Chapter 2. Typology of Polymers

2.1 Types of bonds in Polymers

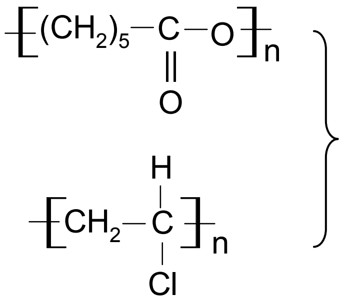
1. primary covalent and metallic bonds
2. hydrogen bonding
3. dipole interaction
4. dispersion force
5. ionic bond

(2.–5.) 2nd force (van der Waals force)

e.g.) polycaprolactone,

\+

PVC,



miscible polymer blends

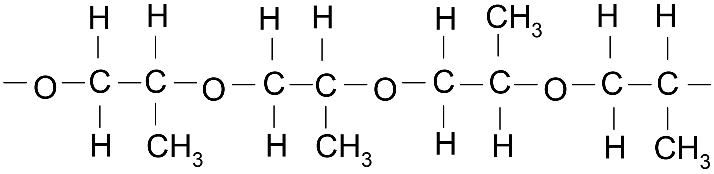
2.2 Stereoisomerism

· Polymer configuration – arrangements of atoms which cannot be altered except by breaking and reforming primary chemical bonds.

– Configuration in vinyl polymers –

i) Atactic – a random arrangement of the unsymmetrical group.

[(e.g.) polypropylene oxide]



ii) Isotactic – the structure in which all of the groups are lined up on the same side of the backbone.

e.g.) PPO, i-PP (T_m = 176 °C)

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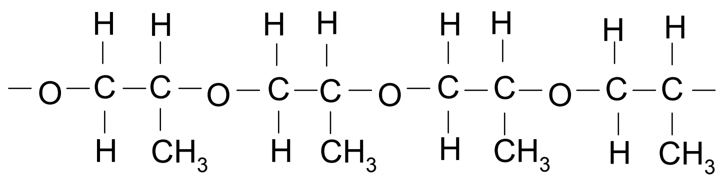
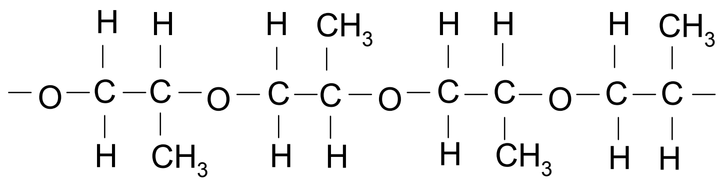


iii)Syndiotactic – alterating placement of the group on either side of the chain.



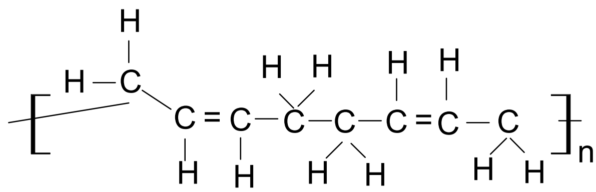
· Configuration- specifies the relative spatial arrangement of bonds in a molecule (of given constitution) without regard to the changes in molecular shape which can arise because of rotations about single bonds. A change in configuration reguires the breaking and reforming of chemical bonds.

· Conformation- the conformation of a macromolecule of given constitution and configuration specifies the spatial arrangements of the various atoms in the molecule that may occur because of rotations about single bonds.

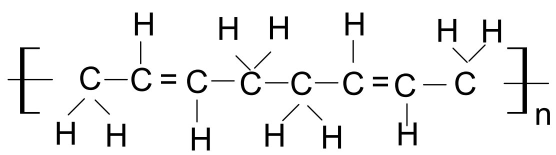
- vinyl polymer에서는 stereoregularity가 증가할수록 crystallinity가 증가함.
- no configurational isomers in PE

· Polymer conformation- changes in structure caused by rotation about single bond.
- stereoisomerism in diene polymer
  ex) polybutadiene,

i) cis-PBD : the substituent groups on the double-sided carbons may either be on the same side.



ii) trans-PBD : the substituent groups on the double-sided carbons may either be on the opposite side.



1.3 Crystallinity

1. Reguirements for crystallinity

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

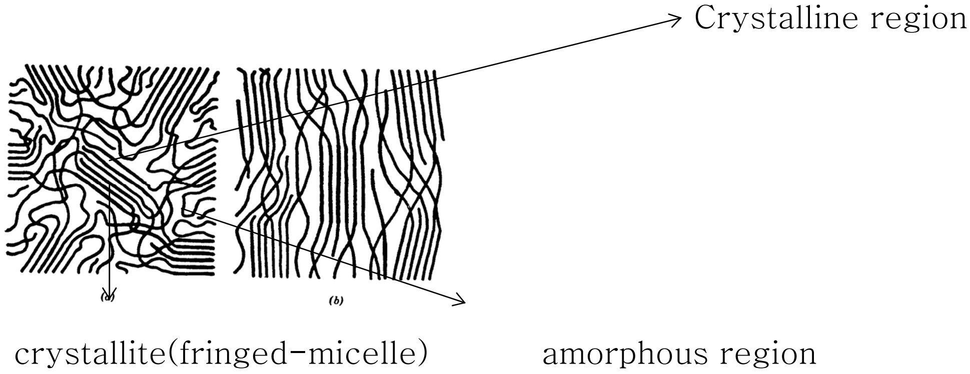
2. The Fringed-Micelle Model

· solid state polymer의 분류

i) completely amorphous

ii) partially crystalline

iii) almost completely crystalline.



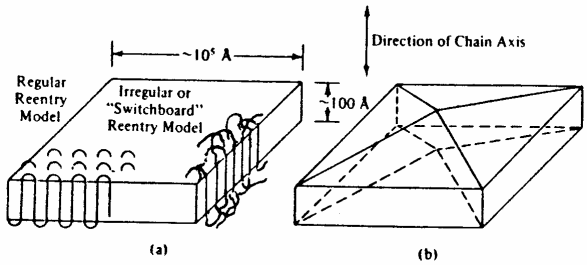
-several hundred Å

If they are stretched→increase crystallinity.

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

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.

4. Extended-chain crystals

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

5. 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.

6. 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.

7. Determination of Crystallinity
i) density measurement

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

ρ : density of the sample
ρ_a: density of amorphous polymer
ρ_c: density of crystalline polymer – X-ray의 unit cell dimension.

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

ii) Specific heat (cal/g·°c)

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

iii) melting enthalpy (enthalpy of fusion)

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

iv) IR

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

e.g.)P.E : 7.67μm 에서 amorphous.

v) NMR

Broad band : crystalline regions

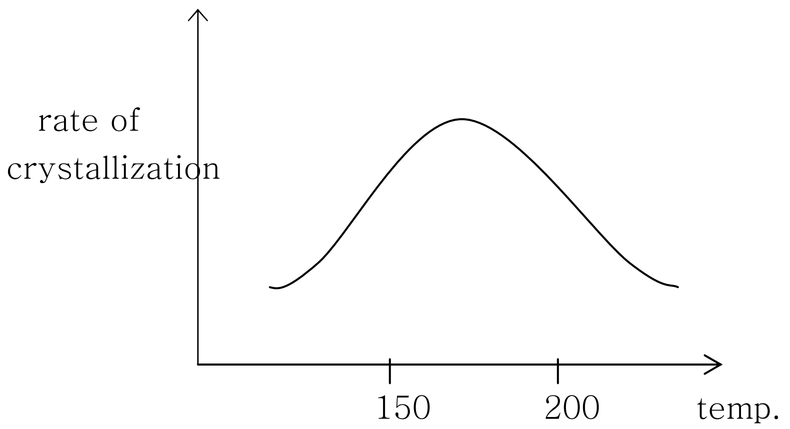
Sharp band : amorphous regions

vi) X-ray

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

Ic= integrating the intensities of crystalline reflections.

8. 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.