

Chapter 11. Polymer Structures

Polymers: materials consisting of long molecules

- the word "polymer" comes from the Greek

Polys	=	many	} many parts
Meros	=	parts	

Macromolecules (long size of the chains)

- typically, the molecules are organic and held together by *covalent C-C bond*
- adjacent "chains" are held together by *secondary (vdW) bonding*
- may be additional covalent bonds *between chains* (referred to as cross-links)

Chapter 10 in Smith & Hashemi
Chapter 14 in Callister

Chapter 11

1

Natural vs man-made

There is a very wide range of polymer types:

Proteins

Rubber

Spider silk (gossamer, is a fiber
spun by spiders)

DNA

Polyethylene

Polyvinyl chloride

Polytetrafluoroethylene (Teflon)

Polycarbonate

Good control over the properties!!!

Chapter 11

2

Hydrocarbon: the simplest polymers

Saturated



Unsaturated



As the molecule gets longer, the melting temperature goes up

CH_4 (C1)	-182.5°C	C12	-9.65°C
C_2H_6 (C2)	-183.5°C	C23	48°C
C_3H_8 (C3)	-189.7°C	C37	71°C
C_4H_{10} (C4)	-138.7°C	C60	96°C
C_6H_{14} (C6)	-95.3°C		

Chapter 11

3

How do you synthesize a polymer?

General reaction of chain polymerization:

If a particular type of polyethylene has an average molecular mass of 150,000g/mol, what is its degree of polymerization?

Chapter 11

4

Some common polymers

Chapter 11

5

Chapter 11

6

Chain polymerization steps

1. **Initiation step:** by free radical formers ($R\bullet$)*, typically *organic peroxides*

*A free radical can be defined as an atom (often part of larger group, that has an unpaired (free) electron

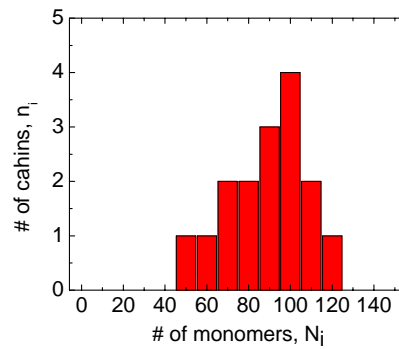
Chain polymerization steps (2 and 3)

2. **Propagation** (there is still an active site, so process continues)

3. **Termination**

Molecular Weight

- Polymers have very high molecular weight (MW)
- For polymer, molecular weight is always a distribution
- Can plot a histogram
- suppose we have 16 polymer chains, with $M_{\text{mer}} = 100$



Chapter 11

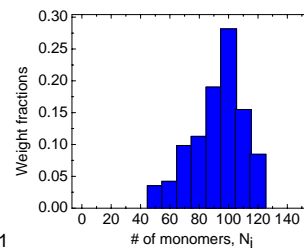
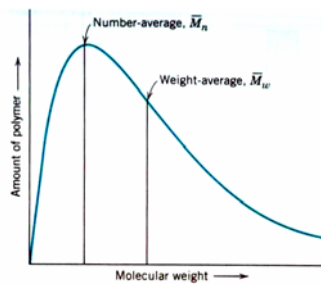
9

Number-Averaged MW

Chapter 11

10

Weight-average MW



Chapter 11

11

How to measure MW?

1. Viscosity

2. Light scattering

Chapter 11

12

Degree of Polymerization (DP)

Chapter 11

13

Molecular Shape

Polymer chains typically arranged at random

Chapter 11

14

Molecular Structure

Since monomers are the building blocks, their chemical composition and functionality will influence the structure and properties of the polymer

- if during polymerization monomer forms bonds in 2 directions, we call it **bifunctional**

- if monomer uses three active bond to form network (3D) polymer material, we call it **trifunctional**

1. Linear polymers
2. Branched polymers
3. Crosslinked polymers
4. Network polymers

Chapter 11

15

Polymer molecular structures

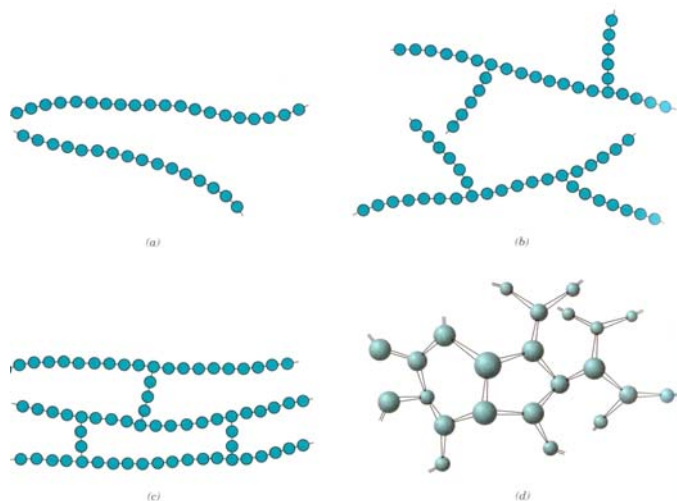


FIGURE 14.7 Schematic representations of (a) linear, (b) branched, (c) crosslinked, and (d) network (three-dimensional) molecular structures. Circles designate individual mer units.

16

Homopolymers and Copolymers

- **Homopolymer:** a polymer consisting of only one type of monomeric unit
- take unit A \Rightarrow polymer ...AAAAAAAAAAAAA...
- **Copolymers:** a polymer chain consisting of 2 or more types of monomeric units
- take units A and B

Four distinct types of copolymers can be identified:

1. Random copolymer: AABBBABABABBBAAAABABBAB
2. Alternating copolymer: ABABABABABABABABABABA
3. Block copolymers: AAAAABBBBBAAAAABBBBB
4. Graft copolymers: AAAAAAAAAAAAAAAAAAAAAA
 B B B
 B B B
 B B B

Chapter 11

17

Other Polymerization Methods

- **Stepwise Polymerization:** monomers chemically react with each other to produce linear polymers; often small molecules (H_2O) are produced as by product
- **Network Polymerization:** chemical reactant attacks **more than 2 sites**

Chapter 11

18

Geometrical Isomerism

Geometrical isomers are possible within mer units with double bond between chain carbon atoms

cis structure

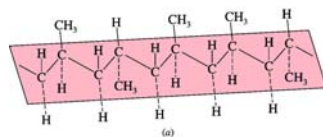
trans structure

Chapter 11

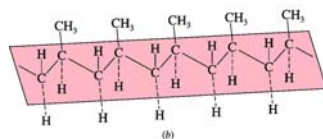
19

Stereoisomerism in Thermoplastics

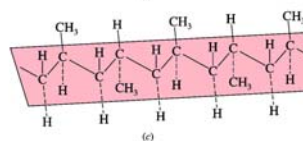
Stereoisomers: molecular compounds that have the same chemical composition, but different structural arrangement



Random (*atactic* isomer)



All methyl groups on the same side (*isotactic* isomer)



Methyl groups on the alternating sides (*syndiotactic* isomer)

Ziegler &
Natta
catalysts
(metallocene)

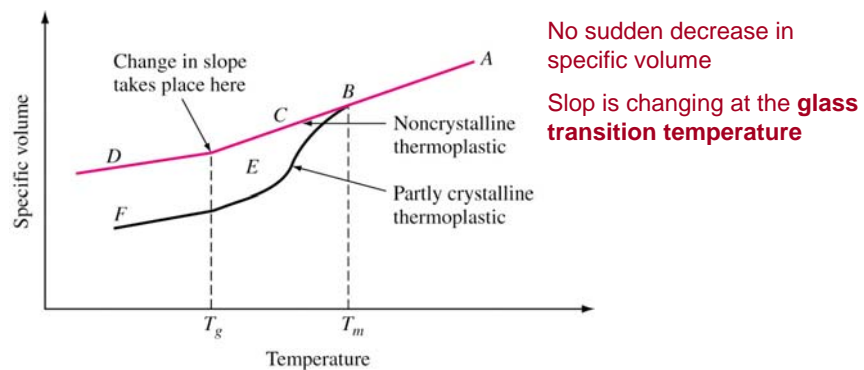
Chapter 11

20

Classification scheme for polymer molecules

Crystallinity in polymers

Thermoplastic polymers: a plastic material that require heat to make it plastic (formable) and upon cooling retains its shape



Distinct specific volume drop during cooling of partially crystalline polymer

Structure of Partially Crystalline Polymers

The longest dimension of crystalline regions in polycrystalline polymeric materials is usually ~5-50nm

⇒ much less compared to the fully extended length

Polymer crystals

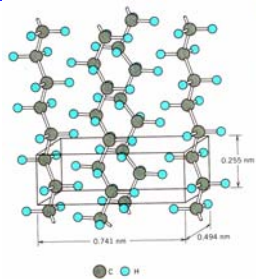


FIGURE 14.10 Arrangement of molecular chains in a unit cell for polyethylene. (Adapted from C. W. Bunn, *Chemical Crystallography*, Oxford University Press, Oxford, 1945, p. 233.)

Crystalline regions are more dense!

