

## 1.4 Copolymer

- ▶ Random, Block, Graft copolymers
- ▶ Random copolymer from two different monomers --- See the following.

Copolymer Eq: [Finemann Ross Eq](#)

## COPOLYMER EQUATION

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left\{ \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \right\}$$

or

$$\frac{d[M_1]}{d[M_2]} = \frac{(r_1[M_1]/[M_2]+1)}{(r_2[M_2]/[M_1]+1)}$$

remember

$$r_1 = \frac{k_{11}}{k_{12}} \quad r_2 = \frac{k_{22}}{k_{21}}$$

The above is for an instantaneous composition and changes with reaction time.

For copolymer property, additive rules are applied.

Ex) Fox Eq (An inverse additivity)

$$\frac{1}{T_g} = \frac{w_A}{T_{g,A}} + \frac{w_B}{T_{g,B}}$$

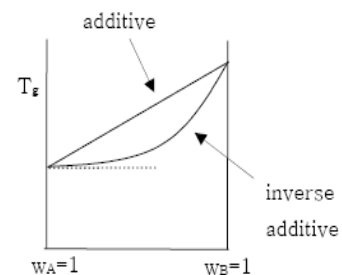
For EPR

$T_g$  of EPR is controlled by E/P ratio.

Homo PE and PP : crystalline

But, between 2/8 ~ 8/2 (E/P), copolymer is amorphous  $\Rightarrow$  EPR (rubber)

A small amount of diene monomer is copolymerized for sulfur cure (EPDM)



**Important to note:**

Reactivity: ethylene  $\gg$  propylene (ca 40 times)

$\therefore$  At similar monomer composition, long ethylene sequence is produced!

→ Could cause whitening in winter season.  
 (Should be avoided in EPR production)

► Block copolymer

Diblock, triblock, multiblock copolymers

Length, composition of block control crystallinity, compatibility and identity.

Useful for surfactant, colloid, compatibilizer etc.

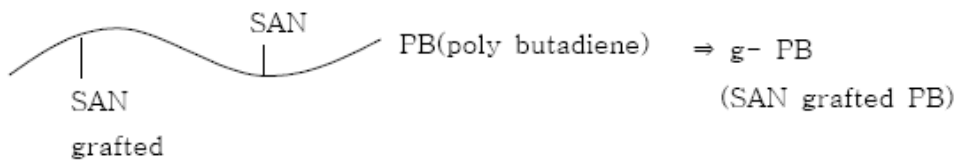
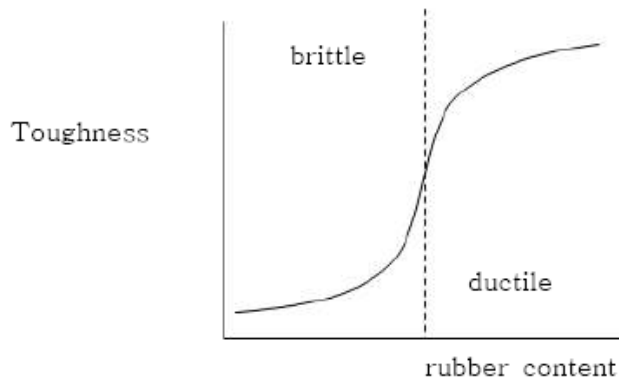


► Graft copolymer:

Modifies the property of stem polymer.



ABS (rubber toughened plastics) ⇒ Rubber particles are imbedded in brittle matrix (SAN)



⇒ Increase miscibility with matrix SAN

⇒ BT curve moves toward lower rubber content as miscibility increases.

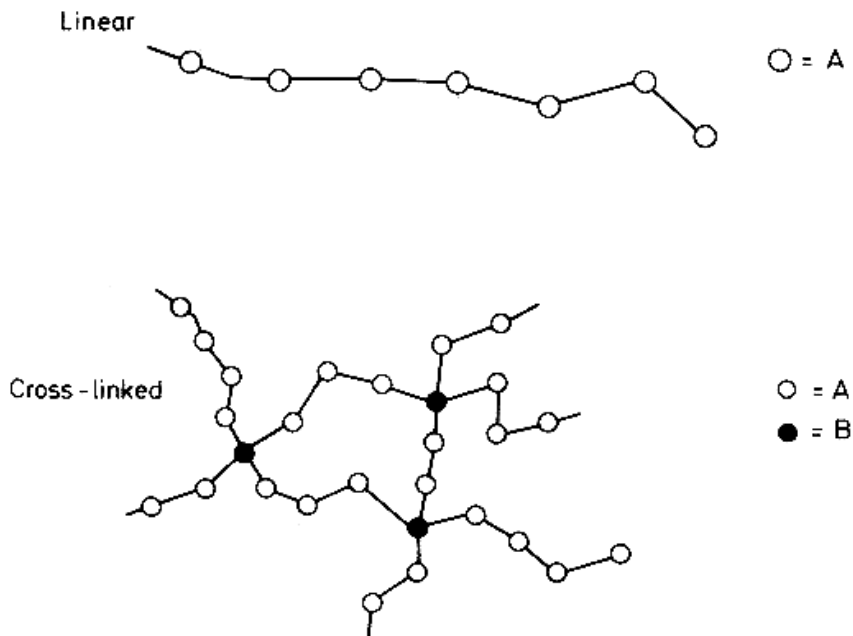
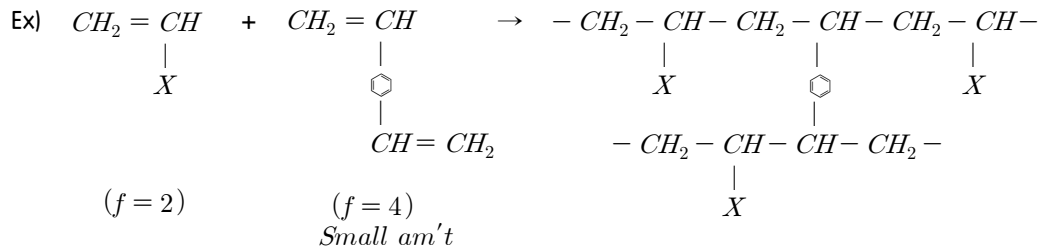
(Keep strong mechanical properties)

## 1.5 Crosslinked polymers

f ≡ Functionality (average)

f = 2 : Linear polymer

f > 2 : Branch or x-linked polymer (See [Figure 1.6](#))



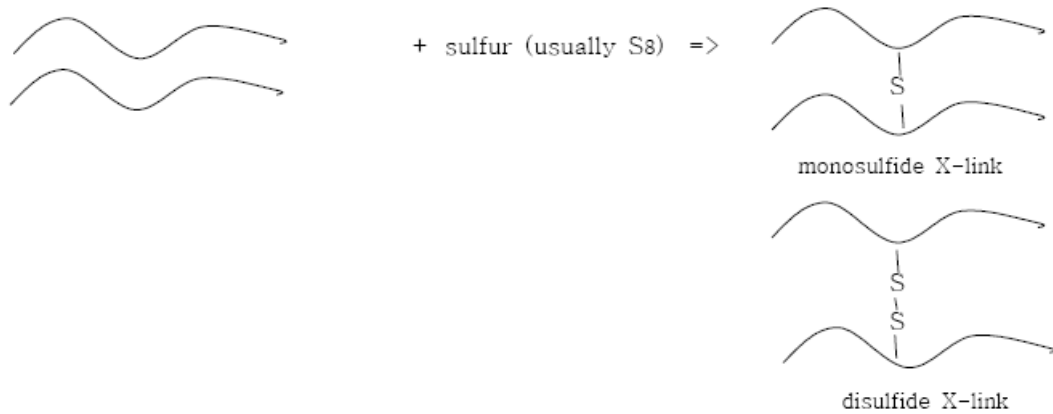
**1.6** Monomer A (functionality 2) yields a linear homopolymer when polymerized, but when polymerized with a small amount of monomer B (functionality 4) it yields a cross-linked copolymer.

Figure 1.6

Ex) X-linking of commercial product → Post reaction X-linking

(PE → X/L PE)

Ex) Vulcanization of rubber



## 1.6 Molecular symmetry and tendency to form crystal

- ▶ Crystalline polymer = crystalline region + amorphous region
- ▶ Amorphous polymer = only amorphous region
- ▶ Crystalline (=high modulus, high density) lamella is sandwiched between amorphous regions(=low modulus, high elongation) rubbery phase→high mechanical strength and ductility for semicrystalline polymer



**1.7** Lamellae within adjacent bands of a banded spherulite of linear polyethylene crystallized at 125°C. The specimen was cut open after crystallization, and lamellae are revealed by permanganic etching of the cut surface. The electron micrograph is of a carbon replica of the etched cut surface (after D. C. Bassett). Scale bar = 10  $\mu\text{m}$ .

**Fig. 5.3** Electron micrographs of single crystals of polyethylene crystallised from dilute solution in xylene: (a) diamond-shaped crystals and (b) truncated crystals. (Reprinted by permission of John Wiley & Sons, Inc.)

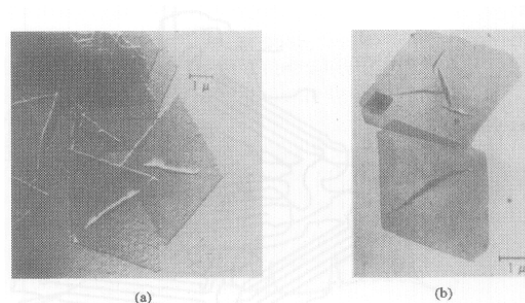


Fig 1.7 Lamellae are extremely thin (~10nm). Amorphous polymers are entrapped between the lamellae. The interconnection of this two phase structure provides the materials with toughness, modulus (crystalline domain) and ductility (amorphous domain). Three dimensional growth of the lamellae becomes spherulite.

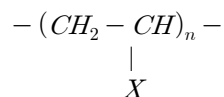
#### Basic requirements for crystallization

##### Molecular regularity

- ABABAB . . .

Regular sequence (Nylon, PET, condensation polymers)

- Irregular side chains disturb packing into crystal (LDPE, PS, PMMA...)
- Tacticity of vinyl monomer



- H, CH<sub>3</sub> : okay with Ziegler-Natta
- Polystyrene , PMMA: amorphous and transparent
- Isotactic; Crystallizes
- Syndiotactic; Very little
- Atactic; Amorphous

##### Tacticity check ?

iPP = hexane insoluble

aPP= " soluble

#### 1.7 Distribution of relative molar mass (RMM)

RMM : Relative molar mass based on mass of C<sup>12</sup> ≡ 12.

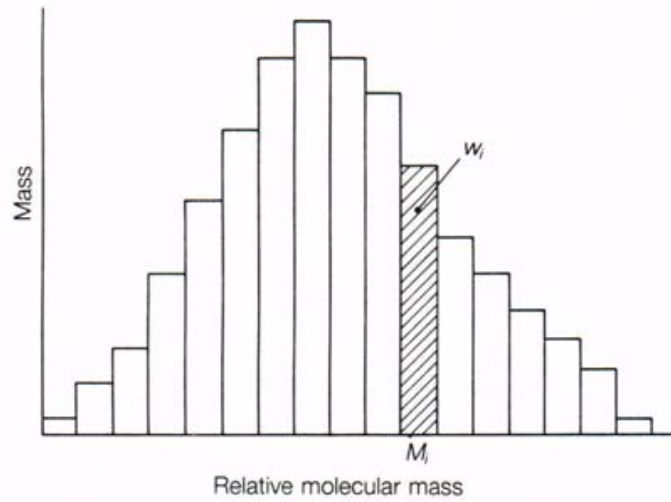
Property of polymer = f(MW, MWD)

Polymer = Polydisperse = Mixture of various MWs

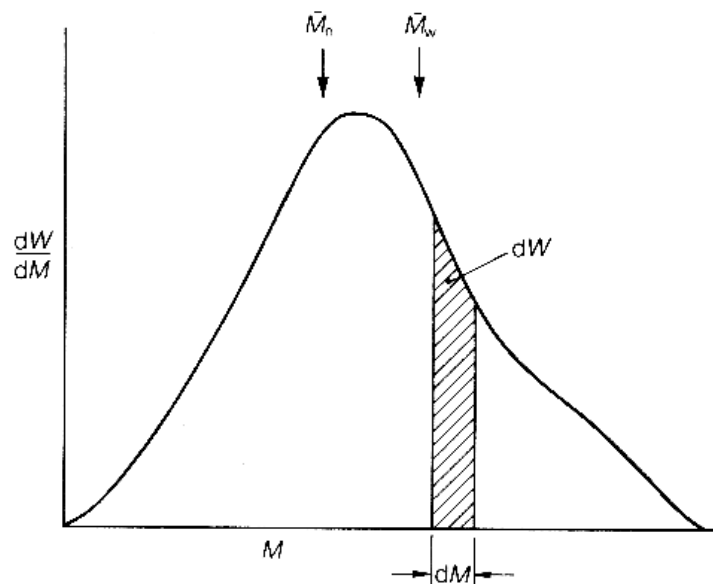
-> Sample w/o fractionation always shows MWD

-> Expressed in terms of average MW ( $\overline{M}_n$ ,  $\overline{M}_w$ ).

Total mass(W) of the sample (See Figures 1.10, 1.11):



**1.10** The distribution is thought of as a series of closely spaced fractions. The  $i$ th fraction, of which the specimen contains a mass  $w_i$ , is of relative molecular mass  $M_i$ .



**1.11** Illustration of a distribution of molecular mass. The area shaded represents the mass of the specimen with molecular mass between  $M$  and  $M + dM$ . A measure of the breadth of the distribution is provided by the two averages  $\bar{M}_n$  and  $\bar{M}_w$ , which are defined by eqns 1.3 and 1.4.

$$W = \sum w_i$$

$$w_i = n_i M_i \quad (n_i: \text{Number of moles having } MW = M_i)$$

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{\sum w_i}{N} = \frac{W}{N} \quad (N: \text{total of moles}) \quad (1.3)$$

$$\overline{M}_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum n_i M_i^2}{W} = \frac{\sum n_i M_i^2}{W} \quad (1.4)$$

$$\frac{\overline{M}_w}{\overline{M}_n} = PDI (= MWD) \quad \text{Polydispersity index}$$

► Example

$M_i$	10	$10^3$	$10^5$	(g/mol)
$n_i$	10	10	10	(moles)

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{10^2 + 10^4 + 10^6}{30}$$

$$\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{10^3 + 10^7 + 10^{11}}{10^2 + 10^4 + 10^6}$$

Note: High MW tail is much more important with weight average MW.

Determination of MW, MWD = GPC (mostly), light scatterings, viscosity

All make use of dilute solution properties.

GPC (Gel Permeation Chromatography):

polymer + solvent => dilute solution

- Column packed with porous X-linked PS gel (Stragel)
- Pore size distribution
- Pore size (in the bead) = O(polymer size)

The amount of polymer appeared at the bottom of the column as a function of time (retention time) is determined by optical or spectrometric method, or compared with STD sample -> Determine MW, MWD.

► Note

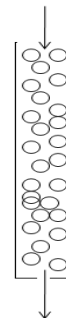
Large molecules : flow outside the bead => short retention time

Small molecules : path through pores => long retention time

∴ As MW ↑ → retention time ↓

As RMM ↑ -> i) Mechanical properties ↑

Ex) tensile modulus, strength, impact strength



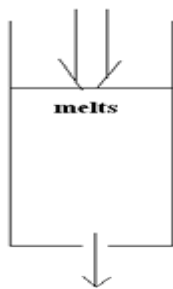


Notched impact specimen-Izod, Charpy

ii) Viscosity ↑ -> Processability

Note: Easy access to processability =>MI(melt flow index)(g/10min, at given load and temperature)

190° C for PE and 230° C for PP with 2.16 (low MI) or 5 kg (high MI) weight.



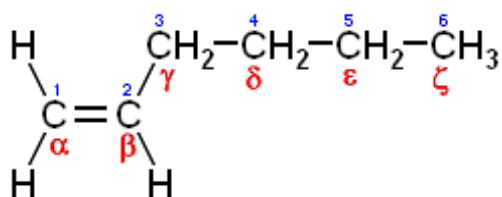

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## Bucknall Ch 1- Supplementary

### Ziegler-Natta catalyst (Coordination polymerization)

$AlR_3 + TiCl_4$  etc.....

**Alpha-olefins** ( $\alpha$ -olefins) are a family of [organic compounds](#) which are olefins with a [chemical formula](#)  $C_xH_{2x}$ , having a [double bond](#) at the primary or alpha ( $\alpha$ ) position.†





### MFI (Melt flow index)

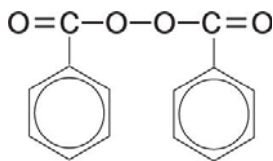
4 to 5 g of sample is taken in the specially designed MFI apparatus (a miniature extruder).

Heated and extruded at 190°C for PE and 230°C for PP with 2.16 kg (low MI) or 5 kg (high MI) weight.

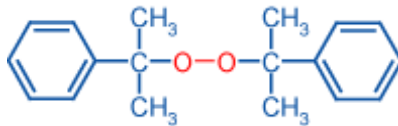
MFI is expressed as grams of polymer/10 minutes of flow time.

### Peroxide Cure

BPO



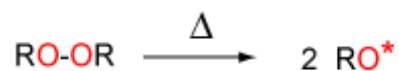
DCP (Dicumyl peroxide or isopropyl benzene peroxide)



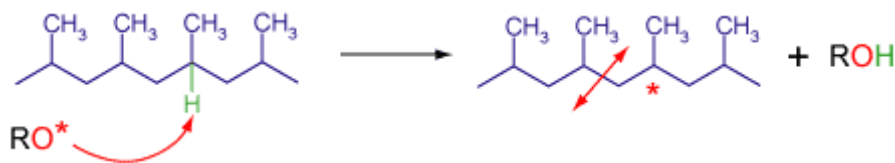
### Beta scission of PP

The degradation of polypropylene is achieved in a 3 step process:

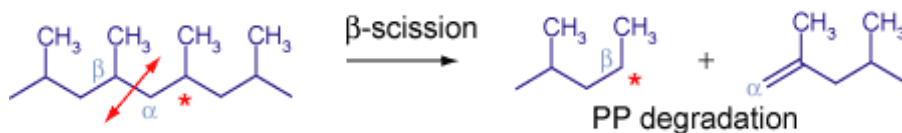
**Initiation:** Free radical formation by thermal decomposition of organic peroxide



**Macroradical formation:** transfer of alkoxy radical to PP backbone



**Beta scission:** Macroradical rearrangement leading to chain scission



The macroradical can then be transferred to another PP chain.

### ESC, ESCR

Mechanical stress+chemical attack→Easy crack initiation+growth

**Environmental Stress Cracking (ESC)** is a most common cause of unexpected [brittle](#) failure of [thermoplastic](#) (especially amorphous) which accounts for around 15-30% of all [plastic](#) component failures in service. The exposure of polymers to liquid [chemicals](#) tends to accelerate the [crazing](#) process, initiating crazes at stresses that are much lower than the stress causing crazing in air. The action of either a tensile stress or a [corrosive](#) liquid alone would not be enough to cause failure, but in ESC the initiation and growth of a crack is caused by the combined action of the stress and a corrosive environmental liquid.

### Copolymer equation (Interpretations)

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1] r_1 [M_1] + [M_2]}{[M_2] r_2 [M_2] + [M_1]} \quad (23)$$

This copolymer equation can be used to predict chain structure as follow.

► The regular alternating copolymers of the type ABAB... is favoured when each growing radical prefers to add to monomer of the opposite type. In this case

$$r_1 \approx r_2 \approx 0 \quad (24)$$

and Equation (23) therefore becomes

$$\frac{d[M_1]}{d[M_2]} = 1 \text{ or } d[M_1] = d[M_2]$$

► An ideal copolymer will tend to form when each type of chain end shows an equal preference for adding on to either monomer. In this case ([Students try](#))

$$r_1 = \frac{1}{r_2} \quad (25)$$

and the copolymer equation becomes

$$\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]} \quad (26)$$

Hence composition depends on the relative amounts of monomer present at any time and the relative reactivities of the two monomers.

► Block copolymers are formed when the growing chain end has a marked preference for adding on to the same kind of monomer. In this case

$$r_1 > 1$$

$$r_2 > 2$$

## Impact test types

