

P 129 Chapter 6. Transition Temperature

- 1) glass-rubber transition temperature (T_g)
- 2) crystalline melting temperature (T_m)
 - can be correlated with the chemical structure by means of a method based on group contributions.
- 3) there may be three transitions below T_g
 - $0.5 T_g \sim 0.8 T_g$, $0.35 T_g \sim 0.5 T_g$,
 - and very low temp ($4 \sim 40$ K).
- 4) Between T_g and T_m
 - rubbery amorphous state and in the crystalline state.
- 5) liquid state transition “liquid crystals”

A : The Glass Transition Temperature

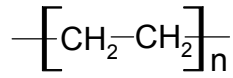
An additive molar function for the calculation of T_g .

(empirical approach)

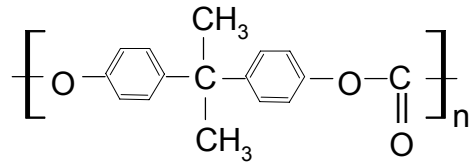
- the product $T_g \cdot M$ behaves as an additive function ; the Molar Glass Transition Function (Y_g)
- T_g (glass transition temp) – the onset of segmental motion of the polymer backbone. The noncrystalline portion of the material exhibits a T_g .
- T_m (melting point) – temp. where the largest and most perfect crystallites would melt.
- T_g sets an upper temp limit for the use of amorphous thermoplastics like poly(methyl methacrylate) (PMMA) or polystyrene (PS) and a lower temp. limit for rubbery behavior of an elastomer like SBR or PBD.

4) Effect of Polymer Structure on T_g

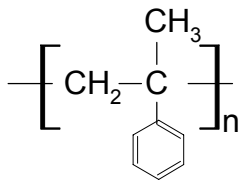
- a) Flexibility of the macromolecules and the intensities of intermolecular forces,
Ex>



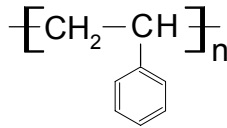
Polyethylene(PE), $T_g = -120\text{ }^\circ\text{C}$



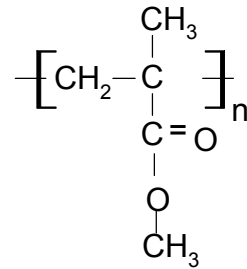
Polycarbonate(PC), $T_g \approx 150\text{ }^\circ\text{C}$



Poly(α -methyl styrene)
 $T_g \approx 168\text{ }^\circ\text{C}$



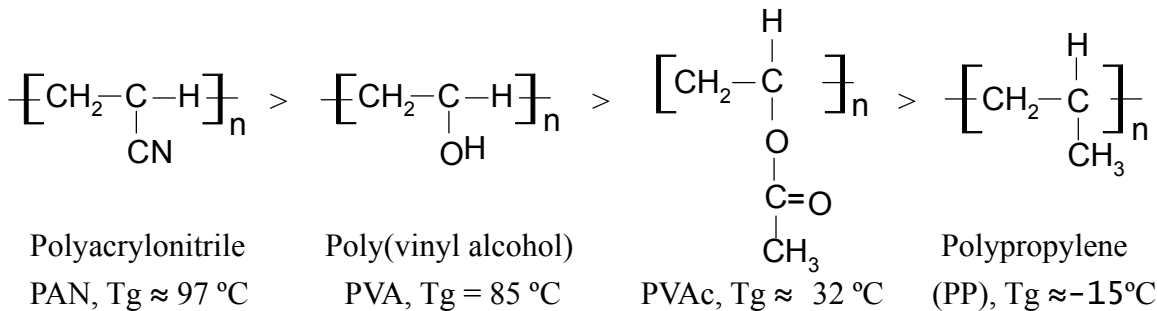
Polystyrene(PS)
 $T_g = 100\text{ }^\circ\text{C}$



Poly(methacrylate)(PMMA)
 $T_g \approx 105\text{ }^\circ\text{C}$

- Strong intermolecular attractive forces pull the chain together and hinder relative motions of segments of different macromolecules. Also polar polymers and those with hydrogen bonding are important therefore have a high T_g .

Ex>



- b) Chain Length : T_g is increased with number-average molecular weight.

$$T_g = T_g^\infty - u/M_n$$

$T_g^\infty = T_g$ of an infinitely long polymer chain

$U =$ constant that depends on the polymer

ex> polystyrene ($M_n=10000$, $T_g=88^\circ \text{C}$)

Polystyrene ($M_n>50000$, $T_g=100^\circ \text{C}$)

c) crosslinking increases the T_g of a polymer.

Large shifts of T_g with increased cross-linking are observed, (ex) epoxy or phenolic thermosetting resin.

d) The free volume of the polymer V_f .

- free volume is the volume of the polymer mass not actually occupied by the molecules themselves:

that is, $V_f = V - V_s$

where V is the specific volume and V_s is the volume of solidly packed molecules.

The higher the V_f , the more room the molecules will have in which to move around and the lower the T_g .

ex> T_g is increased at high pressures, why ?

5) T_g of Copolymers and miscible mixture.

$$T_g = W_1 T_{g1} + W_2 T_{g2} \quad (\text{Wood equation})$$

Where T_g is the observed T_g of the copolymer, W_1 is the weight fraction of homopolymer1 having T_{g1} , and W_2 is the weight fraction of homopolymer2 having T_{g2} .

(Ref.) L.A.Wood, J.Polym.Sci., 28, 319(1958).

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

(Fox equation)

(Ref: T.G.Fox, Bull.Am. Phys.Soc.,1(2),123(1956))

$$\ln T_g = \frac{W_1 \Delta C_{p1} \ln T_{g1} + W_2 \Delta C_{p2} \ln T_{g2}}{W_1 \Delta C_{p1} + W_2 \Delta C_{p2}}$$

(Couchman eq.)

(Ref: P.R.Couchman, Macromolecules,11, 1156(1978)

Kim and Burns,J.Appl.polym.Sci.,34,945(1987))

Where $\Delta C_p = C_p^L(T_g) - C_p^S(T_g)$ = difference in molar heat capacity at T_g , where $C_p^L(T_g)$ is the molar heat capacity at T_g , and $C_p^S(T_g)$ is the molar heat capacity of the solid at T_g

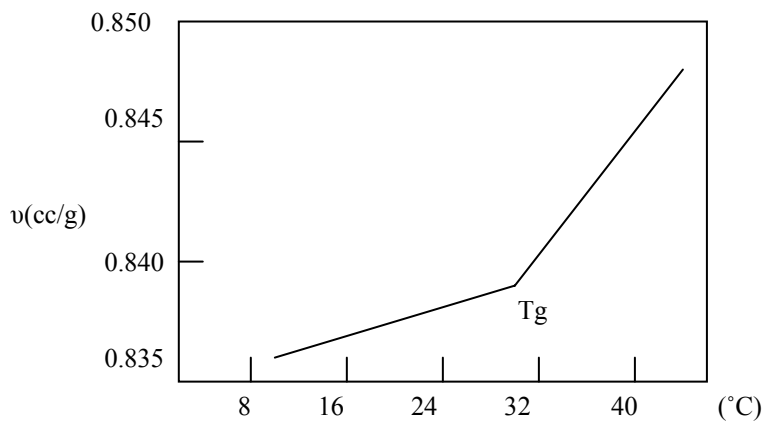
Ex> polycarbonate and poly(e-caprolactone) are known to be miscible. What is the T_g of the mixture if $W_{pc}=0.5$?

$$T_{gpc}=150^\circ\text{C} \quad , \quad T_{gpcL}=-40^\circ\text{C}$$

(sol) using Fox eq.

$$\frac{1}{T_g} = \frac{0.5}{(273 + 150)} + \frac{0.5}{(273 + (-40))}$$

6) Measurement of T_g



T_g : second order transition

$$\left\{ \begin{array}{l} v \text{ vs } T : \text{continuous} \\ dv/dT \text{ vs } T : \text{discontinuous} \end{array} \right\}$$

P 132

$$Y_g = \sum_i Y_{gi} = T_g \cdot M$$

$$T_g = Y_g / M = \sum_i Y_{gi} / M$$

1. The unbranched polymethylene chain

Ex) amorphous polymethylene 의 T_g 는 약 $195 \pm 10K$.

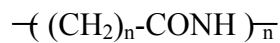
$$\begin{aligned} Y_g(-CH_2-) &= 195 \times 14.03 \\ &= 2736 \pm 140 \text{ (K}\cdot\text{g/mol)} \\ &= 2.74 \pm 0.14 \text{ (K}\cdot\text{kg/mol)} \end{aligned}$$

(see Table 6.1) for T_g

· Comparison between calculated and experimental values. (see Table 6.4)

(Ex 6.1) Estimate the limiting value of T_g for poly lactams (aliphatic polyamides) at increasing number of CH_2 groups in the chain.

(sol)



From Table 6.1

$$Y_g = n \cdot Y_g(-CH_2-) + Y_g(-CONH-) = 4.3n + 15$$

$$M = nM(CH_2) + M(-CONH-) = 14n + 43$$

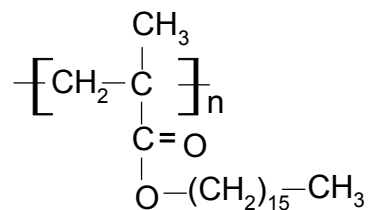
For Nylon-6

$$T_g = \frac{4300n + 15000}{14n + 43} = \frac{Y_g}{M}$$

$n \rightarrow 5$ 일 때

$$= \frac{36500}{113} = 323K = 50^\circ C \quad (\text{for Nylon-6})$$

p 142 (Ex 6.2) Estimate the T_g of poly(hexadecyl methacrylate)



From Table 6.2. (p 139) and 식 (6.8). (p 137)

$$N > 9 \quad Y_g \approx Y_{g9} + 7.5(N-9)$$

$$\text{여기서 } Y_{g9} = 45.2$$

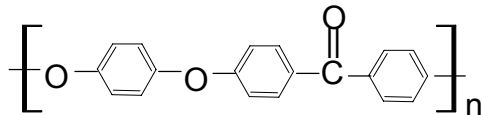
$$Y_g = Y_{g9} + 7.5(N-9) = 45.2 + 7.5(15-9) = 90.2 (\text{K} \cdot \text{Kg/mol})$$

$$M = M_0(100.1) + 15 \times 14.02 = 311$$

$$\therefore T_g = \frac{Y_g}{M} = \frac{90.2 \times 1000}{311} = 290 \text{K}$$

($T_{g \text{ exp}} = 288 \text{K}$) ← (see Table 6.4, p 144)

P 145 (EX 6.3) Estimate the T_g of PEEK



(sol) the molar mass = 288.3g/mol

$$Y_g \left(\text{---O---} \langle \text{C}_6\text{H}_4 \rangle \text{---O---} \right) = 37.4 \text{ (Table 6.1)}$$

$$(29.5 + 4 + 4) = 37.5$$

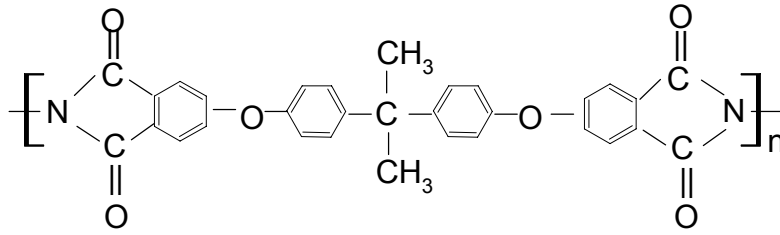
$$Y_g \left(\text{---} \langle \text{C}_6\text{H}_4 \rangle \text{---C(=O)---} \langle \text{C}_6\text{H}_4 \rangle \text{---} \right) = 84 \text{ (Table 6.3)}$$

$$\overline{\sum Y_g} = 121$$

$$\therefore T_g = \frac{121.4 \times 1000}{288.3} = 420 \text{K}$$

(exp. $T_g = 414 \sim 433$) *DSC, 실제 exp. $T_g = 425 \text{K}$

P 146 (Ex 6.4) Estimate the T_g of the polyimide, Ultem 1000 (G.E.Co).



$$(sol) \quad T_g = \frac{285 \times 1000}{578} = 493K$$

$$T_g(\text{exp}) = 490K$$

P 146 • Other factors influencing the value of T_g .

1. Pressure dependence of T_g .

$$T_g(\rho) = T_g(0) + S_g \cdot \rho$$

$$S_g \approx 0.55K / MPa$$

2. The influence of molecular weight

$$T_g = T_g(\infty) - \frac{A}{M_n}$$

3. The influence of tacticity.

$$Tg(\text{syndiotactic}) - Tg(\text{isotactic}) \approx 112^\circ$$

4. The influence of cross-linking.

Cross-linking increases the T_g of a polymer.

B. The Crystalline Melting Point

• An additive molar function for the calculation of T_m

- Molar Melt transition Function

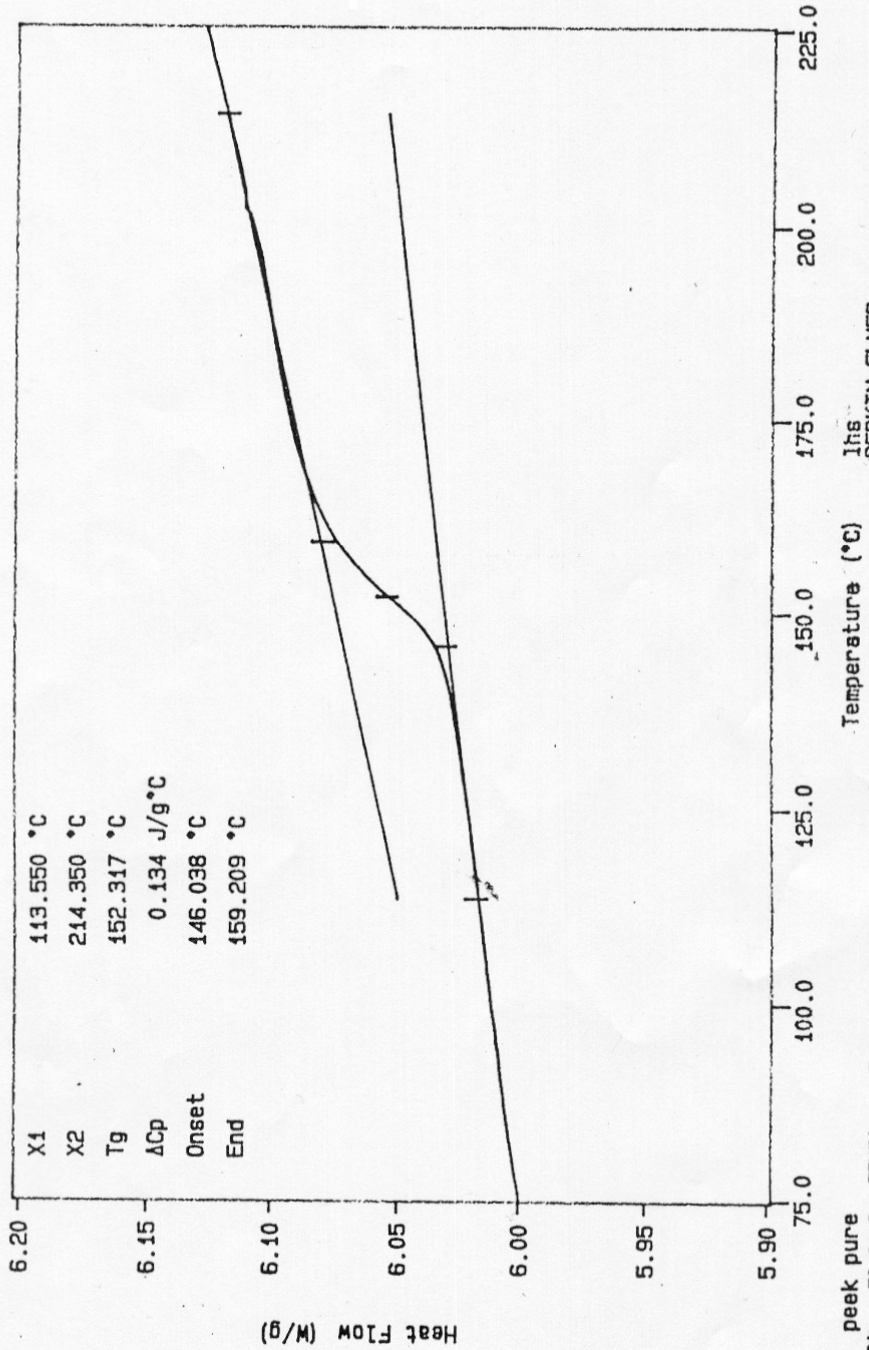
$$\rightarrow Y_m = \sum_i Y_{ni} = T_m \cdot M (K \cdot kg / mol) \quad , \quad T_m = \frac{Y_m}{M} = \frac{\sum Y_{mi}}{M} \quad (6.1.8)$$

Curve 1 DSC

File info: peek9.5 Thu Jul 7 21:08:23 1994

Sample Weight: 9.500 mg

peek



peek pure
TEMP: 50.0 °C
TIME: 500.0 s

5.0 °C/min RATE: 50.0 °C/min

PERKIN-ELMER
7 Series Thermal Analysis System
Fri Aug 5 21:32:37 1994

PEEK DSC Themogram (95.4.27)

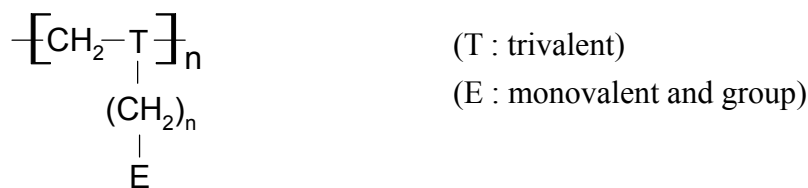
- Derivation of the group contributions of Y_m .

1. The unbranched polymethylene chain

- the melting point of pure polymethylene is 409K.(136°C)

$$Y_n(-CH_2-) = 409 \times 14.03 = 5738 \text{ (K}\cdot\text{kg/mol)}$$

- Aliphatic carbon chains with “small” side groups. (see Table 6.6)
- Aliphatic carbon(main-) chains with “long” side chains (“Comb” polymers)



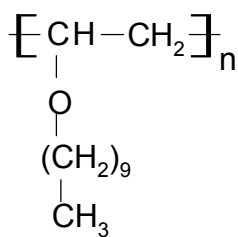
P 156 $\left\{ \begin{array}{l} N=5 \\ N<5 \end{array} \right. \quad Y_m \approx 0.235M_5 = Y_5 \quad (6.19)$

$\left. \begin{array}{l} N<5 \\ N>5 \end{array} \right\} \quad (6.20)$

P 161 $\left. \begin{array}{l} N>5 \end{array} \right\} \quad (6.21)$

- P 163 · Comparison between calculated and experimental values.

(ex.6.5) Estimate the crystalline melting points of poly(vinyl 1-decyl ether), the structural formula is



(sol) For $n > 5$

$$Y_n = Y_{m5} + 5.7(N-5) \quad (6.21) \text{ (P. 152)}$$

From Table 6.7(p.155) gives for poly(ethers),

$$Y_{m5} = 30.1 \text{ (K}\cdot\text{Kg/mol)}$$

$$M_0 = 58.1 \text{ (g/mol)}$$

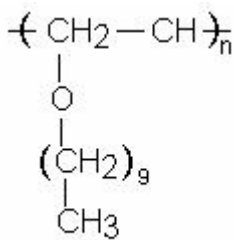
$$\therefore Y_n = 30.1 + 5.7(9 - 5) = 52.9$$

$$M = 58.1 + 14.02 \times 9 = 184$$

$$\therefore T_m = \frac{52.9 \times 1000 K (g/mol)}{184 (g/mol)} = 288 K$$

$$T_m(\text{exp}) = 280 (K) \quad \text{“good agreement”}$$

- the structural formula is



(sol.) For $N > 5$

$$Y_m = Y_{m5} + 5.7 (N - 5) \quad (6.21)$$

from Table 6.7 (p.155) gives for poly(ethers);

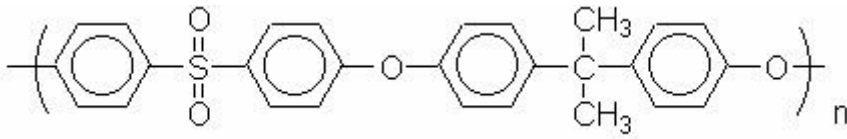
$$Y_{m5} = 30.1 \text{ and } M_o = 58.1$$

$$Y_m = 30.1 + 5.7(4) = 52.9, \quad M = 58.1 + 9 \times 14.02 = 184$$

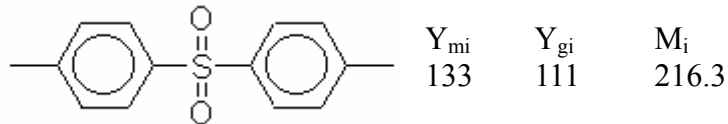
$$T_m = \frac{52.9 \times 1000}{184} = 288 K$$

$$T_m(\text{exp}) = 280 K \quad \text{(fair agreement)}$$

p.163 (EX 6.6) Estimate the crystalline melting point of UDEL polysulfone,



From Table 6.10 (p.162)

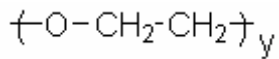


From Table 6.6 (P153)

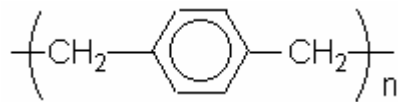
2 -O-	27	87	32.0
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• T_m 에 영향을 주는 것은:

① structure flexibility :



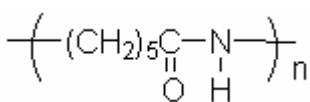
poly(ethylene oxide)
 $T_m=66^\circ\text{C}$



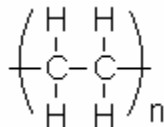
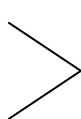
poly(p-xylene)
 $T_m=375^\circ\text{C}$

② strong intermolecular forces :

ex) polyamide-strong hydrogen bonding
has higher T_m than polyethylene.



N-6



PE

ex) Nylon-6 has higher T_m than N-11.

$T_m=225\text{ }^\circ\text{C}$

$T_m=194\text{ }^\circ\text{C}$

● Crystallinity 에 영향을 주는 것:

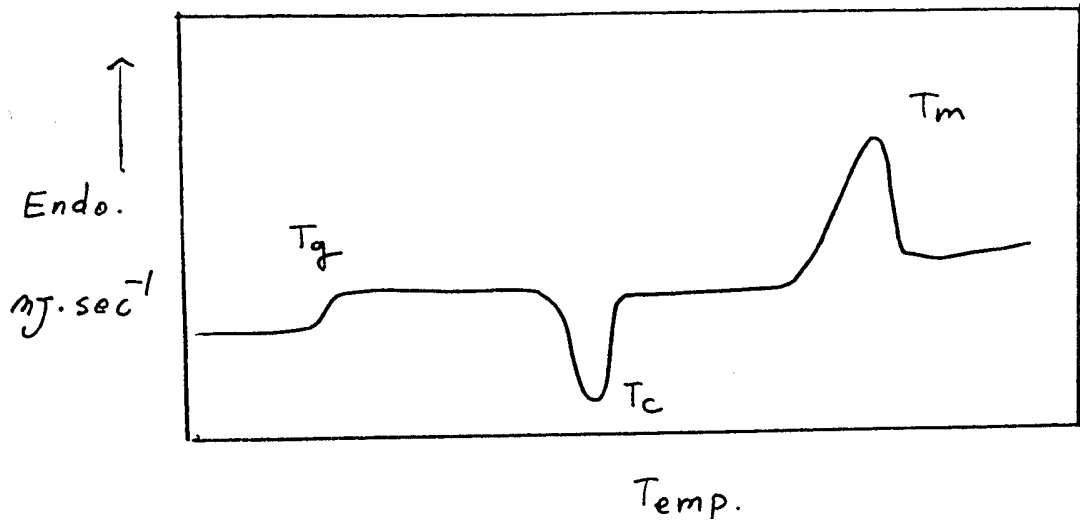
a periodic, regular placement of the atoms of the chain – isotactic.

bulky side group 은 crystallization rate 를 줄인다. (by preventing the close approach of different chain segments).

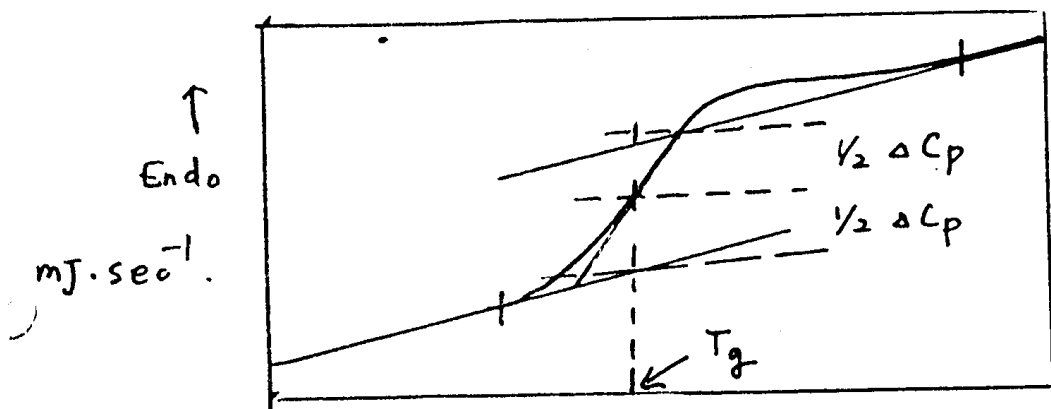
③ crystallization occurs between T_m and T_g . Because of the effects of increasing concentrations of stable nuclei.

Crystallization rates are zero at T_m and T_g . Because the cooler conditions reduce the rate of conformational changes

● By DSC (Differential Scanning Calorimetry)



Typical DSC thermogram of partially crystalline polymer



Determination of Tg by midpoint-method

(Ref. Shultz and Young, J. Appl. Polym. Sci., 28, 1677(1983))

- Temp. Calibration : indium ($T_m=156.60\text{ }^\circ\text{C}$, $\Delta H_f=28.5\text{ J/g}$)
- Heating Rate : 10 ~ 20 K.min
- Sample Size : 5~ 15 mg using aluminum sample pan
- Atmosphere : nitrogen or Helium

●Maker : Perkin- Elmer or Dupont.

Also, we can measure T_g by DTA(Differential Thermal Analysis) or DMA(Dynamic Mechanical Analyzer)

$$T_m = T_m^o \left[1 - \frac{1}{\Delta H_f^o} \left(\frac{2\sigma_e}{L} + \frac{4\sigma}{X} \right) \right]$$

여기서 T_m=melting point of the crystalline component.

T_m^o= equilibrium melting point of the pure crystalline component.

ΔH_f^o=the perfect crystal heat of fusion

σ_e= surface free energy associated with the top or fold surfaces

σ=side surfaces

L=square crystal with thickness

X=lateral crystal size

(Ref) Hoffman et al, "In treatise on solid stste Chemistry", Hannay Ed., Plenum Press, N. Y., 1975, Vol.3.

Rim and Runt, Macromolecules, 17, 1520 (1984)

Table III

Crystal Dimensions for PET Determined From WAXS

	Ray Reflection			T _m , °C	Reference
	010	110	100		
Annealed at 270 °C for 472.5 h	160	140	130	286.0	(1)
Annealed at 250 °C	96	62	60	-	(2)
Annealed at 250 °C for 5 min	82	-	58	255.0	(3)
PEC/PET (9/1) ^a blend	55	80	65	-	(4)

^a Poly(ester carbonate)/poly(ethylene terephthalate).

- (1) C. M. Roland, Polym. Eng. Sci., 31, 849 (1991).
- (2) A. M. Hideleh, and D. J. Johnson, Polymer, 19, 27 (1978)
- (3) Jain, A.k., and V. B. Gupta, J. Macromol. Sci., -phys., B29, 49 (1990)
- (4) S. M. Aharoni, J. Macromol. Sci., - phys., B22, 813,(1983-84)

Y _{mi}	Y _{gi}	M
125	87	194.3
<hr/> 285	<hr/> 206	<hr/> 442.6

$$\therefore T_m = \frac{Y_{mi}}{M} = \frac{285 \times 10^3}{442.6} = 645$$

$$T_g = \frac{Y_{gi}}{M} = \frac{206 \times 10^3}{442.6} = 466$$

$$T_g/T_m = 466/645 = 0.71$$

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○ other factors influencing the value of T_m

- 1. Pressure dependence of T_m
- 2. 3. 4. 등.

○ C. Relationship between glass transition temperature and T_m of Polymers.

$$T_g/T_m \approx 0.667$$

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$$T_g/T_m \cong \begin{cases} 1/2 & \text{for symmetrical polymers} \\ 2/3 & \text{for unsymmetrical} \end{cases} \quad (6.24)$$

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D. Relationship between T_g , T_m and other Transition temperatures.

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1. The local mode relaxation, ($T \ll T_g$) in Boyer's rotation.

– called β -relaxation

$$T(<T_g) \approx 0.75 T_g \text{ (at 100Hz)}$$

- found in both glassy amorphous and semicrystalline polymers
a very short section

2. A liquid-liquid relaxation above T_g : T_{λ}

- discovered recently in some unvulcanized amorphous polymers and copolymers.

- at 1.2 Tg

3. A second glass transition in semi crystalline polymers.

– in some semi crystalline polymers, two Tg's can be distinguished.

Tg(L) : a lower Tg. – from purely amorphous material

Tg(U) : an Upper Tg. – arises from amorphous material which is under restraint due to the vicinity of crystallites.

4. A premelting transition (T_{α})

-the temp. at which hindered rotation of polymer chains inside the folded crystals can occur.

$$T_{\alpha} \approx 0.9T_m \quad (\text{see Table 6.12}) \quad \text{p171}$$

○ The β -relaxation

- polymers are brittle below T_{β} and establish creep and ductile fracture between T_{β} and T_g

- start of free movement of special short section of the polymer chain.

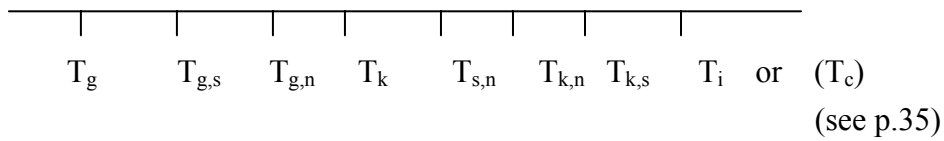
- Boyer's rule is very approximation

$$\left[\begin{array}{l} T_{\beta} \approx 0.8 T_g - 40 \approx 0.5 T_m - 25 \\ \quad \quad \quad (\text{for semi crystalline}) \\ - T_{\beta} + T_g \approx 635K \\ \quad \quad \quad (\text{for glassy polymers}) \end{array} \right.$$

E. Transitions in Thermotropic Liquid Crystal Polymers.

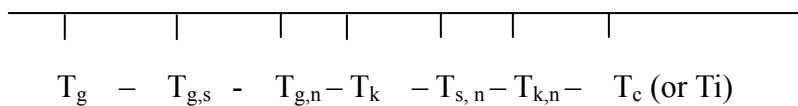
- one heating, yielding mesophase (liquid crystal melts)
so called mesogenic polymers or liquid crystal polymers.

Several phase states of the LCP



- T_g = glass Transition
- $T_{g,s}$ = smectic glass Transition
- $T_{g,n}$ = nematic glass Transition
- T_k = “disordering temp” of the crystalline state into the first liquid crystal state
- $T_{s,n}$ = transition of the smectic into the nematic phase
- $T_{k,n}$ = Crystalline phase into the directly nematic phase
- $T_{k,s}$ = Crystalline phase into the directly smectic phase
- T_i (or T_c) = final transition into the isotropic Liquid.

*several phase states of the LCP



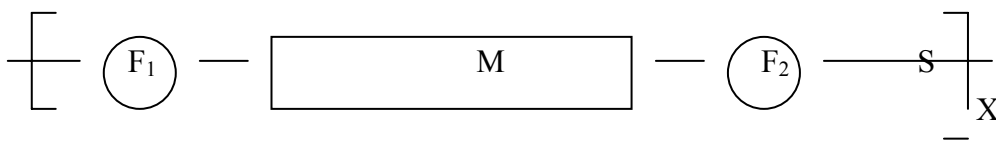
- T_g = glass Transition
- $T_{g,s}$ = smectic glass Transition
- $T_{g,n}$ = nematic glass Transition
- T_k = “disordering temp” of the crystalline state into the first liquid crystal state
- $T_{s,n}$ = transition of the smectic into the nematic phase
- $T_{k,n}$ = Crystalline phase into the directly nematic phase
- $T_{k,s}$ = Crystalline phase into the directly smectic phase

T_i (or T_c) = final transition into the isotropic Liquid

See P.36

See P 35

(1) Polymers with mesogenic groups in the main chain.



M : megogenic group

F : functional group (linking group)

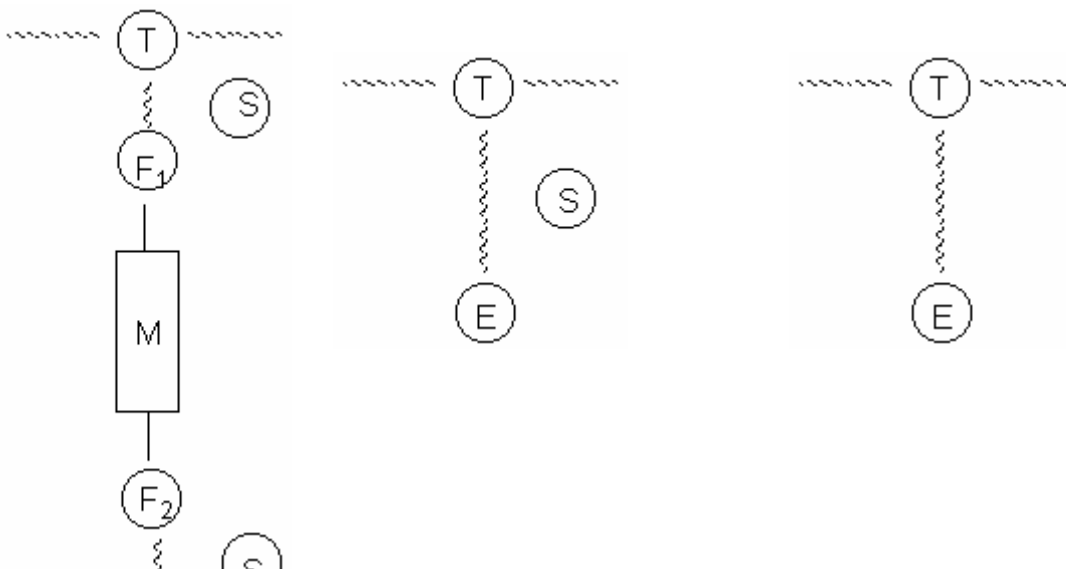
S : flexible spacer

$$T_k = 0.95 T_m (\text{calc}), \quad T_i = 1.05 T_m (\text{calc}) \quad (6.31)$$

-Eq. (6.31) is, as a matter of fact, no quarantee that an anisotropic phase will really be obserable

- In the present state of art, it is impossible to predict the nature and even the possible existence of a mesophase from the structural formula of a polymer

(2) Polymers with megogen groups in the side chain



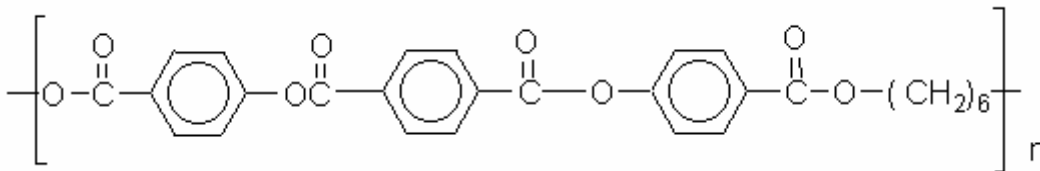
Normal
Comb Polymer

“Basci Polymer”

LCP

P.177

Ex 6.7 Estimate the characteristic temp of
the following Liquid-Crystalline Main-Chain Polymer :



1	Megogenic	Y_g 145	Y_m 205 (Table 6.15, p.178)
2	- COO -	25	50
6	- CH ₂ -	$\frac{16}{186}$	$\frac{10}{265}$ (p.160)

- molar weight = 488

$$T_g = \frac{186}{488} \times 1000 = 381K$$

$$\text{“}T_m\text{”} = \frac{265}{488} \times 1000 = 543K$$

so that $T_k = 0.95 \times 543 = 515k$
 $T_i = 1.05 \times 543 = 570k$

$T_{k(\text{exp})} = 500k$, $T_{i(\text{exp})} = 563k$
(good agreement)