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1. (35 points) Acrylonitrile is polymerized via a free radical polymerization using benzoyl peroxide as the initiator in cumene at 60 °C. The rate of polymerization, R_p , is found to be 9.41×10^{-5} moles/liter-s when the monomer concentration, which is held constant, is 9.6 moles/liter. The rate constant for propagation is found in the Polymer Handbook to be 1.96×10^3 liters/mole-s for these conditions. The rate of initiation, R_i , is measured as 3.91×10^{-8} moles/liter-s.

a) Find the concentration of propagating radicals.

$$R_p = k_p [M][P\cdot] \rightarrow [P\cdot] = \frac{R_p}{k_p [M]} = \frac{9.41 \cdot 10^{-5} \frac{\text{mol}}{\text{L}\cdot\text{s}}}{(1.96 \cdot 10^3 \frac{\text{L}}{\text{mol}\cdot\text{s}}) (9.6 \frac{\text{mol}}{\text{L}})}$$
$$= 5.00 \cdot 10^{-9} \frac{\text{mol}}{\text{L}}$$

b) Find the number average degree of polymerization, N_n , assuming termination is by disproportionation only.

$$N_n = \bar{v} = \frac{R_p}{R_i} = \frac{9.41 \cdot 10^{-5} \frac{\text{mol}}{\text{L}\cdot\text{s}}}{3.91 \cdot 10^{-8} \frac{\text{mol}}{\text{L}\cdot\text{s}}} = 2407$$

note: using $p = \frac{\bar{v}}{1+\bar{v}} \Rightarrow N_n = \frac{1}{1-p} = 2410$ yields the same answer within significant figures
 $= 0.9996$

c) A small amount of 1-butane thiol is added and N_n drops to 90% of the value in part b above. Calculate the concentration of 1-butane thiol in the reaction mixture, if the transfer constant for 1-butane thiol is $C_{RX} = 1.69$ and chain transfer to the monomer and solvent are negligible.

Basing our N_n calculation on \bar{v} , we want

$$\bar{v}_{tr} = 0.9 \cdot \bar{v}_0 = 2166$$

And hence

$$\frac{1}{\bar{v}_{tr}} = \frac{1}{\bar{v}_0} + \sum_{RX} C_{RX} \frac{[RX]}{[M]}$$

$$\frac{1}{2166} = \frac{1}{2407} + 1.69 \cdot \frac{[RX]}{9.6 \frac{\text{mol}}{\text{L}}} \Rightarrow [RX] = 2.63 \cdot 10^{-4} \frac{\text{mol}}{\text{L}}$$

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d) At what temperature (in °C) should the reaction be run in order to triple the rate of polymerization?

We find in the Polymer Handbook that for this system:

$$E_p^* = 16.2 \text{ kJ/mole}$$

$$E_d^* = 120.5 \text{ kJ/mole}$$

$$E_t^* = 1.5 \text{ kJ/mole}$$

$$R_p = k_{app} [M][I]^{1/2} = \left(\frac{k_t d}{k_t}\right)^{1/2} k_p [M][I]^{1/2}$$

$$k_{app} = A_{app} \exp(-E_{app}^*/RT) = \underbrace{A_p \left(\frac{f A_d}{A_t}\right)^{1/2}}_{A_{app}} \exp\left[-\frac{(E_p^* + \frac{E_d^*}{2} - \frac{E_t^*}{2})}{RT}\right]$$

$$E_{app}^* = E_p^* + \frac{E_d^*}{2} - \frac{E_t^*}{2} = 75.7 \text{ kJ/mol}$$

$$\frac{R_{p,T_{new}}}{R_{p,160^\circ C}} = \frac{A_{app} \exp\left(\frac{-E_{app}^*}{RT_{new}}\right)}{A_{app} \exp\left(\frac{-E_{app}^*}{R(333 \text{ K})}\right)} = \exp\left[\frac{-E_{app}^*}{R} \left(\frac{1}{T_{new}} - \frac{1}{333 \text{ K}}\right)\right] = 3$$

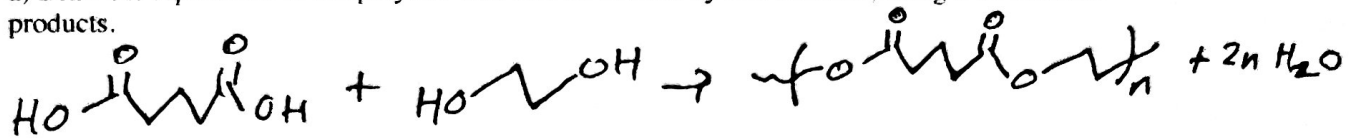
$$\frac{-75.7 \cdot 10^3 \frac{\text{J}}{\text{mol}}}{8.31 \frac{\text{J}}{\text{mol K}}} \left(\frac{1}{T_{new}} - \frac{1}{333 \text{ K}}\right) = \ln 3$$

$$T_{new} = 347 \text{ K} = 73.9^\circ \text{C}$$

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2. (40 points) Glutaric acid ($\text{HOOC}-(\text{CH}_2)_3-\text{COOH}$) is reacted with ethylene glycol ($\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$)

a) Draw the repeat unit of the polymer that will be formed by this reaction, along with the side products.



b) Assume that the concentration of glutaric acid and ethylene glycol are initially both at 2 moles/liter, and the rate constant of the reaction is $k = 0.5 \text{ liter}/(\text{mole}\cdot\text{min})$. At what time will the reaction produce a solution with a number average degree of polymerization equal to 500?

$$N_n = 500 = \frac{1 + k_c [A]_0 t}{1 - k_c [A]_0 t} = \frac{1 + 0.5 \frac{\text{L}}{\text{mol}\cdot\text{min}} \cdot (2 \cdot 2 \frac{\text{mol}}{\text{L}}) t}{1 - 0.5 \frac{\text{L}}{\text{mol}\cdot\text{min}} \cdot (2 \cdot 2 \frac{\text{mol}}{\text{L}}) t}$$

was two groups per molecule

$$\Rightarrow t = 299.5 \text{ min}$$

$[A]_0 = [B]_0$, so stoichiometrically balanced and above holds. Units indicate it is catalyzed

c) Instead of timing the reaction, what is the ratio of glutaric acid to ethylene glycol that will produce the same number average degree of polymerization at infinite times?

At $t \rightarrow \infty$, $p \rightarrow 1$. Hence,

$$N_n = 500 = \frac{1+r}{1+r-2pr} = \frac{1+r}{1-r} \Rightarrow r = \frac{499}{501} \frac{\text{glutaric}}{\text{ethylene}}$$

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To the same mixture, 1 mole/liter of 1,2,3,4-butanetetrol is added.

d) What is the critical extent of reaction for gelation if the initial concentration of glutaric acid and ethylene glycol are the same as in part b? Be conservative in your estimate.

1,2,3,4-butanetetrol contributes to hydroxy group concentration. Thus

swapped [A] and [B] from typical convention,

$$[A]_0 = 2.2M + 4.1M = 8M$$

$$[B]_0 = 2.2M = 4M$$

$$r = \frac{4M}{8M} = 0.5$$

$$\rho = \frac{v_A^0 \text{ from } A_4}{v_A^0 \text{ total}} = \frac{4M}{8M} = 0.5$$

$$\langle f \rangle = \frac{2.2M + 2.2M + 4.1M}{5M} = \frac{\sum n_i f_i}{\sum n_i} = 2.4$$

Two estimates: $P_c = \frac{1}{\sqrt{r + \rho \langle f \rangle - 2}} = \frac{1}{\sqrt{0.5 + 0.5 \cdot 0.5 \cdot 2}} = 1$

$$P_c = \frac{2}{\langle f \rangle} = \frac{5}{6} = 0.8\bar{3}$$

e) At what time will the critical extent of reaction for gelation be reached?

As $P_c = 5/6$, $[B] = (1 - P_c) [B]_0 = \frac{1}{6} \cdot 4M = \frac{2}{3}M$ *more conservative*

$$[A] = [A]_0 + [B] - [B]_0 = 8M - \frac{10}{3}M = \frac{14}{3}M$$

As stoichiometrically imbalanced, relation between time and concentration is given by

$$\frac{1}{[A]_0 - [B]_0} \ln \left(\frac{[A][B]_0}{[A]_0[B]} \right) = k_c t$$

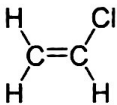
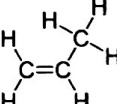
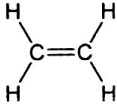
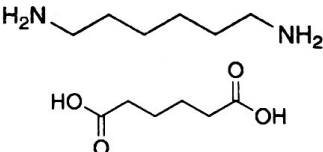
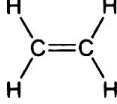
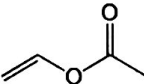
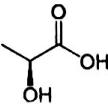

$$t = \frac{1}{0.5 \frac{L}{mol \cdot min}} \cdot \frac{1}{8M - 4M} \cdot \ln \left(\frac{\frac{14}{3}M \cdot 4M}{8M \cdot \frac{2}{3}M} \right) = 0.626 \text{ min}$$

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Short answer questions: (25 points)

3 a) In the following table, **choose any five**, and select the polymerization mechanism from the list below that could be used to prepare the polymer directly. If you attempt more than five, only the first five will be graded.

Possible mechanisms: step-growth, free radical, anionic, cationic, Ziegler-Natta

Polymer	Monomer Structure(s)	Polymerization mechanism
Poly(vinyl chloride)		Free radical, anionic
Isotactic polypropylene		Ziegler-Natta
Low density polyethylene		Free radical
Nylon 6,6		step-growth
High density polyethylene		Ziegler-Natta
Poly(vinyl acetate)		Free radical
Poly(lactic acid)		Step-growth
Poly(isobutylene)		Cationic

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b) In the table below, check the box that corresponds to the type of polymerization reaction that the statement describes:

Characteristic:	Step-growth	Chain-growth
Any two species present in the reaction mixture can react	✓	
The molecular weight of the product polymer changes little throughout the reaction		✓
An initiator is typically required		✓
A small molecule side product is often produced	✓	
The monomers typically contain a carbon-carbon double bond		✓

c) A plant is using free radical polymerization to produce a certain polymer. They observe that after 50 s, 2% of the monomer is converted into polymer. If we want to increase the conversion while keeping the time fixed, which of the following methods can achieve this goal? Describe briefly why or why not, using equations if needed. Also indicate the direction of the change (increase or decrease). (Assume the rate constants and initiator efficiency factor are fixed)

(i) Change the initial monomer concentration

The fundamental equation for all of these is $[M]/[M]_0 = 1 - p = \exp(-k_{app} [I]_0^{1/2} t)$

As the ratio of $[M]/[M]_0$ will be same, changing $[M]_0$ does not affect p

(ii) Change the initial initiator concentration

Yes, increasing $[I]_0$ as from the above will increase conversion

(iii) Change the temperature when $E_p^* = 22$ kJ/mol, $E_d^* = 108$ kJ/mol, and $E_t^* = 14$ kJ/mol

As $E_{app}^* = E_p^* + \frac{1}{2} E_d^* - \frac{1}{2} E_t^* = 69$ kJ/mol,
increasing temperature will increase $k_{app} \Rightarrow$ higher conversion

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d) Graph how M_n varies with time for step-growth, radical with termination by disproportionation, and living polymerization.

