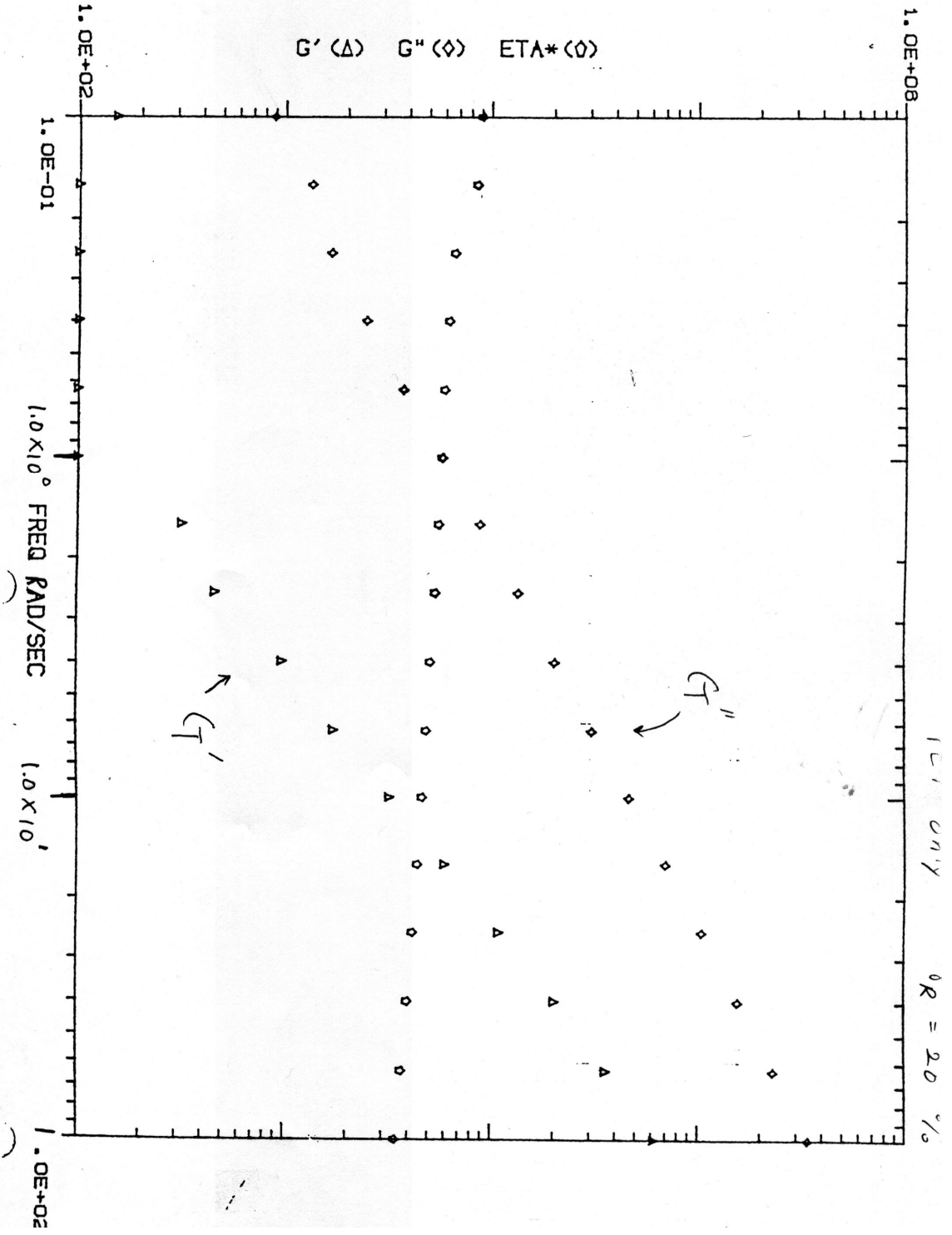
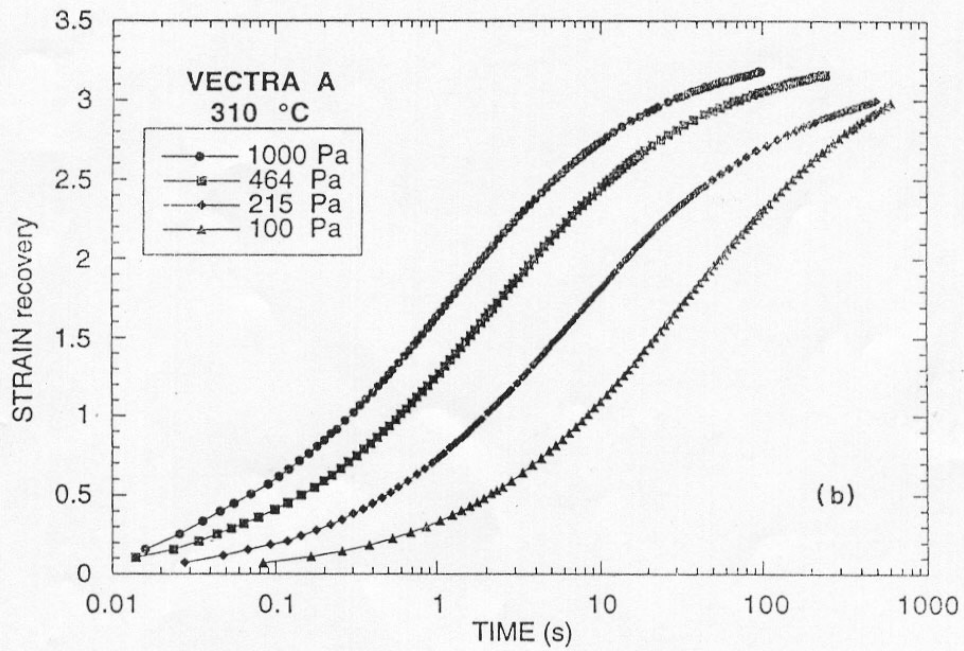
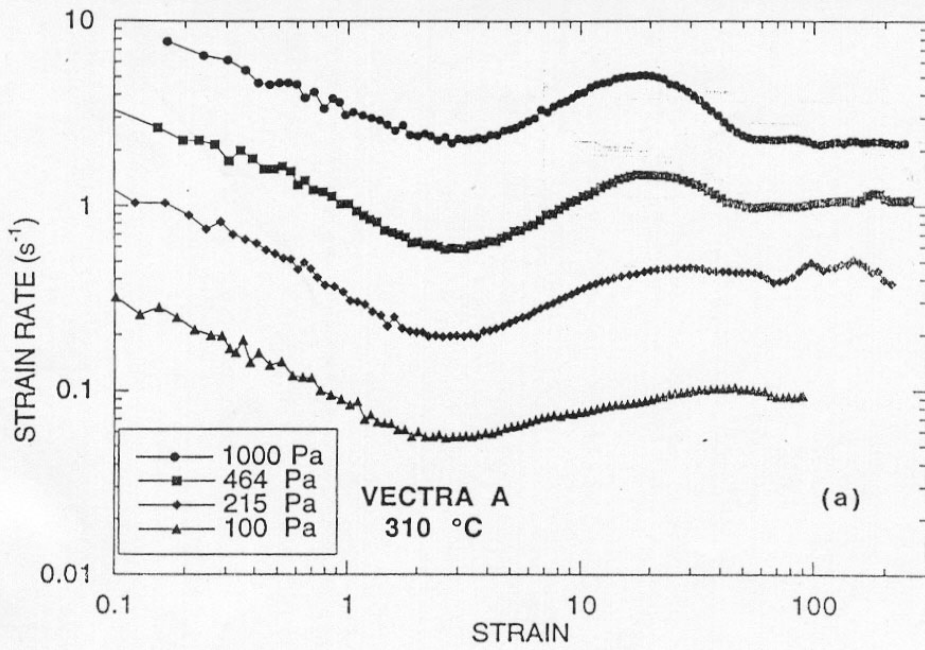


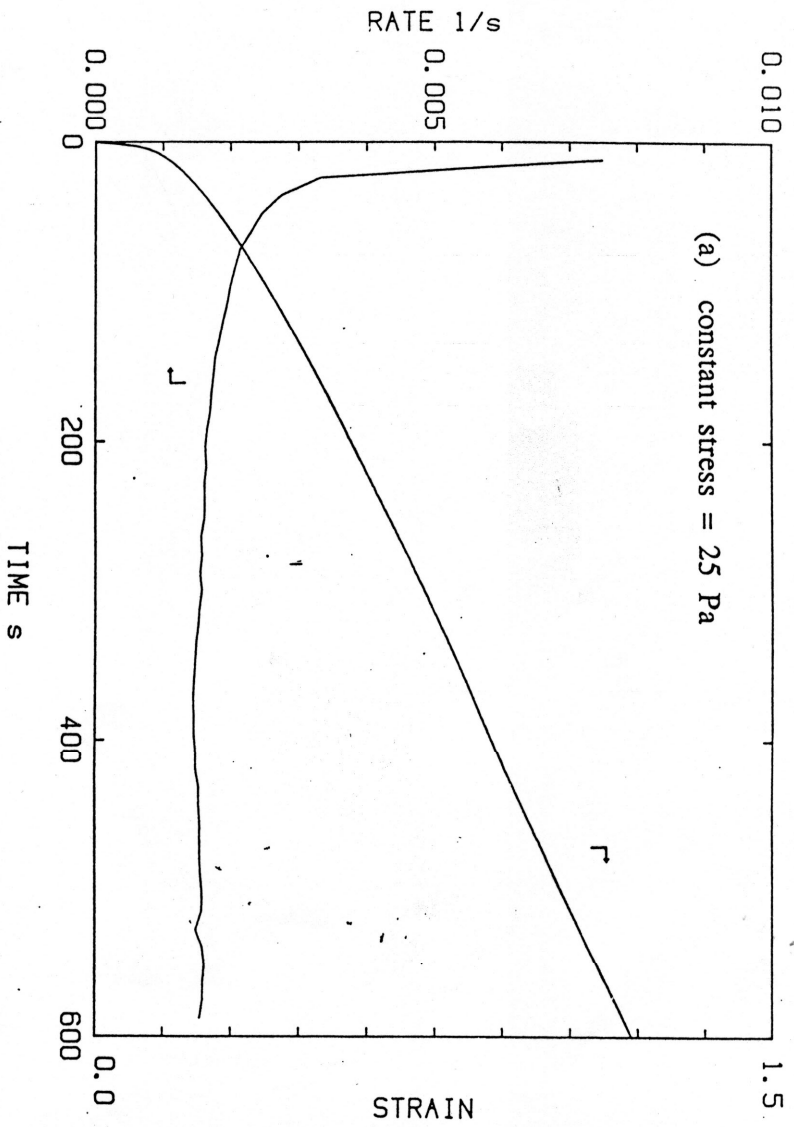
105





Steady Shear Test by Constant Stress Rheometer

101



- i) Strain rate vs time
- ii) Strain vs time for Veena only (Liquid Crystalline Polymer)

고분자의 Rheological Property 측정방법

i) Rotational type viscometer 종류

- RMS (Rheometrics Mechanical Spectrometer)
- RDS (Rheometrics Dynamic Spectrometer)
- RSR (Rheometrics Stress Rheometer)
- ARES (Advanced Rheometric Expansion System)
- Weissenberg Rheogoniometer, etc

측정가능한 물성

- Steady shear viscosity (η_0, η)
- Dynamic viscosity(η^*)
- Storage modulus (G')
- Loss modulus(G'')
- First normal stress difference 등

(a) dynamic test(η^*) –

oscillatory shear, using the cone&plate fixtures, is recommended for materials which are very strain sensitive (i.e, exhibit linear visco-elastic behavior only for small deformations) since the strain is essentially constant throughout the sample volume,

- oscillatory parallel plate measurements ;
useful for materials in approximately the same range of modulus, also preferred when making measurements over a wide range of temp, since the plate separation may be varied and the use of a relatively wide plate separation minimizes errors due to thermal expansion of the fixture, 주로 temp sweep 때 사용함

(b) steady shear test (η) –

the most widely used fixture is the cone&plate, which has the advantage that each volume element of fluid within the sample experiences the same shear rate – This is especially important for fluids which are shear thinning

- steady shear viscosity(η) 와 first normal stress difference 측정가능
- viscosity 측정시 사용하는 transducer 가 10 gr-cm이면 torque 는 1dyne/cm² 까지 측정가능, 이것은 약 10sec⁻¹ shear rate 에서 점도 10 poise 에 해당됨.

- 예로서(단위 환산); poise \equiv dyne \cdot sec/cm² = g/cm \cdot s
 1 Pa \cdot sec = 10 poise = 10g/cm \cdot sec
 1 Pa = 10g/cm \cdot sec² = 10 (g \cdot cm/sec²)(1/cm²) = 10(dyne/cm²)

참고로 dyne = g \cdot cm/sec², N = kg \cdot m/sec², Pa = N/m²

- steady shear can also be performed between parallel plates if a sample is to be tested at a variety of temp.
- when fluids are manipulated in processes of interest such as extrusion, fiber spinning, etc., they are almost invariably subjected to a shear field involving continuous deformation.
- For this reason, it is often desirable to examine the behavior of fluids in steady shear rather than oscillatory shear

P 499 Chap 16. Rheological Properties of Polymer solutions

A Dilute Polymer solutions

$$[\eta] = \lim(c \rightarrow 0) \frac{\eta_{sp}}{c}$$

p 512 The glass transition temperature of polymer solutions

- the T_g of a plasticized polymer

$$T_g = \frac{T_{gp} + (KT_{gs} - T_{gp})\theta_s}{1 + (K-1)\theta_s}$$

$$k : \text{constant} \approx \frac{\alpha_{ls} - \alpha_{gs}}{\alpha_{lp} - \alpha_{gp}}$$

α_l : volume coefficient of expansion above T_g

α_g : volume coefficient of expansion below T_g

$$\frac{T_{gp} - T_g}{T_{gp} - T_{gs}} = \frac{1 - \phi_p}{1 - \phi_p \left(1 - \frac{1}{K}\right)} \quad (16.24)$$

ϕ_p : volume fraction of polymer

p 515 (Ex 16.2) Estimate the T_g for a solution of PS in benzyl alcohol with $\phi_p = 0.85$

(sol.) According to Fig. 16.5 at $\phi_p = 0.85$ and $K=2.5$ (from page 513, bottom)

$$\frac{T_{gp} - T_g}{T_{gp} - T_{gs}} = 0.29 \quad (16.24)$$

PS 의 $T_g = 373K$

Benzyl alcohol 의 T_g 는 T_m 으로부터 estimation

$$\text{(From Table 16.2)} \quad \frac{T_{gs}}{T_{ms}} = \frac{2}{3} \quad \therefore T_{gs} = \frac{2}{3} \times (258K) = 172K$$

식 (16.24) 에 대입,

$$T_{g,est} = 315K \quad , \quad T_{g,exp} = 324K$$

P 515 A new method for estimating the viscosity of concentrated polymer solutions

P 516 (Ex 16.3) For concentrated solutions of polyisobutylene in decalin($\phi_p > 0.1$), estimate the viscosity as a function of the volume fraction of polymer at a temp of 20°C. The viscosity of the bulk polymer at this temp is $\eta_p = 6.5 \times 10^9 \text{ (N} \cdot \text{S / m}^2\text{)}$

(sol) (1) $T_{g,p} = 198\text{K}$, $T_{g,s} = 2/3 T_{m,s} = 2/3(230\text{K}) = 150\text{K}$

$$\text{From } K=2.5, \frac{T_{gp} - T_g}{T_{gp} - T_{gs}} = \frac{1 - \phi_p}{1 - \phi_p + \frac{\phi_p}{K}} \text{ 로부터 } T_g \text{ 를 계산할 수 있음}$$

(2) 그림(15.4)와 $\eta_p / \eta_p(1.2T_g)$ vs T_g/T

PIB의 $A = 12.5$ (P 469 Table)

$$\frac{T_g}{T} = \frac{198}{293} = 0.676$$

$$\log(\eta_p^* / \eta_p(1.2T_g)) = -3.5$$

$$\log \eta_p^* = 9.8, \quad \therefore \log \eta_p(1.2T_g) = 9.8 + 3.5 = 13.3$$

(3) From Eq.(16.26)

$$\eta = \eta_p^* \text{ at } \phi_p = 1.0$$

$$\log \eta = \log \eta_p^* + 5 \log \phi_p \quad (16.26)$$

여기서 $\log \eta$ 를 구할 수 있음 (see Table 16.3)

(η 의 unit 은 $\text{N} \cdot \text{S / m}^2$)

여기서 η = viscosity of diluted polymer

η^* = viscosity of undiluted polymer

Chap 17. Transport of Thermal Energy

- P 530 (Ex 17.1) Estimate the Heat conductivity of amorphous PMMA,
 (a) at room temp
 (b) at 200°C

(Sol) From Eq(17.4), with $C_p=1380(\text{J/kg}\cdot\text{K})$

$$\frac{\lambda}{C_p \cdot \rho} = L \left(\frac{U_R}{V} \right)^3 \left[\frac{3(1-\nu)}{1+\nu} \right]^{1/2}$$

여기서 λ : heat conductivity

C_p : specific heat capacity

ρ : density

L : distance between the molecules in “adjacent isothermal layers”

U : velocity of elastic wave(sound velocity)

$$U_R = V \cdot U_L^{1/3} \left[\frac{1+V}{3(1-V)} \right]^{1/6} \quad (\text{P. 443})$$

↪ Molar Sound velocity function or Rao function

$$U_{\text{log}} = \left(\frac{U_R}{V} \right)^3 \left(\frac{3(1-\nu)}{1+\nu} \right)^{1/2} \quad (17.3)$$

P 525 $\lambda \approx C_p \rho u L \quad (17.2)$

λ : heat conductivity

$$U_{\text{long}} = \left(\frac{U_R}{V} \right)^3 \left[\frac{3(1-\nu)}{1+\nu} \right]^{1/2} \quad (7.3)$$

ν : poisson ratio (p374) chap 13

- 먼저 chap 14 (p 447 Table 14.2) 로부터 Rao function 을 구한다.

$$2 \text{ -CH}_3 \quad 1400 \times 2 = 2800$$

$$1 \text{ -COO-} \quad 1225/4945$$

$$\text{So } U_R / V = \frac{U_R}{\frac{M}{\rho}} = \frac{4945}{101.1/1.17} = 5.8 \text{ (m/s)}$$

$$(U_R / V)^3 = 1.97 \times 10^3 \text{ (m/sec)}$$

P 531 According to eq.(17.4)

$$\frac{\lambda}{C_p \cdot \rho} = L \left(\frac{U_R}{V} \right)^3 \left[\frac{3(1-\nu)}{1+\nu} \right]^{1/2}$$

$$\Rightarrow C_p = 1380 \text{ (J/kg}\cdot\text{K)} \quad (\text{From P.112})$$

$$\rho = 1170 \text{ (Kg/m}^3\text{)}$$

$$L = 5 \times 10^{-11} \text{ (m)} \quad (\text{From Table 17.1})$$

$$(U_R / V)^3 = 1.97 \times 10^3 \text{ (m/sec)}$$

$$\nu = 0.40$$

$$\therefore \lambda = 1380 \times 1170 \times 5 \times 10^{-11} \times 1.97 \times 10^3 \times 1.13 = 0.180 \text{ (J/s}\cdot\text{m}\cdot\text{K)}$$

P 527의 Table 17.1과 비교

$$\lambda_{\text{exp}} = 0.193 \text{ (J/s}\cdot\text{m}\cdot\text{K)}$$

(b) at 200°C

$$\text{먼저 } 25^\circ\text{C에서, } T/T_g = 298/387 = 0.77$$

from fig. 17.2

$$\lambda(T) / \lambda(T_g) = 0.96$$

$$\lambda(T_g) = \frac{1}{0.96} (0.180) = 0.188$$

p 531 at $T = 200 + 273 = 473\text{K}$

$$\frac{T}{T_g} = \frac{473}{387} = 1.22$$

From Fig 17.2

$$\frac{\lambda(473)}{\lambda(T_g)} = 0.95$$

$$\therefore \lambda(473) = 0.188(0.95) = 0.178(J/s \cdot m \cdot K)$$

P 532 (Ex 17.2)

Calculate the λ of PET at 40% crystallinity

$$\Rightarrow \lambda(\text{at room}) = 0.218 (J/s \cdot m \cdot K)$$

(Sol.) $\rho_c = 1.465$, $\rho_a = 1.335$

Eq.(17.7)로부터

$$\frac{\lambda_c}{\lambda} - 1 = 5.8 \left(\frac{\rho_c}{\rho_a} - 1 \right)$$

$$\lambda_c = 0.218 \left(1 + 5.8 \left(\frac{1.465}{1.335} - 1 \right) \right) = 0.218 \times 1.56 = 0.340$$

$$\text{여기서 } \frac{\lambda_c}{\lambda_a} = 0.340 / 0.218 = 1.58 \text{ and } X_c = 0.4$$

(see Fig.17.4 in P.531)

$$\frac{\lambda - \lambda_a}{\lambda_c - \lambda_a} \approx 0.36 \text{ or (From P.531 Fig 17.4)}$$

$$\frac{\lambda - 0.218}{0.340 - 0.218} = 0.36$$

$$\lambda = 0.044 + 0.218 = 0.262 (J/s \cdot m \cdot K)$$

$$\lambda_{\text{exp}} = 0.272 (J/s \cdot m \cdot K)$$

Chap.18

Properties Determining Mass Transfer in Polymeric Systems

A. Permeation of simple Gases.

P : (permeability)

S : (solubility)

D : (diffusivity)

$$P = S \times D$$

P 536 - permeation is a sequential process, starting with solution of the gas on the outer surface of the polymer, followed by slow inward diffusion

P 542 Ex 18.1) Estimate the solubility and the heat of solution (sorption) of oxygen in PET, both in the quenched amorphous glassy state and semi-crystalline state ($X_c = 0.45$).

Sol) i) $T_g(\text{PET}) = 345\text{K}$, For O_2 , $\epsilon/k=107$

From Eq.(18.7b) ϵ (potential energy constant)
k(Boltzman const.)

$$\begin{aligned}\log S(298) &= -7.4 + 0.010\epsilon/k \pm 0.6 \\ &= -6.33 \pm 0.6\end{aligned}$$

$$\therefore S = 5.6 \times 10^{-7}$$

$$S_{\text{Exp}} = 9.9 \times 10^{-7}$$

ii) For semicrystalline state ;

$$\begin{aligned}S_{\text{sc}}(298) &= S_{\text{a}}(298)(1-X_c) \\ &= 5.6 \times 10^{-7}(0.55) = 3.1 \times 10^{-7}\end{aligned}$$

$$S_{\text{sc}}(\text{Exp}) = 7.4 \times 10^{-7}$$

P 552 (Ex 18.2) Estimate the diffusivity at 298K and the activation energy of diffusion for oxygen in PET, both in the glassy and in the semicrystalline state.

(sol.) For the derivation of E_D (activation energy of diffusion)
we use Fig. 18.3

$$T_g = 345\text{K}, P = 6.75 \pm 1.5$$

(from Eq.18.12b p 552)

$$\frac{E_D}{R} \cdot 10^{-3} = \left(\frac{6O_2}{6N_2}\right)^2 \cdot P = \left(\frac{347}{38}\right)^2 \cdot (6.75 \pm 1.5) = 0.83(6.75 \pm 1.5) = 5.6 \pm 1.25 \text{ (KJ/mol)}$$

$$10^{-3} \times E_D = \{(8.3)5.6 \pm (8.3)1.25\} = 46.5 \pm 10.5 \text{ (KJ/mol)}$$

$$E_{D,Exp} = 46.1 \sim 48.5$$

From Eq.(18.13b) (p.552)

$$\log D_0 = 10^{-3} E_D / R - 5.0 \pm 0.8 = 0.6 \pm 0.8$$

From Eq(18.15)

$$\log D(298) = \log D_0 - 1.46 \times 10^{-3} E_D / R = 7.6 \pm 0.8$$

$$\therefore D_a(298) = 2.5 \times 10^{-8} \text{ (cm}^2\text{/sec)}$$

P 560 Ex 18.3 Estimate the permeability $P(298)$ for oxygen of two polymer films :
one a neoprene rubber film and the other a PVC film.

P 571 Ex 18.4 Estimate the moisture content of nylon-6 at 25°C and a relative humidity of
0.7. The crystallinity is 70%.

P 581 Ex 18.5 Estimate the rate of dissolution of PS in toluene at $35^{\circ}\text{C}(308\text{K})$

(a) at a very low Reynolds number ($N_{\text{Re}} \approx 0$)

(b) at a Reynolds number of 100D

PS(M_w)=150000 , $D = \text{toluene in PS at } 35^{\circ}\text{C}$ is 1.5×10^{-6}

Chap. 19 Crystallization and Recrystallization

A₁. Crystallinity :

- the change from a random liquid structure to a well ordered, periodic crystalline structure can occur, this transformation is called crystallization : the reverse is called melting.
- Many polymeric solids consist largely of folded chain lamellae.

A₂. Nucleation and Growth.

- P 586
- the theory is based on the assumption that in supercooled melts there occur fluctuations leading to the formation of a new phase.
The phase transformation begins with the appearance of a number of very small particles of the new phase (nucleation)

(Ex 19.1) Estimate for isotactic PS.

- a. the temperature of maximum crystallization velocity
- b. the linear growth rate at this temp.
- c. the probable(maximum) degree of crystallization

a) Two methods of estimation are available

: eq(19.8) and Fig(19.6b)

i) From eq(19.8)

$$\begin{aligned} T_k &\cong 0.5 (T_m + T_g) \\ &= 0.5 (513 + 373) = 443 \text{ K} \end{aligned}$$

ii) using Fig(19.6b) with $T_g/T_m = 373/513 = 0.7$

$$\text{여기서 } \frac{T_{x,\max}}{T_m} = 0.86, \text{ so } T_{x,\max} = 441\text{K}, T_{\text{exp}} = 449 \text{ K}$$

b) applying Eq(19.16), with $T=T_{x,max}=442K$

$$i) \log \frac{v}{v_0} \approx -2.3 \frac{T_m}{T} \left\{ \frac{T_m}{T_m - T_g} + \frac{50}{T_m - T} \right\} \quad (19.16)$$

여기서 $v_0 = 10^{12}$ (nm/sec) (universal const. For crystalline polymer)

P 661 $\log v = 12 - 2.3 \frac{513}{442} \left(\frac{513}{513 - 373} + \frac{50}{71} \right) = 12 - 4.7 = 0.3$, $v_{max} = 2.0$

ii) From Fig 19.6-a, $T_g/T_m = 0.725$

그림으로부터 $\log v_{max} = 0.5$

$$\text{the average } \log v_{max} = \frac{0.3 + 0.5}{2} = 0.4$$

$$\therefore v_{max} = 10^{0.4} = 2.5(\text{nm/sec}) , v_{max,exp} = 4.2(\text{nm/sec})$$

c) Maximum degree of crystallinity;

Applying Fig 19.6c, $T_g/T_m = 0.725$

{ $X_{c,max} = 0.3$, $X_{c,max,exp} = 0.34$ } in good agreement.