一、 The glass transition temperature Tg, of a linear polymer with number average molar mass M_n = 2300 was found to be 121 ℃. The value of Tg increased to 153 ℃ for a sample of the same linear polymer with M_n =9000. A branched version of the same polymer with M_n = 5200 was found to have a Tg of 115 ℃. Determine the average number of branches on the molecules of the branched polymer. (6%)

二、 The relaxation modulus of poly(isobutylene) (PIB) was found to reach 10^5 N/m^2 in 100 hours at 25 ℃(see Fig. 1). What would the relaxation modulus of PIB be in 1000 hours at -80 ℃ ? The Tg of PIB is -70 ℃. (8%)

Stress-Relaxation Experiments on Polyisobutylene

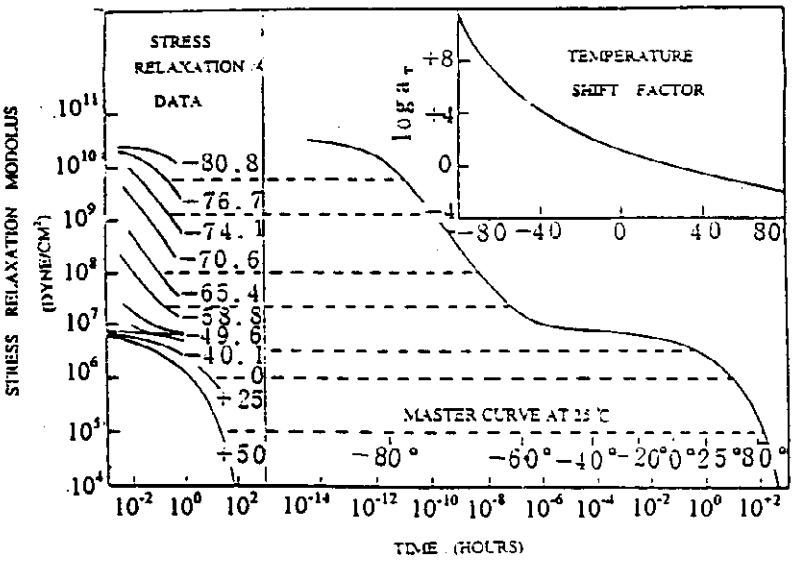


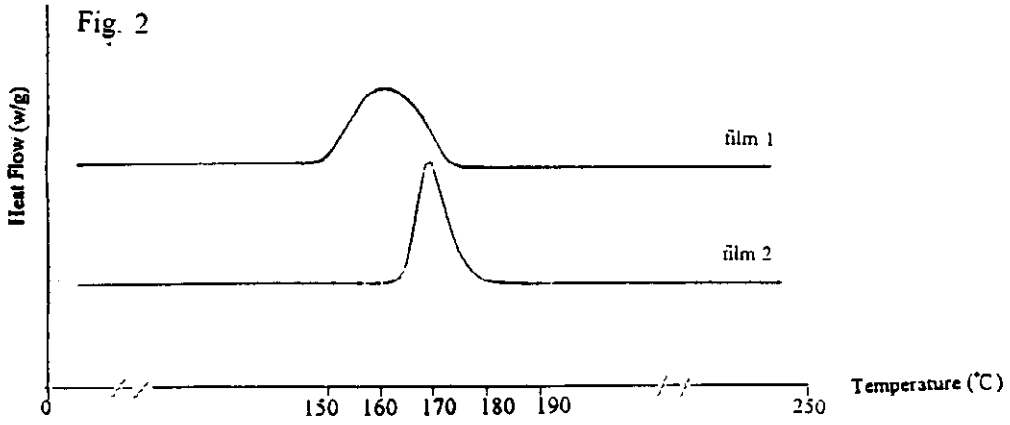
Fig. 1

三、 Explain the following terminology (15 %)

(a) The most probable value of r (end-to-end distance).
(b) Characteristic ratio.
(c) universal calibration curve.
(d) Boltzmann superposition principle.
(e) tie molecules.
(f) equilibrium melting temperature

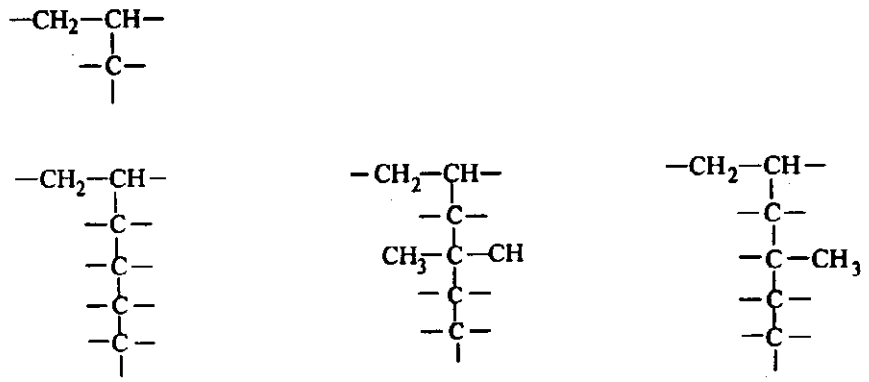
四、Two polymer films were prepared from the same polymer melt. One film was prepared by maintaining the extruded film at 100 ℃ in an air environment and then quickly quenching the extruded film into ice water (film 1), while the other extruded film was maintained at 140 ℃ for 5 seconds and then quickly cooled by ice water (film 2). The DSC (differential scanning calorimetry) thermograms of these two films are shown in Fig. 2. Film 1 had a rather broad melting point centered at approximately 163 ℃. Film 2 had a sharper melting point which was approximately at 170 ℃ but had a lower percentage of crystallinity than that of film 1. (30 % v.s. 50 %). Explain this observation. (6 %) Draw diagram and describe how the percentage of crystallinity of films 1 and 2 will change as a function of time, if the two films are allowed to crystallize for a long period of time. (4 %)

Fig. 2

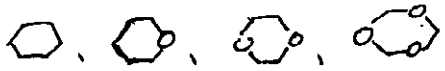


五、(a) What types of molecular motions are possibly accounting for the secondary transition peaks determined by dynamic mechanical analysis (DMA)? (5%)

(b) Rank the melting temperatures of the following polymers in each series. (must give reasons of ranking) (6%)



六.

有環狀化合物，  等，請問

(1) 有那些可以進行開環反應，那些不行？(5%) 原因如何？(3%)

(2) 能進行反應者，以何種方式進行（陰離子、陽離子或自由基）？(3%)

(3) 請選一單体，以化學方程式表示其反應机構（必要時可加入其他藥劑或催劑）(4%)

七.

(1) 試述以直接法及間接法測定高分子分子量的優缺点。(4%)

(2) 列出五种測定高分子分子量的方法，並分別說明其屬於何種方法？(5%)
所測出的分子量屬於何种平均分子量，$\overline{M}_n$, $\overline{M}_w$ 或其他？(3%)

(3) $\overline{M}_v = [\Sigma w_i M_i^a]^{1/a}$, w_i = Weight fraction
兩种分子量分別為 39,000 及 292,000 的 monodisperse polystyrene，以等重量混合後，其在苯溶液中的極限粘度 (intrinsic viscosity) 是多少？
polystyrene 在苯溶液中 Mark-Houwink 常數為 $K = 9.18 \times 10^{-5}$ dl/g，$a = 0.74$
(本實驗是在 25°C 下進行)。(4%)

八.

Mayo Equation, $(\overline{X}_n)^{-1} = (\overline{X}_n)_0^{-1} + C_I \frac{[I]}{[M]} + C_S \frac{[S]}{[M]} + C_Y \frac{[Y]}{[M]} + C_{polymer} \frac{[P]}{[M]}$
式中，C_I, C_S, C_Y 及 $C_{polymer}$ 為鏈轉移常數，[I], [S], [Y], [P] 及 [M] 分別為 initiator, solvent, chain transfer agent 及 polymer 的濃度，請回答下列問題：

(1) 此方程式規範了幾种轉移反應？(3%)

(2) 鏈轉移反應对高分子分子量的大小及分佈的影响如何？(3%)

(3) 如何利用此方程式測出 $(\overline{X}_n)_0$ 及各种鏈轉移常數？(3%)

(4) 1M 的 styrene 以苯為溶劑，於 60°C 下行聚合反應，設苯濃度為 10M 並含有 10^{-3} M 的 n-butyl mercaptan，試問所得聚苯乙烯的聚合度將為多少？已知苯乙烯在無溶劑下於 60°C 行聚合反應所得聚合度為 168，苯及 n-butyl mercaptan 的鏈轉移係數分別為 1.8×10^{-6} 及 22。(4%)

九.

陽離子及陰離子聚合反應各有幾種起始 (initiation) 式？試分別舉例說明之。(6%)