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100

PSC 302
Examination 3
Dr. Storey

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$z, 1.5 - (1.5 \times 0.1)$

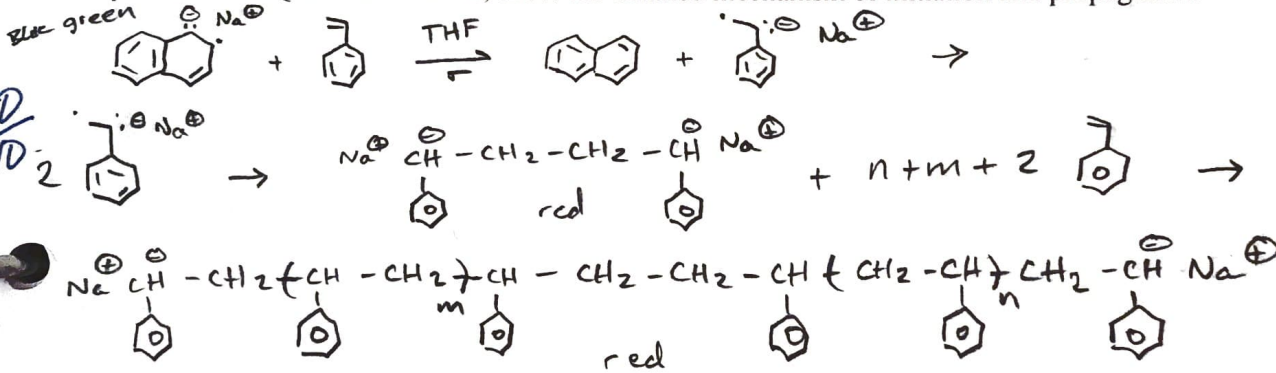
10 pts 1. Anionic polymerization of styrene (F.W. = 104 g/mol) was carried out in THF at room temperature using sodium naphthalene as the initiator. The initial styrene and sodium naphthalene concentrations were 1.5 M and 1×10^{-4} M, respectively. What is the molecular weight of the polystyrene produced at 90% conversion, assuming fast initiation?

1/10

$$\bar{X}_n = \frac{[M]_0 - [M]}{0.5[I]} \rightarrow \frac{1.5 - (1.5 \times 0.90)}{0.5(1 \times 10^{-4})} = \frac{27,000}{3,000} \times 104 \text{ g/mol}$$

$$= 312,000 \text{ g/mol}$$

10 pts 2. For Question 1 above, show the detailed mechanism of initiation and propagation.



12 pts 3. Kinetics of anionic polymerization of isoprene in THF at 10°C were measured. The following dilatometric data were recorded, where H_m represents the theoretical maximum change in capillary height associated with complete monomer conversion and H_t represents the change in height at the given time. Calculate the apparent first-order rate constant, k_{app} .

12/12

Time (min)	4	7	12	22	38	56
$\Delta H_m / (\Delta H_m - \Delta H_t)$	1.13	1.23	1.43	1.93	3.13	5.37

My calculator cannot do a linear regression so I'll have to take the slope.

$$\text{slope} = \frac{\ln(5.37) - \ln(1.13)}{(56.60) - (4.60)} = k_{app} = \boxed{4.996 \times 10^{-4} \text{ s}^{-1}}$$

$$\frac{\text{slope}}{[M]} = k_p^{app}$$

This is non-sensical. Crosslinking?

- 10 pts 4. For both butadiene and isoprene, the best elastomeric properties are obtained when the proportion of cis-1,4 content is maximized. What disadvantages (with respect to elastomeric properties) are produced by each of the other possible structures?

$\frac{6}{10}$



For ideal elastomeric properties, a system would need a high amorphous characteristic (natural rubber is 100%). Trans conformations configuration would promote crystallization by crosslinking. This would heighten T_g and lower the elastomeric properties. The more crystalline these structures are, the less amorphous they would be.

- 8 pts 5. Which of the three methods below is used for commercial production of poly(styrene-*b*-diene-*b*-styrene) triblock copolymers? (Circle correct answer)

$\frac{0}{8}$

- Simple sequencing (styrene followed by diene followed by styrene)
- Use of a difunctional initiator with a polymerization sequence: 1) diene, 2) styrene
- Coupling reaction between two diblocks produced using the polymerization sequence: 1) styrene, 2) diene

- 12 pts 6. A series of cationic polymerizations of isobutylene was carried out in CH_2Cl_2 at -78°C using TiCl_4 as catalyst. Within the series, the initial monomer concentration $[M]_0$ was varied, and all other conditions were held constant. The degree of polymerization of the first-formed polymer was calculated from GPC data acquired, as shown in the table below.



$\frac{5}{12}$

What is the value of the monomer transfer constant, C_M ?

$[M]_0$ (mol/L)	0.10	0.20	0.30	0.50	1.5
X_n	602	862	1,010	1,160	1,380

From Eq: VIII-7

$$C_M = \frac{1}{X_n} - \frac{1}{k_{p2}} - \frac{1}{k_{p1}} \rightarrow \frac{1}{602} - \frac{1}{k_{p2}} - \frac{1}{k_{p1}}$$

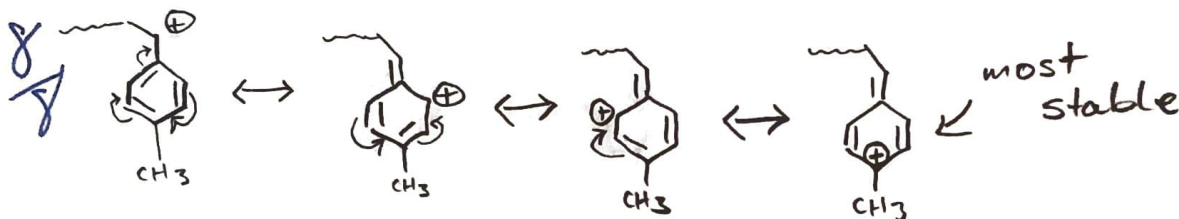
$$\left(\frac{1}{k_{p2}} - \frac{1}{k_{p1}} \right) [M]$$

$$\rightarrow \frac{1}{602} - \frac{\frac{1}{862} - \frac{1}{602}}{\left(\frac{1}{.2} - \frac{1}{.1} \right) 10}$$

$$\frac{1}{602} - 1.002 \times 10^{-5} =$$

$$\boxed{1.651 \times 10^{-3}}$$

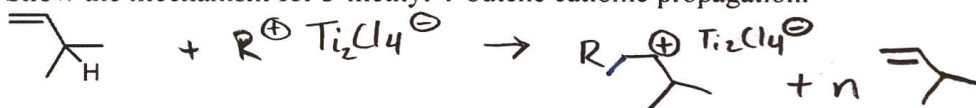
8 pts 7. Draw the various resonance structures for the growing carbenium ion derived from p-methylstyrene.



10 pts 8. Explain the concept of back strain as it relates to formation of a carbenium ion by direct ionization.

Back strain is the phenomena whereby the larger and more bulky the substituents attached to a carbenium ion, the faster the carbenium ion will form. This is due to the change from sp^3 to sp^2 , ~~where the relief in steric hindrance~~ ^{which releases strain} ~~with the three groups,~~ ^{the bulkier are} the higher the ground state energy and thus the lower the Eact. *Not well stated at all.*

10 pts 9. Show the mechanism for 3-methyl-1-butene cationic propagation.



the higher the ground state energy and thus the lower the Eact.

This is all I could think of in the moment.

10 pts 10. Show the mechanism for unimolecular β -proton transfer (i.e., transfer to the counterion) in isobutylene propagation with AlCl_4^- counterion.

