

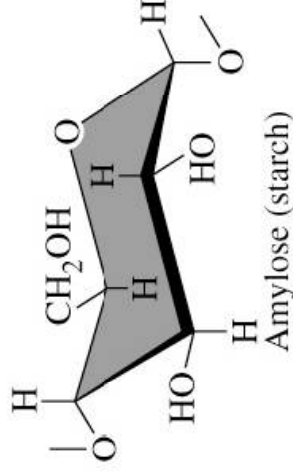
Polymers

- **Polymers** are the giant molecules of chemistry.
- Chemists also call them **macro-molecules**.
- The small building-block molecules are called **monomers**.
- Synthetic polymers are a mainstay of modern life, but nature also makes polymers; they are found in all living matter.

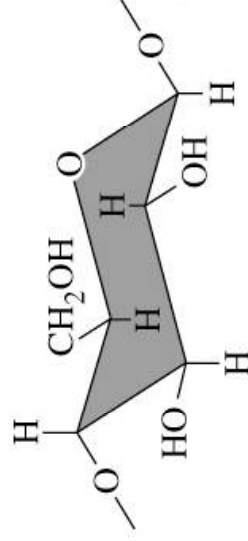
Natural Polymers

Three types of natural polymers are polysaccharides, proteins, and nucleic acids.

polysaccharides



Amylose (starch)



Cellulose

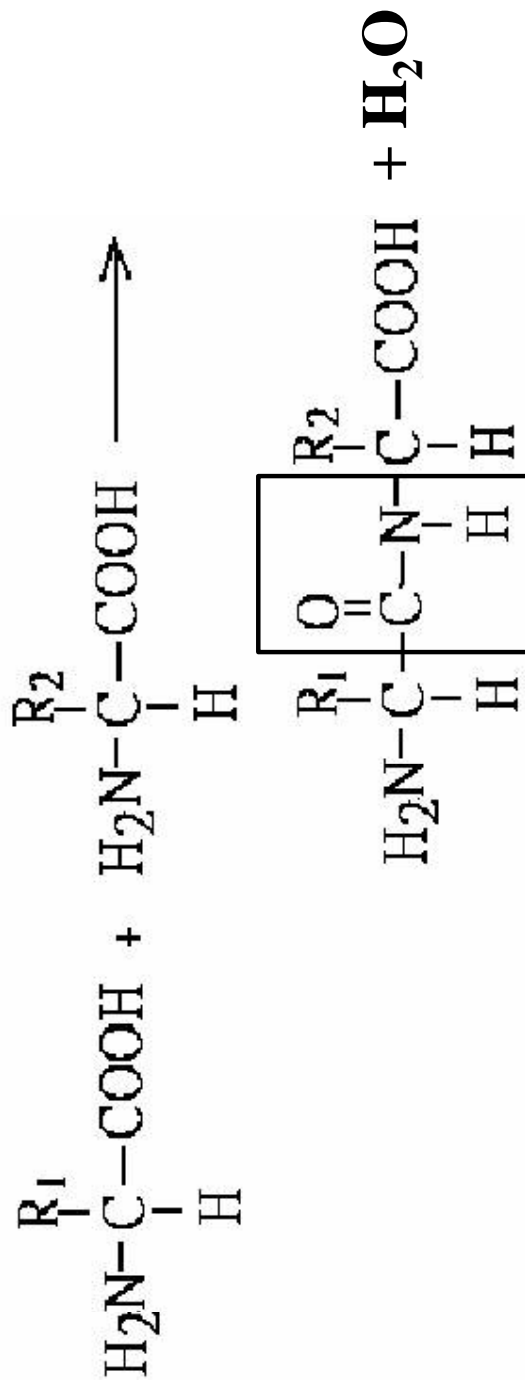


Amylose (starch)



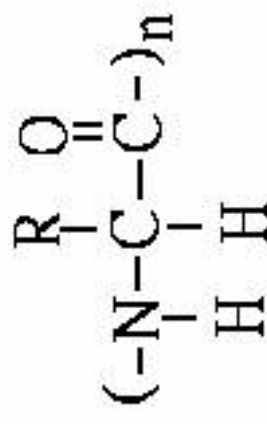
Cellulose

proteins



Peptide Bond

Primary Structure of Protein - Polypeptide Chains



20 Common Amino Acids

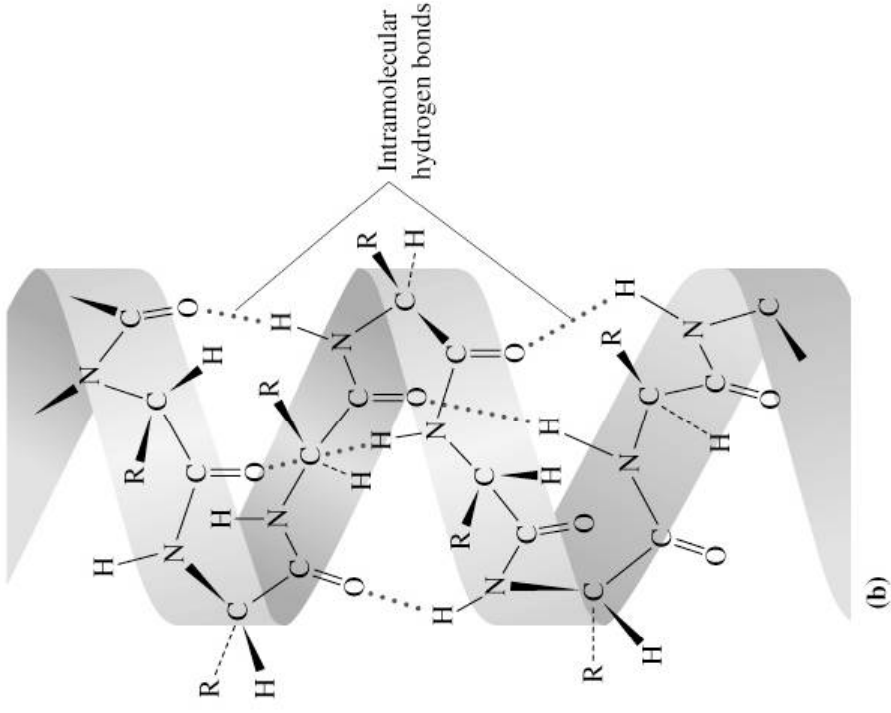
TABLE 23.2 The 20 Amino Acids Commonly Found in Proteins

Name	Symbol	Condensed Structural Formula	pI ^a
Neutral amino acids			
Glycine	Gly	HCH(NH ₂)COOH	6.03
Alanine	Ala	CH ₃ CH(NH ₂)COOH	6.10
Valine ^b	Val	(CH ₃) ₂ CHCH(NH ₂)COOH	6.04
Leucine ^b	Leu	(CH ₃) ₂ CHCH ₂ CH(NH ₂)COOH	6.04
Isoleucine ^b	Ile	CH ₃ CH ₂ CH(CH ₃)CH(NH ₂)COOH	6.04
Phenylalanine ^b	Phe	C ₆ H ₅ CH ₂ CH(NH ₂)COOH	5.74
Serine	Ser	HOCH ₂ CH(NH ₂)COOH	5.70
Threonine ^b	Thr	CH ₃ CHOHCH(NH ₂)COOH	5.6
Methionine ^b	Met	CH ₃ SCH ₂ CH ₂ CH(NH ₂)COOH	5.71
Cysteine ^b	Cys	HSCH ₂ CH(NH ₂)COOH	5.05
Tyrosine	Tyr	<i>p</i> -HOC ₆ H ₄ CH ₂ CH(NH ₂)COOH	5.70
Tryptophan ^b	Trp	C ₈ H ₆ NCH ₂ CH(NH ₂)COOH	5.89
Asparagine	Asn	H ₂ NCOCH ₂ CH(NH ₂)COOH	5.4
Glutamine	Gln	H ₂ NCOCH ₂ CH ₂ CH(NH ₂)COOH	5.7
Proline ^c	Pro	C ₄ H ₈ NCOOH	6.21
Acidic amino acids			
Aspartic acid	Asn	HOOCCH ₂ CH(NH ₂)COOH	2.96
Glutamic acid	Glu	HOOCCH ₂ CH ₂ CH(NH ₂)COOH	3.22
Basic amino acids			
Lysine ^b	Lys	H ₂ N(CH ₂) ₄ CH(NH ₂)COOH	9.74
Arginine	Arg	H ₂ NC(=NH)NH(CH ₂) ₃ CH(NH ₂)COOH	10.73
Histidine ^b	His	C ₃ H ₃ N ₂ CH ₂ CH(NH ₂)COOH	7.58

^apH of at the *isoelectric point*.

^bEssential amino acids.

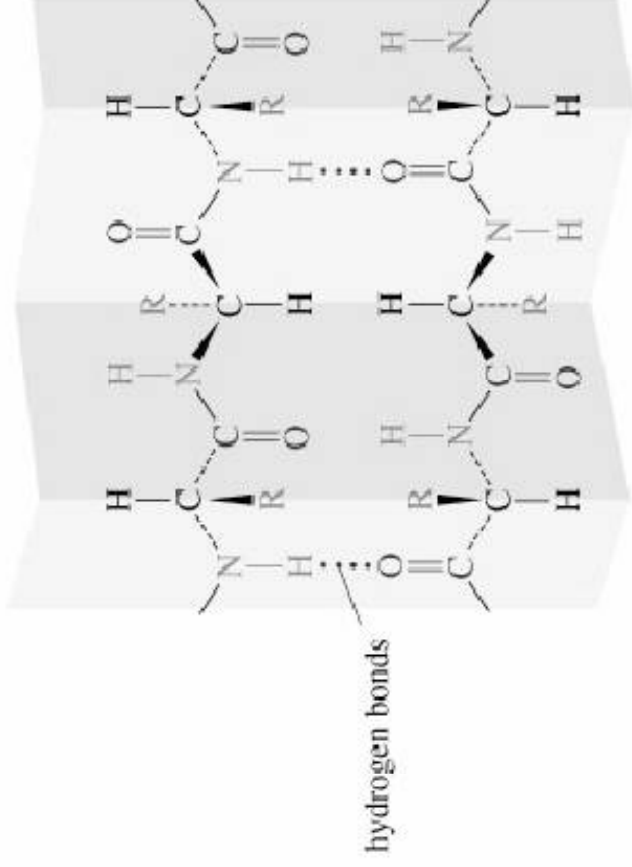
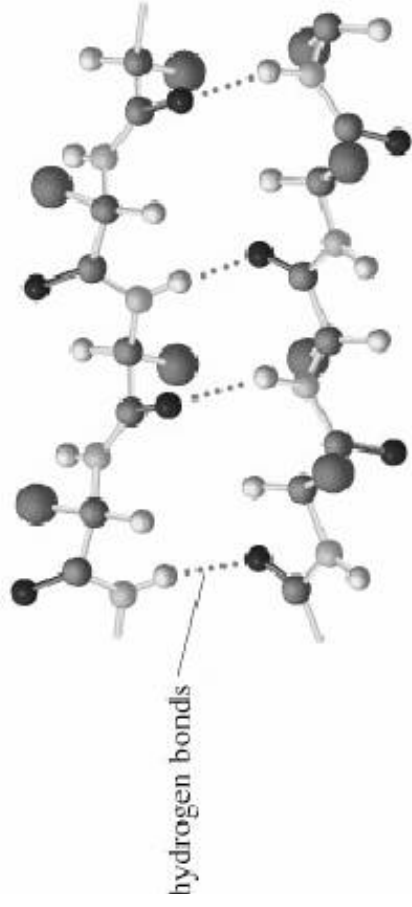
^cProline has a *secondary* amine functional group —NH— making it an *imino* acid.



Hydrogen Bonding in Polypeptide Chains

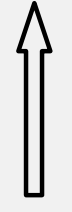


Secondary Structure



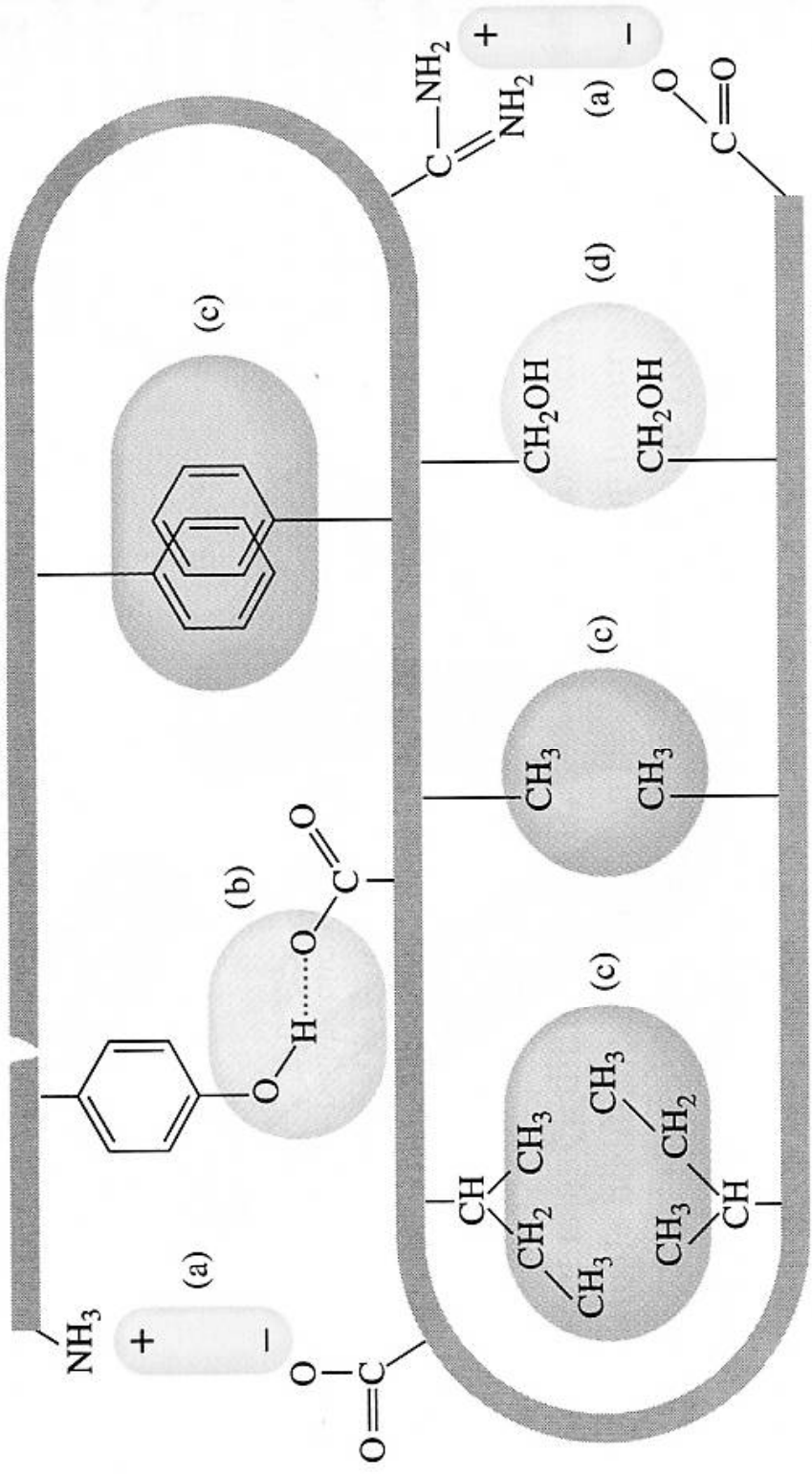
(a)

Hydrogen Bonding in Polypeptide Chains



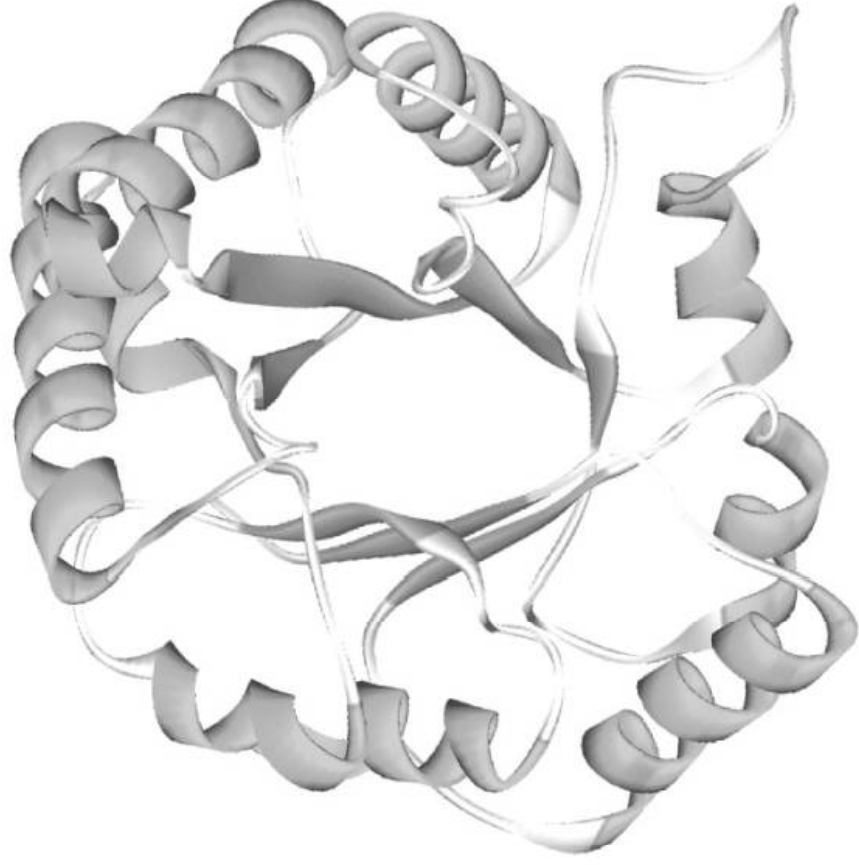
β -pleated sheet

Secondary Structure

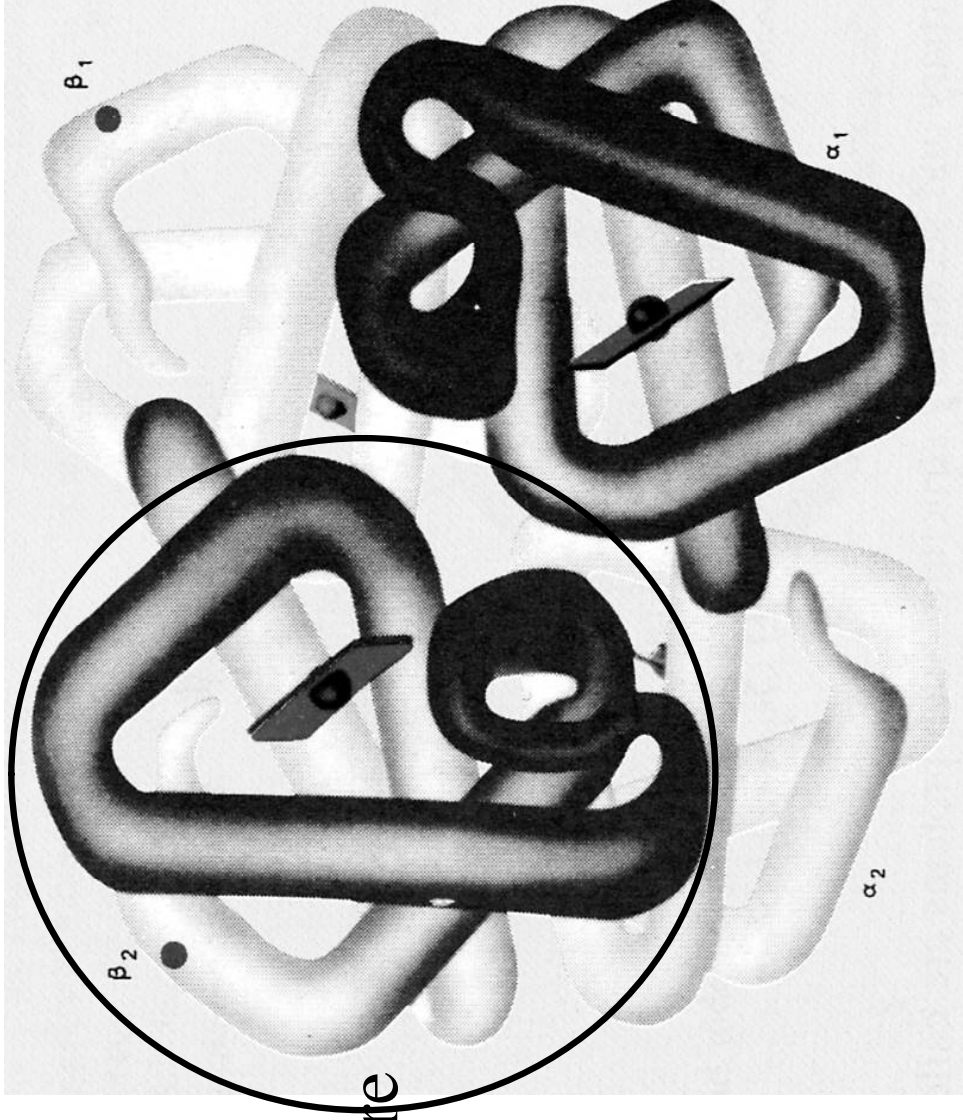


Interaction Forces in Polypeptide Chains
To form Tertiary Structure

Tertiary Structure of a Protein

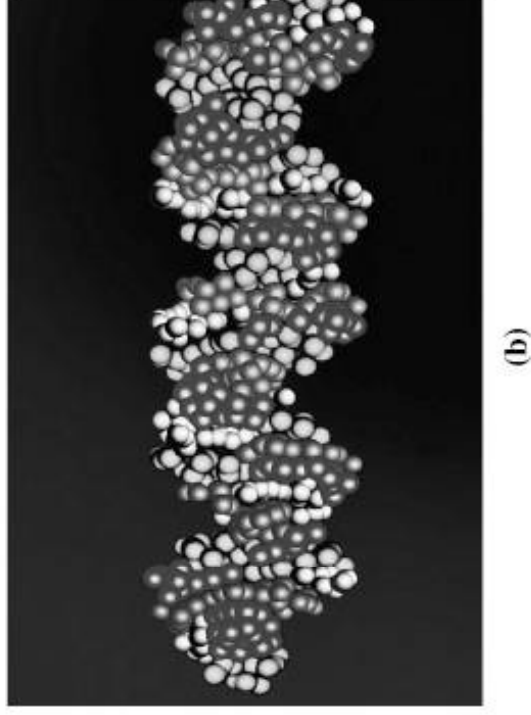
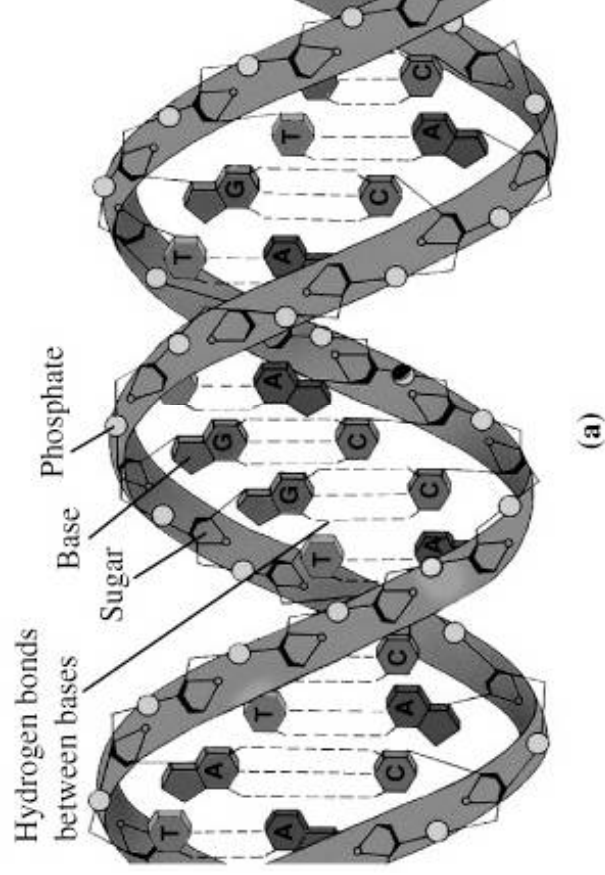


Tertiary Structure

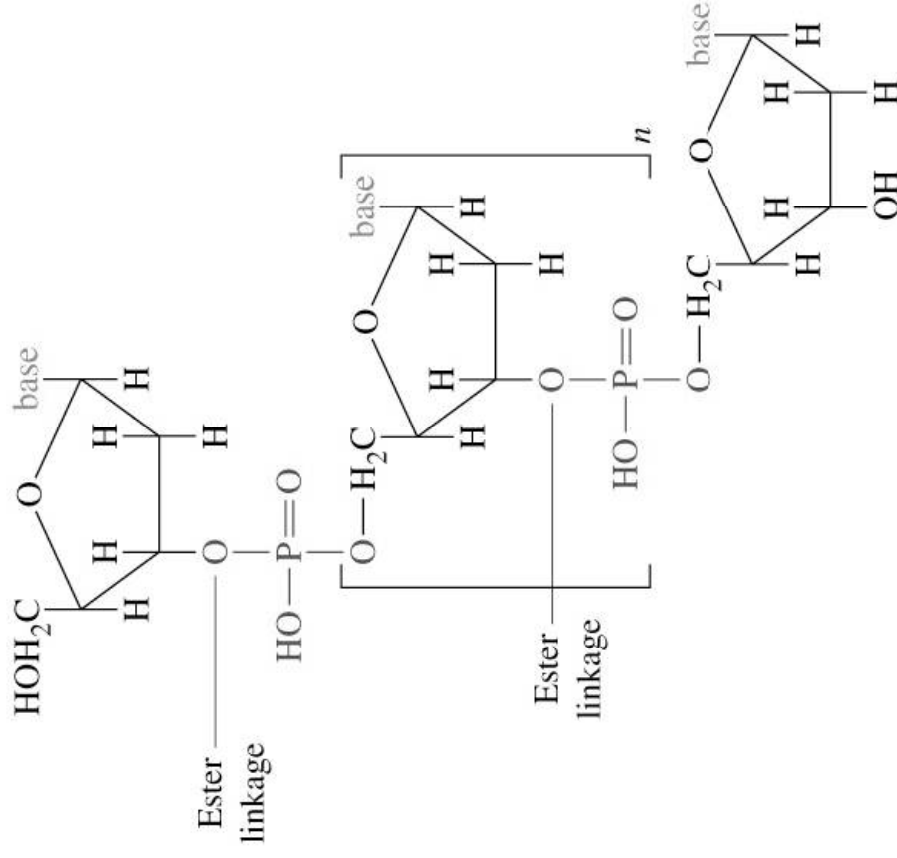


Quaternary Structure of Polypeptide (hemoglobin)

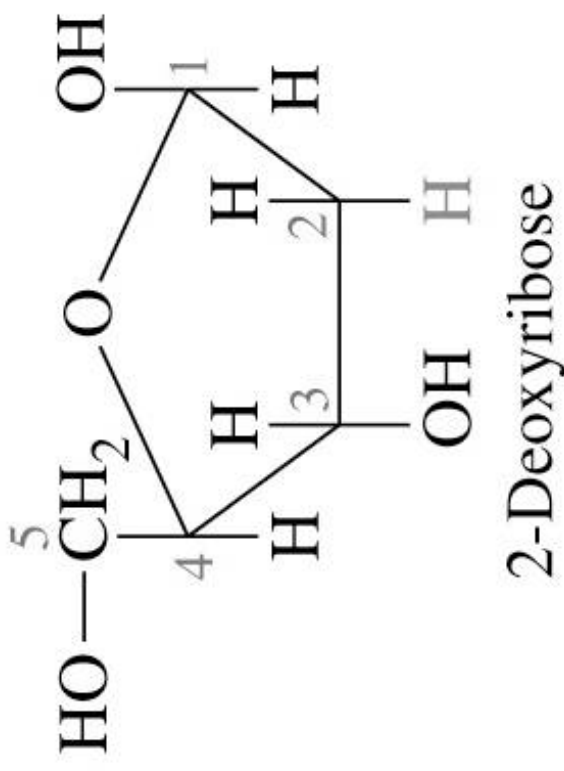
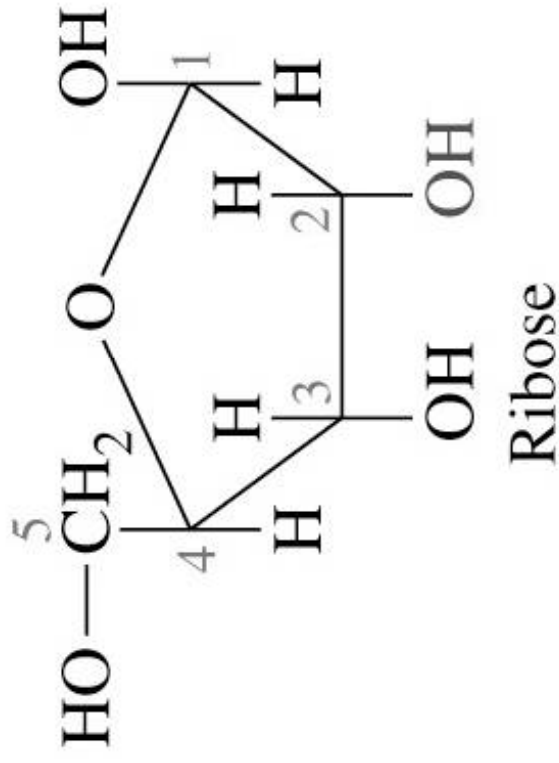
The DNA Double Helix



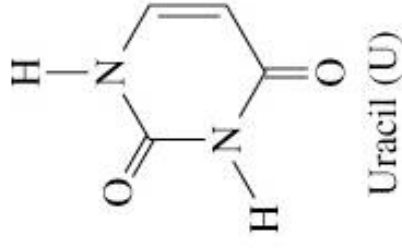
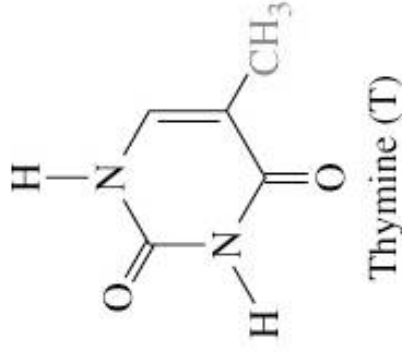
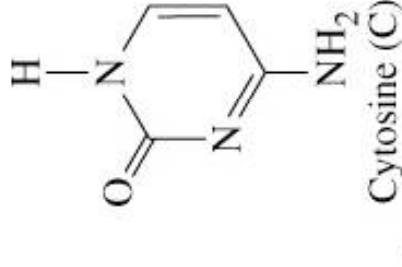
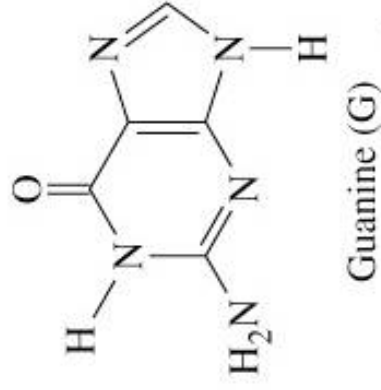
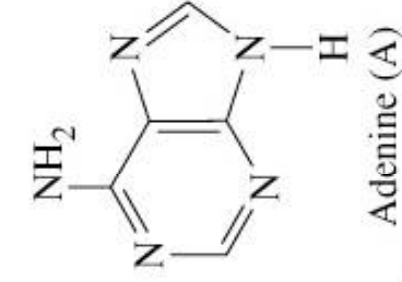
The Backbone of a Deoxyribonucleic Acid Molecule



Sugars Found in Nucleic Acids



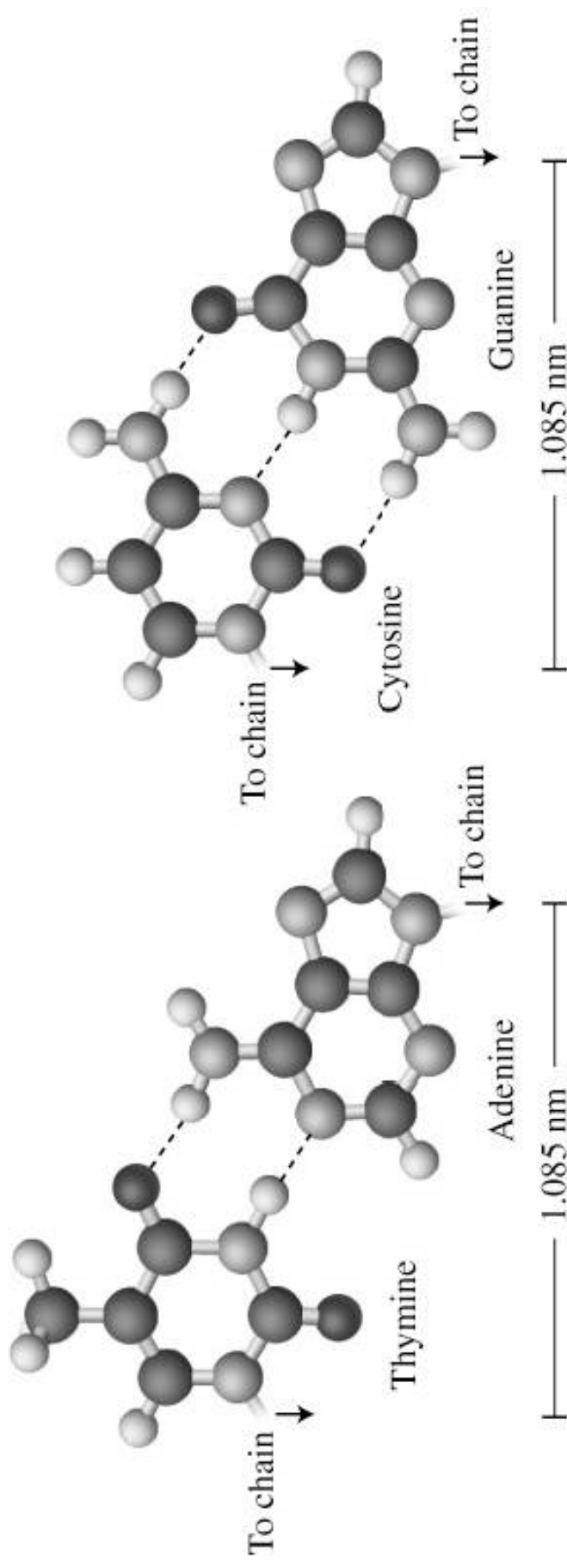
Heterocyclic Bases Found in Nucleic Acids



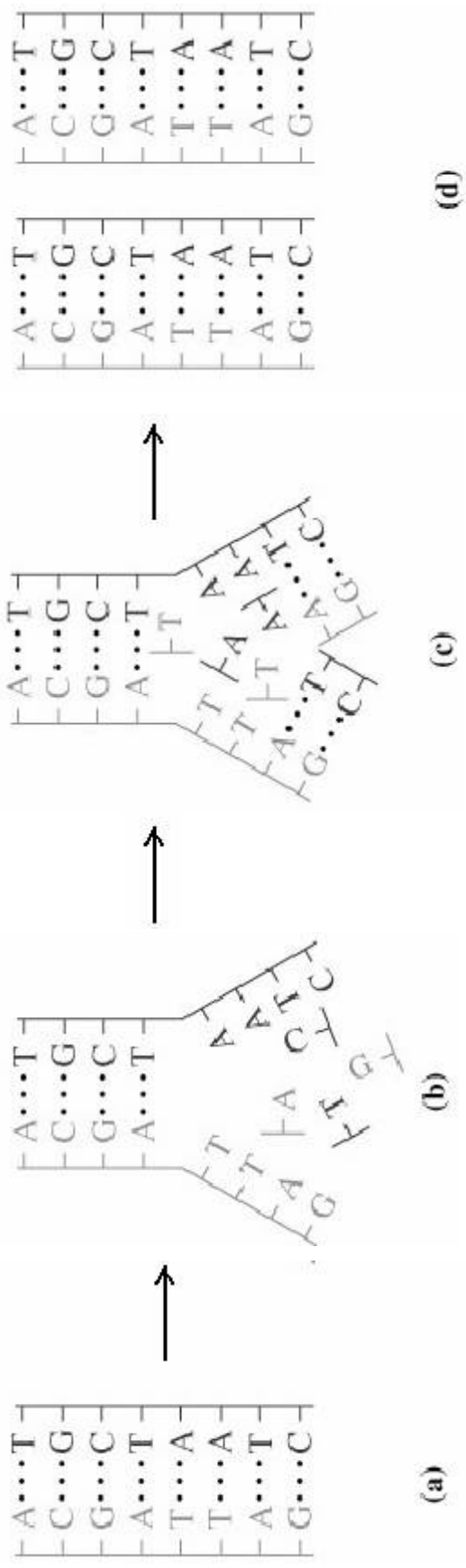
Purine bases

Pyrimidine bases

The Pairing of Bases in the DNA Double Helix



DNA Replication

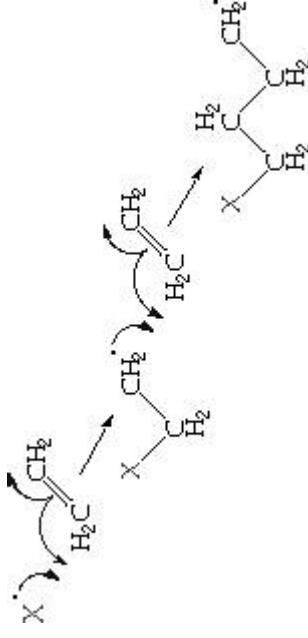


Polymers

- Addition Polymers
- Condensation Polymers
- Rubbers & Co-polymers

Addition Polymerization

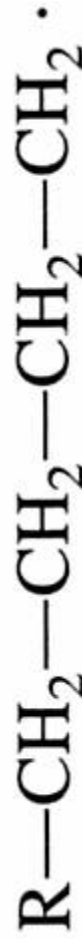
- The key feature of **addition polymerization** is that monomers add to one another in such a way that the polymeric product contains all the atoms of the starting monomers.
- The steps for addition polymerization include:
 - *Initiation* - often through the use of free-radicals.
 - *Propagation* - radicals join to form larger radicals.
 - *Termination* - occurs when a molecule is formed that no longer has an unpaired electron.



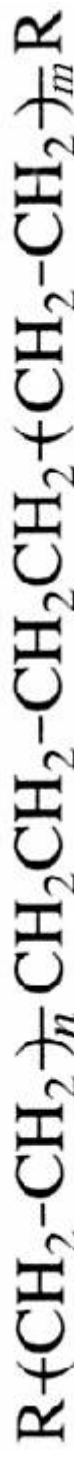
Initiation



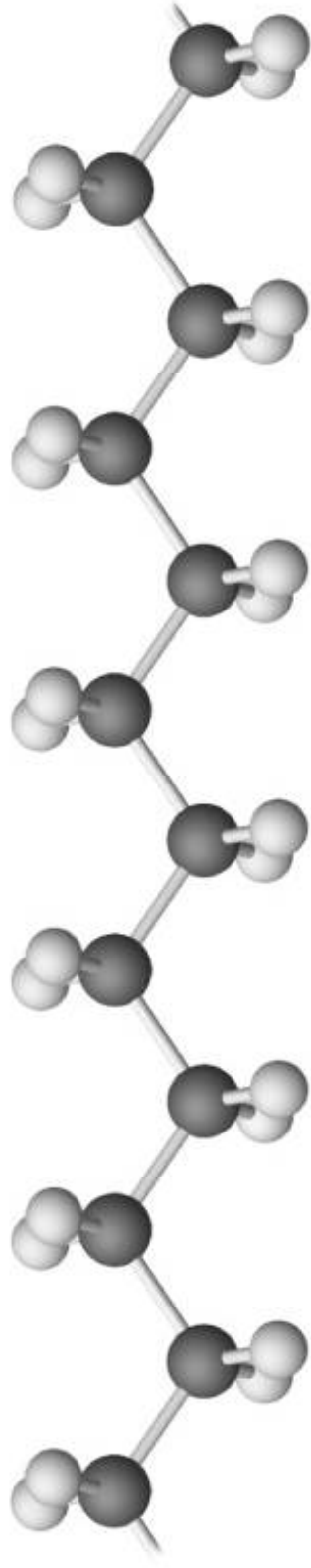
Propagation



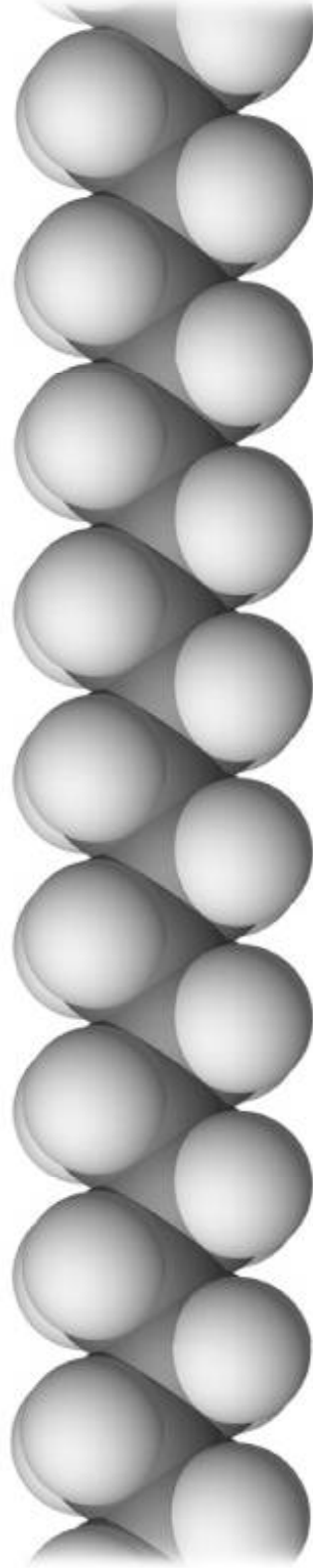
Termination



Molecular Models of a Segment of a Polyethylene Molecule











Ball-and-stick model











Space-filling model

Ethylene polymer derivatives

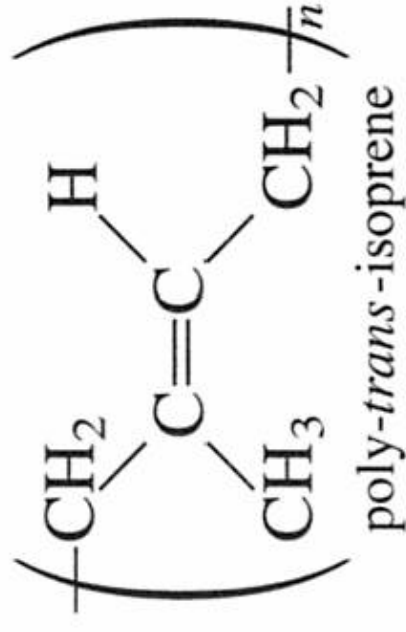
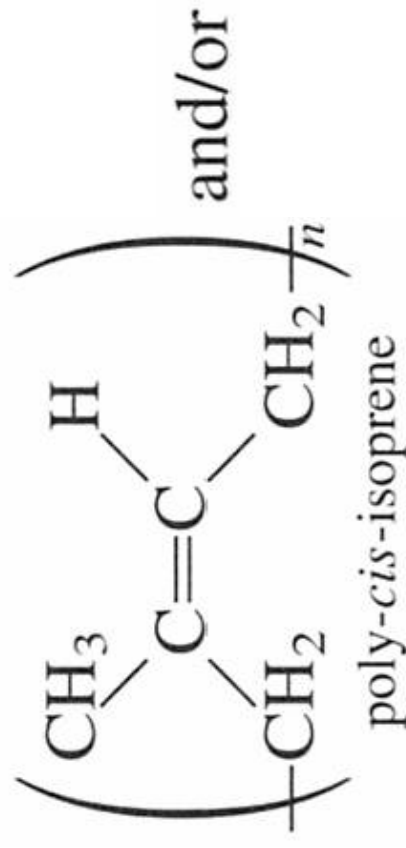
Formula	Monomer name	Polymer name	Uses
$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	Ethylene 	Polyethylene 	Bottles, bags, films, toys
$\begin{array}{c} \text{H} & & \text{CH}_3 \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	Propylene 	Polypropylene 	Bottles, films, carpets
$\begin{array}{c} \text{H} & & \text{Cl} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	Vinyl chloride 	Polyvinyl chloride 	Floortiles, coats, pipe
$\begin{array}{c} \text{H} & & \text{CN} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	Acrylonitrile 	Polyacrylonitrile 	Carpets, fabric

Ethylene polymer derivatives

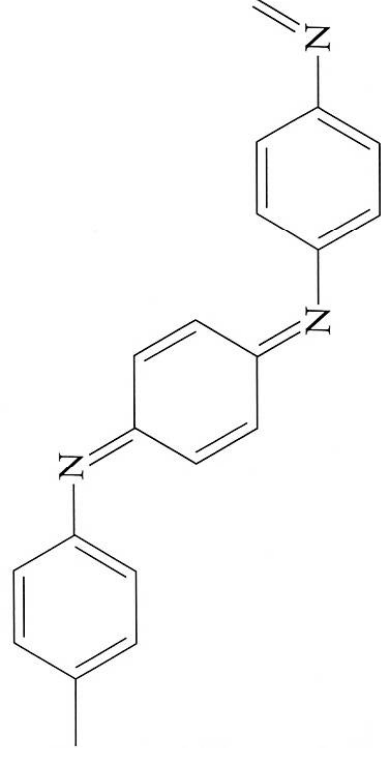
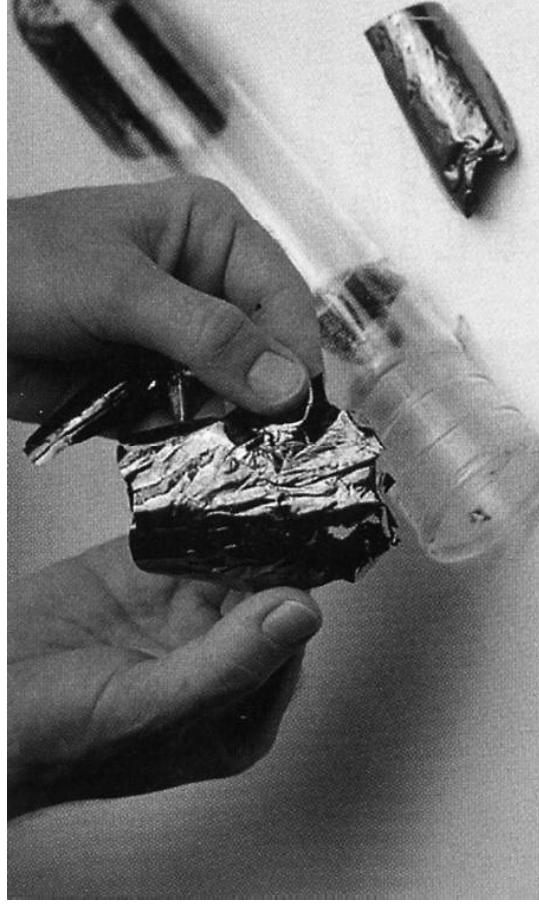
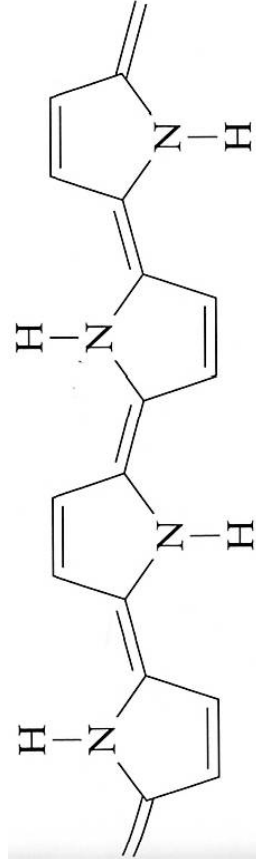
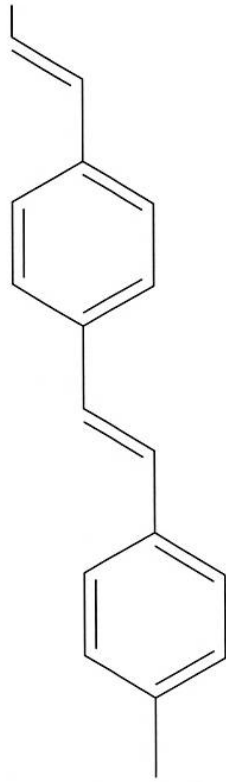
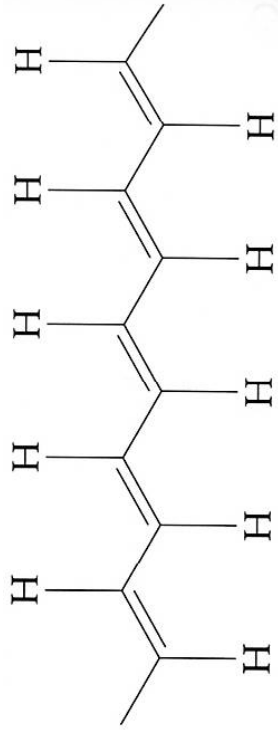
Formula	Monomer name	Polymer name	Uses
$ \begin{array}{c} \text{H} \\ \\ \text{C} \\ \\ \text{H} \end{array} = \begin{array}{c} \text{H} \\ \\ \text{C} \\ \\ \text{H} \end{array} - \begin{array}{c} \text{C}_6\text{H}_5 \end{array} $	Styrene 	Polystyrene 	Food containers, building insulation
$ \begin{array}{c} \text{H} \\ \\ \text{C} \\ \\ \text{H} \end{array} = \begin{array}{c} \text{H} \\ \\ \text{C} \\ \\ \text{O} - \text{C} - \text{CH}_3 \\ \\ \text{O} \end{array} $	Vinylacetate 	Polyvinylacetate 	Latex paints, adhesives
$ \begin{array}{c} \text{H} \\ \\ \text{C} \\ \\ \text{H} \end{array} = \begin{array}{c} \text{CH}_3 \\ \\ \text{C} \\ \\ \text{H} \end{array} - \begin{array}{c} \text{C} \\ \\ \text{O} - \text{C} - \text{CH}_3 \\ \\ \text{O} \end{array} $	Methyl methacrylate 	Polymethyl methacrylate 	High quality transparent objects, contact lenses
$ \begin{array}{c} \text{F} \\ \\ \text{C} \\ \\ \text{F} \end{array} = \begin{array}{c} \text{F} \\ \\ \text{C} \\ \\ \text{F} \end{array} $	Tetrafluoroethylene 	Polytetrafluoroethylene 	Engine gaskets, bearings, non-stick pan coatings



isoprene

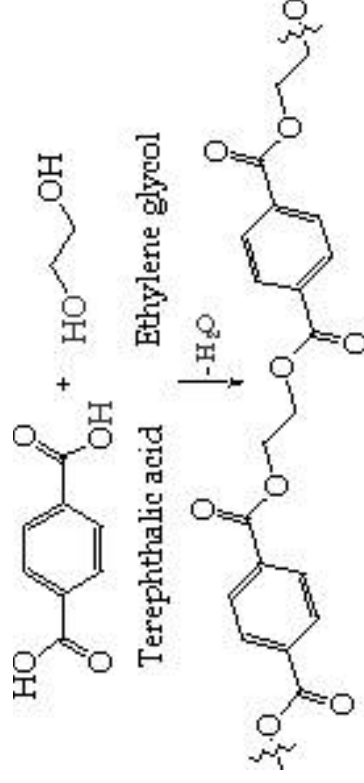


Conducting Polymers



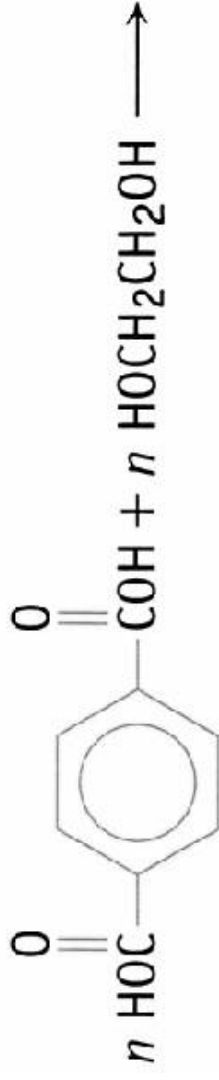
Condensation Polymerization

- In **condensation polymerization**, a small portion of the monomer molecule is not incorporated in the final polymer.
- The monomers are held together by a certain kind of bond (such as an amide bond) and a molecule is eliminated in the process (such as a water molecule).
- This is the type of process used to make nylons and silicones.



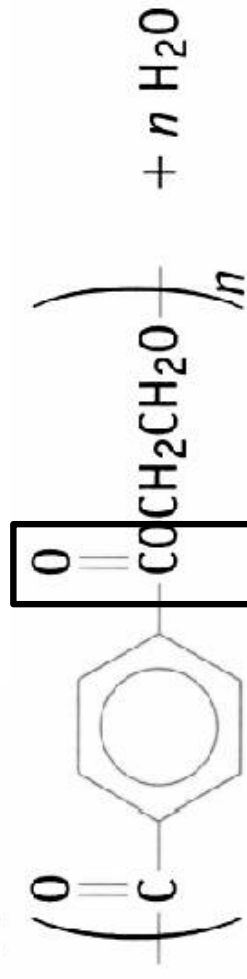
Terylene - Polyester

Polyester



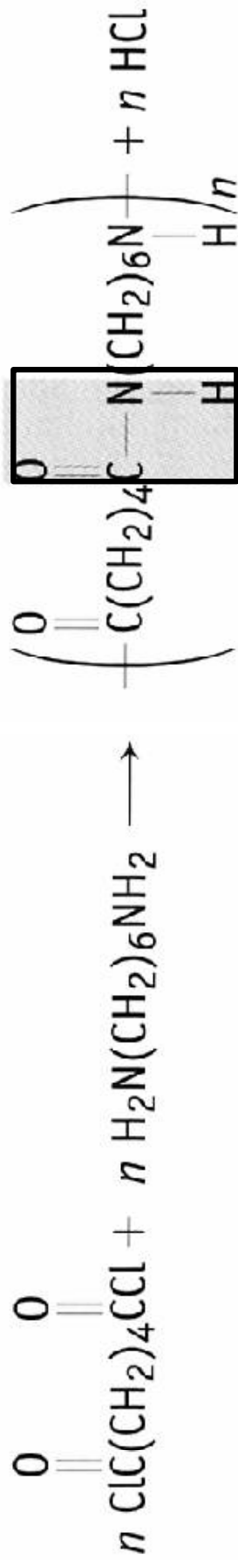
terephthalic acid

ethylene glycol



polyethylene terephthalate (PET), a polyester Dacron

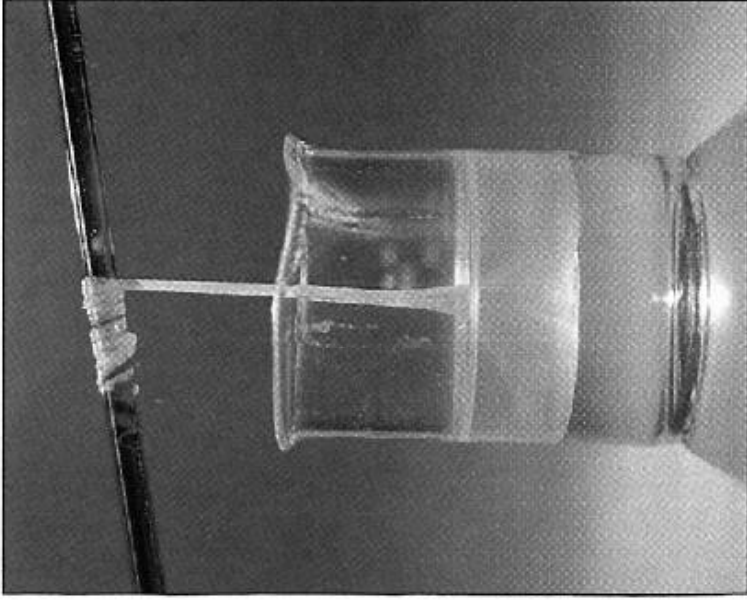
Polyamide



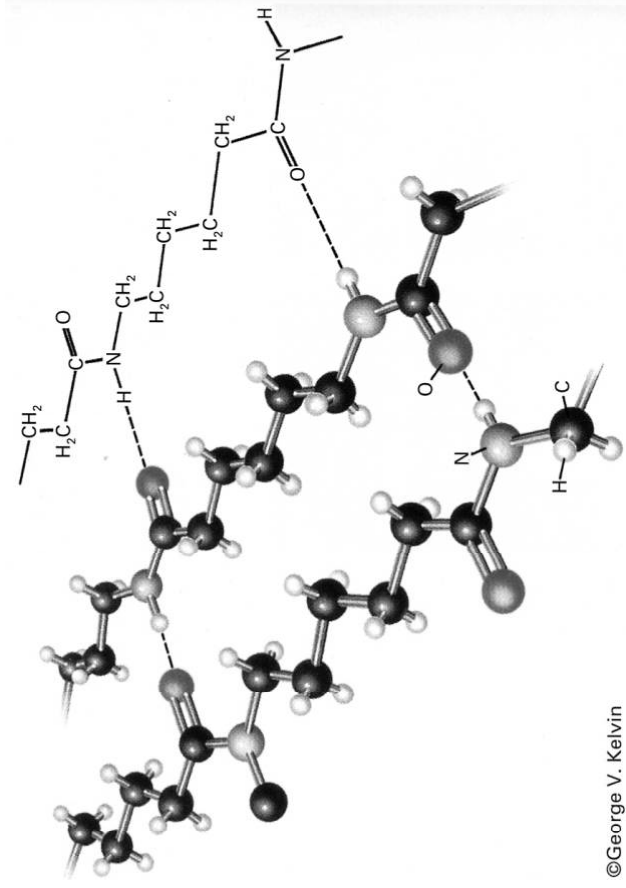
adipoyl chloride

hexamethylenediamine

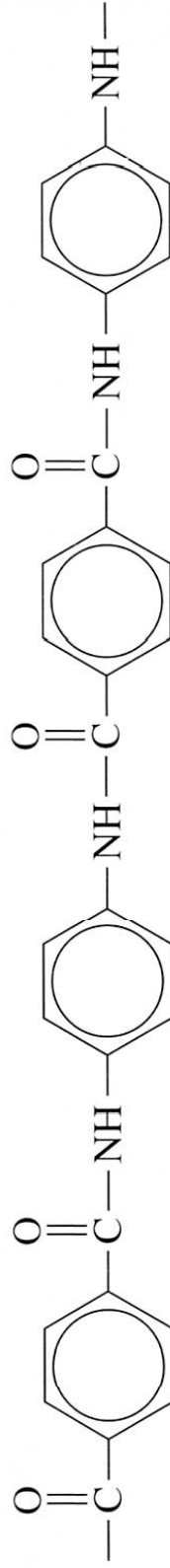
amide link in nylon-66, a polyamide



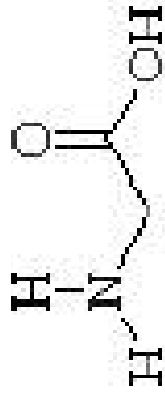
Nylon-6,6.



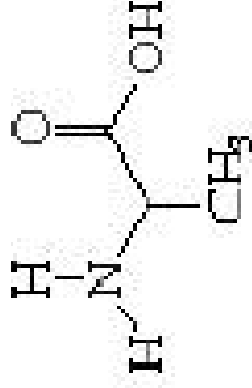
Kevlar



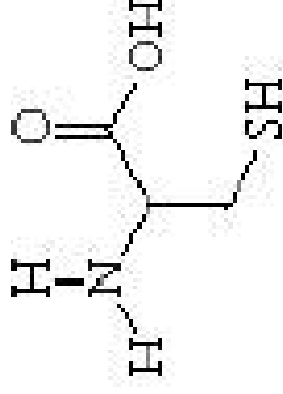
- Silk is a polymer of the amino acids *glycine* and *alanine*
- Wool is having **disulphide** (sulphur-sulphur) bonds to link the polymer chains together. The sulphur is present due to the amino acid *cysteine*



Glycine 



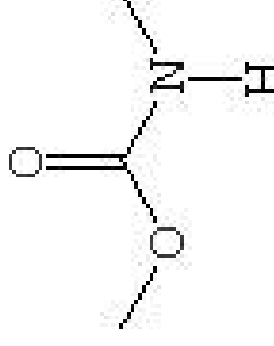
Alanine 



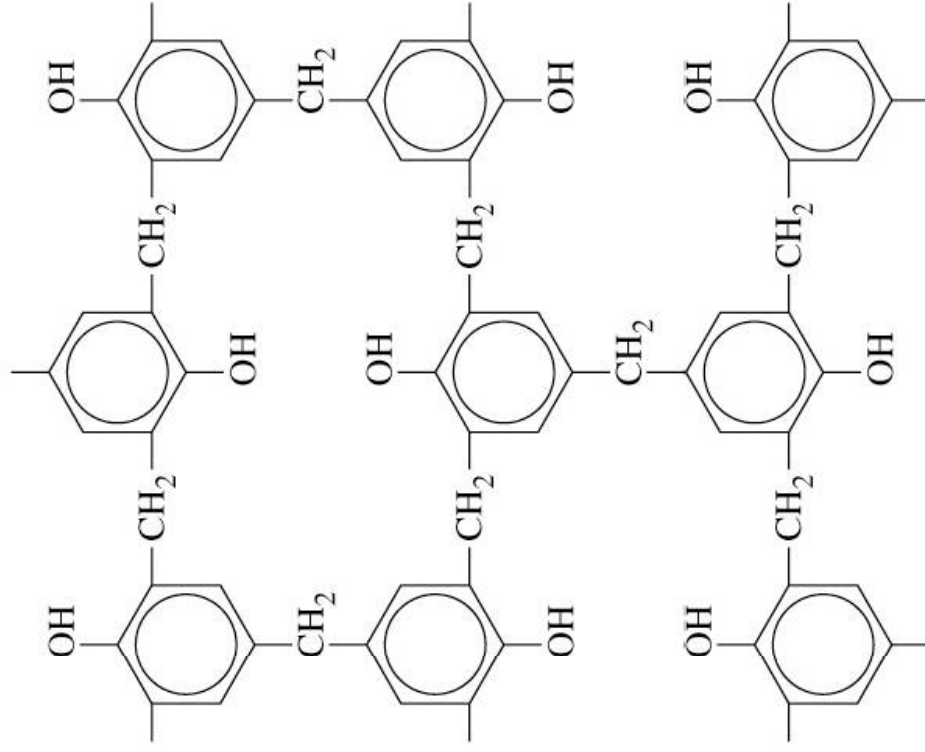
Cysteine 

Polyurethanes

These polymers have a similar structure to the polyamides, which have the urethane (carbamate) group as part of the polymer backbone.



Cross-linking Polymer



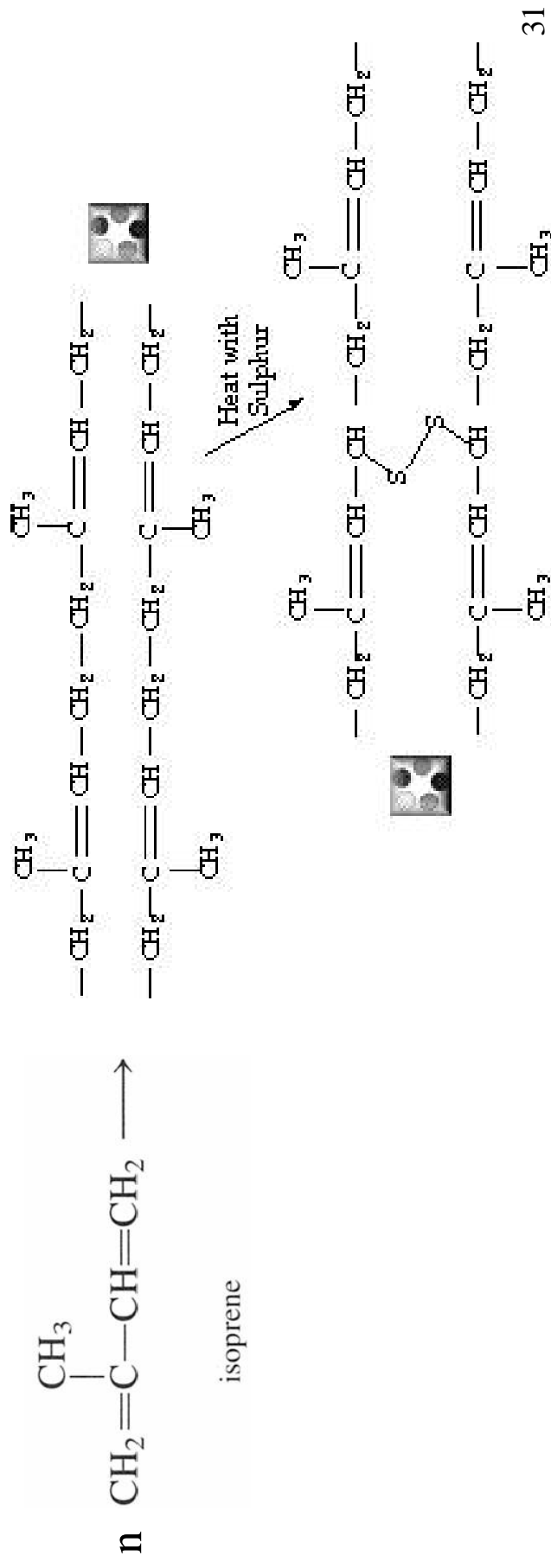
Bakelite®

Elastomers

- **Elastomers** are flexible, elastic materials.
- Natural rubber is soft and tacky when hot. It can be made harder in a reaction with sulfur, called *vulcanization*.
- Several kinds of synthetic rubber were developed during and after World War II. *Neoprene* (polychloroprene) is one example of this.
- *Copolymerization* is a process in which a mixture of two different monomers form a product in which the chain contains both monomers as building blocks.

Rubber

Natural rubber was first introduced to Europe in the mid. 18th century - and is an example of an **elastomer** - an elastic polymer. A problem was that natural rubber is a very weak, soft thermoplastic when heated - but very brittle when cold. A process, **vulcanisation**, was invented by Goodyear, where rubber heated with sulphur produces a harder, less tacky elastic material.



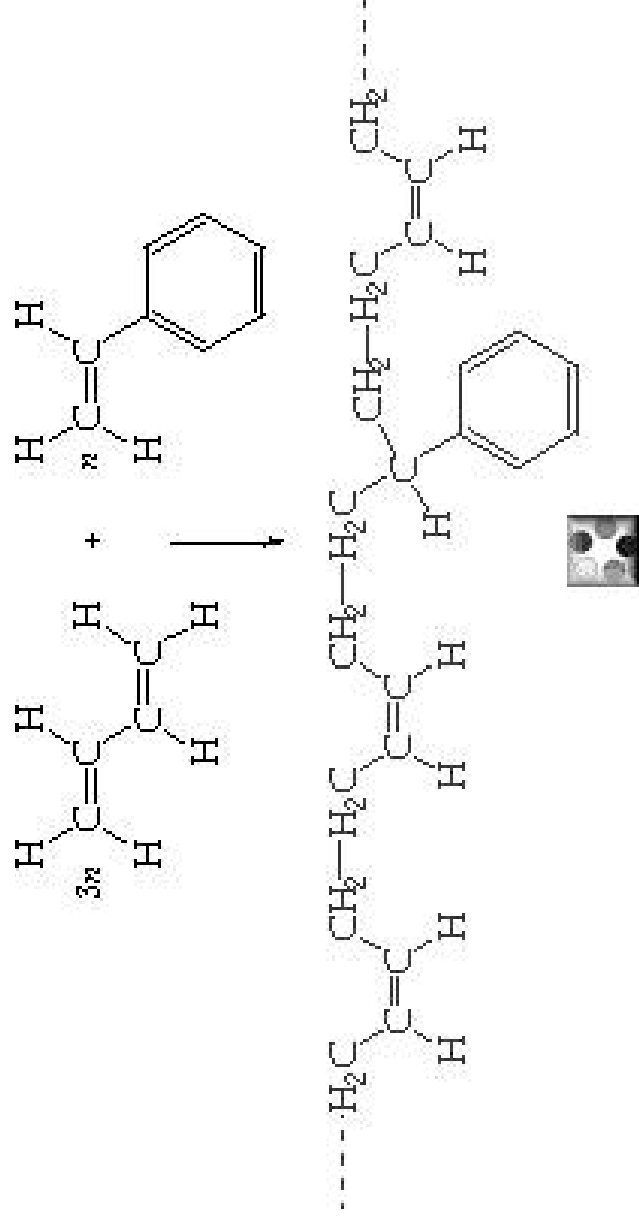
Extent of Cross-linking in Rubber Products

TABLE 24.3 Extent of Cross-linking in Rubber Products

Product	Monomer Units Between Cross-links
Surgical gloves	100–150
Kitchen gloves	50–80
Artificial heart membrane	30–40
Bicycle inner tube	20–30
Bicycle tire	10–20

Copolymers

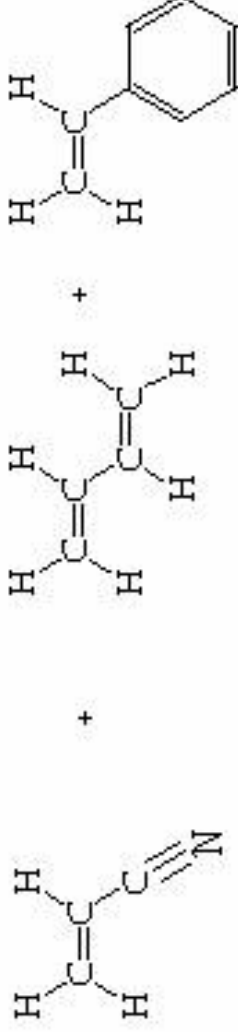
Some of the most commercially important addition polymers are the **copolymers**. There are polymers made by polymerizing a mixture of two or more monomers. An example is styrene-butadiene rubber (**SBR**) - which is a copolymer of butadiene and styrene. Most is vulcanized and used in tire production - though some is used for bubble-gum (unvulcanised form).



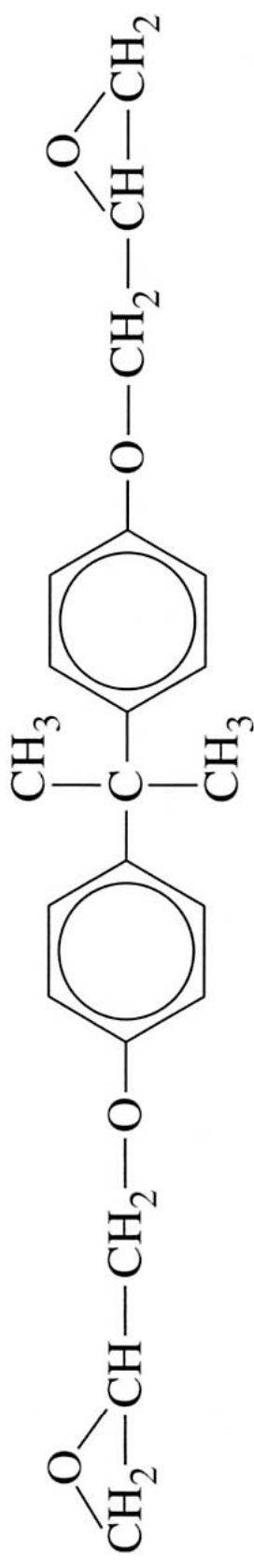
Styrene-butadiene rubber (SBR)

ABS - Poly(Acrylonitrile, Butadiene, Styrene)

- ABS is a copolymer of Acrylonitrile, Btadiene, and Stylene.
- ABS plastics generally possess medium strength and performance and medium cost.
- ABS is often used as the cost and performance dividing line between standard plastics (PVC, polyethylene, polystyrene, etc.) and engineering plastics (acrylic, nylon, acetal, etc.).
- ABS polymers can be given a range of properties, depending on the ratio of the monomeric constituents and the molecular level connectivity. Typically, a styrene-acrylonitrile glassy phase is toughened by an amorphous butadiene/butadiene-acrylonitrile rubber phase.



Epoxy Resin



A Composite Material (Fiber Glass with Epoxy Resin)



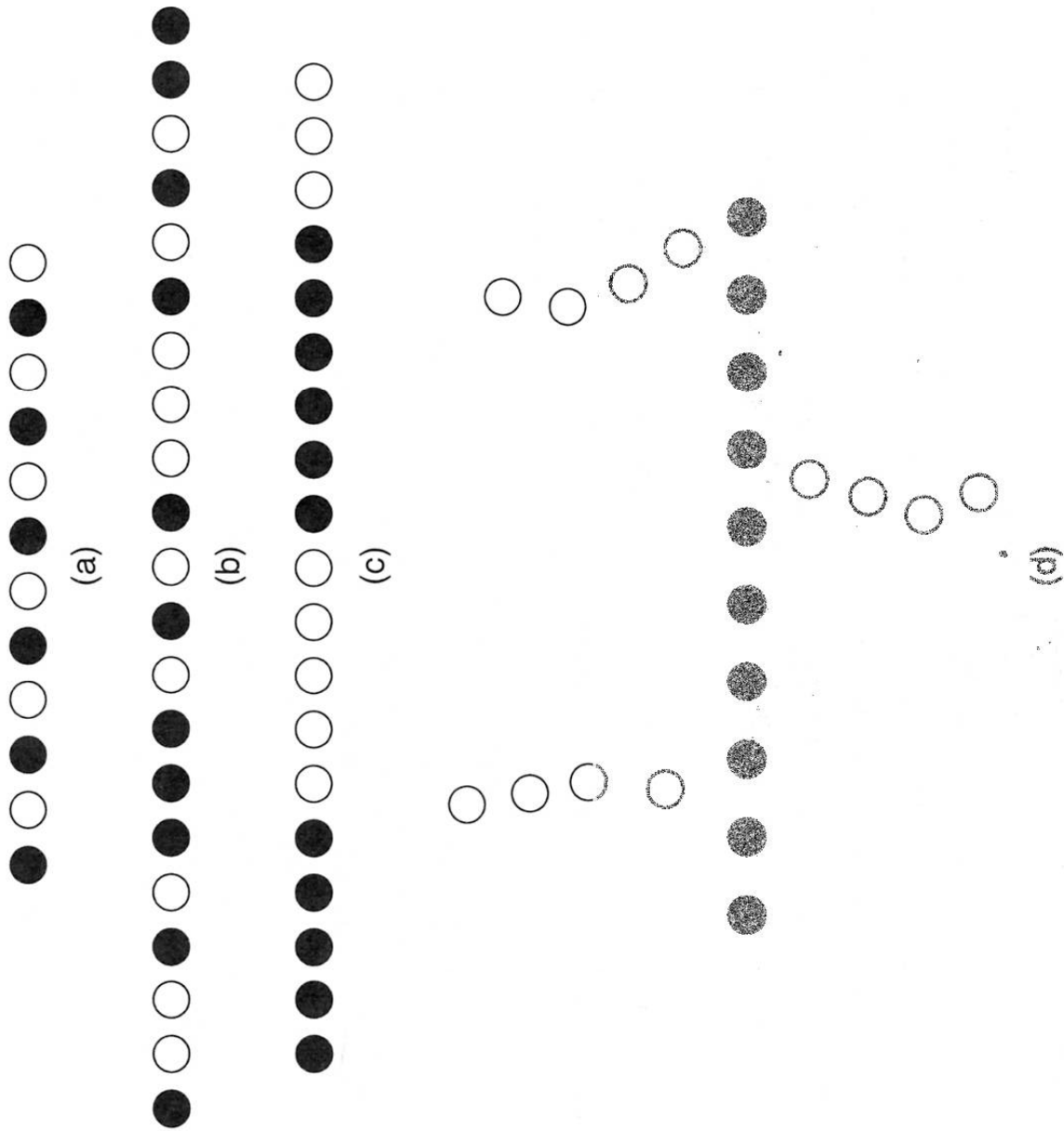
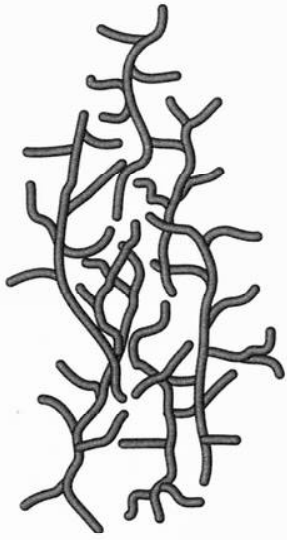


Figure 1.58 Summary of copolymer classifications: (a) alternating, (b) random, (c) block, and (d) graft.

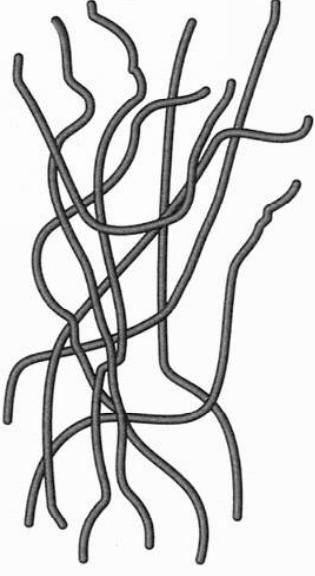
Physical Properties Of Polymers

- A **thermoplastic polymer** is one that can be softened by heating and then formed into desired shapes by applying pressure.
- **Thermosetting polymers** become permanently hard at elevated temperatures and pressures.
- *High-density polyethylene (HDPE)* consists primarily of linear molecules and has a higher density, greater rigidity, greater strength, and a higher melting point.
- *Low-density polyethylene (LDPE)* has branched chains and is a waxy, semi-rigid, translucent material with a low melting point.

Organization of Polymer Molecules



LDPE



HDPE



(a)



(b)

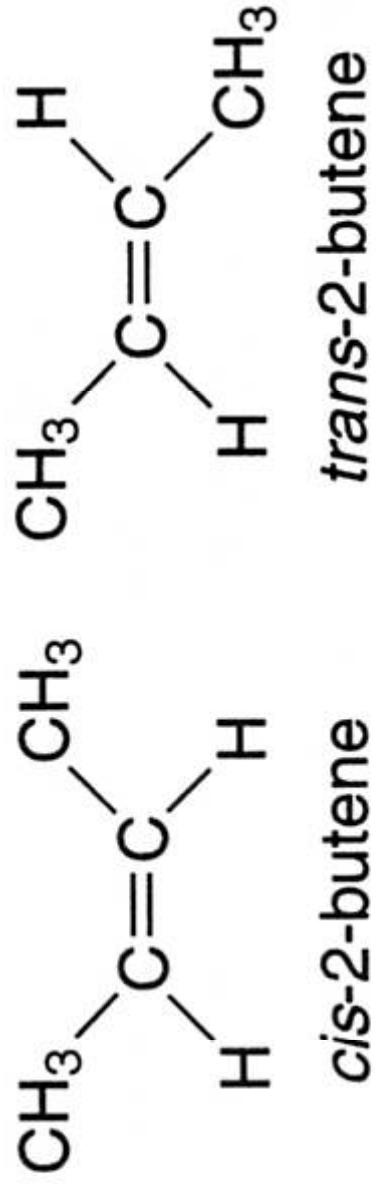


Figure 1.54 An example of polymer stereoisomers.

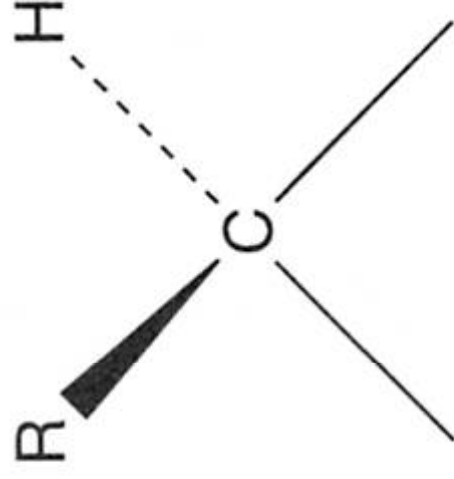


Figure 1.56 An example of an asymmetric carbon atom

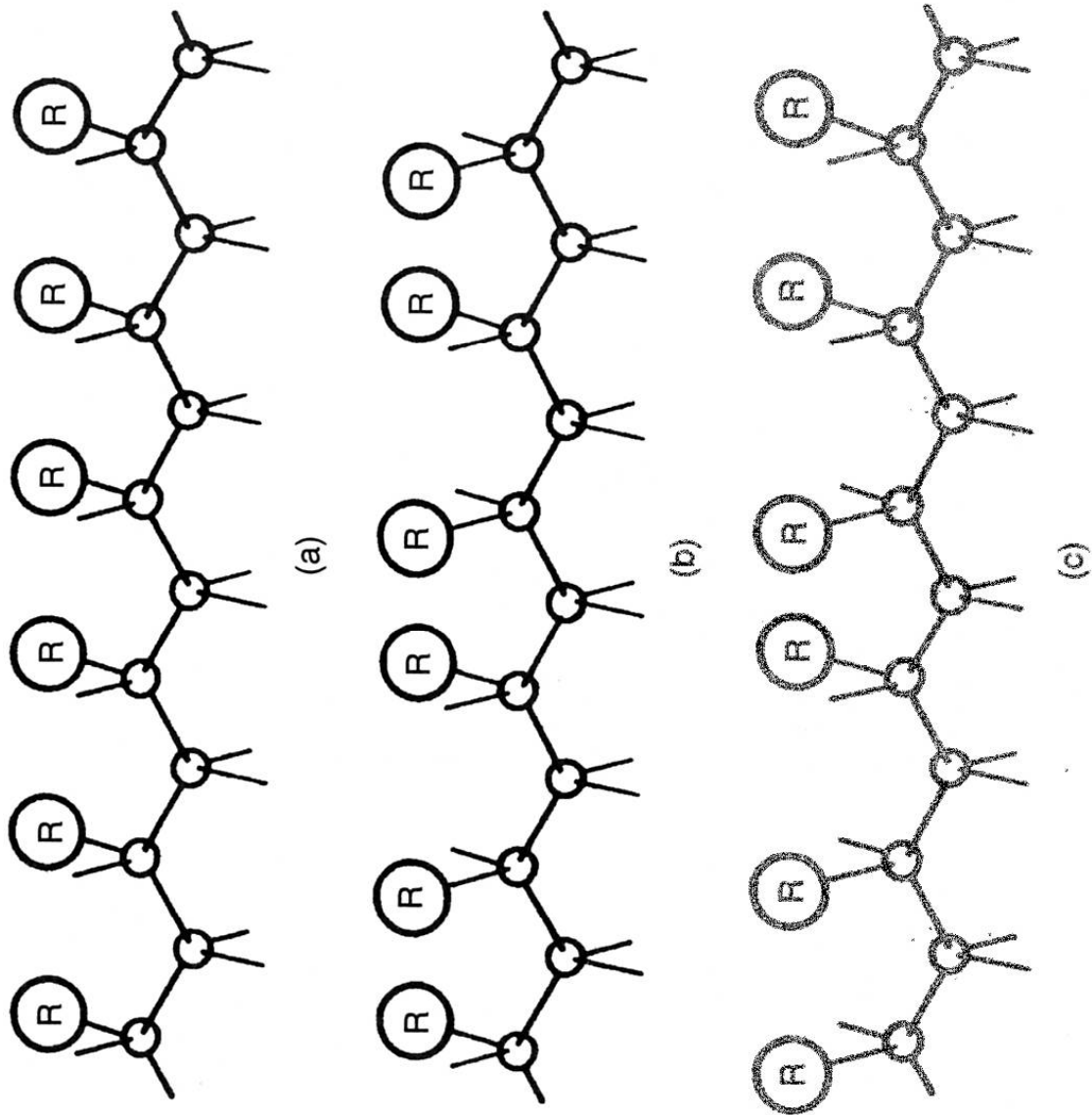


Figure 1.57 Summary of different types of tacticity, where R represents an atom other than hydrogen: (a) isotactic; (b) syndiotactic; and (c) atactic. Reprinted, by permission, from P. Hiemenz, *Polymer Chemistry: The Basic Concepts*, p. 27. Copyright © 1984 by Marcel Dekker, Inc.

Gel Permeation Chromatography (GPC)

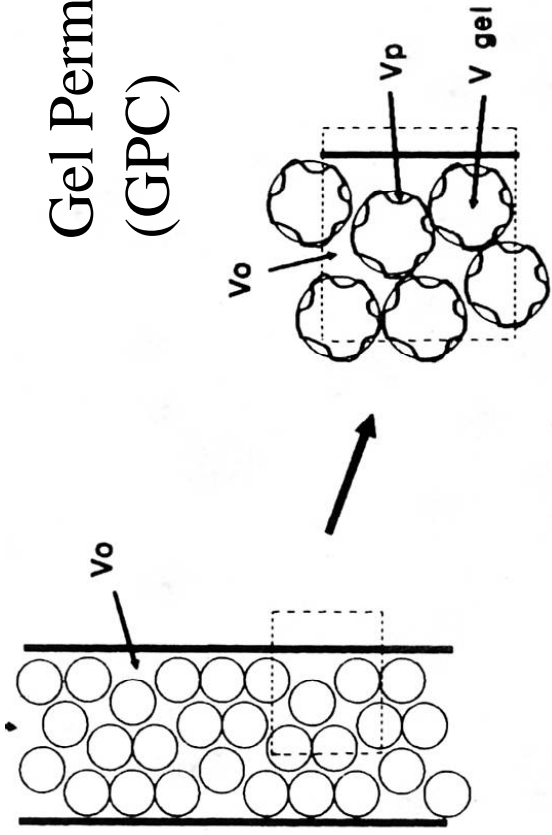
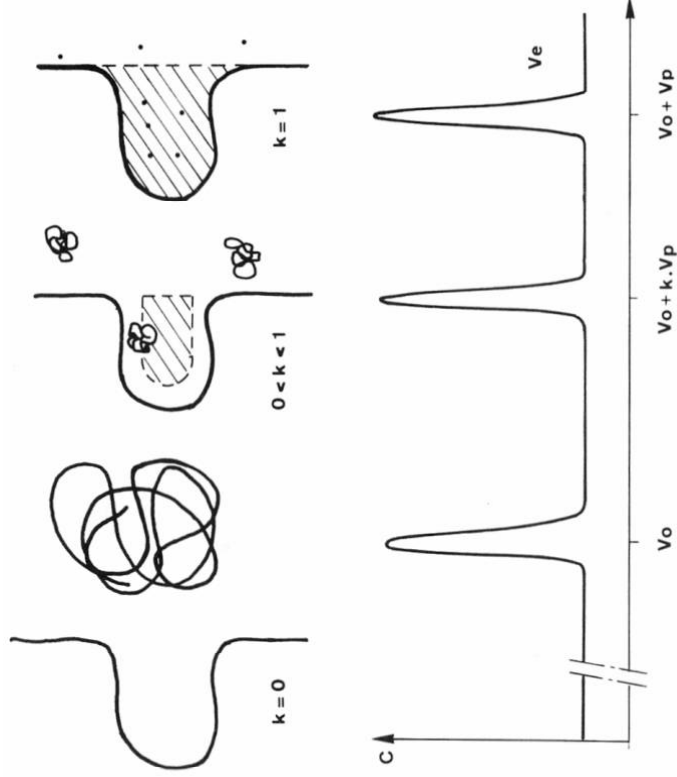


Fig. 1. Representation of the GPC column; V_0 is the dead volume, V_p is the porous volume and V_{gel} is the gel volume



$k =$ partition coefficient

Fig. 7. Representation of the size exclusion of a macromolecule in a GPC column. $k = 0$: excluded macromolecule; $0 < k < 1$: selective permeation 42

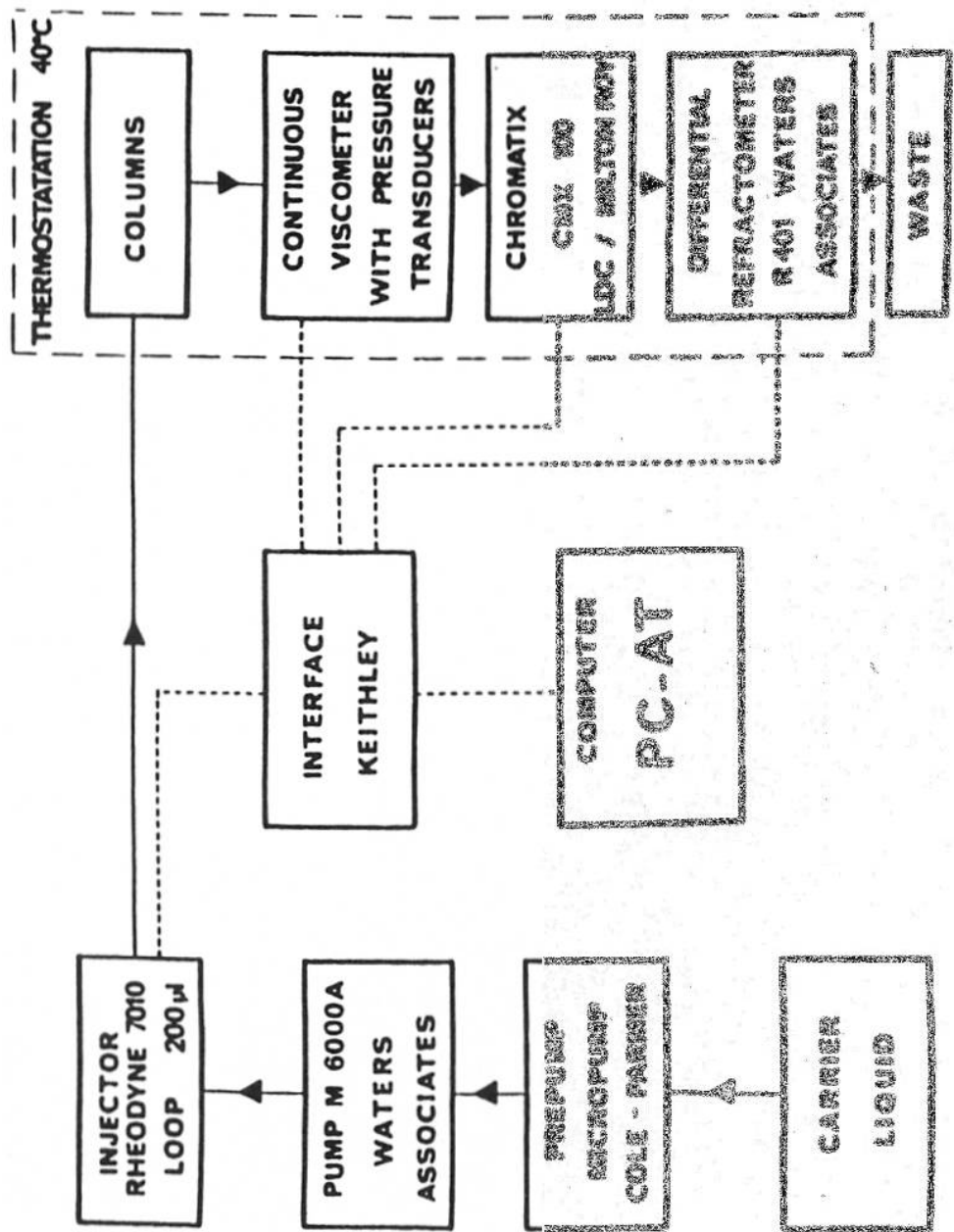


Fig. 12. Schematic diagram of a GPC instrument with triple detection (light scattering, viscometer, refractometer)

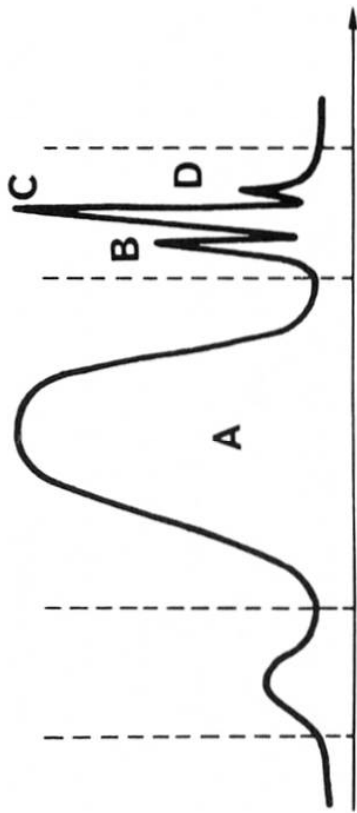


Fig. 14. Evidence of additives in plastics by GPC. (A): polymer peak; (B): plasticizer; (C): stabilizer; (D): dye

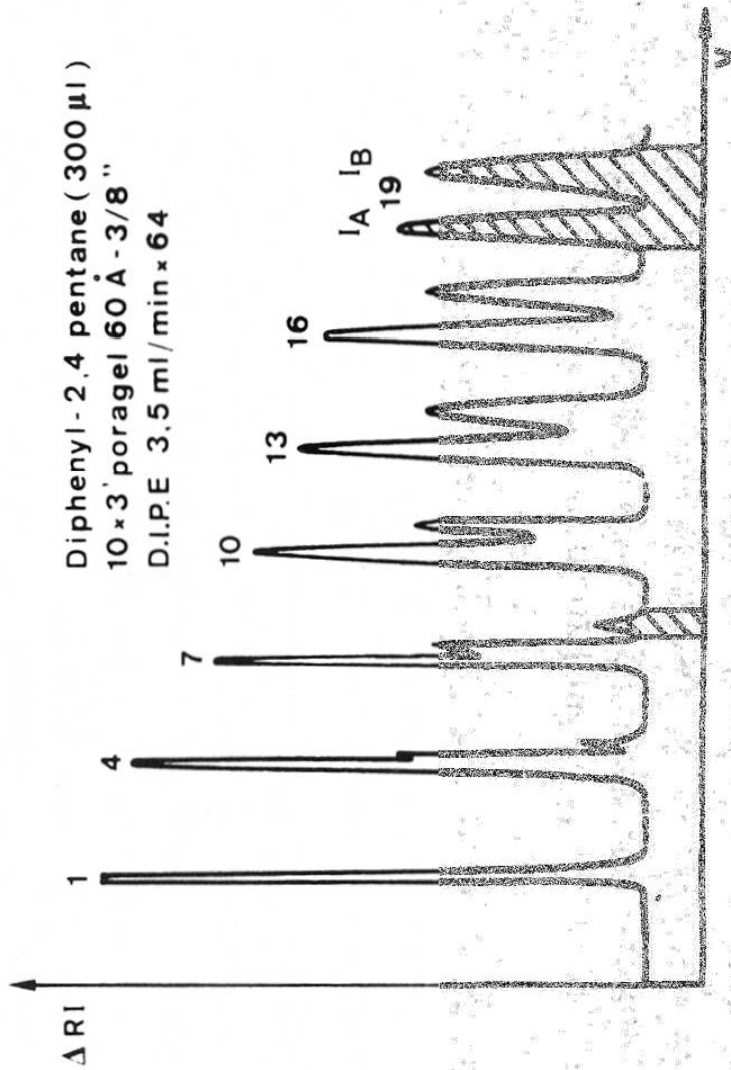


Fig. 15. Separation of diphenyl-2,4-pentane stereoisomers by recycle-GPC in di-isopropyl ether (DIPB), [78]. 19 cycles were necessary to separate the two isomers I_A and I_B

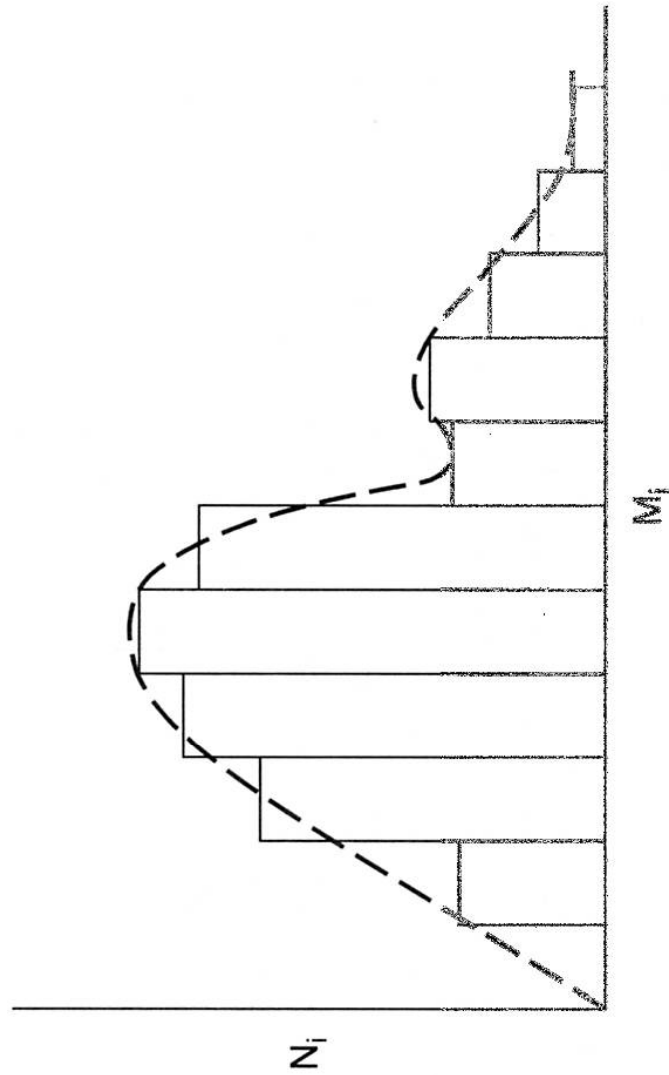


Figure 1.59 Histogram showing the number of molecules, N_i , having the molecular weight M_i . Reprinted, by permission, from P. Heimez, *Polymer Chemistry: The Basic Concepts*, p. 35. Copyright © 1984 by Marcel Dekker, Inc.

Table 1.23 Summary of the Most Common Molecular Weight Averages

Average	Definition	Methods of Determination
\bar{M}_n number ave.	$\frac{\sum N_i M_i}{\sum N_i}$	Osmotic pressure, colligative properties, end group analysis
\bar{M}_w weight ave.	$\frac{\sum N_i M_i^2}{\sum N_i M_i}$	Light scattering, sedimentation velocity
\bar{M}_z z-average	$\frac{\sum N_i M_i^3}{\sum N_i M_i^2}$	Sedimentation equilibrium
\bar{M}_v viscosity ave.	$\left(\frac{\sum N_i M_i^{1+a}}{\sum N_i M_i} \right)^{1/a}$	Intrinsic viscosity (<i>a</i> is characteristic of a system and lies between 0.5 and 1.0)

Polydispersity index $I_p = \bar{M}_w / \bar{M}_n$

For example,
Commercial PVC compound, Geon 87402
weight-average molecular weight (M_w) 73,800
number-average molecular weight (M_n) 37,800

$$\begin{aligned}\text{Polydispersity index } I_p &= M_w/M_n \\ &= 73,800/37,800 = 1.95\end{aligned}$$

TGA

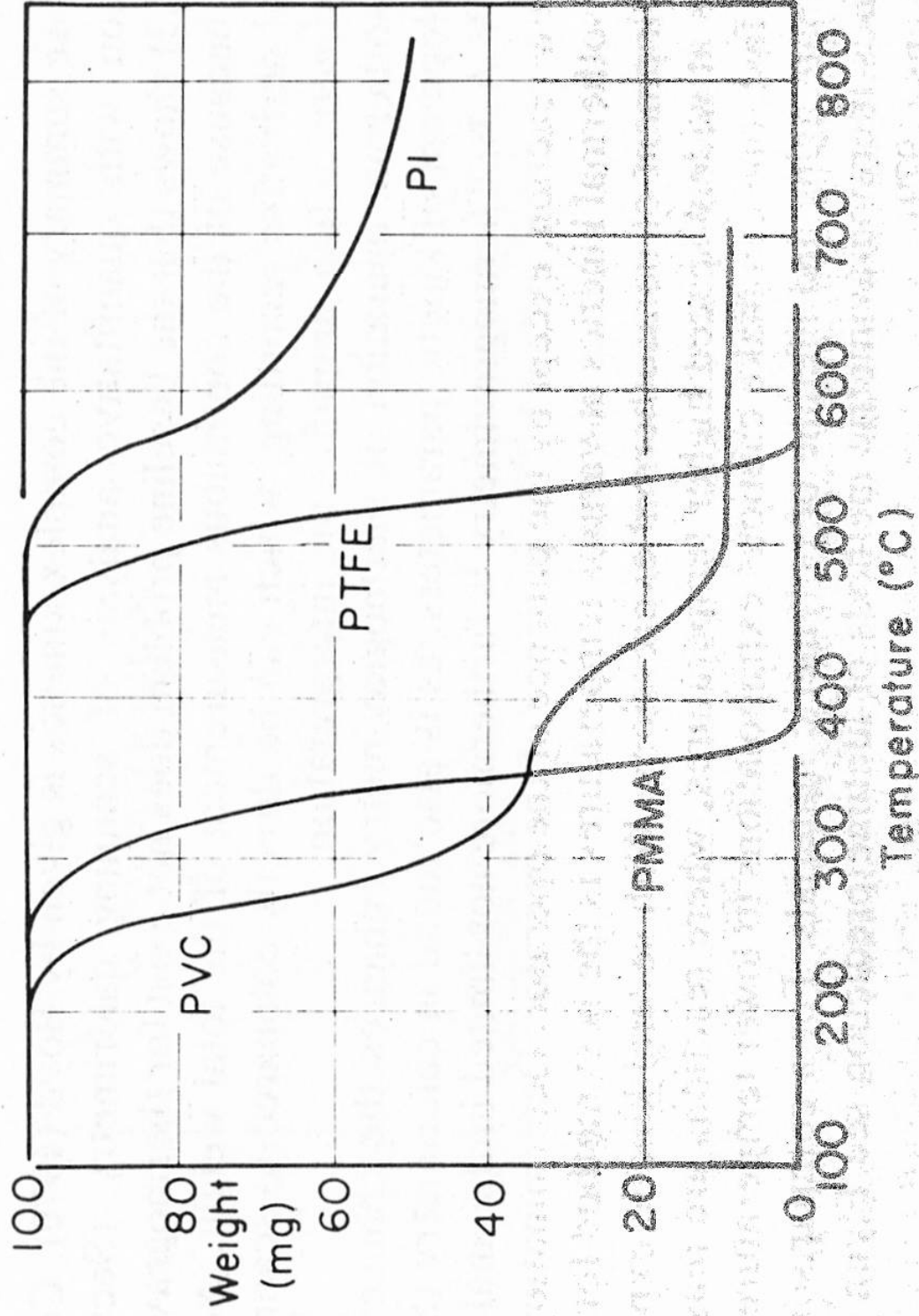


Fig. 56 Thermogravimetry curves of poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA), polytetrafluoroethylene (PTFE), and a polyimide (PI). Curves drawn after Chiu (1966). Experimental conditions, 10 mg sample heated at 5 K min⁻¹ in N₂ atmosphere.

DSC (differential scanning calorimetry) or DTA (differential thermal analysis)

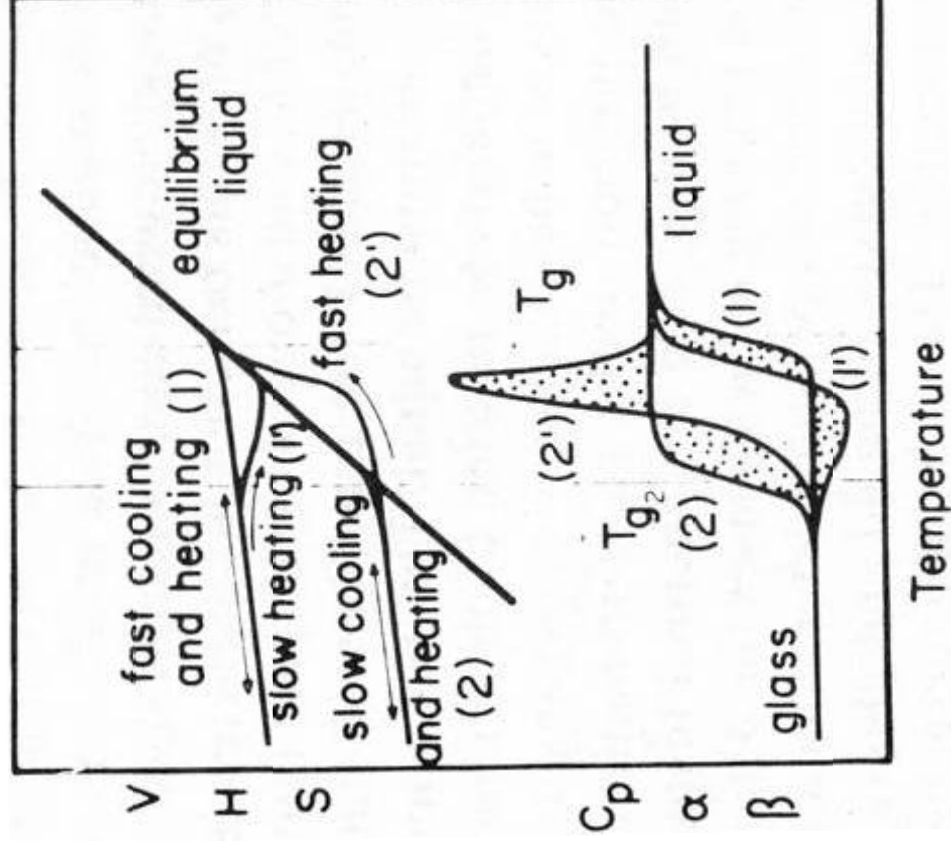


Fig. 30 Schematic drawing of changes in enthalpy, entropy, volume, and the derivative properties heat capacity, expansion coefficient, and compressibility on heating and cooling through the glass transition region. From Weitz and Wunderlich (1974). Reprinted with permission, courtesy J. Wiley and Wiley, Inc.

TABLE I

EFFECT OF CHAIN POLARITY AND HYDROGEN BONDING
ON T_g AND T_m IN POLYESTERS AND POLYAMIDES

Polymer	T_g ($^{\circ}\text{K}$)	T_m ($^{\circ}\text{K}$)
Nylon 6, 6	322	500
Nylon 6, 10	318	499
Nylon 12, 2	332	509
Nylon 10,, 2	329	515
Nylon 8, 2	366	552
Nylon 6, 2	432	599
Poly(ethylene adipate)	210	325
Poly(ethylene terephthalate)	342	529

Double glass transition

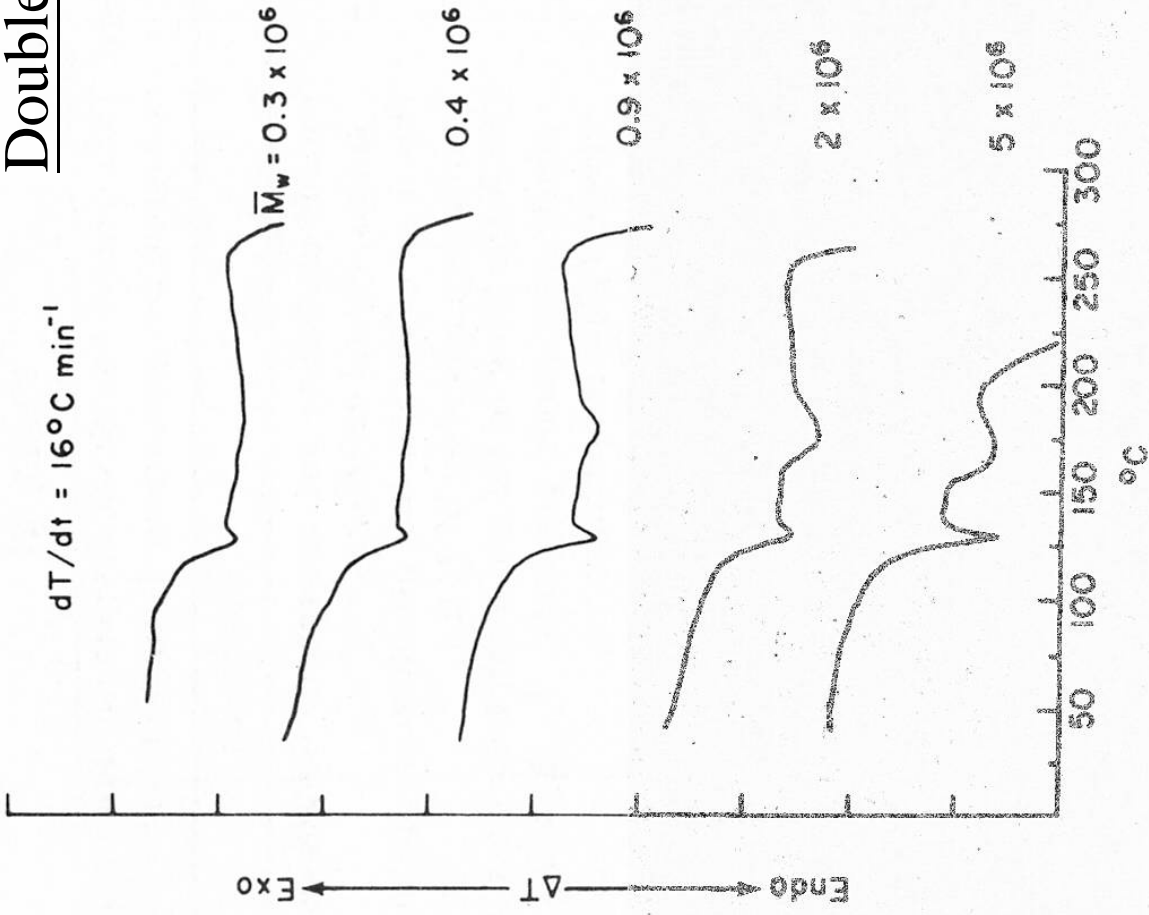


Fig. 9 DSC curves of PMMA samples with different molecular weight. (From Parke and Wunderlich, 1974.)

TABLE XI

CHARACTERISTIC TRANSITIONS FOR SEMICRYSTALLINE POLYMERS ARRANGED
IN ORDER OF ASCENDING TEMPERATURE"

Designation	Comments
$T < [T < T_g (L)]$	Various crystalline and amorphous transitions arising from side groups, crystal defects, etc
$T < T_g (L)$	This is an in-chain motion usually occurring at $0.75 T_g (L)$ and is probably a precursor of $T_g (L)$
$T_g (L)$	This is the lower of the two amorphous glass transitions. In completely amorphous polymers, $T_g (L) \equiv T_g$, where T_g is the classical glass temperature
$T_g (U)$	This is the upper of the two amorphous glass transitions. It should disappear as crystallinity approaches zero
T_c	This is a crystalline transition that appears to be a premelting phenomenon. It is seen with the least ambiguity in crystals grown from solution under equilibrium conditions. Its value depends on fold length. This definition of T_c , as used by Boyer (1973a), will be limited to this section of the chapter. In the rest of this chapter, T_c is generally used to symbolize crystallization temperature
T_m	Crystalline melting temperature

" From Boyer (1973c).

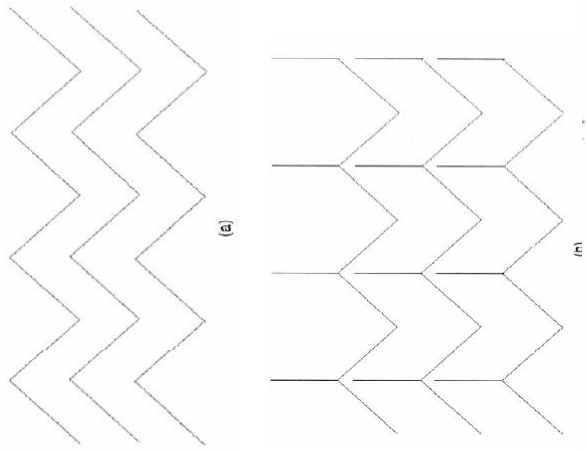


Figure 1.60 Schematic illustration of extended chain crystallinity in polymers (a) polyethylene and (b) polypropylene.

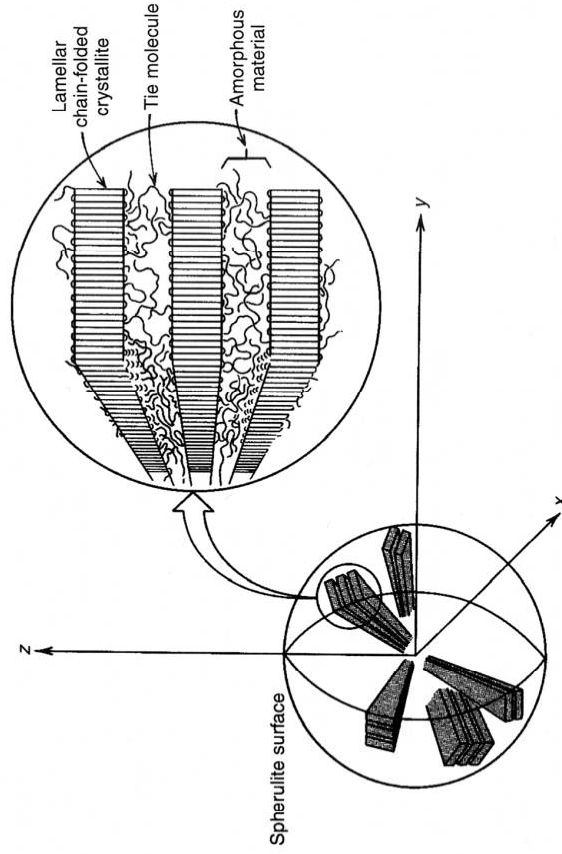


Figure 1.61 Schematic illustration of chain folding leading to lamellar crystallinities (*inset*) and

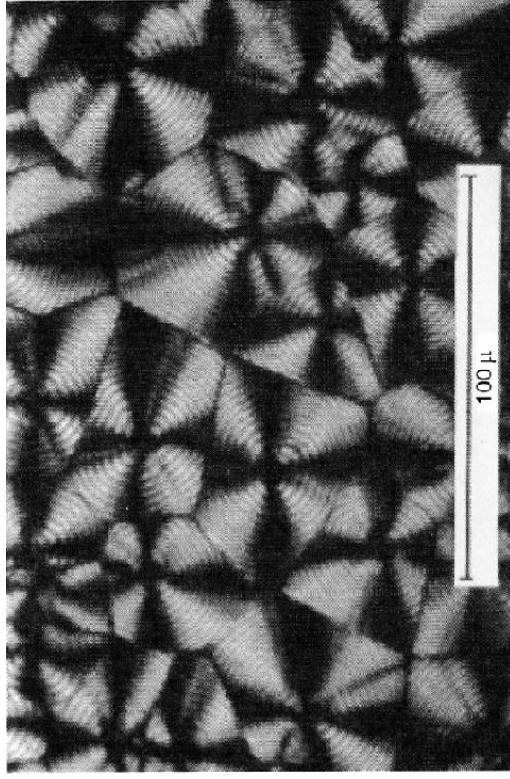


Figure 1.62 Cross-polarized micrograph of polyethylene show spherulitic structure.

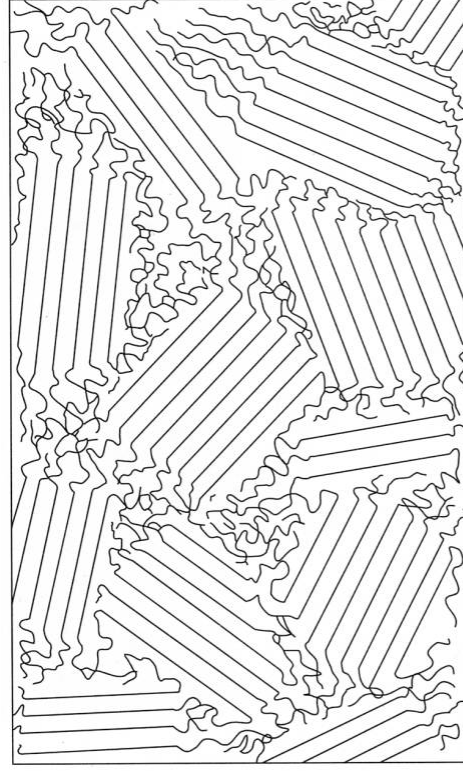


Figure 1.63 The fringed-micelle model of polymer crystallinity. From K. M. Ral T. H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*. Copyright © 1976 by John Wiley & Sons, Inc. This material is used by permission of John Wiley Sons, Inc.

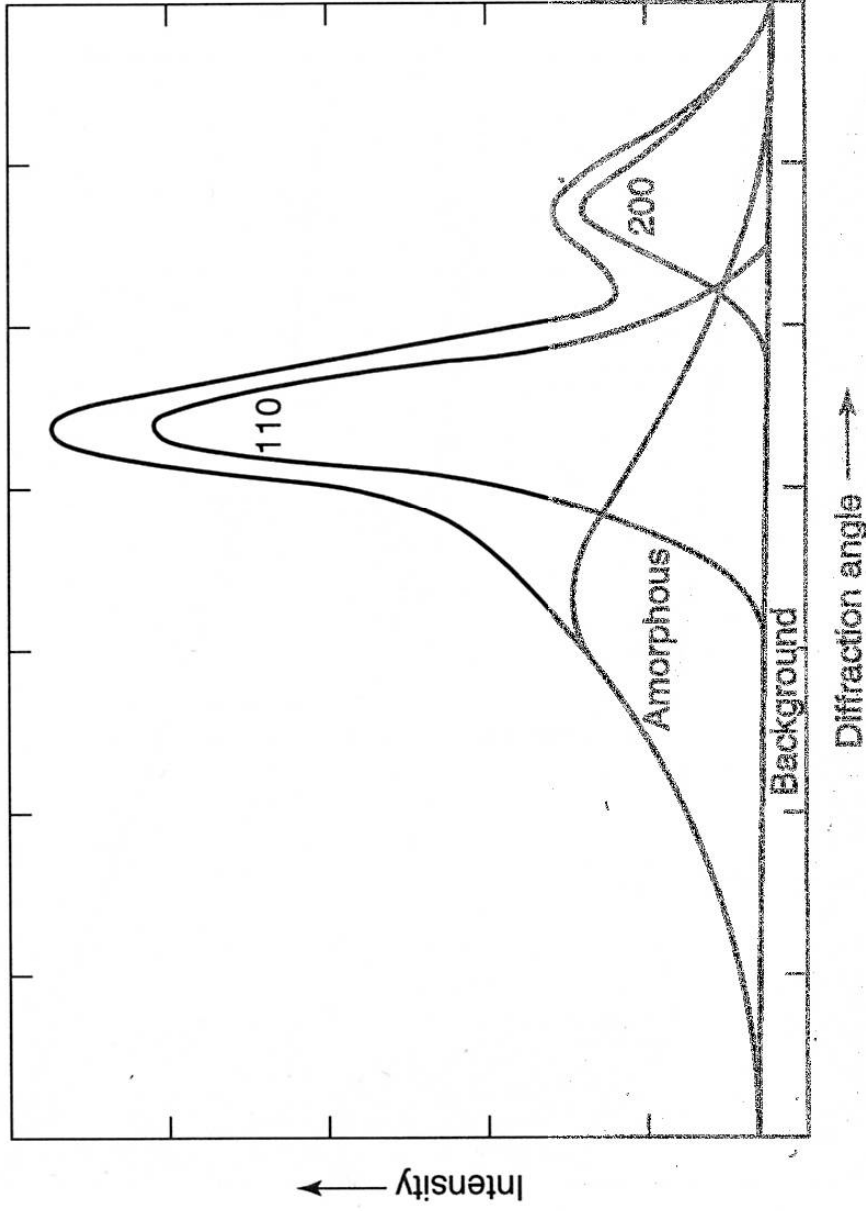


Figure 1.66 Resolution of the X-ray scattering curve of a semicrystalline polyethylene sample into contributions from crystalline (110 and 200 planes) and amorphous components. From F. W. Billmeyer, *Textbook of Polymer Science*, 3rd ed. Copyright © 1984 by John Wiley & Sons, Inc. This material is used by permission of John Wiley & Sons, Inc.

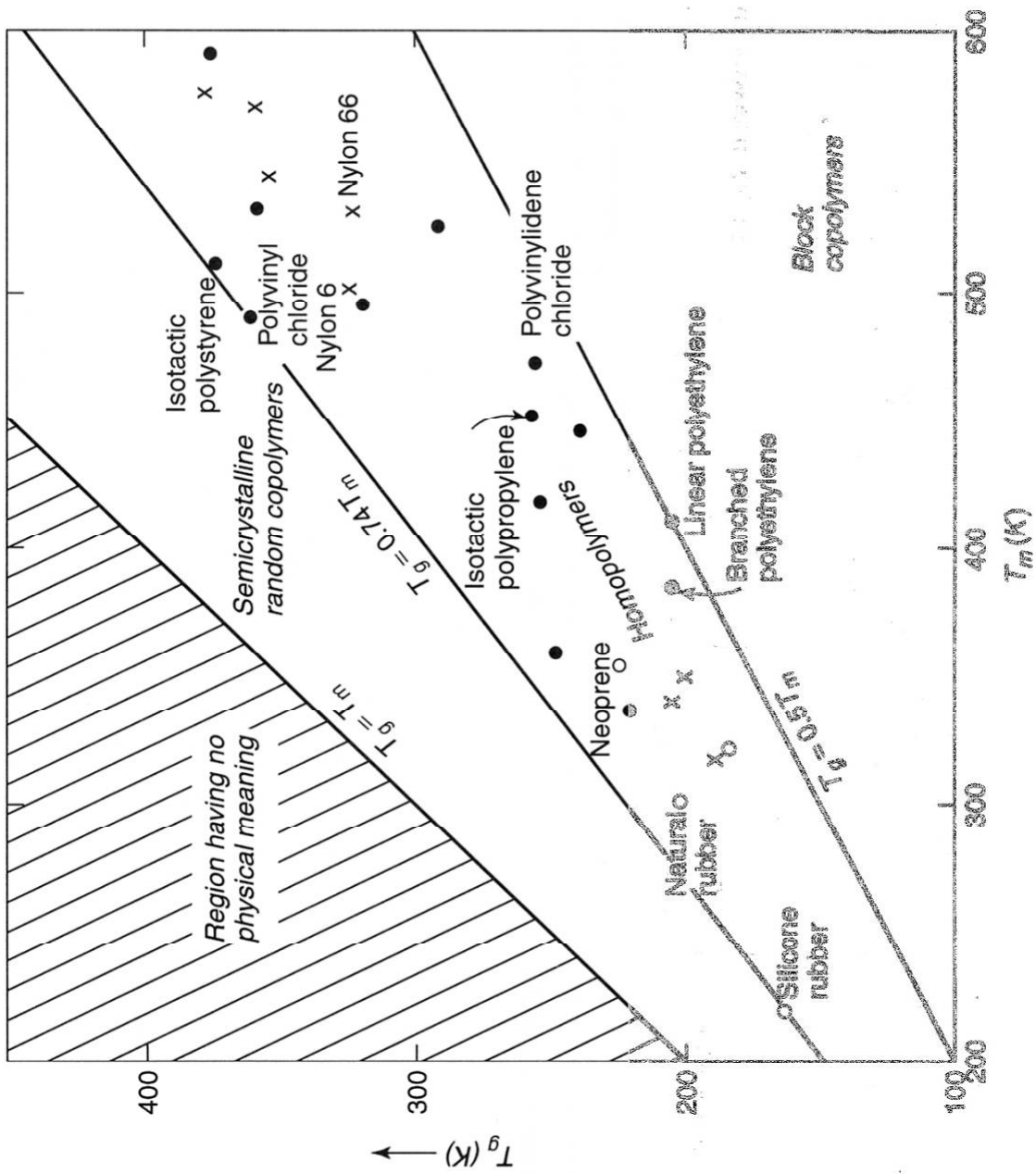


Figure 1.71 The glass transition temperature, T_g , as a function of crystalline melting point, T_m , for homopolymers. Filled circles are addition homopolymers, open circles are elastomers, and crosses are condensation homopolymers. From K. M. Ralls, T. H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*. Copyright © 1976 by John Wiley & Sons, Inc. This material is used by permission of John Wiley & Sons, Inc.

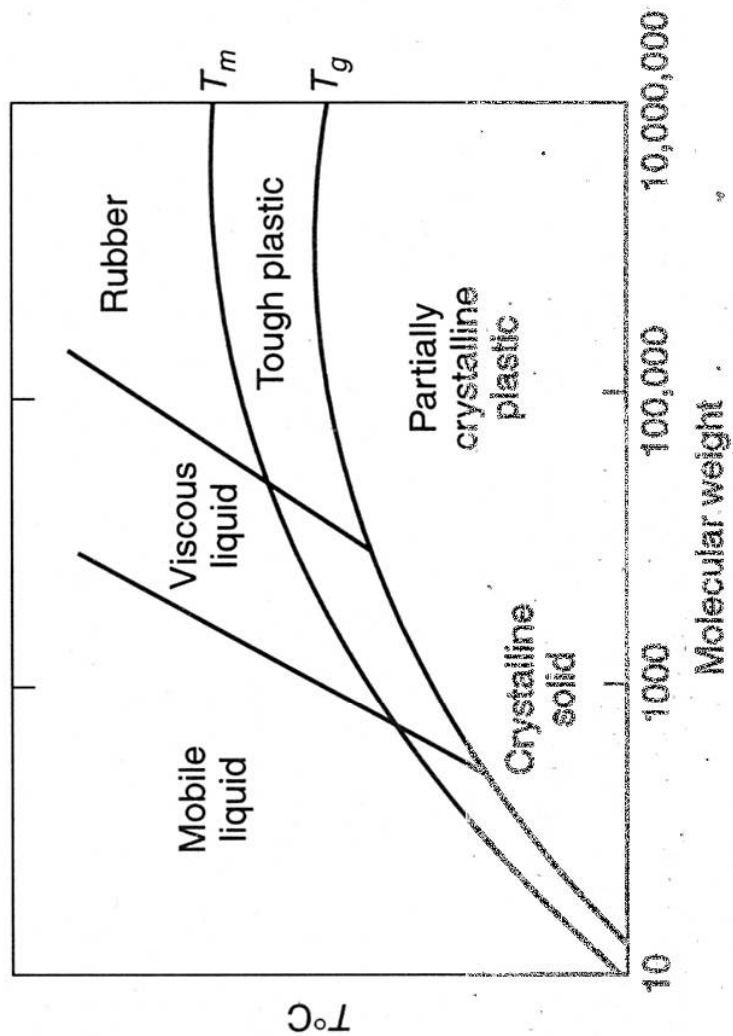


Figure 1.72 Approximate relations among molecular weight, T_g , T_m and polymer properties From F. W. Billmeyer, *Textbook of Polymer Science*, 3rd ed. Copyright © 1984 by John Wiley & Sons, Inc. This material is used by permission of John Wiley & Sons, Inc.

Table 1.26 Predominant Properties of Crystalline Polymers

	Degree of Crystallinity		
Temperature Range	Low (5–10%)	Intermediate (20–60%)	High (70–90%)
Above T_g	Rubbery	Leathery, tough	Stiff, hard, brittle
Below T_g	Glassy, brittle	Hornlike, tough	Stiff, hard, brittle

Additives in Polymers- Plasticizer, Thermal stabilizer, Dye

PVC

one of the most used polymers, because it is easily processed and compounded, the raw materials involved in its formulation have a relative low cost and because a wide range of properties can be obtained.

Plasticizers

- The most widely used primary plasticizers have a low molecular weight (known as monomeric plasticizers)
- The most common monomeric plasticizers are esters derived from phthalic acid, although other derived from different organic acids can be used, as phosphates, trimellitates, citrates, sebacates, adipates, etc.
- Polymeric plasticizers are generally saturated polyesters.

- The permanence of a plasticizer in a flexible PVC compound depends upon three major factors which include structure, molecular weight/viscosity, and polarity.
- Branched plasticizers are more permanent than the equivalent but linear plasticizers, since branching tends to hinder movement or entangle the plasticizer within the polymer matrix making it more difficult to migrate or to be removed by volatilization or extraction.
- Plasticizers of linear structures provide less permanence, but they do yield better low temperature properties.

TABLE I
Weight Loss % of PVC Films during the Heating Process

Temperature (°C)	Time (min)		
	15	30	45
140°C	9.00	10.39	11.66
160°C	12.68	25.63	—

PVC problems:

Its low thermal stability, leading to

- discoloration,
- hydrogen chloride loss
- serious corrosion phenomena
- changes in its mechanical properties with a decrease or an increase in molecular weight as a result of chain-scission or cross-linking of the polymer molecules.

<Polymer Degradation and Stability 82 (2003) 387–393>

The defect sites in the polymer chains are proposed to be responsible for the instability.

Possible defect structures in PVC: branching, chloroallyl groups, end groups, oxygen-containing groups and head-to-head structures

Thermal stabilizers include basic compounds, metallic soaps, and organotin compounds, such as barium–cadmium–zinc stearate complex (Ba–Cd–Zn stearate), dibasic lead carbonate (DBLC) (Rolite lead), Di- (n-butyl) tin maleate, N-acryloyl-N'-p-substituted phenylthiourea derivatives.




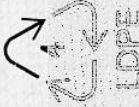



Thermal stabilizers

Table 1

Induction period (T_s) as a function of the type of the investigated *N*-acryloyl-*N'*-*p*-substituted phenylthiourea derivatives acting as thermal stabilizers for rigid PVC, at 180 °C, in air

Type of stabilizer	Code name	T_s (min)
PVC Blank	PVC	0
Dibasic lead carbonate	DBLC	7
Barium-cadmium-zinc stearate	Ba-Cd-Zn stearate	6
Dibutyl tin maleate	DBTM	11
<i>N</i> -acryloyl- <i>N'</i> -phenylthiourea	<i>N</i> -A- <i>N'</i> 4~TU	12
<i>N</i> -acryloyl- <i>N'</i> - <i>p</i> -NO ₂ phenylthiourea	<i>N</i> -A- <i>N'</i> - <i>p</i> -NO ₂ - Ω TU	19.5

Polymer Recycle

Code	Material	Percent of total bottles recycled
 1 PETE	----- Polyethylene terephthalate (PET)*	20-30
 2 HDPE	----- High-density polyethylene	50-60
 3	----- Poly(vinyl chloride) (PVC)*	5-10
 4 LDPE	----- Low-density polyethylene	5-10
 5 PP	----- Polypropylene	5-10
 6 PS	----- Polystyrene	5-10
 7 OTHER	----- All other resins and layered multi-material	5-10

*Bottle codes are different from standard industrial identification to avoid confusion with registered trademarks.