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"On my honor, as an Aggie, I have neither given nor received unauthorized aid on this academic work."

[signature]

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Exam III, April 10, 2014, 100 pts Polymer Chemistry, CHEM 466, Spring 2014 Texas A&M University, College Station, TX, USA

- 1. For the copolymerization of styrene (M_1) with vinyl chloride (M_2), the reactivity ratio values are $r_1 = 17$ and $r_2 = 0.02$ (data from the textbook, Table 5.1).
 - (a) Draw a line on the following plot that represents F₁, the expected mole fraction of M₁ that would be incorporated in the copolymer, as a function of feed composition, f₁. [6 points]



(b) Provide the polymer structure(s) for the expected sample, qualitatively, that would result from the following copolymerization conditions. [7 points]



(c) Provide the polymer structure(s) for the expected sample, qualitatively, that would result from the following copolymerization conditions. [7 points]



[printed]

 (a) Cite one of the advantages and one of the drawbacks of free radical polymerizations over ionic polymerizations. What makes free radical polymerization so attractive from an industrial viewpoint? [4 points]

Adubulages: a talerant to functional groups Drawbooks: Radical species can react w/ each other " towards protic solvents [Lairreversible termination] Attractive become lots of cheop monomers & purity of respents is not critical + can be run in water >> (b) Describe (with reaction equations) the unwanted side reactions that can occur during a free radical polymerization. Use the polymerization of styrene initiated by AIBN as a model reaction. How could you minimize such reactions? [10 points] Termination due to radical reativity DRadical couplings: Home + State - Horas and EDispopertionation: Holding + ETGAL -> Holding + "ETGAL the the tragent on the the 3 Transfer Minimize terminations by decreasing the instantaneous concentration of radical in the reaction mixture (c) During free radical polymerizations, and unlike during controlled radical polymerizations,

(c) During free radical polymerizations, and unlike during controlled radical polymerizations, it is difficult to exert a control over the DP_n of the polymers that are generated. Compare the DP_n vs. % monomer conversion plots for a free, and a controlled radical polymerization. Propose a way to limit the DP_n that are achieved during a free radical polymerization. Show how this mechanism would affect the plot of DP_n vs. % monomer conversion for a free radical polymerization. [6 points]

Method to limit DPn: DPna Scontrolled radical polym Add on efficient transfer agent in the polymerization mixture free radical polymerization + CT gent Free radical polymerization + CT gent have - high CT este (= ktr kprop) -R° + Br-CBrs - R-Br HBrs To Anonomentaulursion

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- 3. For the atom transfer radical polymerization of tert-butyl acrylate:
 - (a) Provide the chemical structure of the polymer. [3 points]



(b) Provide an electron arrow-pushing mechanism above, labeling the initiation, propagation and reversible termination steps. [5 points]

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(c) Calculate the % monomer conversion after 8 h of polymerization, given the ¹H NMR spectra at reaction times of 0 and 8 h, using the assumption that 0% conversion had occurred at 0 h. Please note that the integration lines and values are given for the three vinylic protons resonating between 5.5 and 6.5 ppm and for the three methoxy protons of the anisole solvent resonating at 3.8 ppm (which may be used as an internal reference). [4 points]



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(d) Because the protons of the chain ends cannot be integrated accurately, use the numberaveraged molecular weight, $M_n = 7970 \text{ Da}$, obtained from GPC to calculate the degree of polymerization, n. [4 points]

7970 Da - 115 Da - 80 Da = 7775 Da (chain ends) 802 (w-chain) $\frac{7775 \, D_{\rm h}}{128 \, D_{\rm h}} = 61 = DP_{\rm h}$ C7 H12 2 Cotting 128 Da 115 Da (repeat

(e) Calculate the initiator efficiency, f, given that the initial monomer and initiator concentrations were 7.8 M and 0.078 M, respectively. [4 points]

 $DP_n = [M]_{\circ} \cdot 2 conv.$ [I].f

(from part (c)) = 7.8 M · 50 % conv.

 $60 = \frac{50}{f}$ f = 83 %

4. Provide retrosynthetic analyses of the following polymer structures, giving also the forward reaction conditions that would be required to conduct the transformations.

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(a) [10 points]

OCH₃ CI 'n С m n OCH3 Cull PMDETA ocH3 n n oct3 1) 7 (cation i polym) 3cl3 (on other Lewis acid) 2) XS [O] X (terminator) l Cl

Name: ANSWER KEY [printed] (b) [15 points] ЮH 1-x n x X n / cat.) 1-x ΗO OH pt-x シリ 0 かみら D O (xy) S Ú₿ Θ 2 (avioric polym HO 3 H₽ 4 \bigcirc 100 0

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- 5. Provide the chemistry involved with a standard "super glue" (you may use R as the alkyl substituent).
 - (a) Give the monomer structure. [3 points]
 - (b) Draw the electron arrow-pushing mechanism for the polymerization. [6 points]
 - (c) Give the polymer structure. [3 points]

c٨ CN 2C n 1 mir 0 1-yanoacyl 0 D - yanoacrylate N lerminatio 1Ta' CN cN CN CEN CN Ð 1-1 e D 0 H R

(d) Explain (in words and through chemical structures) why polymerization is facile. [3 points]

R R R R R	C ^{IIIN} C ^{IIIN} P P P P P P P P P P P P P	attack by	O_K_O FO Micleophiles
monomer is in cn = 1 in termediate	Bu GEORES Vu GEORES R carbanion is	Du Jorde Nu Jorde R resonance	Stabilized