

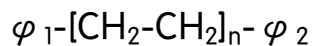
1 Structure of Molecule

1.1 Introduction

Polymer = poly (many) + meros (members)

Note: Macromolecule

Ex) Polyethylene



$$n = O(10^4)$$

Typically, 10^3 (Wax) < MW < 10^6 (UHMWPE)

UHMWPE needs gel spinning in solvent such as decalin.

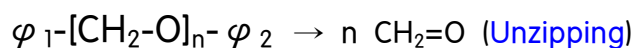
At given temperature and pressure, state of matter changes as the molecular weight increases as:

Gas → Liquid → Slurry → Wax → Solid

φ_1, φ_2 = end group = initiator fragment = minute amount →

Exerts negligible effect on property.

Exception: POM (INI) (Developed by Staudinger in 1920s)



With only the development of stable end cap, POM has been commercialized in 1959 as engineering plastics as gear and appliance.

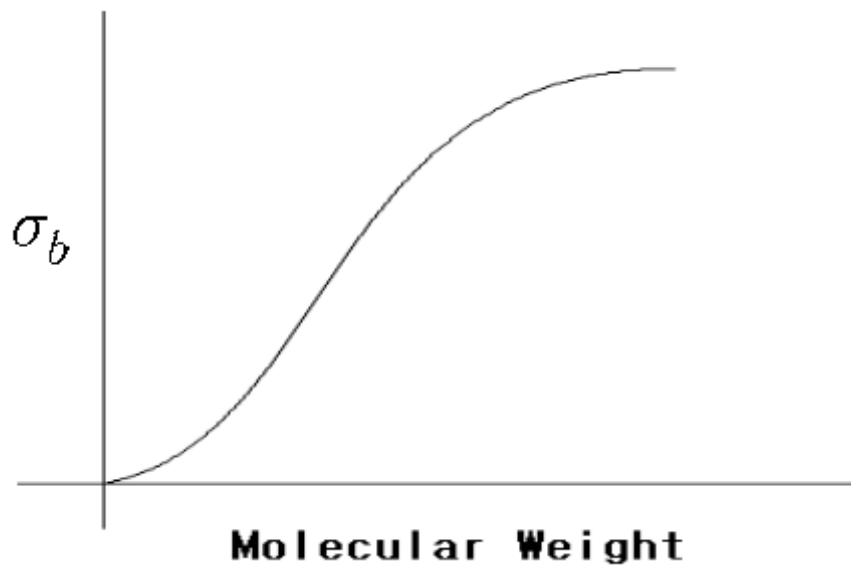
Mechanical properties of polymer = f (MW, Structure)

► Effect of MW

Break strength = A - B/Mn

A, B = Constant

Mn = Number average MW



► Processing method controls the MW:

Injection grade < Extrusion grade < Film grade

Injection=Flow is most important.

Film=Melt strength is most important.

► Effect of molecular structure

Linear PE = easy to crystallize = high density PE(HDPE)

Produced by [Ziegler-Natta catalyst](#) (low pressure method)

Less than 1 branch per 100 main chain C atoms

High crystallinity → high density ($\rho = 0.97-0.98 \text{ g/cm}^3$) → for heavy duty

Branched PE (BPE)

Short chain branch disturbs chain packing into crystal structure → low crystallinity → low density

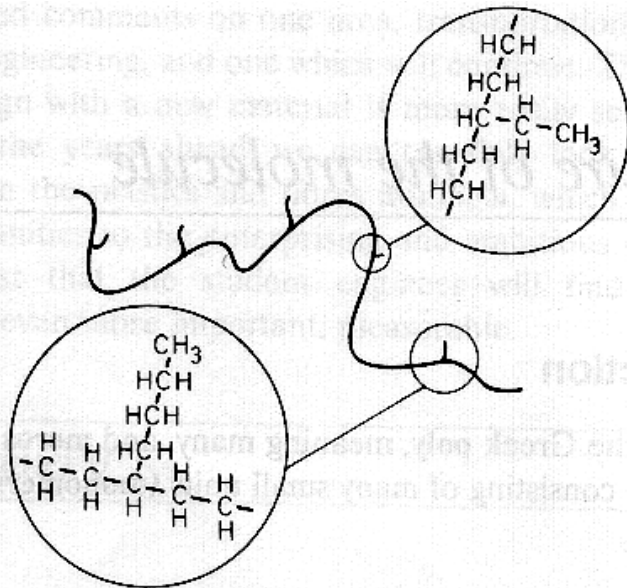
Small amount [SCB](#) exerts significant effects on [solid state property](#) - modulus, creep resistance, impact toughness.

Long chain branch exerts significant effect on melt property.

Low density PE = LDPE (SCB) (High pressure method).

2-3 branches per 100 main chain C atoms.

Mostly 2 or 4 carbon atoms per branch (SCB).

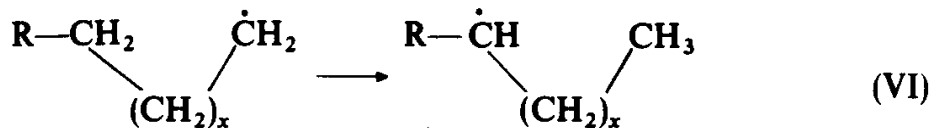


1.1 Side-branched polyethylene.

Low crystallinity → low density ($\rho = 0.92-0.93$).

Type of BPE

LDPE by back biting mechanism (Eq VI)



LLDPE, ULDPPE, VLDPE

Density ($0.86 < \rho < 0.89$)

Produced by copolymerization w/ α -olefin

Typically 1-butene, 4-methyl pentene-1 (Z-N catalyst) (Figure 1.4)

Type and content of α -olefin governs the property and applications.

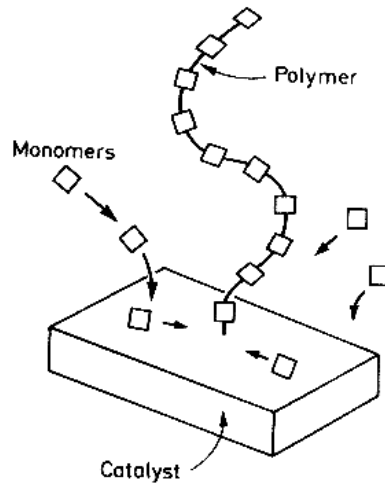
LLDPE-vinyl sack (high tear strength!!!)

ULDPE, VLDPE-olefin modifier, hot melt, adhesives...

Toughmer (Mitsui, commercialized in 1986) --- See Table 1 Figure 2

Series A=copolymer with butene-1, $T_m = 70-80^\circ\text{C}$

Series B=copolymer with 4-methylpentene-1, $T_m \sim 40^\circ\text{C}$



1.4 An illustration of polymerization by Ziegler-Natta catalyst. The monomers diffuse on to the catalyst surface. They then migrate across the surface to the growth point.

Table 1. Characteristics of ULDPEs and HDPE

Sample	Density (g/cm ³)	T _m (°C)	MI (g/10min)*	M _n (10 ⁴)	M _w (10 ⁴)	Comonomer	C ₂ units	Maker
A-4085	0.887	75.2	3.7/ 23.0	5.52	9.95	butene-1	86% mol	Mitsui
A-4090	0.893	82.0	3.9/ 24.0	3.75	6.99	butene-1	86% mol	Mitsui
A-20090	0.895	84.2	18.2/114.5	2.81	4.78	butene-1	86% mol	Mitsui
P-0480	0.865	40.8	1.0/ 6.6	6.66	14.20	4-methylpentene	76% wt	Mitsui
P-0680	0.867	40.0	0.4/ 3.1	8.88	17.21	4-methylpentene	76% wt	Mitsui
E308 (HDPE)	0.956	129	0.84/ 11.2	2.13	8.59	—	100% wt	Korea Petrochem.

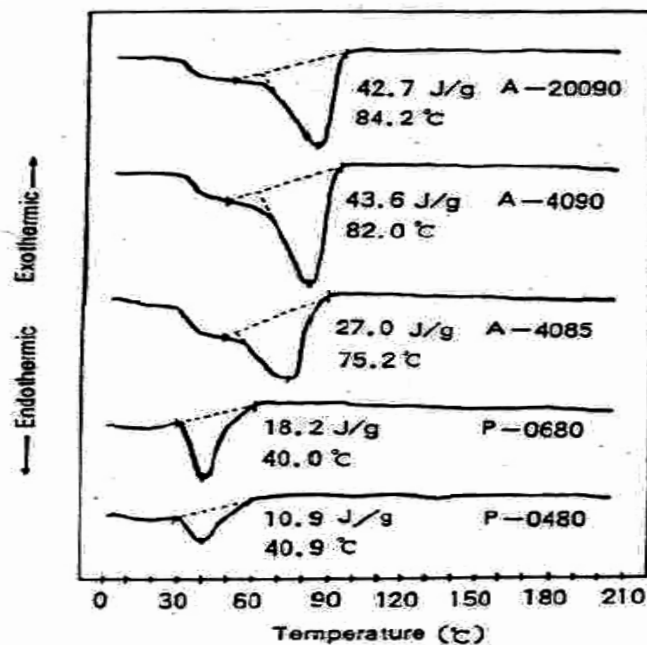
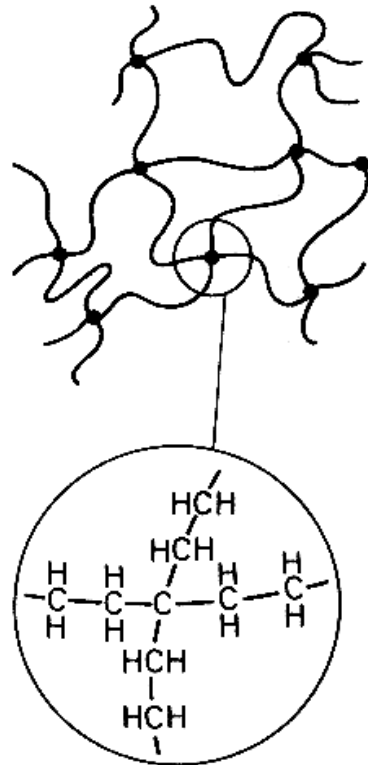


Fig. 2. DSC thermograms of ULDPEs.

Crosslinked PE (X/L PE)



1.2 Illustration of the molecular structure of cross-linked polyethylene in the liquid state. The spaces between the sketched net are filled with other parts of the network.

Produced by melt extrusion in the presence of peroxide (DCP, BPO).

Properties of X/L PE

High ESCR (Environmental stress crack resistance).

High impact strength.

Used for hot water pipeline.

Peroxide cure of PP

Chain scission (β -scission)

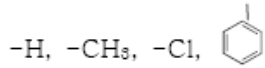
Called rheology controlled PP.

1.2 Additional polymers

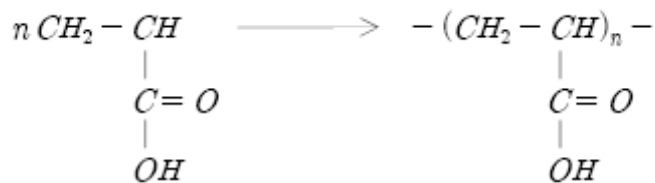
► Vinyl monomer



PE, PP, PVC, PS
(4 Commodity Polymers)



► Acrylate : Acrylic acid derivative



Methyl acrylate

Ethyl acrylate

Butyl acrylate...w/ increasing length, T_g decreases until the branch is crystallized.

Methacrylic acid

MMA.....

► Mechanism & Kinetics



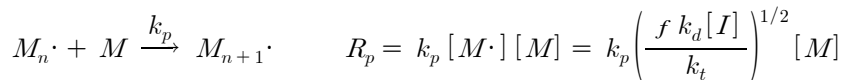
Decomposition



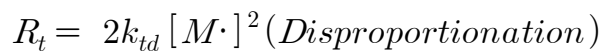
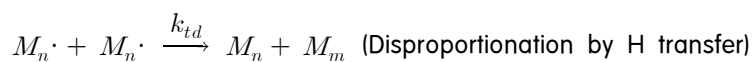
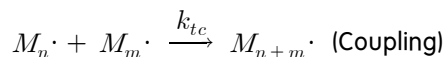
Initiation



Propagation



Termination

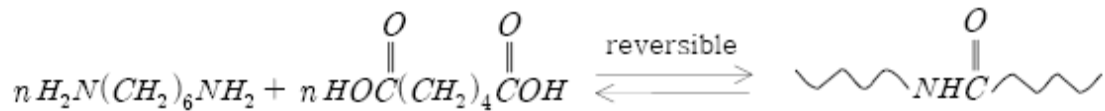


$$\text{@s.s } R_t = R_i = 2k_{td} [M\cdot]^2$$

$$[M\cdot] = \left(\frac{2f k_d [I]}{2k_{td}} \right)^{1/2}$$

1.3 Condensation polymers

- Polyamide 66(Nylon 66)



Polyester (PET), PBT.....

- MW controlled by the stoichiometric imbalance as follow:

$$\overline{X}_n = \frac{1+r}{1+r-2rp} = \frac{1+r}{1-r} \quad (p=1)$$

- Condition for high MW by condensation polymerization

- i) 1:1 stoichiometry
- ii) Pure monomer
- iii) Long reaction time

- Radical polymerization vs Condensation polymerization

- Radical polymerization : Initiation + Propagation + Termination
occur in a few seconds

- For condensation polymerization high MW is obtained only at long reaction time with exact 1:1 stoichiometry

