

Polymers and Their Mechanical Behavior

Polymer classifications

Molecular weight

Chemical structure

Secondary bonding forces

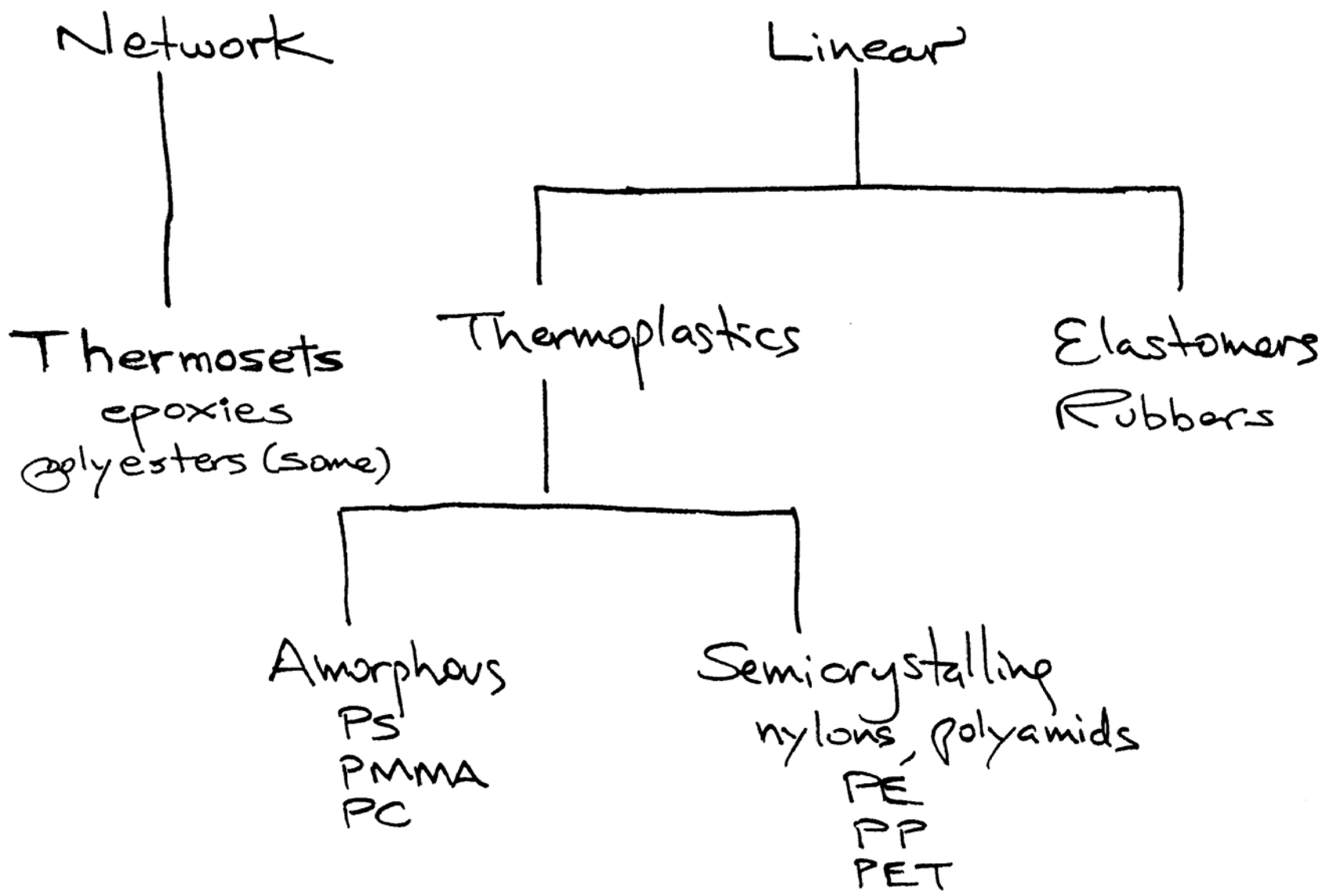
Crystallization

Glass transition

Crazing

Stress-strain response/mechanical behavior

POLYMER CLASSIFICATIONS



MOLECULAR WEIGHT

molecular size
⇓
flexible, chain-like structure

} ⇒ key to unusual properties of polymers

large total force fields between molecules
(secondary bond forces acting over large distances)

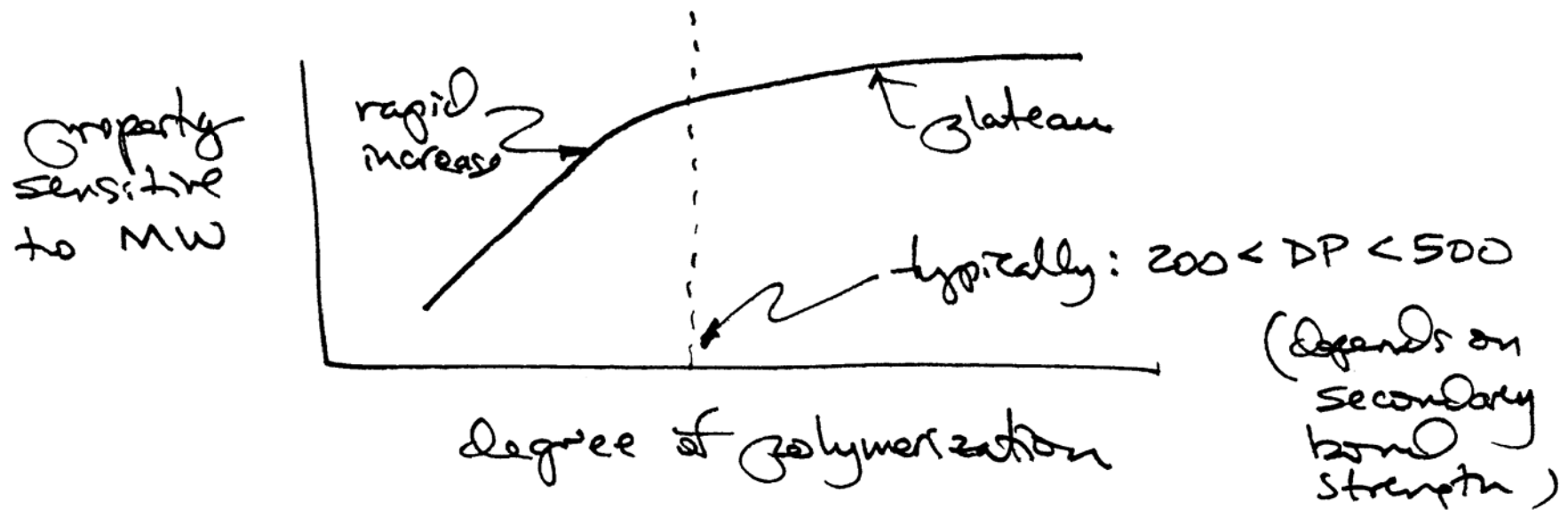
+
high degree of physical entanglement and interaction

Effect of MW on polymer behavior:

as MW \uparrow T_g
melt-flow T
melt & solution viscosities
tensile / impact strengths


} \uparrow

* "High MW" needed to get polymeric behavior



CHEMICAL STRUCTURE

Backbone :

- substituting C with O increases chain flexibility ($\therefore T_{mp} \downarrow$)
- substituting  for C decreases chain flexibility ($\therefore T_{mp} \uparrow$)

Pendant groups:

- if the substituent is linear, loose packing results (\therefore transition temperatures will be low)
- if the substituent is bulky and close to the backbone, stiffening of chain results (\therefore transition temperatures will be increased)

Crosslinking :

- stiffens polymer

NATURE OF SECONDARY INTERMOLECULAR BONDING FORCES

primary bonding {
metallic
covalent 30-220 kcal/mole
ionic 40-200 kcal/mole

* polymers → covalent primary bonds

	<u>energies (kcal/mole)</u>
<u>secondary bonding</u> { van der Waals induced dipole polar hydrogen ionic	0.5 - 2
	1.5 - 3
	3 - 7
	10 - 20

* polymers → secondary bonding very significant
(forces acting along great molecular lengths)

van der Waals bonding in polymers:

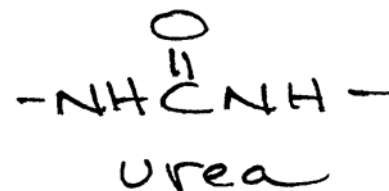
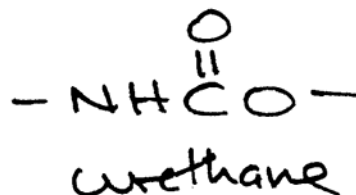
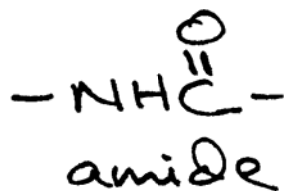
- associated with $-CH_2$ sequences in backbone
- lower T_{mp} ex: PE

polar bonding in polymers:

- associated with molecules containing $-O-$
- associated with side-chain units of:
 - CN
 - F
 - Cl
 - NO_2ex: PVC, PAN

hydrogen bonding in polymers:

H-F, H-N, H-O most highly polarized bonds



CRYSTALLIZATION IN POLYMERS

Occurs in some thermoplastics if:

- molecular structure is favorable
(spatial issues: packing of chains)
- secondary bonding is favorable
(e.g. nylon 6,6)
- slow cooled from melt; allowed to crystallize between T_m & RT; annealed

Mechanisms:

- chain folding
- spherulite formation

CRYSTALLITES & SPHERULITES

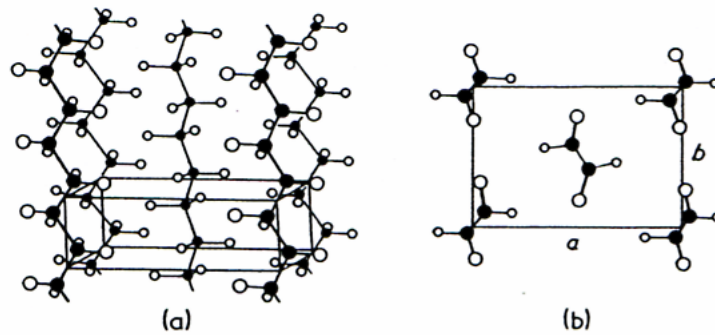


Fig. 4.5 Crystal structure of orthorhombic polyethylene. (a) General view of unit cell. (b) Projection of unit cell parallel to the chain direction, c. (● . . . carbon atoms, ○ . . . hydrogen atoms).

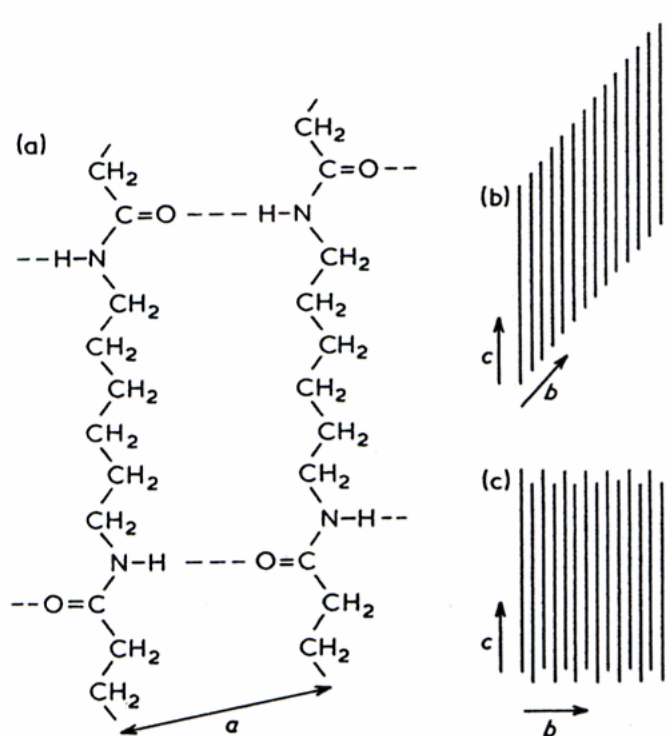


Fig. 4.7 Schematic representation of the α and β forms of nylon 66. (a) Molecular arrangement of hydrogen-bonded sheets common to both forms. (b) Stacking of sheets in the α form, viewed parallel to the sheets. (c) Stacking of the sheets in the β form. (After Wunderlich).

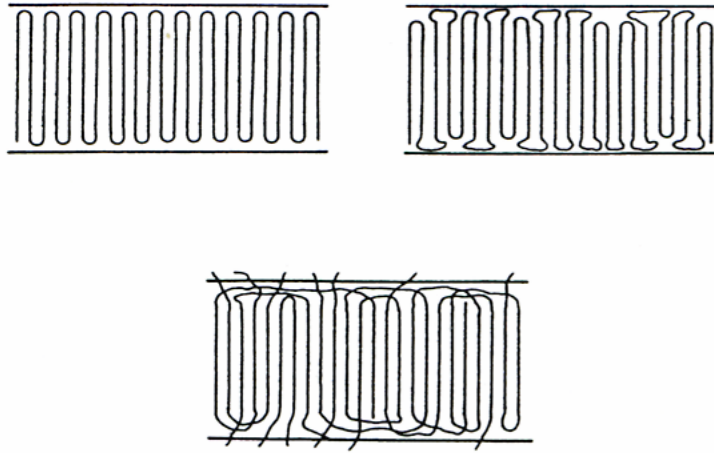


Fig. 4.11 Schematic illustrations of the different types of folding suggested for polymer single crystals. (a) Adjacent re-entry with sharp folds. (b) Adjacent re-entry with loose folds. (c) Random re-entry or 'switch-board' model.

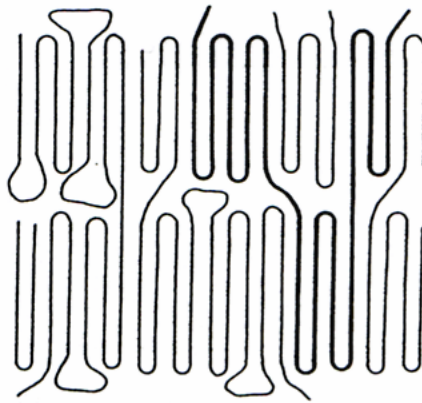


Fig. 4.17 A schematic representation of one possible model for the conformation of a deuterated polymer molecule (heavy line) in a matrix of protonated molecules (light lines).

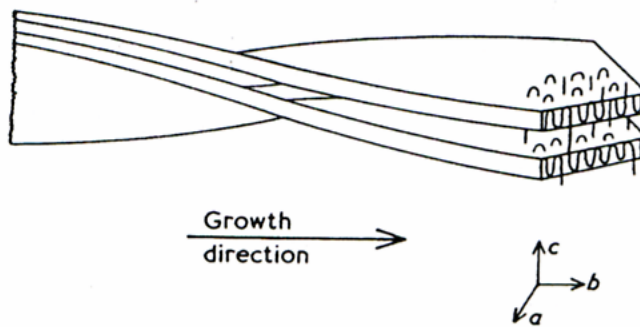


Fig. 4.16 Schematic representation of a possible model for twisted lamellae in spherulitic polyethylene showing chain-folds and intercrystalline links.

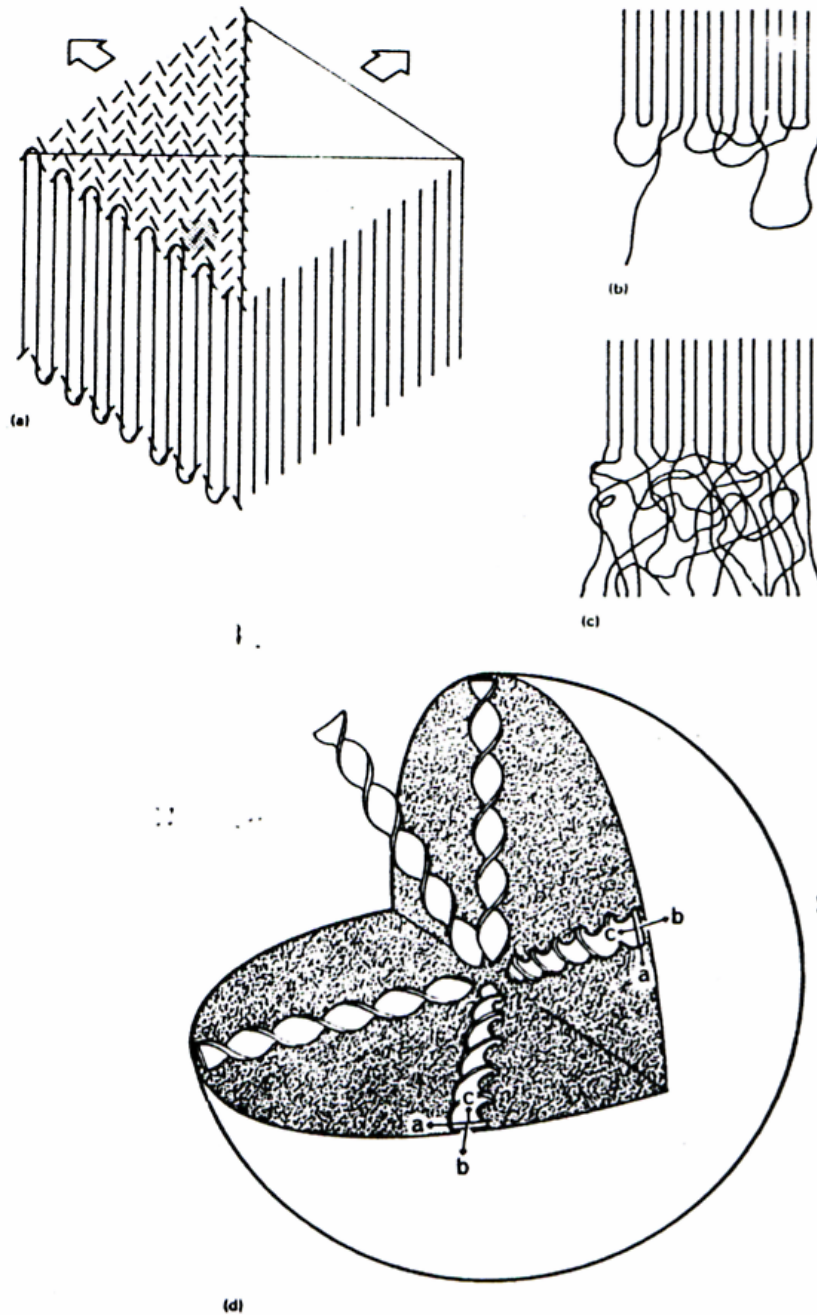


Figure 2.6 (a) Model of part of a lamellar polyethylene crystal with a regular folded chain structure. The unit cell, see figure 2.4(a), is shown shaded. The vertical lines represent the axes of the individual molecular chains. The loops at the fold surface depict orderly chain folding. (b), (c) Alternative models of the lamellar polymer crystal with disordered material at the fold surface, including switchboard loops and loose ends. (d) Structural organisation within the spherulite showing orientation of crystallographic axis: [reproduced by permission from P. J. Barham and A. Keller, *J. materials Sci.*, 12, 2141–2148 (1977)]

POLYMER MATERIALS (John Wiley, 1980)
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