IntroductiontoEngineeringMaterials

PolymerStructures

- Classification.
- Monomersandchemicalfunctionalgroups.
- Nomenclature.
- Polymerizationmethods.
- Molecularweight&degreeofpolymerization.
- Molecularstructures.
- Copolymers.
- Crystallinity.

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Polymers

-Verylargemolecules(**macromolecules**)thatarecomposedof smallerrepeatingunits(**monomers**).

A+A ⟶ A-A $\xrightarrow{A}$ A-A-A ⟶.....

- Examples:
  - Textile fibers:polyester,nylon…
  - ICpackagingmaterials.
  - Resistsforphotolithography/microfabrication.
  - Plasticbottles(polyethyleneplastics).
  - Adhesivesandepoxy.
  - High-strength/light-weightfibers:polyamides,polyurethanes, Kevlar…
  - Biopolymers:DNA,proteins,cellulose…

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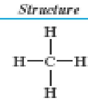
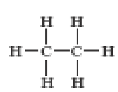
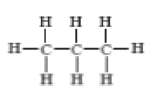
Classification

- **Thermoplastics**:polymers that flow more easily when squeezed,pushed,stretched,etc.by a load (usuallyat elevated T).
  - Canbereheatedtochangeshape.
- **Thermosets**: polymers thatflow and can be molded initiallybuttheir shapebecomesset uponcuring.
  - Reheatingwill resultinirreversiblechangeordecomposition.
- Otherwaysto classify polymers.
  - Bychemicalfunctionality(e.g.polyacrylates,polyamides, polyethers,polyeurethanes…).
  - Vinyl vs. non-vinylpolymers.
  - Bypolymerizationmethods(radical,anionic,cationic…).
  - Etc…

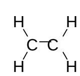
Chemicalfunctionalgroups

Table 14.1 Compositions and Molecular Structures for Some of the Paraffin Compounds: C_nH_{2n+2}

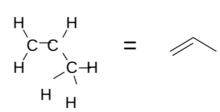
Name	*Composition*	*Structure*	*Boiling Point (°C)*
Methane	CH_4		−164
Ethane	C_2H_6		−88.6
Propane	C_3H_8		−42.1
Butane	C_4H_{10}	.	−0.5
Pentane	C_5H_{12}	.	36.1
Hexane	C_6H_{14}	.	69.0

Saturatedhydrocarbons

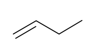
Ethylene (ethene)



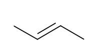
Propylene (propene)



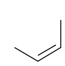
1-butene



2-butene



trans



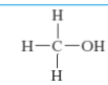
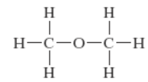
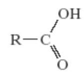
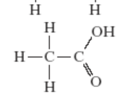
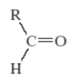
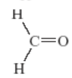
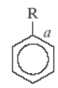
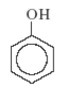
cis

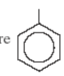
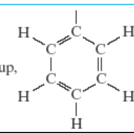
Acetylene (ethyne)

Unsaturated hydrocarbons

Chemicalfunctionalgroups

Table 14.2 Some Common Hydrocarbon Groups

Family	Characteristic Unit		Representative Compound
Alcohols	R—OH		Methyl alcohol
Ethers	R—O—R′		Dimethyl ether
Acids			Acetic acid
Aldehydes			Formaldehyde
Aromatic hydrocarbons			Phenol

[a] The simplified structure  denotes a phenyl group, 

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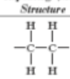
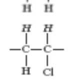
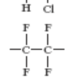
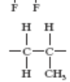
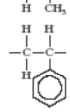
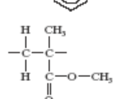
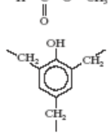
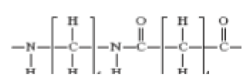
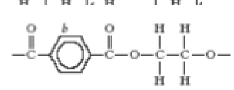
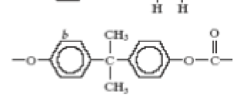
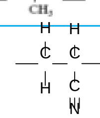
Somecommonpolymers

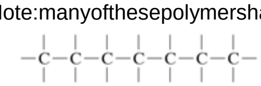
	Repeating (Mer) Structure
Polyethylene (PE)	
Polyvinyl chloride (PVC)	
Polytetrafluoroethylene (PTFE) teflon	
Polypropylene (PP)	
Polystyrene (PS)	
Polymethyl methacrylate (PMMA)	
Phenol-formaldehyde (Bakelite)	

Polyhexamethylene adipamide (nylon 6,6) 

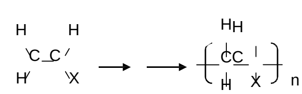
Polyethylene terephthalate (PET, a polyester) 

Polycarbonate 

Polyacrylonitrile(PAN) 

Note:manyofthesepolymershave  backbone.

Vinylpolymers(oneormoreH'sofethylenecanbesubstituted)



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Nomenclature

Monomer-basednaming:
poly________

Monomer namegoes here

e.g.ethylene->polyethylene

ifmonomer namecontains more than one word:
poly(____________)

Monomer namein parentheses

e.g.acrylic acid->poly(acrylicacid)

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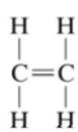
polymethylene

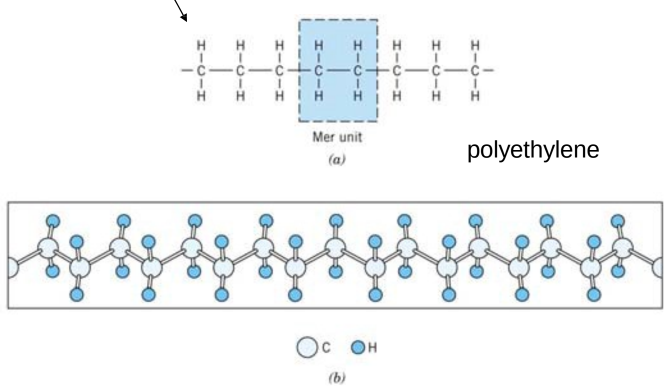
Monomerstopolymers



ethylene

polymerization

FIGURE 14.1 For polyethylene, (*a*) a schematic representation of mer and chain structures, and (*b*) a perspective of the molecule, indicating the zigzag backbone structure.

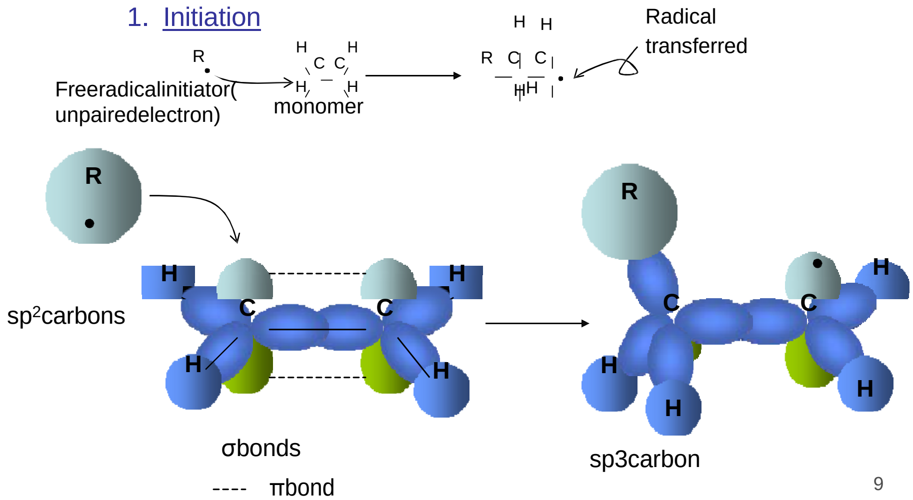


polyethylene

Polymerizationmethods

A. FreeRadicalPolymerization

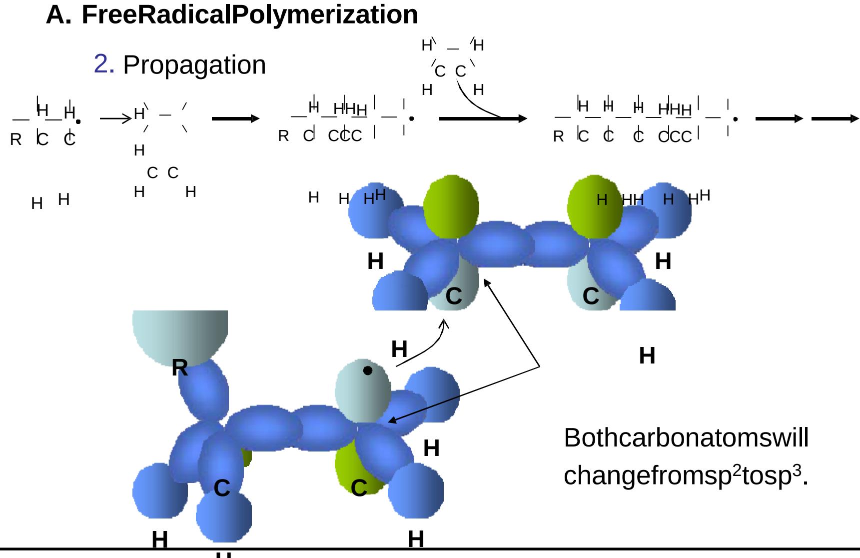
1. Initiation



Polymerizationmethods

A. FreeRadicalPolymerization

2. Propagation

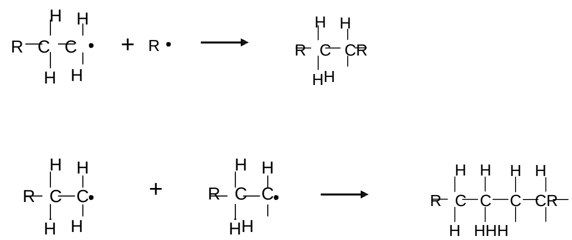


subShi

Polymerizationmethods

A. FreeRadicalPolymerization

3. Termination



Intentionalorunintentionalmolecules/impuritiescanalsoterminate.

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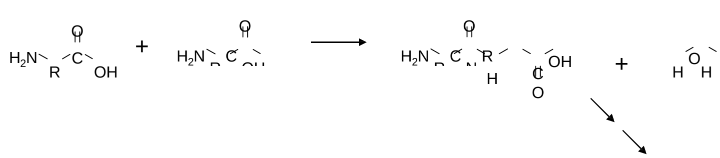
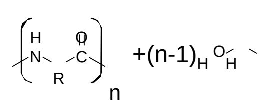
Polymerizationmethods

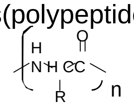
B. Stepwisepolymerization

Losewater
(condensation)





Proteins(polypeptideshavesimilarcomposition)



VariousRgroups…

C. Othermethods

Anionicpolymerization,cationic
polymerization,coordination
polymerization…

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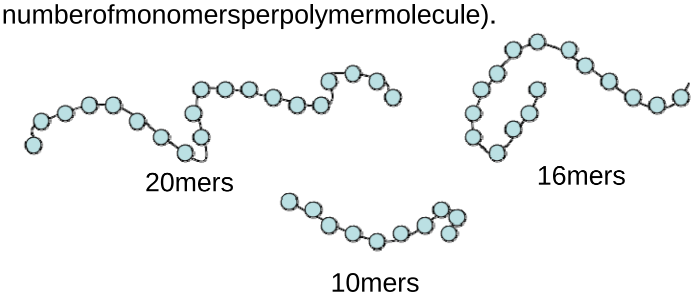
MolecularWeight

Notonlyaretheredifferentstructures(moleculararrangements) buttherecanalsobeadistributionofmolecularweights(i.e. numberofmonomersperpolymermolecule).



Averagemolecularweight= $\frac{20+16+10}{3} M_{monomer} = 15.3 M_{monomer}$

Thisiswhatiscallednumberaveragemolecularweight.

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MolecularWeight

Numberaveragemolecular weight:

[redacted] $= \frac{m_o \sum_j N_j j}{\sum_j N_j}$

N_j=numberofpolymerchainswithlength$j$ $M_j = jm_o$ =massofpolymerchainwithlength$j$
m_o=monomermolecularweight

Note: $\sum_j N_j M_j =$ Totalweight $\sum_j N_j$ =Total#ofpolymerchains

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Molecular Weight

Weight average molecular weight:

[redacted]

$W_j = N_j M_j$

In general:

[redacted]

If α=0 then $\overline{M_n}$

If α=1 then $\overline{M_w}$

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Molecular Weight: Different Notations

In Lecture Notes

[redacted]

N_j=number of polymer chains with length j $M_j = jm_o$=mass of polymer chain with length j

In Callister Textbook

[redacted]

$$x_i = \frac{N_i}{\sum_j N_j}$$

[redacted]

$$w_i = \frac{N_i M_i}{\sum_j N_j M_j}$$

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MolecularWeight

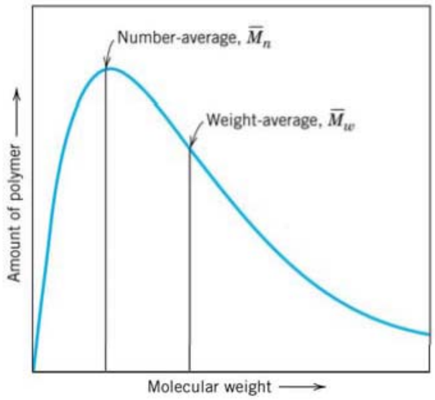

FIGURE 14.4 Distribution of molecular weights for a typical polymer.

Weightaveragecountsthe heavierchainsmore–certain propertiescanbedependenton molecularweight(i.e.largerMW polymerchainscancontributeto theoverallpropertydifferently thansmallerones).

NOTE: $\overline{M_w}$ isalwayslargerthan $\overline{M_n}$ unlesspolydispersity=1

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Polydispersity& Degree of polymerization

Polydispersity= $\frac{\overline{M_w}}{\overline{M_n}} \geq 1$

Whenpolydispersity=1,**monodisperse.**

Degreeofpolymerization:

Numberavgdegreeofpolymerization $n_n = \frac{\overline{M_n}}{m_o}$

Monomer molecular weight

Weightavgdegreeofpolymerization $n_w = \frac{\overline{M_w}}{m_o}$

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Example1

A. Calculatenumberandweightavgdegreesofpolymerizationand polydispersityforapolymersamplewiththefollowingdistribution.

Avg#ofmonomers/chain	Relativeabundance
10	5
100	25
500	50
1000	30
5000	10
50,000	5

B. IfthepolymerisPMMA,calculatenumberandweightaverage molecularweights.

C. Ifweaddpolymerchainswithavg#ofmonomers=10suchthat theirrelativeabundancechangesfrom5to10,whatarethenew numberandweightaveragedegreesofpolymerizationand polydispersity?

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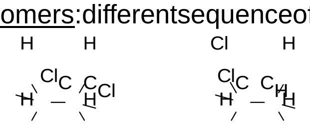
Isomerisminpolymers

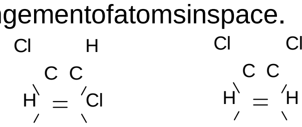
Sofar,we'veconsideredpolymersasif theywerebeadsonastring, thereismorestructuralcomplexity.

Isomers:moleculeswithsameempiricalformulabutdifferent structure.

geometricalisomers:differentsequenceofbonds.



stereoisomers:samebondsequencebutdifferent arrangementofatomsinspace.



Similartomoleculespolymersalsohaveisomers…

sequence,stereoandstructuralisomers

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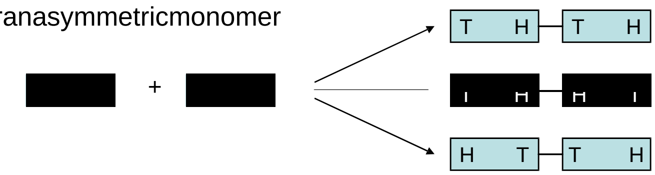
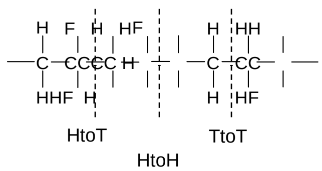
Sequenceisomerism

Foranasymmetricmonomer

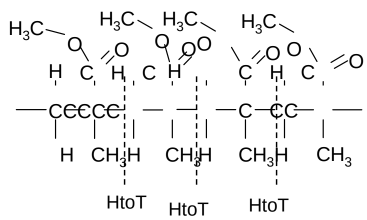


e.g.poly(vinyl fluoride):



Randomarrangement

e.g.PMMA



ExclusiveHtoTarrangement(Why?)

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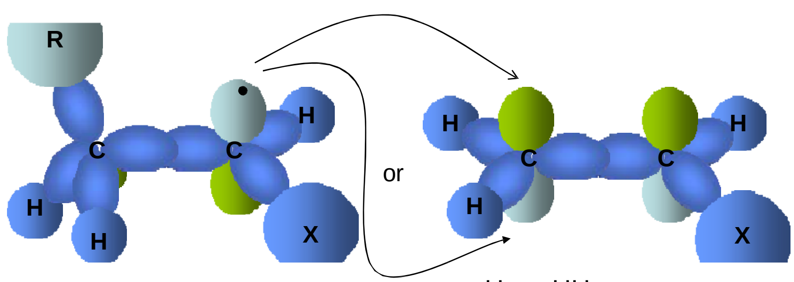
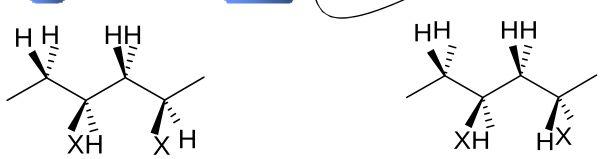
Stereoisomerism(tacticity)

Evenwithexclusivehead-to-tailarrangement,therecanstill bevariations





meso-diad

racemic-diad

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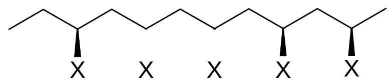
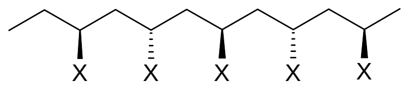
Stereoisomerism(tacticity)

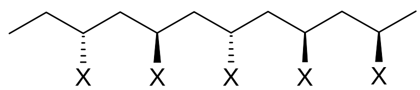
Isotactic:onlymeso-diads



Syndiotactic:onlyracemic-diads



Atactic:randommixture



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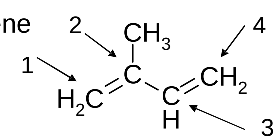
StructuralIsomers

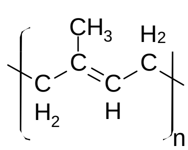
Somepolymerscontainmonomerswithmorethan1reactivesite

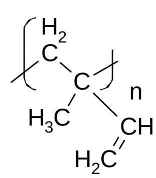
e.g.isoprene

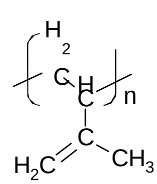


trans-isoprene

trans-1,4-polyisoprene *trans*-1,2-polyisoprene 3,4-polyisoprene







Note:therearealso*cis*-1,4-and*cis*-1,2-polyisoprene

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Molecularstructure

Sofar,we'veconsideredpolymersassimplelinearchainofonetypeof monomer…

Linearstructures

a) Linearhomopolymer:
…--A—A—A—A—A—A—A—A—A—A—A—A—A—A—A--…

b) Linearcopolymer:

…--A—B—A—B—A—B—A—B—A—B--…alternatingcopolymer

…--A—A—A—A—A—B—B—B—B—B--…blockcopolymer

…--A—B—B—A—B—A—A—A—B—B--…randomcopolymer

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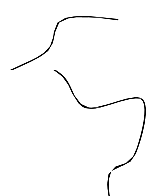
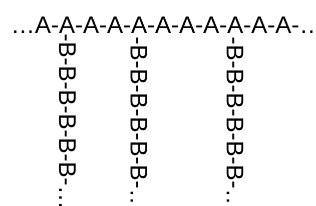
Molecularstructure

Branchedstructures

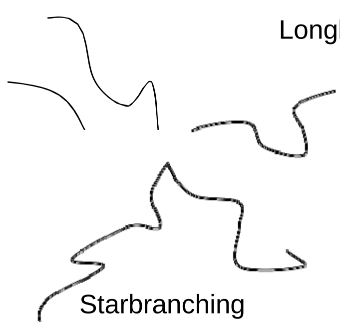
Shortbranching



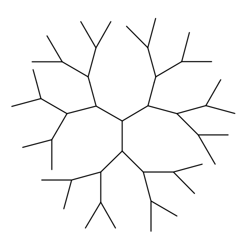
Longbranching



Graftcopolymer



Starbranching



Dendrimers

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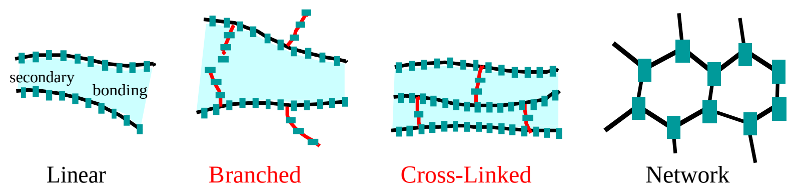
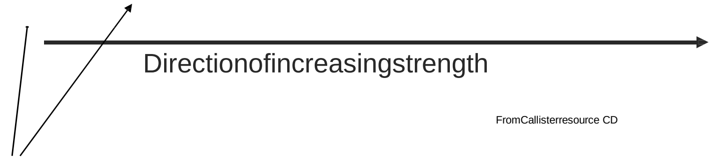
Molecularstructure

Secondary bonding
betweenchains

Covalentlylinked
chains





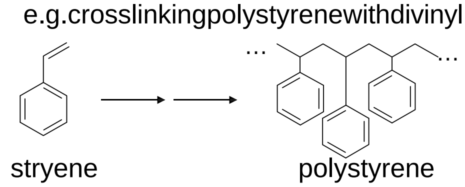
FromCallisterresource CD

Notalwaysin thisorder(e.g.high-densityvs.low-densitypolyethylene).
Why?

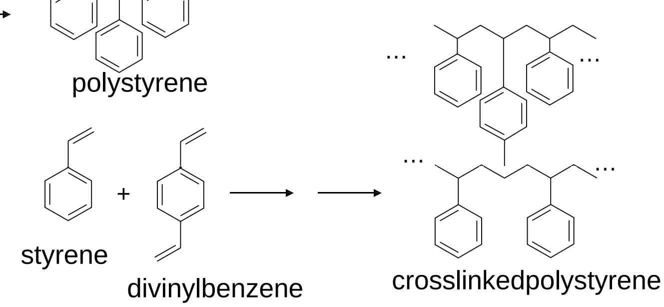
Molecularstructure

Howdo**crosslinking**and**branching**occurinpolymerization?

1.Startwithoraddinmonomersthathavemorethan2sitesthat bondwithothermonomers.
e.g.crosslinkingpolystyrenewithdivinylbenzene



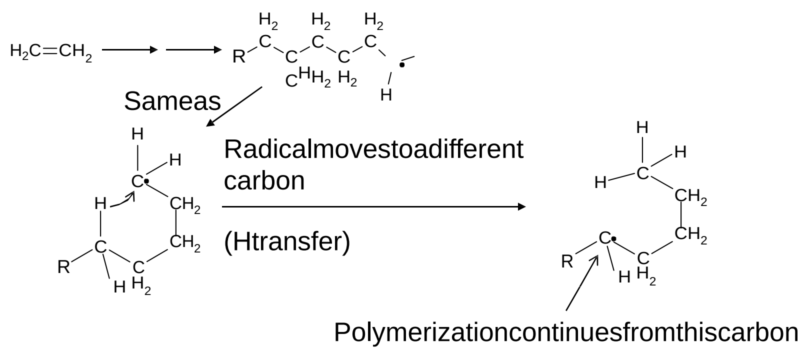
Controldegree
ofcrosslinking
bystyrene-
divinylbenzene
ratio



Monomerswiththreeormorepolymerizablegroupsleadtonetworkpolymers.

Molecularstructure

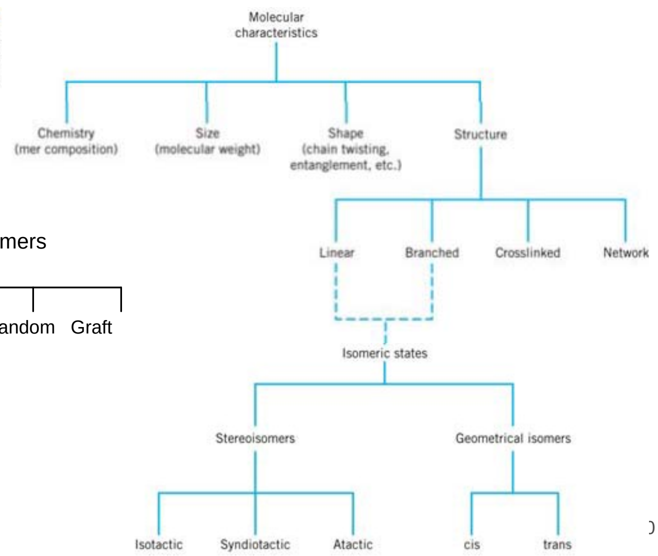
Branchinginpolyethylene(back-biting)

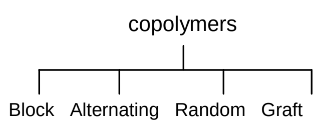


Thisprocessis usuallydifficulttoavoidandleadsto**low-densitypolyethylene** (highlybranched).
Whenthereis small degreeofbranching:**high-densitypolyethylene.**

Molecularstructure

FIGURE 14.8 Classification scheme for the characteristics of polymer molecules.





Example2

Anitrilerubber copolymer,co-poly(acrylonitrile-butadiene),is foundtohave

$\overline{M_n} = 106{,}740\, g/mol$ and $n_n = 2000$

Calculatethe ratioof number ofacrylonitrileto number ofbutadiene.

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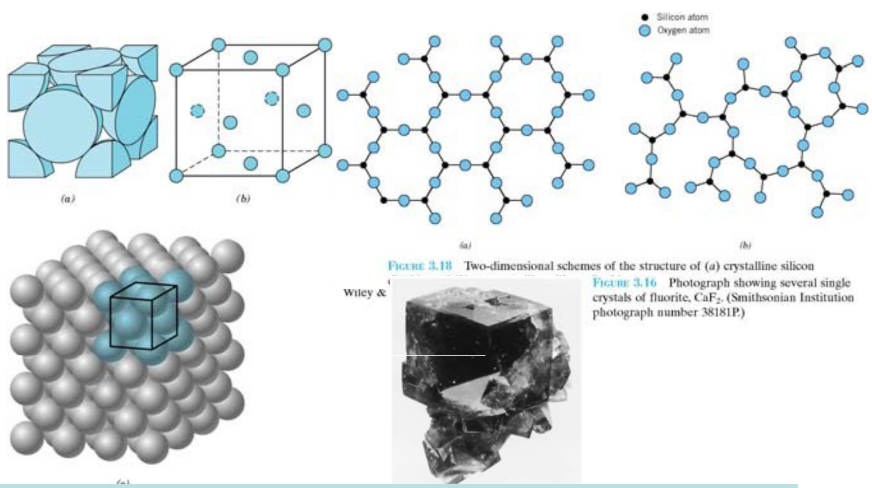
Crystallineor Amorphous



We've seen crystallineand amorphousmaterialsin metalsand ceramics. Whatabout polymers?

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Polymercrystallinity

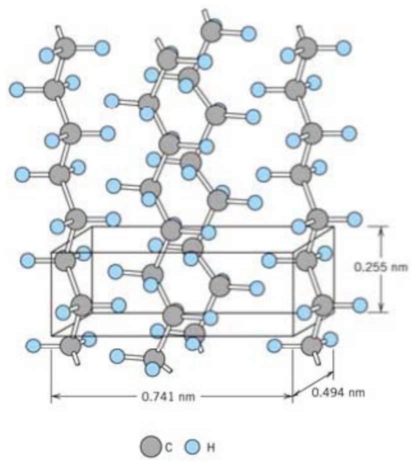

Figure 14.10 Arrangement of molecular chains in a unit cell for polyethylene. (Adapted from C. W. Bunn, *Chemical Crystallography,* Oxford University Press, Oxford, 1945, p. 233.)

Someareamorphous,someare partiallycrystalline(semi-crystalline).
-Whyis it difficult tohavea 100% crystallinepolymer?

$$\%crystallinity = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100\%$$

ρ_s=densityofspecimeninquestion
ρ_a=densityoftotallyamorphouspolymer
ρ_c=densityoftotallycrystallinepolymer

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Polymercrystallinity

$$\%crystallinity = \frac{M_{crystalline}}{M_{total}} \times 100\% = \frac{\rho_c V_c}{\rho_s V_s} \times 100\% = \frac{\rho_c}{\rho_s} f_c \times 100\%$$

Whatisf_c?Volumefractionofcrystallinecomponent.

Togetf$_c$:

$$M_{total} = M_{crystalline} + M_{amorphous}$$

$$M_s = M_c + M_a$$

$$\rho_s V_s = \rho_c V_c + \rho_a V_a$$

$$\rho_s = \rho_c \frac{V_c}{V_s} + \rho_a \frac{V_a}{V_s}$$

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Polymercrystallinity

Usingdefinitionofvolumefractions: $f_c = \frac{V_c}{V_s}$ and $f_a = \frac{V_a}{V}$

$$\rho_s = \rho_c f_c + \rho_a f_a = \rho_c f_c + \rho_a (1 - f_c)$$

$$\rho_s = f_c(\rho_c - \rho_a) + \rho_a$$

$$f_c = \frac{\rho_s - \rho_a}{\rho_c - \rho_a}$$

Substitutingin f_c intotheoriginal definition,weget:

$$\%crystallinity = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100\%$$

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Polymercrystallinity

Degreeofcrystallinitydependsonprocessingconditions(e.g. coolingrate)andchainconfiguration.

Coolingrate:duringcrystallizationuponcoolingthroughMP, polymersbecomehighly viscous.Requiressufficienttimefor random&entangledchainstobecomeorderedinviscousliquid.

Chemicalgroups and chainconfiguration:

MoreCrystalline	LessCrystalline
Smaller/simperside groups	Larger/complexsidegroups
Linear	Highlybranched
Isotacticorsyndiotactic	Crosslinked,network
	Random

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Semicrystallinepolymers

Fringedmicellemodel:crystallineregionembeddedinamorphous region.Asinglechainofpolymermaypassthroughseveral crystallineregionsaswellasinterveningamorphousregions.

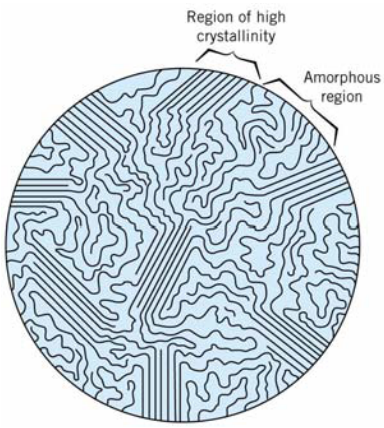

FIGURE 14.11 Fringed-micelle model of a semicrystalline polymer, showing both crystalline and amorphous regions. (From H. W. Hayden, W. G. Moffatt, and J. Wulff, *The Structure and Properties of Materials,* Vol. III, *Mechanical Behavior.* Copyright © 1965 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

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Semicrystallinepolymers

Chain-foldedmodel:regularlyshapedplatelets(~10–20nmthick) sometimesformingmultilayers.Averagechainlength>>than plateletthickness.

FIGURE 14.13 The chain-folded structure for a plate-shaped polymer crystallite.

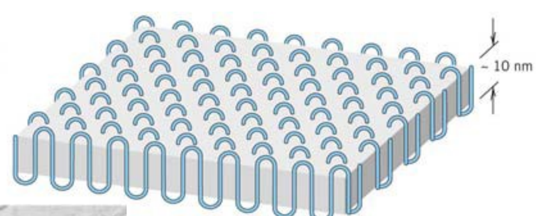
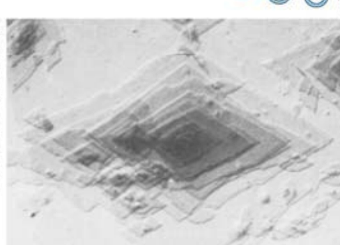


FIGURE 14.12 Electron micrograph of a polyethylene single crystal. 20,000×. [From A. Keller, R. H. Doremus, B. W. Roberts, and D. Turnbull (Editors), *Growth and Perfection of Crystals.* General Electric Company and John Wiley & Sons, Inc., 1958, p. 498.]



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Semicrystallinepolymers

Spherulites: Sphericalshapecomposedofaggregatesofchain-foldedcystallites.

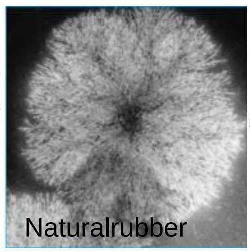


FIGURE 14.14 Schematic representation of the detailed structure of a spherulite. (From John C. Coburn, *Dielectric Relaxation Processes in Poly(ethylene terephthalate)*, Dissertation, University of Utah, 1984.)

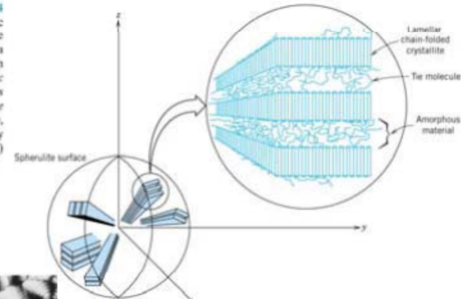
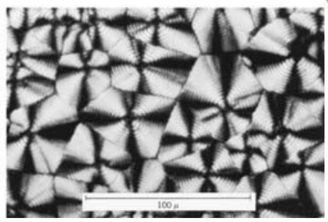


FIGURE 14.15 A transmission photomicrograph (using cross-polarized light) showing the spherulite structure of polyethylene. Linear boundaries form between adjacent spherulites, and within each spherulite appears a Maltese cross. 525×. (Courtesy F. P. Price, General Electric Company.)



Cross-polarizedlight throughspherulitestructur eofpolyethylene.

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Diblockcopolymers

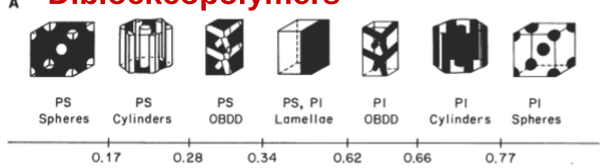
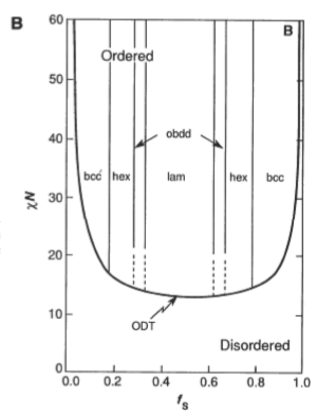


Fig. 6. (**A**) Effect of varying composition on the ordered phase symmetry in polystyrene-polyisoprene (PS-PI) diblock copolymer; f_s refers to the overall volume fraction of polystyrene. (**B**) Phase diagram for polystyrene-polyisoprene (PS-PI) diblock copolymers (46, 47). Ordered phases correspond to those illustrated in (A).



F. Bates,*Science*1991.

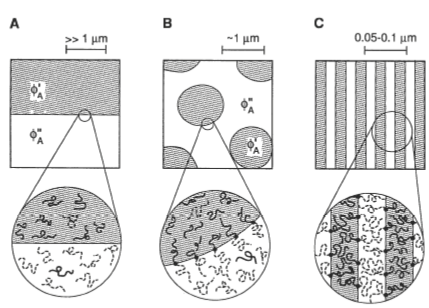


Fig. 2. (**A–C**) Representative polymer-polymer phase behaviors that can be realized with different molecular architectures. Macrophase separation (A) results when thermodynamically incompatible linear homopolymers are mixed. The covalent bond between blocks in a diblock copolymer leads to microphase segregation (C). A mixed architecture of linear homopolymers and the corresponding diblock copolymer produces a surfactant-like stabilized intermediate-scale phase separation (B).

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Conceptsto remember…

- Classification:thermosetsandthermoplastics.
- Monomers andchemicalfunctionalgroups.
- Nomenclature.
- Polymerizationmethods: free radical,addition,andother polymerization.
- Number & weightaveragemolecularweights, polydispersity& degreeof polymerization.
- Sequenceisomerism,tacticity,structuralisomerism
- Molecularstructures:linear,branched,crosslinked, network…
- Copolymers: block, alternating,randomandgraft.
- Crystallinity:fringedmicelles&chain-foldedmodelsand spherulites.

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