

Polymerization of Acrylamide Using the Hydrogen Peroxide–Hydroxylamine Couple*

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Synopsis

The large heat of polymerization for acrylamide makes the measurement of conversion by temperature rise in an adiabatic system quite convenient. The initial monomer concentration in the reaction medium ranged from 0.2 to 0.8 mol/kg while the concentration of the two initiator components was varied from 1 to 100 mmol/kg. The adiabatic reactor was an aluminum beaker with a thin internal organic liner. The reactor was insulated and shielded. Approximate reactor charge was 200 g. Iron has a pronounced accelerating effect on the rate. The predominant reaction appears to be the iron-catalyzed decomposition of hydrogen peroxide in the presence of small amounts of hydroxylamine hydrochloride. At hydroxylamine to peroxide ratios greater than about 1:2, there seems to be no further benefit from hydroxylamine additions. The activation energy is lowered by the addition of iron decreasing from 18.7 kcal/mol with no added iron to 4.5 kcal/mol when the system contains 1 ppm iron.

INTRODUCTION

The value of redox couples lies in their ability to carry out a polymerization at a lower temperature, with a shorter induction period and possibly to a higher conversion than with a peroxide alone. The interaction between the oxidizing and reducing agent speeds up the formation of radicals, thus decreasing the time necessary for polymerization. The reducing agent usually consists of some type of inorganic ionic species. An electron transfer between the two initiators is associated with the increased free radical formation.

This work was concerned with the redox couple hydrogen peroxide–hydroxylamine hydrogen chloride. An advantage of this couple over many others is that the residual ions left in solution are minimized which results in lower impurities in the polymer. The main objective of this work was to study the kinetics of the reaction between the redox couple and acrylamide.^{1,2}

Das,³ in the only reported study of acrylamide polymerization initiated by the redox couple hydrogen peroxide–hydroxylamine, found the rate to be first-order dependent on monomer concentration and half-order dependent on each initiator concentration. A maximum peroxide concentration of 0.01M was reported, above which half-order dependence no longer holds. The author explained this by oxygen quenching due to peroxide decomposition at high concentrations. An overall activation energy of 6.5 kcal/mol was given.

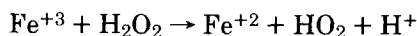
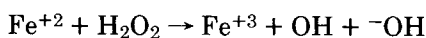
Hydrogen peroxide has been coupled with many other reducing agents. Sugimura⁴ studied the redox couple hydrogen peroxide–thiourea in conjunction

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with the aqueous solution polymerization of acrylonitrile. The rate dependency on concentration was found to be first order for monomer and half-order for each initiator. Substituted derivatives of thiourea were found to increase the polymerization rate as the electron withdrawing ability of the substituents increased. This enabled the author to suggest a plausible mechanism for the reaction between the two initiators which results in accelerated polymerization rates.

Ghosh^{5,6} developed a dye interaction technique which is used to estimate the number of hydroxyl end groups. In an investigation of the polymerization of methyl methacrylate, initiated by peroxide alone and by the redox couple peroxide-iron, the dye technique was used to obtain information on the termination mechanism. A decrease in polymer yield at high peroxide concentrations (greater than 0.1*M*) was attributed to the photooxidation of monomer molecules to nonpolymerizable products.

Peroxide and iron is among the oldest of redox couples.⁷ The electron transfer reaction between the ferrous ion and hydrogen peroxide resulting in a peroxide radical has been extensively studied in various monomer solutions^{5,8,9}:



Iron is successively oxidized and reduced, resulting in the production of radicals.

Kwang-Fu¹⁰⁻¹⁵ has studied a number of different radical initiated systems for the aqueous polymerization of acrylamide. He has examined the effect of pH on the polymerization rates. In a peroxide initiated system, the rate increases as pH is decreased below a value of 4 or increased above 9. No generalizations were drawn concerning other initiation systems.

Other redox couples which have been studied in conjunction with acrylamide polymerization include persulfate-bisulfite,² persulfate-thiosulfate,¹ chlorate-sulfite,¹⁶ and ferric-bisulfite.¹⁷

EXPERIMENTAL

The large heat of polymerization for acrylamide makes the measurement of conversion by temperature rise particularly convenient.² There are some assumptions inherent in using an adiabatic system to measure conversion.¹⁸ These include the following:

1. There is no evaporation of water from the solution.
2. The monomer and polymer have the same heat capacity (0.5 cal/mol°C).
3. All the heat produced by the polymerization results in a temperature rise of the solution.

Evaporation of water can occur in this system, although at 30°C (the temperature at which most rates were recorded) it is negligible.

The initial monomer concentration in the reaction medium ranged from 0.2*M* to 0.8*M* while the concentration of the two initiators was varied from 0.001*M* to 0.10*M*. In a typical run with initial monomer and initiator concentrations of 0.4*M* and 0.02*M*, respectively, the initial rate of polymerization was observed to be 0.011 mol/kg·min.

The adiabatic reactor consists of an aluminum beaker with a very thin internal organic liner (Fig. 1). It is equipped with a heating element which serves to bring

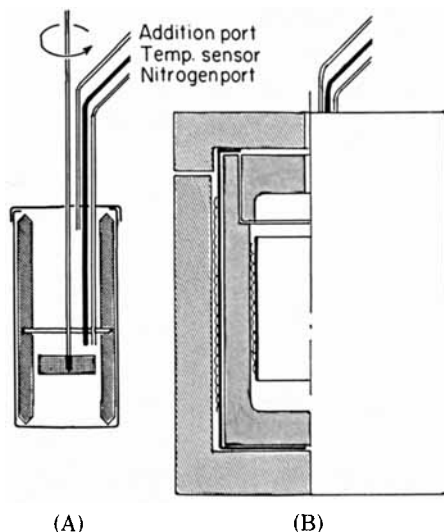


Fig. 1. The adiabatic reactor (A) has stainless steel baffles and stirrer blade. The insulated housing (B) has an inner heating panel for adjusting the original reaction temperature along with a heated shield which is kept at the same temperature as the contents of the reactor.

the reactor contents up to the desired initial temperature (usually 30°C). A $\frac{3}{4}$ in. thick layer of urethane foam surrounds the reactor, the outer surface being wrapped in an aluminum shield. Two thermocouples, one directly beneath the reactor and the other on the surface of the shield, are connected to a differential thermometer. The differential thermometer in turn is connected to a control instrument which was designed by Professor R. Phelan of Cornell University. This instrument directs a current to the aluminum shield on the urethane foam when its temperature is less than that of the reactor. This serves to maintain the inner layer of foam at the same temperature as the reactor. Therefore, no heat should be lost from the reactor during polymerization.

The heat capacity of reactor contents, excluding the aqueous monomer solution, (i.e., stirrer, baffles, etc.) was estimated by measuring the rate of temperature rise at 30°C for various volumes of water. By extrapolation to zero volume, the heat capacity of the contents was estimated at 28.05 cal/°C. This correction factor is included in all the reported rates.

To get an estimation of the heat loss from the system, 200 mL of water was heated to 40°C. In a period of 20 min the 0.11°C that was lost from the system can be considered negligible in measuring initial rates.

Acrylamide was recrystallized from chloroform and dried in a vacuum oven at room temperature. The two initiators, 3% hydrogen peroxide and hydroxylamine hydrogen chloride, were of reagent grade and not further purified.

The precise concentration of the hydrogen peroxide was determined by titrating with standardized KMnO_4 .¹⁹ Water, the solvent, represented the largest source of metal ions, of which certain types were shown to greatly accelerate the polymerization rate. To obtain water with a consistent (and low) metal ion concentration, distilled water was run through an ion exchanger (Millipore, Milli-Q) before redistillation in all glass apparatus.

In all runs the solvent consisted of 200 g of water (including the water added

with the initiators). A monomer solution of the desired concentration was prepared and added to the reactor. Any metal ions or complexing groups to be added were injected at this time. The reactor contents were brought up to the desired temperature. Nitrogen was bubbled through the solution for 15 min to sparge oxygen from the system. A fresh hydroxylamine solution of the necessary concentration was prepared for each run because of the risk of premature oxidation of the initiator. The nitrogen flow was terminated. A 10 mL aliquot of hydroxylamine was injected. 30s later the peroxide was injected. The polymerization, being exothermic and adiabatic, produced a temperature rise which was plotted on a chart recorder as a function of time. The polymerization was allowed to proceed until the rate of temperature increase was less than $0.02^{\circ}\text{C}/\text{min}$. The polymer was precipitated by adding acetone, and dried and stored for viscosity measurement. Final conversion always exceeded 90%.

RESULTS AND DISCUSSION

Making the assumptions listed above, a linear relationship between temperature rise and monomer disappearance may be written:

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

where ΔH_p = heat of polymerization (cal/mol) and C_p = heat capacity of system (cal/ $^{\circ}\text{C}$). It follows from integrating this equation that the total temperature rise ($T_f - T_0$) is proportional to the initial monomer concentration:

$$T_f - T_0 = \left(\frac{\Delta H_p}{C_p} \right) [M]_0 \quad (2)$$

From eqs. (1) and (2) one may determine the conversion X at any time during the polymerization from the temperature:

$$X = \frac{T - T_0}{T_f - T_0} \quad \text{or} \quad X = 1 - \frac{[M]}{[M]_0} \quad (3)$$

Typically for free radical polymerizations the rate is expressed in the form:

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

where $[M]$ = monomer concn., $[I]$ = initiator concn., and k_p , k_i , and k_t are the rate constants for polymerization, initiation, and termination, respectively.

Initial Rate Dependency on Monomer and Initiator Concentrations with No Iron Added

The rate dependence on monomer concentration was measured at 30°C using equimolar initiator concentrations of $0.02M$, where M is mol/kg. The rate was found to be proportional to the monomer concentration raised to the 1.03 power (Fig. 2). Likewise the dependence of rate on initiator concentrations was found to be proportional to the peroxide and hydroxylamine concentrations raised to the 0.44 and 0.52 power, respectively (Fig. 3). The monomer concentration was held constant at $0.4M$ each case with $0.02M$ peroxide in the hydroxylamine de-

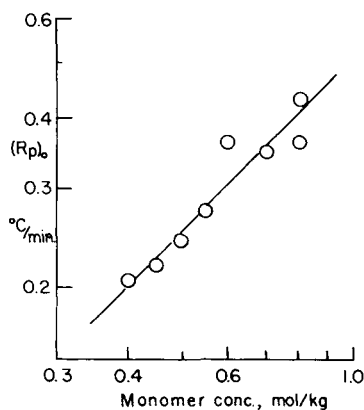


Fig. 2. The initial rate of polymerization varies with the monomer concentration with the 1.03 power when peroxide and hydroxylamine concentrations are each 20 mmol/kg at 30°C.

pendency measurements and 0.1M hydroxylamine in the peroxide concentration dependency measurements.

Das,⁴ using gravimetric methods, studied the kinetics of acrylamide polymerization with the same redox couple. In a typical run of 0.4M monomer and 0.01M initiator a polymerization rate of 0.0154 mol/kg-min was reported. This is slightly higher than the rate measured in this work at similar conditions. This may be attributed to a higher metal ion concentration in his solutions which will be discussed in the activation energy section. Das cited first-order dependence on monomer concentration and half-order dependence on each initiator concentration (provided peroxide concentration is less than 0.01M). At peroxide concentrations greater than 0.01M a decreasing dependence on peroxide was reported. This was explained by him as a retarding affect due to the decomposition of peroxide to oxygen which quenches the free radicals.

Similar results were obtained from this work concerning monomer and initiator concentration dependencies. The decreasing rates at higher peroxide concentrations were not observed although there is scatter in the data [Fig. 3(A)].

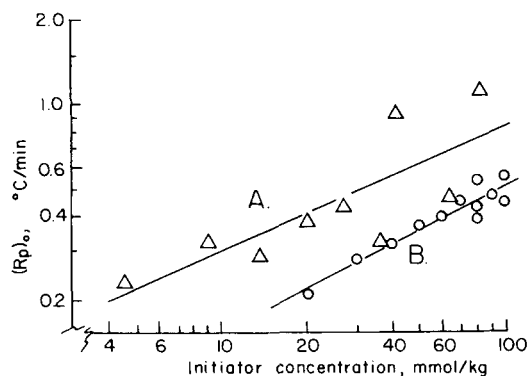


Fig. 3. Initial rate dependence (30°C) on initiator concentrations with 0.40 mol/kg acrylamide: (A) H_2O_2 varied with 100 mmol/kg of hydroxylamine hydrochloride; (B) hydroxylamine hydrochloride varied with 20 mmol/kg of H_2O_2 .

Effect of Metal Ions

Small variations in metal ion concentration were found to have a large effect on the polymerization rates. Copper and iron ions were added, in the form of cupric acetate and ferrous sulfate, to assess their influence on the rate. Addition of 10 ppm of copper metal increased the rate fourfold. The same acceleration required less than 1 ppm of iron.

Dainton⁸ makes the statement that the cupric ion more readily oxidizes polyacrylamide radicals than the ferric ion. This implies that the cupric ion is a more effective chain terminator and thus may explain the lower rates obtained for copper than for iron.

At concentrations around 1 ppm the rate is proportional to the iron concentration to the 0.67 power (Fig. 4). From the rate with no iron added, the adventitious iron concentration is estimated to be 0.010 ppm. This would include the traces of iron in the recrystallized acrylamide, the initiators and the distilled deionized water.

For a peroxide-iron initiation system, Bond²⁰ found a critical iron concentration of around 100 ppm above which polymerization rate is not markedly increased. The author states that, although the number of free radicals increase with increasing iron concentration, many more are lost at high concentrations due to side reactions.

Initial Rate Dependency on Concentration with 1 ppm Iron

Since a small concentration of iron has such a significant effect on the polymerization rate and is, for all practical purposes, impossible to eliminate, further experiments were carried out to assess the effects on reaction order at a standard concentration of 1 ppm iron.

The results in Figure 5 indicate a very nearly first order dependence on monomer concentration in a system with 1 ppm iron added. The data, replotted as rate vs. initiator concentration at four set values of monomer concentration (Fig. 6), show initiator dependence to a power between 0.5 and 0.6. It is con-

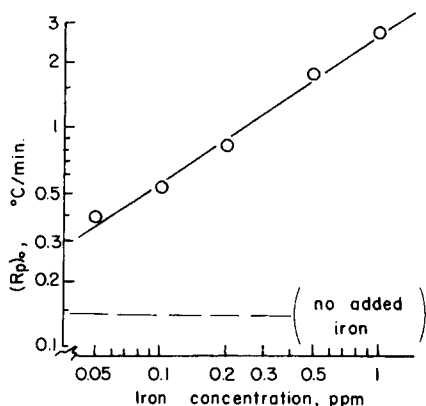


Fig. 4. Initial rate dependence (30°C) on iron concentration with acrylamide at 0.40 mol/kg and both initiators at 10 mmol/kg.

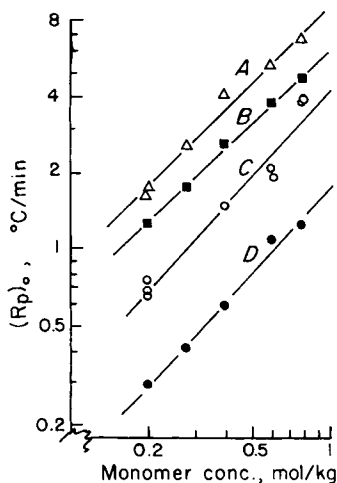


Fig. 5. Initial rate (30°C) with 1.0 ppm iron added. Equimolar concentrations (mmol/kg) of peroxide and hydroxylamine hydrochloride each held at: (A) 20; (B) 10; (C) 5.0; (D) 1.0.

cluded from the data that at *equimolar* initiator concentrations the peroxide concentration dependency is nearly half-order. The hydroxylamine concentration dependency need not be independently half-order, however.

As will be shown in the following discussion, at nonequimolar initiator concentrations with 1 ppm iron in the system the hydroxylamine concentration seems to have little effect on the kinetics of the reaction.

When the concentration of hydroxylamine was varied at constant monomer and peroxide concentrations, no simple rate dependency on concentration was observed (Fig. 7). In each set of runs the peroxide concentration was in excess or equal to the hydroxylamine concentration. In all three cases a leveling of the rate dependency on hydroxylamine concentration was observed as the hydroxylamine concentration increases relative to the peroxide concentration. At concentrations in excess of peroxide (in the presence of 1 ppm iron) further increases in the hydroxylamine appear to have virtually no effect on the initial rate. These results are consistent with the rate data in Figures 5 and 6. The concentration dependence is the greatest at very low hydroxylamine concentrations

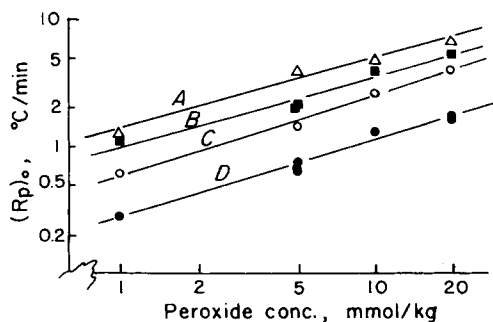


Fig. 6. Crossplot of Figure 5. Equimolar initiator concentrations with monomer concentrations (mol/kg) of: (A) 0.8; (B) 0.6; (C) 0.4; (D) 0.2.

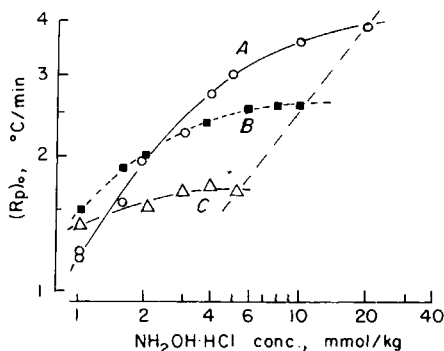


Fig. 7. Initial rate (30°C) dependence on reducing agent concentration with 1 ppm iron and with acrylamide at 0.4 mol/kg and peroxide (mmol/kg) at (A) 20; (B) 10; (C) 5.

and decreases as hydroxylamine concentration increases until it appears to have no further effect on the rate.

Similarly, the peroxide dependency was determined by holding monomer and hydroxylamine concentrations constant and varying the peroxide concentration. Figure 8 shows the results of two sets of runs. In each case half-order dependence on peroxide concentration was observed. The rates for the two sets of runs at 0.02M and 0.04M hydroxylamine (with the same monomer and peroxide concentrations) are almost identical. Again it appears that at high relative hydroxylamine concentrations, in the presence of 1 ppm of iron, there is little dependency of the rate on hydroxylamine concentration.

An empirical equation was developed which is consistent with the observed rate data. The results are consistent with

$$R_{p0} \propto [M]^{1.0} [H_2O_2]^{0.5} \quad (5)$$

The rate dependency on hydroxylamine concentration is not as obvious. The hydroxylamine concentration can be expressed as a fraction of the peroxide concentration:

$$\sigma = [NH_2OH \cdot HCl] / [H_2O_2] \quad (6)$$

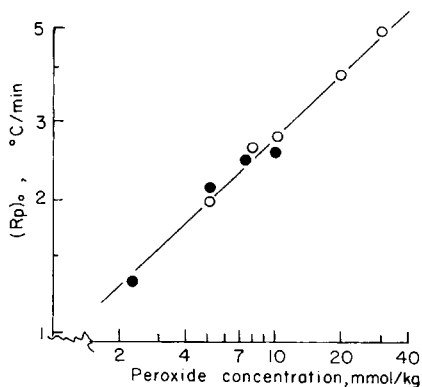


Fig. 8. Initial rate (30°C) dependence on peroxide concentration with 1 ppm iron and 0.4 mol/kg acrylamide and 40 mmol/kg (O) and 20 mmol/kg (●) hydroxylamine hydrochloride.

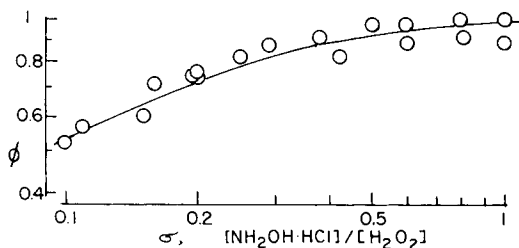


Fig. 9. Data of Figure 7 replotted as reduced rate ϕ vs. the ratio of reducing agent to oxidizing agent (mol basis). The line corresponds to eq. (10).

The rate can be expressed in terms of a reduced rate ϕ , which is the ratio of the rate at some hydroxylamine concentration divided by the rate at equimolar initiator concentrations.

$$\phi = R_{p0}(\sigma)/R_{p0}(\sigma = 1) \tag{7}$$

A log-log plot of ϕ vs. σ for all the data from Figure 7 can be fitted by a curve (Figs. 9 and 10) with the following equation:

$$\phi = 1.10\sigma/(0.10 + \sigma) \tag{8}$$

or

$$R_{p0}(\sigma)/R_{p0}(\sigma = 1) = 1.10\sigma/(0.10 + \sigma) \tag{9}$$

Since it has been shown that $R_{p0}(\sigma = 1) \propto [H_2O_2]^{1/2}$, the above expression may be rewritten as:

$$R_{p0}(\sigma) = K[H_2O_2]^{1/2} (1.10\sigma)/(0.10 + \sigma) \tag{10}$$

This expression is consistent with the observation that at large σ (close to 1) the rate is essentially independent of the hydroxylamine concentration. The overall rate expression derived from the results when the system contains 1.0 ppm of

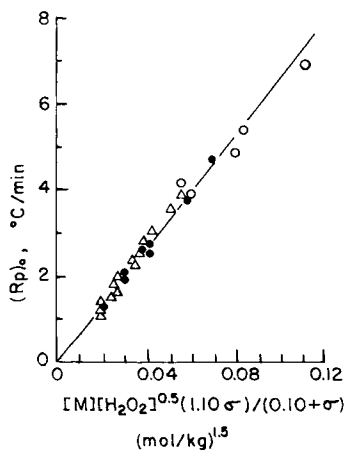


Fig. 10. Linearized data according to eqs. (10) and (11): (O) acrylamide concentration was varied; (●) peroxide concentration was varied; (Δ) hydroxylamine concentration was varied.

added iron (2×10^{-5} gatom/kg) can be represented as

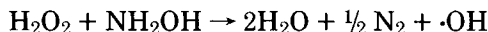
$$\frac{-d[M]}{dt} = K_{30^\circ\text{C}} \exp \left[2265 \left(\frac{1}{303} - \frac{1}{T} \right) \right] \times [\text{AAM}]^{1.0} [\text{H}_2\text{O}_2]^{0.5} \left(\frac{1.10 [\text{NH}_2\text{OH}\cdot\text{HCl}]/[\text{H}_2\text{O}_2]}{0.10 + [\text{NH}_2\text{OH}\cdot\text{HCl}]/[\text{H}_2\text{O}_2]} \right) \quad (11)$$

The value of $K_{30^\circ\text{C}}$ (Fig. 10) is 65.1, where all concentrations are in mol/kg and time is in min. It is to be expected that the rate would vary with iron concentration to the 0.67 power in the vicinity of 1 ppm, but the total form of the equation was not tested at all iron levels. It would not be wise to extrapolate the equation beyond the limits of σ between 0.10 and about 1.5. On the other hand, the prediction that at low values of σ , the rate might decrease with added peroxide is not without foundation. Das³ speculated that high concentrations of peroxide could lead to oxygen formation with consequent retardation.

The following equation appears to correlate the data when no iron is intentionally added to the system and all possible precautions are taken to diminish ionic contamination:

$$\frac{-d[M]}{dt} = 21.0 \exp \left[9411 \left(\frac{1}{303} - \frac{1}{T} \right) \right] \times [\text{AAM}]^{1.03} [\text{H}_2\text{O}_2]^{0.44} [\text{NH}_2\text{OH}\cdot\text{HCl}]^{0.52} \quad (12)$$

In the equation, concentrations are in mol/kg and time is in min. The equation has to be used with caution since the iron concentration (if there is any) is adventitious. The results in the absence of added iron seem to be consistent with the initiation reaction postulated by Das³:



The hydroxyl radical added to monomer then is the chain initiator for the usual propagation reaction.

Activation Energy

The activation energy is determined from plots of $\ln R_{p0}$ vs. $1/T$ (slope = $-E_a/R$).

The overall activation energy, in this work, was found to be a direct function of the iron concentration in the system (Table I). Since the added iron affects

TABLE I
Activation Energies for Various Iron Concentrations

Run no. ^a	Iron added (ppm)	Activation energy (kcal/mol)	
		From $(R_p)_0$	From M_0
1	none	18.7	-9.8
2	0.10	12.6	-6.7
3	0.50	5.5	Not run
4	1.0	4.5	-4.9

^a For runs 1 and 2: acrylamide = 0.8M; peroxide and hydroxylamine each = 0.04M; for runs 3 and 4: acrylamide = 0.4M; peroxide and hydroxylamine each = 0.01M.

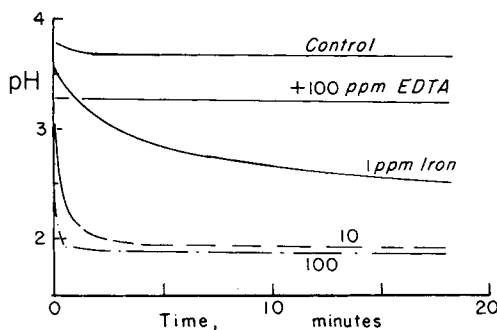


Fig. 11. Stability of pH for solutions with 20 mmol/kg each of H_2O_2 and $\text{NH}_2\text{OH}\cdot\text{HCl}$ (30°C , no monomer). Added iron accelerates the drop in pH. EDTA (ethylene diamine tetraacetic acid, disodium salt) with no added iron is more stable than the control with no iron or EDTA.

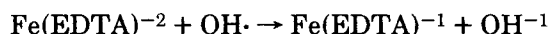
activation energy so much, the fact that Das³ reported an energy of 6.5 kcal/mol can be interpreted to mean that his polymerization system may have contained iron or some other transition metal. For that matter, the present study with no added iron does not offer proof that absolutely no iron is present. It can be said with some confidence that the adventitious contamination level of iron is probably less than 0.01 ppm.

pH Measurements

The pH of a solution of 0.02M in initiators (with no monomer present) was measured as a function of time (Fig. 11). The drop in pH is rapid with the addition of iron. A chelating agent, EDTA (ethylene diamine tetraacetic acid, sodium salt), when added to a solution of the redox couple, resulted in virtually no change in pH with time. The EDTA is expected to complex any metal ions in solution and to prevent their interaction with the redox couple. Whether this result implies that a trace of iron is necessary for the reaction between the initiators to form radicals still can be debated.

In a polymerization reaction at standard conditions with 100 ppm EDTA added, no polymer was produced. Without the EDTA, as the same reaction conditions the polymerization proceeded at a reasonable rate. It appears that the pH drop may be an indication of the extent of the reaction between the initiators.

Bond²⁰ found that in a polymerization reaction initiated by hydrogen peroxide and iron a complexing agent was essential. Without EDTA to chelate the iron, complete oxidation occurred. An electron transfer reaction between the chelated iron and peroxide was proposed. This work is definitely not in agreement with that of Bond. However, the fact that no polymerization occurs in a reaction medium containing EDTA may not necessarily be due to the complexing of iron. Hydroxylamine and peroxide may still generate the hydroxyl radicals which may be rapidly reduced by the EDTA anion:



No attempts were made to control the pH during polymerization due to the complexity introduced by adding buffers to the reaction medium.

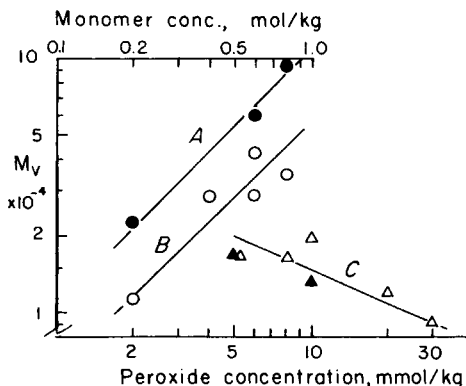


Fig. 12. Dependence of molecular weight M_v on monomer and peroxide concentrations (30°C, 1 ppm iron): (A) equimolar concentrations of peroxide and hydroxylamine hydrochloride of 1.0 mmol/kg; (B) equimolar concentrations of 5.0 mmol/kg; (C) acrylamide concentration of 0.4 mol/kg and hydroxylamine hydrochloride concentrations of 20 (▲) and 40 mmol/kg (△).

Molecular Weight

A Ubbelohde viscometer was used to measure the flow times of a series of dilute aqueous polymer solutions prepared from samples retained from the rate experiments. Viscosity average molecular weights were calculated from a Mark-Houwink relationship for aqueous polyacrylamide¹⁶ at 30°C:

$$[\eta] = 3.73 \times 10^{-4} M_v^{0.66} \quad (13)$$

Intrinsic viscosity and the weight and number average molecular weights were correlated for a similar system of aqueous polyacrylamide (peroxide initiated) at 30°C by Klein.²¹

From the rate expression, it is expected that the molecular weight would be more dependent on monomer concentration than on the initiator concentrations (Fig. 12). Also, from the rate data it is expected that the hydroxylamine concentration (at equal molar initiator concentrations) would have essentially no effect on the molecular weight (Fig. 13). The data show the expected trends.

As the iron concentration in the reaction medium is increased, a lower molecular weight polymer is produced (Fig. 14). This is quite consistent with the acceleration in rate by iron. Changes in molecular weight with temperature (Fig. 15, Table I), followed the expected pattern. That is to say, an increase in tem-

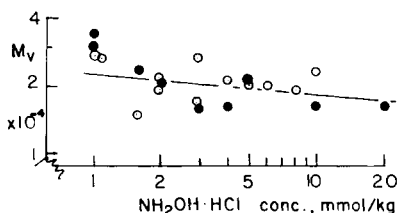


Fig. 13. Dependence of molecular weight M_v on reducing agent concentration (30°C, 1 ppm iron). Acrylamide concentration of 0.4 mol/kg and peroxide concentrations of 10 (●) and 20 (○) mmol/kg.

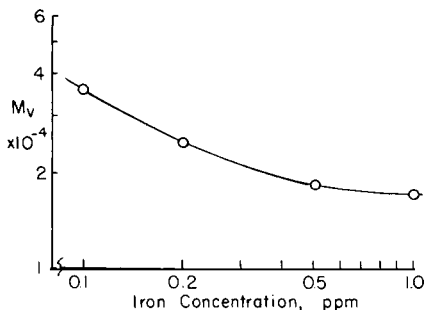


Fig. 14. Decrease in M_v caused by added iron. Acrylamide concentration of 0.4 mol/kg, peroxide and hydroxylamine hydrochloride each at 10 mmol/kg.

perature results in a lowered molecular weight. For idealized kinetics,²² the sum of the activation energy for polymerization and that for molecular weight should be twice that of $k_p/k_t^{1/2}$. For the rate of polymerization,

$$(E_a)_p = E_i/2 + E_p - E_t/2 \tag{14}$$

where the total activation energy is made up of contributions from initiation, propagation, and termination reactions. For molecular weight dependence,

$$(E_a)_m = E_p - E_t/2 - E_i/2 \tag{15}$$

Thus

$$(E_a)_p + (E_a)_m = 2E_p - E_t \tag{16}$$

In this work, with no added iron (Table I), $(E_p - E_t/2)$ is 4.5 kcal/mol. Pohl reported a value of 3.7 kcal/mol by measuring the activation energy of the initi-

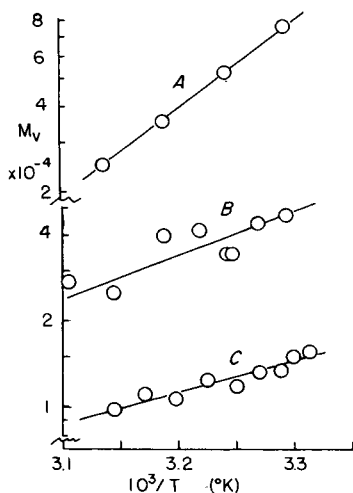


Fig. 15. Arrhenius-type plots for M_v : (A) no added iron; (B) 0.1 ppm added iron; (C) 1.0 ppm added iron. For curve C, acrylamide concentration was 0.4 mol/kg and each initiator concentration was 10 mmol/kg. For curves A and B, acrylamide was 0.8 mol/kg and each initiator was 40 mmol/kg.

ation reaction separately for a redox system with acrylamide.² Both of these values are quite a bit higher than Dainton's value of 1.5 kcal/mol.

Added iron (Table I) decreases activation energy for both rate of polymerization and for molecular weight. The idealized analysis would be expected to be less applicable with large amounts of iron since substantial chain transfer may be involved.

CONCLUSIONS

The redox couple hydrogen peroxide-hydroxylamine hydrochloride is an effective initiator for aqueous acrylamide solutions. The reaction can be carried out most reliably in the presence of a small amount of iron. The reaction appears to be the iron-catalyzed decomposition of peroxide in the presence of small amounts of hydroxylamine. At hydroxylamine to peroxide ratios of greater than 1:2, there appears to be no further benefit from hydroxylamine additions.

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