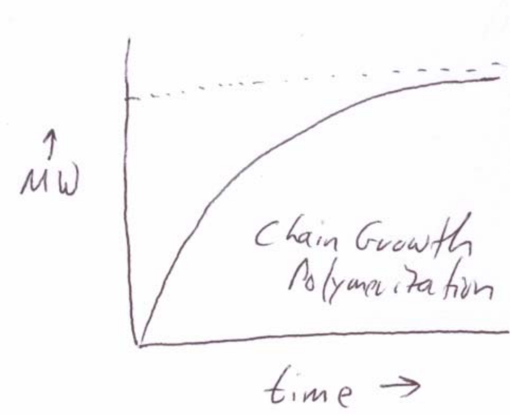
Copy of (051013 Quiz 3 Introduction to Polymers)

This week we saw a demonstration of nylon synthesis, we generally discussed step-growth (or condensation) and chain-growth (or addition) polymerization and went through a list of about 30 common polymers and copolymers including their chemical structure.

1) Vinyl polymers are generally made by addition polymerization.
   a) Give 4 vinyl polymers and their chemical structure.
   b) Give the 4 monomers used for the addition polymerization and their chemical structure.
   c) By comparing the monomer to the polymer repeat unit explain why these polymers are not made by condensation (step) polymerization.

2) Nylon is commonly made by step-growth polymerization. In class we made nylon 6,10.
   a) Give the structure of Nylon 6,10 circling the chemical group that defines this polymer as nylon.
   b) Draw the structure of the two chemicals that were used in class to make nylon 6,10.
   c) Explain why this is a condensation polymerization and what molecule condenses (is a byproduct). What is added to the reaction mixture to neutralize this molecule?
   d) How is this reaction driven to completion and why is driving the reaction to completion important to condensation polymerizations?

3) The following three statements are true of Chain Growth (Addition) Polymerization. Make 3 contradictory statements for Step Growth Polymerization (e.g. the Nylon reaction from class).
   a) Mechanism: Initiation step followed by Propogation steps followed by a Termination step.
   b) Monomer Concentration: Monomer is left even at the end of the reaction.
   c) Polymer Molecular Weight Graph:

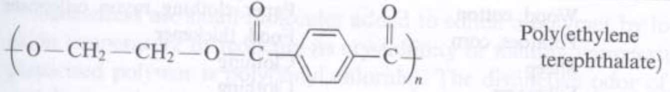


4) a) Give a function that describes the relationship between n_1 and the extent of reaction p for a step growth polymerization (this is called the "*Most Probable Distribution*").
   b) Explain how this function is obtained by i) writing an expression for the extent of reaction, p, in terms of the original number of molecules N_0 and the number of molecules at a given time of reaction, N; ii) writing an expression for n_1 in terms of N and N_0. iii) Relating n_1 and p.
   c) n_w for a bifunctional monomer (2 reactive atoms) made by step-growth is, $n_w = (1+p)/(1-p)$ What is the polydispersity index (PDI) for a step growth polymerization that has fully reacted, p = 1? What is the standard deviation, σ, for this polymer in terms of n_1?
   d) The *Most Probable* distribution is also found for a randomly degraded (cleaved) polymer, regardless of initial distribution. Can you explain why this might be the case? (Hypothesize what the similarity is between random cleavage and step growth polymerization.)

Copy of (051020 Quiz 4 Introduction to Polymers (Chemistry))

This week we looked at synthesis of a polyester network polymer "glyptal", Carother and Flory/Stockmayer (Miller/Macosko)'s interpretation of network formation and the swelling of a hydrogel (sodium polyacrylate).

1) PET or PETE is a polyester. Propose a synthesis for PETE based on the synthesis of glyptal in class.

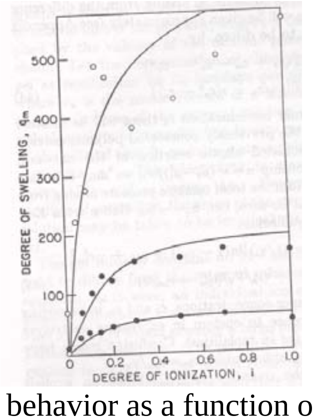


For your synthesis propose
i) monomer(s),
ii) reaction conditions (temperature etc.) and
iii) suggest the PDI that might result from this synthesis.
iv) How might you qualitatively monitor the extent of reaction, p, in this system?

2) i) If a network polymer was desired what monomer could be added to your PET synthesis?
ii) What would be the average functionality, $\langle f_{avg} \rangle$ for this system (write an equation)?
iii) Using the Carothers equation what would be the critical extent of reaction based on your equation for average functionality?

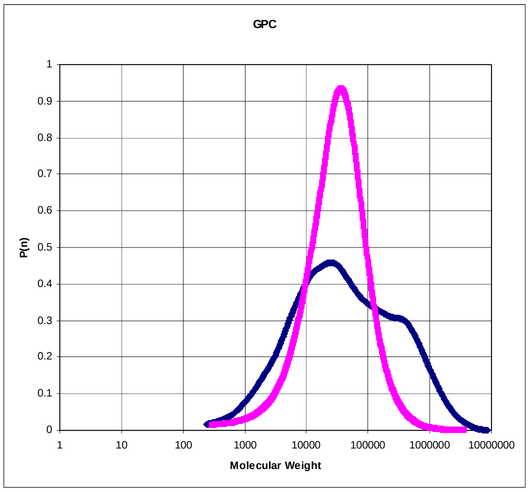
3) i) How would you measure/observe when the system forms a gel? (Define a gel) That is how did we determine the system was a gel in class? (Sketch a plot of this versus reaction time).
ii) Give three definitions of a gel based on molecular weight and topology (network structure). These are due to Carothers; Miller/Macosko; and Flory/Stockmayer.
iii) Percolation is a feature of many disordered, complex systems. Percolation was first seriously considered in polymers by Flory and Stockmeyer. Explain in your own terms what "percolation of a network" means .

4) The hydrogel we observed in class can swell more than 100 times (q_m = 10,000!) its volume with water. The plot below, from Flory's first book, shows the swelling ratio of an early polyacrylic acid hydrogel as a function of the degree of ionization (ionized fraction) and molecular weight between crosslinks, n.



i) Explain in your own words the behavior as a function of n (top curve is highest n).
ii) Explain in your own words the behavior as a function of Degree of Ionization, i.
iii) Guess at the reason for the plateau in swelling ratio.
iv) Why does salt make the hydrogel deswell?

New Quiz for Final (Parts of Quiz 2)



(a)

1) In Plot "(a)", Pick 5 or 6 equally spaced points in molecular weight including the peak position(s) for the ***unimodal*** curve and make a table of P(n) and n. Use this table to calculate a) the mean (number average, n_1), b) second moment, n_2, c) weight average, n_w, d) the polydispersity index, PDI, and e) the standard deviation, σ, about the mean.

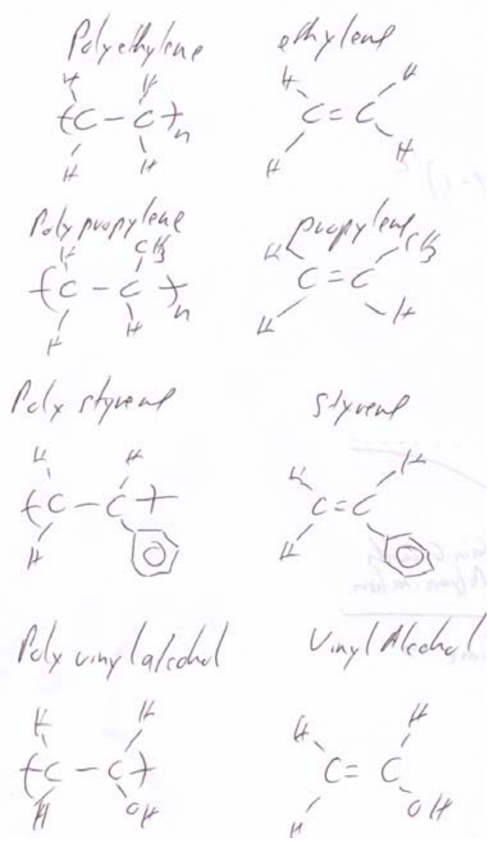
2) For free radical polymerization of polystyrene using benzoyl peroxide:
   - a) Write a stoichiometric expression for the three reactions involved in this chain polymerization.
   - b) Write an expression for the rate of reaction for each of the three reactions in terms of monomer concentration, initiator concentration and free radical concentration.
   - c) Sketch a plot of overall rate versus time and show where steady state occurs
   - d) How is steady state defined in terms of the rates listed in part b?
   - e) Assuming that the reaction is at steady state write an expression for the overall rate of polymerization in terms of monomer and initiator concentrations.

3) a) Explain what the kinetic chain length is, ν. (describe this in words)
   - b) Give an expression for the kinetic chain length if the monomer concentration is M and the initiator concentration is I. The answer should include a function of 3 rate constants, I and M.
   - c) List the two main mechanisms for termination of chain growth.
   - d) How will the molecular weight be related to the kinetic chain length for these two conditions of termination reaction?

4) We looked at Ziegler-Natta polymerization briefly.
   - a) What two compounds would you mix to make a Ziegler-Natta catalyst system?
   - b) Why does one of these include a transition metal?
   - c) Sketch the electronic structure of a transition metal and an alkene π bond (double bond), showing bonding and anti-bonding orbitals, that can explain the effectiveness of Ziegler-Natta catalysts.
   - d) Name the polymer that was first polymerized using Ziegler-Natta catalysts.

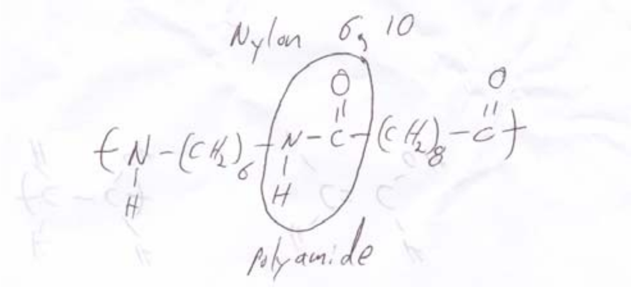
ANSWERS: ***051013 Quiz 3 Introduction to Polymers***

1) a&b)

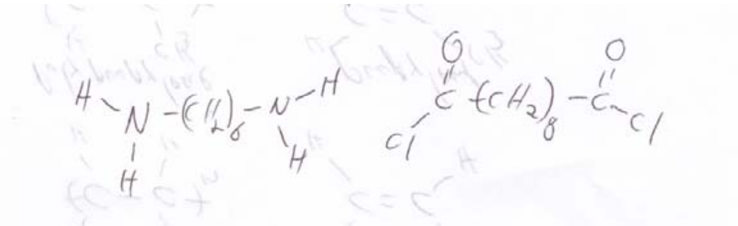


c) The polymers are not made by condensation (step-growth) because no mass is lost to a byproduct in the polymerization reaction. (monomer and repeat unit have the same molar mass).

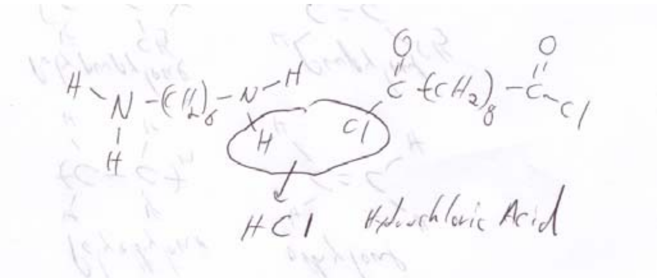
2). a)



b)



c) It is a condensation reaction because HCl is condensed (appears as a byproduct) during the polymerization. HCl is neutralized by NaOH which is added to the aqueous phase to produce water and NaCl salt.

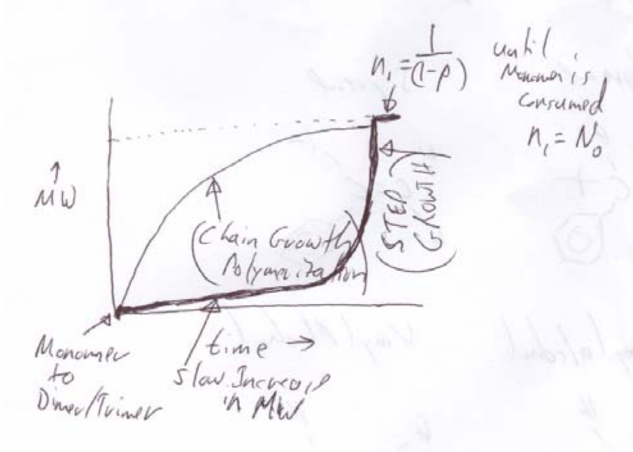


d) Removing the product (Nylon) and byproduct HCl drives the reaction to completion at the interface between the organic and aqueous phase.

3) a) There is only one reaction in step growth, the reaction terminates when the last condensation occurs.

b) Monomer in the step growth reaction is consumed almost immediately as it is transformed into dimers and trimers.

c)



4) a) $n_1 = 1/(1-p)$

b) i) The extent of reaction is given by $p = 1-N/N_0$

- ii) $n_1 = N_0/N$
- iii) $p = 1 - 1/n_1$ or $n_1 = 1/(1-p)$

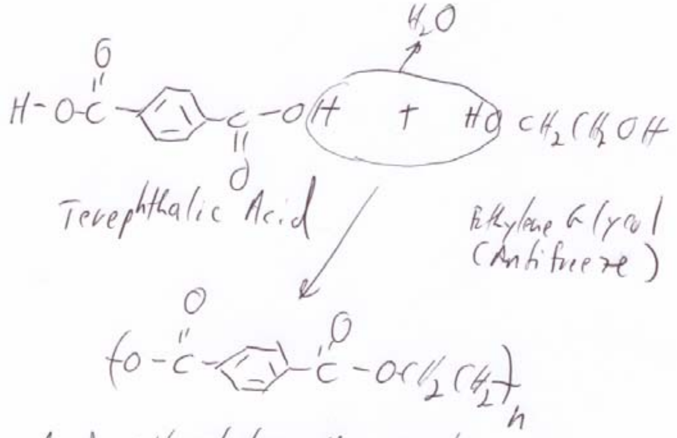
c) PDI = 2 and $\sigma = n_1$

d) In random cleavage the largest chains are more likely to break by a factor of (N_{large}/N_{small}). For step polymerization smaller chains are more likely to react on a per mass basis by the same factor since the number density of reactive chain ends is 2/N. The same distribution results from chain cleavage and step growth because the same probability factor governs both reactions. (This is a difficult question intended as a test of your reasoning using what we covered in class.)

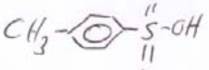
ANSWERS: 051020 Quiz 4 Introduction to Polymers (Chemistry)

1) i) You would use terephthalic acid and ethylene glycol in a condensation reaction,

i)

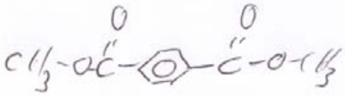


ii) Acid will catalyse this reaction
(typically p-toluene sulfonic acid)



Raise Temperature to drive off water $T > 100°C$

If you use



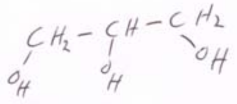
You Make CH_3CH $T_{boil} = 65°C$
So it is easier to drive reaction
(Methanol is toxic)

$\boxed{T \text{ typically } 150°C}$

iii) PDI = 2 for condensation

iv) As the reaction proceeds water is produced and acid is consumed so the reaction could be monitored by the pH of the system.

2) i) Glycerol (glycerin) can be added to give branching.



glycerol glycerin, glycerine,
1,2,3 propanetriol

ii) If the mole fractions of terephthalic acid, ethylene glycol and glycerin are A, B and C, then the average functionality is $\langle f_{avg} \rangle = 2\,(A+B) + 3{*}C$

iii) $p_c = 2/\langle f_{avg} \rangle$. If C = 0.1 then $\langle f_{avg} \rangle = 2.1$ and $p_c = 0.95$.

3) i) The (low shear rate) viscosity becomes infinite for a gel as shown in Flory's Plot.

[IX-1b] DISTRIBUTIONS IN NONLINEAR POLYMERS 355

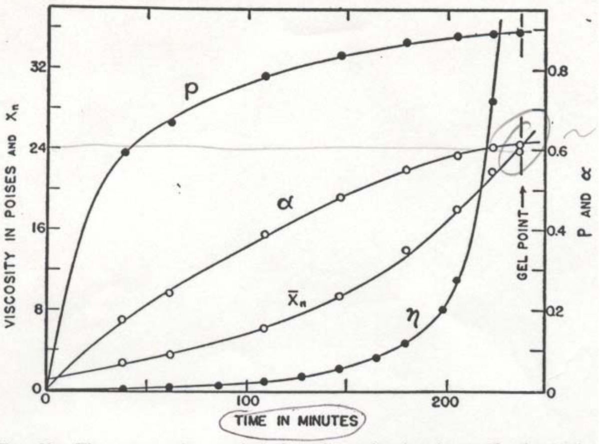


FIG. 62.—The course of a typical three-dimensional polyesterification.[1] The results shown are those for the third experiment reported in Table XXXI.

ii) Carothers: n_1 => infinity
Miller/Macosko: n_w => infinity
Flory/Stockmayer: α => 1

where α is a way to measure when you have reached the percolation threshold, that is when the network connects across the sample. α is the average number of bonds a crosslink site sees in looking away from a networked chain.

iii) Percolation means that there is a connecting pathway across the system in 3d.

4) i) The functionality can be described by the Flory-Rehner equation:

$$\ln(1-v_2)+v_2+\chi v_2^2=\frac{V_1}{n}\left[\frac{v_2}{2}-v_2^{1/3}\right]K_{dangling\ chain}$$

where n is the molecular weight between crosslinks, v_2 is $1/q_m$, χ is the interaction parameter and V_1 is the molar volume of the solvent. q increases with n because the elastic response of the network to swelling is smaller for longer chains, that is the single chain modulus or spring constant k_{spring} is proportional to kT/n. With a smaller elastic response the enthalpic attraction of ionic groups and water drives more swelling.

ii) The more ionic groups the stronger the enthalpic interaction and the greater the swelling.

iii) Several reasons, the elastic response of the network is non-linear at high extensions, at high charging levels the charging is screened (as described by Debye) and the effect of addition of more charges is diminished, the Flory Rehner equation is non-linear.

iv) The addition of salt effectively blocks the ionic groups so salt reduces the average interaction parameter between the polymer and water.

1) Unimodal Curve

n	P(n)	nP(n)	$n^2P(n)$
10^3	0.02	20	20,000
10^4	0.4	4000	4×10^7
5×10^4	0.92	46,000	2.3×10^9
10^5	0.5	50,000	5×10^9
5×10^5	0.08	40,000	2×10^{10}
Sum	1.92	140,020	2.734×10^{10}

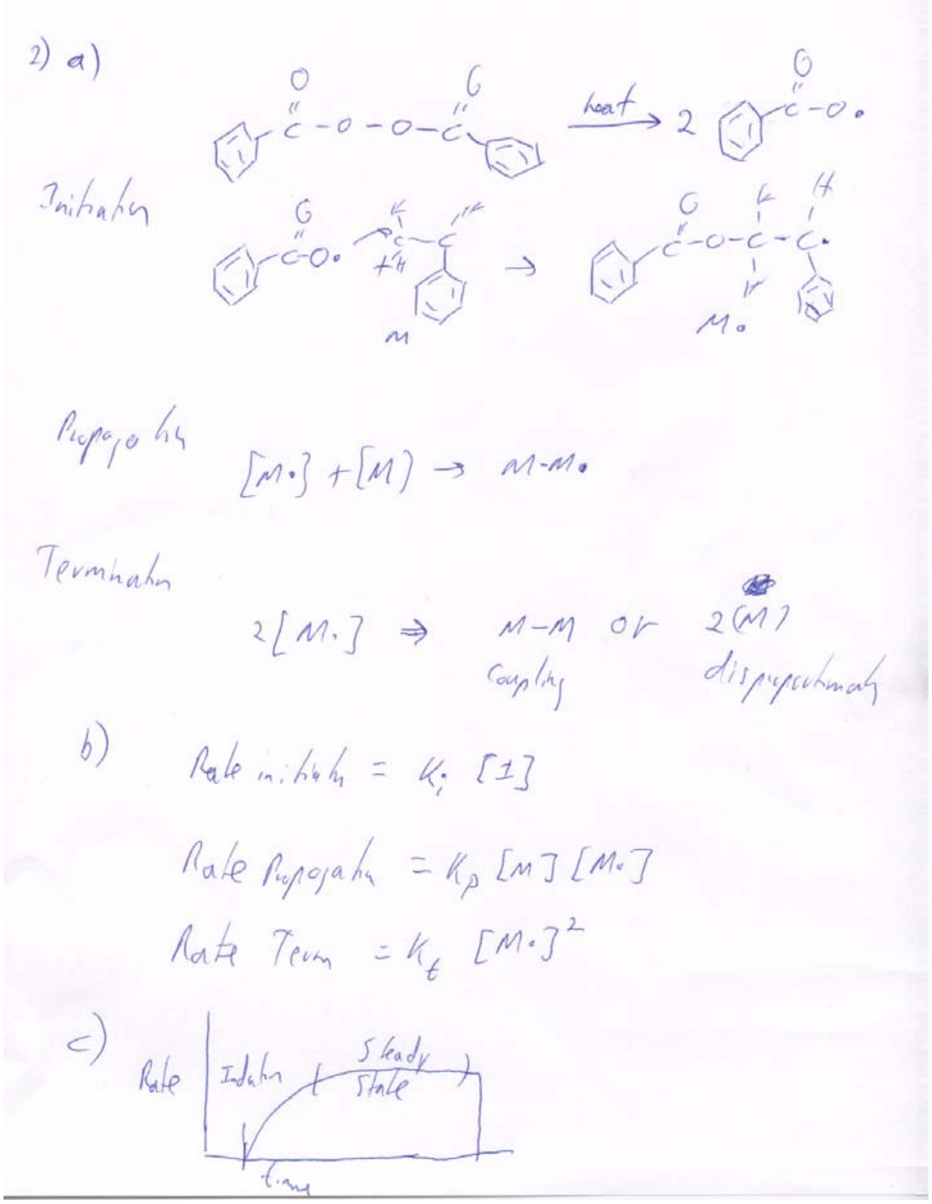
a) n_1 = 140,020/1.92 = 72,927 g/mol

b) $n_2 = 2.734 \times 10^{10}/1.92 = 1.42 \times 10^{10}$ (g/mol)^2

c) $n_w = 1.42 \times 10^{10}$/72,927=195,300 g/mol

d) PDI = 195,300/72,927 = 2.677

e) σ = 72,927 g/mol $(2.677-1)^{1/2}$ = 94,450 g/mol



2) a)

heat → 2

Initiation

M

M•

Propagation $[M\cdot] + [M] \rightarrow M\text{-}M\cdot$

Termination

$2[M\cdot] \Rightarrow M\text{–}M$ or $2(M)$

coupling

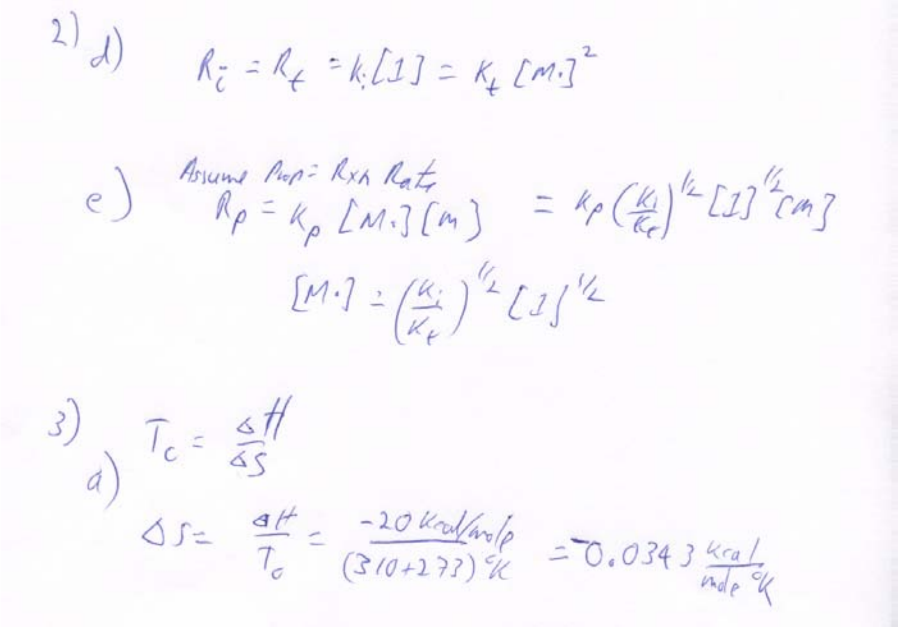
disproportionation

b) Rate initiation $= k_i\ [I]$

Rate Propagation $= k_p\ [M]\ [M\cdot]$

Rate Term $= k_t\ [M\cdot]^2$

c)



2) d) $R_i = R_t = k_i[I] = k_t[M\cdot]^2$

e) Assume Prop = Rxn Rate

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

$$[M\cdot] = \left(\frac{k_i}{k_t}\right)^{1/2}[I]^{1/2}$$

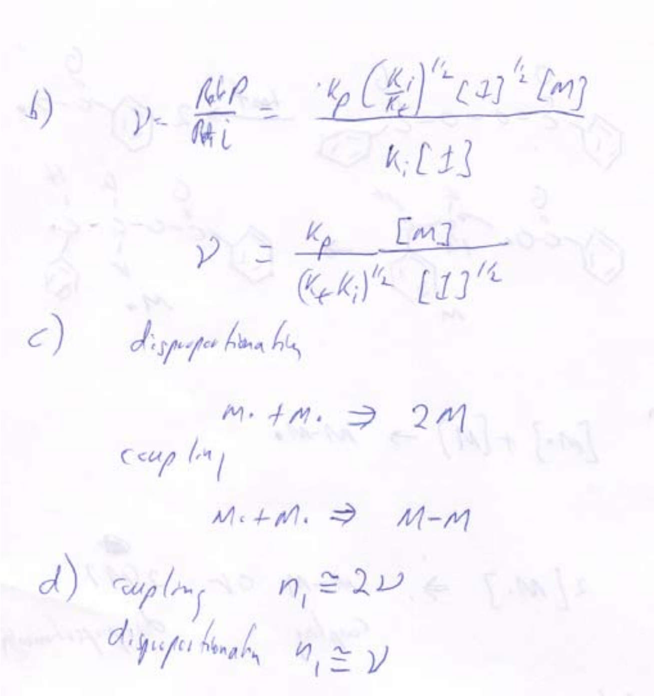
3) a) $T_c = \frac{\Delta H}{\Delta S}$

$$\Delta S = \frac{\Delta H}{T_c} = \frac{-20\ \text{kcal/mole}}{(310+273)\ °\text{K}} = -0.0343\ \frac{\text{kcal}}{\text{mole}\ °\text{K}}$$

b) The entropy change is negative because the polymer is less random than the free monomer. This is the norm for polymerization.

c) Heating would not enhance polymerization since the free energy change would be lower when heated since ΔG = ΔH - T ΔS and ΔH an dΔS are negative.

3) a) The kinetic chain length is the rate of propogation divided by the rate of initiation.



b) $\nu = \frac{RoP}{RoI} = \frac{k_p\left(\frac{k_i}{k_t}\right)^{1/2}[I]^{1/2}[M]}{k_i[I]}$

$$\nu = \frac{k_p}{(k_t k_i)^{1/2}}\frac{[M]}{[I]^{1/2}}$$

c) disproportionation

$M\cdot + M\cdot \Rightarrow 2M$

coupling

$M\cdot + M\cdot \Rightarrow M-M$

d) coupling $n_1 \cong 2\nu$

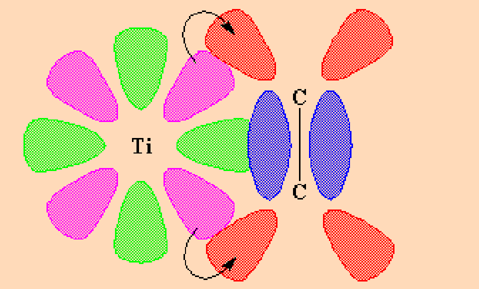
disproportionation $n_1 \cong \nu$

New Quiz answers

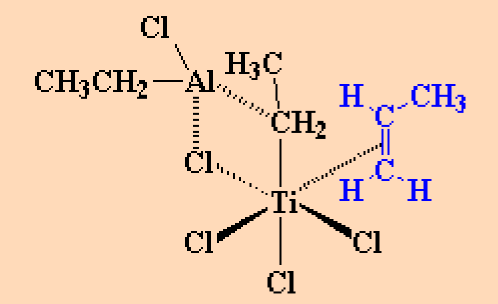
4) a) $TiCl_3$ and $Al(C_2H_5)_2Cl$ or $TiCl_4$ $Al(C_2H_5)_3$ or VCl_4 and $Al(C_2H_5)_2Cl$.

b) 6 bonding orbitals with only 5 filled leaves one for coordination with a vinyl bond.

c) Sketch the electronic structure of a transition metal and a π bond (bonding and anti-bonding orbitals) that can explain the effectiveness of Ziegler-Natta catalysts.



Then electrons from one of the filled orbitals can slip into the alkene's π-antibonding orbital, making the titanium alkene complex stronger.



The π-electrons from propylene end up filling titanium's empty orbital.

From USMiss web page.

d) Polypropylene.