Chapter 5. Crystallinity

5.1 Reguirements for crystallinity

- Regular chain structure.   ex) iso-PP, iso-PS
- Hydrogen bonding
- Strong dipole interaction.   ex) nylon-6

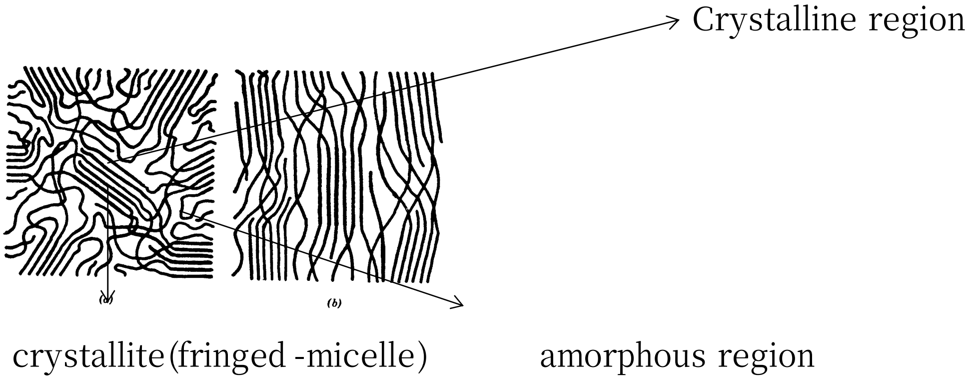
5.2 The Fringed-Micelle Model

· solid state polymer의 분류

i) completely amorphous

ii) partially crystalline

iii) almost completely crystalline.



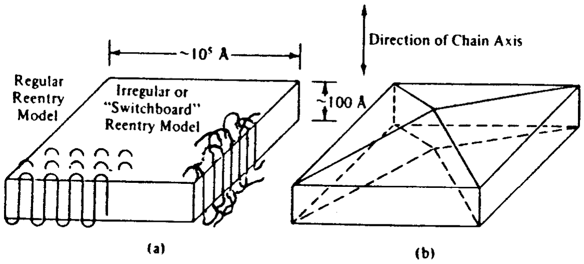
-several hundred Å

If they are stretched→increase crystallinity.

- crystallites tie the individual chains together
- the crystallites will generally melt before the polymer degrades

5.3 Folded-chain Crystallites

- the growth of single crystals from dilute solution



i) regular reentry model
ii) adjacent reentry model
iii) irregular or “switchboard” reestry model

- 두께는 분자량에 무관하고 온도가 증가할수록 두께는 증가하고 growth rate 가 감소할수록 more perfect crystal 이 얻어진다.
- Chain folding why? 1000 Å 의 길이가 100 Å 두께에 들어갈려면 folding이 일어나야 한다.
- Solution state : lamellae (plate like polymer crystal)
- Melt state : a model combining the folded-chain lamellae with the interlamellar amorphous material.

5.4 The effects of crystallinity on polymer properties

· LDPE (low density polyethylene)
- long branched branches : made by high-pressure process.(25,000-50,000 psi)
  δ=0.915g/cm^3 42-53% crystallinity   Tm= 110-120 °C

· LLDPE (linear low density polyethylene)
- short, straight branch : low-pressure (100 psi)
  Tm= 120-130 °C   54-63% crystallinity

· HDPE (high density PE)

- no branches, linear : made by low pressure process
  δ=0.97 g/cm^3 64-80% crystallinity
- more tightly packed in the crystalline than in the amorphous areas.
  e.g.) iso-PP: crystalline, hard and rigid plastics.

· crystalline polymers have two-phase systems with a crystalline phase dispersed in an amorphous matrix - mostly opague.

· In general, transparent polymers are completely amorphous.

5.5 Determination of Crystallinity

1. density measurement

$$\phi_C = \frac{\rho - \rho_a}{\rho_c - \rho_a}$$

(volume fraction of material in the crystalline state)

ρ : density of the sample

ρ_a: density of amorphous polymer

ρ_c: density of crystalline polymer – X-ray의 unit cell dimension.

$$\omega_c = \frac{\rho_c(\rho - \rho_a)}{\rho(\rho_c - \rho_a)}$$

2. Specific heat (cal/g·°c)

$$\chi = \frac{c_a - c}{c_a - c_c}$$

3. melting enthalpy (enthalpy of fusion)

$$\chi = \frac{\Delta H}{\Delta H_f}$$

4. IR

$$\chi = \frac{\varepsilon_{\lambda}}{\varepsilon_{\lambda_c}}$$

e.g.)P.E : 7.67μm 에서 amorphous.

5. NMR

Broad band : crystalline regions

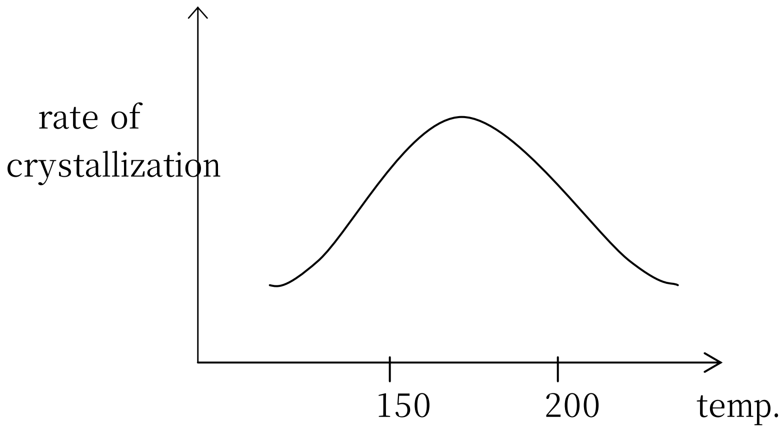
Sharp band : amorphous regions

6. X-ray

$$\chi = \frac{I_c}{I_c + I_a}$$

Ic = integrating the intensities of crystalline reflections.

. Rate of crystallization



- rate of crystallization is maximum between Tg and Tm of the polymer.

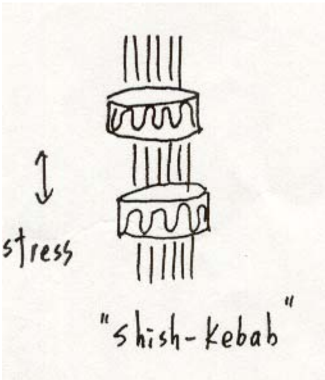
. Secondary crystallization

quenching of specimen at melt temperature and then store at temp. higher than Tg

→ the disordered regions will mobile enough to rearrangement into lower energy, more ordered structure.

5.6 Extended -chain crystals

. fibrillar structure – polymers crystallized from a melt while subjected to extensional flow (eztended – chain crystals)



5.8 spherulties (구정)

. polycrystal이란 개념이며 single crystal 이 아니다. – spherulites are aggregates of lamellar crystallites.

특징)

i) grow radially from a point of nucleation.

ii)nuclei가 많으면 작은 sphrulite 가 많이 생긴다. Shock cooling → smaller spherulites.

iii)크기는 약 0.01mm(diameter) - "Maltese Cross"구조 편광현미경으로 관찰

iv)semicrystalline polymer 에서 볼 수 있는 특징.