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## Aqueous Redox Polymerization of Acrylamide Initiated by Lactic Acid/Permanganate

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### ABSTRACT

Acrylamide was polymerized in aqueous solution at  $35 \pm 0.2^\circ\text{C}$  with the redox pair potassium permanganate/lactic acid. The kinetics of polymerization was followed iodometrically. The effect of monomer, potassium permanganate, and lactic acid concentration and temperature on the rate of polymerization was studied. The dependence of the number-average degree of polymerization on the initial rate of polymerization and temperature was also determined.

The study of the polymerization of acrylamide has been undertaken on account of the increasing importance of polyacrylamide as a flocculant, a sizing agent and various other biochemical uses.

Acrylamide has been polymerized by various redox pairs such as permanganate/tartaric acid [ 1 ], permanganate/oxalic acid [ 2 ],  $\text{K}_2\text{S}_2\text{O}_8$ -ascorbic acid [ 3 ], etc. The permanganate/lactic acid-initiated polymerization of this monomer has been investigated with a view to study the kinetic course of the reaction as compared to other redox systems as well as to elucidate the mechanism of free-radical formation.

## EXPERIMENTAL

Preparation and Purity of Materials

Monomer. The purification of acrylamide was done by recrystallization from the methanol and subsequent drying under vacuum.

Activator. Lactic acid was a B. D. H. (Analar) reagent.

Catalyst.  $\text{KMnO}_4$  was a B. D. H. (Analar) grade product.

Solvent. Conductivity water, used in all experiments, was prepared by redistilling distilled water to which a small quantity of alkaline permanganate had been added.

Technique

The apparatus employed was a modification of a known one [4]. The method was the same as that followed by Misra et al. [2, 5-8]. Known quantities of acrylamide and lactic acid, together with the requisite quantity of water were taken in a Pyrex reaction flask protected from light. The flask was immersed up to the neck in a thermostat maintained at  $35 \pm 0.2^\circ\text{C}$  and a controlled stream of oxygen-free, dry nitrogen was passed through the contents of the flask. After 1 hr, to determine the initial monomer concentration, two equal aliquots were withdrawn from the reaction mixture and introduced into ice-cold brominating reagent [9], known amounts of which were previously taken in separate iodine flasks. Bromination was done by using an aqueous  $\text{KBr-KBrO}_3$  solution in the presence of an excess of 1 M  $\text{H}_2\text{SO}_4$ . A calculated amount of  $\text{KMnO}_4$  was then introduced to initiate the polymerization reaction. Several aliquots were withdrawn at desired time intervals and introduced into ice-cold brominating reagent to quench the polymerization reaction. The iodine flasks were quickly stoppered, shaken well, and kept in the dark for complete bromination of the monomer double bonds. The remaining bromine was back-titrated with excess  $\text{KI}$  and  $\text{Na}_2\text{S}_2\text{O}_3$  solution to a starch end point [6, 8].

Different induction periods were encountered in experiments which were due mainly to the residual oxygen in the system and sometimes, probably due to chance impurity. All precautions were taken to obtain a reproducibility of within 5% conversion. Graphs were plotted after eliminating the induction periods.

Determination of Molecular Weights

For molecular weights determination the samples of polyacrylamide were prepared and purified by two reprecipitations from

methanol (AR). The samples were then dried at 40°C. The viscosity of very dilute aqueous solution of the polymer (< 0.4%) was determined at 30°C. Finally, the molecular weights were determined by using the relationship of Suen et al. [10]

$$[\eta]_{30^\circ\text{C}} = 6.8 \times 10^{-4} M^{0.66}$$

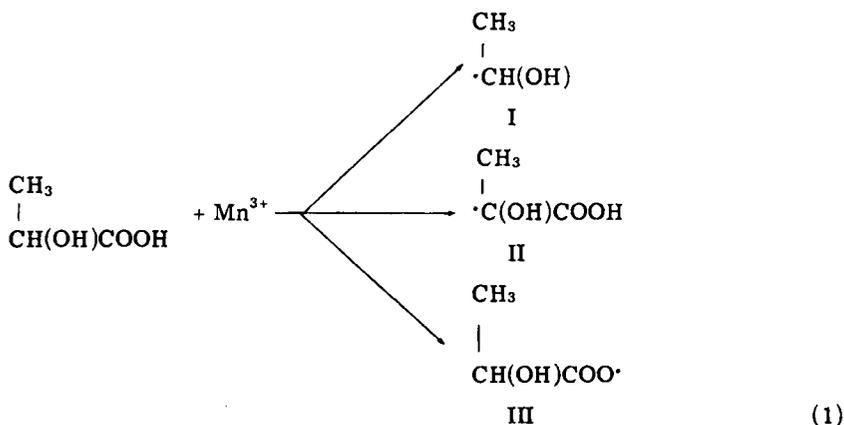
where  $[\eta]$  is the intrinsic viscosity of the polymer solution and M denotes molecular weight of the sample.

RESULTS AND DISCUSSION

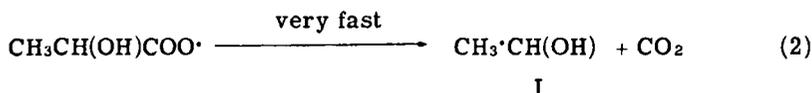
Mechanism

In the aqueous polymerization of acrylamide initiated by the KMnO<sub>4</sub>-lactic acid system, the permanganate first reacts with acrylamide producing manganese dioxide, which then dissolves in lactic acid, producing highly reactive Mn<sup>3+</sup> ions. These Mn<sup>3+</sup> ions react with lactic acid to produce active free-radicals which are capable of initiating the polymerization of acrylamide.

A plausible reaction mechanism may be put forward [ Eq. (1) ] to explain the experimental facts.



In the aliphatic series, reactions such as that of Eq. (2)



are very fast indeed, and consequently the formation of radicals such as (I) above would be favored. The formation of radicals (I), (II), and (III) can be postulated, but (I) would be the main polymerizing initiator due to reasons explained above. The formation of carbon free radical (I) has also been confirmed by mercuric chloride test.

### Activator and Catalyst Dependence

A half order rate dependence on the concentration of both the oxidant and the reductant is predicted by the following equation:

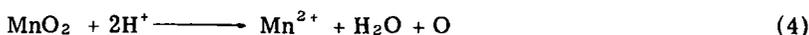
$$R_p = K[M] [\text{Oxidant}]^{1/2} [\text{Reductant}]^{1/2} \quad (3)$$

where

$$K = k_p k_r^{1/2} / (2k_t)^{1/2}$$

The various terms have the usual meaning, and  $k_r$  is the rate constant of the redox reaction. Equation (3) is followed in many redox systems in homogeneous and heterogeneous polymerization [11-14].

Although many redox systems show a half order dependence on the activator concentration, yet more often it is found that the  $R_p$  is independent of the concentration of activator. Such behavior has been reported by Palit et al. [15, 16], Misra et al. [7, 17-20] and Shukla et al. [21-23]. It may be due to the balance existing between the rates of radical generation step and the side reaction occurring in the system



The above behavior is more or less also shown in the acrylamide polymerization initiated by the present redox system.

As the pH of the system varies with the amount of activator (lactic acid), a study of the activator dependence indirectly reveals the effect of the pH of the medium on the polymerization. The pH decreases with increasing concentration of activator. The initial rate and the limiting conversion both increase with decreasing pH in the range 3.1 to 2.6. Both the initial rate and limiting conversion approach a maximum at pH 2.6. On further decreasing the pH value, both the above decrease appreciably.

The order of the reaction with respect to the catalyst concentration

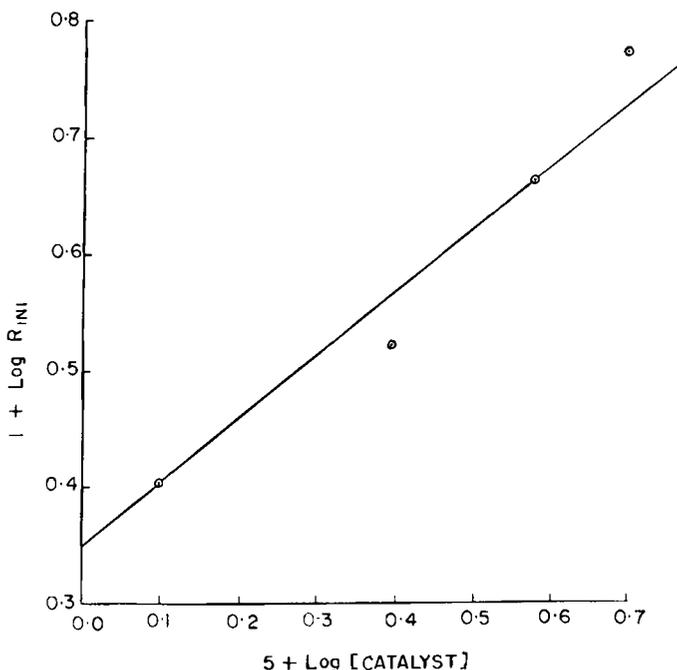


FIG. 1. Double logarithmic plot of initial rate of polymerization ( $R_{in}$ ) in % conversion per minute vs. concentration of the catalyst ( $KMnO_4$ ) in mole/dm<sup>3</sup>.

has been determined from the double logarithmic plot of  $R_{in}$ , obtained from the initial slope of conversion curves and expressed in percent conversion per minute versus the logarithm of catalyst concentration (in mole/dm<sup>3</sup>) (Fig. 1). Within the studied range ( $1.25$  to  $5.00 \times 10^{-4}$  mole/dm<sup>3</sup>) of catalyst concentration the catalyst exponent is found to be 0.52. A bimolecular mechanism of termination is thus indicated in the studied range.

The dependence of the rate of polymerization on molecular weight on increasing the catalyst concentration, keeping the concentrations of activator and monomer constant, has also been studied (Fig. 2 and Table 1). The samples of polyacrylamide were prepared by short-stopping the reaction at the point up to which the steady state is observed and the molecular weight of the sample as obtained was determined. The relationship between the rate and reciprocal of the

TABLE 1. Time vs. Conversion Curves for the Polymerization of Acrylamide with Varying Initial Concentration of  $\text{KMnO}_4$ <sup>a</sup>

Expt. no.	$[\text{KMnO}_4] \times 10^4$ (mole/dm <sup>3</sup> )	Extent of conversion (%) with reaction time				
		2 min	4 min	6 min	8 min	10 min
1	1.00	0.8	0.8	2.2	3.2	4.1
2	2.00	1.3	2.4	3.8	5.0	6.2
3	2.50	1.7	3.2	4.8	6.5	8.0
4	3.00	2.0	4.1	6.2	8.0	10.2
5	4.00	2.6	5.0	7.4	10.2	12.3
6	5.00	3.0	5.9	8.6	12.0	14.6

<sup>a</sup>[Acrylamide] = 0.35 mole/dm<sup>3</sup>; lactic acid =  $7.45 \times 10^{-2}$  mole/dm<sup>3</sup>; pH = 2.6; temperature =  $35 \pm 0.2^\circ\text{C}$ .

degree of polymerization (Table 2) at different catalyst concentrations has been plotted in Fig. 3. As is evident, the plot is nearly a straight line.

### Monomer Dependence

The initial polymerization rate and the percentage conversion are found to increase with increasing monomer concentration. The curve in Fig. 4 represents the results of variation of rate against the monomer concentration. It is seen that the rate of polymerization increases linearly within a certain range of monomer concentration ( $1.25$  to  $5.00 \times 10^{-2}$  mole/dm<sup>3</sup>). A deviation from this behavior is observed at higher concentration of the monomer (above  $75.0 \times 10^{-2}$  mole/dm<sup>3</sup>), which may be due to the viscosity of the medium more than due to the higher conversion of the monomer into polymer.

### Temperature Dependence

When the temperature at which the polymerization is done is raised above  $35^\circ\text{C}$ , it is found that the initial rate of polymerization increases and the maximum conversion falls. At higher temperature side reactions of the type (5) may set in, thereby increasing the possibility of the primary radicals undergoing a change at a faster rate.

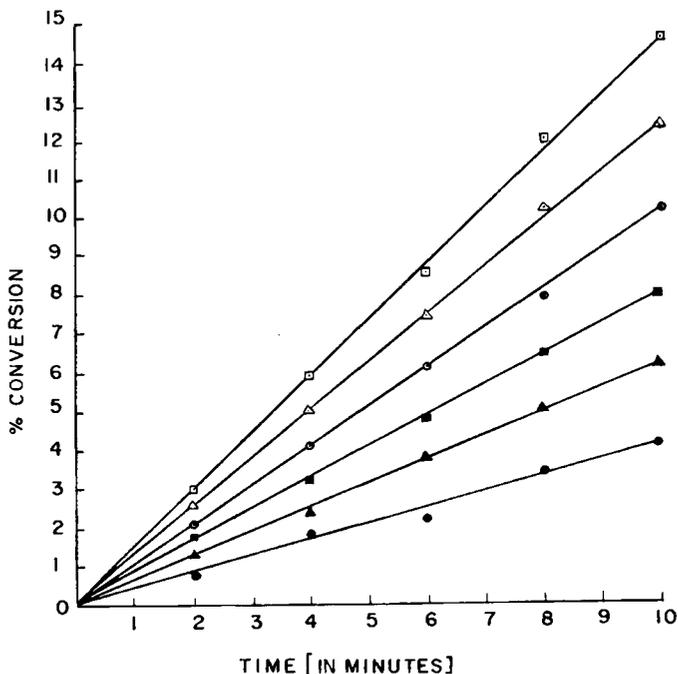


FIG. 2. Time vs. conversion curves for the polymerization of acrylamide with varying initial concentration of  $\text{KMnO}_4$ : ( $\bullet$ )  $[\text{KMnO}_4] = 1.0 \times 10^{-4}$  mole/dm<sup>3</sup>; ( $\blacktriangle$ )  $[\text{KMnO}_4] = 2.0 \times 10^{-4}$  mole/dm<sup>3</sup>; ( $\blacksquare$ )  $[\text{KMnO}_4] = 2.5 \times 10^{-4}$  mole/dm<sup>3</sup>; ( $\circ$ )  $[\text{KMnO}_4] = 3.0 \times 10^{-4}$  mole/dm<sup>3</sup>; ( $\triangle$ )  $[\text{KMnO}_4] = 4.0 \times 10^{-4}$  mole/dm<sup>3</sup>; ( $\square$ )  $[\text{KMnO}_4] = 5.0 \times 10^{-4}$  mole/dm<sup>3</sup>.  $[\text{Acrylamide}] = 35.0 \times 10^{-2}$  mole/dm<sup>3</sup>;  $[\text{lactic acid}] = 7.45 \times 10^{-2}$  mole/dm<sup>3</sup>; temperature =  $35 \pm 0.2^\circ\text{C}$ ; pH = 2.6.

TABLE 2. Dependence of the Average Molecular Weight of Polyacrylamide on the Varying Rate of Initiation<sup>a</sup>

Expt. no.	$R_{in}$ (% conversion/min)	$M \times 10^{-5}$	$\bar{P}$	$(1/\bar{P}) \times 10^4$
1	0.41	1.15	1617.89	6.18
2	0.62	1.10	1547.55	6.46
3	0.80	1.05	1477.20	6.76
4	1.02	0.98	1378.72	7.25
5	1.23	0.967	1360.43	7.35
6	1.46	0.961	1351.99	7.36

<sup>a</sup> Polymerization conditions as in Table 1.

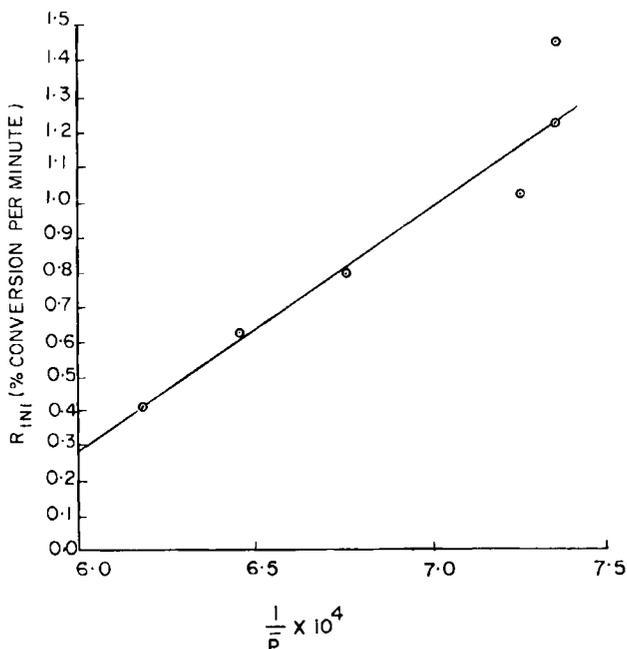


FIG. 3. Plot of reciprocal of degree of polymerization ( $1/\bar{P}$ ) vs. the rate of initiation ( $R_{in}$ ).



This may be the reason for the increase in the limiting conversion. Similar observations were made by Palit et al. [15] and Misra et al. [1, 2, 5, 6, 7, 17-20].

The overall energy of activation as calculated from the Arrhenius plot (Fig. 5) is found to be 15.6 kcal/mole (65.0 kJ/mole) within the temperature range 30 to 50°C. This is of the same order as the value found in other similar redox systems.

The molecular weight of the polymer was found to decrease with increasing temperature of the polymerization medium. Figure 6 shows an inverse relationship between the molecular weight and the temperature.

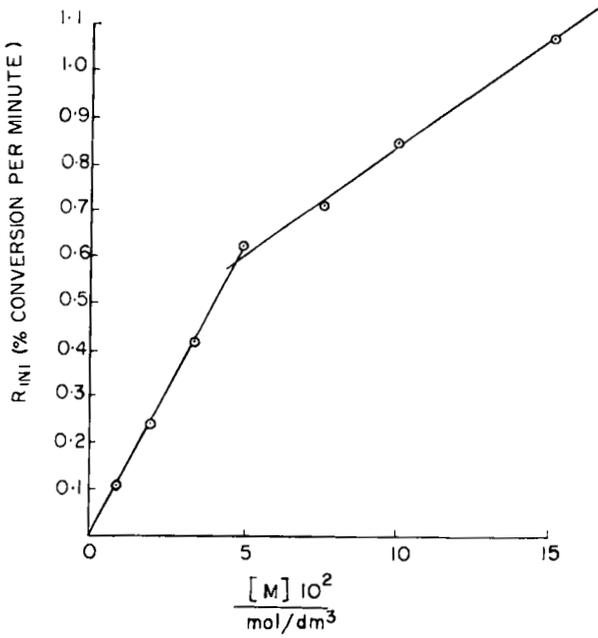


FIG. 4. Dependence of initial rate of polymerization ( $R_{in}$ ) in % conversion per minute on monomer concentration.

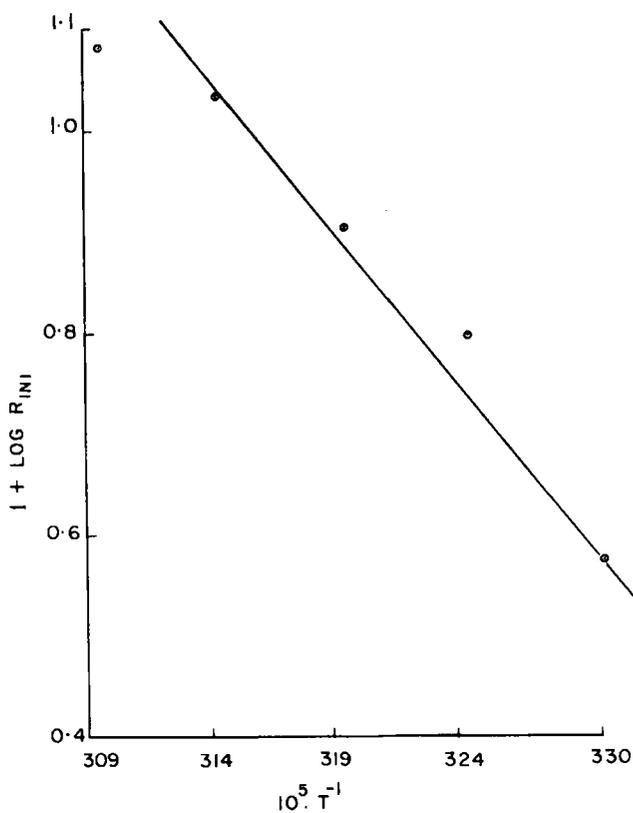


FIG. 5. Arrhenius plot of the initial rate of polymerization ( $R_{in}$ ) vs. reciprocal of absolute temperature ( $T$ ) of polymerization.

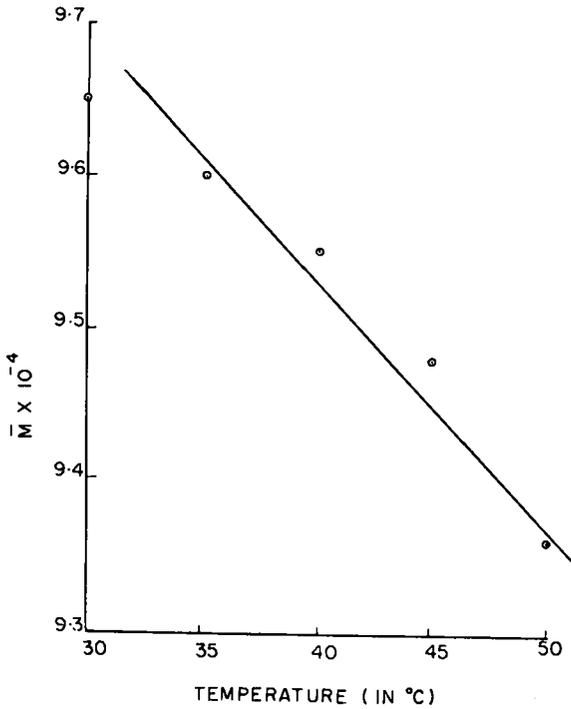


FIG. 6. Variation of molecular weight with temperature of polymerization.  $[\text{Acrylamide}] = 5.0 \times 10^{-2}$  mole/dm<sup>3</sup>;  $[\text{lactic acid}] = 7.45 \times 10^{-2}$  mole/dm<sup>3</sup>;  $[\text{KMnO}_4] = 5.0 \times 10^{-4}$  mole/dm<sup>3</sup>.

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