss of optical clarity (increase in opacity)

3) Nucleation

    a) adventitious nucleation agents

    b) purposely added nucleation agents

C) <u>Structures of Crystallites & Crystallite - Amorphous Boundaries</u>

    1) Size of crystallites

        a) determination

            i) X-Ray Diffraction
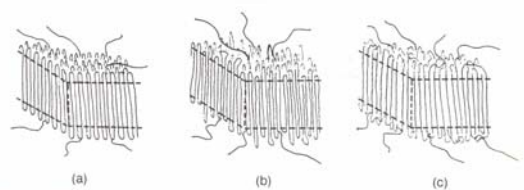
                ➢ Peak Shape Analysis

FIGURE 3.16. Folded-chain lamella model: (a) regular adjacent folds; (b) irregular adjacent folds; and (c) nonadjacent switchback.

                ➢ $\Rightarrow$ average size & size distribution

        b) ≈ 100 Å thick plates

    2) Folded-Chain Lamella Model

        a) <mark>Figure 3.16 in Stevens</mark>

        b)

    3) Crystallite Morphologies
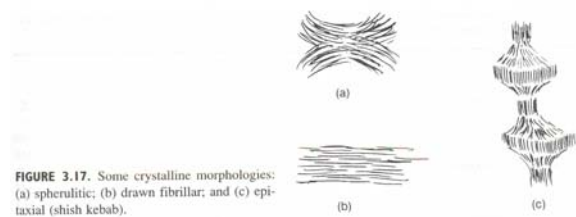
        a) Determination

            i) Electron Microscopy

FIGURE 3.17. Some crystalline morphologies: (a) spherulitic; (b) drawn fibrillar; and (c) epitaxial (shish kebab).

                ➢ freeze fracturing

                ➢ glassy *vs*. fibrillar morphologies

b) Figure 3.17 in Stevens

c) Spherulitic

    i)   aggregates of fibrils (small hair like strands)

    ii)   most common morphology in melt crystallizations or crystallizations from

        solution

d) Drawn Fibrillar

    i)   caused by fiber drawing

e) Epitaxial (shish kebab)

    i)   crystallization from stirred solutions or melts

D) Effects of Crystallinity

1) Mechanical Property Improvements

a) Tougher

b) Stiffer

c) Due to greater total interchain forces

    i)   i.e., average interchain distance decreases

2) More Opaque

a) due to light scattering from crystallites

3) Higher Density

4) More Solvent Resistant

a) c.f., polymer dissolution model

b) $\therefore$ degree of non-dissolution is an approximate measure of degree of crystallinity

E) <u>Melting Points</u>

    1) Typically quite broad for polymers

        a) broad for amorphous regions

        b) narrow(er) for crystalline regions

    2) T_m is the crystalline melting point

    3) T_g and T_m are highly correlated

        a) Table 3.5 in Stevens

        b) this is a reflection of the common factors influencing them

        c) T_g values are typically 1/2 to 2/3 of T_m in K

TABLE 3.5. Approximate Glass Transition Temperatures (T_g) and Crystalline Melting Temperatures (T_m) of Some Common Polymers[a]

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-Polyisoprene	−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

[a]Data from Peyser[4a] and Miller[4b] (average of reported values).

VI   <u>Liquid Crystallinity</u>

A) <u>Nature & Origins</u>

    1) Intermediate orientational and positional order

        a) i.e., intermediate between liquid and crystalline phases

        b) ordered regions called Mesophases

        c) occur between conventional mp and true isotropic solution

    2) Small molecule liquid crystallinity

        a) polarizable molecules

            i) delocalized π systems

            ii) extended conjugation

        b) relatively rigid molecules

        c) rod-like or disk-like molecules

        d) "tails"

3) Unique properties of Liquid Crystalline phases

    a) structures influenced by external electric and magnetic fields

    b) color and/or opacity changes with temperature

    c) extremely high optical rotations

4) Classification of Liquid Crystals

    a) Lyotropic Liquid Crystals

        i)   form in solution

    b) Thermotropic Liquid Crystals

        i)   form in neat materials

    c) Degree of Ordering

        i)   Nematic, Smectic, Cholesteric, etc.

5) Importance of liquid crystallinity to polymer science

    a) effects on viscosity

    b) maintenance of ordered configurations in the solid state

B) **Example of Copolyester**

1) Ingredients

    a) Terephthalic Acid

    b) Ethylene Glycol

    c) para-Hydroxybenzoic Acid

        i)   relatively rigid in backbone

HO_2C—⬡—CO_2H $HOCH_2CH_2OH$ HO—⬡—CO_2H

     55   56   57

d)   Molecules 55-57 in Stevens

2)   Melt Viscosity as a function of relative concentrations of components

a)   Figure 3.18 in Stevens

b)   Stage 1

i)   viscosity increase

ii)   due to increased concentration of more rigid monomer

c)   Stage 2

i)   viscosity decrease

ii)   melt becomes opaque

iii)   due to liquid crystalline behavior (thermotropic)

d)   Stage 3

i)   viscosity increase
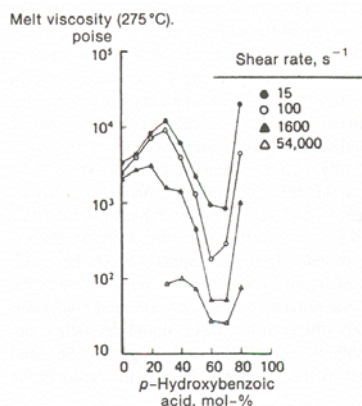
ii)   due to too much rigidity to form liquid crystal

FIGURE 3.18. Effect of p-hydroxybenzoic acid concentration on melt viscosity of a terephthalic acid/p-hydroxybenzoic acid/ethylene glycol co-polyester. [From Jackson and Kuhfuss,[37] copyright 1976. Reprinted by permission of John Wiley & Sons, Inc.]

3)   Ordering retained on cooling

a)   ⇒ improved processability

i)   due to decreased viscosity

b)   also ⇒ improved mechanical properties

i)   the order ⇒ stronger interchain forces

C)   Disadvantages & Solutions

1)   Very high melting points

58
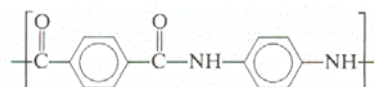
2) Very low solubilities in normal solvents

   a)   e.g., Kevlar and concentrated H_2SO_4

   b)   <mark>Molecule 58 in Stevens</mark>
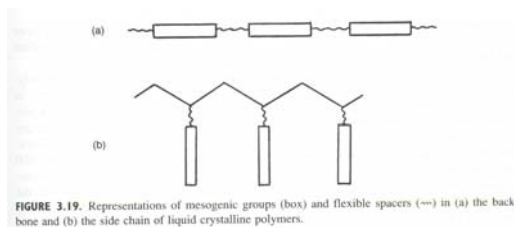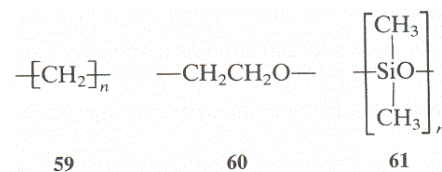
3) Separate Mesogens with flexible spacers

   a)   <mark>Molecules 59-61 in Stevens</mark>

4) Main Chain and Side Chain Liquid Crystalline "Spaced" Polymers

   a)   <mark>Figure 3.19 in Stevens</mark>

$$-[CH_2]_n \qquad -CH_2CH_2O- \qquad \left[\begin{array}{c} CH_3 \\ | \\ SiO \\ | \\ CH_3 \end{array}\right]_n$$

59   60   61

FIGURE 3.19. Representations of mesogenic groups (box) and flexible spacers (~~) in (a) the backbone and (b) the side chain of liquid crystalline polymers.

VII   **Chemical Crosslinking**

A) Generation of Crosslinks

1) During Polymerization

   a)   e.g., styrene & divinylbenzene copolymers

2) During Separate Curing stage

   a)   e.g., natural rubber & S_8 vulcanization

B) Measurement & Evaluation of Crosslinks

1) Degree of swelling

2) Loss of flow properties

3) Crosslink Density is key property for a particular system

VIII   Physical Crosslinking

A) Nature

1) Chemical Crosslinking involves covalent or ionic links between chains

2) Physical Crosslinking involves use of phase separation to produce crosslinks

   a) Figure 3.20 in Stevens

   b) Thermoplastic Elastomers

   c) microphase separation based on mutual polymer faction insolubility
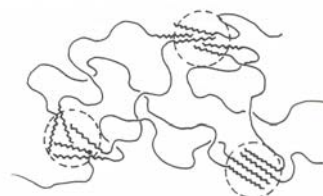
   d) Table 3.6 in Stevens

FIGURE 3.20. Representation of aggregation in an ABA block thermoplastic elastomer (— represents end blocks, circle represents microdomains).

B) ABA Block Copolymers

1) B blocks "flexible"

   a) e.g., polybutadiene

2) A blocks "hard"

   a) e.g., polystyrene

TABLE 3.6. Commercially Important Thermoplastic Elastomers

Type	End Blocks	Middle Block
Styrenic	Polystyrene	Polybutadiene or polyisoprene
Polyolefin[a]	Isotactic polypropylene	Ethylene–propylene copolymer
Polyurethane	Rigid polyurethane	Flexible polyester or polyether
Copolyester	Rigid polyester[b]	Flexible polyester
Polyamide	Rigid polyamide[c]	Flexible polyether

[a] Also manufactured by mechanical blending of isotactic polypropylene and ethylene–propylene–diene copolymer.
[b] Principally poly(ethylene terephthalate).
[c] Nylons 6, 66, 11, 12, and 612.

IX   Polymer Blends (Polyblends)

A) Rationale

1) Production costs

   a) monomer production

   b) polymerization line

2) Safety costs

TABLE 3.7. Types of Polyblends

Type	Description
Mechanical blends	Polymers are mixed at temperatures above T_g or T_m for amorphous and semicrystalline polymers, respectively
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
Chemical blends	
Interpenetrating polymer networks (IPN)	Crosslinked polymer is swollen with different monomer, then monomer is polymerized and crosslinked
Semi-interpenetrating polymer networks (semi-IPN)	Polyfunctional monomer is mixed with thermoplastic polymer, then monomer is polymerized to network polymer (also called pseudo-IPN)
Simultaneous interpenetrating polymer networks (SIN)	Different monomers are mixed, then homopolymerized and crosslinked simultaneously, but by noninteracting mechanisms
Interpenetrating elastomeric networks (IEN)	Latex polyblend is crosslinked after coagulation

3) Engineering costs of new blend convert commodity materials into higher profit engineering materials

4) Types of Polyblends

    a) Table 3.7 in Stevens

B) Interactions in Polyblends

    1) Types & Effects

        a) Figure 3.21 in Stevens

        b) Additive

            i) no new interactions between chains

FIGURE 3.21. Hypothetical property–concentration relationships for a binary miscible polyblend.

        c) Synergistic

            i) new types of interactions between chains

            ii) e.g., ionic or hydrogen bonds occur or are strengthened

        d) Non-Synergistic

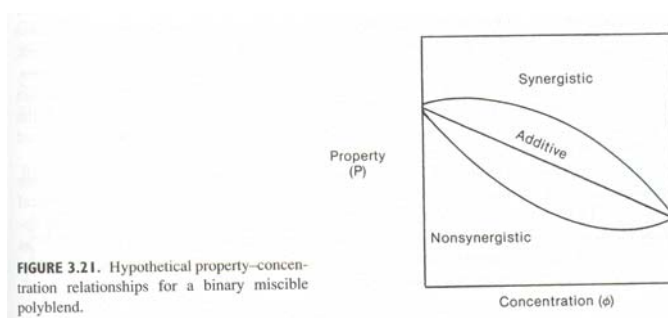   i) e.g., prevention or disruption of crystallinity

    2) Prediction of Properties of Polyblends

        a) challenging for miscible blends

            i) hard even to predict miscibility

            ii) hard to evaluate new interactions quantitatively

            iii) may add compatibilizers

        b) very very challenging for immiscible blends

            i) properties primarily determined by continuous phase

3) Microphase Separation

    a) Structure of phase boundary

    b) is fundamental to immiscible blends

        i)   use tends to increase

    c) Compatibilizers

        i)   AB block copolymers

        ii)   Figure 3.22 in Stevens

FIGURE 3.22. Representation of the use of an AB block copolymer to improve interfacial adhesion in an immiscible polyblend.

        iii)   graft copolymers

            ➢ relatively low production costs