

Adiabatic Polymerization of Acrylamide Using a Persulfate–Bisulfite Redox Couple

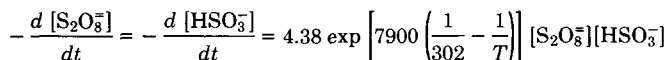
KARIN POHL and FERDINAND RODRIGUEZ, *School of Chemical Engineering, Olin Hall, Cornell University, Ithaca, New York, 14853*

Synopsis

The temperature rise during the adiabatic polymerization of acrylamide in water has been used to characterize the kinetic parameters. Based on initial rate data, the following equation is obtained:

$$-\frac{d[M]}{dt} = 99.7 \exp \left[5767 \left(\frac{1}{303.6} - \frac{1}{T} \right) \right] [M]^{1.53} [PS]^{0.53} [BS]^{0.47}$$

where concentrations of monomer, persulfate, and bisulfite are in mole/kg, T is in K, and t is in min. The order with respect to monomer is confirmed by an analysis of the entire temperature–time record during polymerization. The persulfate–bisulfite couple was studied also in the absence of monomer. Concentrations were measured by UV absorbance and by permanganate titration. The reaction can be represented by:



where concentrations are in mole/liter, T is in K, and t is in min.

INTRODUCTION

Many initiators have been used for the polymerization of acrylamide. Among these persulfate salts both alone and in combination with a reducing agent have played a prominent role.¹

When acrylamide—like other vinyl monomers—polymerizes in an adiabatic system, the temperature of the reaction mixture rises because of the heat of polymerization. The progress of the polymerization can be followed quantitatively in an isolated and insulated system by measuring the temperature rise.

In the present work, the adiabatic polymerization of acrylamide was studied using persulfate–bisulfite as the redox couple. The reaction mechanism of the redox couple alone was also investigated. Rates of reaction were measured under various conditions to establish the dependence of rate on monomer and on initiator concentration.

EXPERIMENTAL

The polymerizations were run in a 700-ml Dewar flask fitted with a nitrogen inlet tube, a stirrer, an injection tube, and a thermistor probe. The increase in temperature of the reaction was measured by a digital thermometer, reading to 0.01°C, connected to a recorder with scale expansion.

In a typical polymerization 20 g of Eastman acrylamide recrystallized from chloroform were dissolved in 400 ml distilled water. The solution was allowed to come to constant temperature and was purged with a stream of nitrogen for 20–30 min, after which it was transferred to the Dewar flask and sparged for an additional 5 min with nitrogen. The initiator solutions were injected—first the persulfate, then the bisulfite—from separate syringes. The polymerization started usually within a few seconds after injection. The reaction was allowed to proceed until the maximum temperature had been reached. The total exotherm for a monomer concentration of 0.66 mole/kg was about 12.2°C. This represents over 99% conversion since no monomer is detectable in the final solution (using NMR). In all runs conversion exceeded 90%. The final solutions all were readily pourable and the Trommsdorff effect (which sometimes occurs when persulfate alone is used) was not observed.

Analysis of the recrystallized acrylamide by atomic absorption showed a copper content of less than 0.1 ppm and iron of about 0.1 ppm. The system is not highly sensitive to copper. An intentional addition of 5 ppm copper based on monomer increases the rate only 15%. An addition of 115 ppm increases the rate by 210%.

For the kinetic measurement of the persulfate–bisulfite couple alone, potassium persulfate and sodium metabisulfite were used without further purification. It was found that the rate of reaction could only be measured in a buffered solution, with pH about 6.5.² A 2*M* phosphate buffer stock solution was made which was used to make up all persulfate and bisulfite solutions and which was also used as the blank in the UV measurements. Before preparing any bisulfite solution, the buffer–solvent was purged with nitrogen for 20 min. The bisulfite and persulfate solutions were made up separately, allowed to come to constant temperature, and then mixed. Aliquots from this reaction were taken at given intervals and the absorbance at 260 nm was measured. The extinction coefficients of bisulfite and persulfate in a 0.2*M* phosphate buffer had been determined to be 7.67 and 15.53, respectively.

RESULTS AND DISCUSSION

The change in temperature during the course of the polymerization is used as a quantitative measure of monomer being converted to polymer. Assuming that (1) monomer and polymer have about the same heat capacity, (2) no evaporation occurs, (3) heat of solution for monomer and polymer are about equal, and (4) the reaction goes to completion, then the rate of temperature increase is proportional to the rate of monomer disappearance

$$\frac{dT}{dt} = -\frac{\Delta H_p}{C_p} \left(-\frac{d[M]}{dt} \right) \quad (1)$$

where ΔH_p is the heat of polymerization in cal/mole and C_p is the heat capacity of the system in cal/degree. The total rise in temperature $T_{\text{final}} - T_0 = \Delta T_{\text{max}}$ is proportional to the initial monomer concentration.

Hence,

$$\int_{T_0}^T dt = -\frac{\Delta H_p}{C_p} \int_{[M]_0}^{[M]} d[M] \quad (2)$$

from which follows

$$\frac{\Delta T}{\Delta T_{\max}} = \frac{[M]}{[M]_0} \quad (3)$$

where $\Delta T = T_{\text{final}} - T$ and $[M]$ is the monomer concentration at T . For a polymerization at constant temperature, the rate of reaction often is assumed to have the form

$$R_p = -\frac{d[M]}{dt} = k_p (k_i/k_t)^{1/2} [M]^a [I]^b \quad (4)$$

where k_p is the rate constant for polymerization reaction; k_i is the rate constant for initiation reaction; k_t is the rate constant for termination reaction; $[I]$ is the initiator concentration. The rate constant as a function of temperature is given by the Arrhenius equation

$$k = Ae^{-\Delta E_a/RT} \quad (5a)$$

where ΔE_a is the energy of activation, or

$$\ln(k/k_0) = -\frac{\Delta E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (5b)$$

To use the adiabatic temperature rise to measure kinetic parameters, eqs. (1), (3), (4), and (5) are combined to give

$$\frac{dT}{dt} = K_0 \exp \left(\frac{-\Delta E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right) \cdot (\Delta T)^a \left(\frac{[M]_0}{\Delta T_{\max}} \right)^{a-1} [I]^b \quad (6)$$

The simplest application of eq. (6) uses only the initial rate $(dT/dt)_0$ at T_0 . A plot of $\ln(dT/dt)$ vs. $1/T$, $\ln[M]_0$ or $\ln[I]_0$ gives the activation energy and monomer and initiator dependence, respectively. Initial rates were obtained in two ways: (1) by taking the slope of the initial reaction directly from the temperature-time plot drawn by the recorder and (2) by plotting ΔT (i.e., $T_{\text{final}} - T$) logarithmically versus the time for each run. Such a plot often gives straight line to about 80% conversion. This relationship can be expressed by

$$\Delta T = \Delta T_{\max} e^{-t/\tau} \quad (7)$$

where τ is the time at which $\Delta T = \Delta T_{\max}/e$. The initial rate $(dT/dt)_0$ is equal to $\Delta T_{\max}/\tau$.

The thermal decomposition of the persulfate ion in aqueous solution has been shown to proceed with a first-order dependency on persulfate concentration.³ The radicals produced in the initiation step by the decomposition of the persulfate ion then start the radical chain reaction of the vinyl monomer. In its classical form, the rate of this reaction is expressed by

$$-\frac{d[M]}{dt} = k_{\text{obs}} [M] [I]^{1/2} \quad (8)$$

where $[M]$ is the monomer concentration and $[I]$ is the initiator concentration. Many people have found the initiator dependence to be 0.5. However, the monomer dependence is often greater than 1.0 (refs. 4 and 5).

In the present work, the power of the monomer concentration was found to be 1.53 at 30°C. The dependence on initiator concentration was 0.53 with respect to persulfate and 0.47 with respect to bisulfite at 30°C (Figs. 1 and 2). The energy of activation was found to be 11.5 kcal/mole (Fig. 3), and the overall rate constant

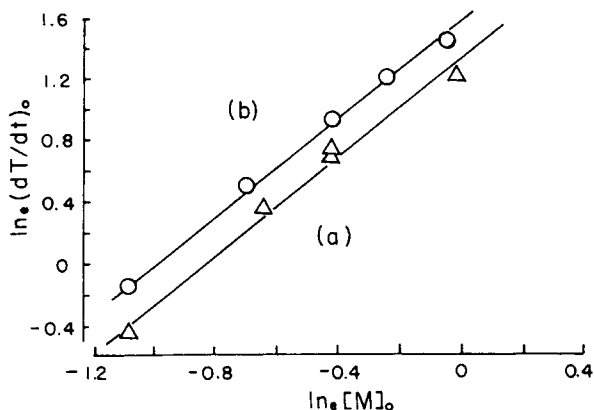


Fig. 1. Rate of polymerization dependence on monomer concentration. For both curves $[S_2O_8^{2-}] = 0.873 \times 10^{-3}$ mole/kg: (a), $[HSO_3^-] = 1.746 \times 10^{-3}$ mole/kg, slope = 1.54; (b), $[HSO_3^-] = 2.481 \times 10^{-3}$ mole/kg, slope = 1.52. Rate, dT/dt , is in $^{\circ}C/min$.

$k_{obs} = 99.7$ at $30.6^{\circ}C$ for the following empirical equation:

$$-\frac{d[M]}{dt} = k_{obs}[M]^{1.53}[PS]^{0.53}[BS]^{0.47} \quad (9)$$

where concentrations are given in mole/kg and time is in minutes.

The reaction of the redox couple by itself was found to be first order, both with respect to persulfate and to bisulfite (Fig. 4). The rate constant is 0.438 liter/(mole min).

Analysis of Course of Polymerization

Since the reaction of the initiator couple is much slower than the polymerization (see following section), it is reasonable to assume that the persulfate and bisulfite concentrations do not change significantly during the beginning of the reaction (say up to 15 min). Equation (6) can then be used to calculate the

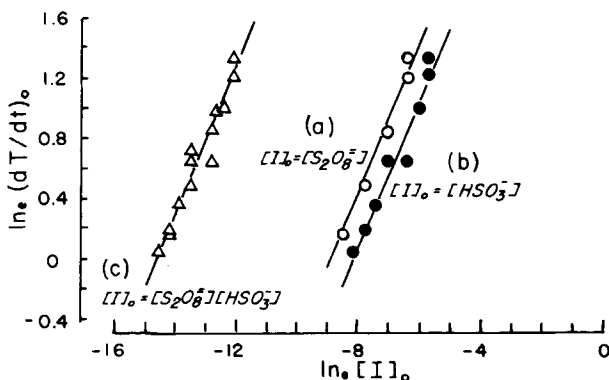


Fig. 2. Rate of polymerization dependence on initiator concentrations. Curve (a), $[HSO_3^-] = 3.45 \times 10^{-3}$ mole/kg, slope = 0.54; (b), $[S_2O_8^{2-}] = 1.75 \times 10^{-3}$ mole/kg, slope = 0.47. In (c), product of initiator concentrations are plotted, slope = 0.47. For all points, monomer concentration = 0.663 mole/kg, initial temperature = $30.7^{\circ}C$.

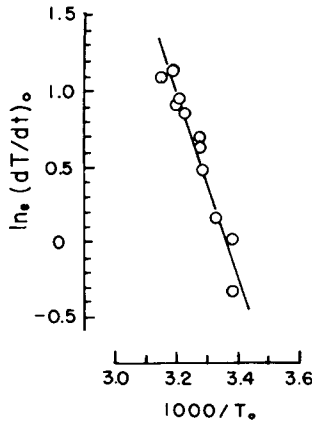


Fig. 3. Arrhenius plot for polymerization rate. $[M]_0 = 0.663$ mole/kg, $[HSO_3^-] = 1.74 \times 10^{-3}$ mole/kg, $[S_2O_8^{2-}] = 0.873 \times 10^{-3}$ mole/kg.

monomer dependence, a , during the course of a given polymerization. The slope at any point during the polymerization can be obtained by differentiating eq. (7)

$$\frac{d\Delta T}{dt} = -\Delta T_{\max} \cdot \frac{1}{\tau} e^{-t/\tau} \tag{10}$$

Eliminating dT/dt between eqs. (6) and (10), and defining a new lumped parameter, y :

$$y = \frac{\Delta E_a}{RT} - \frac{t}{\tau} = a \ln \Delta T + \text{constants} \tag{11}$$

y was plotted versus $\ln \Delta T$ for a variety of runs at $T_0 = 30.65^\circ\text{C}$. In each case,

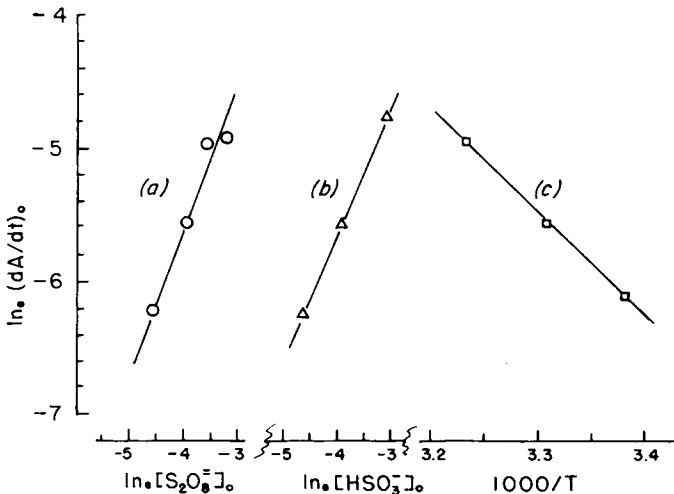


Fig. 4. Initial rate of change of absorbance, A , as function of reactant concentrations (mole/liter), and temperature (K). For (a) slope = 1.04; (b) slope = 0.98; (c) energy of activation = 15.7 kcal/mole.

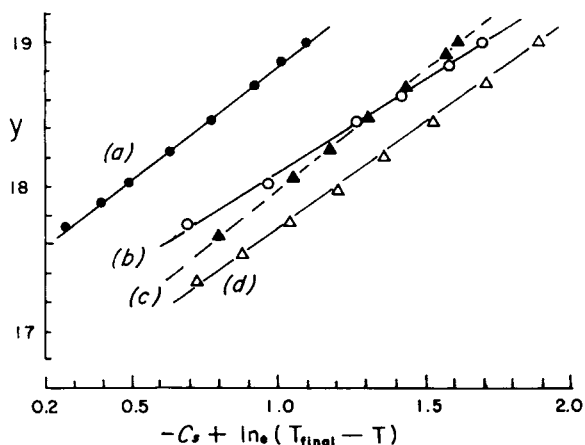


Fig. 5. Evaluation of exponent a in eq. (11) for four typical runs (details in Table I). Constant C_s is arbitrary shift factor to put data on single plot.

a straight line out to about 60–70% conversion was obtained with slope a (Fig. 5). Table I lists the range of values for eight runs. The value for a obtained from the initial rate of polymerization ($a = 1.53$) compares well with the monomer dependence during the course of a given polymerization except for the lowest monomer concentrations. This method of plotting does not require an independent measure of the finite heat capacity of the Dewar system since ΔH_p is not used as an independent constant. It does assume rapid equilibration between apparatus and contents.

Reaction between Persulfate and Bisulfite Ions

In order to postulate a mechanism of polymerization of acrylamide initiated by the persulfate–bisulfite redox couple, it seemed desirable to study the rate of reaction of the initiator couple in the absence of acrylamide.

Stoichiometry of Reaction

To determine the stoichiometry of the reaction, persulfate and bisulfite were mixed in a ratio of 1:2 in an aqueous solution at room temperature. The solution was purged with nitrogen and the pH kept at 6 to avoid loss of HSO_3^- by air oxi-

TABLE I
Monomer Dependence during Course of Given Polymerization

Run No.	Line in Fig. 5	Concentrations \times mole/kg			Slope a
		$[\text{M}]_0$	$[\text{S}_2\text{O}_8^{2-}] \times 10^3$	$[\text{HSO}_3^-] \times 10^3$	
61	—	0.34	0.873	1.346	1.115
36	—	1.003	0.873	1.746	1.58
52	—	0.663	0.873	1.746	1.45
65	—	0.663	0.219	0.436	1.47
35	(a)	0.530	0.873	1.746	1.59
29	(b)	0.34	0.873	2.481	1.20
56	(c)	0.663	1.745	1.740	1.40
67	(d)	0.663	0.46	0.290	1.51

dation and SO_2 evaporation. After 40 hr, the solution was analyzed for unreacted bisulfite in two ways: (1) by titrating acidified samples with standard potassium permanganate, and (2) by measuring the UV absorbance at 260nm (see Experimental Section). Both methods gave the same result: half the original bisulfite was left, which means that one molecule of $\text{S}_2\text{O}_8^=$ indeed reacts with one molecule of HSO_3^- .

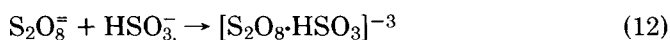
Reaction Kinetics

The rate of reaction of the redox couple was followed by measuring the UV absorbance at 260 nm, where both the persulfate and the bisulfite ions absorb. Both ions follow Beer's law in the concentration range studied, and the absorbances are additive. Since the reaction product (bisulfate) does not show an absorbance at 260 nm,^{2b} one can follow the course of reaction by observing the decrease of absorbance at 260 nm. The decrease in concentration of either persulfate or bisulfite is proportional to the decrease in absorbance, the proportionality factor being the sum of the extinction coefficients of the two ions (see Experimental section).

The order of reaction both with respect to persulfate and bisulfite was found to be one (see Fig. 4). The energy of activation was found to be 15.7 kcal/mole (Fig. 4). The rate constant at 29°C was determined to be $4.38 \times 10^{-1} \text{ l mole}^{-1} \text{ min}^{-1}$. Table I lists the summary of rate data.

In order to confirm that reaction proceeds via a radical mechanism in a buffered solution, the polymerization of acrylamide was successfully performed at pH 6.85.

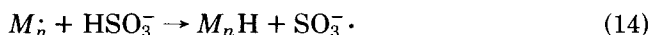
Tsuda⁶ studied the polymerization of acrylonitrile in aqueous solution at 25°C using labeled persulfate ($\text{K}_2\text{S}_2^{35}\text{O}_8$) and labeled bisulfite ($\text{NaHS}^{35}\text{O}_3$) as redox initiators. He determined an empirical equation for the ratio of sulfonate to sulfate end groups, with the sulfonate being the major end group under every condition of polymerization. In order to account for the increase in the number of sulfate end groups with increasing concentration of persulfate, Tsuda postulated the intermediate $[\text{S}_2\text{O}_8 \cdot \text{HSO}_3]^{-3}$ in the primary reaction



because the increase in the concentration of persulfate reduces the concentration of free bisulfite and accordingly reduces the formation of bisulfite radicals by the following side reaction

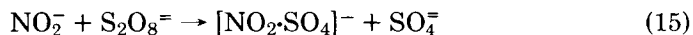


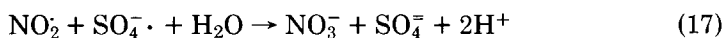
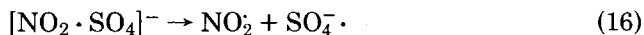
Tsuda also considered the following chain transfer reaction



where M_n^{\cdot} represents a polymer radical. This side reaction becomes important when the bisulfite concentration is high, causing an increase in the number of sulfonate end groups and a reduction in the degree of polymerization and overall rate of polymerization.

A system similar to the persulfate-bisulfite couple, was studied in detail by R. E. Ball.^{2c} He found the reaction to proceed via a free-radical bimolecular mechanism and proposed the following reaction scheme:





These observations suggest that the reaction between the persulfate and the bisulfite ions proceeds via a bimolecular, radical mechanism first order both with respect to persulfate and bisulfite ions.

CONCLUSIONS

In summary, it can be said that the initiator couple behaves "normally," producing radicals in the initiating step by the reaction of one persulfate ion with one bisulfite ion. The rate constant of this radical producing reaction (k_1) is much greater than the rate constant for the dissociation reaction of persulfate (k_i).

Assuming that the difference in the rates of polymerization of acrylamide using the redox couple as compared to persulfate alone is due only to the difference in rate constants for the initiation step and not to differences in the rate constant for propagation or the rate constant for termination, it is then possible to calculate the rate of polymerization (R_p) for a given set of conditions, both for the persulfate-initiated and the redox-initiated polymerization. The ratio of these calculated values can then be compared to the experimental values under the same conditions.

$$R_{p1}(\text{persulfate}) = (k_p/k_t^{1/2}) \times k_i^{1/2} [\text{M}]^{1.25}[\text{I}]^{0.5} \quad (18)$$

$$R_{p2}(\text{this work}) = (k_p/k_t^{1/2}) \times k_1^{1/2} [\text{M}]^{1.53}[\text{I}_1]^{0.53}[\text{I}_2]^{0.47} \quad (19)$$

$k_i = 3.18 \times 10^{-6} \text{ min}^{-1}$ (Riggs and Rodriguez⁷) and $k_1 = 0.438 \text{ liter}/(\text{mol min})$ (this work). For the conditions of $[\text{M}]_0 = 0.238 \text{ mole/liter}$ and $[\text{I}] = [\text{I}_1] = [\text{I}_2] = 0.010 \text{ mole/liter}$, the calculated and experimental values are R_{p1}/R_{p2} (calculated from k_i and k_1) = 0.038 and R_{p1}/R_{p2} (experimental results of this work and Riggs and Rodriguez) = 0.016. Since the two numbers are similar in magnitude, we conclude that the difference in rate of polymerization in the presence of bisulfite is due primarily to the difference in radical production rate. This calculation does not try to explain the difference in monomer dependence between the two. Perhaps the termination mechanism is altered sufficiently by the presence of the bisulfite to change the exponent from 1.25 with persulfate alone to 1.53 with the redox couple.

The authors wish to thank the Eastman Kodak Co. for financial support of this project.

References

1. R. H. Yocum and E. B. Nyquist, *Functional Monomers*, Vol. 1, Marcel Dekker, New York, 1973, Ch. 1.
2. E. Ball, Ph.D. thesis, Brown University, Providence, RI, 1967, p. 21; (b) p. 12; (c) p. 72.
3. *Peroxide Reaction Mechanisms*, J. O. Edwards, Ed., Wiley, New York, 1960, p. 176.
4. J. P. Riggs and F. Rodriguez, *J. Polym. Sci. Part A-1*, **5**, 3167 (1967).
5. M. M. Husain and A. Gupta, *J. Macromol. Sci., Chem.*, **11**, 2977 (1977).
6. Y. Tsuda, *J. Appl. Polym. Sci.*, **5**, 104 (1961).
7. J. P. Riggs and F. Rodriguez, *J. Polym. Sci. Part A-1*, **5**, 3151 (1967).

Received June 26, 1980

Accepted July 31, 1980