

of ligand basicity. Since PA values are known<sup>15</sup> for a variety of anions ( $A^-$ ) (e.g.,  $F^-$ ,  $CN^-$ ,  $CH_3CO_2^-$ ,  $C\equiv CH^-$ , and  $CH_3^-$ ), eq 3 allows one to estimate basicities of a range of  $CpOs(PPh_3)_2(A)$  complexes. Perhaps in other complexes, one might also find that the basicity of the metal increases as the PA values of its  $A^-$  ligands increase.

**Acknowledgment.** We thank the National Science Foundation (Grant No. CHE-9103948) for support of this work. The loan of  $OsO_4$  from Johnson Matthey, Inc., is greatly appreciated.

### Periodic Polymerization of Acrylonitrile in the Cerium-Catalyzed Belousov-Zhabotinskii Reaction

John A. Pojman,\* Danna C. Leard, and William West

Department of Chemistry and Biochemistry  
University of Southern Mississippi  
Hattiesburg, Mississippi 39406-5043  
Received June 12, 1992

We have studied the effects of acrylonitrile on the cerium-catalyzed Belousov-Zhabotinskii (BZ) reaction and have found that they depend on when the monomer is added to the batch reaction. Moreover, we have found that the polymerization of acrylonitrile occurs periodically. We believe this to be the first report of an isothermal, periodic polymerization.

The study of polymerization reactions as dynamical systems is relatively rare although the potential utility is great. Ray and co-workers have investigated oscillatory thermal phenomena in a continuous-flow stirred-tank reactor (CSTR) for vinyl polymerizations.<sup>1-3</sup> Propagating fronts of addition polymerization have been studied in the former Soviet Union<sup>4-8</sup> and in the U.S.<sup>9-11</sup>

Váradí and Beck observed that acrylonitrile could inhibit oscillations in the ferroin-catalyzed BZ reaction and a white precipitate would form.<sup>12</sup> Because ferroin can complex with the polymer, we have chosen the cerium-catalyzed system instead.

Acrylonitrile (Aldrich) was obtained with MEHQ inhibitor. The presence of the inhibitor was found to not alter the results. All other chemicals were of reagent grade (Aldrich) and used without further purification. Reactions were performed in a beaker open to the air at ambient conditions (23 °C) with magnetic stirring. The BZ reaction was prepared<sup>13</sup> from 10 mL of each of the following stock solutions: 0.23 M sodium bromate ( $NaBrO_3$ ), 0.31 M malonic acid ( $CH_2(COOH)_2$ ), and 0.019 M ammonium cerium(IV) nitrate ( $Ce(NH_4)_2(NO_3)_6$ ) in 2.7 M  $H_2SO_4$ .

The malonic acid and bromate solutions were mixed. The cerium solution was then added, and the data acquisition was begun. The signals from the bromide-selective electrode (Orion) and the platinum electrode (Rainin) (both referenced to a  $Hg/HgSO_4$  electrode (Rainin)) were digitized on a Strawberry Tree 12 bit A/D board and collected on a Macintosh IICx computer.

(1) Uppal, A.; Ray, W. H.; Poore, A. B. *Chem. Eng. Sci.* **1974**, *29*, 967-985.

(2) Teymour, F.; Ray, W. H. *Chem. Eng. Sci.* **1989**, *44*, 1967-1982.

(3) Schmidt, A. D.; Clinch, A. B.; Ray, W. H. *Chem. Eng. Sci.* **1984**, *39*, 419-432.

(4) Davtyan, S. P.; Zhirkov, P. V.; Vol'fson, S. A. *Russ. Chem. Rev.* **1984**, *53*, 150-163.

(5) Chechilo, N. M.; Enkolopyan, N. S. *Dokl. Phys. Chem.* **1974**, *214*, 174-176.

(6) Chechilo, N. M.; Enkolopyan, N. S. *Dokl. Phys. Chem.* **1975**, *221*, 392-394.

(7) Surkov, N. F.; Davtyan, S. P.; Rozenberg, B. A.; Enkolopyan, N. S. *Dokl. Phys. Chem.* **1976**, *228*, 435-438.

(8) Begishev, B. P.; Volpert, V. A.; Davtyan, S. P.; Malkin, A. Y. *Dokl. Phys. Chem.* **1985**, *279*, 1075-1077.

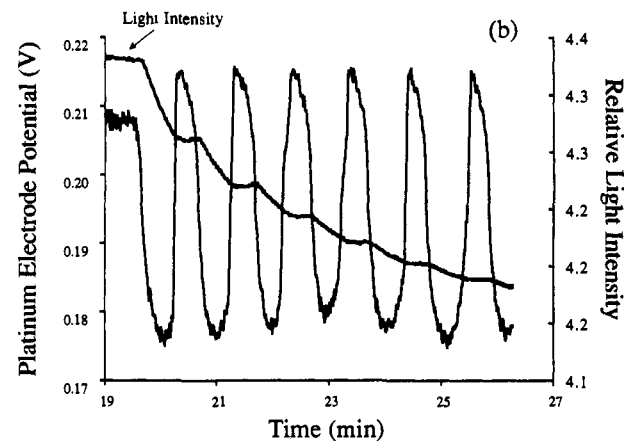
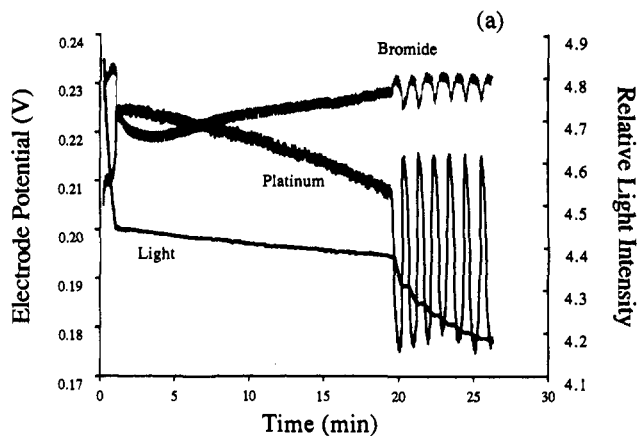
(9) Pojman, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 6284-6286.

(10) Pojman, J. A.; Khan, A. M.; West, W. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1992**, *33*, 1188-1189.

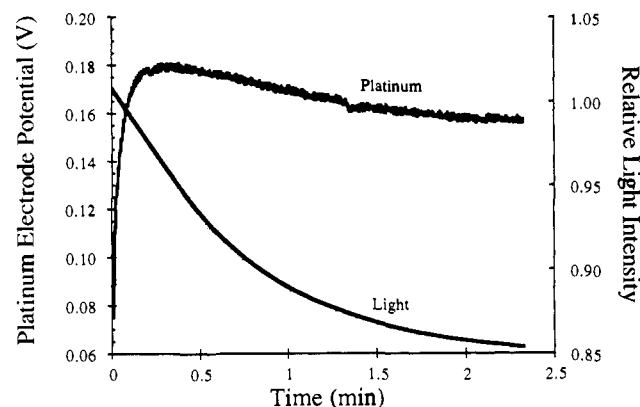
(11) Pojman, J. A.; Craven, R.; Khan, A.; West, W. *J. Phys. Chem.*, in press.

(12) Váradí, Z.; Beck, M. T. *J. Chem. Soc., Chem. Commun.* **1973**, 30-31.

(13) Shakhshiri, B. Z. *Chemical Demonstrations: A Handbook for Teachers*; University of Wisconsin Press: Madison, WI, 1985.



**Figure 1.** (a) Evolution of a BZ reaction in which 1.0 mL of acrylonitrile was present before addition of  $Ce(IV)/H_2SO_4$  solution: total volume = 30.0 mL;  $[NaBrO_3]_0 = 0.077$  M;  $[malonic\ acid]_0 = 0.10$  M;  $[Ce(IV)] = 0.0063$  M;  $[H_2SO_4]_0 = 0.90$  M. (b) Enlargement of the oscillatory region.



**Figure 2.** Acrylonitrile polymerization initiated by  $Ce(IV)$  and malonic acid. The acrylonitrile (1.0 mL) and malonic acid were stirred before the  $Ce(IV)/H_2SO_4$  solution was added. Reagents:  $[malonic\ acid]_0 = 0.10$  M;  $[Ce(IV)] = 0.0063$  M;  $[H_2SO_4]_0 = 0.90$  M.

Because polyacrylonitrile is insoluble in water, the qualitative progress of the polymerization was monitored by measuring the relative decrease in transmitted light due to scattering of an incandescent light beam passed through the solution. A simple CdS detector was used without calibration by converting the current to a voltage and using that voltage as a measure of the relative intensity.

Figure 1 shows that the oscillations do not commence for 20 min, although the normal induction period for the reaction with these concentrations is 2.8 min. The system remains in the oxidized, low-bromide state. If the acrylonitrile is added before the cerium, polymer forms when the cerium solution is added, but

no more visibly appears until oscillations commence. As the system begins to oscillate, white polymer precipitate is observed. However, small amounts of polymer do form, as can be seen from Figure 1a in which the transmittance slowly decreases during the inhibition period.

The polymerization does not occur continuously but rather in a stepwise manner, in phase with the oscillations in the cerium(IV) concentration. Figure 1b shows that the polymer appears as the cerium(IV) is reduced, but while the cerium is being oxidized, the amount of polymer remains constant. This observation is consistent with experiments which indicate that radical intermediates' concentrations oscillate. Försterling et al. measured oscillations in  $[\text{BrO}_2^*]$  on the micromolar level.<sup>14</sup> Venkataraman and Sørensen<sup>15</sup> measured oscillations in the malonyl radical concentrations on the nanomolar level.

To eliminate the possibility that the precipitation process is itself periodic, acrylonitrile polymerization was initiated by cerium(IV)/ $\text{H}_2\text{SO}_4$  and malonic acid. Figure 2 shows that the polymer appears monotonically as the cerium is reduced. This experiment also indicates that malonyl radicals formed by the oxidation of malonic acid<sup>15-19</sup> can initiate polymerization. The same experiment was performed using bromomalonic acid synthesized according to the procedure of Försterling et al.<sup>20</sup> Polymer formed, but much more slowly than with malonic acid.

We determined that the initiation is not from  $\text{BrO}_2^*$  radicals formed during the oxidation of cerium. Using cerium(III)/ $\text{H}_2\text{SO}_4$  and bromate solution of the same concentrations as with the Ce(IV) experiments, acrylonitrile did not polymerize. Also, cerium(IV) does not react at a significant rate with acrylonitrile.

The inhibition period is proportional to the amount of acrylonitrile initially present in the system up to 1.0 mL, and then it reaches a plateau. The addition of bromide or bromomalonic acid shortens the inhibition period. If acrylonitrile is added after 21 min, no inhibition period occurs. This suggests that acrylonitrile is scavenging bromomalonyl radical, interfering with the production of bromide, and preventing the system from switching to the reduced state. After 21 min, enough bromomalonic acid has accumulated that scavenging by acrylonitrile does not prevent bromide release.

The central problem is why little polymer is observed after the initial burst even though Ce(IV) is present with malonic acid. We believe that polymerization is started initially by malonyl radicals formed as the Ce(IV) is reduced. The Ce(III) is reoxidized in an autocatalytic process involving  $\text{HBrO}_2$  and  $\text{BrO}_2^*$ .<sup>21</sup> The  $\text{BrO}_2^*$  radical can terminate growing polymer chains via disproportionation, thus stopping the polymer from growing to a sufficient length to precipitate while regenerating  $\text{HBrO}_2$ . The rate of disproportionation is much greater than the rate of polymer chain termination because the concentration of  $\text{BrO}_2^*$  ( $\sim 10^{-6}$  M) is a thousand times greater than the polymer chain concentration ( $\sim 10^{-9}$  M, assuming all of the malonyl radicals initiate polymerization). Support for this scenario was provided by adding acrylonitrile 1.6 min after the cerium was added, when  $\text{BrO}_2^*$  would be present. No polymer was observed.

The appearance of polymer while oscillations continue in the standard BZ reaction is not a general property of vinyl monomers. The addition of other monomers such as methyl methacrylate and styrene stops oscillations completely unless the  $[\text{H}_2\text{SO}_4]_0 \geq 3$  M, but butyl acrylate behaves similarly to acrylonitrile.

**Acknowledgment.** Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We acknowledge support from the National Science Foundation's Mississippi EPSCoR Program. We also thank David Creed and Kenneth Showalter for helpful discussions.

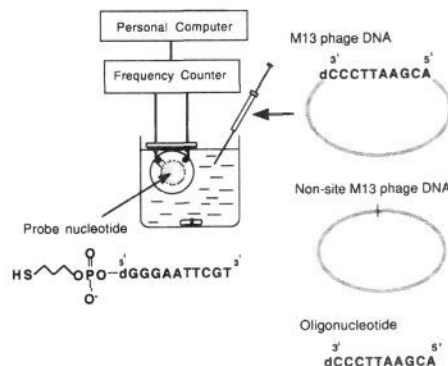
## Hybridization of Nucleic Acids Immobilized on a Quartz Crystal Microbalance

Yoshio Okahata,<sup>\*,1a</sup> Yuka Matsunobu,<sup>1a</sup> Kuniharu Ijiri,<sup>1a</sup> Masayuki Mukae,<sup>1b</sup> Akira Murakami,<sup>1b</sup> and Keisuke Makino<sup>1b</sup>

Department of Biomolecular Engineering  
Tokyo Institute of Technology  
Ookayama, Meguro-ku, Tokyo 152, Japan  
Faculty of Textile Science, Kyoto Institute of  
Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan  
Received July 6, 1992

Current methods of gene analysis are dependent upon the ability to detect specific DNA sequences in a heterogeneous mixture. The immobilization of DNA on a solid support has been used to separate complementary DNAs from solution by procedures such as the affinity capture method<sup>2,3</sup> and the sandwich hybridization method<sup>4</sup> using radioisotope-labeled or hapten-labeled DNA. These conventional methodologies have some difficulties: (i) pre- and posttreatments are required to modify DNAs with probes or proteins and to analyze hybridizations, respectively; (ii) it takes a relatively long time to analyze the results; and (iii) it is difficult to detect quantitatively the absolute amount and the time course of hybridization.

In this communication, we propose a new methodology to detect in situ, quantitatively, the one-to-one hybridization between the oligonucleotides immobilized on Au electrodes of a quartz crystal microbalance (QCM) and target M13 phage DNAs in aqueous solutions from the frequency changes of the QCM. QCMs are known to provide very sensitive mass measuring devices because their resonance frequency decreases upon the increase of a given mass on the QCM on a nanogram level.<sup>5,6</sup>



The QCM employed is a crystal of commercially available 9-MHz, AT-cut quartz on which Au electrodes were deposited on both sides (area: 16 mm<sup>2</sup> × 2). The QCM was connected to

(14) Försterling, H. D.; Murányi, S.; Noszticzius, Z. *J. Phys. Chem.* **1990**, *94*, 2915-2921.

(15) Venkataraman, B.; Sørensen, P. G. *J. Phys. Chem.* **1991**, *95*, 5707-5712.

(16) Försterling, H.-D.; Noszticzius, Z. *J. Phys. Chem.* **1989**, *93*, 2740-2748.

(17) Brusa, M. A.; Perissinotti, L. J.; Colussi, A. J. *J. Phys. Chem.* **1985**, *89*, 1572-1574.

(18) Försterling, H.-D.; Stuk, L. *J. Phys. Chem.* **1992**, *96*, 3067-3072.

(19) Ganipthisubramanian, N.; Noyes, R. M. *J. Phys. Chem.* **1982**, *86*, 5158-5162.

(20) Försterling, H. D.; Idstein, H.; Pachl, R.; Schreiber, H. *Z. Naturforsch.* **1984**, *39a*, 993-997.

(21) Field, R. J.; Körös, E.; Noyes, R. *J. Am. Chem. Soc.* **1972**, *94*, 8649-8664.

(1) (a) Tokyo Institute of Technology. (b) Kyoto Institute of Technology.

(2) Meinkoth, J.; Wahl, G. *Anal. Biochem.* **1984**, *138*, 267.

(3) Syvänen, A.-C.; Laaksonen, M.; Söderlund, H. *Nucleic Acids Res.* **1986**, *14*, 5037.

(4) (a) Dunn, A. R.; Hassel, J. A. *Cell* **1977**, *12*, 23. (b) Keller, G. H.; Cumming, C. U.; Huang, D.-P.; Manak, M. M.; Ting, R. *Anal. Biochem.* **1988**, *170*, 441. (c) Ebersole, R. C.; Miller, J. A.; Moran, J. R.; Ward, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 3239.

(5) Sauerbrey, G. *Z. Phys.* **1959**, *155*, 206.

(6) (a) Okahata, Y.; Ebato, H. *Anal. Chem.* **1989**, *61*, 2185; **1991**, *63*, 203. (b) Okahata, Y.; Ebato, H. *J. Chem. Soc., Perkin Trans. 2* **1991**, 457. (c) Okahata, Y.; Kimura, K.; Ariga, K. *J. Am. Chem. Soc.* **1989**, *111*, 9190. (d) Okahata, Y.; Ebara, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 116.