

# 习题解答

## 习题 1A

1-1: 几何异构体(顺式, 反式), 旋光异构体(全同, 间同, 无规)

1-2: 1,4 聚合产生几何异构体(顺式, 反式), 1,2 聚合和 3,4 聚合各产生三种旋光异构体(全同, 间同, 无规)。

1-3:  $r\%$ 指  $r$  在全部二元组中的百分数, 指  $rrrr$  在全部五元组中的百分数。

1-4:  $rr\%=8/13$ ,  $rrrr\%=4/10$

1-5: 结晶聚合物: 聚乙烯, 等规聚丙烯, PET, 等规聚苯乙烯, 聚乙烯醇, 乙/丙 98/2 无规共聚物  
无定形聚合物: 无规聚苯乙烯, 聚醋酸乙烯酯, 乙/丙 50/50 无规共聚物

1-6: 低氯含量时由于氯原子的引入破坏了聚乙烯结构的规整性, 降低了结晶的完善程度, 导致熔点降低; 高氯含量时结晶能力已完全丧失, 由于氯原子的极性, 导致玻璃化温度的升高。

1-7 : 丁烯-1 可得到全同、间同和无规结构的旋光异构体, 其中无规结构的聚(丁烯-1)结晶性最差。

氯丁烯 1, 4 加成聚合可得到顺式和反式的几何异构体, 1, 2 或 3, 4 加成聚合可得到全同、间同和无规结构的旋光异构体, 其中全同结构的结晶性最好。

1-8: 乙烯与丙烯的交替共聚物。能

1-9: 高抗冲聚苯乙烯。

1-10: 略。

1-11: 完全水解得到聚乙烯醇, 部分水解得到醋酸乙烯酯与乙烯醇的无规共聚物。

1-12: 结晶聚合物具有较高的力学性能和耐热性能。

1-13: 比容-温度曲线可判断是否嵌段(本章内容尚不足以解此题, 可作为后续内容及其它课程内容的综合思考)。

## 习题 1B

1-14: 重量分数  $w_1 = 0.2$ ,  $w_2 = 0.4$ ,  $w_3 = 0.4$

$$\overline{M}_n = \frac{1}{\sum \frac{w_i}{M_i}} = \frac{1}{\frac{0.2}{10000} + \frac{0.4}{50000} + \frac{0.4}{100000}} = 3.125 \times 10^4$$

$$\overline{M}_w = \sum w_i M_i = 0.2 \times 10000 + 0.4 \times 50000 + 0.4 \times 100000 = 6.2 \times 10^4$$

$$\overline{M}_z = \sum \frac{w_i M_i^2}{w_i M_i} = \frac{0.2 \times 10000^2 + 0.4 \times 50000^2 + 0.4 \times 100000^2}{0.2 \times 10000 + 0.4 \times 50000 + 0.4 \times 100000} = 8.1 \times 10^4$$

1-15: 由式(1-27),  $\int_{1000}^{100000} w(M) dM = 1$ , 且重量分数均匀分布并与分子量无关, 可求得  $w = \frac{1}{10^5 - 10^3}$

利用式(1-28)~(1-30):

$$\overline{M}_n = \frac{1}{\int_{1000}^{100000} \frac{w(M)}{M} dM} = (10^5 - 10^3) \times (\ln 10^5 - \ln 10^3)^{-1} = 2.1 \times 10^4$$

$$\overline{M}_w = \int_{1000}^{100000} w(M) M dM = \frac{1}{10^5 - 10^3} \times 0.5 \times (10^{5 \times 2} - 10^{3 \times 2}) = 5.05 \times 10^4$$

$$\overline{M}_z = \frac{\int_{1000}^{100000} w(M) M^2 dM}{\int_{1000}^{100000} w(M) M dM} = 6.7 \times 10^4$$

$$1-16: \quad \overline{M}_n = \frac{1}{\sum \frac{w_i}{M_i}} = \frac{1}{\frac{0.5}{35000} + \frac{0.5}{150000}} = 5.68 \times 10^4$$

$$\overline{M}_w = \sum w_i M_i = 0.5 \times 90000 + 0.5 \times 300000 = 1.95 \times 10^5$$

1-17: 纯PVC的 $M_n=18900$

1-18: 纤维素的链节分子量为 26.95, 丙烯腈的链节分子量为 53。

设每根纤维素分子上链中接有 x 根丙烯腈链, 则有:

$$\frac{x \cdot 2.7 \times 10^4 / 53 \times 14}{x \cdot 2.7 \times 10^4 + 1.46 \times 10^5} = 0.0713$$

求得 x=2

1-19: 一个分子链中有一个 $-NH_2$ , 所以可知尼龙 6 的数均分子量为

$$\overline{M}_n = \frac{1}{4.45 \times 10^{-5}} = 2.25 \times 10^4 \text{ g/mol}$$

$$\text{平均聚合度: } \bar{x}_n = \frac{2.25 \times 10^4}{113} = 199$$

$$1-20: \quad \overline{M}_n = 2.2 \times 10^4, \quad \overline{M}_w = 1.8 \times 10^5$$

$$1-21: \quad \bar{x}_n = 3, \quad \bar{x}_w = 3.33$$

$$1-22: \quad \overline{M}_n = 2.35 \times 10^5, \quad \overline{M}_w = 4.72 \times 10^5$$

## 习题 2A

2-1:  $C_\infty=6.96$ ,  $b=1.31\text{nm}$ ,  $z=96$ , 重复单元数 5.24

$$2-2: \langle AA'^2 \rangle = pL^2 \quad \langle AB^2 \rangle = \left( \frac{p}{2} + q \right) L^2$$

$$2-3: \text{平均链段长度 } R = \frac{(p/2)L + qM}{p/2 + q}, \quad \langle AB^2 \rangle = \left( \frac{p}{2} + q \right) R^2$$

2-4: 由于聚合物的分子链在 $\theta$ 溶剂与本体中均为无扰链，而其它溶剂中或大于或小于无扰链。

2-5: 聚乙烯在  $140^\circ\text{C}$  为熔体，处于无扰态， $C_\infty=7.4$

$$\langle r_0^2 \rangle = C_\infty nl^2 = 7.4 \times 2 \times \frac{10^7}{28} \times 0.154^2 = 1.25 \times 10^5 \text{ nm}^2$$

$$2-6: \text{由式(2-25), 最可几的末端距出现在 } \frac{\partial(W(r)4\pi r^2)}{\partial r} = 0$$

$$\text{即: } \left( \frac{3}{2\pi nl^2} \right)^{3/2} \times \left( -\frac{3r}{nl^2} \right) \exp\left( -\frac{3r^2}{2nl^2} \right) \cdot 4\pi r^2 + \left( \frac{3}{2\pi nl^2} \right)^{3/2} \exp\left( -\frac{3r^2}{2nl^2} \right) \cdot 8\pi r = 0$$

$$\text{则有: } \left( -\frac{3r}{nl^2} \right) 4\pi r^2 + 8\pi r = 0, \text{ 得到 } r = (2nl^2/3)^{1/2}$$

$$2-7: \text{(a) } r_{\max} = nl \sin \frac{\theta}{2} = 1000 \times 0.164 \times \left( \sin \frac{142}{2} + \sin \frac{110}{2} \right) = 289 \text{ nm}$$

$$\text{(b) } r_{\max} = nl \sin \frac{\theta}{2} = 1000 \times \left( 2 \times 0.154 \times \sin \frac{116}{2} + 2 \times 0.143 \times \sin \frac{113}{2} \right) = 498 \text{ nm}$$

$$\text{(c) } r_{\max} = nl \sin \frac{\theta}{2} = 1000 \times 2 \times 0.154 \times \sin \frac{109.5}{2} = 251 \text{ nm}$$

$$\text{(d) } r_{\max} = nl \sin \frac{\theta}{2} = 1000 \times 0.143 \times \left( \sin \frac{110}{2} + \sin \frac{108}{2} \right) = 233 \text{ nm}$$

2-8:

$$\text{由于: } \langle r^2 \rangle_0 = zb^2 = C_\infty \langle r^2 \rangle_{f,j} = 9.85 nl^2 = 9.85 \times 2 \times \frac{1 \times 10^5}{104} \times 0.154^2 = 449 \text{ nm}^2$$

$$r_{\max} = zb = nl \sin \frac{\theta}{2} = \frac{1 \times 10^5}{104} \times 0.154 \times \sin \frac{109.5}{2} = 121 \text{ nm}$$

$$\text{所以: } b = \frac{\overline{r_0^2}}{r_{\max}} = \frac{449}{121} = 3.7 \text{ nm}$$

$$2-9: \text{平均链段长度 } R = \frac{xL_a + yL_b}{x + y}$$

$$\text{均方末端距} = (x+y)R^2$$

$$2-10: \text{根据: } \frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c, \text{ 可知 } [\eta] = 1.5 \text{ mL/g}, \quad k'[\eta]^2 = 0.9 (\text{mL})^2 / \text{g}^2$$

求得  $k' = 0.4$  (无量纲)

2-11: 由  $[\eta]_{PS} M_{PS} = [\eta]_{PMMA} M_{PMMA}$ , 进行分子量的换算, 即可做出 PMMA 的 GPC 校正曲线。

2-12: (a)  $[\eta] = 1.32$ , (b)  $M_{\eta} = 5.45 \times 10^5$

2-13:  $\bar{M}_{\eta} = [\sum w_i M_i^{\alpha}]^{1/\alpha} = (0.5 \times 39000^{0.74} + 0.5 \times 292000^{0.74})^{1/0.74} = 1.5 \times 10^5$

$$[\eta] = k M_{\eta}^{\alpha} = 9.18 \times 10^{-3} \times (1.5 \times 10^5)^{0.74} = 62 \text{ mL/g}$$

2-14:  $M_{PVC} = 2.06 \times 10^5$

2-15: (a)  $[\eta] = 0.9$ ,  $k_H = 0.23$ , (b)  $M_{\eta} = 2.5 \times 10^5$

2-16:  $M_{PMMA} = 7.6 \times 10^4$

2-17: 由  $H = \frac{64\pi^3 n^2}{3\lambda^4 N_A} \left( \frac{dn}{dc} \right)^2$  和  $\left( H \frac{c}{R_{\theta}} \right)_{\theta=0} = \frac{1}{M_w} + 2 \langle A_2 \rangle_z c + \dots$ , 做图  $\left( H \frac{c}{R_{\theta}} \right) \sim c$ , 通过直线的

截距和斜率即可求出重均分子量及第二维利系数。

2-18: 同一种聚合物的  $k$  和  $\alpha$  值相同。由  $[\eta]_A = k M_A^{\alpha}$  和  $[\eta]_B = k M_B^{\alpha}$ :

$$M_A = \left( \frac{[\eta]_A}{k} \right)^{1/\alpha}, \quad M_B = \left( \frac{[\eta]_B}{k} \right)^{1/\alpha}$$

所以共混物的特性粘度  $[\eta] = k M^{\alpha} = k (w_A M_A + w_B M_B)^{\alpha} = (w_A [\eta]_A^{1/\alpha} + w_B [\eta]_B^{1/\alpha})^{\alpha}$

2-19: (a) 产物全为嵌段共聚物: 以  $115000 \text{ g/mol}$  为平均分子量的单峰分布;

(b) B 单体一半构成嵌段共聚物一半形成均聚物: 分别以  $100000 \text{ g/mol}$ 、 $15000 \text{ g/mol}$  和  $115000 \text{ g/mol}$  为平均分子量的三峰分布;

(c) 产物全为共混物: 分别以  $100000 \text{ g/mol}$  和  $15000 \text{ g/mol}$  为平均分子量的双峰分布。

2-20: 由普适校正曲线读出淋洗体积为  $160 \text{ cm}^3$  时  $[\eta]M$  约等于  $10^5$ , 所以该新聚合物的分子量为  $1.8 \times 10^4$ 。

## 习题 2B

2-19: (a)  $\Omega = \frac{100 \times 99 \times \dots \times 91}{10 \times 9 \times \dots \times 1} = 1.7 \times 10^{13}$

$$(b) \Omega = 100 \times 0.99z \cdot 0.98(z-1) \cdot \dots \cdot 0.91(z-1) = 62.8z \cdot (z-1)^8$$

2-21: 利用式(2-101)

$$(1) \bar{\Delta S}_1 = -k(0.5 \ln 0.5 + 0.5 \ln 0.5) = 0.693k$$

$$(2) \bar{\Delta S}_2 = -k(0.5 \ln 0.5 + \frac{0.5}{100} \ln 0.5) = 0.35k$$

$$(3) \overline{\Delta S}_3 = -k \left( \frac{0.5}{100} \ln 0.5 + \frac{0.5}{100} \ln 0.5 \right) = 0.0069k$$

2-22: 由式(2-114),

$$\Phi_1 = \frac{10}{10 + \frac{1 \times 2 \times 10^5}{1.06 \times 10^6}} = 0.98, \quad \Phi_2 = 0.02$$

$$\begin{aligned} \overline{\Delta G}_m &= 1.38 \times 10^{-23} \times 298 \times \left( 0.98 \ln 0.98 + \frac{0.02}{2 \times 10^5 / 104} \ln 0.02 + 0.37 \times 0.98 \times 0.02 \right) \\ &= -5.2 \times 10^{-23} J / \text{格位} \end{aligned}$$

2-23: 聚合物的分子量越大, 分子链的扩张体积越大, 所以重叠浓度越小。重叠浓度应与链长的-0.8次方成正比。

2-24: 1229

2-25: 利用  $\frac{\pi}{RTc} = \frac{1}{M_n}$  求得数均分子量为 13.9 万。

2-26: 利用  $\pi = \rho gh$  求得渗透压如下表:

| c (g/L) | $\pi$ (cm 溶剂) | $\pi$ (Pa) | $\pi/RTc$ |
|---------|---------------|------------|-----------|
| 3.2     | 0.70          | 58.31      | 0.007355  |
| 6.6     | 1.82          | 151.6      | 0.009271  |
| 10      | 3.10          | 258.2      | 0.010423  |
| 14      | 5.44          | 453.2      | 0.013064  |
| 19      | 9.30          | 774.7      | 0.016457  |

作图得截距为 0.00531, 斜率为  $5.69 \times 10^{-4}$ , 得到数均分子量为  $1.88 \times 10^5 g/mol$ , 第二维利系数为  $5.69 \times 10^{-4} mol.mL/g^2$

2-27: (a)两个  $1/M$  不相同, 因为渗透压方法测定的是数均分子量, 光散射方法测定的是重均分子量。

(b)通过公式可以发现两个斜率也不相同。渗透压的是  $A_2$ , 光散射的是  $2A_2$

2-28: (a)聚合物 A 同 2-26 题。

聚合物B按同样方法作图求解, 数均分子量为  $1.0 \times 10^5 g/mol$ , 第二维利系数为  $7.97 \times 10^{-4} mol.mL/g^2$ 。

$$(b) \overline{M}_n = 1.13 \times 10^5$$

$$(c) \overline{M}_w = 2.44 \times 10^5$$

2-29: 由  $\overline{\Delta G}_m = kT(\Phi_1 \ln \Phi_1 + \Phi_2 \ln \Phi_2 + \chi \Phi_1 \Phi_2)$

$$\frac{\partial}{\partial \Phi_2} \left( \frac{\Delta G}{RT} \right) = -(\ln \Phi_1 + 1) + (\ln \Phi_2 + 1) + \chi(\Phi_1 - \Phi_2) = 0$$

$$\frac{\partial^2}{\partial \Phi_2^2} \left( \frac{\Delta G}{RT} \right) = \frac{1}{\Phi_1} + \frac{1}{\Phi_2} - 2\chi = 0$$

所以 spinodal 方程为:  $\chi = \frac{1}{2} \left[ \frac{1}{\Phi_1} + \frac{1}{\Phi_2} \right]$

## 习题 2C

2-30: 利用式(2-190),  $\lambda=2$

$$\frac{\rho RT}{M_c} = \frac{1.0 \times 10^6 \text{ g/m}^3 \times 8.314 \text{ J/K} \cdot \text{mol} \times 300 \text{ K}}{5000 \text{ g/mol}} = 0.5 \text{ MPa}$$

$$\sigma = 0.5 \times (2 - 2^{-2}) = 0.875 \text{ MPa}$$

$$E = 0.5 \times 3 = 1.5 \text{ MPa}$$

2-31: 利用式(2-196)

$$G = \frac{\rho RT}{M_c} \left( 1 - \frac{2M_c}{M} \right) = \frac{0.95 \times 8.314 \times 300}{5000} \left( 1 - \frac{2 \times 5000}{100000} \right) = 0.43 \text{ MPa}$$

2-32:  $\frac{10}{10 \times 10^{-6}} = \frac{N \cdot 1.38 \times 10^{-23} \times 300}{V} (2 - 2^{-2}),$

可求得  $\frac{N}{V} = 1.38 \times 10^{26} \text{ m}^{-3}$

2-33:  $\frac{10}{15 \times 1.5 \times 10^{-6}} = \frac{0.9 \times 10^3 \times 8.314 \times 300}{M_c} (3 - 3^{-2})$

可求得:  $M_c = 1.46 \times 10^4 \text{ g/mol}$

2-34: (a)  $1.5 \times 10^4 = \frac{N \cdot 1.38 \times 10^{-23} \times 298}{V} (2.5 - 2.5^{-2})$

可求得  $\frac{N}{V} = 1.56 \times 10^{24} \text{ m}^{-3}$   $\frac{\mu}{V} = \frac{2}{\phi} \frac{N}{V} = 0.78 \times 10^{24} \text{ m}^{-3}$

(b)  $\frac{\sigma_1}{\sigma_2} = \frac{\lambda_1 - \lambda_1^{-2}}{\lambda_2 - \lambda_2^{-2}} = \frac{1.5 - 1.5^{-2}}{2.5 - 2.5^{-2}} = 0.45$ , 所以  $\sigma_1 = 6.8 \times 10^3 \text{ Pa}$

(c)  $\frac{\sigma_1}{\sigma_2} = \frac{T_1}{T_2} = \frac{373}{298} = 1.25$ , 所以  $\sigma_1 = 1.88 \times 10^4 \text{ Pa}$

2-35: 由  $\frac{\rho V_1}{M_c \left( \frac{1}{2} - \chi \right)} = \Phi_2^{5/3}$ , 求得  $\frac{\rho}{M_c} = 70.8 \text{ mol/m}^3$

所以  $G = \frac{\rho RT}{M_c} = 70.8 \times 8.314 \times 298 = 1.75 \times 10^5 \text{ Pa}$ ,

2-36:  $G = \frac{E}{3} = 1 \times 10^4 \text{ Pa}$

$\sigma = G(\lambda - \lambda^{-2}) = 1 \times 10^4 \times (2.5 - 2.5^{-2}) = 2.34 \times 10^4 \text{ Pa}$

2-37: 设 A 带的拉伸比为  $\lambda_A$ , B 带的拉伸比为  $\lambda_B$

则有:  $\frac{NkT_A}{V}(\lambda_A - \lambda_A^{-2}) = \frac{NkT_B}{V}(\lambda_B - \lambda_B^{-2})$

$\lambda_A + \lambda_B = 4$

两式联立, 可求得  $\lambda_B = 1.75$ , 所以 B 带的长度为 17.5cm。

2-38: (a)

$\sigma = \frac{\rho RT}{M_c} \left( 1 - \frac{2M_c}{M} \right) (\lambda - \lambda^{-2}) = \frac{0.98 \times 10^3 \times 8.314 \times 298}{10000 \times 10^{-3}} \left( 1 - \frac{2 \times 10000}{100000} \right) (2 - 2^{-2}) = 3.4 \times 10^5 \text{ Pa}$

$G = \frac{\rho RT}{M_c} \left( 1 - \frac{2M_c}{M} \right) = \frac{0.98 \times 10^3 \times 8.314 \times 298}{10000 \times 10^{-3}} \left( 1 - \frac{2 \times 10000}{100000} \right) = 1.94 \times 10^5 \text{ Pa}$

(b)  $\sigma = 7.65 \times 10^5 \text{ Pa}$ ,  $G = 4.37 \times 10^5 \text{ Pa}$

2-39: 由  $\sigma = \frac{NkT}{V}(\lambda - \lambda^{-2})$ , 可知  $\sigma_0 = 0.015 \cdot 8.314 \times 300 \times (1.1 - 1.1^{-2}) = 15.6 \text{ Pa}$

$\frac{\sigma_0}{\sigma_{10}} = \frac{(N/V)_0}{(N/V)_{10}} \cdot \frac{T_0}{T_{10}} \quad \frac{15.6}{10} = \frac{0.015}{x} \cdot \frac{300}{400} \quad \text{解得 } x=0.0072$

2-40: 由题意可知  $M_c = \frac{5000}{3} \times (12 \times 3 + 16 + 6) = 9.67 \times 10^4 \text{ g/mol}$ ,

$V_1 = 102/0.8 = 127.5 \text{ cm}^3/\text{mol}$

由  $\frac{\rho V_1}{M_c \left( \frac{1}{2} - \chi \right)} = \Phi_2^{5/3}$ , 可求出  $\phi_2 = 0.083$ ,

溶胀后的密度  $\rho = 0.083 \times 1.2 + (1 - 0.083) \times 0.8 = 0.833 \text{ g/cm}^3$

2-41:  $V_1 = 112.5/1.10 = 102.27 \text{ cm}^3/\text{mol}$

$\rho/M_c = 2.10/14/2 = 0.075 \text{ mol/L} = 7.5 \times 10^{-5} \text{ mol/cm}^3$

求得 $\Phi_2 = 0.266$ , 最后体积 =  $3.76\text{cm}^3$

2-42: 由式(2-213)求得 $\Phi_2=0.113$ , 得到溶胀网络 $\rho = 0.8452$

### 习题 3A

3-1: 约为 380K。

3-2: 利用Fox公式(3-38):  $\frac{1}{218} = \frac{w_1}{373} + \frac{1-w_1}{203}$ ,  $w_1 = 0.151$

3-3: 利用Fox公式:  $\frac{1}{303} = \frac{1-w_1}{356} + \frac{w_1}{188}$ ,  $w_1=0.2$

3-4: (a)证明: 由  $T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2}$

$$\text{可得 } T_g (w_1 + k w_2) = w_1 T_{g1} + k w_2 T_{g2}, \quad (T_{g1} - T_g) w_1 = k w_2 (T_g - T_{g2})$$

$$\text{所以 } (T_{g1} - T_g) w_1 / w_2 = k (T_g - T_{g2})$$

(b)作图结果:  $k=3.25$ 。

3-5: 利用 Fox 公式, B 均聚物的玻璃化温度约为 190K。

3-6: 根据  $T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2}$ , 可求出丁二烯的玻璃化温度为 184K,  $k$  值为 1.85

丁二烯/醋酸乙烯酯(50/50w/w)共聚物的 $T_g$ 为 225K。

### 习题 3B

3-7: 瞬时应变由弹簧贡献, Kelvin 模型 1000s 的应变为 0.002。

$$0.002 = 0.004(1 - e^{-1000/\tau}), \quad \tau = 1443\text{s}$$

3-8: 由  $1.0 = 2.0e^{-t/\tau}$ ,  $\tau = 1.443\text{s}$

$$\varepsilon(t) = \varepsilon(\infty)(1 - e^{-t/\tau}) = \frac{100 \times 10^6}{2.0 \times 10^9} (1 - e^{-1000/1443}) = 0.025$$

3-9:  $\tau = 100\text{s}$ 。

(a)样品在不同时刻受四个应力, 分别为 0.1MPa, -0.1MPa, 0.1MPa, -0.1MPa, 作用时间不同。应用 Boltzmann 叠加原理:

$$\gamma(240) = \frac{0.1}{1}(1 - e^{-240/100}) - \frac{0.1}{1}(1 - e^{-200/100}) + \frac{0.1}{1}(1 - e^{-160/100}) - \frac{0.1}{1}(1 - e^{-120/100}) = 0.144 \quad \gamma = 0 \text{ 时}$$

(b)与上题同解法。

3-10:  $\tau = \frac{\eta}{E} = \frac{10^{10}}{10^8} = 100\text{s}$



$$\text{所以 } \sigma = \sigma_1 + \sigma_2 = 10^8 \times 0.01 \cdot e^{-50/100} + 10^8 \times 0.02 \cdot e^{-25/100} = 2.16 \times 10^6 \text{ Pa}$$

$$3-11: \text{蠕变过程: } \gamma = \gamma_1 + \gamma_2 + \gamma_3 = \frac{\sigma_0}{G_1} + \frac{\sigma_0}{G_2}(1 - e^{-t/\tau}) + \frac{\sigma_0}{\eta_3}t$$

$$\text{蠕变回复过程: } \gamma = \gamma_2 + \gamma_3 = \frac{\sigma_0}{G_2}(1 - e^{-t_1/\tau})e^{-t/\tau} + \frac{\sigma_0}{\eta_3}t_1$$

3-12: 设模型的弹簧模量为  $E$ , 粘壶的粘度为  $\eta$ , 则有:

$$\varepsilon_1 = \frac{\sigma}{E} + \frac{\sigma}{\eta} \cdot t = \frac{10^3}{E} + \frac{10^3}{\eta} \cdot 10 = 0.15$$

$$\varepsilon_2 = \frac{\sigma}{\eta}t = \frac{10^3}{\eta} \cdot 10 = 0.1$$

$$\text{计算可得 } E = 2 \times 10^4 \text{ Pa}, \quad \eta = 10^5 \text{ Pa.s}, \quad \tau = 5 \text{ s}$$

$$3-13: \text{由题意可知在受到恒定应力时: } \varepsilon = \varepsilon_E + \frac{\sigma}{\eta} \cdot t = \varepsilon_E + \frac{1000}{\eta} \cdot 3 = 2,$$

$$\text{永久应变 } \varepsilon_\eta = \frac{\sigma}{\eta} \cdot t = \frac{1000}{\eta} \cdot 3 = 0.75$$

$$\text{所以恒定 } 1000 \text{ Pa 时橡胶带的伸长为 } \varepsilon_E = 1.25, \quad \lambda_E = 2.25$$

在  $127^\circ\text{C}$  固定应变为 1.5 时

$$\frac{\sigma}{1000} = \frac{T_1(\lambda_1 - \lambda_1^{-2})}{T_2(\lambda_2 - \lambda_2^{-2})} = \frac{400 \times (2.5 - 2.5^{-2})}{300 \times (2.25 - 2.25^{-2})} = 1.52, \quad \text{初始应力为 } 1.52 \times 10^3 \text{ Pa}$$

$$3-14: \text{橡胶球损失的能量为: } E = mgh = 9.8 \times 0.4m = 3.92m$$

$$\text{升高的温度为 } T = \frac{E}{m \cdot C_p} = \frac{3.92m}{m \cdot 1.83 \times 10^3} = 0.002 \text{ K}$$

$$3-15: \lg a_{T,1} = \lg \frac{\eta_{25}}{\eta_{10}} = \frac{-17.44(25-10)}{51.6 + (25-10)} = -3.93$$

$$\lg a_{T,2} = \lg \frac{\eta_{40}}{\eta_{10}} = \frac{-17.44(40-10)}{51.6 + (40-10)} = -6.41$$

$$\text{所以 } \lg \frac{\eta_{40}}{\eta_{25}} = \lg a_{T,2} - \lg a_{T,1} = -6.41 + 3.93 = -2.48, \quad \eta_{40} = 2 \times 10^5 \text{ Pa} \cdot \text{s}$$

$$3-16: (1) \lg a_T = \frac{-17.44(150-100)}{51.6 + (150-100)} = -8.58$$

$$(2) \lg a_T = \frac{-13.7(150-100)}{50.0 + (150-100)} = -6.85$$

$$3-17: (a) \lg a_{T,1} = \lg \frac{\eta_{140}}{\eta_{110}} = \frac{-17.44(140-110)}{51.6 + (140-110)} = -6.41$$

$$\lg a_{T,2} = \lg \frac{\eta_{160}}{\eta_{110}} = \frac{-17.44(160-110)}{51.6 + (160-110)} = -8.58$$

$$\text{所以 } \lg \frac{\eta_{160}}{\eta_{140}} = \lg a_{T,2} - \lg a_{T,1} = -8.58 + 6.41 = -2.17, \quad \eta_{160} = 676 \text{ Pa} \cdot \text{s}$$

(b) 提高温度、降低分子量。

### 习题 3C

3-20: 因为在流道内分子链已发生弹性回复, 故出口膨胀程度降低。

$$3-21: \eta = KZ_w^{3.4}, \quad 2 \times 10^4 = K(700 \times 2)^{3.4}, \quad K = 4.02 \times 10^{-7}$$

$$\eta_{500} = 4.02 \times 10^{-7} \times (500 \times 2)^{3.4} = 6371 \text{ Pa} \cdot \text{s}$$

$$\log \frac{\eta_{145}}{\eta_{T_g}} = \log \frac{6371}{\eta_{T_g}} = \frac{-17.44(145-75)}{51.6 + (145-75)} = -10$$

$$\log \eta_{T_g} = 13.8$$

$$\log \frac{20000}{\eta_{T_g}} = \frac{-17.44(x-75)}{51.6 + (x-75)} = -9.5 \quad x = 136.6^\circ \text{C}$$

3-22: 相互推开

$$3-23: DP_w = 300000/211 = 1422 \quad Z_w = 1422 \times 5 = 7110$$

$$\eta = KZ_w \quad 150 = K \times 7110^{3.4} \quad K = 1.2 \times 10^{-11}$$

$$\eta = K \times 14220^{3.4} = 1583 \text{ Pa} \cdot \text{s}$$

$$3-24: \text{利用第一个条件: } \frac{\tau}{\dot{\gamma}} = 10 = \frac{A}{1 + \sqrt{B\dot{\gamma}}} = A$$

$$\text{利用第二个条件: } \frac{\tau}{\dot{\gamma}} = 1.0 = \frac{10}{1 + \sqrt{B\dot{\gamma}}}, \quad B = 0.081$$

$$\tau = \frac{A\dot{\gamma}}{1 + \sqrt{B\dot{\gamma}}} = \frac{10 \times 4000}{1 + \sqrt{0.081 \times 4000}} = 2105 \text{ Pa}, \quad \eta = 0.53 \text{ Pa} \cdot \text{s}$$

$$3-25: 1000 = 2.70 \times 10^2 \dot{\gamma}^{0.635}, \quad \dot{\gamma} = 7.86$$

$$\eta = 1000/7.86 = 127 \text{ Pa} \cdot \text{s}$$

溶液为假塑体, 很可能为触变体。

$$3-26: \tau = 98 \text{ Pa}, \quad \dot{\gamma} = 192.08 \text{ s}^{-1}$$

$$\text{移动距离} = 192.08 \text{ s}^{-1} \times 10 \text{ s} \times 0.01 \text{ cm} = 19.208 \text{ cm}$$

## 习题 4

4-1: 100nm 的聚乙烯晶片的熔点为:

$$T_m = T_m^0 \left( 1 - \frac{2\sigma}{L_c \rho_c \Delta H^0} \right) = 415 \times \left( 1 - \frac{2 \times 90 \times 10^{-3}}{100 \times 10^{-9} \times 1000 \times 293 \times 10^3} \right) = 412 K$$

类似的 50nm、10nm、5nm 的聚乙烯晶片的熔点分别为 410K, 390K, 364K。

4-2: 重量结晶度  $w_c = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)}$ , 在分子与分母上同除以  $\rho_s$ , 则有  $w_c = \frac{\rho_c(1 - \rho_a/\rho_s)}{(\rho_c - \rho_a)}$ ,

$$\text{令 } A = \frac{\rho_c}{\rho_c - \rho_a}, \text{ 则有 } W_c = A(1 - \rho_a/\rho_s)$$

$$(a) \rho_a = 1.335 g/cm^3, \rho_c = 1.454 g/cm^3$$

$$(b) w_c = A(1 - \frac{\rho_a}{\rho_s}) = 12.2 \times (1 - \frac{1.335}{1.357}) = 0.2$$

4-3: A 的结果可判断为玻璃化温度; C、D 可以判断为熔点; B 的实验结果可能有误

4-4: (a)PET 的链节分子量为 192g/mol, 所以完全结晶 PET 密度为:

$$\frac{192}{2.15 \times 10^{-22} \times 6.02^{23}} = 1.48 g/cm^3$$

(b)

(1)以熔融焓对密度作图外推到密度为 1.48 处即得 100%结晶的熔融焓 126.1 J/g

(2)密度最大样品的结晶度为  $110.1/126.1=0.87$

(3) 以密度对结晶度作图(如下图所示)推至结晶度为零处即得完全无定形PET的密度为 1.338 g/cm<sup>3</sup>。

(a)PET 的链节分子量为 192g/mol, 所以完全结晶 PET 密度为:

4-5: 当聚氧化乙烯中水含量为体积分数 0.01 时熔点为:

$$\frac{1}{T_m} - \frac{1}{T_m^*} = \frac{R}{\Delta H_u} \cdot \frac{V_u}{V_1} \cdot (\Phi_1 - \chi \Phi_1^2) = \frac{8.314}{8284} \times \frac{44/1.33}{18} \times (0.01 - 0.45 \times 0.01^2) = 1.84 \times 10^{-5}$$

$$T_m = \frac{1}{1.84 \times 10^{-5} + 1/339} = 337 K = 64^\circ C$$

4-6: (1)利用 Fox 公式: 得增塑剂的重量分数为 0.12, 可近似看作体积分数用于下题

$$(2) \frac{1}{T_m} - \frac{1}{T_m^*} = \frac{R}{\Delta H_u} \cdot \frac{V_u}{V_1} \cdot (\Phi_1 - \chi \Phi_1^2) = \frac{8.314}{1960} \times \frac{226/1.088}{200} \times (0.12 - 0.4 \times 0.12^2) = 5 \times 10^{-4}$$

$$T_m = \frac{1}{0.0005 + 1/538} = 424 K = 151^\circ C$$

4-7: 利用公式  $1 - \alpha = \exp(-Kt^n)$ , 10s 后的结晶度为:

$$\alpha = 1 - \exp(-Kt^n) = 1 - \exp(-10^{-2} \times 10^2) = 1 - 0.368 = 0.632$$

$$4-8: \langle \cos^2 \theta \rangle = 0.2 \times 1/3 + 0.5 \cos^2(30) + 0.3 \cos^2(0) = 0.74$$

$$f = \frac{1}{2} (3 \langle \cos^2 \phi \rangle - 1) = \frac{1}{2} (3 \times 0.74 - 1) = 0.61$$

$$4-9: f = \frac{\Delta n}{\Delta n_0} = \frac{0.03}{0.05} = 0.6, \text{ 所以 } \langle \cos^2 \theta \rangle = 0.73, \text{ 夹角 } \theta = 31.1^\circ$$

$$4-10: 0.8 = 0.5 \times 0.95 + 0.5 f_a, f_a = 0.65$$

4-11: 图略, 参考教材图 4-59

4-12: 举例略。可通过 DSC 方法, 观察玻璃化转变温度、熔点及液晶相转变温度来进行辨别。

## 习题 5

$$5-1: \sigma_r = \frac{f}{A}, \sigma = \frac{f}{A_0}$$

因为是不可压缩材料, 所以泊松比  $\nu = 0.5$ , 即:  $A \cdot L = A_0 \cdot L_0$

$$\text{所以 } \frac{\sigma_r}{\sigma} = \frac{A_0}{A} = \frac{L}{L_0} = \lambda = 1 + \varepsilon。$$

5-2: 聚酰胺没有晶区  $\alpha$  转变。

5-3: 银纹, 塑性形变, 产生新表面

5-4: 由表 3-1, 聚苯乙烯的  $7M_c$  尚低于 155,000, 此举提高加工性能, 不损失力学性能。可取

5-5: 对图中应变速率为 5%/min 的曲线积分求曲线下面积, 再乘以样品的体积即可得出断裂功。

$$5-6: \text{由 } K_{IC} = \sigma_c \sqrt{\pi a}, \text{ 可知 } 0.8 \times 10^6 = \sigma_c \sqrt{3.14 \times 0.01}, \text{ 得出 } \sigma_c = 4.5 \times 10^6 \text{ Pa}$$

$$5-7: \text{由 } K_{IC} = 4\sqrt{6} \frac{Fa}{BT^{3/2}}, \text{ 可知: } 2 \times 10^6 = 4\sqrt{6} \frac{F \cdot 0.04}{0.003 \times 0.02^{3/2}}, \text{ 解出 } F = 43.3 \text{ N}$$

$$\text{所以 } \sigma = \frac{F}{A_0} = \frac{43.3}{0.02 \times 0.003} = 7.2 \times 10^5 \text{ Pa}$$

$$5-8: E = \frac{\sigma}{\varepsilon} = \frac{200 / (3.14 \times 0.005^2)}{0.25 / 100} = 1 \times 10^9 \text{ Pa}$$

$$G = \frac{F^2}{2B} \frac{dC}{da} = \frac{F^2}{2B} \frac{192a^2}{EBT^3} = 8090 \text{ N/m}$$

$$5-9: \text{由 (5-46) } \delta = \frac{64a^3}{EBT^3} F \text{ 得到 } a = \left( \frac{\delta EBT^3}{F} \right)^{1/3}$$

$$\text{代入 (5-48) } G_{IC} = \frac{F^2}{2B} \frac{192a^2}{EBT^3} = \frac{F^2}{2B} \frac{192}{EBT^3} \left( \frac{\delta EBT^3}{F} \right)^{2/3} = \frac{6}{T} \left( \frac{F^4 \delta^2}{EB^4} \right)^{1/3}$$

$$G_{IC} = \frac{6}{0.02} \left( \frac{10^4 \times 0.0025^2}{2.5 \times 10^9 \times 0.004^4} \right)^{1/3} = 3.08 J / cm^2$$