Chapter 4. Structures of Polymers

Natural polymers: wood, rubber, cotton, wool, leather, silk

Synthetic polymers: plastics, rubbers, fibers

특징: 경량성, 저가, 만족할만한 물성, 가공성 용이

→ metals, ceramics 대체

Hydrocarbon Molecules

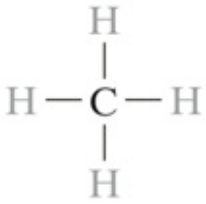
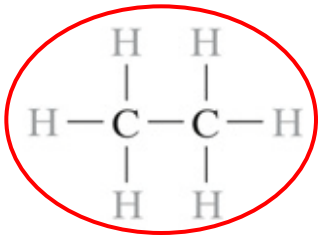
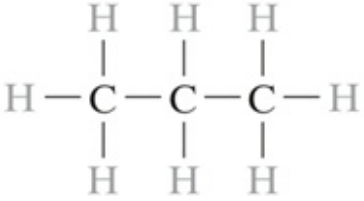
→ C & H로 구성

분자내 주된 결합은 공유결합

Saturated hydrocarbon (포화탄화수소): 모든 결합이 single bond

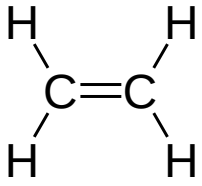
→ Paraffin 화합물 (C_nH_{2n+2})

Table 4.1 **Compositions and Molecular Structures for Some of the Paraffin Compounds: C_nH_{2n+2}**

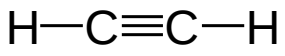
Name	*Composition*	*Structure*	*Boiling Point (°C)*
Methane	CH_4		−164
Ethane	C_2H_6		−88.6
Propane	C_3H_8		−42.1
Butane	C_4H_{10}	·	−0.5
Pentane	C_5H_{12}	·	36.1
Hexane	C_6H_{14}	·	69.0

Unsaturated hydrocarbon (불포화탄화수소)

→ double bond or triple bond를 갖는 탄화수소

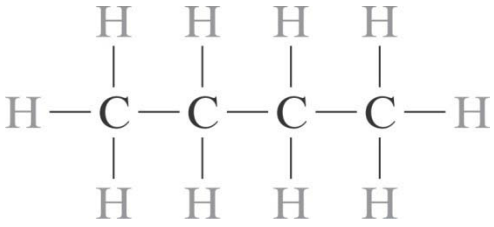


ethylene

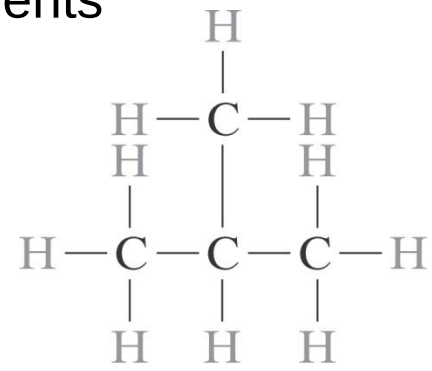


acetylene

- Isomerism (이성질): same composition, but different atomic arrangements

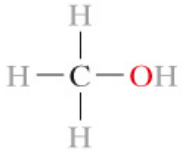
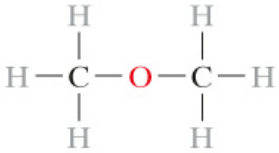
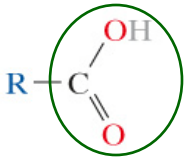
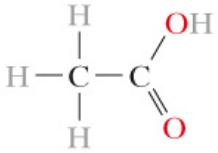
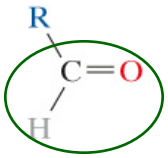
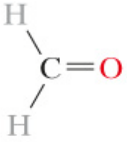
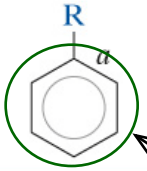
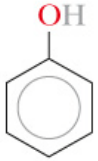


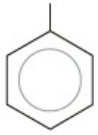
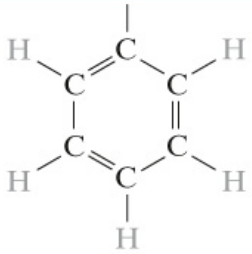
normal butane
(b.p. = -0.5 °C)



isobutane
(b.p. = -12.3 °C)

Table 4.2 Some Common Hydrocarbon Groups (고분자 구조에 흔한 유기화학 작용기)

Family	*Characteristic Unit*	*Representative Compound*
Alcohols		Methyl alcohol 
Ethers		Dimethyl ether 
Acids		Acetic acid 
Aldehydes		Formaldehyde 
Aromatic hydrocarbons		Phenol 

[a] The simplified structure  denotes a phenyl group, 

R & R' : alkyl group
(포화탄화수소 작용기)

ex.)

CH_3- (methyl)

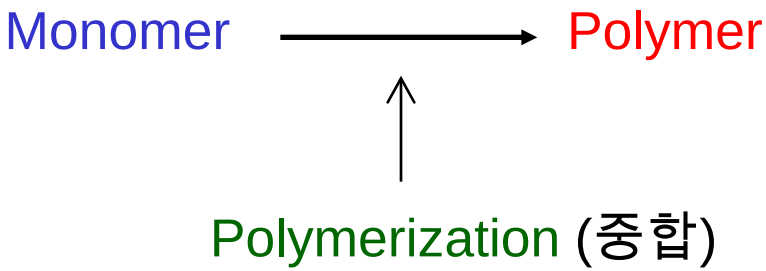
C_2H_5- (ethyl)

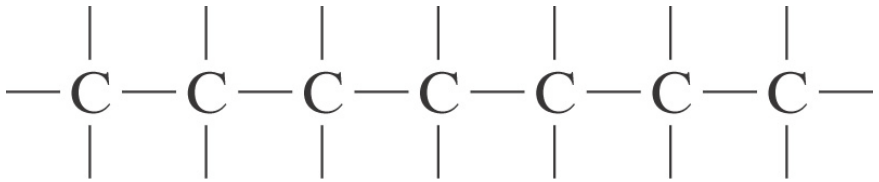
C_6H_5- (phenyl)

Polymer Molecules

→ "macromolecules" (거대분자)

Polymer (고분자, 폴리머): "poly" (many) + "mer" (part)
즉, many parts (여러 개의 부분이 합쳐진 것)
Monomer (단량체): 고분자 합성에 사용되는 기본 분자

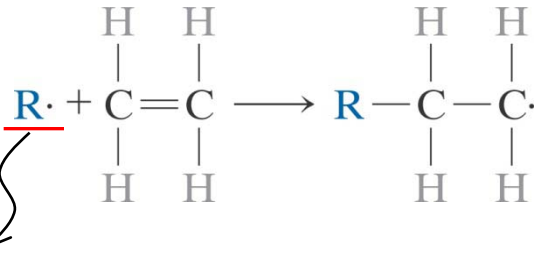




: Polymer backbone의 예
(공유결합으로 연결)

Chemistry of Polymer Molecules

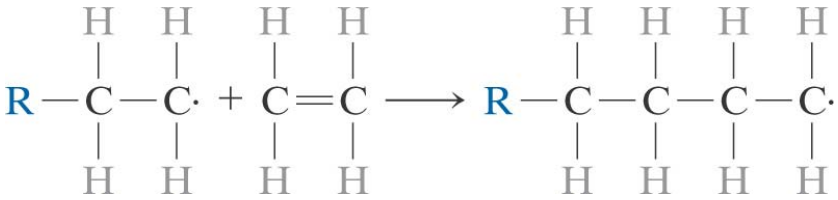
Ex.) Polyethylene (PE)의 중합 과정



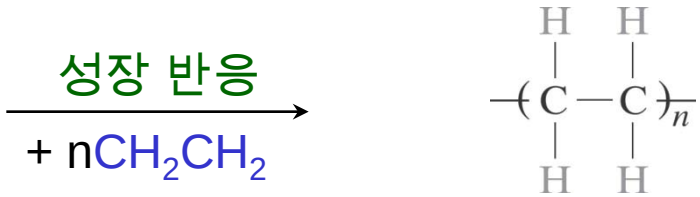
(개시 반응)

Active species (from initiator or growing radical)

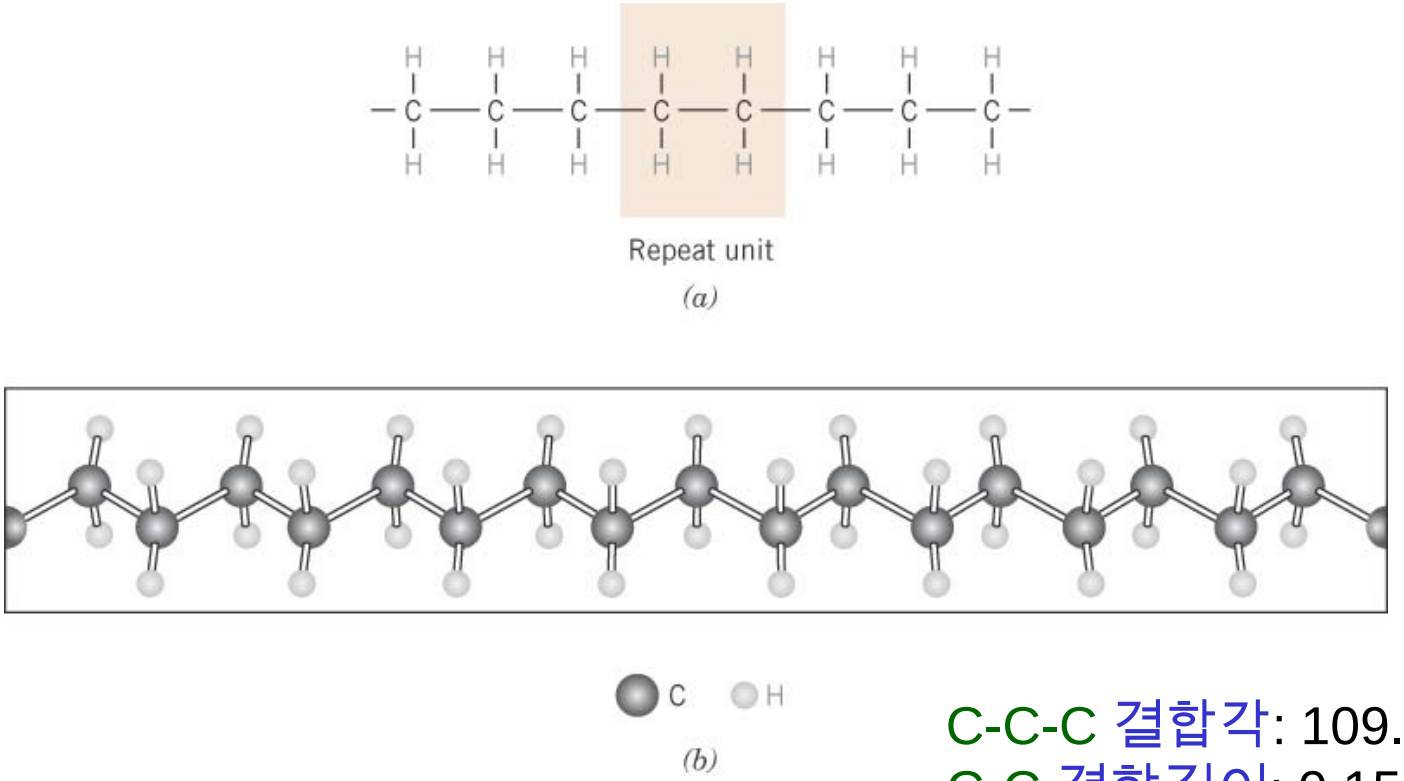
Radical (·): active site, unpaired electron, free radical



(성장 반응)

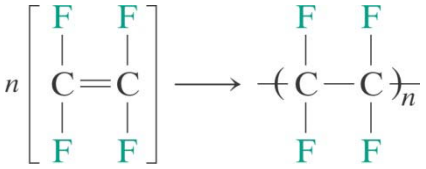


: PE (폴리에틸렌)

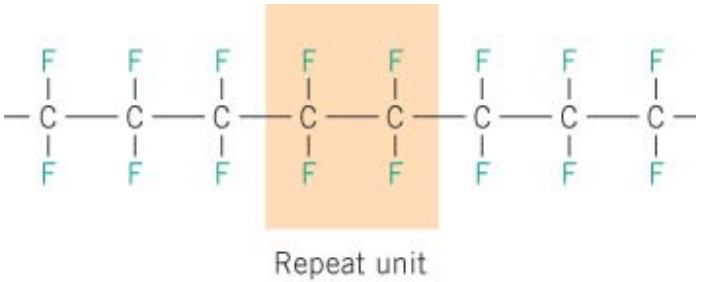


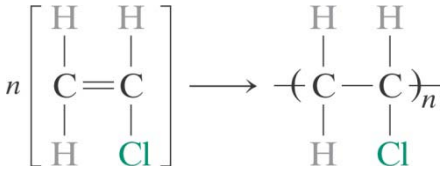
C-C-C 결합각: 109.28°
C-C 결합길이: 0.154 nm

Fig. 4.1 Polyethylene의 구조: (a) 사슬(chain) 구조와 반복 단위, (b) zigzag backbone 구조를 표시한 3차원 모형.



tetrafluoroethylene





vinyl chloride

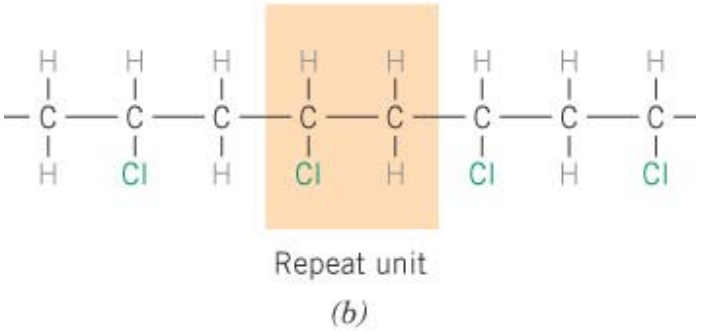
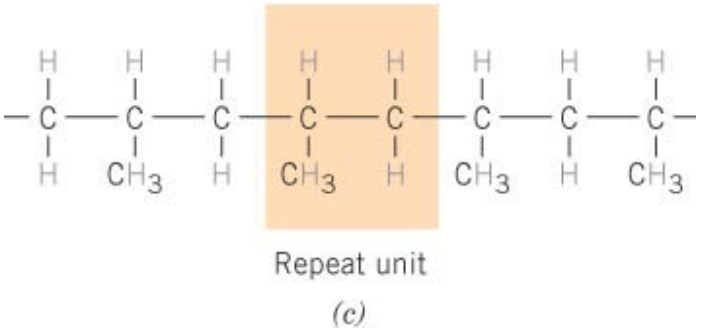
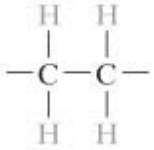
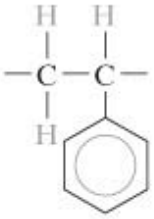


Fig. 4.2 몇 가지 고분자의 반복단위와 사슬구조:
(a) polytetrafluoroethylene (PTFE),
(b) polyvinyl chloride (PVC),
(c) polypropylene (PP).



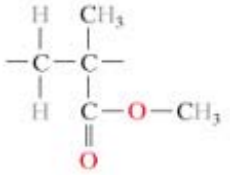
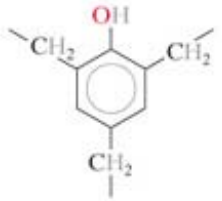
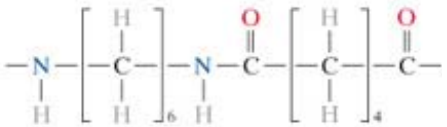
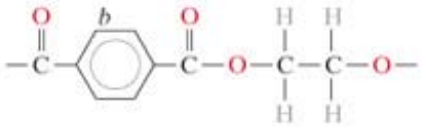
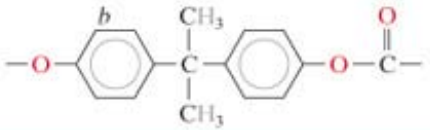
VMSE
► Repeat Unit Structures

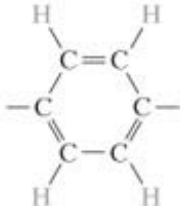
Table 4.3 A Listing of Repeat Units for 10 of the More Common Polymeric Materials

Polymer	*Repeat Unit*
 Polyethylene (PE)	
 Poly(vinyl chloride) (PVC)	
 Polytetrafluoroethylene (PTFE)	
 Polypropylene (PP)	
 Polystyrene (PS)	

(*Continued*)

Table 4.3 (Continued)

Polymer	Repeat Unit
VMSE ► Repeat Unit Structures  Poly(methyl methacrylate) (PMMA)	
 Phenol-formaldehyde (Bakelite)	
 Poly(hexamethylene adipamide) (nylon 6,6)	
 Poly(ethylene terephthalate) (PET, a polyester)	
 Polycarbonate (PC)	

[b] The  symbol in the backbone chain denotes an aromatic ring as 

- Homopolymer (단일중합체)
  : 사슬을 따라 반복되는 반복단위가 동일한 고분자

- Copolymer (공중합체)
  : 둘 이상의 서로 다른 반복단위로 구성된 고분자

- Bifunctional monomer (이작용성 단량체)
  : 다른 단량체와 두 개의 공유결합을 형성해 이차원 사슬형 분자구조를 형성하는 단량체 (예: ethylene)

- Trifunctional monomer (삼작용성 단량체)
  : 다른 단량체와 세 개의 공유결합을 형성해 삼차원 망상형 분자구조를 형성하는 단량체 (예: phenol-formaldehyde)

Molecular Weights (분자량)

Polymer는 중합시 chain length가 다양

→ molecular weight distribution (MWD)를 지님

∴ Average molecular weight (평균 분자량)을 사용

- Number-average molecular weight (수평균 분자량)

$$\overline{M}_n = \sum x_i M_i$$

x_i: number fraction (수분율)

i 범위에 있는 고분자의 분자량

- Weight-average molecular weight (중량평균 분자량)

$$\overline{M}_w = \sum w_i M_i$$

w_i: weight fraction (중량분율)

i 범위에 있는 고분자의 분자량

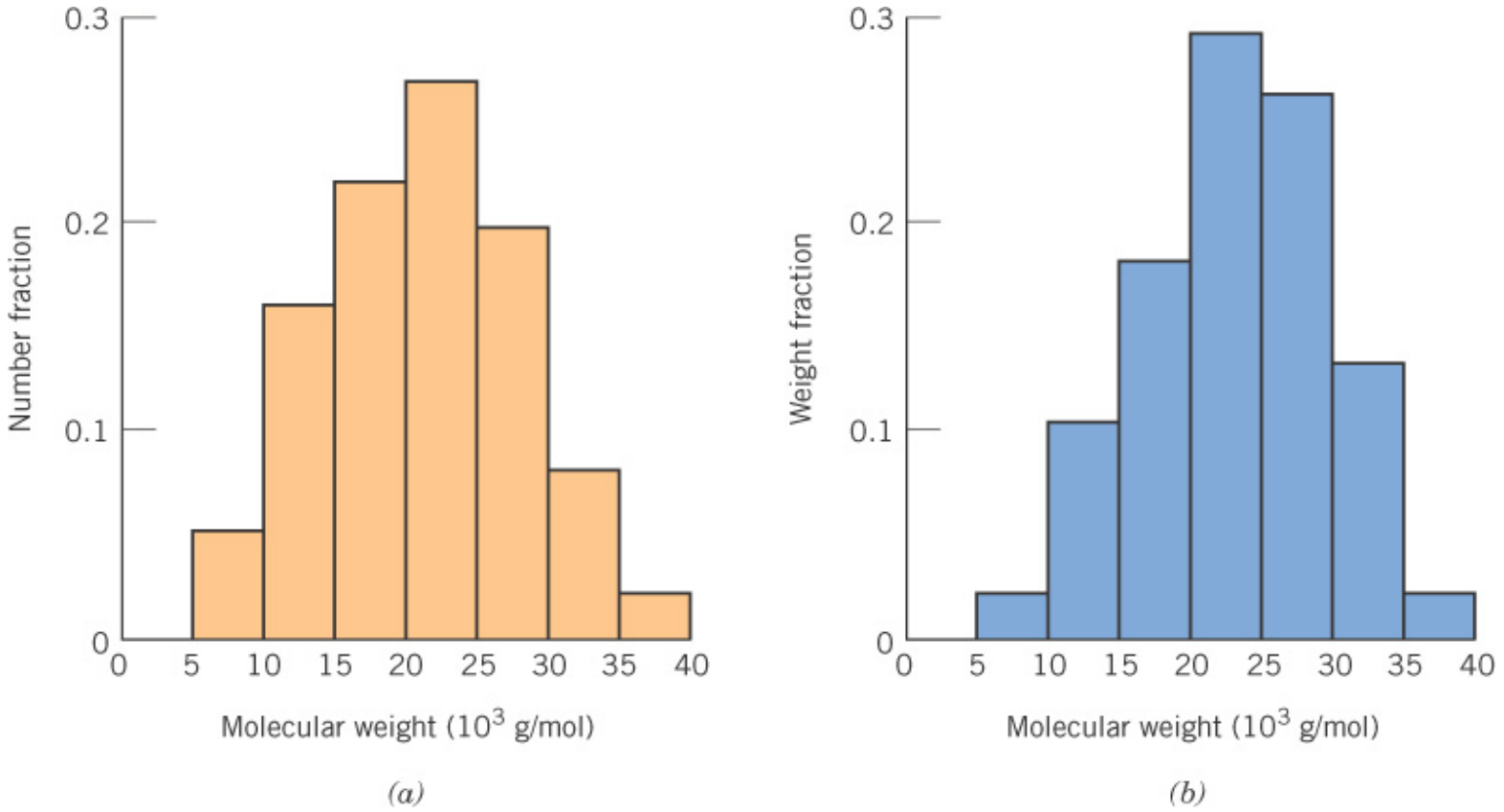


Fig. 4.3 고분자의 분자량 분포(MWD)에 대한 막대 그래프:
(a) 수분율로 표시한 분자량 분포, (b) 중량분율로 표시한 분자량 분포.

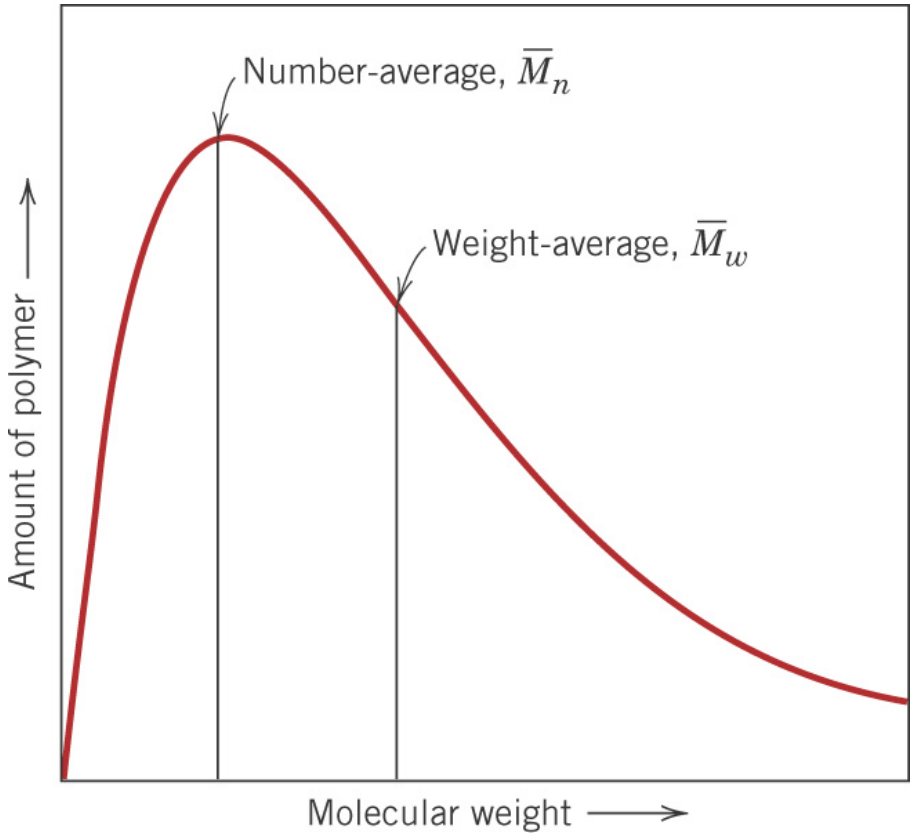


Fig. 4.4 전형적인 고분자에 대한 분자량 분포 (MWD), 수평균 분자량 ($\overline{M}_n$) 및 중량평균 분자량 ($\overline{M}_w$).

- Degree of Polymerization (중합도)

: 고분자 사슬 속의 평균적인 반복단위(repeat units) 수

$$DP = \frac{\overline{M}_n}{m}$$

$\overline{M}_n$ ⟶ 수평균 분자량

m ↘ 반복단위의 분자량

Ex. 4.1) Fig. 4.3의 그래프로 표시된 PVC의 분자량 분포 자료로부터 (a) 수평균 분자량, (b) 중합도, (c) 중량평균 분자량을 계산

→ 예제 풀이를 참고하여 각자 풀어 볼 것.

Molecular Shape

↘ Single bond(단일 결합)로 된 사슬은 rotating, bending 가능

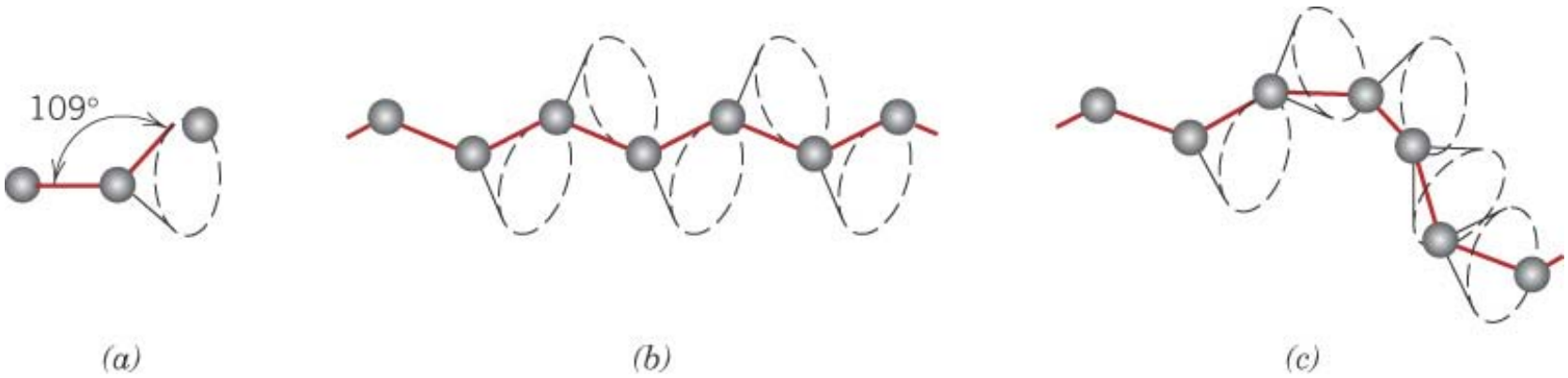
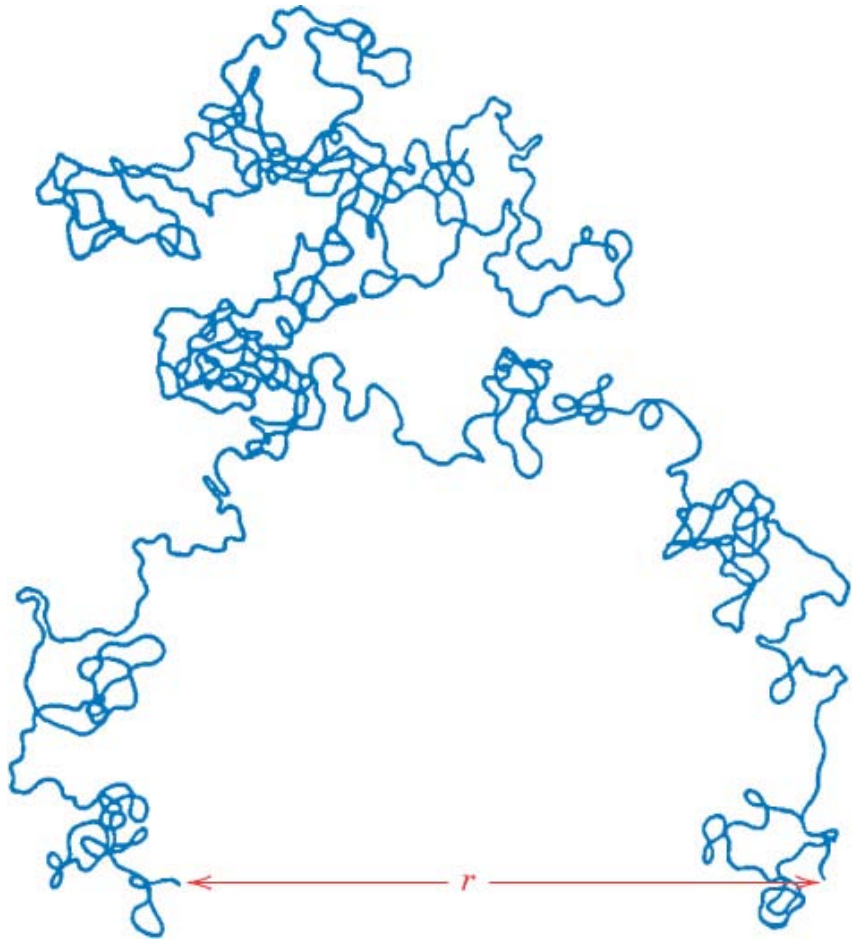


Fig. 4.5 주사슬 탄소 원자의 위치에 따른 고분자 사슬 형상의 모식도:

(a) 결합각을 유지하면서 점선 표시한 위치에 존재 가능

(b) 주사슬 분절(segment)이 선형 구조로 배열된 고분자 사슬

(c) 주사슬 분절이 꼬인(twisted) 구조로 된 고분자 사슬.



r (end-to-end distance):
고분자 사슬의 크기를
나타내는 양단간 거리

Fig. 4.6 임의의 형상을 갖는
고분자 사슬의 개략도.

* Conformation: 단일결합 사슬 원자의 회전에 의해 변경될 수 있는 사슬 배열

Polymer properties (고분자 물성)

: chain length(즉, 분자량)에 영향을 받음

예) 고분자의 상온에서의 대략적 상태

short chain (M ≈ 수백 g/mol): liquids

M ≈ 수천 g/mol 근처: oligomers (wax or soft resins)

long chain (M ≈ 만 g/mol 이상): solid polymers

Rotational flexibility (회전 유연성)

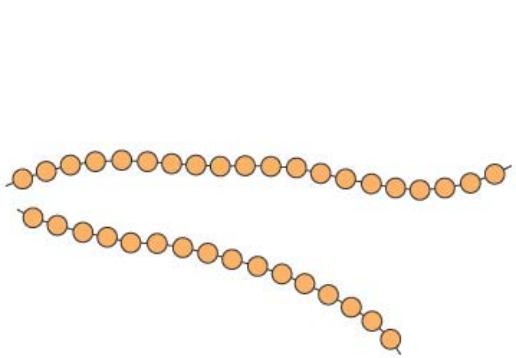
: repeat unit 구조 및 chemistry에 의존

예) C=C (이중결합) 및 C≡C (삼중결합): 회전운동 못함 (rigid)

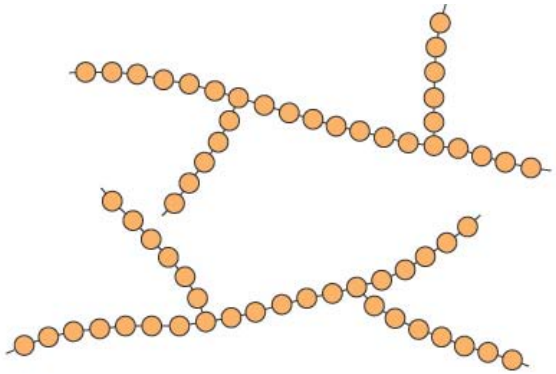
bulky side group (부피 큰 곁가지 화학기): 회전운동 제약

Polymer Structure

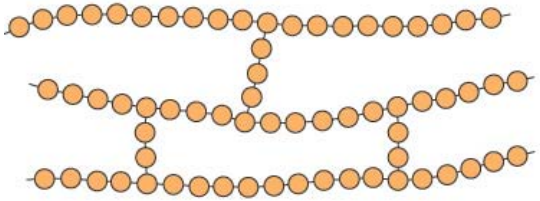
→ Polymer chain은 선형, 가지형, 가교형, 망상형 구조 등 다양



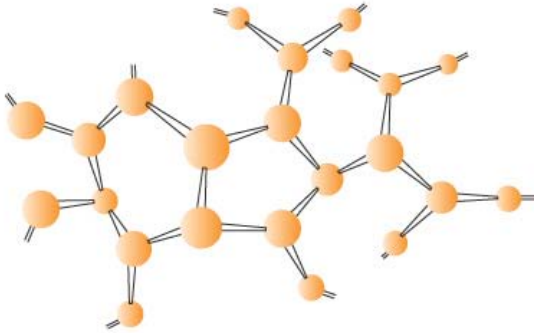
linear (선형)



branched (가지형)



crosslinked (가교형)



network (망상형)

Linear polymers: high-density PE (HDPE), PS, PVC, PMMA, nylon, etc.

Branched polymers: low-density PE (LDPE)

Crosslinked polymers: vulcanized rubbers

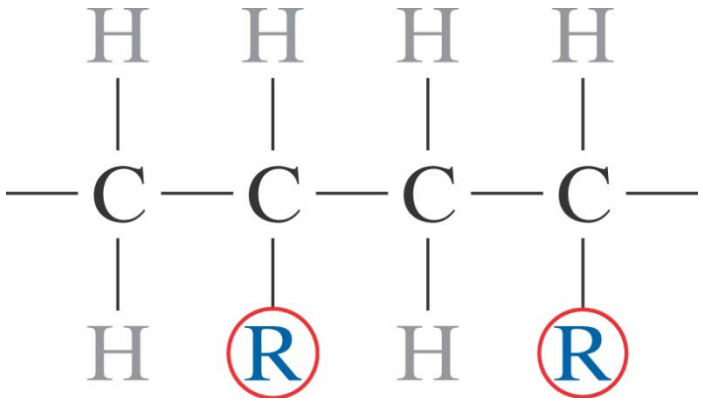
Network polymers: epoxy, polyurethane, phenol-formaldehyde

Fig. 4.7 고분자의 다양한 분자 구조.

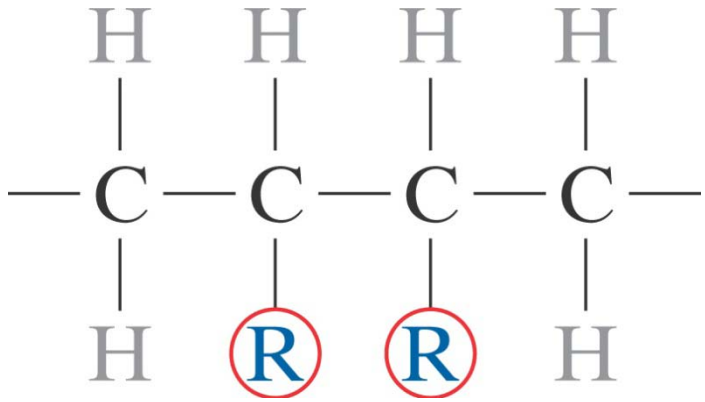
Molecular Configurations

↘ 주결합을 끊어 재형성하지 않고는 바뀔 수 없는 사슬 배열

- **Head-to-tail & head-to-head configuration**



Head-to-tail configuration
→ 일반적으로 선호

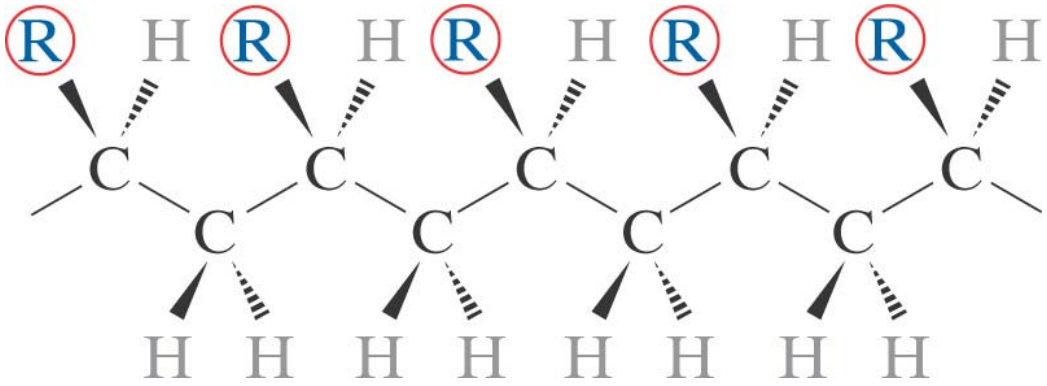


Head-to-head configuration
→ R 기 사이에 극성반발이 일어날 수 있음

- **Stereoisomerism** (입체 이성질체)

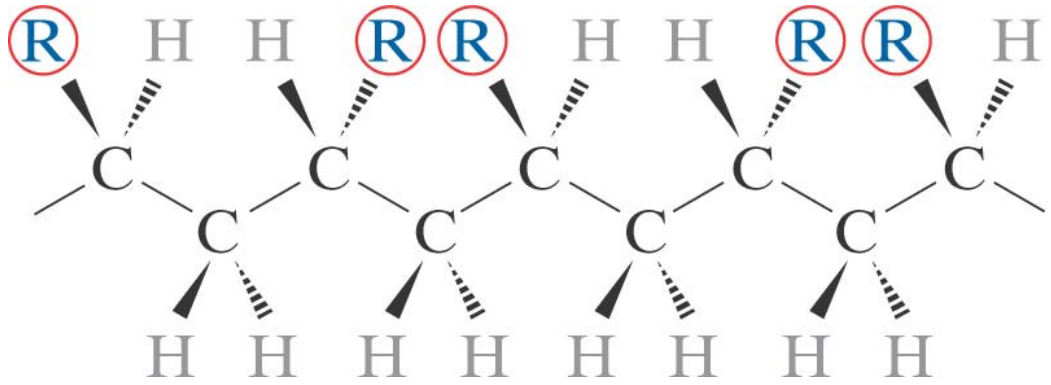
  - Isotactic configuration:

    → R 기가 모두 같은 면에 위치



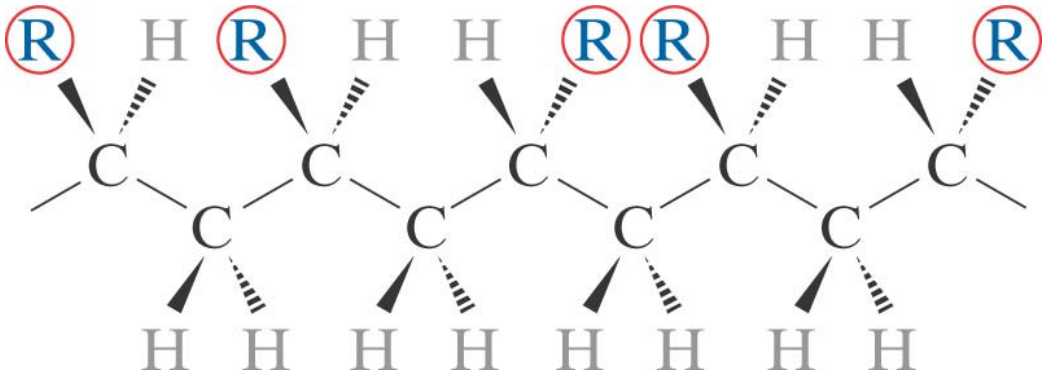
- Syndiotactic configuration:

→ R 기가 면 앞뒤로 번갈아 가며 위치



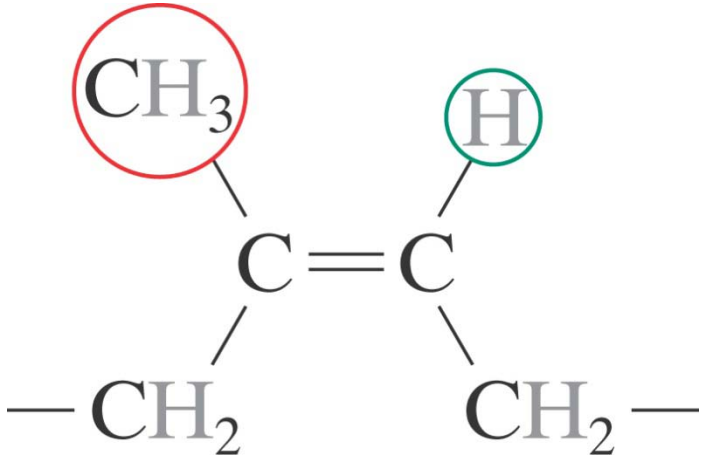
- Atactic configuration:

→ R 기의 배열에 규칙성이 없이 위치

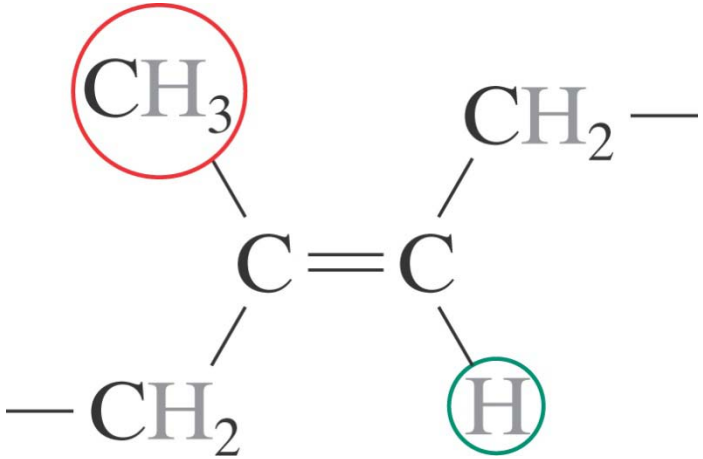


- **Geometrical isomerism** (기하 이성질체)

- Cis structure:



- Trans structure:



→ Polyisoprene의 *cis* 구조와 *trans* 구조에 대한 예

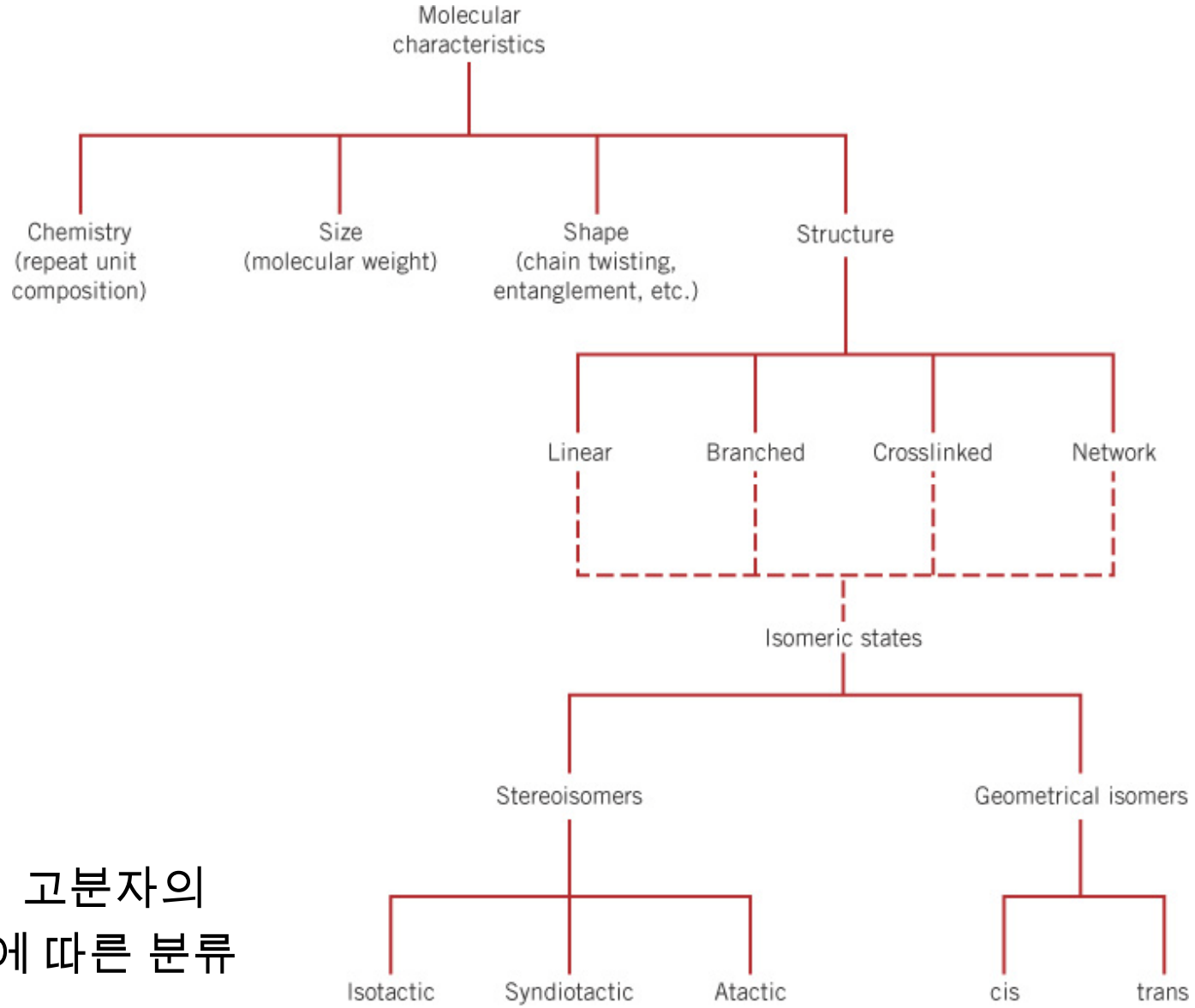


Fig. 4.8 고분자의 특징에 따른 분류

Thermoplastic & Thermosetting Polymers

Thermoplastic polymers (열가소성 고분자)

→ Soften when heated
& harden when cooled
(reversible), 유연함
(예: 선형 및 가지형 범용 고분자)

Thermosetting polymers (열경화성 고분자)

→ Permanently hard when heated
(irreversible), 단단함
dimensional stability ↑
(예: epoxy, phenol, polyester 수지 등)

Copolymers (공중합체)

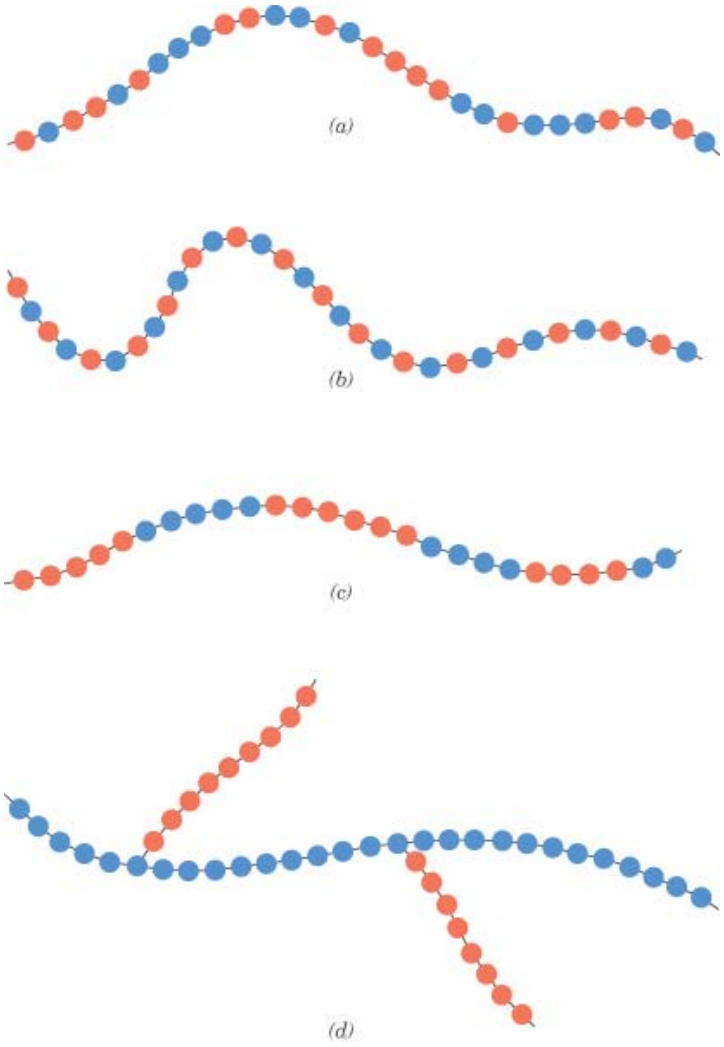
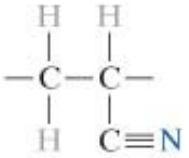
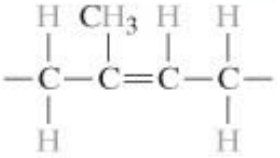
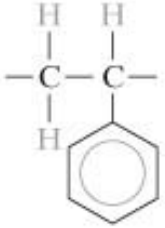
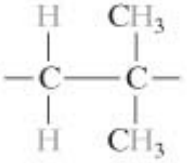
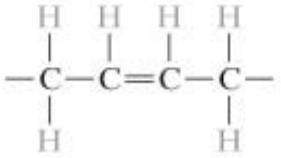
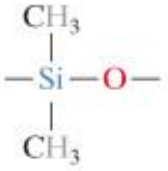
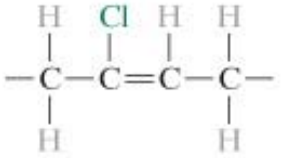


Fig. 4.9 다양한 공중합체에 대한 개략도: (a) random copolymer (임의, 불규칙 공중합체), (b) alternating copolymer (교대, 교호 공중합체), (c) block copolymer (블록 공중합체), (d) graft copolymer (그래프트, 접목 공중합체).

VMSE
► Repeat Units
Rubbers

Table 4.5 Chemical Repeat Units That Are Employed in Copolymer Rubbers

Repeat Unit Name	Repeat Unit Structure	Repeat Unit Name	Repeat Unit Structure
Acrylonitrile		Isoprene	
Styrene		Isobutylene	
Butadiene		Dimethylsiloxane	
Chloroprene			

Polymer Crystallinity

→ 고분자는 atoms, ions 대신 사슬로 된 분자로 이루어져 metal, ceramic보다 원자 배열이 복잡

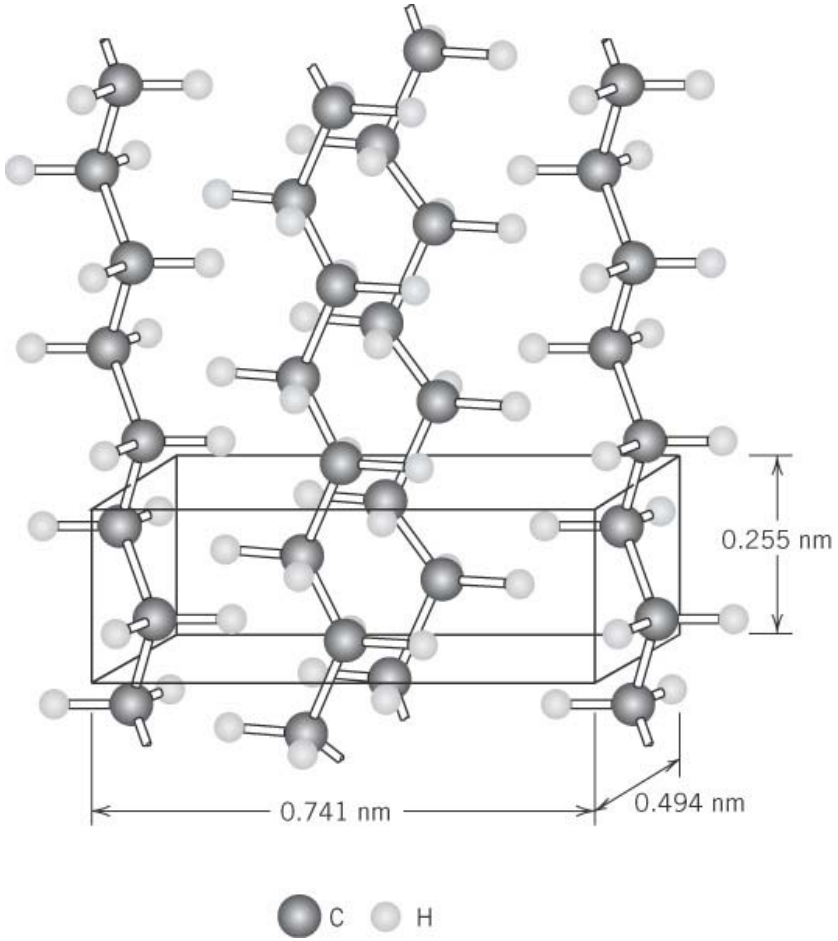


Fig. 4.10 폴리에틸렌 결정구조에 대한 모형: 직육면체는 PE의 unit cell을 나타내는 것으로 orthorhombic geometry ($a \neq b \neq c$, $\alpha=\beta=\gamma=90^{o}$)를 보여줌.

- 고분자의 결정성은 0 ~ 95% 까지 존재

→ Semicrystalline (반결정성)

금속 ~ 완전 결정

세라믹 ~ 완전 결정 or 무정형

- Degree of crystallinity (결정화도)

→ 원자 배열 (결정성은 무정형보다 구조가 조밀) 및 냉각 속도 (급랭보다 서랭의 경우가 결정화도↑)에 의존

- 결정성 고분자는 밀도↑ , 강도↑, 내화학성↑, 내열성↑

Polymer Crystals

→ 작은 결정 영역(crystallites)과 무정형 영역이 혼재된 구조로 이루어짐

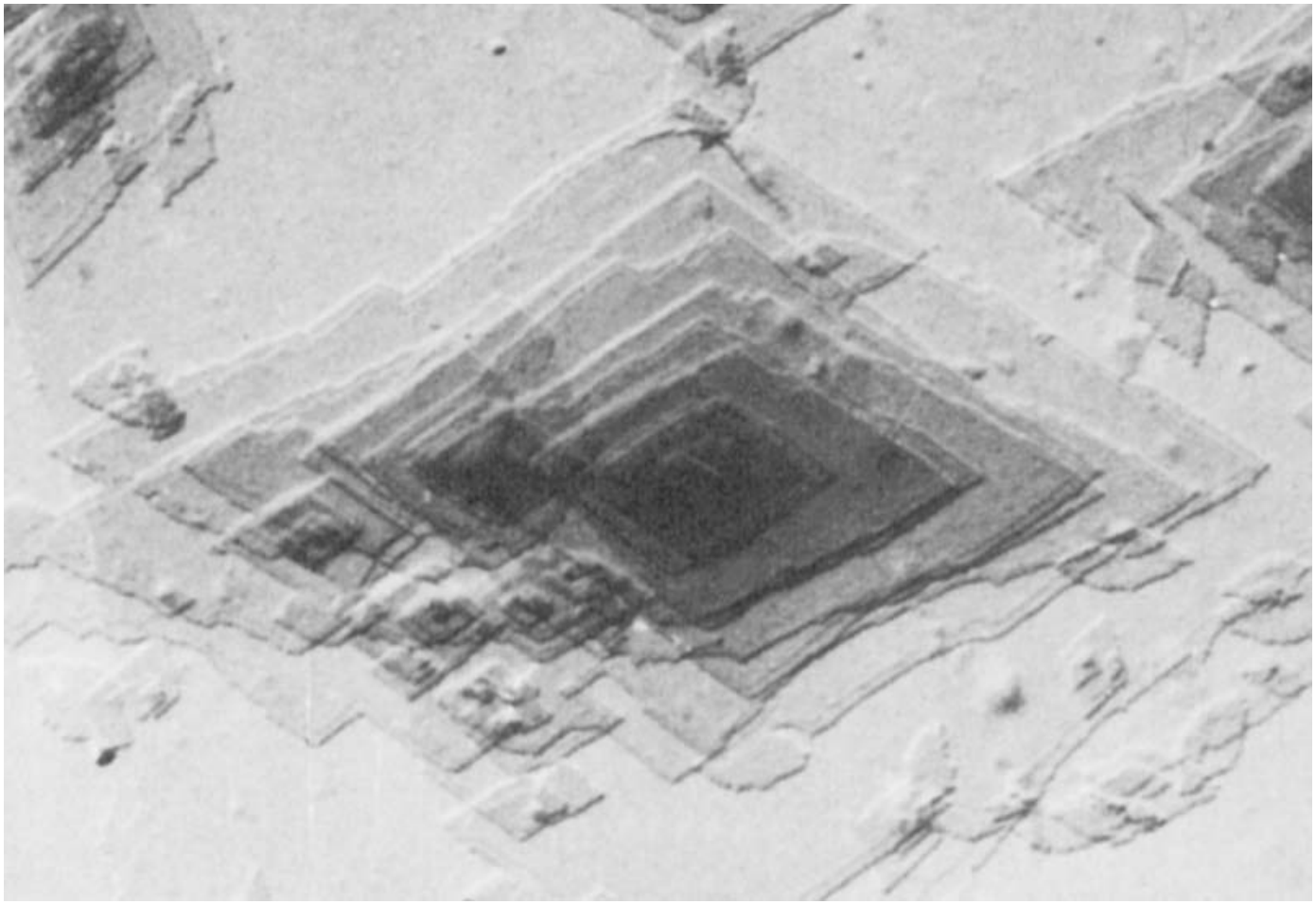


Fig. 4.11 폴리에틸렌 단결정 (single crystal)의 전자현미경 사진.

- Chain-folded model (사슬 접힌 모형)

  → 작은 결정 영역(crystallites)과 무정형 영역이 **혼재**된 구조로 이루어짐

  → 묽은 고분자 용액에서 성장시킨 고분자 단결정에 대한 모형

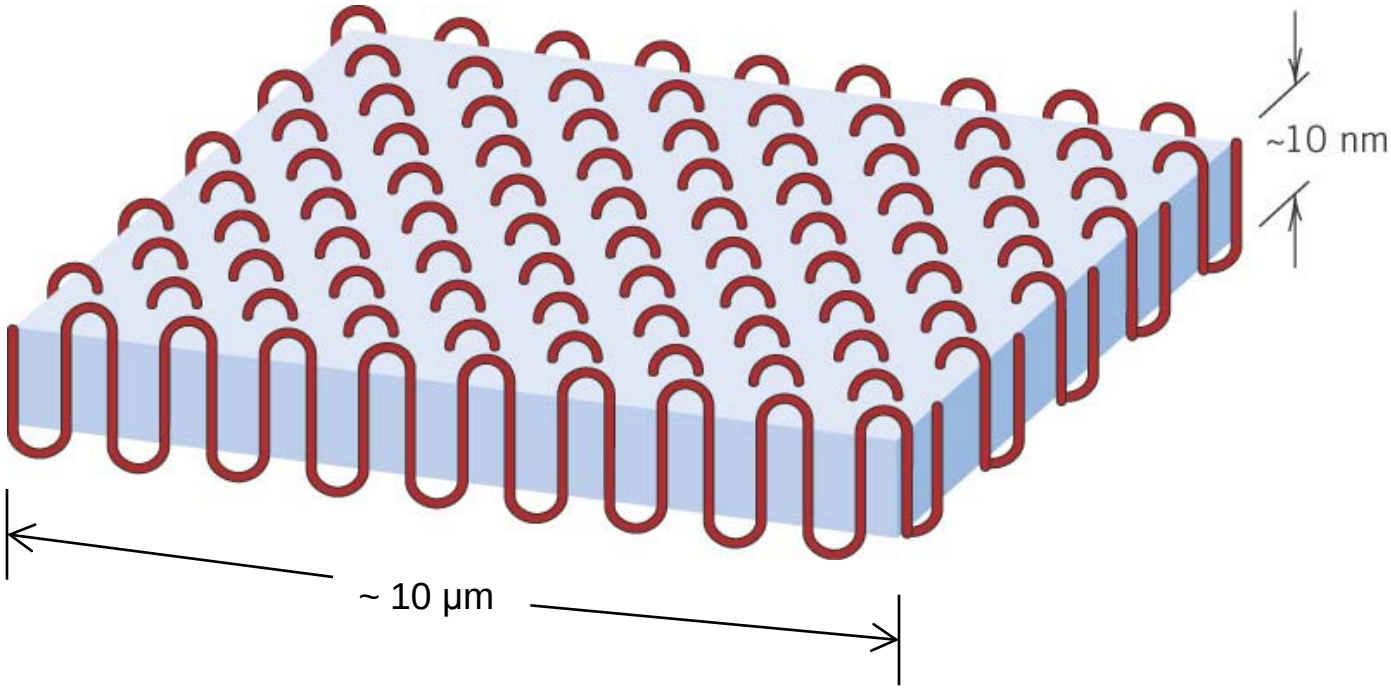


Fig. 4.12 판상 고분자 결정체 (단결정)에 대한 사슬접힌 모형.

- Spherulites (구정)

  → 용융체(melt)로부터 결정화된 고분자의 결정구조

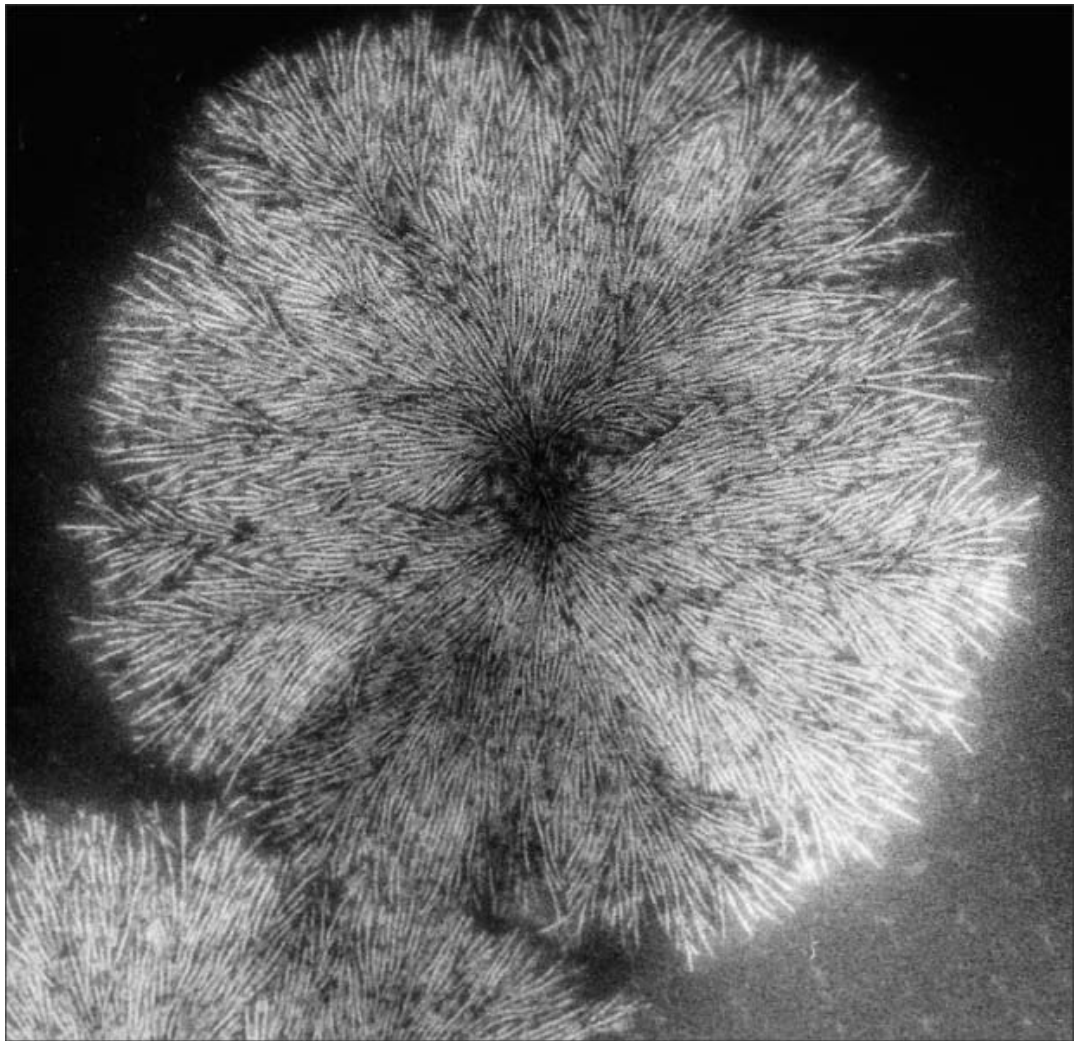


Fig. 4.0 (4장 표지 그림) 천연고무의 구정 구조에 대한 전자현미경 사진 (30,000 배 확대).

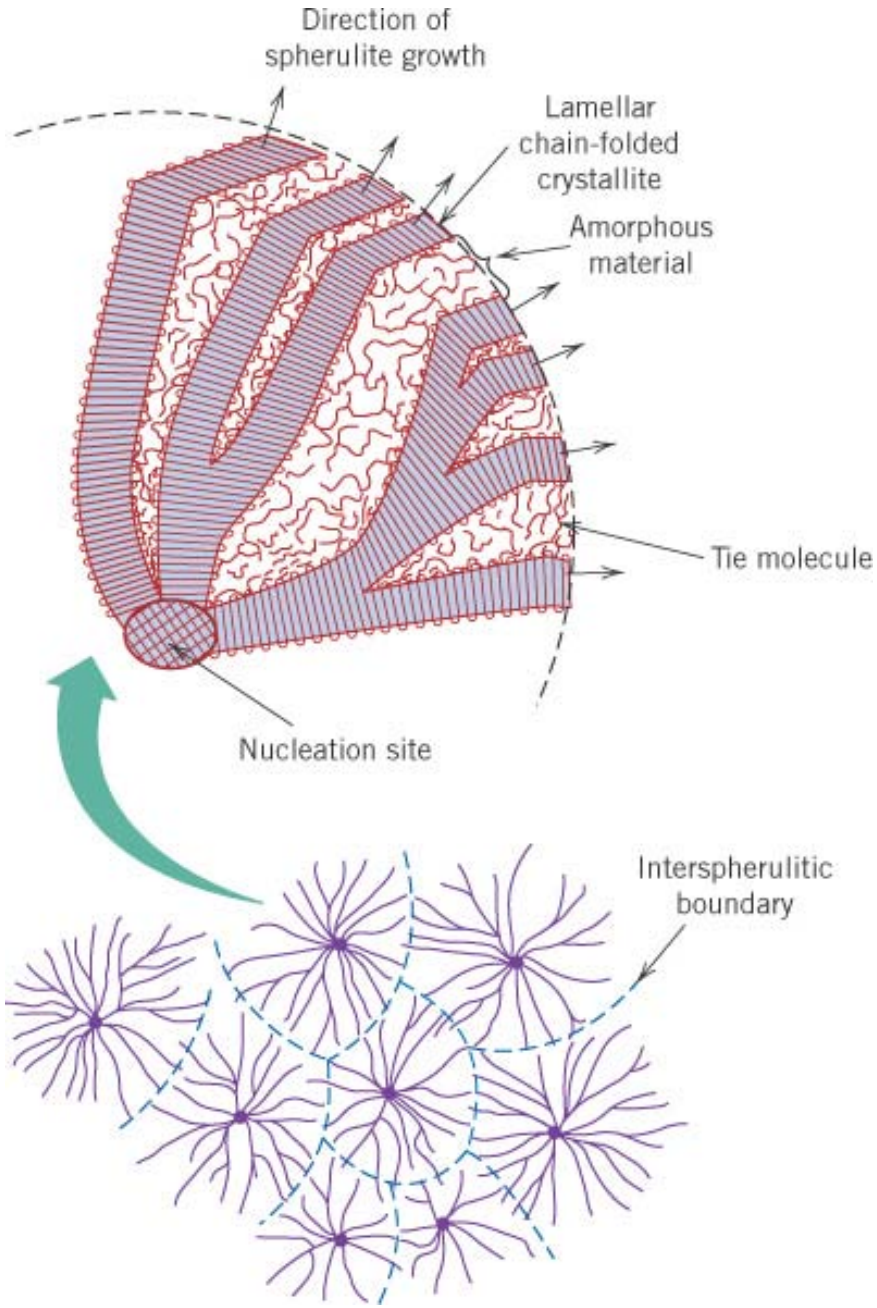


Fig. 4.13 Spherulite의 상세 구조에 대한 개략도: 각 구정은 복잡한 다결정으로 이루어짐.

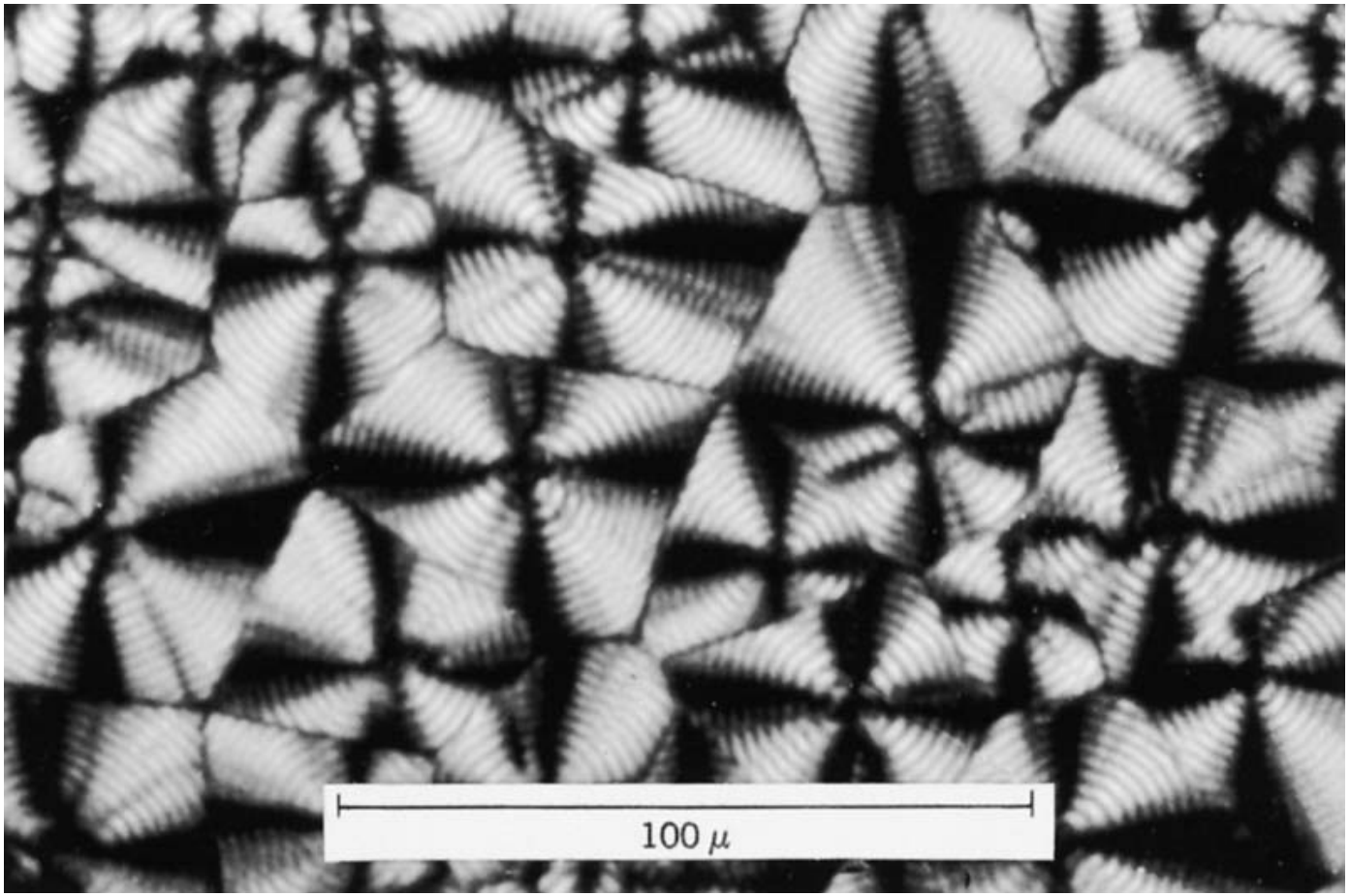


Fig. 4.14 Polyethylene 구정 구조의 편광현미경 사진: 각 구정 내에 (ring band에 의한) Maltese cross 형태가 나타남.