Chapter 15-1. Introduction to Polymer Chemistry

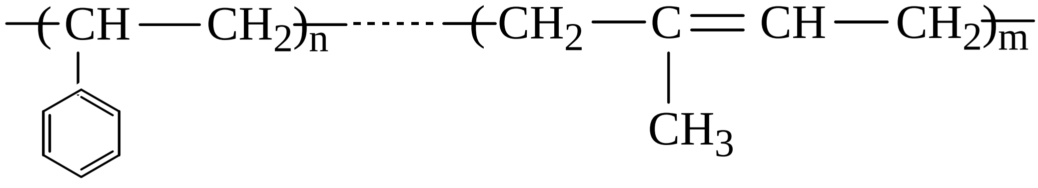
• Polymer - a macromolecule which contains large number of molecules joined together.

• Polymer의 구조 :

┌ Linear Polymer
├ Graft or Branched Polymer
└ Crosslinked Polymer

(i) Linear Polymer

┌ Homopolymer - the same monomer is used
| -A -A -A -A -A -
| ex) PE, PP, PS, PC, PMMA등
└ Copolymer - a polymer formed from more than one
  | type of monomer
  | ┌ Block Copolymer : AAABBBB
  └ | Random " : ABAABABBAB
    | ex) SAN, Vectra -> Poly(HBA -HNA)
    └ Alternating " : ABABABAB

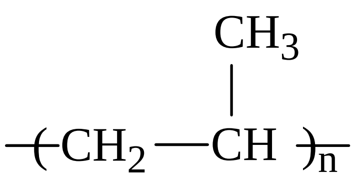


Styrene

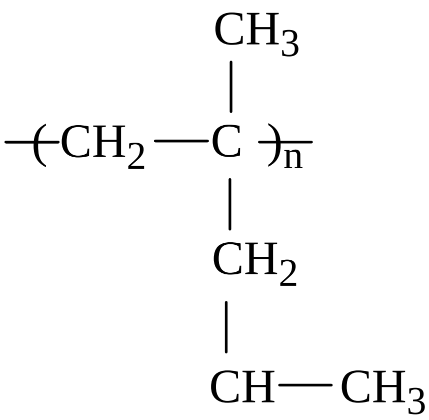
Isoprene block copolymer

(ii) Graft or Branched polymer - have a side chain branching from the polymer backbone.

(ex)



linear polyethylene



branched polyethylene

(iii) Crosslinked Polymers (or Network Polymers)

- 경화(crosslinking) 때문에 Polymer chain의mobility가 감소되어 flow가 일어나지 않는다.

(열경화성 고분자 : (ex)Phenol resin, epoxy resin, 불포화 polyester resin등)

(1) 고분자의 분류 (classification)

Polymer ┏ Plastics - 고분자를 이용하여 최종 제품의 형태로 만들어 진것 (PVC, PE, PS, PC등)

┣ Fiber - 섬유형태로서 (L/D) 가 큰것 (ex) PET, N -6, N -66등

┗ Elastomer - 탄성체로서 polybutadiene, SBR등

(2) 구조(structure) 에 따른 분류

(a) 열가소성 고분자 (Thermoplastic) – 열을 가했을 때flow가 일어나고, 열을 제거하면 다시 flow가 멈춤

(ex) 대부분의 linear polymer 로서 PE, PP, PS, PET, NYLON -6등

(b) 열경화성 고분자 – (Thermosetting polymer)

- 열을 가하면 경화 반응 (curing reaction) 이 일어나고, 일단 경화 후에는 flow가 일어나지 않음. 계속해서 열을 가하면 분해 (degradation) 이 일어남

(ex) 에폭시 수지, 페놀수지, 불포화 폴리에스터 수지등

(3) Grade에 따른 분류

(a) 범용(commodity) 고분자

- easy process
- low price

(ex) PS, PE, PP, PVC등

(b) 엔지니어링(Engineering) 고분자

- good mechanical properties
- 범용성 고분자보다2-3배 비싸다

(ex) Nylon, PET, PBT, Polycarbonate

Polyacetal (or polyoxymethylene(POM)

(c) 특수고분자(specialty Polymers)

- high temp stability
- high modulus, high price

(ex) Poly(ether ether ketone) (PEEK)

Polyimide, Liquid crytalline polymer (LCP)

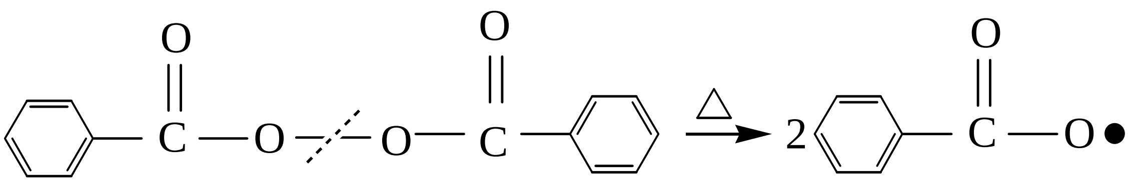
Polyetherimide, Polysulfone등

(2) Polymerization Reactions

(a) Addition Polymerization

- free radical에 의하여 반응이 제거됨

(i) Free radical polymerization



Benzoyl Peroxide
(free radical initiator)

$$C_6H_5C(=O)-O\bullet + CH_2=CH_2 \longrightarrow C_6H_5C(=O)O-CH_2-CH_2\bullet$$

$I \xrightarrow{\triangle} 2R\bullet$] Initiation(개시)

$R\bullet + M \longrightarrow M_1\bullet$ ┓

$M_1\bullet + M \longrightarrow M_2\bullet$ ┃ Propagation (전개)

$M_2\bullet + M \longrightarrow M_3\bullet$ ┛

:

$M_n\bullet + M_m\bullet \longrightarrow$ Polymer] Termination (종결)

(ii) Ionic Polymerization ┏ Cationic Polymerization ┗ Anionic Polymerization

- Cationic Polymerization : induced by chemical initiators, the active species are carbonium ions which is an exceedingly reactive particle. Vinyl polymers and dienes can be polymerized using cationic initiators. Phenol, Formaldehyde resin, isobutylene등 생산.

- Anionic polymerization : initiated by bases such as $Li^{+}NH_2^{-}$

Polystyrene, ethylene oxide 등 생산. 고분자의 구조를 control 하는데 좋음, High molecular weight 를 얻음.

(iii) Ziegler-Natta 촉매

($\underline{Al/TiCl_3}$, $\underline{Al/TiCl_4}$)

PE PP

Aluminium-titanium 촉매

- The most important catalysts

(장점) 1. linear polymer 생산에 적합

2. stereochemical control 이 용이함

(ex) High dansity polyethylene (HDPE) :

- high degree of crystallinity

(up to 80%)

- greater strength than LDPE

(ex) Low density polyethylene (LDPE)

- a polymer with branched structure

- crystallinity (up to 53%)

• Polymer 의 Tacticity

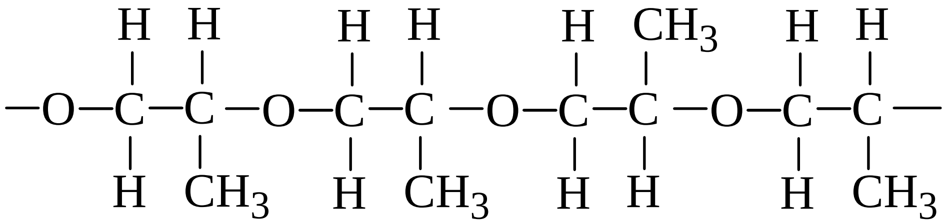
(i) Atactic 구조 - unsymmetric group such as methyl groups distributed at random.

(ii) Isotactic - all methyl groups located on one side of the extended polymer chain.

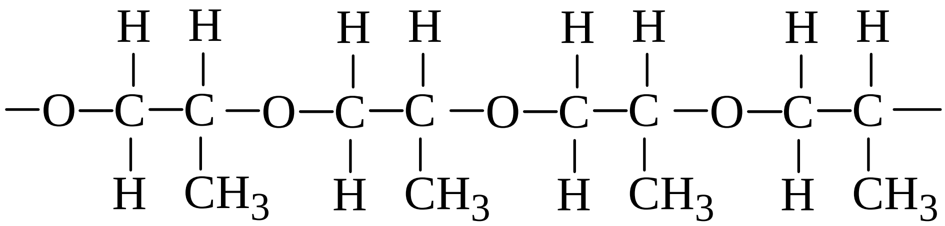
(iii) Syndiotactic - the unsymmetric groups alternate regularly from side to side

(ex) polypropylene oxide

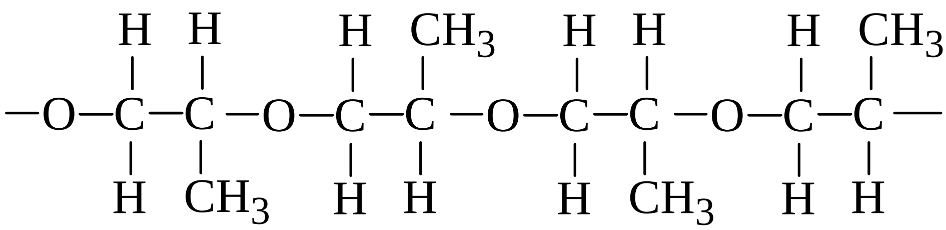
(i) atactic



(ii) isotactic



(iii) syndiotactic

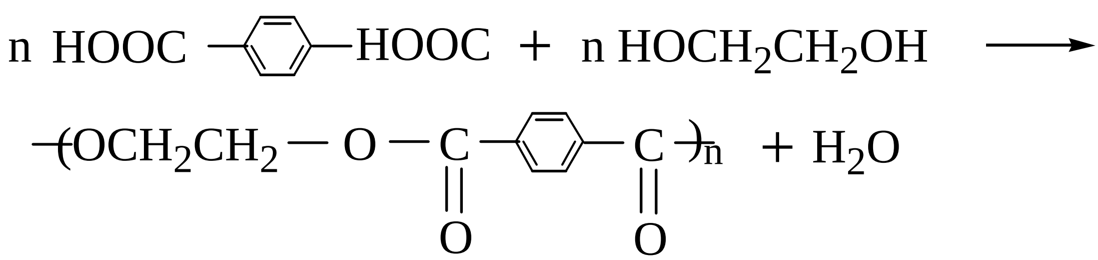


(b) Condensation polymerization

(step - growth 중합)

(ex) Nylon-6, Nylon-66, PET 등

(i) Terephthalic acid + ethylene glycol → PET + H_2O



(ii) Hexamathylene diamine + adipic acid $\rightarrow$ Nylon-66 + H_2O

$$H_2N\text{-}(CH_2)_6\text{-}NH_2 + HOOC\text{-}(CH_2)_4\text{-}COOH \longrightarrow$$

$$\left(\underset{\substack{\| \\ O}}{C} - (CH_2)_4 - \underset{\substack{\| \\ O}}{C} - NH - (CH_2)_4 - NH \right)_n + H_2O$$

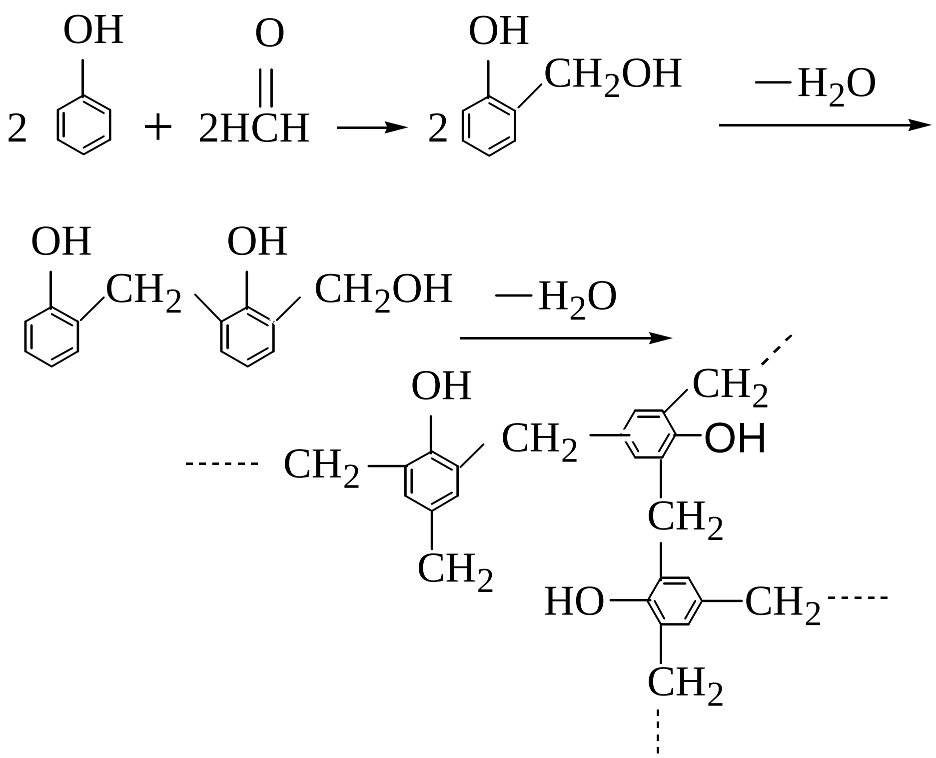
Nylon-66 (hexamethylene adipamine)

(iii) Formaldehyde condensation

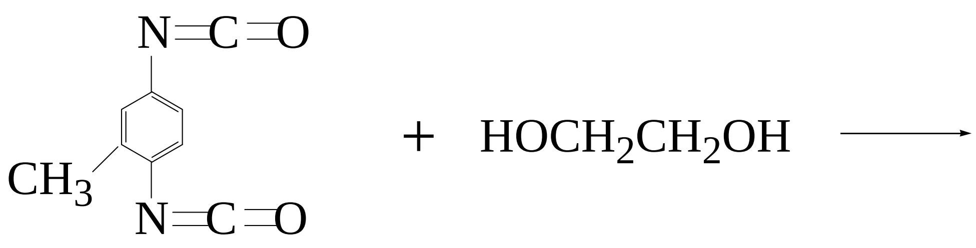
$$n\overset{\substack{O \\ \|}}{HCH} \longrightarrow -(CH_2 - O - CH_2 - O)- \text{ ------}$$

polyacetal, polyoxymethylene

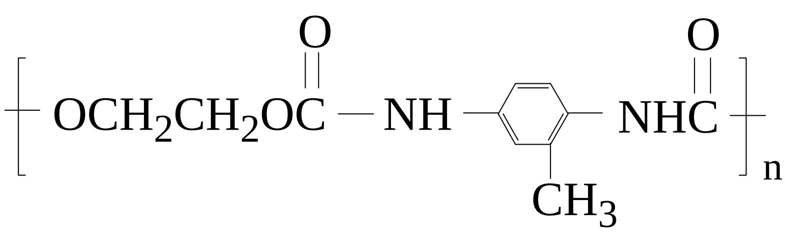
- The first synthetic resin : Bakelite



• Polyurethanes :



TDI Ethylene glycol



PU (polyurethane)

(3) Polymerization Technics

(a) Bulk polymerization

- monomer 를 그대로 또는 중합개시제를 첨가하여 중합

- solvent 없이 중합

(ex) PE, PP, PAN, Nylon, PET, PS 등

(b) solution 중합 (용액 ")

- monomer 를 녹이는 용매(solvent)에서 중합

- 용매가 polymer 를 녹일 경우 : 투명한 polymer

- 용매가 polymer 를 안녹일 경우 : 분말상 polymer

(ex) cis - polybutadiene, cis - polyisoprene, 접착제등

(c) Suspension 중합 (현탁중합)

- 물을 용매로 사용하여 잘 저으면서 monomer 가 물속에 분산이 되어 중합이 됨

- Initiator 는 monome에 잘 녹는것을 선택함

- used in free radical olefin 중합

  (pearl or bead 중합)

  (ex) styrene foam, PVC 분말, PS ion exchange 등

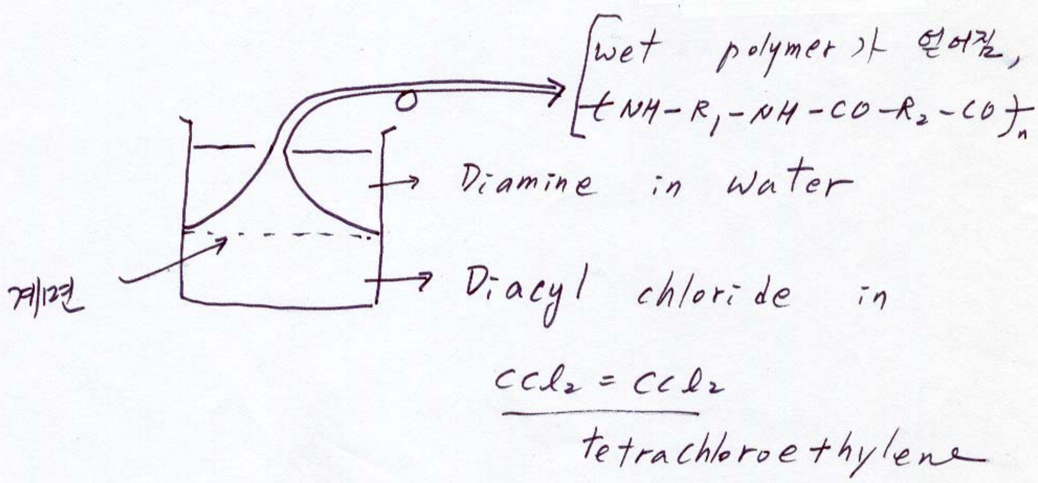
(d) Emulsion 중합 (유화 중합)

- 용매로서 물을 사용하고, 수용성의 개시제(initiator)를 사용하고, 비누나 세제같은 유화제 (emulsifier) 를 첨가해서 중합

  (ex) PS, PVC, SBR, NBR 등

(e) Interfacial (계면중합) Polymerization

- 반응이 두 immiscible liquid 사이의 interface 에서 일어남



(Sebacoyl chloride 을 많이 사용함)

- heat sensitive polymer 생산시 이용함.

- Physical Properties

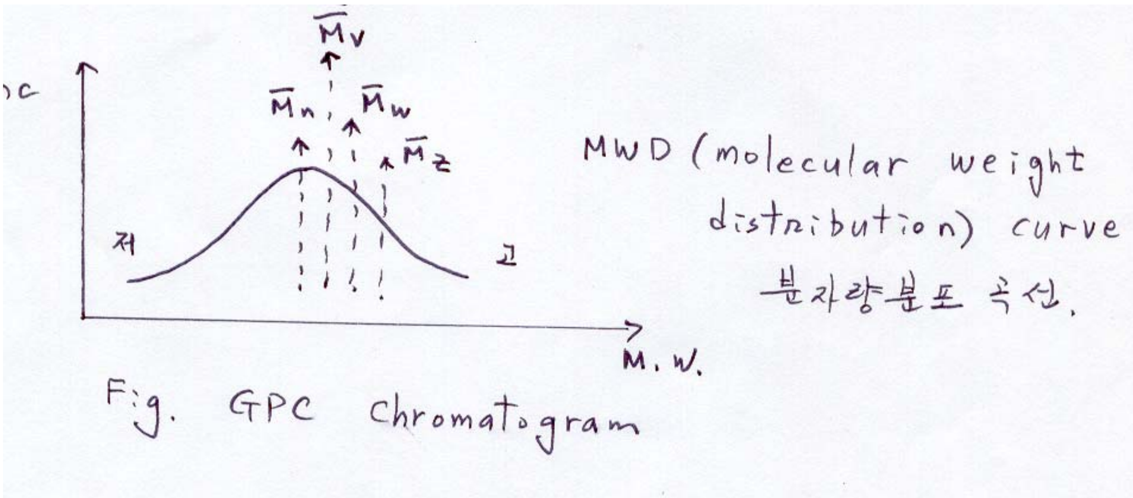
  · Molecular weight (분자량)

    (a) number-average molecular weight ($\overline{M}_n$)

    (b) weight-average molecular weight ($\overline{M}_w$)

    (c) viscosity-average " " ($\overline{M}_v$)

    (d) z-average " " ($\overline{M}_z$)



($\overline{M}_z$) ≥ ($\overline{M}_w$) ≥ ($\overline{M}_v$) ≥ ($\overline{M}_n$)

when MWD = 1.0, ($\overline{M}_z$) = ($\overline{M}_w$) = ($\overline{M}_v$) = ($\overline{M}_n$)

여기서 MWD = $\dfrac{\overline{M}_w}{\overline{M}n}$

· $\overline{M}_n$ = 수평균 분자량

$$= \frac{\sum N_i M_i}{\sum N_i}$$ 여기서 N_i = the number of each species

M_i = molecular weight of each polymer species

· $\overline{M}_w = \dfrac{\sum N_i M_i^2}{\sum N_i M_i}$ (중량평균 분자량)

여기서 $N_iM_i = W_i$ (the weight of each polymeric species)

$\therefore\ \overline{M}_w = \dfrac{\sum W_i M_i}{\sum W_i}$ (참고서적 : By A. Rudin "The Elements of Polymer Science and Engineering", page 53)

(ex)

N_i	M_i
2	600
3	1000
1	2000

calculate $\overline{M}_{n,}$ $\overline{M}_w$, MWD

$$\overline{M}_n = \frac{2(600)+3(1000)+1(2000)}{2+3+1} = \frac{6200}{6} \qquad 1033$$

$$\overline{M}_w = \frac{2(600)^2+3(1000)^2+1(2000)^2}{2+3+1} = 1245$$

$$\therefore\ \text{MWD} = \frac{\overline{M}_w}{\overline{M}_n} = \frac{1245}{1033} \qquad 1.21\ \text{(polydisperse)}$$

if MWD = 1.0 (즉 $\overline{M}_w = \overline{M}_n$ 이면 monodispersi polymer 임)

· 고분자의 분자량 측정방법

(a) Gel Permeation Chromatography (GPC)

또는 size exclusion chromatography (SEC)

(b) Light scattering

- $\overline{M}_w$ 측정

(c) Membrane osmometry

- $\overline{M}_w$ 측정

(참고문헌 : By A. Rudin "The Elements of Polymer Science and Engineering", Academic press, chapter 3)

· Crystallinity (결정화도)

- requirements for crystallinity :

(i) regular chain structure,

(ex) i-PS, i-PP

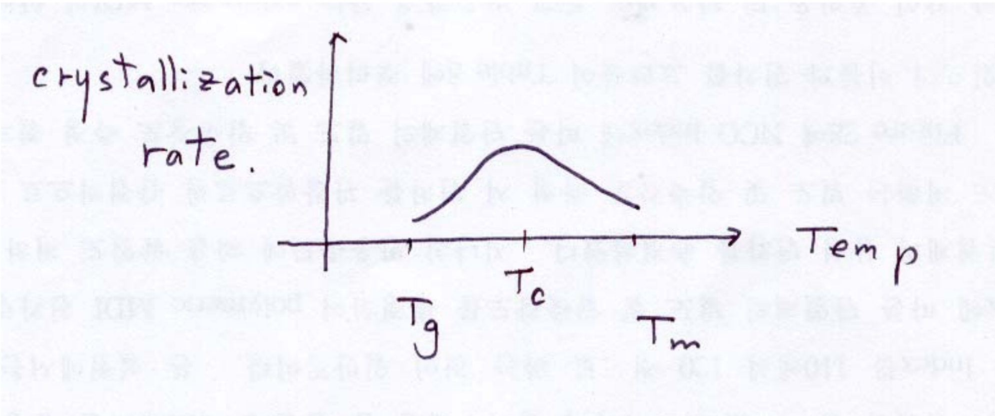
(ii) need hydrogen bonding or strong dipole interaction

(ex) Nylon-6

· Cristallization

(a) Primary crystallization - Polymer molecules crystallize when they are cooled from melted state.

고분자의 결정화는 T_g 와 T_m 사이에서 일어남.

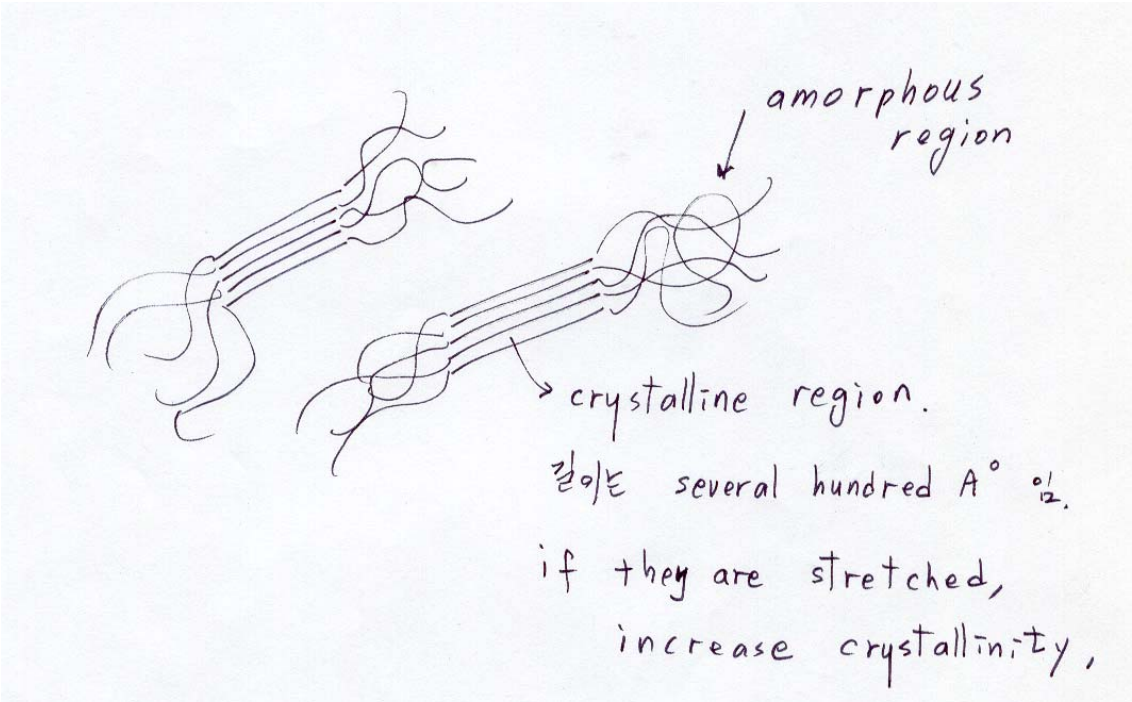


(b) Secondary crystallization - melted state (용융상태) 의 sample 을 급냉(quenching) 한 후, T_g 와 Tm 사이의 온도, 즉 T_c (결정화온도 : crystallization temperture) 에 오랜시간동안 열처리하면, 분자사슬들이 움직여 좀더 완전한 결정격자를 이루어 결정화도가 증가함

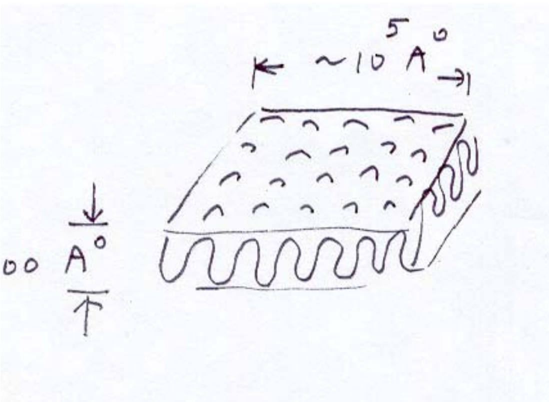
• 고분자의 결정 model

* The fringed-micelle model : 고분자는 무정형부분 (amorphous region) 과 결정성 부분 (crystalline region) 이 서로 함께 연결되어 이루어져 있

음



* Folded - chain crystallires :



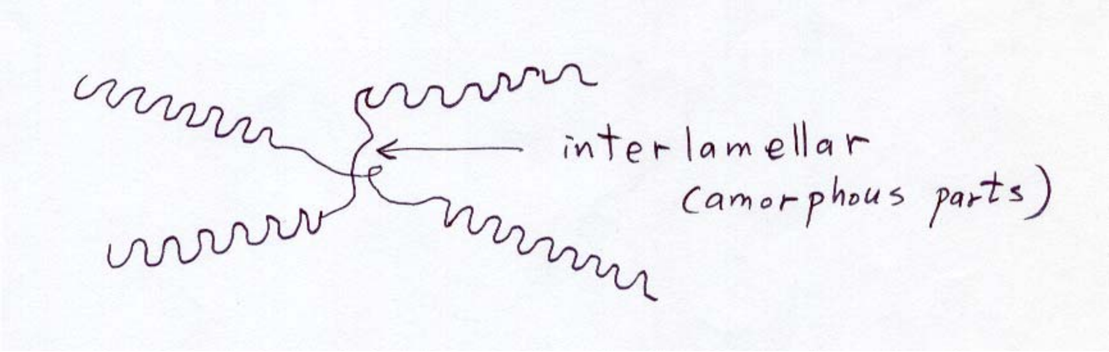
- Lamellar : platelike polymer crystal (판상구조)
- 두께는 분자량에 무관하고, growth rate가 감소할수록 more perfect crystal 이 얻어짐
- 예를들어, 1000Å 길이의 polymer molecule 이 100Å 두께의 Lamellar 에 들어가려면 folding 이 일어남.

• Solution 및 melted state 에서의 결정생성

(i) solution 상태에서의 결정 생성 - solution 상태에 있는 고분자는 solvent 가 증발 (evaporate) 하면서 single crystal (lamellar, 즉 folded chain crystal) 이 생성됨.

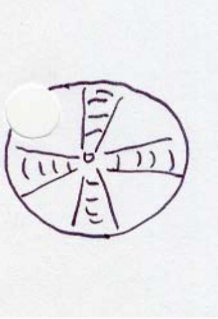
(ex) PE single crystal

(ii) melt 상태에서의 결정 생성 - a model combining the folded - chain lamellar with the interlamellar amorphous material



• Extend - chain crystals : fibrillar structure - polymers crystallized from a melt while subjected to extensional flow.

• Spherulite : (구정)



- spherulites are aggregates of lamellar crystallites
- polycrystal 이란 개념이며, single crystal 이 아님
- grow radially from a point of nucleation
- 크기는 약 0.01 mm(diameter) , "Maltese Cross" 구
- semicrystalline polymer 에서 볼수 있는 특징

• Thermoplastics

· 대표적인 열가소성 고분자 : PE, PP, PVC, PS, PMMA, SAN, ABS

· The crystallinity of polyethylene (PE)

(i) low density polyethylene (LDPE)

- long branched polymer
- made by high - pressure process

(about 25000 ～ 50000 psi)

- density (d) = 0.910 ～ 0.925(g/cm^3)
- 결정화도 (crystallinity) = 42 ～ 53 %
- 녹는점 (melting point, T_m) = 110 ～ 120 ℃

(ii) linear low density polyethylene (LLDPE)

- short, straight branch
- low pressure process (100 psi)
- 밀도 = 0.926 ～ 0.940 (g/cm^3)
- 결정화도 = 54 ～ 63 %
- T_m = 120 ～ 130 ℃

(iii) high density polyethylene (HDPE)

- no branches, linear polymer
- made by low pressure process
- 밀도 = 0.941 ～ 0.965 (g/cm^3)
- 결정화도 = 64 ～ 80 %

Tm = 130 ～ 136 ℃

Table 5.1 The Influence of Crystallinity on Some of the Properties of Polyethylene[a]

Commercial product	Low density	Medium density	High density
Density range, g/cm^3	0.910–0.925	0.926–0.940	0.941–0.965
Approximate % crystallinity	42–53	54–63	64–80
Branching, equivalent CH_3 groups/1000 carbon atoms	15–30	5–15	1–5
Crystalline melting point, °C	110–120	120–130	130–136
Hardness, Shore D	41–46	50–60	60–70
Tensile modulus, psi	$0.14–0.38 \times 10^5$	$0.25–0.55 \times 10^5$	$0.6–1.8 \times 10^5$
(N/m^2)	$(0.97–2.6 \times 10^8)$	$(1.7–3.8 \times 10^8)$	$(4.1–12.4 \times 10^8)$
Tensile strength, psi	600–2300	1200–3500	3100–5500
(N/m^2)	$(0.41–1.6 \times 10^7)$	$(0.83–2.4 \times 10^7)$	$(2.1–3.8 \times 10^7)$
Flexural modulus, psi	$0.08–0.6 \times 10^5$	$0.6–1.15 \times 10^5$	$1.0–2.6 \times 10^5$
(N/m^2)	$(0.34–4.1 \times 10^8)$	$(4.1–7.9 \times 10^8)$	$(6.9–18 \times 10^8)$

[a] It must be kept in mind that mechanical properties are influenced by factors other than the degree of crystallinity (molecular weight, in particular).

100-1