EMAC 276

Lecture 9 : The Polyolefin Family

Polyethylene – PE: Part 1

Polypropylene - PP

Poly(1-butene) – Polybutylene – PB

Andy Olah, Ph.D.

February 10, 2024

EMAC 276 - Homework Assignment #2

Due: Friday, February 14

Dr. Olah

During our classes we identified several common polymers that when initially discovered were described as "value-less", "impossible to process", "a useless mass", etc. We also identified several methods ("tricks") that were subsequently utilized to develop these polymers into successful products; many which are still with us today.

Your exercise is to select one polymer (either from our in-class discussion or from outside our class discussion) and describe 1) the polymer and the initial performance deficiency, 2) the action taken to overcome this deficiency, and, 3) the ensuing product(s) developed from this modification.

If you choose to use an "in class" example your maximum score will be 10.

If you choose to use an "outside the class" example your maximum score will be 12. (i.e., final score +2)

Your answer shall be short comprising between one-half to one page.

Your answer is shall be structured accordingly:

Paragraph #1: Identify and describe the polymer and it's initial deficiency **(3 Points)**

Paragraph #2: Identify the modification or "trick" which was utilized to overcome this deficiency. **(5 Points)**

Paragraph #3: Identify the commercial product or products resulting from this modification. **(2 Points)**

What is a "Olefin" Type Polymer?

Vinyl polymers are the most common type of polymers derived from "vinyl-type" monomers having the general structure:

$$CH_2 = CHR.$$

Where,

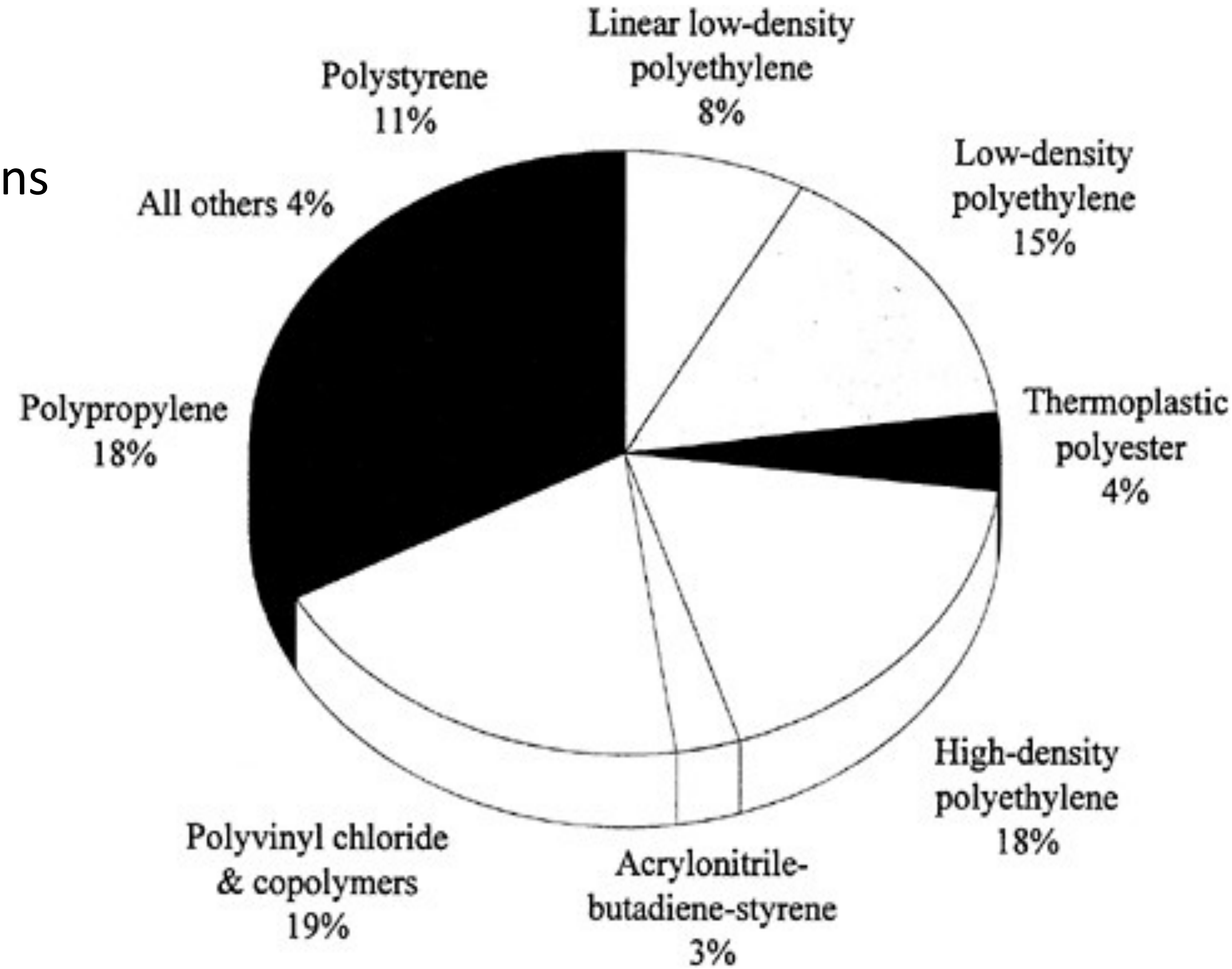
polystyrene – R = C_6H_5
polyvinyl chloride – R = Cl
polyvinyl acetate – R = O_2CCH_3
polyacrylonitrile - R = CN

Not to be confused with poly(vinyl chloride) (PVC) materials which have traditionally been identified as "Vinyls"; i.e., vinyl siding, vinyl records, etc.

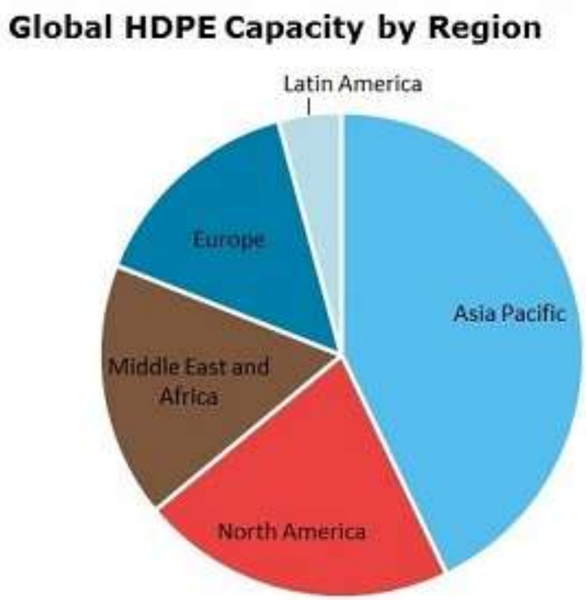
Olefin polymers are a subgroup of vinyl monomers produced from alkenes having a C_nH_{2n} monomer structure:

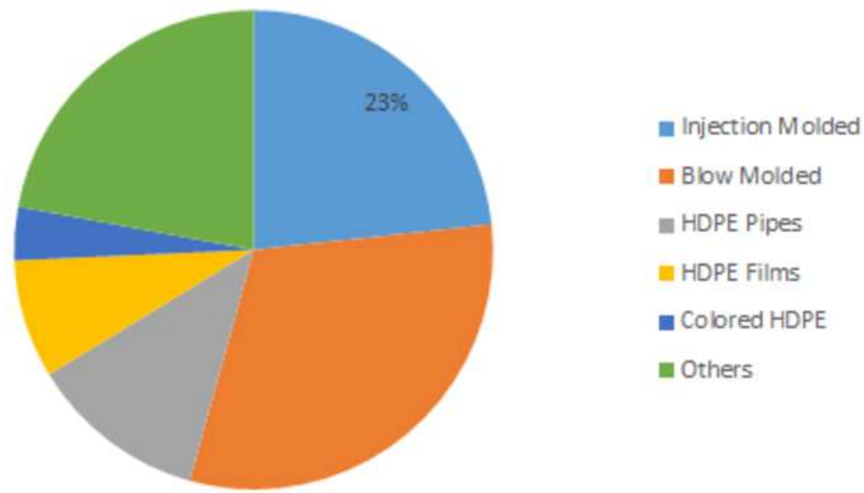
polyethylene – R = H => $CH_2 = CH_2$; (n = 2) => C_2H_4
polypropylene – R = CH_3 => $CH_2 = CH\text{-}CH_3$; (n = 3) => C_3H_6
polybutylene – R = $CH_2\text{-}CH_3$ => $CH_2 = CH\text{-}CH_2\text{-}CH_3$; (n=4) => C_4H_8

The Polyolefin Resins Represent the Largest Volume of Polymer Resins in the Global Market Comprising 59%

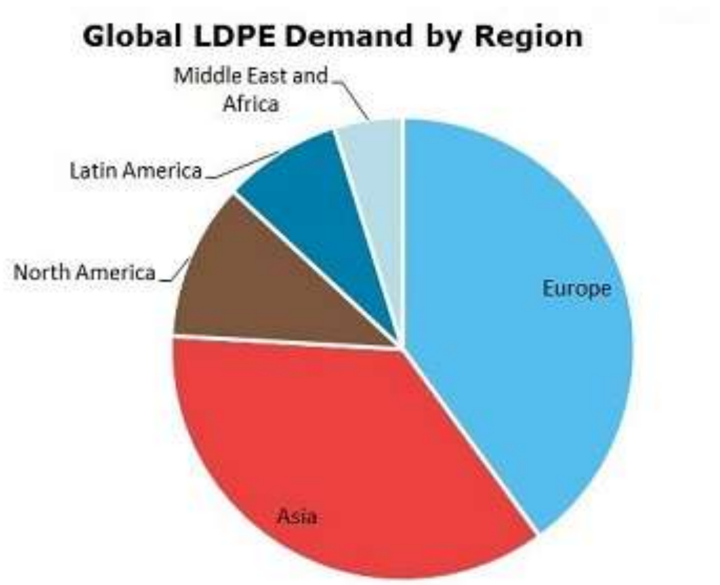


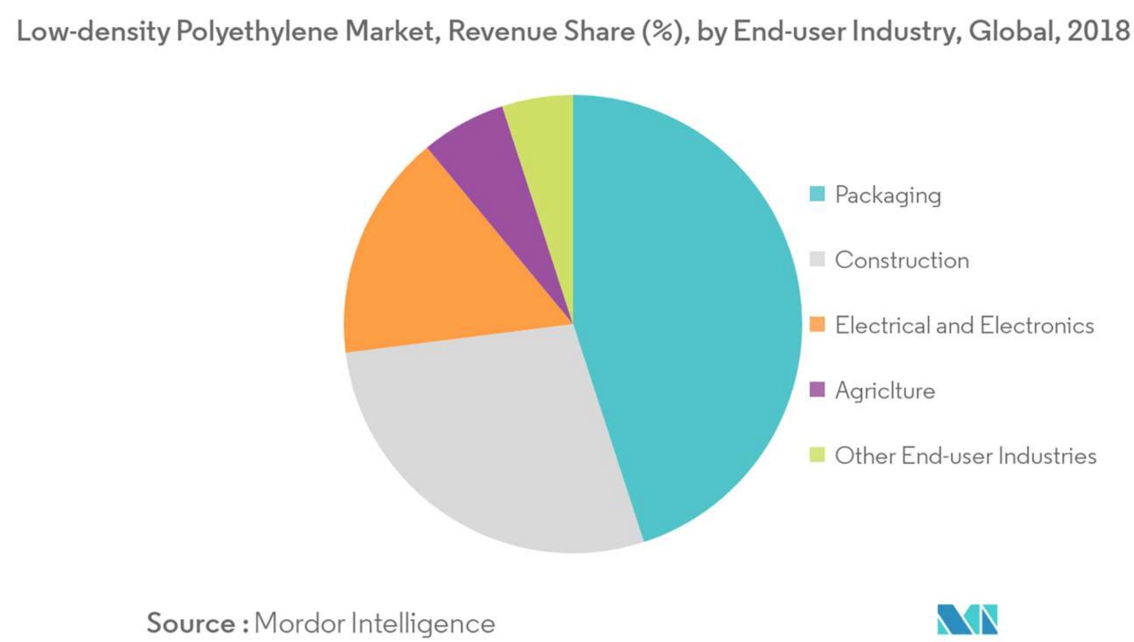
Global HDPE Production and Market





Global LDPE Demand and Market





Early History of Polyethylene Polymerization

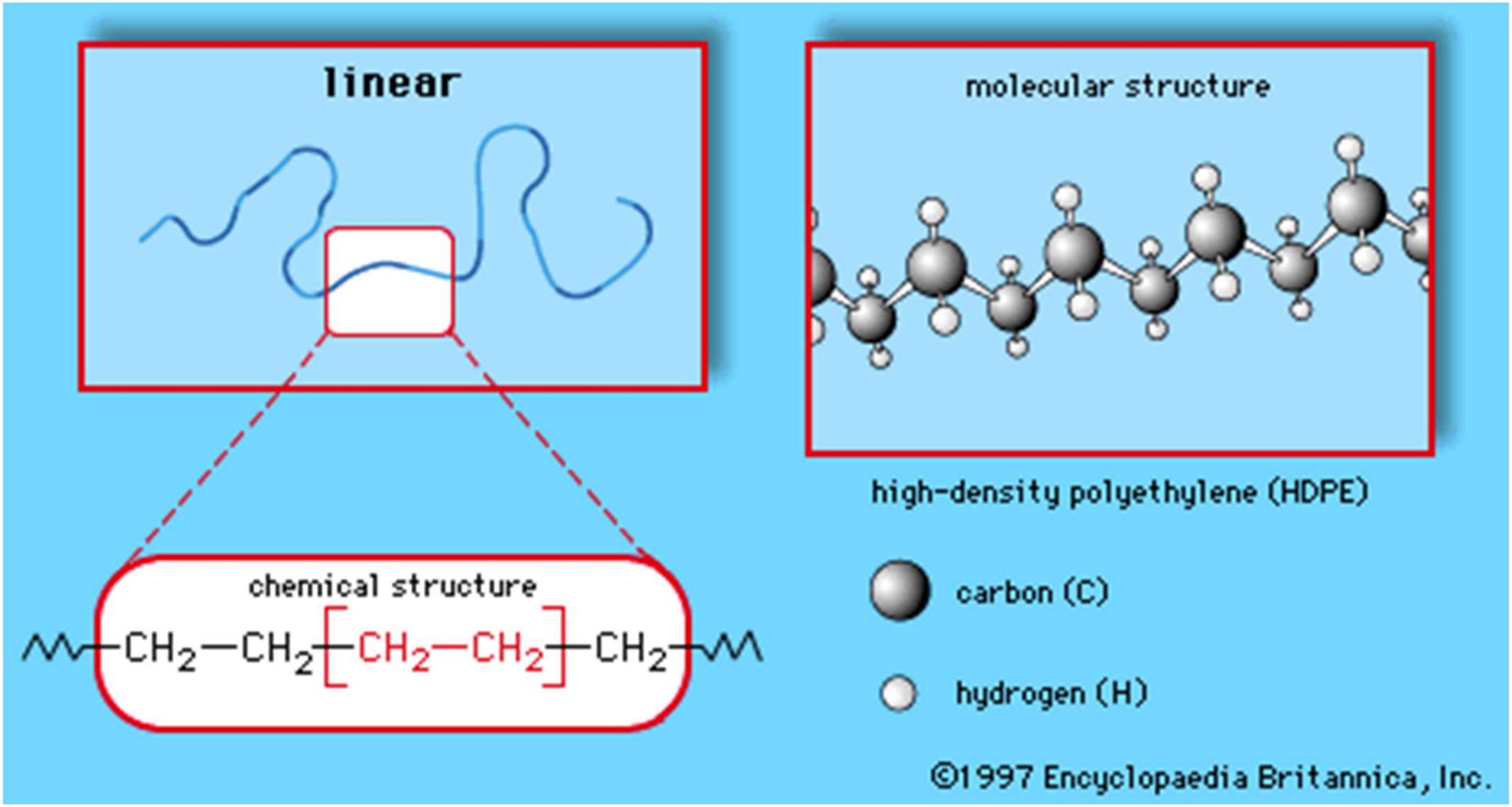
1894 - Accidentially discovered by Hans von Peckmann by decomposition of diazomethane producing a white powder. Analysis indicated it was simply made up of carbon and hydrogen with repeat units of (– CH2 -).

1929 - Friedrick and Marvil produced a low molecular weight material by reacting ethylene with n BuLi.

1933 – Eric Fawcett and Reginald Gibson at Imperial Chemical Industries (ICI) studying ethylene and benzaldehyde at high temperatures. A white waxy material was produced. The reaction was caused by free radicals produced by retained oxygen in the system.

1939 – Michael Perrin at ICI was able to produce large quantities of polyethylene by the high pressure polymerization method which allowed commercial production to ensue.

Polyethylene is a Very Basic Polymer



The Simplest of Molecular Structures Can Lead to a Large Diversity of Structure and Morphology

Three fundamental features of polyethylene leading to the diversity of structures and in turn performance are:

a. Short chain and long chain branching.

b. Co-monomer content and distribution.

c. Molecular weight and molecular weight distribution.

These Variations of Polyethylene Lead to a Diversity of Products

Linear Versions:

High density polyethylene (HDPE)
Ultra-high molecular weight polyethylene (UHMWPE)

Branched Versions:

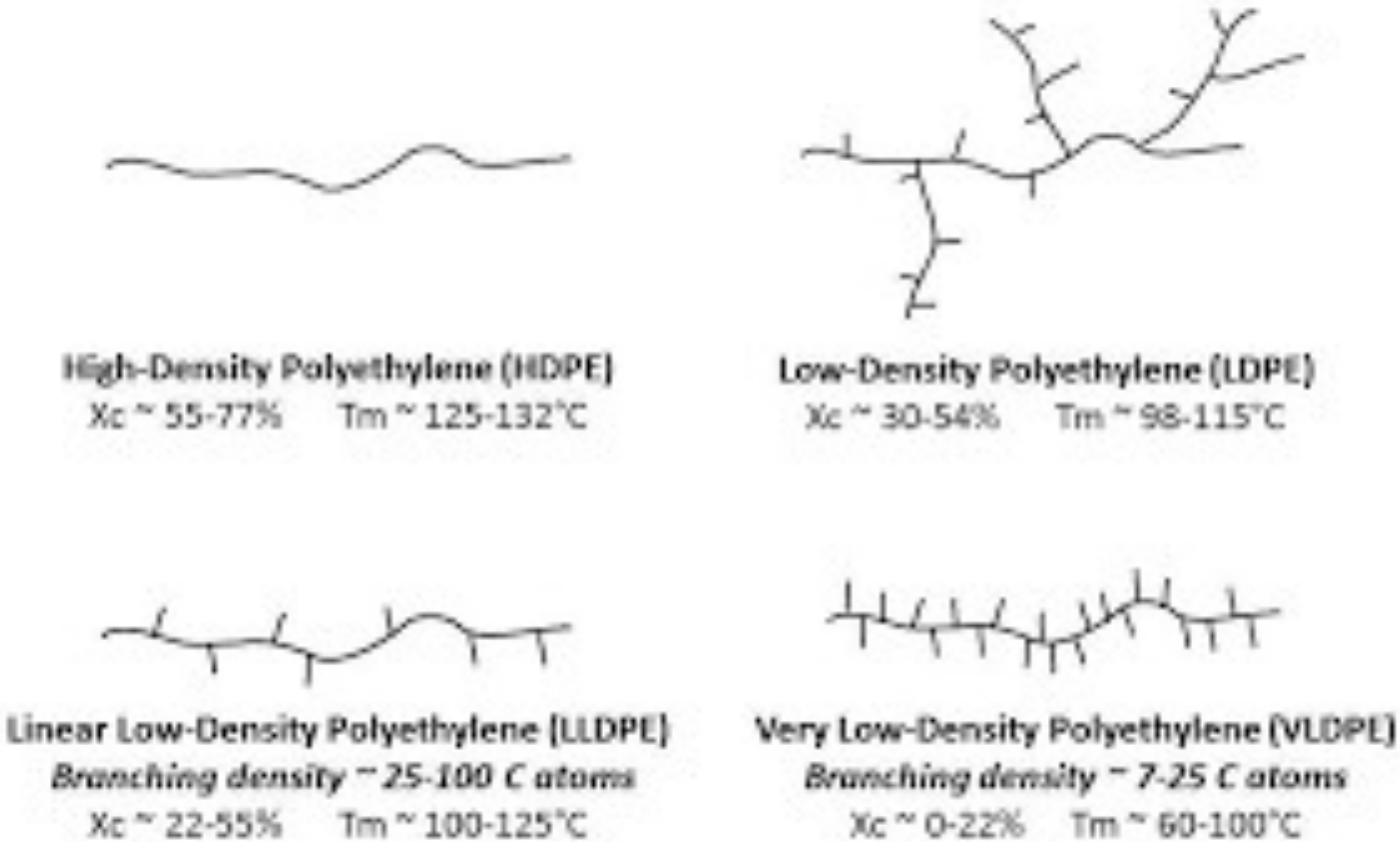
Low-density polyethylene (LDPE)
Linear low density polyethylene (LLDE)

Medium-density polyethylene (MDPE)
Very-low-density polyethylene (VLDPE)
High-molecular-weight polyethylene (HMWPE)
Ultra-low-molecular-weight polyethylene (ULMWPE)
Chlorinated polyethylene (CPE)

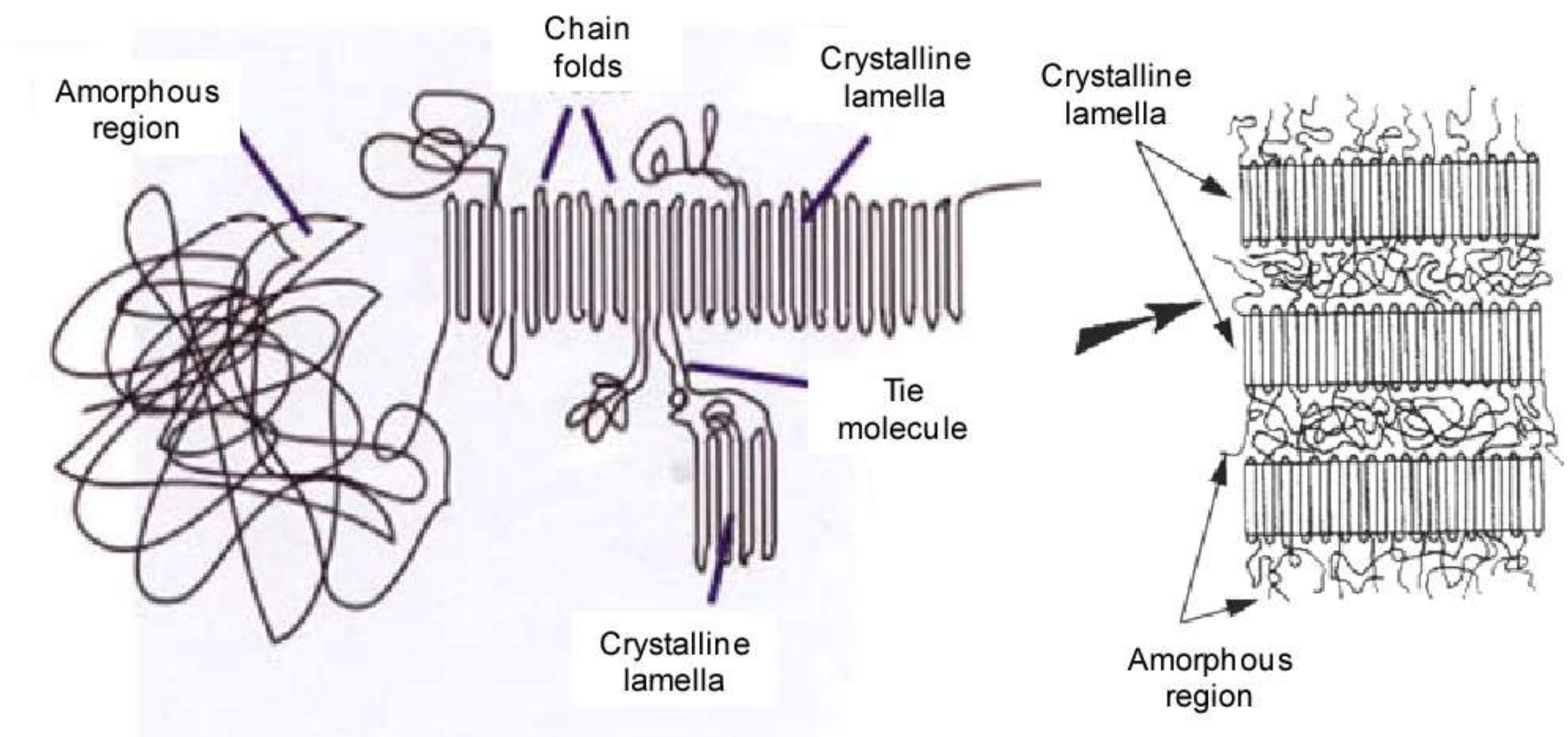
Bimodal and Trimodal Polyethylene

Cross-linked polyethylene (PEX): four forms (PEX-a, PEX-b . . etc)

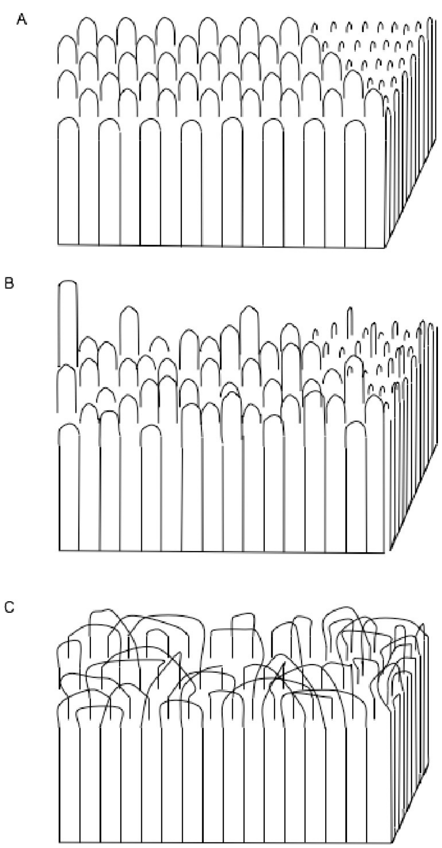
The Variance of Most Polyethylene Products is Based on Branching

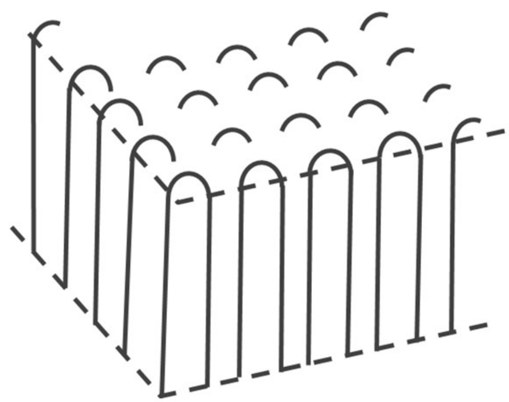


Polyethylene is a Semi-crystalline Material having both Amorphous and Crystalline Regions

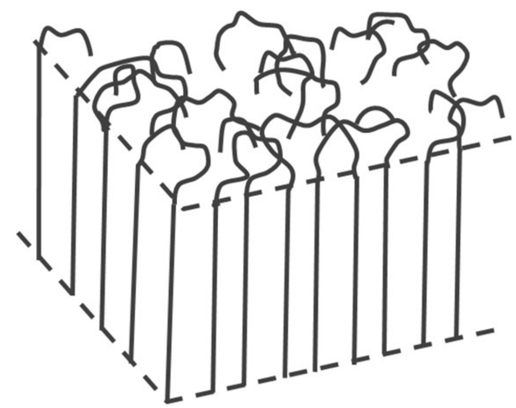


The Polyethylene Molecules in the Crystalline Domains are Chain Folded





Adjacent Re-entry Model

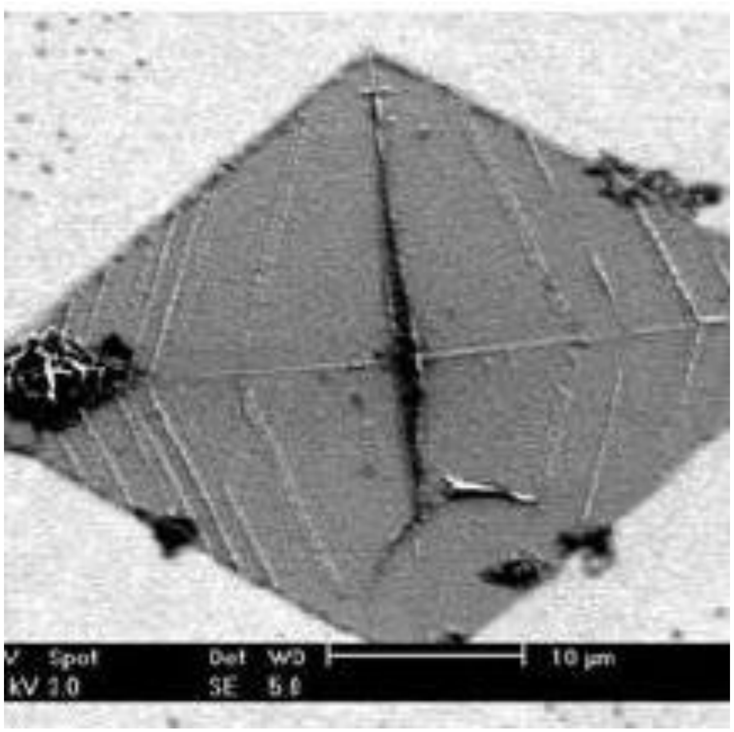


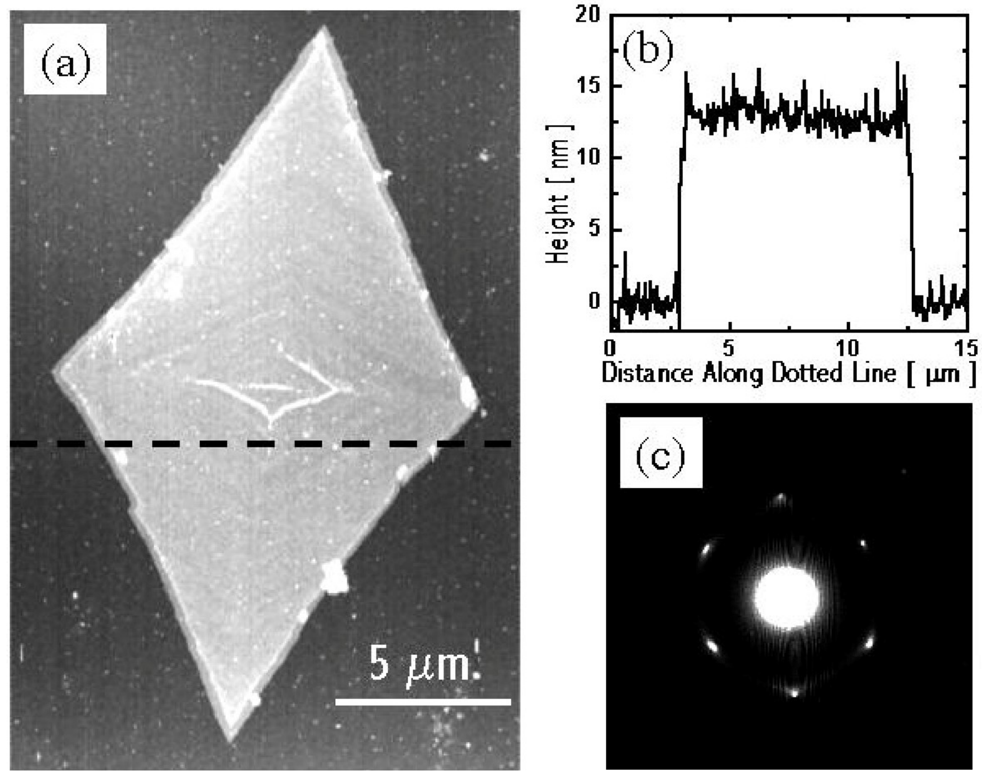
Switchboard Model

Polyethylene Single Crystal Growth from Solution

- Polyethylene was of M_w=32,100 and M_w/M_n=1.11 (32 K fraction), and of M_w=119,600 and M_w/M_n=1.19 (120 K fraction).
- From octane and hexadecane solutions, single crystals were obtained by isothermal crystallization at 94.0 and 99.0 °C, respectively. After the crystallization, the dispersion of single crystals was dropped on an aqueous solution of poly(vinyl alcohol) (PVA). Aqueous solution was 7 wt%. After drying PVA at room temperature, the single crystals distributed on the surface of PVA were observed with an atomic force microscope in a dynamic force mode in air.

Results of Growing a Polyethylene Single Crystal from Solution





Schematic Representation of a Polyethylene Single Crystal Grown from Solution

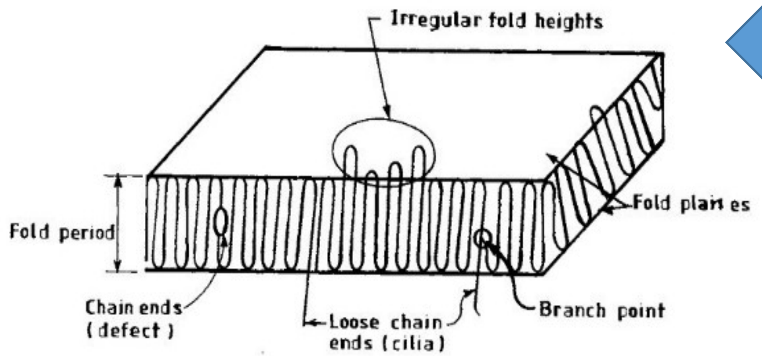


Figure 3.16 *Schematic diagram of chain folding showing conformational imperfections.*

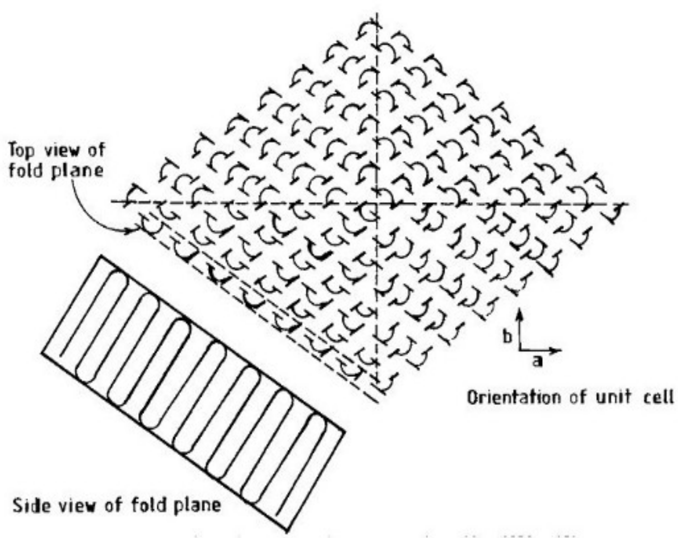
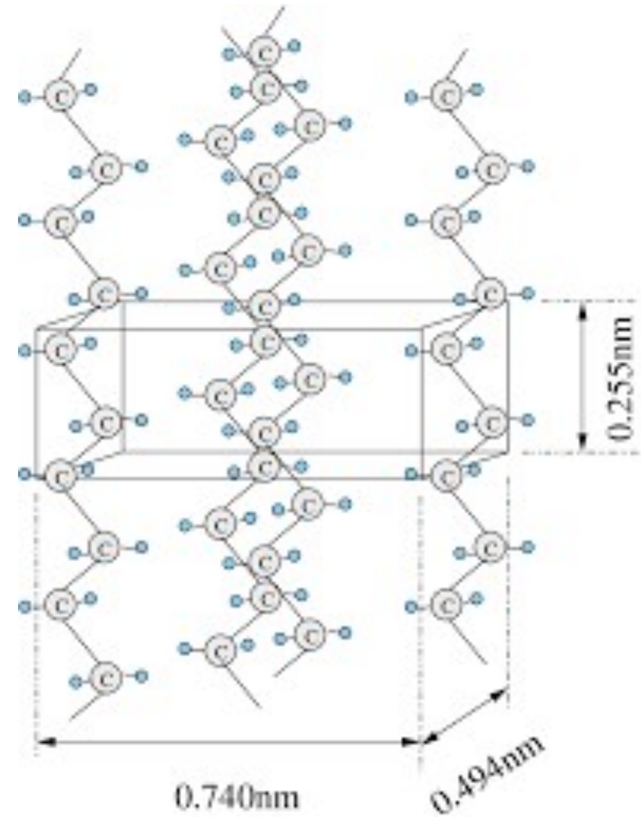


Figure 3.17 *Fold packing in a polyethylene single crystal. (From Reneker, D.H. and Geil, P.H., J. Appl. Phys., 31, 1916, 1960. With permission.)*

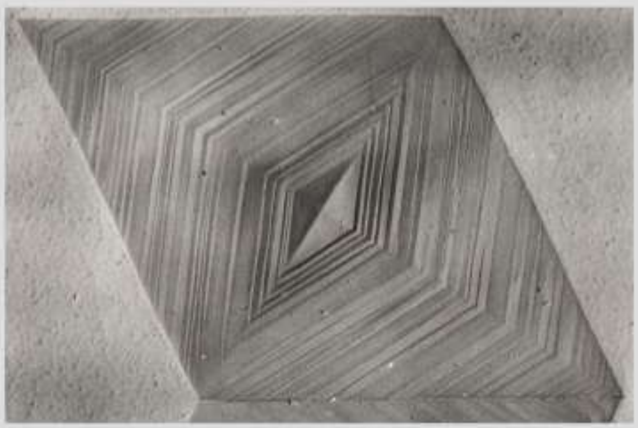


Unit Cell Dimensions of Crystalline Polyethylene

Polyethylene Single Crystals have Three Dimensional Structure

Polyethylene single crystals

(A fantastic electron micrograph by D.C. Bassett)



PE crystallised from solution can form beautiful crystals. Here is an electron micrograph of a stack of PE Chain Folded crystals that have grown on top of each other. The symmetry is incredible when you think that these crystals are formed from one of the most flexible polymer chains in the world.

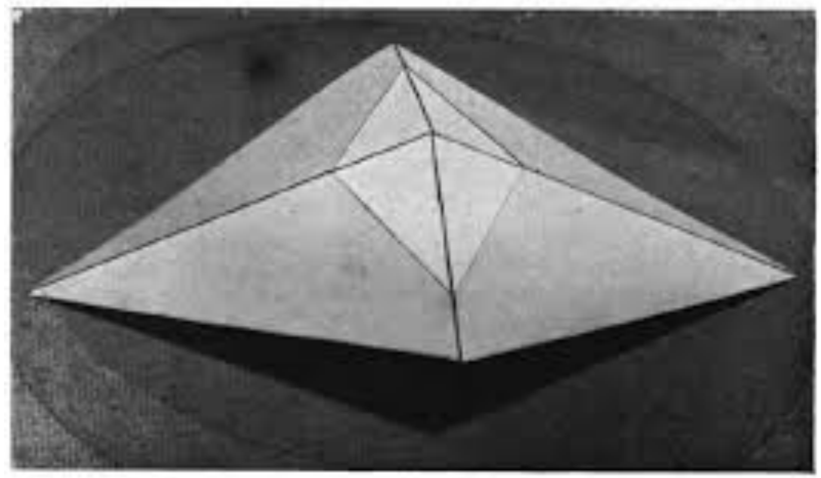
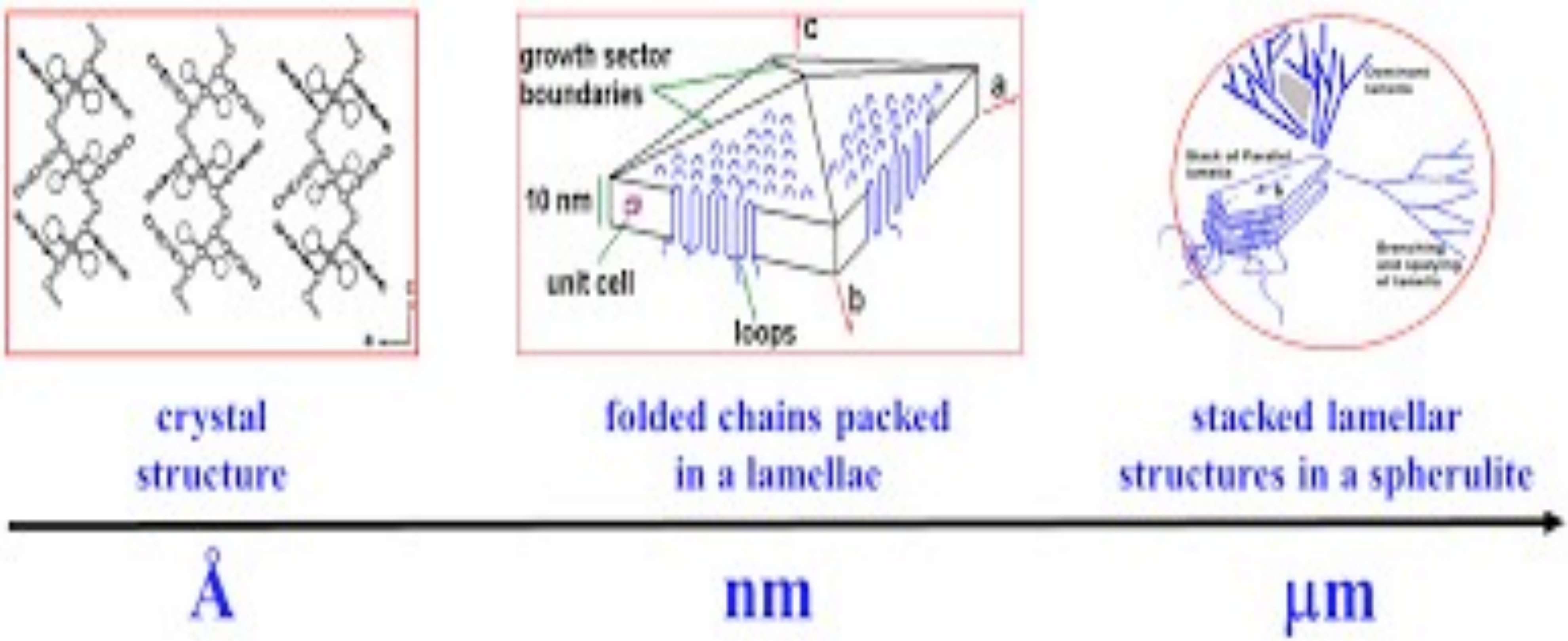
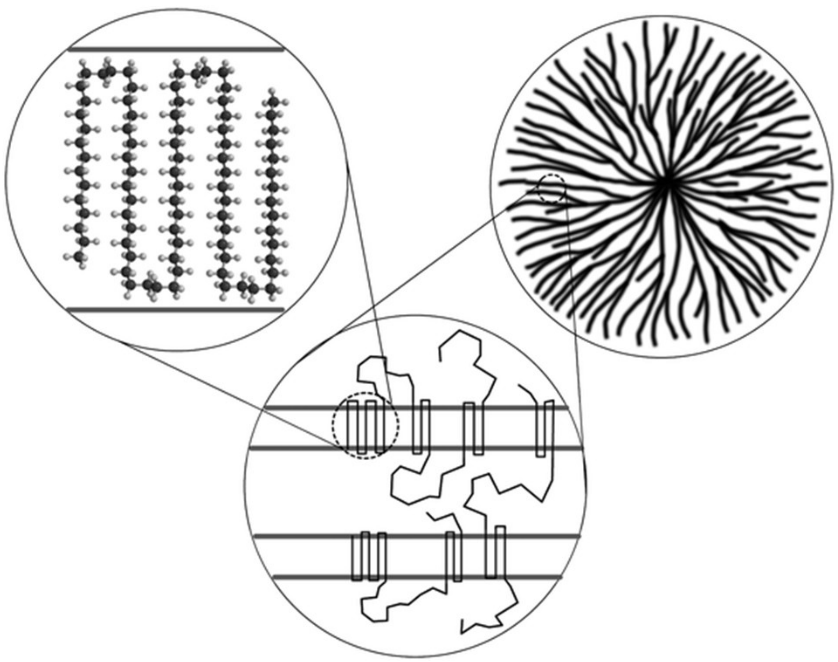


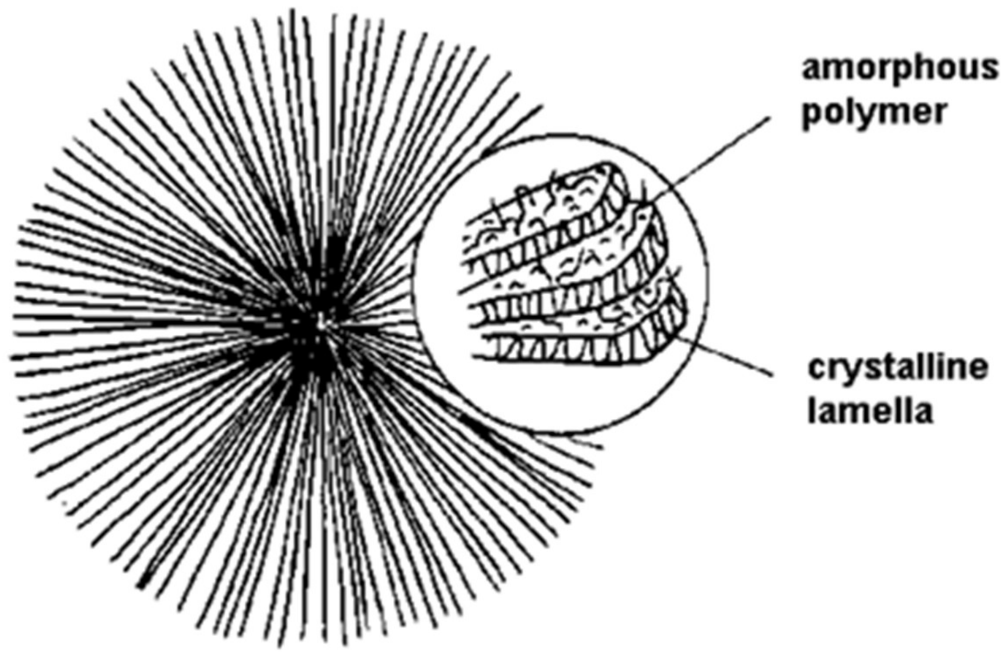
Figure 9—Model of a non flat-based hollow pyramid. This is the true three-dimensional configuration of some of the simplest monolayer polyethylene crystals. The transparent disc illustrates the relation of the pyramid to a flat base (plane perpendicular to the pyramid axis)

Spherulitic Growth from Propagating Polyethylene Lamella

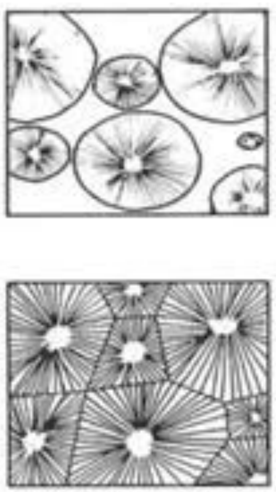


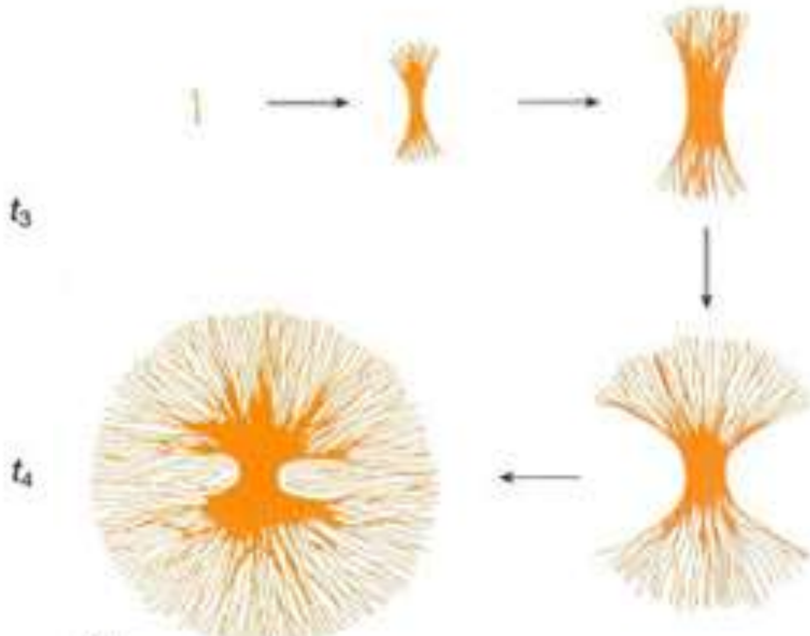
Spherulitic Growth from Propagating Polyethylene Lamella



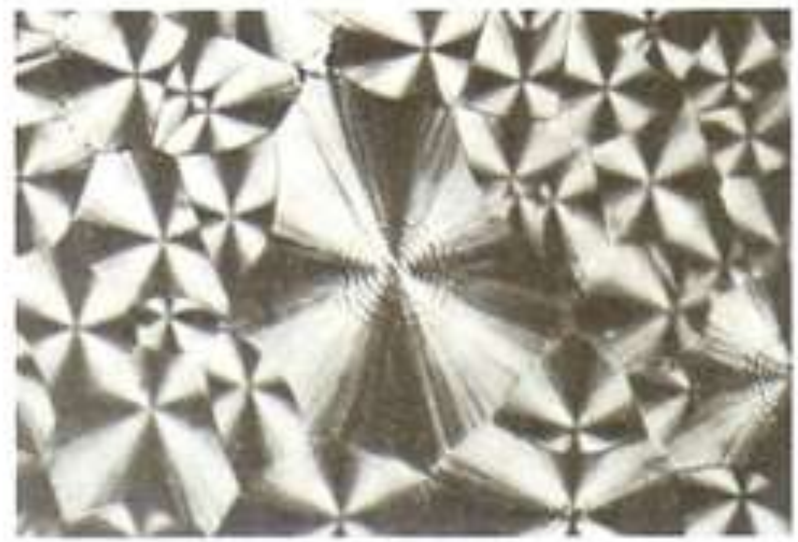


Formation of Bulk Polyethylene by Spherulitic Growth



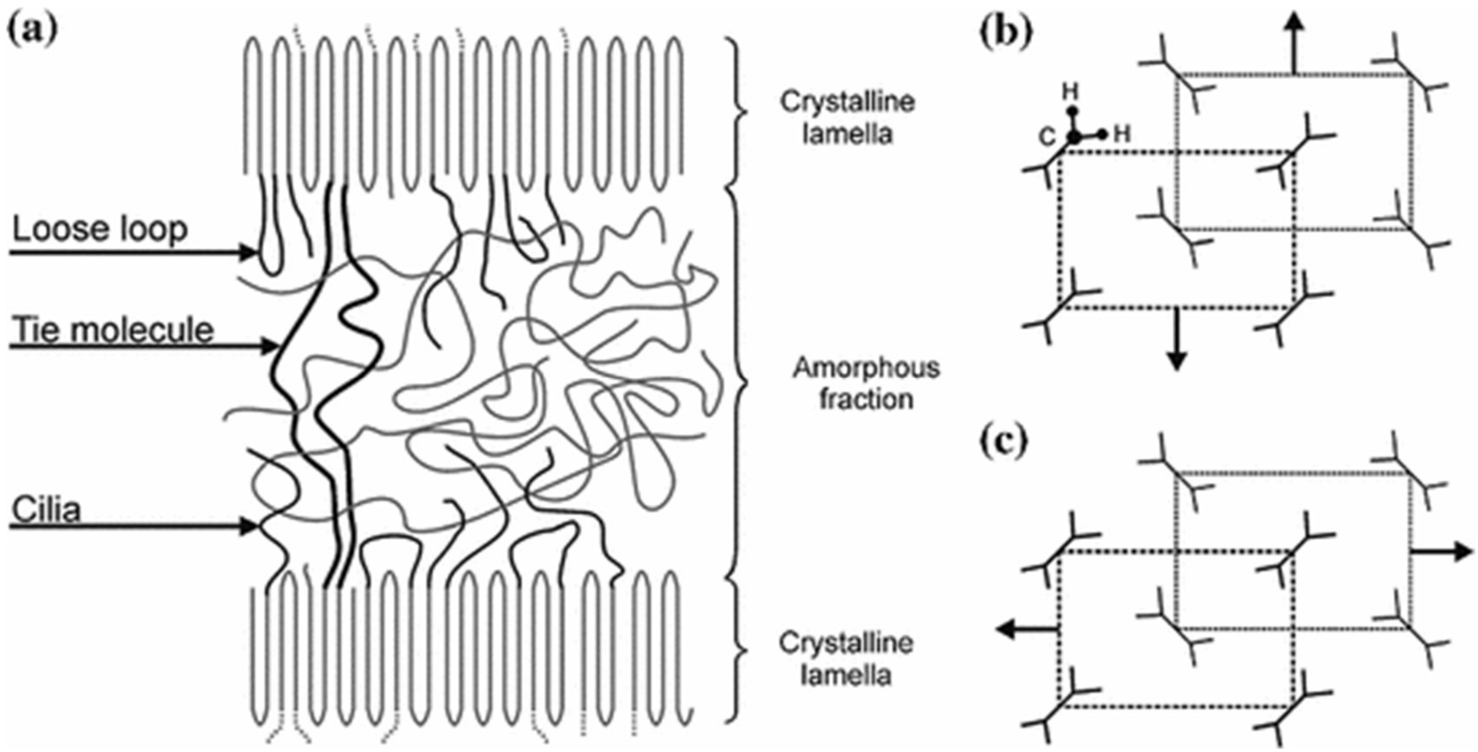


(a)



(b)

The Interlamellar and Interspherulitic Regions are the Amorphous Regions of Polyethylene



Boyer proposed that there exists two glass transition temperatures for polyethylene.

Glass Temperatures of Polyethylene

Raymond F. Boyer

The Dow Chemical Company, Midland, Michigan 48640.
Received July 3, 1972

Macromolecules, <u>6</u>, 288 – 299 (1973)

J. Poly., Sci., Symposium No. 50, 189 – 242 (1975)

“Linear and branched polyethylenes, especially in the Range of 50 – 75% crystallinity,, exhibit three amorphous Phase transitions or relaxation phenomena at the fol-Lowing temperature regions: 145 ± 10 K (-128 ± 10 C), 195 ± 10 K, (-78 ± 10 C) and 240 ± 20K (-33 ± 20 C).”

“Each of these regions has one or more characteristics of a true glass transition, i.e., an abrupt increase in the Coefficient of thermal expansion, and an abrupt increase in the specific heat; a dynamic mechanical loss peak Whose magnitude increases with amorphous content; . . .”

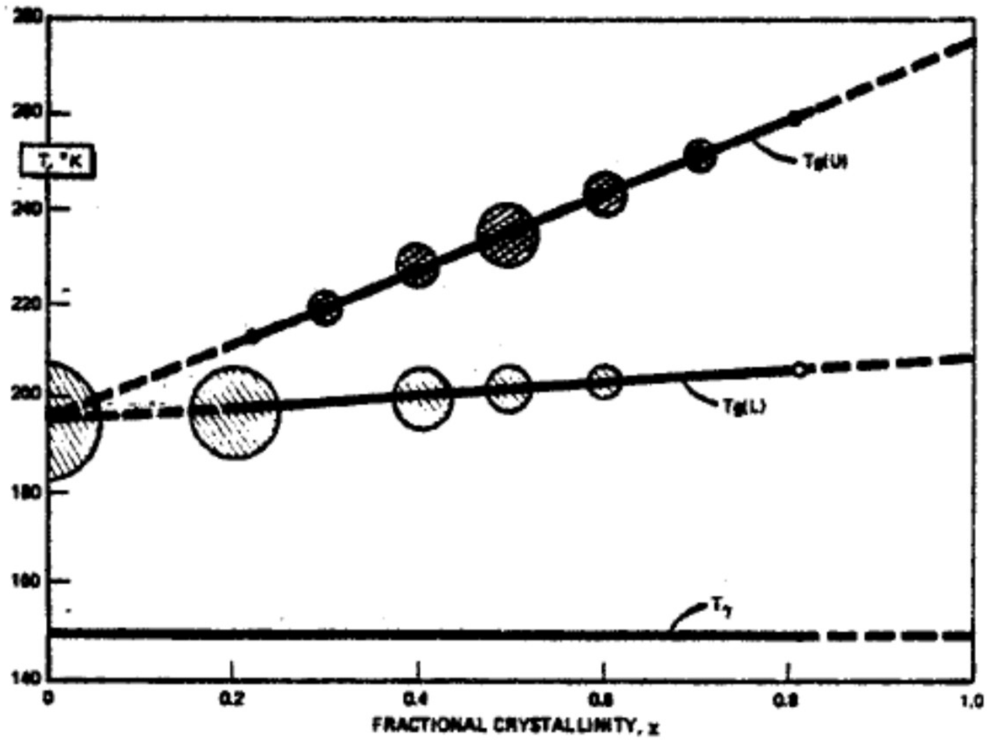


Figure 1. The double glass transition, T_g(L) and T_g(U), and the T_γ amorphous relaxation in linear polyethylene. The size of the circles indicate the intensity of the two glass transitions. Intensity of the T_γ transition increases continuously to the left. We associate T_g(L) with cilia and polymer chains rejected by crystallites; and T_g(U) with loose loops and/or tie molecules. This plot has been estimated by us from the thermal expansion data of Stehling and Mandelkern.[2]

Proposed Origin of Tg(L) and Tg(U)

(4) Partially crystalline polyethylenes exhibit two glass transitions: a Tg(L) around 195 K (-78 C) and a Tg(U) around 240 K (-33 C) but both increase linearly with crystallinity. (5) These are ascribed to the existence of two types of amorphous material. For example, Tg(L) may be associated with cilia and Tg(U) may arise from loose loops and or tie molecules.

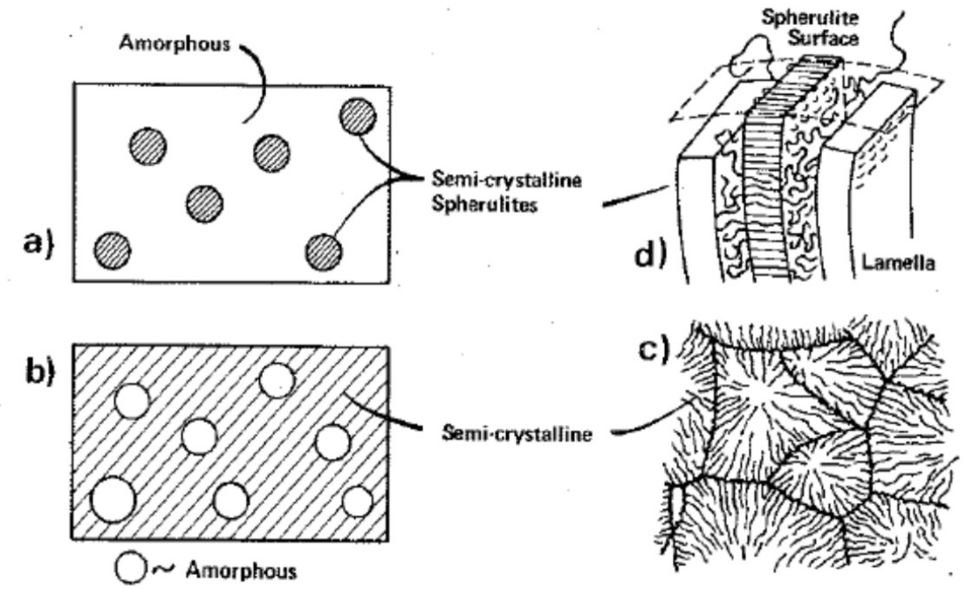
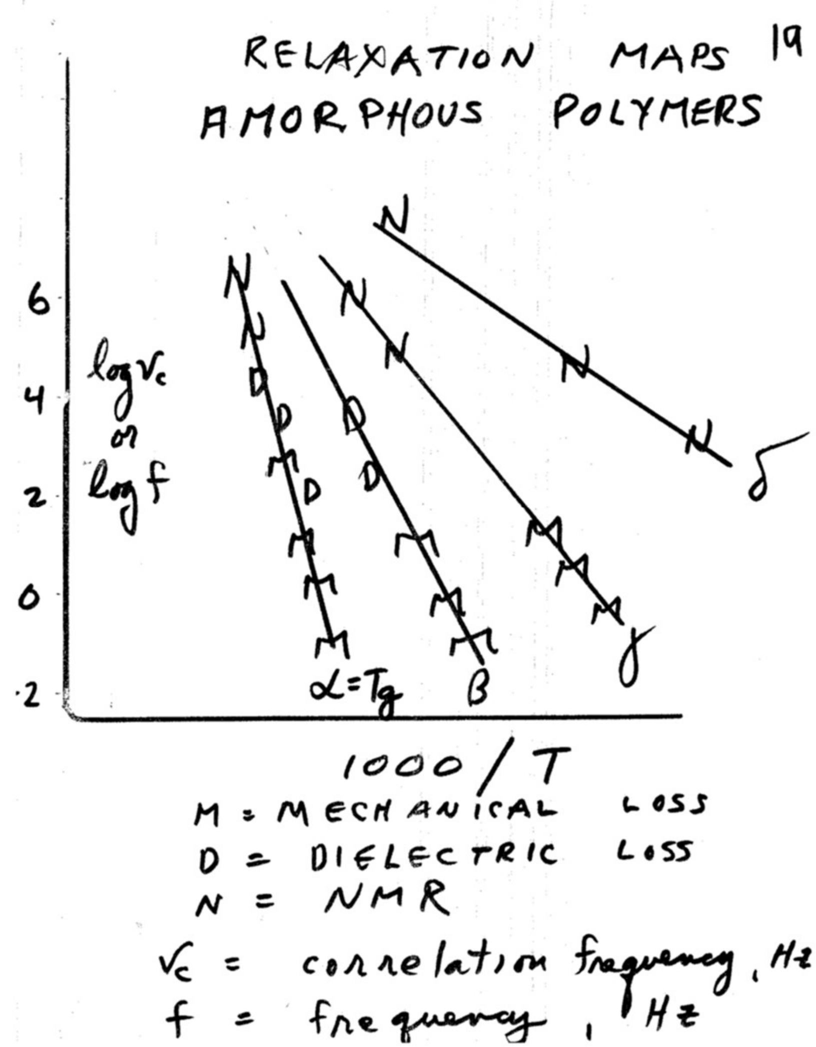


FIG. 9. Schematic morphology for the existence of a double glass transition. (a) isolated spherulites in continuous amorphous phase of $T_g = T_g(L)$; (b) rejected amorphous material of $T_g(L)$ at high x_c, actually appearing in grain boundaries as at (c); (d) Takayanagi model [34] showing interlamellar disorganized, or amorphous, material which may give rise to $T_g(U)$.

Image of Ray Boyer and Ray Boyer's class notes.

Plastics Hall of Fame Inductee



Critical Properties for the Differentiation of the Polyethylene Types

Density

Crystalline Region	
Perfect	1.00 g/cm3
Unit Cell Calculation (orthorhombic)	0.996
Single Crystal Determination	0.972
Amorphous Region	0.850 – 0.855

Transition Temperatures

Glass Transition Temperature	-78 C
Melt Transition Temperature (density dependent)	130-140 C

The Most Common Classification of Polyethylene is by Density

Table 1. Classification of polyethylenes by density

Resin family	*Lower density limit g/cc*	*Higher density limit g/cc*
High Density Polyethylene (HDPE)	0.941	0.975
Medium Density Polyethylene (MDP)	0.928	0.941
Linear Low Density Polyethyl-ene(LLDPE/LDPE)	0.915	0.928
Very Low Density Polyethylene (VLDPE)	0.900	0.915
Elastomers/Plastomers	0.865	0.900

Lesson 9: Polyolefins – PE 1

Questions?

Dr. Andy Olah, amo5@case.edu, O: 216-368-0606, C: 216-272-0505

"You always had the power my dear, you just had to learn it for yourself."

Glenda, (the good witch)
The Wizard of Oz (1939)