

April 1999 CUME

Organic Chemistry

Department of Chemistry

University of Missouri—Columbia

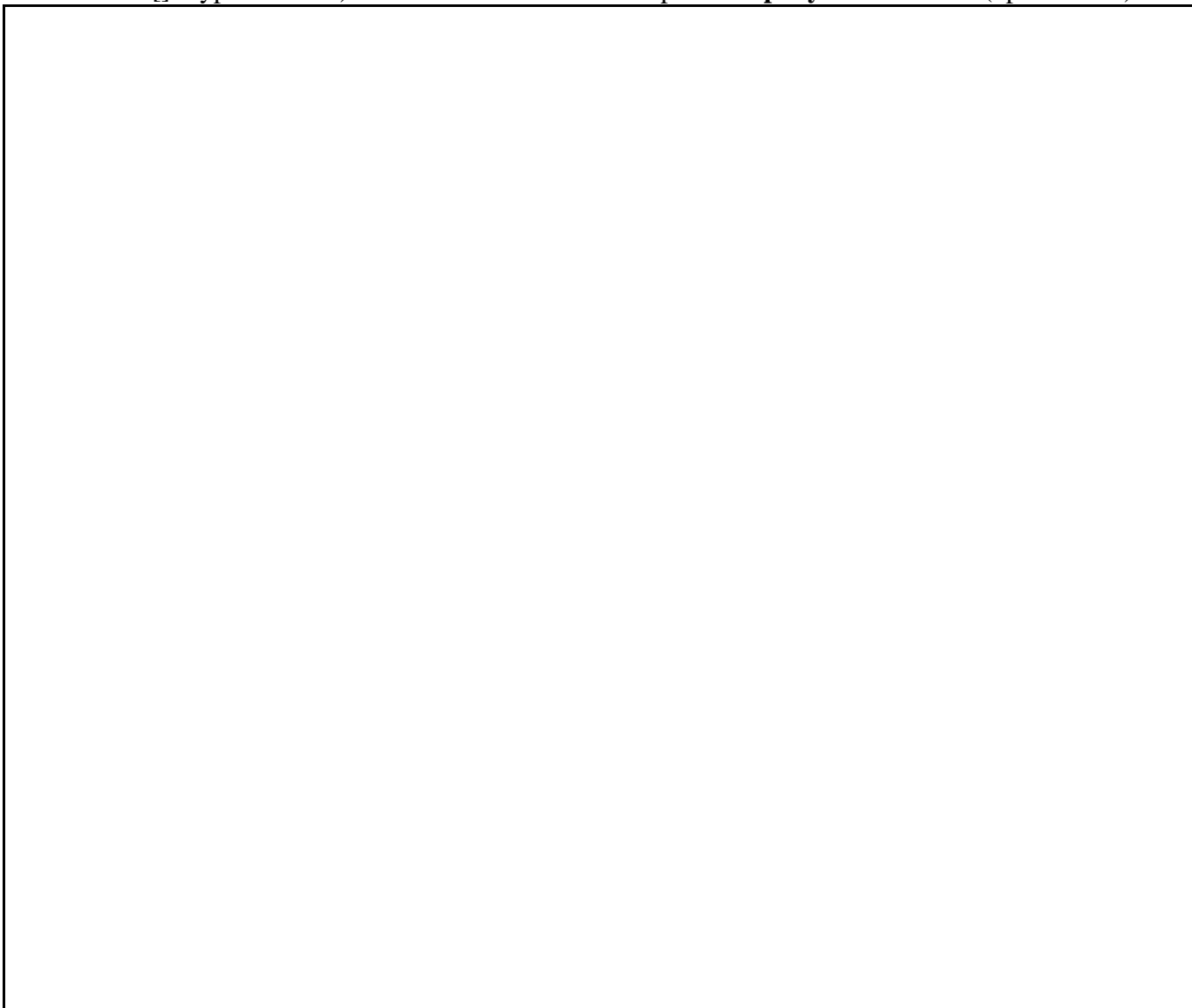
Saturday, April 3, 1999, @Nine O' Clock, 125I Chemistry

Dr. Rainer Glaser

Announced Reading: "Synthetic Polymers"

Question 1. Super Glue - Superstar of Modern Adhesion. (15 points)

(a) Super glue is cyanoacrylate and is sold under many names (SuperBonder, Permabond, Pronto, Black Max, Alpha Ace, Krazy Glue). The June 1993 issue of the Magazine of Fantasy and Science Fiction celebrated the advantages of super glue as follows: “Cyanoacrylate is an especially lovely and appealing glue, because it is (relatively) nontoxic, very fast-acting, extremely strong, needs no other mixer or catalyst, sticks with a gentle touch, and does not require any fancy industrial gizmos such as ovens, presses, vices, clamps, or autoclaves. Actually, cyanoacrylate does require a chemical trigger to cause it to set, but with amazing convenience, that trigger is the hydroxyl ions in common water. And under natural atmospheric conditions, a thin layer of water is naturally present on almost any surface one might want to glue.” Draw the structures of **monomer** and **polymer** (e.g. draw the repeating unit inbetween “[]”-type brackets) and outline the first few steps of the **polymerization** (up to trimer).



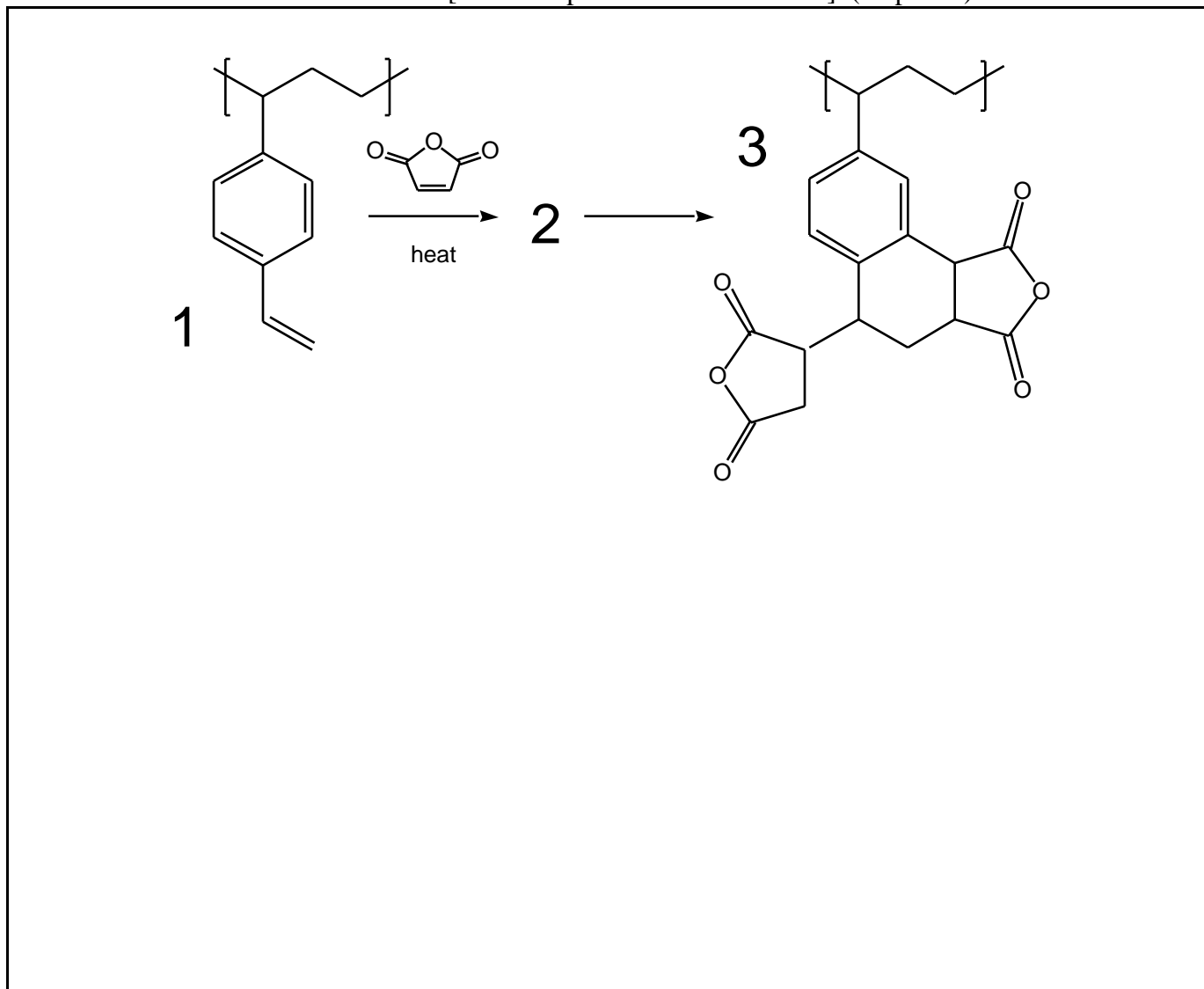
Question 2. Functional Polymers From Vinylpolystyrene. (30 points)

“Functional Polymers From Vinylpolystyrene. Diels-Alder Reactions with Olefins.” Stranix, B. R.; Darling, G. D. *J. Org. Chem.* **1998**, 62, 9001-9004. Conventional ways of making functional polymers often lead to features that are harmful to their use as solid-state reagents. The present authors describe a simple method for the preparations of divinyl-benzene rich resins highly functionalized with cyclic anhydrides, imide, or acyl or alkyl halide groups.

(a) Provide a mechanism for the radical chain polymerization of *para*-divinylbenzene (*para*-vinylstyrene). Suggest a radical chain initiator. Show the mechanism up to the “trimer radical.” Assume that the polymerization only involves “1,2-additions.” (10 points)

(b) Assume that the polymerization of *para*-divinylbenzene (*para*-vinylstyrene) does not involve 1,2-addition but that polymerization occurs by way of both methylene groups of *para*-divinylbenzene. Show the repeating unit of the resulting polymer inbetween “[]”-type brackets. (5 points)

(c) The reaction of polymer **1** with maleic anhydride gives an intermediate **2** which reacts on to the product **3**. Polymer **3** can, for example, be reacted with NaOH to the polycarboxylic acid functionalized resin. Draw the structure of **2** and explain the mechanisms for the reactions of **1** to **2** and of **2** to **3**. Give the names of the two reactions. [Hint: Keep track of the H-atoms.] (10 points)



(d) Show the structure of the product formed in the reaction of polymer **1** with perchlorocyclopentadiene. Pay attention to connectivity and stereochemistry. (As always, only show one repeating unit.) (5 points)



Question 3. Addition Polymerization. (20 points)

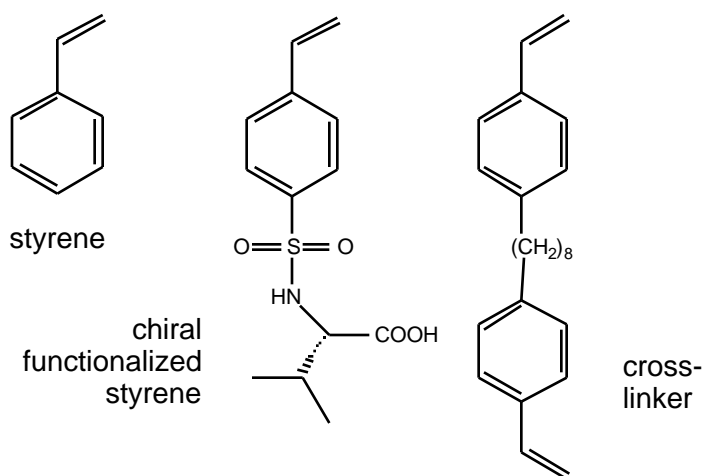
“LFER (Linear Free Energy Relation) Correlation of ^{13}C Chemical Shift in Para-Substituted Phenyl Isocyanide: Implications for formation of a Unique Polymer.” Kim, M.; Euler, W. B.; Rosen, W. J. *Org. Chem.* **1997**; 62, 3766-3769. Rosen *et al.* prepared a series of *para*-substituted isocyanobenzenes, X-Ph-NC with X = H, NO₂, CO₂CH₃, OCH₃, CH₃, NH₂, and OH. The ^{13}C chemical shifts of the isonitrile C-atoms correlated fairly well with the Hammett substituent constants of the substituents X. There was, however, one exception. The ^{13}C chemical shifts of the *para*-hydroxy compound deviated from the correlation and this chemical shift showed a high concentration dependency.

(a) Explain the origin of the concentration dependency of the ^{13}C chemical shift of the isocyano C-atom in *para*-hydroxyisocyanobenzene. (10 points)

(b) Considering your answer to (a), provide the structure of the addition polymer formed by *para*-hydroxyisocyanobenzene and suggest a mechanism for its formation. (10 points)

Question 4. Highly Enantioselective Polymeric Catalysts. (10 points)

“Asymmetric Diels-Alder Reactions of Methacrolein with Cyclopentadiene Using Polymer-supported Catalysts: Design of Highly Enantioselective Polymeric Catalysts.” Kamhori, K.; Ito, K.; Itsuno, S. *J. Org. Chem.* **1996**, *61*, 8321-8324. The authors describe the synthesis of a chiral polymeric catalyst and the stereochemical outcome (% yield, % ee) of one specific Diels-Alder reaction is monitored to evaluate the quality of the catalysts. Let’s just take a look at how the polymeric catalyst is put together. The polymer is a co-polymer of styrene, a chiral styrene derivative (formed from 4-vinylbenzenesulfonyl chloride and L-valine), and a cross-linking agent such as the one shown. The polymer is formed by benzoyl peroxide initiated radical chain reaction. Explain the function of the cross-linking agent?



Question 5. Polymer Supported BINAP Hydrogenation Catalysts. (25 points)

“Preparation and Use of a Polymer Supported BINAP Hydrogenation Catalysts.” Bayston, D. J.; Fraser, J. L.; Ashton, M. R.; Baxter, A. D.; Polywka, M. E. C., Moses, E. *J. Org. Chem.* **1998**, *63*, 3137-3140. Fill in the missing structures and reagents in the route map for the ligand synthesis. PS-NH₂ stands for amino-functionalized polystyrene.

