

## Chapter 8. Transition in Polymer

### 1) Thermal Transitions

-Polymer molecules crystallize when they are cooled.(crystalline polymer)

### Definitions

1. Specific volume-the product of specific volume and molar weight.

$$v \equiv \frac{1}{\rho} \quad (\text{cm}^3/\text{g} \quad \text{or} \quad \text{m}^3/\text{kg})$$

2. Molar volume-the product of specific volume and molar weight

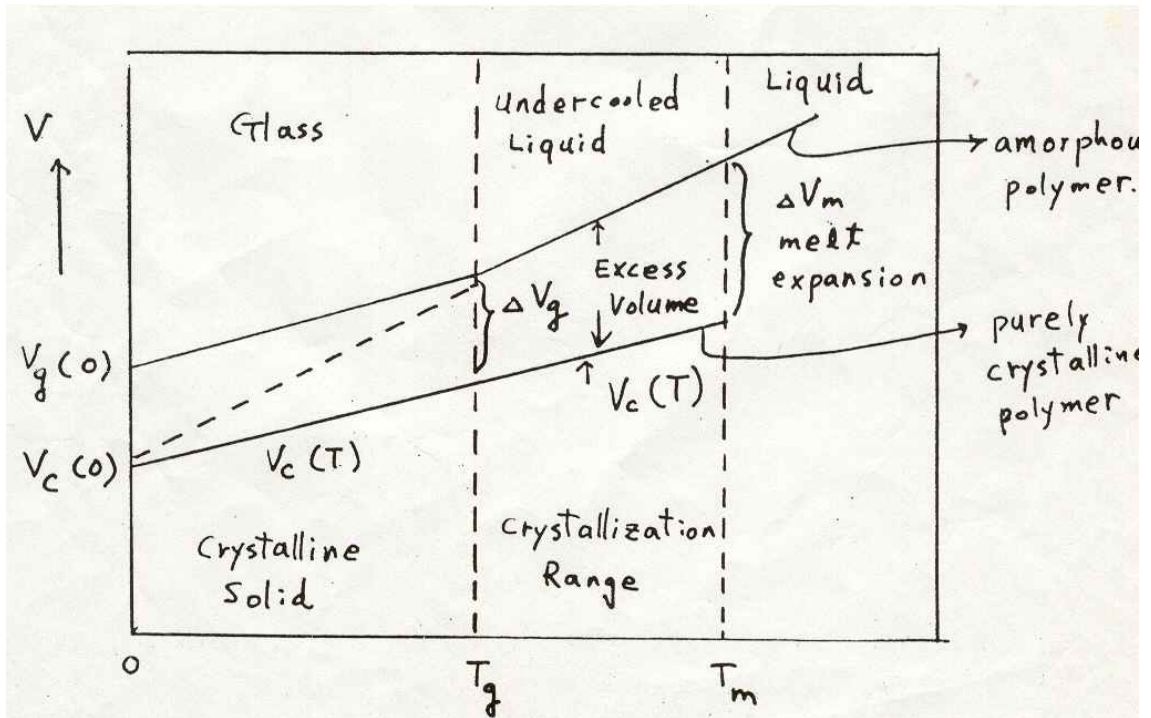
$$V \equiv Mv \equiv \frac{M}{\rho} \quad (\text{cm}^3/\text{mol} \quad \text{or} \quad \text{m}^3/\text{mol})$$

3. The coefficient of thermal expansion:

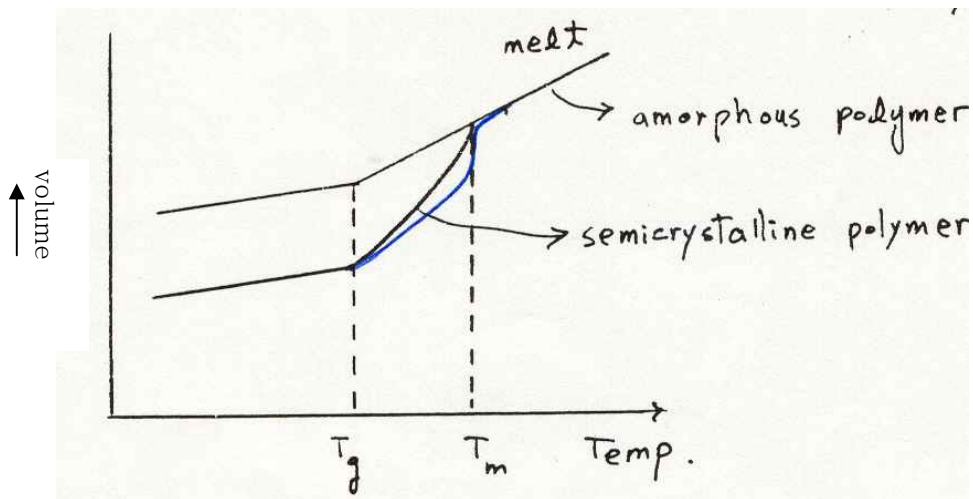
$$\frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p \equiv \alpha \quad (\text{K}^{-1})$$

4. The linear coefficient of thermal expansion :

$$\frac{1}{L} \left( \frac{\partial L}{\partial T} \right)_p \equiv \beta \quad (\text{K}^{-1})$$



Temp →



Volume-Temperature relation for an amorphous and semicrystalline polymer.

- o low molecular weight polymer-melt and crystallize quickly and completely.
- o high molecular weight polymer-need reorganization to fit into crystal

lattices and crystallization rate is slow.

o  $T_m$ (melting point): temperature where the largest and most perfect crystallites would melt.

o  $T_g$ (glass transition temp): the onset of segmental motion of the polymer backbone. The noncrystalline portion of the material exhibits a  $T_g$ .

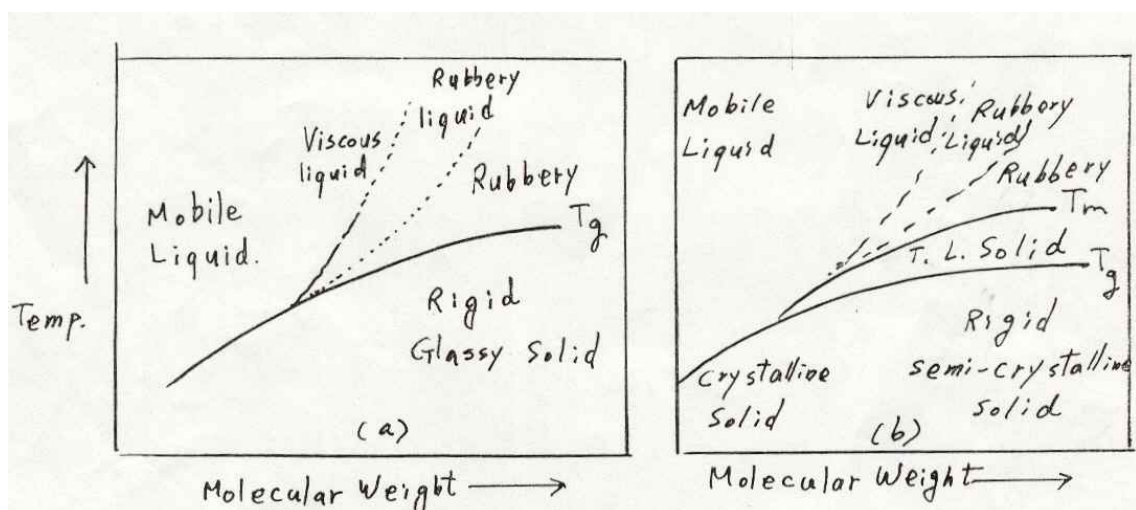
o  $T_g$  sets an upper temperature limit for the use of amorphous thermoplastics like poly(methyl methacrylate)(PMMA) or polystyrene(PS) and a lower temperature limit for rubbery behavior of an elastomer like SBR or 1,4-cis-polybutadiene.

o For semicrystalline polymer- $T_m$  or the onset of the melting range determines the upper service temperature.

## 2) Crystallization of Polymer

-polymer chain must be capable of packing together in ordered periodic arrays of crystallization to occur.

-Random copolymerization of atactic structure will prevent crystallization.



Approximate relations between temp, molecular weight, and physical state for (a) amorphous

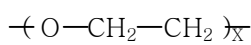
(b) semicrystalline polymer

- at the melting point,  $\Delta G_m = 0$

$$T_m = \frac{\Delta H_m}{\Delta S_m}, \quad \Delta S_m \text{ 이 감소, } T_m \text{ 증가.}$$

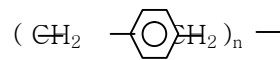
$T_m$  에 영향을 주는 것은 :

(1) structure flexibility :



poly(ethylene oxide)

$$T_m = 66^\circ\text{C}$$

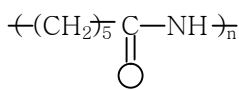


poly(p-xylylene)

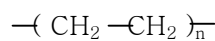
$$T_m = 375^\circ\text{C}$$

(2) strong intermolecular forces :

ex> polyamide-strong hydrogen bonding has higher  $T_m$  than polyethylene



N-6



PE

ex> Nylon-6 has higher than N-11

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

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

crystallinity 에 영향을 주는 것 :

(1) a periodic, regular placement of the atoms of the chain - isotactic

(2) 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 at  $T_g$ . Because the cooler conditions reduce the rate of conformational changes.

Molecular orientation : the oriented molecules need only be aligned without regard to location of atoms in particular positions.

Orientation -> increase crystallization

When the polymer melts become elongated and oriented under high pressure and temperature, and this reduces their entropy, the equilibrium

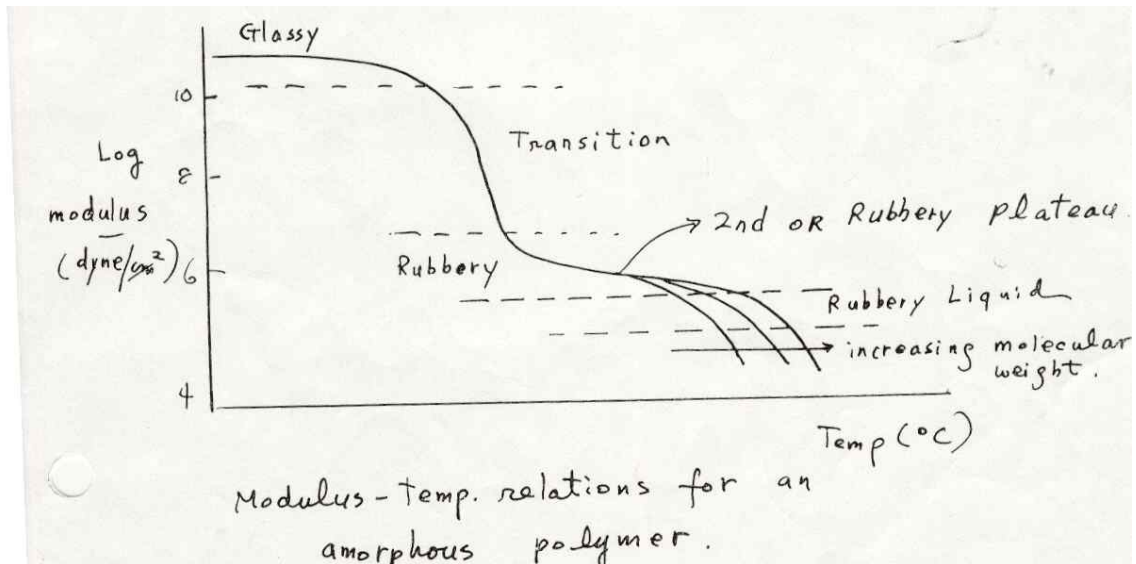
crystallization temperature is increased.

### (3) The Glass Transition

#### Modulus-Temperature Relations

At sufficiently low temp - a polymer will be a hard, brittle material (modulus  $> 10^9$  n/m<sup>2</sup>)

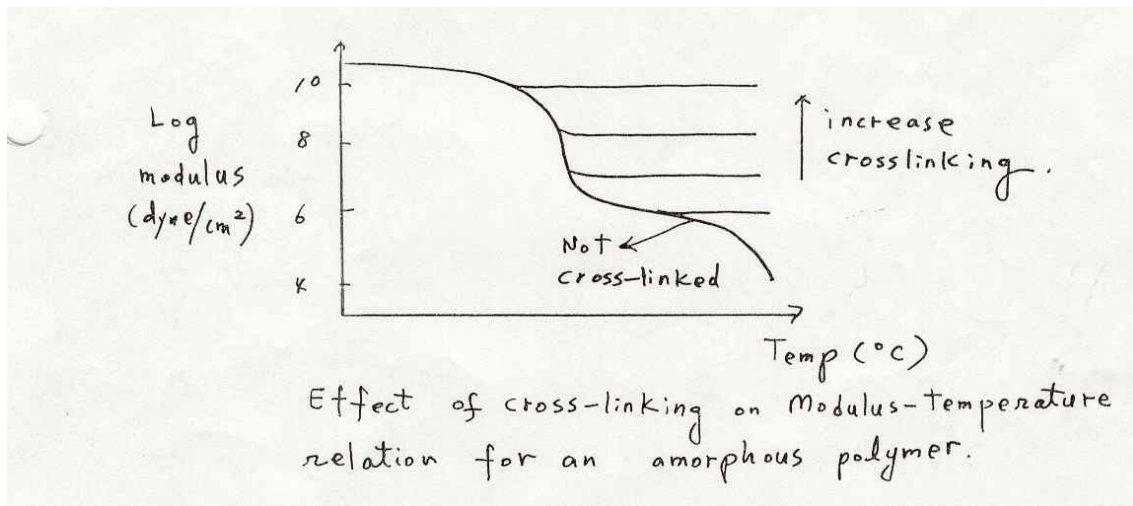
This is the glassy region



The glass transition region is a temperature range in which the onset of motion on the scale of molecular displacements can be detected in a polymer specimen

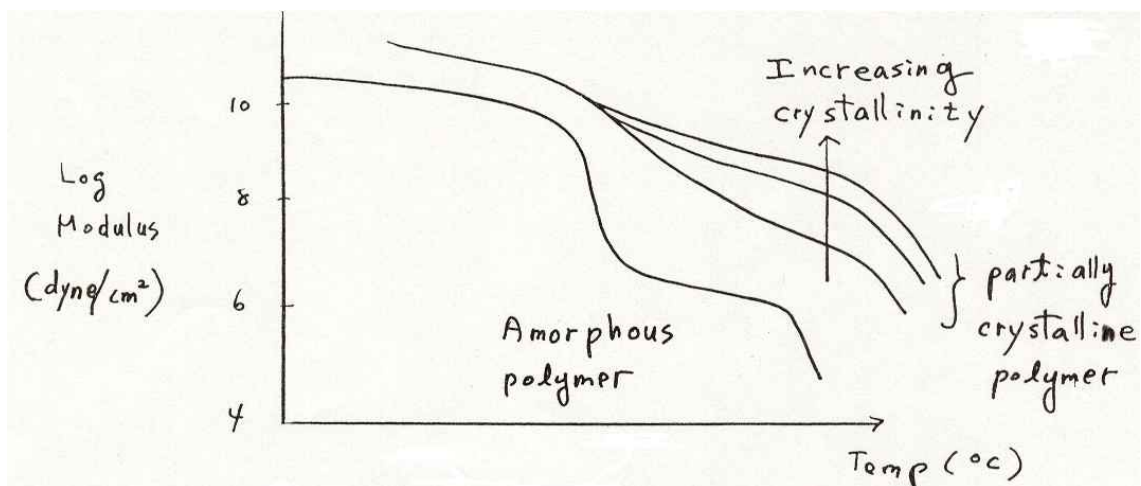
(glass- to- rubber transition region)

Rubbery Region : Polymer molecules do not flow past each other to a significant extent, because their rate of transition is restricted by mutual entanglements



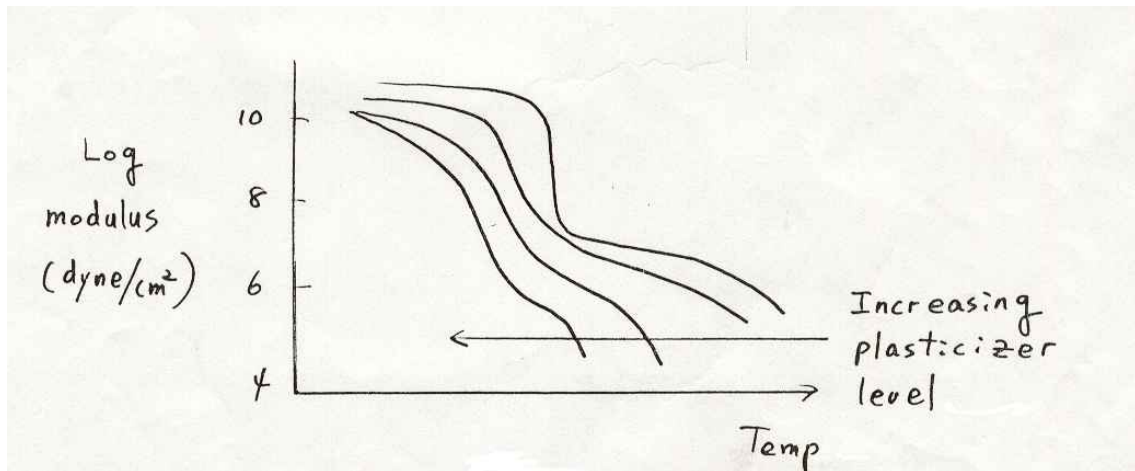
At high cross-linked polymers, the intermolecular linkages will be spaced so closely. Then the material remains glassy at all usage temperatures

- typical of tight network structures such as in cured phenolics.



Modulus-Temp relation for amorphous and partially crystalline polymer

- In a semicrystalline polymer, large scale segmental motion occurs only at temperatures between  $T_g$  and  $T_m$  and only in amorphous regions.
- At low degrees of crystallinity the crystallites act as virtual cross-links, and the amorphous regions exhibit rubbery or glassy behavior.



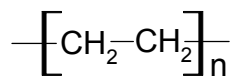
Modulus-Temp relation for a plasticized amorphous polymer

- Plasticizer reduces  $T_g$ (e.s.) PVC( $T_g=85^\circ\text{C}$ ) with 50% DOF(Diethyl Phthalate  $T_g=-30^\circ\text{C}$ )
- The Plasticizer molecules reduce the bonding forces.

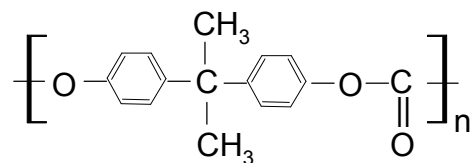
#### 4) Effect of Polymer Structure on $T_g$

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

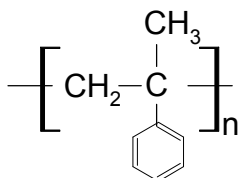
Ex>



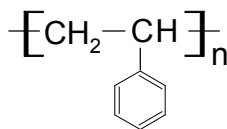
Polyethylene(PE),  $T_g = -120^\circ\text{C}$



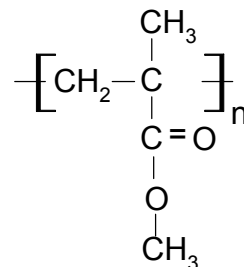
Polycarbonate(PC),  $T_g \approx 150^\circ\text{C}$



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



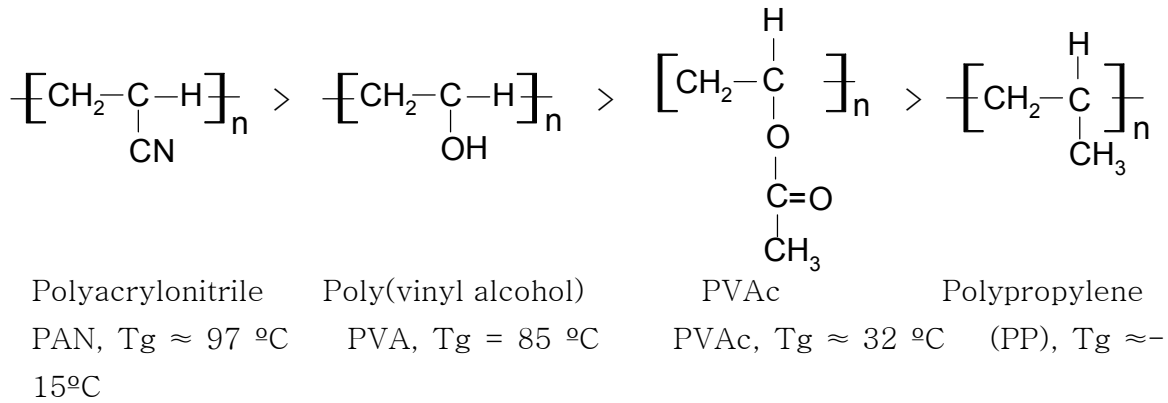
Polystyrene(PS)  
 $T_g = 100^\circ\text{C}$



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

- Strong intermolecular attractive forces pull the chain together and hinder relative motions of segments of different macromolecules. Also polar polymers and those in which 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:

$$\text{that is, } V_f = V - V_s$$

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  $T_g$

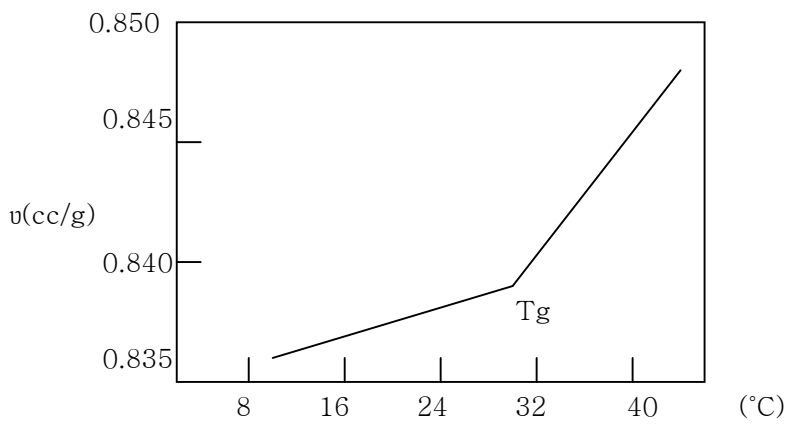
Ex> polycarbonate and poly(e-caprolactone) are known to be miscible. What is the  $T_g$  of the mixture if  $W_{pc}=0.5$  ?

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

(sol) using Fox eq.

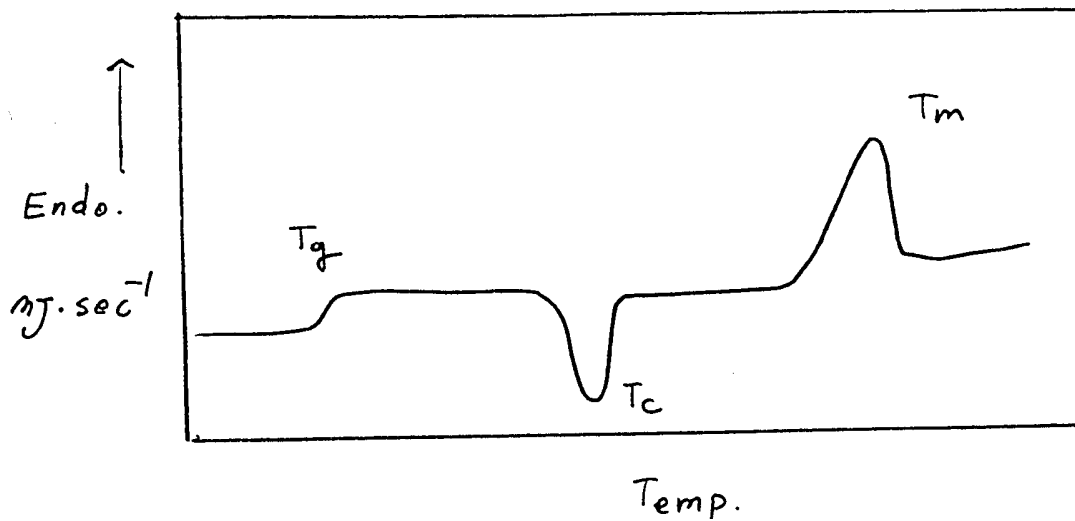
$$\frac{1}{T_g} = \frac{0.5}{(273+150)} + \frac{0.5}{(273+(-40))}$$

6) Measurement of  $T_g$

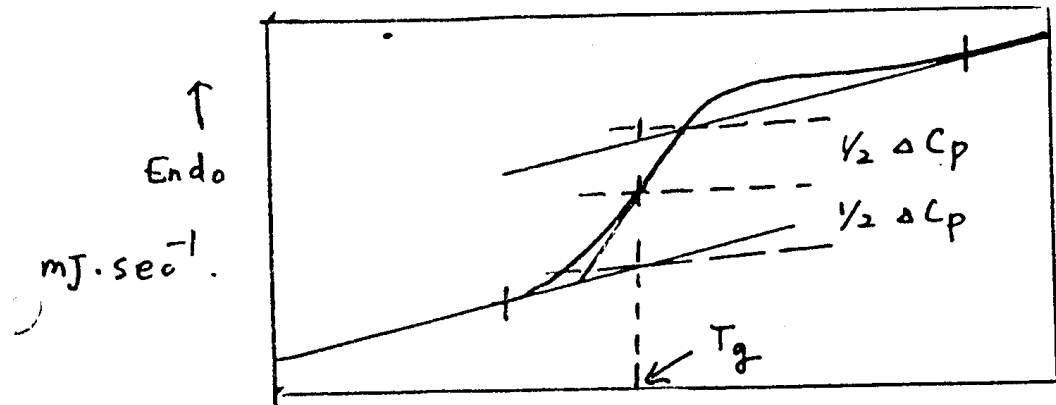


$T_g$  : second order transition  
{  $v$  vs  $T$  : continuous }  
{  $dv/dT$  vs  $T$  : discontinuous }

● By DSC (Differential Scanning Calorimetry)



Typical DSC thermogram of partially crystalline polymer



Determination of  $T_g$  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)