

八十五學年度國立台灣工業技術學院研究所碩士班招生考試

所別：纖維及高分子工程技術研究所 組別：高分子組

科目：高分子原理

- 一. State the methods you would use to determine:
 (a) $\bar{M}_n$ for samples of poly(ethylene glycol) with values in the range 4×10^2 to $5 \times 10^3 \text{ g mol}^{-1}$; (b) $\bar{M}_n$ for samples of polyacrylonitrile with values in the range 5×10^4 to $2 \times 10^5 \text{ g mol}^{-1}$, and (c) the polydispersity indices of samples of polystyrene with molar masses in the range 10^4 to 10^6 g mol^{-1} .
 For each method, discuss briefly possible errors in the determinations. (9%)

- 二. The tables below give the mean flow times (t) in a suspended-level viscometer recorded for solutions of two of five monodisperse samples of polystyrene at various concentrations (c) in cyclohexane at 34°C . Under these conditions, the mean flow time (t_0) for cyclohexane is 151.8 s

(Sample B)		(Sample E)	
$10^3 \times c/\text{g cm}^{-3}$	t/s	$10^3 \times c/\text{g cm}^{-3}$	t/s
1.586	158.5	1.040	176.1
5.553	178.6	1.691	195.4
7.403	189.6	2.255	214.8
8.884	199.5	2.706	232.4

Determine the intrinsic viscosities, $[\eta]$, of these samples. The intrinsic viscosities of the other three polystyrene samples were evaluated under the same conditions and are given in the following table together with M_w values determined by light scattering.

Polystyrene sample	$M_w/\text{g mol}^{-1}$	$[\eta]/\text{cm}^3 \text{g}^{-1}$
A	37000	15.77
B	102000	---
C	269000	42.56
D	690000	68.12
E	2402000	---

Using these data together with the calculated values of $[\eta]$ for samples B and E, evaluate the constants of the Mark-Houwink equation for polystyrene in cyclohexane at 34°C . What can you deduce about the conformation of the polystyrene chain under the conditions of the viscosity determinations? (10%)



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(a) A viscoelastic polymer is subjected to an oscillating sinusoidal load applied at angular frequency, ω . Assuming that the variation of the strain, e , and the stress, σ , with time, t , can be represented by equations of the form:

$$e = e_0 \cos \omega t$$

$$\sigma = \sigma_0 \cos(\omega t + \delta)$$

where δ is the phase lag between the stress and strain, show that the energy dissipated per cycle of the deformation (ΔU). (6%)

(b) How can one avoid thermal failure of the polymer given in (a) when the heat accumulated in the polymer is significantly larger than that transferred out of the sample? (4%)

四、

- (1) The glass transition temperature of a polymer is mostly affected by the (a) degree of crystallinity (b) chain length (c) crystal defect (d) free volume of the polymer. (2.5%)
- (2) The unit cell dimensions of the polymer crystal are usually determined by using (a) small angle X-ray scattering (SAXS) (b) differential scanning calorimetry (DSC) (c) transmission electron microscope (TEM) (d) wide angle X-ray scattering (WAXS). (2.5%)
- (3) The creep or stress relaxation behavior of a polymer subjected to a load is mainly due to the fact that (a) degree of crystallinity of polymer changes (b) the length of the polymer decreases (c) the modulus of polymer decreases (d) the amount of heat accumulated in the polymer increases with increasing time. (2.5%)
- (4) The most probable value and root mean square value of the end-to-end distance of a freely jointed chain is equal to (a) $(8/3\pi)^{1/2} l n^{1/2}$, $l n^{1/2}$ (b) $l n^{1/2}/\sqrt{6}$, $l n$ (c) $l n$, $l n^{1/2}$ (d) $(2/3)^{1/2} l n^{1/2}$, $l n^{1/2}$, respectively. (2.5%)
- (5) If we try and crystallize a polymer melt a few degrees above T_g then the rate of growth of crystals is initially governed by the fact that: (a) there are no stable nuclei present. (b) viscosities of polymer melts are very high. (c) crosslinking reactions occurs at high temperatures. (d) tertiary crystallization. (2.5%)
- (6) With regard to polyethylene single crystallization, which of the following statement is correct? (a) crystals get smaller (b) angle of truncation decreases (c) crystals remain constant (d) The percentage of 100 chain folding increases with increasing crystallization temperature. (2.5%)



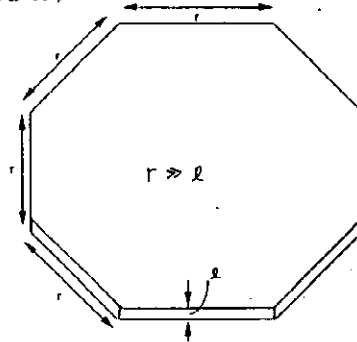
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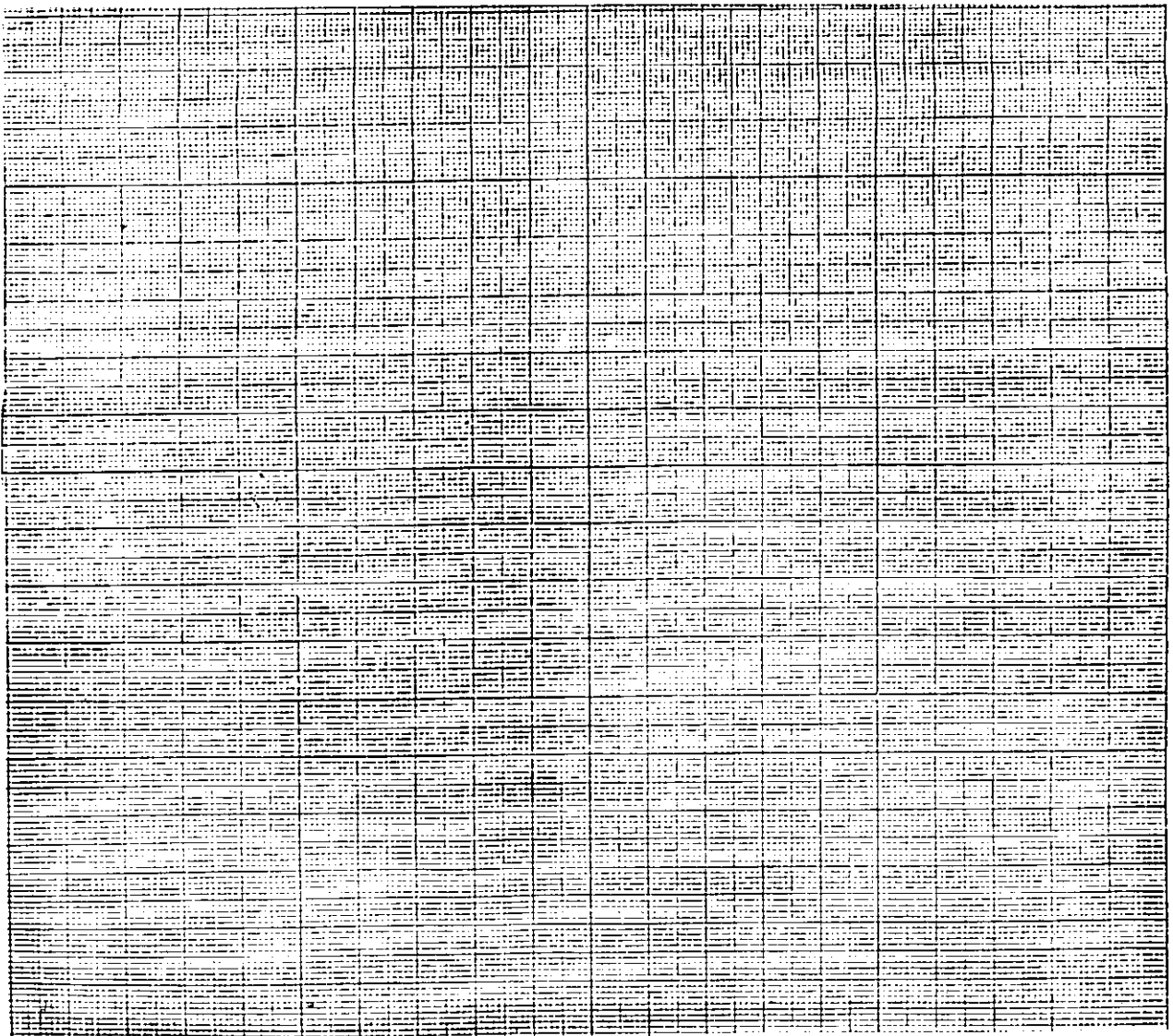
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- 五. Derive the Hoffman-Weeks equation ($T_m = T_m^0(1 - \frac{2\sigma_e l}{\Delta H_f^0 l})$) based on a hexagonal shaped crystal of dimension as shown below: (6%)



where T_m^0 is the equilibrium melting temperature.
 ΔH_f^0 is the enthalpy of fusion per unit volume of crystals.
 σ_e is the top and bottom surface energies.



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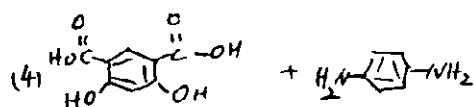
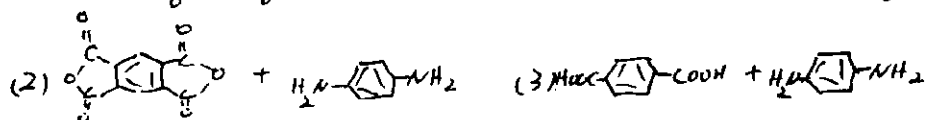
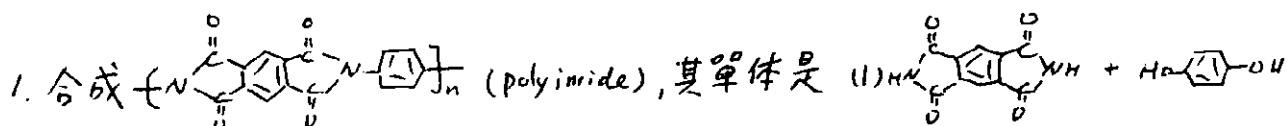
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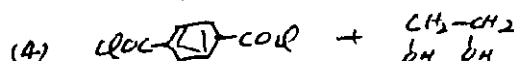
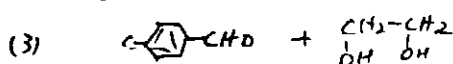
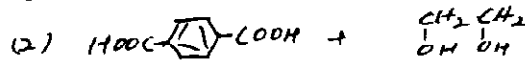
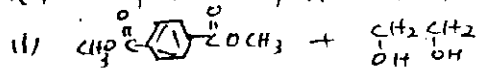
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六、單一選擇題：

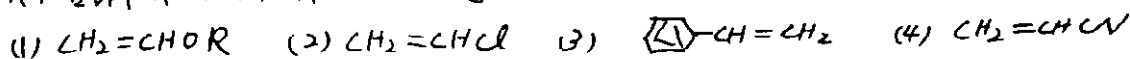
(以下第 1 至 16 題，每題答對者得 3 分，第 17 題答對者得 2 分；第 1 至 17 題答錯者，倒扣題分的四分之一；未答者，得零分；倒扣至本第六大題零分為止)



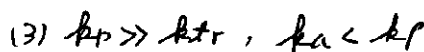
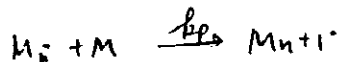
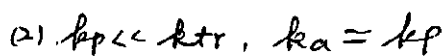
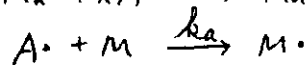
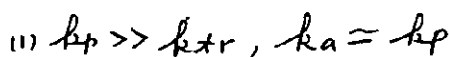
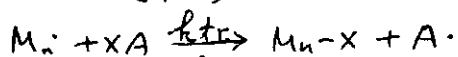
2. 以下四種原料中，那一種不是合成 PET (polyethylene terephthalate) 的原料



3. 以下各種單體中，那一種不適合進行自由基聚合反應

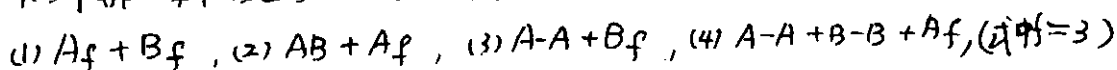


4. 以下凡種鏈轉移 (Chain transfer) 的條件中，何者會降低聚合體的鏈長

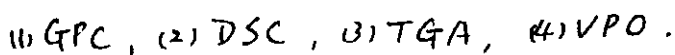


(4) 以上三種情況，均會使聚合體鏈長降低

5. 下列那一種配分合成的高分子不會有架橋現象



6. 下列何種儀器可以測知高分子的分子量分佈



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7. 下列測定高分子分子量的方法中，那一種方法不能直接測出高分子的分子量？

- (1) 光散射法 (2) 末端基法 (3) 粘度法 (4) 渗透壓法

8. 在逐級反應系中，以 Carother Equation (CE) 及 Statistical Approach (SA) 兩種方法來預估反應到達膠點 (gel point) 時的反應率 P_c ，以下四種敘述那一種是正確的？

- (1) 以 CE 及 SA 法預測之 P_c 均較實驗值小，
 (2) 以 CE 及 SA 法預測之 P_c 均較實驗值大，
 (3) 以 CE 法預測之 P_c 較實驗值小，SA 法預測之 P_c 值較實驗值大，
 (4) 以 CE 法預測之 P_c 較實驗值大，SA 法預測之 P_c 值較實驗值小。

9. 1 莫耳之甘油 (glycerol, $\begin{smallmatrix} \text{CH}_2 & -\text{CH}- & \text{CH}_2 \\ | & & | \\ \text{OH} & & \text{OH} \end{smallmatrix}$) 和 5 莫耳之羧酸 (phthalic acid, $\begin{smallmatrix} \text{COOH} \\ | \\ \text{C}_6\text{H}_4 \\ | \\ \text{COOH} \end{smallmatrix}$) 之均相混合液，其平均官能度 (functionality) 是多少？

- (1) 3 (2) $\frac{13}{6}$ (3) 2 (4) 1



10. 下列四種單體 (括號內為 $Q-e$ 值)

Acrylic Acid (AA; 0.83, 0.88), *n*-butyl vinyl ether (BVE; 0.038, -1.500)

Maleic Anhydride (MA; 0.86, 3.69), Methyl Methacrylate (MMA; 0.78, 0.40)

分別與 Styrene (St, 1.00, -0.80) 進行自由基共聚合反應，則其和 St 形成交替式共聚物 (alternating copolymer) 的容易度依序為

- (1) $MA < AA < MMA < BVE$ (3) $BVE < MMA < AA < MA$
 (2) $MA < MMA < AA < BVE$ (4) $MMA < AA < MA < BVE$

11. 下列六種單體 (括弧內為 $Q-e$ 值) 中，若進行自由基共聚合反應則以 何種式配對最好？

Vinyl Acetate (VA; 0.026, -0.88), St (1.00, -0.80)

n-Butyl Acrylate (BA; 0.38, 0.85), vinyl chloride (VC; 0.056, 0.16)

Acrylonitrile (AN; 0.48, 1.23), 2-vinyl pyridine (VP; 1.41, -0.42)

- (1) VA-St; BA-VC; AN-VP (3) VA-VP; BA-AN; St-VC
 (2) VA-VC; AN-BA; St-VP (4) St-AN; VP-VA; VC-BA

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12. monodisperse polymer A 及 B 之分子量分別為 100,000 及 400,000，一重量單位的 A 與兩重量單位的 B 混合均勻後，則混合高分子的重量平均分子量， $\bar{M}_w = ?$
 (1) 2.0×10^5 (2) 3×10^5 (3) 1.33×10^5 (4) 2.5×10^5
13. 苯乙烯在 THF 中進行陰離子聚合反應，苯乙烯初始濃度 $[M]_0 = 1.0 M$ ，正丁基鋰 (n-butyl lithium) 為起始劑 $[I]_0 = 1.0 \times 10^{-3} M$ ，且 $R_i = R_p$ ，假設反應前後體積不變，且仍為均相溶液。當變化率 (conversion%) 到達 50% 時加入水 $[H_2O] = 0.5 \times 10^{-3} M$ ，試問當變化率到達 100% 時，該高分子的平均 $\bar{X}_n$ 是多少？
 (1) 5×10^2 (2) 15×10^2 (3) 20×10^2 (4) 30×10^2
14. 上題 (13 題) 在不加水的情況下，變化率達 100% 時，其 $\bar{X}_n = ?$
 (1) 5×10^2 (2) 10×10^2 (3) 15×10^2 (4) 20×10^2
15. 單體 $HO-CH_2CH_2CH_2CH_2COOH$ 進行縮合反應，形成 $H-(OCH_2CH_2CH_2CH_2C(=O))_n-OH$ ，經測定 $\bar{M}_w = 18400 g/mole$ ，則 $\bar{X}_n = ?$
 (1) 15300 (2) 14150 (3) 11260 (4) 9250 g/mole
16. 2.7 克的線型聚酯高分子，其末端基為 $-COOH$ ，以末端基滴定法測定分子量，共消耗 0.1 N alcoholic KOH 滴定液 15 ml。試問此高分子的分子量是多少？
 (1) 1800 (2) 3600 (3) 7200 (4) 9000
17. 以依數性質 (colligative property) 所測定出某之高分子^{平均}分子量為
 (1) $\bar{M}_n$ (2) $\bar{M}_w$ (3) $\bar{M}_z$ (4) $\bar{M}_{z+1}$

