1.6 Molar mass

- Low molar mass substances (oligomers) : m. p.↑ with MW↑.
- High molar mass substances (polymers) : m. p. constant with MW↑
  but, rheological properties : (ex.) melt viscosity ↑ with MW↑

Molar mass distribution (3 ~ 4 지수 정도의 범위로 분포)

· *Number average molecular weight*

$$\overline{M_n} = \frac{\sum N_i M_i}{\sum N_i} = \sum n_i M_i = \frac{\sum W_i}{\sum \frac{W_i}{M_i}} = \frac{1}{\sum \frac{w_i}{M_i}}$$

N_i = # of molecules
n_i = numerical fraction or number fraction (= mole fraction x_i)
W_i = mass of M_i
w_i = weight fraction or mass fraction

· *Weight average molecular weight*

$$\overline{M_w} = \frac{\sum N_i M_i^{\,2}}{\sum N_i M_i} = \frac{\sum W_i M_i}{\sum W_i} = \sum w_i M_i$$

· *Viscosity average molecular weight*

$$\overline{M_v} = \left(\frac{\sum N_i M_i^{\,1+a}}{\sum N_i M_i} \right)^{1/a} = \left(\sum w_i M_i^{\,a} \right)^{1/a}, \quad 0.5 \le a \le 0.8$$

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta - \eta_0}{c \eta_0} \right)$$

η_0 : η of pure solvent
$[\eta]$: intrinsic viscosity
c : concentration of polymer in solution

· **Mark-Houwink rule** (relationship betw. $[\eta]$ and $\overline{M_v}$)

$$[\eta] = K\overline{M_v}^{a}$$

K, a : Mark-Houwink parameters,
Unique for the combination of polymer & solvent

· $M_n \le M_v \le M_w \le M_z$

· **Polydispersity index**, PI (or heterogeneity index) $\equiv \dfrac{M_w}{M_n}$

$M_n \le M_w$ 의 증명 :

$\sum N_i (M_i - M_n)^2 \ge 0$ 이 성립하므로 풀어 쓰면

$\sum N_i M_i^{\,2} + \sum N_i M_n^{\,2} - 2\sum N_i M_i N_n \ge 0$ 이 된다. 이 식을 $\sum N_i$ 로 나누면

$$\frac{\sum N_i M_i^{\,2}}{\sum N_i} + M_n^{\,2} - \frac{2\sum N_i M_i M_n}{\sum N_i} \ge 0$$ 이므로

$$\frac{\sum N_i M_i^{\,2}}{\sum N_i} \ge M_n^{\,2}$$ 이 된다. 이를 다음과 같이 처리하면

$$\frac{\sum N_i M_i^{\,2}}{\sum N_i} \times \frac{1}{M_n} \ge M_n \quad \Rightarrow \quad \frac{\sum N_i M_i^{\,2}}{\sum N_i} \times \frac{\sum N_i}{\sum N_i M_i} \ge M_n$$ 이 되므로

$M_w \ge M_n$ 이 성립한다.

Experimental techniques for MW determination

Absolute methods (no calibration)
Relative " (calibration)

Table 1.3 Experimental techniques for molar mass determination

Method	Result	Comments
End-group analysis	$\bar{M}_n$	Absolute method, restricted to low molar mass
Colligative methods: ebulliometry, cryoscopy and osmometry	$\bar{M}_n$	Absolute methods, ebulliometry/cryoscopy, restricted to low molar mass
Light scattering	$\bar{M}_w$	Absolute method
Viscometry	$\bar{M}_v$	Relative method, easy to use
Size exclusion chromatography (SEC)	Molar mass distribution	Relative method, requires calibration

- *End group analysis* (by IR, NMR, titration) → low molar mass polymers
- *Colligative properties*

  Boiling point elevation (ebulliometry)
  Freezing point depression (cryoscopy)
  Osmotic pressure

b. p. elevation & f. p. depression

→ $\overline{M_n}$ for low molar mass (≤10000 g/mol)

$$\left(\frac{\Delta T_x}{c}\right)_{c\to 0} = \left(\frac{V_1 R T_0^{\,2}}{\Delta H_x}\right)\frac{1}{\overline{\overline{M_n}}}$$

V_1 : molar volume of solvent

T_0 : b. p. or f. p. temperature for pure solvent

$\triangle T_x$: $\triangle T$ in f. p. or b. p.

$\triangle H_x$: transition enthalpy

Osmometry ($\overline{M_n}$ ≤100,000 g/mol)

van't Hoff equation:

$$\left(\frac{\pi}{c}\right)_{c\to 0} = \frac{RT}{\overline{\overline{M_n}}}$$

$$\leftarrow \quad \frac{\pi}{c} = RT\left(\frac{1}{\overline{\overline{M_n}}} + A_2 c + A_3 c^2 + \cdots\right)$$

- *Light scattering* → $\overline{M}_w$ cf. small-angle neutron scattering(SANS)
  X-ray scattering

- *Viscometry* → $\overline{M}_v$ (relative method)

- *Size exclusion chromatography* (SEC), or *gel permeation chromatography* (GPC)
  : relative method (∴ Calibration is necessary)
  porous gel을 지나는 시간이 다름. 농도를 굴절률이나 IR light absorption을 측정.

- *Degree of polymerization* (X)

$$X = \frac{M}{M_{rep}} \qquad M_{rep} \sim \text{Molar mass of CRU}$$

For step-growth polymerization : Most probable distribution
(Schultz-Flory distribution)

$$n_i = \frac{1}{\overline{X}_n}\left(1 - \frac{1}{\overline{X}_n}\right)^{i-1}$$

n_i : the number fraction of molecules of $X = i$

$\overline{M}_n$: the number average of the degree of polymerization

For chain radical polymerization : Schultz distribution

$$n_i = \frac{4i}{\left(\overline{X}_n - 1\right)^2}\left(\frac{1}{1 + \frac{2}{\overline{X}_n - 1}}\right)^i$$

1.7 Polymerization

Flory scheme (based on polymerization mechanism)

Criterion	Step	Chain
Growth reaction	Reaction proceeds by stepwise intermolecular condensation	Repeating units are added one at a time
Monomer concentration	Almost completely disappears early in the reaction	Decreases steadily throughout the reaction
MW of high polymer	Increases steadily	Is formed at once
Reaction time	Long reaction time is essential to achieve high MW	Long reaction time will increase the yield (not MW)
Reaction mixture	All species are present	Mixture contains high polymer, monomer and small no. of growing chains

- **Step growth** (ex: polyamide, polycarbonate, polyester, PPO, PPS, etc.)

All reactions are reversible ∴ requires the removal of water for high MW.

Number average degree of polymerization

$$\overline{X}_n = \frac{1}{1-p} \qquad p : \text{extent of rxn} \left(= \frac{N_0 - N}{N_0} \right)$$

$$= \frac{\text{no. of groups reacted}}{\text{no. of groups present initially}}, \quad \text{즉 conversion}$$

p	0.1	0.9	. . .	0.9999
$\overline{M}_n$	1.1	10	. . .	10000

- **Chain growth** (ex: PE, PP, PS, PMMA, PVC, PVA etc.)

Radical, anionic, cationic or coordination polymerizations

Initiation, propagation, termination
→ Linear polymer
→ Branched polymer (by chain-transfer)

HDPE (low-pressure PE) vs. LDPE (high-pressure PE)

Anionic & cationic → Living polymerization
→ Molecular design
Possible to prepare exact block copolymer
Impurity (ex, water) leads chain transfer & termination of growing chains (고순도 필요)

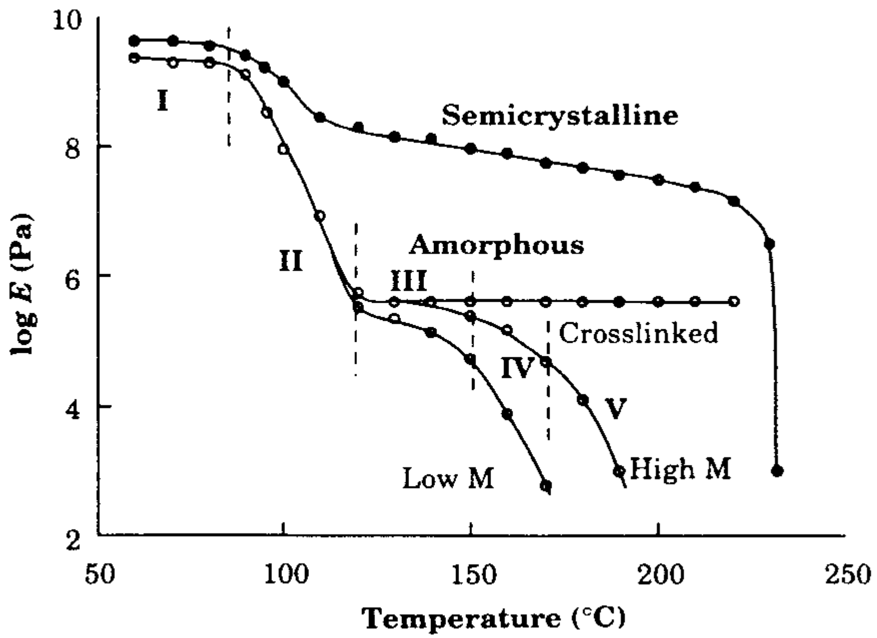
1.8 Thermal transitions and physical structures

Fully amorphous ~ irregular chain structure
Semicrystalline ~ lamella-shaped crystals & amorphous components

Differences in crystallinity
→ differences in physical properties

ex) relaxation modulus $\equiv \left(\dfrac{\text{stress}}{\text{strain}} \right)$

※ Schematic diagram of stress relaxation modulus for isotactic PS and fully amorphous (atatic) PS



I : glassy (below T_g)

II : leather-like (at T_g)

III : rubber-like (rubber plateau)

IV, V : sliding motions of molecules

1.9 Polymer materials

Thermoplastics

Thermosets (phenoxy, epoxy, melamines, etc.)

Rubbers or *elastomers* (SBR, PBD, PI, etc.)

Properties of a polymer material

- by structure of polymers, additives, processing methods & conditions

→ cf. PE fibers 100 GPa (fibrous PE, longitudinal modulus)

1 GPa (conventionally processed)