

1. You are to prepare nylon 46 from an acid and an amine.

(a) Write down the chemical equation showing the structure of the monomers and polymer.



(b) [4 x 2 points] You want to obtain the polymer with high molar mass. One thing you can do is to use high-purity monomers. What are the other four [4] things?

1. accelerate the reaction to high conversion (high temperature, catalyst)
2. removing the small molecules (to shift the equilibrium)
3. (stoichiometric) balancing the feed of the monomers
4. employing bulk polymerization (to avoid cyclization)

(c) The practical method to obtain high molar mass is to use 'nylon salt'. Describe the method.

See p40 Textbook

(d) You can prepare the same polymer via interfacial polymerization. How should the monomer be changed? Explain.

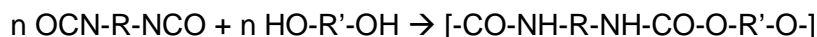
Use of $\text{ClOC}-(\text{CH}_2)_4-\text{COCl}$ instead of $\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$, since interfacial polymerization needs very fast reaction.

(e) In interfacial polymerization of polyester or polycarbonate, NaOH should be added continuously to the system. For nylon you need not. Explain why. [Hint: This is a general chemistry question.]

In both cases, diacid chloride is in organic phase. For diol (for polyester) or bisphenol (for polycarbonate) to be in their conjugate base form [oxide anion] and be located in aqueous phase, pH should be maintained higher than pKa of diol or phenol. NaOH should be added continuously to maintain high pH, as HCl is produced continuously. For nylon amine is in its acidic form [ammonium ion] and is soluble in aqueous phase when pH of the aqueous phase is low by produced HCl. Actually, pH of aqueous phase should be low at the start of the reaction to dissolve the amine.

2. You are to prepare a polyurethane [PU].

(a) Give a general equation for the formation of PU.



(b) The type of the polymerization reaction for PU is different from that for nylon. How is it distinguished?

polyaddition rather than polycondensation. no small molecules produced.

(c) If you want your PU to be elastomeric, i.e. highly stretchable and recoverable, what kind of monomer would you use? Explain.

For PU to be elastomeric it should have flexible chain and crosslinking. The use of multifunctional alcohol with long chain enables it.

Alternatively, the use of the mixture of short and long chain diol may produce segmented copolymer containing hard and soft segments, which behaves as a thermoplastic elastomer.

(d) If you want fabricate PU foam, what would you do? Explain.

Add small amount of water, which produce CO_2 gas through the reaction with isocyanate.

3. For dendrimer and hyperbranched polymer [HBP] answer the following questions.

- (a) You want to prepare a second-generation dendrimer with one molecule of tetrafunctional core. How many molecules of AB₂-type (or ARB₂-type) monomer are needed? What is the branching factor of this dendrimer?

By drawing the structure, you need 12 molecules.

$$\text{Branching factor} = [N(\text{br}) + N(\text{ter})] / [N(\text{br}) + N(\text{ter}) + N(\text{lin})] = (4+8)/(4+8+0) = 1$$

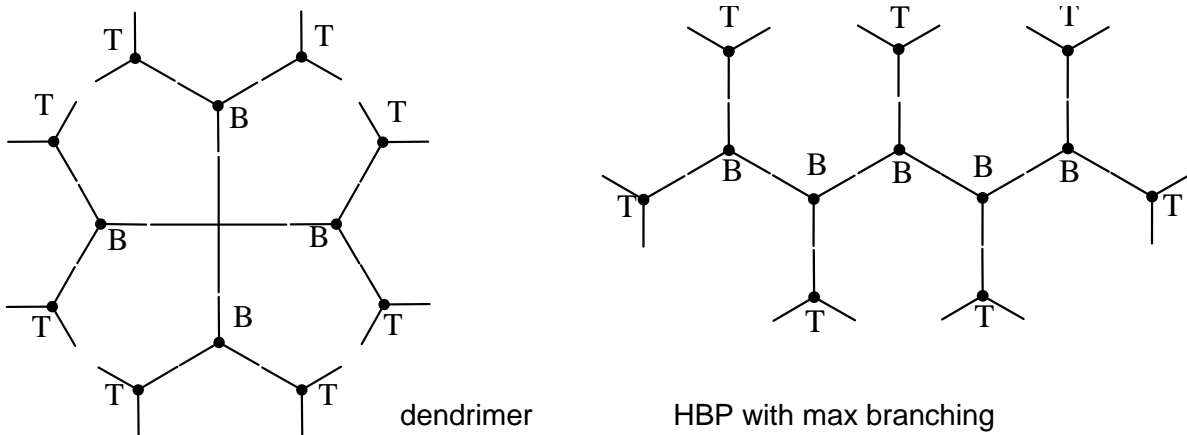
- (b) If you prepare HBP with the same number of AB₂ molecules, what would be the minimum and maximum branching factor you can get?

With minimum branching, N(br) = 0, N(ter) = 2, N(lin) = 10.

$$\text{min branching factor} = 2/12 = 1/6$$

With maximum branching, N(br) = 5, N(ter) = 7, N(lin) = 0

$$\text{max branching factor} = (5+7)/12 = 1$$



- (c) If you prepare HBP with the same number of moles (not molecules), you would get the branching factor of 0.5. What would you do, if you want to obtain a higher branching factor?

Add multifunctional core molecules.

Add monomer slowly.

Both emulate dendrimer synthesis.

4. For a radical polymerization of poly(methyl methacrylate) [PMMA] with the monomer concentration of 1 mol/L and the initiator (with the efficiency of 0.5) concentration of 0.01 mol/L, the following values are determined at steady-state.

$$k_d = 2 \times 10^{-5} \text{ s}^{-1}$$

$$k_p = 1 \times 10^3 \text{ L/mol-s}$$

$$k_t = 1 \times 10^7 \text{ L/mol-s}$$

Neglecting chain transfer reactions, answer the following questions.

- (a) Estimate the steady-state rate of polymerization.

$$R_i = 2 f k_d [I] = 2E-7 = R_t = 2 k_t [M\bullet]$$

$$[M\bullet] = (R_t/2k_t)^{.5} = 1E-7$$

$$R_p = k_p [M] [M\bullet] = 1E-4 \text{ mol/L-s}$$

- (b) Estimate the average lifetime of radical at steady state

$$\tau = [M\bullet]/R_t = .5 \text{ s}$$

(c) [6 points] It is analyzed that the retrieved PMMA at 10% conversion contains an average of 1.2 initiator fragment per chain. Estimate the number average molar mass of this PMMA.

$$q + 2(1 - q) = 1.2, q = .8$$

$$x_n = [2/(1+q)] n = [2/(1+.8)] [R_p/R_t] = 556$$

$$M_n = 556 M_0 = 55600$$

(d) If you want to cut down the molar mass by half, how much CBr_4 (with the chain transfer constant of 2) should be added? [If you are not sure of your answer to (c) above, you may use 100000 as the original molar mass, taking 1 point deduction. Take your chance.]

$$1/x_n = 2/(x_n)_0 = 1/(x_n)_0 + C [S]/[M]$$

$$[S] = 9.0E-4 \text{ mol/L}$$

5. A reagent can retard or inhibit the propagation in radical polymerization.

(a) How is a retardation distinguished from an inhibition in terms of rate of polymerization?

Retardation lowers R_p , while inhibition stops propagation ($R_p = 0$).

(b) Each of (A) quinone, (B) di-*t*-butylphenol, and (C) DPPH can be used as retarder/inhibitor. They retard/inhibit the polymerization by (1) chain transfer, (2) termination, or (3) lowering radical reactivity. Match A, B, and C to 1, 2, and 3.

A-3, B-1, C-2

(c) [3 x 2 points] Show how each of A, B, and C above inhibit or retard the propagation by writing chemical equations.

