Polymerization Coupled To Oscillating Reactions: (1) A Mechanistic Investigation of Acrylonitrile Polymerization in the Belousov–Zhabotinsky Reaction in a Batch Reactor

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Polymerization Coupled To Oscillating Reactions: (1) A Mechanistic Investigation of Acrylonitrile Polymerization in the Belousov−Zhabotinsky Reaction in a Batch Reactor

Randy P. Washington, William W. West, Gauri P. Misra, and John A. Pojman*

Contribution from the Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, Mississippi 39406-5043

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Abstract: When acrylonitrile is added to the Belousov−Zhabotinsky reaction, periodic polymerization is observed. (Pojman, J. A.; Leard, D. C.; West, W. W. *J. Am. Chem. Soc.* **1992**, *114*, 8298). The polymer's structure and the amount of bromine in the polymer sample were determined by ^{13}C NMR and elemental analysis, respectively. Carbon-13-labeled malonic acid indicates that polymerization of acrylonitrile is initiated by malonyl radical. The bromous radicals are believed to terminate the polymer leaving an alcohol group on the polymer end. Further analysis of the polymer sample confirms that the sample is partially brominated. Numerical simulations based on a modified FKN mechanism are found to be in good agreement with experimental findings. Simulations indicate that periodic termination of the polymer chain by bromine dioxide, not the periodic initiation by malonyl radical, is the dominant cause of the periodic polymerization. Similar results were found in the malonyl-controlled variant of the BZ reaction.

I. Introduction

The Belousov−Zhabotinsky (BZ) reaction, which consists of the cerium-catalyzed oxidation of malonic acid by bromate in an acidic medium, is one of the most studied oscillating reactions.[1,2] In the BZ reaction, there are several species that show periodic behavior, particularly the Ce(IV) and bromide concentrations. Radicals such as malonyl and bromine dioxide are formed in the BZ system as well.[2] Researchers have shown that the malonyl radical[3−5] and bromine dioxide radical[3,6] concentrations oscillate with time.

Váradi and Beck observed that the addition of acrylonitrile to the ferroin-catalyzed BZ oscillating reaction inhibited oscillations.[7] The appearance of a white precipitate, presumably polyacrylonitrile, was viewed as a test for the presence of free radicals. Later, Pojman et al. found that acrylonitrile polymerized periodically when added to the cerium-catalyzed BZ reaction.[8] Ferroin can complex with polyacrylonitrile and is therefore not a convenient catalyst.

Studies by Pojman et al. also show that the induction period increases when acrylonitrile is added initially with the malonic
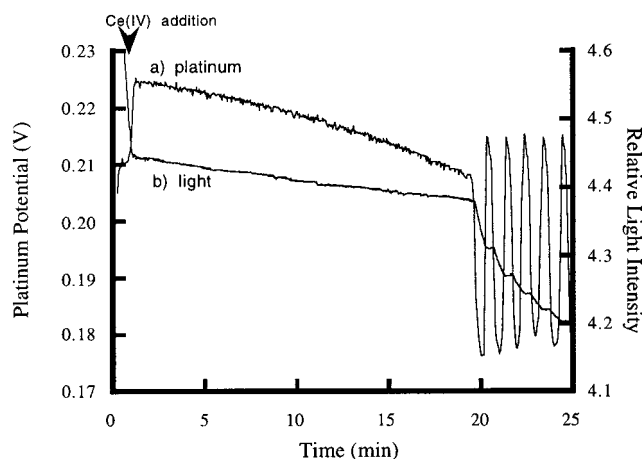
Figure 1. Experimental results of polymerization coupled with oscillations: $[MA]_o = 0.10$ M; $[NaBrO_3]_o = 0.07$ M; $[Ce(IV)]_o = 0.0063$ M in $[H_2SO_4]_o = 0.90$ M.[8]

acid solution as shown in Figure 1.[8] The addition of acrylonitrile to the BZ reaction after the onset of oscillations places the reaction in a high Ce(IV) quasi-steady state (inhibition period), and oscillations commence after a period of time that is a function of the acrylonitrile concentration. General observation shows that acrylonitrile affects the system in two ways: (1) it increases the induction period and (2) it inhibits oscillations. These two observations led us to believe that acrylonitrile is removing HOBr and bromine from the system. As observed later in the characterization of the polymer and proposed model, apparently this is what happens.

We present spectral characterization of the polymer sample to identify the initiating species and propose a mechanism for polymerization coupled to oscillations. Furthermore, simulations of the proposed mechanism are included to show the general behavior of periodic polymerization. The simulations indicate

* Phone: 601-266-5035. Fax: 601-266-6075. E-mail: john.pojman@usm.edu.
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Table 1.   Proposed Model for Periodic Polymerization with Modified FKN Mechanism

| | rate constant | | |
reaction	forward	reverse	reference
$Br^- + HOBr + H^+ \rightleftharpoons Br_2 + H_2O$ (MF1)	$8.0 \times 10^9 \, M^{-2} \, s^{-1}$	$80.0 \, s^{-1}$	Försterling et al.[6]
$Br- + HBrO_2 + H+ \rightleftharpoons 2 \, HOBr$ (MF2)	$2.5 \times 10^6 \, M^{-2} \, s^{-1}$	$2.0 \times 10^5 \, M^{-2} \, s^{-1}$	Försterling et al.[6]
$Br- + BrO3- + 2 \, H+ \rightleftharpoons HOBr + HBrO2$ (MF3)	$1.6 \, M^{-3} \, s^{-1}$	$3.2 \, M^{-1} \, s^{-1}$	Försterling et al.[6]
$2HBrO_2 \rightleftharpoons HOBr + BrO3- + H+$ (MF4)	$3.0 \times 10^3 \, M^{-2} \, s^{-1}$	$1.0 \times 10^{-8} \, M^{-2} \, s^{-1}$	Försterling et al.[6]
$HBrO2 + BrO3- + H^+ \rightleftharpoons Br2O4 + H2O$ (MF5)	$33.0 \, M^{-2} \, s^{-1}$	$2.2 \times 10^3 \, s^{-1}$	Försterling et al.[6]
$Br_2O_4 \rightleftharpoons 2 \, BrO_2\bullet$ (MF6)	$7.5 \times 10^4 \, s^{-1}$	$1.4 \times 10^9 \, M^{-2} \, s^{-1}$	Försterling et al.[6]
$Ce3+ + BrO2\bullet + H+ \rightleftharpoons Ce4+ + HBrO2$ (MF7)	$6.2 \times 10^4 \, M^{-2} \, s^{-1}$	$8.4 \times 10^3 \, M^{-2} \, s^{-1}$	Försterling et al.[6]
$Ce4+ + MA \rightleftharpoons Ce3+ + MA\bullet + H+$ (MF8)	$0.23 \, M^{-2} \, s^{-1}$	$2.2 \times 10^4 \, M^{-2} \, s^{-1}$	Försterling et al.[6]
$HOBr + MA \rightleftharpoons BrMA + H2O$ (MF9)	$1.0 \, M^{-2} \, s^{-1}$		Försterling et al.[6]
$2 \, MA^\bullet \rightarrow$ products (MF10)	$3.2 \times 10^9 \, M^{-2} \, s^{-1}$		Försterling et al.[6]
$MA \rightleftharpoons enol$ (MF11)	$3.0 \times 10^{-3} \, s^{-1}$	$200.0 \, s^{-1}$	Gyorgyi et al.[13]
$enol + Br_2 \rightarrow BrMA + Br^-$ (MF12)	$1.9 \times 10^6 \, M^{-2} \, s^{-1}$		Gyorgyi et al.[13]
$BrMA + Ce(IV) \rightarrow Ce(III) + Br^-$ (MF13)	$5.0 \, M^{-2} \, s^{-1}$		assigned by us
$AN + HOBr \rightarrow$ products (MF14)	$3.0 \, M^{-2} \, s^{-1}$		assigned by us
initiation			
$AN + MA^\bullet \rightarrow P^\bullet$ (MF15)	$0.2 \, M^{-2} \, s^{-1}$		assigned by us
propagation			
$P^\bullet + AN \rightarrow P^\bullet$ (MF16)	$1.45 \times 10^6 \, M^{-2} \, s^{-1}$		Brandrup et al.[14]
termination			
$P^\bullet + P^\bullet \rightarrow P$ (MF17)	$5.0 \times 10^6 \, M^{-2} \, s^{-1}$		assigned by us
$P^\bullet + Ce(IV) \rightarrow P$ (MF18)			assigned by us
$P^\bullet + BrO_2^\bullet \rightarrow P$ (MF19)			assigned by us

that it is not periodic initiation but periodic termination that causes periodic polymerization.

The simulation of polymerization coupled to oscillations was furthered tested by considering a variant of the Belousov–Zhabotinsky reaction, the Rácz system. The two most important features of the Rácz system are the high acidity and high malonic acid/bromate concentration ratio. The FKN mechanism depicts that oscillations in the classic BZ reaction are controlled by bromide ions.[9] However, the FKN model does not explain the occurrence of oscillations in the Rácz system. The effect that acrylonitrile has on the dynamics of the bromide-controlled BZ reaction (induction period and frequency) is apparently based on the necessity of bromide ions. One of the marked differences between the bromide-controlled and radical-controlled oscillating reactions is the presence of an induction period in the former. The latter, the Rácz system, is characterized by a high malonic acid/bromate concentration ratio and 3 M sulfuric acid and exhibits oscillations without an induction period. The oscillations in the Rácz system are believed to be controlled by the malonyl radical.[4,6,10,11] Thus, it is of interest to see whether a modified version of the Radicalator model[6] is sufficient in simulating periodic polymerization in the Rácz system. Furthermore, the malonyl radical acts as a control intermediate as well as an initiating species for polymerization.

II. Experimental Procedure

A. Materials. Sodium bromate (Aldrich), ammonium cerium (IV) nitrate (Aldrich), ammonium Ce(III) sulfate (Aldrich), malonic acid (Aldrich), and sulfuric acid (Fisher Scientific, certified grade) were used as received, while the inhibitor was removed from acrylonitrile (Aldrich) with a column provided by the supplier.

B. Methods. Experiments were performed in a 100 mL double-walled glass cell maintained at 25 ± 0.1 °C using a circulating water bath. A bright platinum electrode (Orion) in conjunction with a Hg/HgSO$_4$ reference electrode (Radiometer) and a thermocouple (Omega) were used to record redox potential and temperature, respectively. The

time course of the polymerization of acrylonitrile was recorded by illuminating the reaction mixture with a fiber optical illuminator (Fiber lite model 190) and following the transmitted light intensity through the cell using a CdS detector. The data were collected at a rate of 10 Hz using a data acquisition board (Strawberry Tree 12 bit A/D board) and stored on a Macintosh IIvx computer. The platinum electrode and CdS detector were connected to the computer through a digital pH meter (Corning) and a high impedance amplifier, respectively.

Equal volumes (20 mL) of 0.31 M malonic acid, 0.23 M bromate, and 0.019 M Ce(III) or Ce(IV) in 2.7 M H_2SO_4 were added to the reactor. The reaction was initiated by the addition of the cerium solution. For polymerization studies, the monomer was added to the malonic acid solution and allowed to premix, followed by bromate and Ce (IV) solutions. Under the Rácz conditions, 56 mL of 0.64 M malonic acid in 3.0 M H_2SO_4, 0.6 mL of 1 M bromate, and 3.4 mL of 0.019 M Ce(IV) in 3.0 M H_2SO_4 were used.

Polyacrylonitrile was collected by suction filtration and purified by reprecipitation from dimethyl formamide with the addition of absolute ethanol. The overall conversion was determined gravimetrically. Polymer samples for NMR analysis were prepared by first dissolving the polymer in DMSO-d_6. Other samples were dissolved in acetone-d_6. The samples were then filtered through a Nalgene 0.45 mm syringe filter (25 mm) to remove dust and other impurities. All NMR spectra were obtained on a Bruker AC-300 300 MHz Fourier transform spectrometer. Elemental analysis was done by Desert Analytics.

## III. Overview of Proposed Mechanism

To ascertain the mechanism describing periodic polymerization coupled to the oscillations, we first considered the initiation and termination steps. The influence of the monomer on the dynamics of the system, delayed oscillations, for instance, provides means by which we could test not only how the monomer polymerizes in the system, but also how it interacts with other species of the oscillating BZ reaction. From that, a model based on a modified version of the FKN mechanism[9] is proposed, explaining how the polymerization of acrylonitrile is initiated and terminated and how the addition of acrylonitrile changes the dynamics of the system. Any model must reproduce three observations, namely, periodic polymerization, lengthening of the induction period, and monomer conversion on the order of 50%.

A proposed model for polymerization coupled with oscillation is presented in Table 1. The general behavior of the BZ reaction

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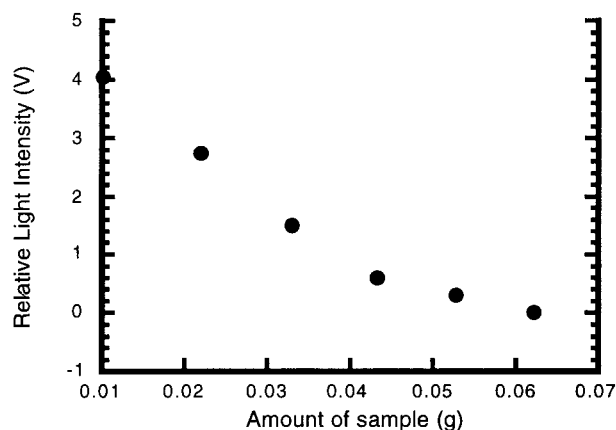
Figure 2. Detector response to the amount of polymer present. The difference corresponds to the decrease in light due to the amount of polymer present.

was simulated using MF1−MF13. The assigned rate constant for the MF13 takes into account all of the bromide-producing reactions, reproducing the induction period that is obtained experimentally. The inclusion of polymerization kinetics completes the proposed model. Details about the assignment of the rate constants associated with the polymerization process are given later. In the model, MA, MA$^{\bullet}$, AN, P$^{\bullet}$, and P refer to malonic acid, malonyl radical, acrylonitrile, polymer radical, and polymer, respectively; Br^{-}, HOBr, Br$_2$, HBrO$_2$, BrO$_3^{-}$, Br$_2$O$_4$, BrO$_2^{\bullet}$, Ce^{4+}, MA, enol, MA$^{\bullet}$, BrMA·, AN, and P$^{\bullet}$ have been considered as dynamic variables. The STIFF3 subroutine[12] was used to solve the equations obtained from the model.

Malonyl radicals are produced in a one-electron Ce(IV) oxidation of malonic acid, MF8. The radicals formed from the oxidation reaction can react with acrylonitrile to yield a polymer radical (MF15), indicated as P$^{\bullet}$. The polymer radicals can propagate consuming more acrylonitrile (MF16). The chain propagates until termination occurs.

A. Measuring Conversion. Figure 1 shows that the light transmittance decreases in a stepwise manner in the BZ reaction with acrylonitrile. To show that this decrease in light was a function of polymer conversion, we investigated the dependence of light transmittance signal on the amount of polymer present. Turbidity measurements were made on a homemade photometer consisting of a light source, a photodiode, and an amplifier. Linearity is observed over a certain range as shown in Figure 2. As is usually the case for instrumental methods of analysis, there is a deviation from linearity at high "analyte" concentration. This seems to be an ideal method for measuring low conversion; however, the proportionality constant changed depending on the settings. The sensitivity or how much the signal decreases depends on the gain and offset of the amplifier, the age of the photodiode, and the "size" of the precipitate. Thus, a quantitative correlation between light transmittance and conversion was not made. An important factor that can be deduced from the above is that the amount of polymer produced at each oscillation decreases as the reaction proceeds because the monomer is being consumed. We consider this factor in the verification of the proposed model.

The experimental conversion at 30 min was determined gravimetrically to be 55%. The discrepancies between the observed and simulated percentage conversion are 2-fold. First, the base model with no acrylonitrile added is assumed to predict the concentration of malonyl radical and bromine dioxide radical

concentration with great precision and accuracy. Second, the rate constants for the polymerization steps are assumed to be independent of chain length and viscosity. The overall conversion is dependent on the initiator's and terminating species' concentrations as well as the rate constants for initiation, propagation, and termination.[15] Thus, only qualitative behavior of conversion time behavior is possible and, in our case, sufficient. The thrust is to only show the general behavior of the conversion with time.

B. Identification of Initiating Species. The temporal behavior of the redox potential and light intensity reveals that the polymer does not precipitate appreciably out of the solution until the onset of oscillations as shown in Figure 1. In trying to identify the initiating species, we initially considered three radicals produced in the BZ reaction, namely, malonyl radical (MA$^{\bullet}$), bromomalonyl radical (BrMA$^{\bullet}$), and bromine dioxide radical (BrO2$^{\bullet}$). Although cerium(IV) ions can initiate polymerization, the rate is too slow with respect to the rate of polymerization observed in the oscillating BZ reaction, and therefore, this initiation is negligible. It was demonstrated that bromine dioxide radicals formed from the cerium (III) and acidic bromate reaction effect no significant polymerization by mixing equal volumes (10 mL) of cerium (III) in sulfuric acid, bromate, and distilled water with 1 mL of acrylonitrile. Therefore, it was concluded that neither bromine dioxide radical nor cerium (IV) was the primary initiating species.

Pojman et al. proposed that the malonyl radical was the primary initiating species, and bromine dioxide radical was able to terminate the polymer chain.[8] In characterizing the sample, it was presumed that malonyl radical would be easily identified if it were the initiating species. However, in some cases, the end groups cannot be detected directly by ^{13}C NMR because their concentrations are so low compared to the rest of the polymer chain. An enhancing technique such as carbon-13 labeling is employed in such situations.

It is well-documented that the Ce(IV)-organic acid redox system can initiate polymerization. Sarac et al. have used the Ce(IV)-malonic acid system to initiate polymerization of acrylamide.[16] Subramanian and Santappa studied the redox polymerization of methyl acrylate and methyl methacrylate by Ce(IV)-malonic acid.[17,18] These researchers have attributed the oxidation of malonic by Ce(IV) as the primary initiating species. We have confirmed the presence of malonyl radical by ^{13}C NMR using labeled malonic acid. The spectrum of polyacrylonitrile showed characteristic shifts of the malonyl radical attachment on the polymer chain at 174 ppm due to the COOH group and 43.5 and 43.2 ppm for methylene group.

C. Identification of Terminating Species. There are three ways through which termination can occur: (1) polymer radical combination, (2) Ce(IV), and (3) BrO$_2$$^{\bullet}$. Although the initiating species was detected by NMR when labeled malonic acid was used, such labeling techniques are not readily available to distinguish among the various modes of termination. Polymer radical combination would result in two initiating groups on the polymer chain. The combination between a bromine dioxide radical and a polymer radical would leave a BrO$_2$ group on the

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end of the polymer. We propose that the bromous ester end group hydrolyzes in the acidic medium of the BZ reaction to leave an alcohol group on the end of the polymer, analogous to the reaction between $BrO_2^\bullet$ and malonyl radical to produce tartaric acid (MA-OH).[19] The bromine dioxide radical can also abstract a hydrogen from the polymer radical terminating the polymer and leaving a vinyl group as an end group. The vinyl group could then be brominated by either Br_2 or HOBr.
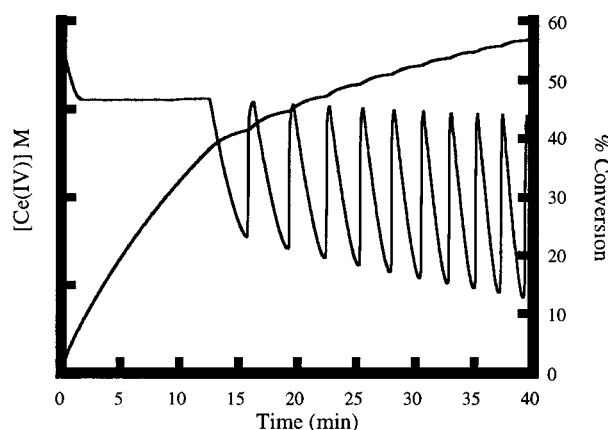
Termination of a polymer radical by cerium(IV) has been observed in polymerization using cerium(IV)/organic substrate redox systems.[20-23] The reaction generally begins when the polymer radical encounters and complexes with a cerium(IV) ion. An electron is transferred from the polymer to the cerium(IV) ion. The oxidized polymer radical, a secondary or tertiary carbocation, is released from the complex and reacts with water, resulting in an alcohol group on the end of the polymer.[20]

It is possible with the considerations above that Ce(IV) and $BrO_2^\bullet$ termination cannot be distinguished using end-group analysis. However, simulations may show which one is likely to be the terminating species. Because each of the possible routes for termination outlined in the model reveals different temporal behavior of the conversion, we show simulations depicting termination by combination and combination along with either $BrO_2^\bullet$ or Ce(IV) interaction with the growing macroradical.

IV. Simulation of the Proposed Model

A. The Cause of Periodic Polymerization. Periodic polymerization is undoubtedly the most intriguing characteristic of polymerization coupled with oscillations. We have confirmed the presence of the malonyl radical on the polymer backbone using ^{13}C NMR, indicating that malonyl radicals initiate the polymerization of acrylonitrile in the BZ reaction. Researchers have demonstrated that the malonyl radical concentration oscillates in the BZ reaction.[3-5] Thus, this phenomenon at first glance may be attributed to the oscillations in the initiating species. If termination solely by polymer radical combination explains experimental findings, then periodic initiation begets periodic polymerization. Oscillatory behavior has also been observed in the concentration of bromine dioxide radical.[3,6] As revealed later, the periodicity in the concentration of $BrO_2^\bullet$ causes periodic polymerization. Simulations are performed and presented below to demonstrate the above considerations.

B. Periodic Initiation (Bimolecular Termination). Bimolecular termination warrants a detailed look at polymerization of acrylonitrile in aqueous media in the assignment of rate constants. Acrylonitrile shows peculiar behavior particularly when it is heterogeneously polymerized. The polymeric radicals grow a critical length and then precipitate out of solution.[24] The propagation involves the interaction of small molecules (monomer) with large molecules (macroradicals), whereas segmental movement is limited for two macroradicals combining for termination to occur. Thus, the value of k_p should not be affected as much as k_t. The reported values for k_t have varied from 10^8 [14]

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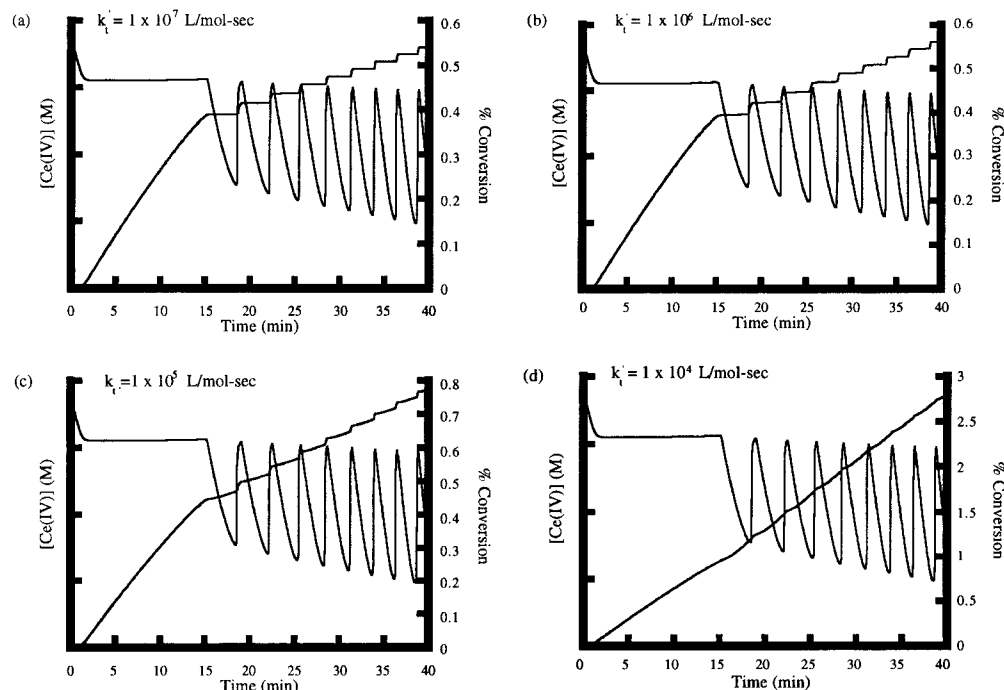(20) Meira, G. R. *J. Macromol. Sci., Rev. Macromol. Chem.* **1981**, C20, 207−241.
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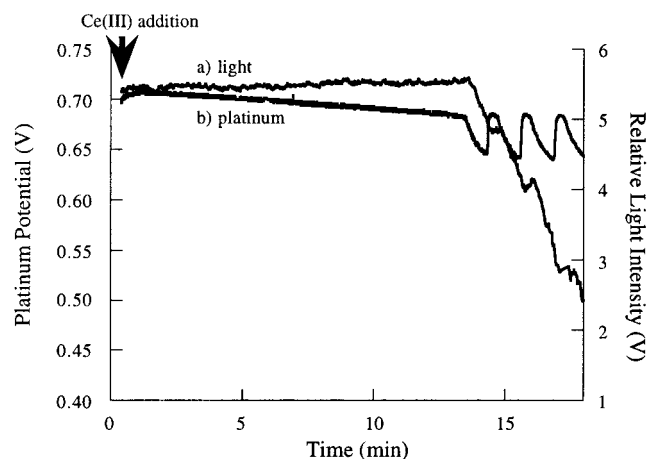(22) Fernandez, M. D.; Guzman, G. M. *J. Polym. Sci, Part A: Polym. Chem.* **1989**, 27, 3703−3720.
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Figure 3. Simulated time course of conversion with polymer radical combination. Conversion corresponds to monomer converted to polymer. The [Ce(IV)] is on a logarithmic scale.

to 10^4 L mol^{-1} s^{-1}.[25] The lower end originates from bulk polymerization of acrylonitrile. We have chosen a value between the two in the present model. The value of k_p was used as reported in the literature.[14] The simulations were performed with the assumption that the rate constants were independent of chain length. Figure 3 shows the calculated conversion with time considering only polymer radical combination, MF17.

The conversion increases during the induction period, contrary to what is found experimentally. The response of the photodiode detector to the amount of polymer indicates that little or no polymer is produced during the induction period. At the onset of oscillations, the conversion increases stepwise and in phase with oscillations. It is found that termination exclusively by combination is sufficient to explain periodic polymerization, yet unable to explain the low conversion observed during the induction period.

C. Termination by Ce(IV). According to the proposed model, Table 1, there are three possible termination steps, MF17−MF19. To identify the most facile step(s), we performed simulations in which termination by polymer radical combination, MF17, along with Ce(IV), MF18, or $BrO_2^\bullet$, MF19, is considered. When Ce(IV) termination is considered, the computational results show periodic polymerization as shown in Figure 4. However, the resultant conversion is much less than the empirical value, and increasing the magnitude of the rate constant does not cause any significant change in the conversion. From the simulation, it can be concluded that the termination step involving Ce(IV), MF18, cannot be a dominant way in which the polymer chain is terminated. It is of interest that termination by Ce(IV) has been observed with a calculated rate coefficient of 1.45×10^4 L mol^{-1} s^{-1}.[18] No matter what value is used in the simulations, the experimental results are not reproduced.

D. Termination by BrO2•. Previously, it was shown that when Ce(IV) was used as the catalyst, periodic polymerization was observed.[8] However, at the time of Ce(IV) addition, as shown in Figure 1, a large amount of polymer is produced and the light intensity decreases. After approximately 18 min, polymerization occurs with oscillations. The initial burst of precipitation is removed with the substitution of Ce(III) for Ce(IV). Figure 5 shows a time course of polymerization coupled with oscillations in which Ce(III) is used instead of Ce(IV). In the case of Ce(III), the initial burst of polymer formation is not observed, owing to the high bromine dioxide radical concentration. Bromine dioxide radicals are produced from the reaction

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Figure 4. Conversion and reaction dynamics under termination by Ce(IV) with varied rate constant for reaction MF18. Termination by combination, MF17, is included as well. The [Ce(IV)] is on a logarithmic scale.

Figure 5. Time course of periodic polymerization in which 1.0 mL of acrylonitrile is added before the Ce(III)/H_2SO_4 solution: $[MA]_o = 0.10$ M; $[NaBrO_3]_o = 0.07$ M; $[Ce(III)]_o = 0.0063$ in $[H_2SO_4]_o = 0.90$ M.
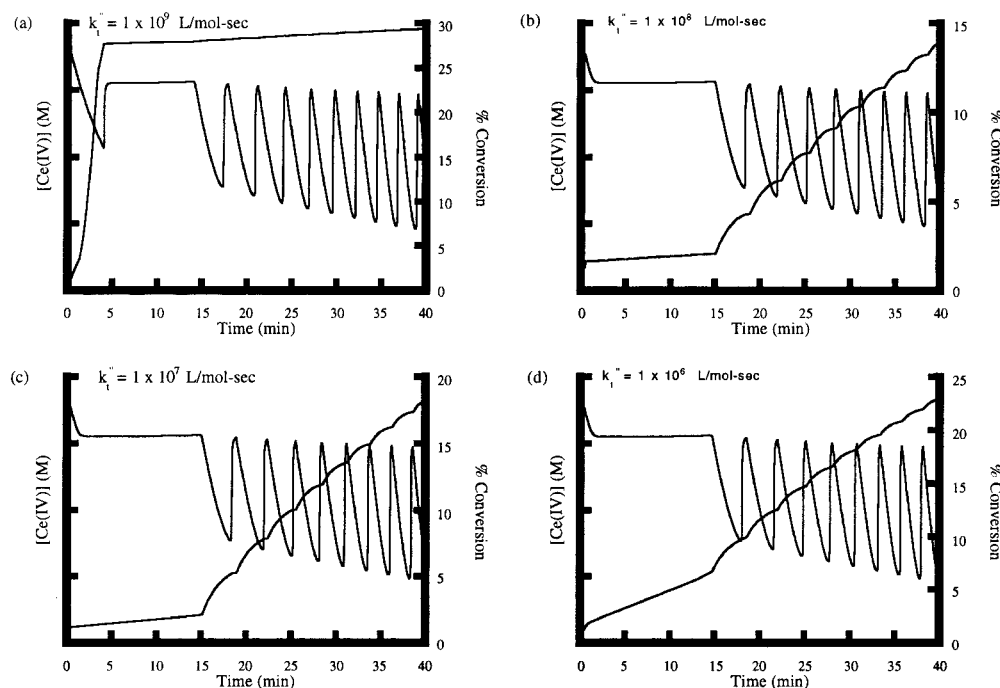
between Ce(III) and BrO_3^-, causing an initial increase in the radical concentration, stunting polymer growth. In the case of Ce(IV), bromine dioxide radical concentration must build up to a critical level before it can "cease" the formation of polymer. At this critical concentration of bromine dioxide radical, no precipitation is observed. Thus, experimental observations suggest that bromine dioxide radical is the terminating species.

With the above in mind, the termination step by $BrO_2^{\bullet}$, MF19, was studied numerically. No literature values for the rate constant for bromine dioxide radical reacting with a polymer radical were available; therefore, we offer the following in suggesting an appropriate value. Initially, the bromine dioxide radical interacting with polymer radical was compared to the reaction between malonyl radical and bromine dioxide radical with a corresponding rate constant of 10^9 L mol^{-1} s^{-1}. However, there is a striking distinction which leads to a different value. The reaction of malonyl radical and $BrO_2^{\bullet}$ occurs in a homogeneous phase, while that of the polymer radical occurs
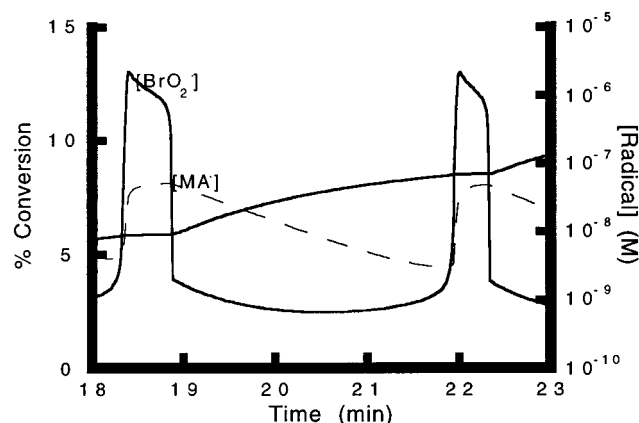
in an inhomogeneous phase. Figure 6 shows how the variation of the termination rate constant for $BrO_2^{\bullet}$ reaction with the polymer chain as well as termination by combination, MF17 and MF19, affects the computed time course of conversion. Figure 6a indicates that a rate constant of 10^9 L mol^{-1} s^{-1} is too high. With this magnitude, a monotonic increase in conversion is observed, not periodic polymerization as noted experimentally. As the rate constant is lowered, periodic polymerization becomes more pronounced. As stated above, the reaction between the bromine dioxide radical and the polymer radical is inhomogeneous. A lower value as used in the model is justified by considering that the $BrO2^{\bullet}$ must diffuse into the precipitated macroradical in order for termination to occur. Thus, the rate constant for heterogeneous termination of polymer growth will be lower than the corresponding solution phase rate constant in the reaction between malonyl and bromine dioxide radicals.

The modeling of the proposed mechanism with lower magnitudes for the termination rate constant for $BrO_2^{\bullet}$ is treated in Figure 6b–d. The simulations show that the conversion does not increase appreciably during the induction period. Periodic increase in the conversion occurs at the onset of oscillations. Figure 6b–d shows the variation of the termination rate constant for $BrO_2^{\bullet}$. As the value is lowered two orders of magnitude, computational results agree closer to experimental observation, namely periodic polymerization and little or no conversion during the induction period. The greater mobility of $BrO_2^{\bullet}$ would probably cause the termination rate constant to be higher than the combination of two growing macroradicals, 10^6 L mol^{-1} s^{-1}. The model with termination by combination and $BrO_2^{\bullet}$, MF17 and MF19, accounts for periodic polymerization and low conversion during the induction period.

E. The Role of $BrO_2^{\bullet}$. The significance of bromine dioxide radical is further realized by noting the dependence of conversion on its concentration. A typical time course of $MA^{\bullet}$, $BrO_2^{\bullet}$, and monomer conversion is shown in Figure 7 to illustrate the role of $BrO_2^{\bullet}$. Consider the order of magnitude in which the initiating species and the terminating species are changing. The

Figure 6. Computational results showing that the time course of conversion with k_t for combination is equal to 5×10^6 L mol^{-1} s^{-1}. The termination rate constants for BrO2$^\bullet$ used in the simulation are (a) 1×10^9, (b) 1×10^8, (c) 1×10^7, and (d) 1×10^6 L mol^{-1} s^{-1}. The [Ce(IV)] is on a logarithmic scale.


Figure 7. Computational results showing the time course of conversion of malonyl and bromine dioxide radical with time.

rate of polymerization is given by the ratio of the rate of initiation to the rate of termination.[15] The MA$^\bullet$ concentration changes only one order of magnitude through one oscillation, while BrO$_2$$^\bullet$ concentration changes three. As shown in Figure 7, there is no appreciable change in conversion until the BrO$_2$$^\bullet$ radical becomes sufficiently low, thus increasing the rate of polymerization. At the same time, there is a gradual decrease in MA$^\bullet$ concentration, which decreases the rate of polymerization. However, the conversion does not decrease until the BrO$_2$$^\bullet$ concentration rises. The periodicity of the maxima and minima of the bromine dioxide radical concentration governs the periodic formation of polyacrylonitrile in the BZ reaction. The oscillatory behavior of the malonyl radical serves only to initiate polymerization, not to cause periodicity in the polymer formation.

F. Induction Period. Another important finding or test for the model is to show that an increase in the induction period is observed with the addition of acrylonitrile. Furthermore, Pojman et al. showed that acrylonitrile inhibited oscillations for a time

period dependent on the concentration if added after oscillations have commenced.[8] Figure 8 shows the simulated results of the oscillating reaction without and with acrylonitrile, respectively. Indeed, the model predicts that an increase in induction period of the BZ reaction is observed in the presence of acrylonitrile. Acrylonitrile can be brominated by both HOBr and bromine. In the model, the reaction between HOBr and acrylonitrile was only considered. The reaction between bromine and acrylonitrile effected little or no change in the induction period. The bromination of acrylonitrile by HOBr explains how acrylonitrile increases the induction period and also inhibits oscillations once it is added after oscillations have started. Since acrylonitrile provides an additional sink for HOBr, the bromomalonic acid concentration decreases resulting in a decrease in the rate of bromide production.[2]

G. Polymer Analyses. Elemental analyses indicate that polyacrylonitrile is partially brominated. The bromination of polyacrylonitrile can proceed via the reaction with Br$_2$ and HOBr. In our setup, the reactor is illuminated to monitor the progress of the polymerization process. This light could be sufficient enough to cleave bromine to produce bromine radicals, which in turn can abstract hydrogens from the polymer chain. To show that bromine was not responsible for the bromination of polymer, we ran the reaction using the conditions in Figure 3 in the absence of light. The absence of light should lessen the importance of the bromine radical attack, suggesting that HOBr is the key brominating species. Elemental analysis shows that samples obtained from the reaction in the dark had a higher bromine content (3.03%) than samples obtained in the presence of white light (1.69%). The findings suggest that the bromine in the sample originates from the reaction of the polymer and HOBr. However, we cannot conclusively say that bromination occurs via HOBr because of the equilibrium that exists between HOBr and Br$_2$.[2] This reaction is not included in the model because it is a postsynthesis process.
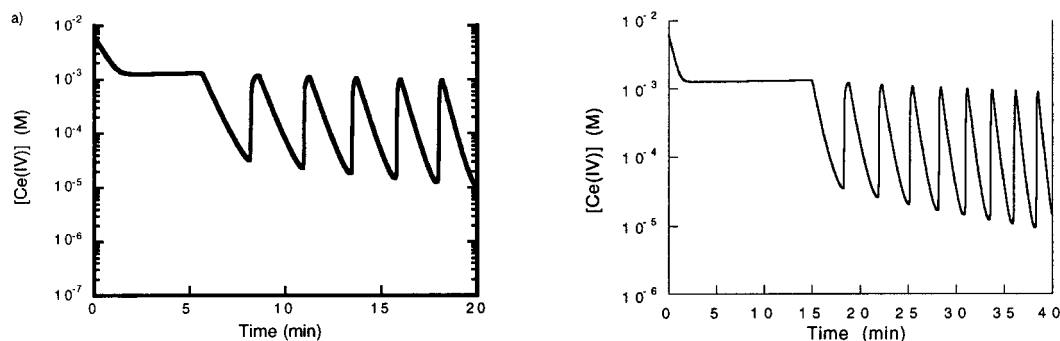
Figure 8. Computational results obtained with the modified FKN model (a) without the addition of acrylonitrile and (b) with acrylonitrile: $[MA]_o$ = 0.1 M, $[BrO_3^-]_o$ = 0.07 M; $[Ce(IV)]_o$ = 0.063 M, $[H^+]$ = 1.0 M, $[AN]_o$ = 2.0 M. $BrO_2^{\bullet}$ and polymer radical combination are used as the terminating species. The $[Ce(IV)]$ is on a logarithmic scale.

Table 2. Periodic Polymerization with Modified Radicalator

| | rate constant | | |
reaction	forward	reverse	reference
$Br^- + HOBr + H^+ \rightleftharpoons Br_2 + H_2O$ (MR1)	$8.0 \times 10^9\,M^{-2}\,s^{-1}$	$80.0\,s^{-1}$	Försterling et al.[6]
$Br^- + HBrO_2 + H^+ \rightleftharpoons 2\,HOBr$ (MR2)	$2.5 \times 10^6\,M^{-2}\,s^{-1}$	$2.0 \times 10^5\,M^{-2}\,s^{-1}$	Försterling et al.[6]
$Br^- + BrO_3^- + 2\,H^+ \rightleftharpoons HOBr + HBrO_2$ (MR3)	$1.6\,M^{-3}\,s^{-1}$	$3.2\,M^{-1}\,s^{-1}$	Försterling et al.[6]
$2HBrO^+ \rightleftharpoons HOBr + BrO_3^- + H^+$ (MR4)	$3.0 \times 10^3\,M^{-2}\,s^{-1}$	$1.0 \times 10^{-8}\,M^{-2}\,s^{-1}$	Försterling et al.[6]
$HBrO_2 + BrO_3^- + H^+ \rightleftharpoons Br_2O_4 + H_2O$ (MR5)	$33.0\,M^{-2}\,s^{-1}$	$2.2 \times 10^3\,s^{-1}$	Försterling et al.[6]
$Br_2O_4 \rightleftharpoons 2\,BrO_2^{\bullet}$ (MR6)	$7.5 \times 10^{4\,s^{-1}}$	$1.4 \times 10^9\,M^{-2}\,s^{-1}$	Försterling et al.[6]
$Ce^{3+} + BrO_2^{\bullet} + H^+ \rightleftharpoons Ce^{4+} + HBrO_2$ (MR7)	$6.2 \times 10^4\,M^{-2}\,s^{-1}$	$8.4 \times 10^3\,M^{-2}\,s^{-1}$	Försterling et al.[6]
$Ce^{4+} + MA \rightleftharpoons Ce^{3+} + MA^{\bullet} + H^+$ (MR8)	$0.23\,M^{-2}\,s^{-1}$	$2.2 \times 10^4\,M^{-2}\,s^{-1}$	Försterling et al.[6]
$HOBr + MA \rightarrow BrMA + H_2O$ (MR9)	$1.0\,M^{-2}\,s^{-1}$		Försterling et al.[6]
$2MA\bullet + H2O \rightarrow MA + TA$ (MR10)	$3.2 \times 10^9\,M^{-2}\,s^{-1}$		Försterling et al.[6]
$MA^{\bullet} + BrO_2^{\bullet} \rightarrow$ products (MR11)	$5.0 \times 10^9\,M^{-2}\,s^{-1}$		Försterling et al.[6]
$2BrO_3^- + 2\,H^+ \rightarrow HBrO_2 + HBrO_4$ (MR12)	$7.0 \times 10^{-7}\,M^{-2}\,s^{-1}$		Försterling et al.[6]
initiation			
$AN + MA^{\bullet} \rightarrow P^{\bullet}$ (MR13)	$0.2\,M^{-2}\,s^{-1}$		assigned by us
propagation			
$P^{\bullet} + AN \rightarrow P^{\bullet}$ (MR14)	$1.45 \times 10^4\,M^{-2}\,s^{-1}$		Brandrup.[14]
termination			
$P^{\bullet} + P^{\bullet} \rightarrow P$ (MR15)	$5.0 \times 10^6\,M^{-2}\,s^{-1}$		assigned by us
$P^{\bullet} + BrO_2^{\bullet} \rightarrow P$ (MR16)	$1.0 \times 10^7\,M^{-2}\,s^{-1}$		assigned by us

V. Periodic Polymerization in the Rácz System

We extended our studies with polymerization coupled to oscillations in the Rácz system. The Radicalator model, given by MR1−13 in Table 2, has successfully explained the chemical dynamics observed in the Rácz system.[6] Reactions involving polymerization, MR14−MR15, are included as well. We consider the initiation of polymerization by malonyl radical $MA^{\bullet}$ (reaction MR13), the growth reaction of polymer chain via reaction 14, and the termination of polymer chain by (1) bromine dioxide radical $BrO_2^{\bullet}$ (reaction MR15) and (2) combination of polymer radical (reaction MR16). We do not consider Ce(IV) as a possible route owing to its low concentration. The following were used as dynamical variables: Br^-, $HOBr$, Br_2, $HBrO_2$, BrO_3^-, Br_2O_4, $BrO_2^{\bullet}$, Ce^{4+}, MA, $MA^{\bullet}$, AN, and $P^{\bullet}$. The STIFF3 subroutine[12] was used to solve the differential equations obtained from this model. The rate constants used in the computation are listed in Table 2.

A. Numerical Simulations. Figure 9 shows an experimental trace of acrylonitrile in the Rácz system. The light transmittance and the redox potential indicate that polymerization occurs in phase with oscillations. It is important to note that the addition of acrylonitrile does not induce an induction period. One of the possible reasons for the absence of an induction period in the presence of acrylonitrile could be the negligible role played by HOBr and Br_2 in the malonyl radical-controlled BZ reaction. There was also a possibility that the acrylonitrile free radical $(CH=C^{\bullet}-CN)$ formed by a reaction between acrylonitrile and Ce^{4+} could quench $BrO_2^{\bullet}$. Such behavior was observed when
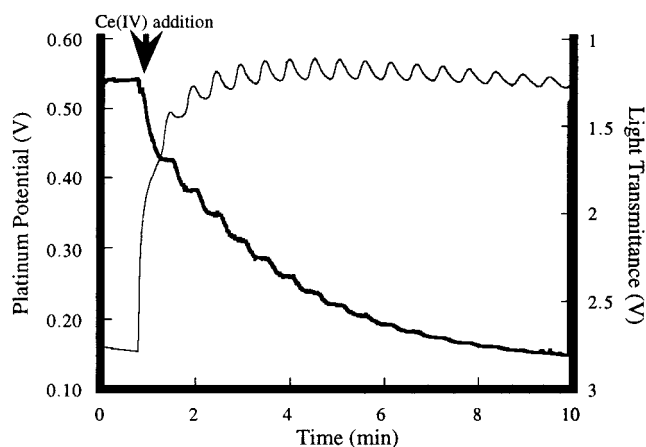

Figure 9. Experimental results for periodic polymerization in the Rácz system. $[MA]_o$ = 0.6 M in 3.0 M H_2SO_4; $[NaBrO_3]_o$ = 0.015; $[Ce(IV)]_o$ = 0.001 M; $[AN]_o$ = 0.25 M.

acetylacetone was added to the Rácz system.[26] Because the Ce(IV) oxidation of acrylonitrile is slower than acetylacetone, no induction period is observed.

The computational result of the model, MR1−MR16, is shown in Figure 10. There is striking similarity between the predicted and experimental conversion with time. Polymerization starts immediately, and conversion increases periodically with
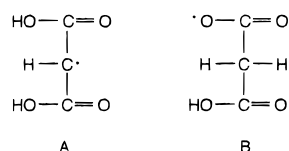
(26) Misra, G. P.; Washington, R. P.; Pojman, J. A. *J. Phys. Chem. A.* **1998**, *102*, 612−619.
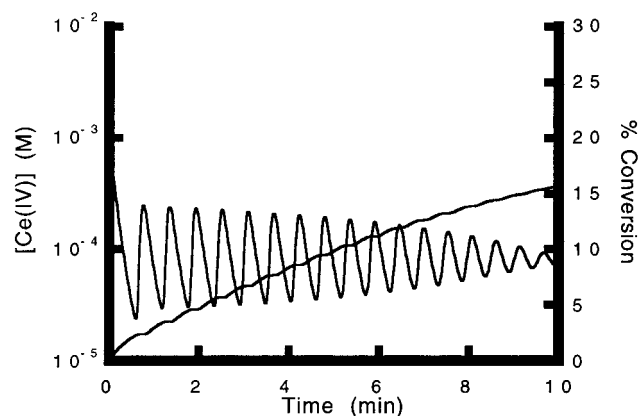
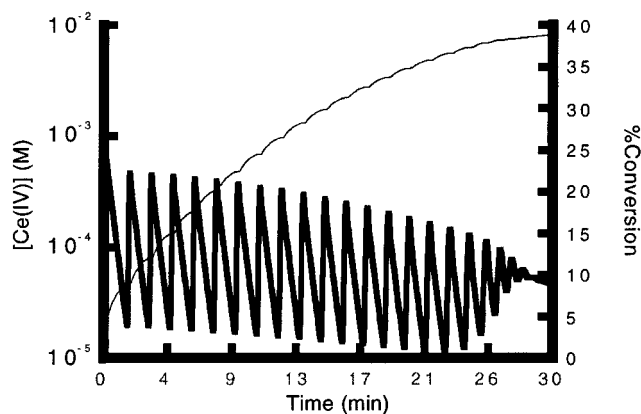**Figure 10.** Simulated results based on model presented in Table 2.

Scheme 1. Structure of Two Types of Malonyl Radicals

decreasing step size as the reaction progresses. It is interesting that simulated results come closer to experimental findings if other factors are included, namely, the existence of two types of malonyl radicals and the lowering of the rate constant associated with the combination of $BrO_2^\bullet$. In 3 M H_2SO_4, Brusa et al. found that two types of malonyl radicals (Scheme 1) exist upon the oxidation of malonic acid by Ce(IV).[27] The researchers found that 85% A and 15% B are formed in 3 M H_2SO_4. Thus, we include in the model the reaction A + B → products with a rate constant of 1×10^9 L mol^{-1} s^{-1} and the proportions indicated.

Zhabotinsky noted that the lifetime of bromine dioxide radical decreases with increasing acid concentration.[28] Thus, a lowering of the rate constant for MR-6 to 1×10^8 L mol^{-1} s^{-1} is justified. It could be equally justified to change the values of the rate coefficients for MR14−MR16, which are inversely proportional to viscosity.[15] The higher acid and malonic acid concentrations contribute to an increase in viscosity, thus decreasing the rate constants. We are not sure how much the rate constants are affected by viscosity, but it is worth noting that viscosity can play a role. Figure 11 shows the simulated results when the above considerations are taken into account. While the behavior is similar to that of the previously simulated case, now there is more profound evidence of periodic polymerization. The periodic nature of the monomer conversion is predicted, and no induction period is noticed.

The monomer conversion is found to be unaffected when reactions between (1) acrylonitrile and HOBr and (2) acrylonitrile and Br_2 are included in the model. These two reactions

(27) Brusa, M. A.; Perissinotti, L. J.; Colussi, A. J. *J. Phys. Chem.* **1985**, *89*, 1572−1574.
(28) Zhabotinsky, A. M. *Acta Chim. Acad. Sci. Hung.* **1982**, *110*, 283−294.

Figure 11. Simulated results for polymerization coupled to oscillations in the malonyl-controlled BZ reaction.

do not induce an induction period. Noszticzius et al. noted that the dynamics of the Rácz reaction was not affected by reactions MR1−MR3. In fact, similar behavior was found if these reactions were removed.[11] In the Rácz system, the bromide concentration is very low ($<10^{-8}$ M).[4,6,10,11] Thus, the concentration of Br_2 and HOBr would also be extremely low. This would explain why less than one percent bromine was found in the polymer samples obtained in this particular system.

VI. Conclusions

Polymerization coupled with oscillations is a unique phenomenon. An understanding of why and how acrylonitrile periodically polymerizes in the BZ reaction lies in the kinetics of the BZ reaction as well as the polymer process. A numerical and experimental investigation of the periodic precipitation of acrylonitrile led us to suggest what causes periodic polymerization. Analysis of samples obtained from the BZ reaction indicates that brominated polyacrylonitrile is a byproduct. However, the bromination of polyacrylonitrile is not inherent to the mechanism itself but is a postsynthesis process. Malonyl radical is shown to initiate polymerization using labeled malonic acid. Simulations of the proposed mechanism agree well with experimental findings, suggesting that the model is suitable for explaining the mechanism associated with periodic polymerization. Furthermore, simulations suggest that bromine dioxide radical is the cause of periodic polymerization. A variant of the BZ reaction was also satisfactorily simulated, taking into account two types of malonyl radicals that are present at high acid concentration and a lower rate constant for bromine dioxide combination. The possibility of the quenching of $BrO_2^\bullet$ by the acrylonitrile free radical in the Rácz system is less likely because the cerium-initiated polymerization of acrylonitrile occurs at a very slow rate, thereby indicating low formation of the acrylonitrile free radical.