

POLYMERIZATION OF ACRYLAMIDE INITIATED AT A LOW TEMPERATURE BY POTASSIUM PERMANGANATE-OXALIC ACID REDOX SYSTEM

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I INTRODUCTION

The heterogenous polymerizations of methyl methacrylate¹⁾²⁾, acrylonitrile³⁾ and methylacrylate⁴⁾ have already been studied using potassium permanganate-oxalic acid redox system as an initiator. Misra et al. have recently reported the homogeneous polymerizations of acrylic acid⁵⁾, methacrylic acid⁶⁾ and acrylamide⁷⁾ initiated by the redox system at temperatures higher than 25°C. They studied the polymerization kinetics from the analysis of the remaining monomer, because the rate of polymerization was fairly high and the concentration of monomer was low. The authors were interested in the polymerization of acrylamide under a considerably concentrated state, because the considerably concentrated polymer solution was obtainable from the polymerization and so the polymer could be easily recovered by precipitation into a nonsolvent from the solution. In the considerably concentrated solution of acrylamide the rate of polymerization was so high even at 25°C that the polymerization mechanism could not be studied. The polymerization at the temperature of 10°C, however, was found to be suitable for studying the polymerization mechanism. Further the chain length of the produced polymer was estimated in the present paper.

II EXPERIMENTAL

2.1. Reagents

Acrylamide was recrystallized from a benzene solution. The melting point was 83.5–84.0°C. Potassium permanganate was recrystallized from an aqueous solution. Ferric chloride as a stopper of polymerization and oxalic acid were special grade.

2.2. Polymerization

The polymerization was carried out at 10°C in a round flask equipped with a stirrer, a tube to stream nitrogen gas and a thermometer. A certain amount of monomer was dissolved in a certain amount of water in the flask after nitrogen gas was made to flow. A given amount of aqueous solution containing potassium permanganate and oxalic acid was added to the monomer

solution to initiate polymerization. The molar ratio of oxalic acid to potassium permanganate was 2.5 which was the optimum for both the polymerization of methyl methacrylate¹⁾ and that of acrylonitrile³⁾. Each sample of 20 ml was drawn off at intervals into a weighed aqueous solution containing the stopper. The amount in each mixture was weighed and the weight of the drawn solution was determined. The mixture was poured into methanol and the polymer was precipitated. The polymer was filtered off and dried in vacuo at 40–50°C. When the aqueous solution containing potassium permanganate and oxalic acid was added to the monomer solution, it changed brownish and faded away in accordance with the progress of polymerization.

2.3. Degree of polymerization

Intrinsic viscosity number $[\eta]$ was determined from the viscosity of the one Normal sodium nitrate solution at 30°C using a Ubbelohde type viscometer. The molecular weight of the polymer was calculated from the equation

$$[\eta] = 3.73 \times 10^{-4} M_w^{0.666}$$

where M_w is the weight average molecular weight. Since the molecular weight in the polymer of each conversion showed almost a constant value up to 50%, that in 50% conversion was determined.

III RESULT

3.1. Effect of initiator

The rates and the degrees of polymerization were determined under several concentrations of potassium permanganate at the fixed monomer concentration of 0.353 mol/l (2.50%) and 10°C. The results are shown in Table 1. The time-conversion curves are shown in Fig. 1. As is evident from Table 1 and Fig. 1, the polymerization started after an induction period which decreased as the concentration of potassium permanganate increased. The plot on the logarithm of the rate of polymerization versus that of the concentration of potassium permanganate is shown in Fig. 2. The rate of polymerization is proportional to the 0.75 power of the concentration of potassium permanganate. The degree of polymerization decreased as the concentration of potassium permanganate increased and ranged between 8000 and 26000.

3.2. Effect of monomer concentration

The rates of polymerization were determined under several conditions of monomer at the fixed concentration of potassium permanganate of 0.127 mmol

Table 1 Effect of initiator concentration
(Acrylamide : 0.353 mol/l)

$\text{KMnO}_4 \times 10^4$ (mol/l)	Induction period (min)	$R_p \times 10^4$ (mol/l·sec)	DP
1.27	25	2.42	26000
2.53	14.5	4.12	21100
5.66	12	7.06	13700
6.33	10.5	8.12	8310

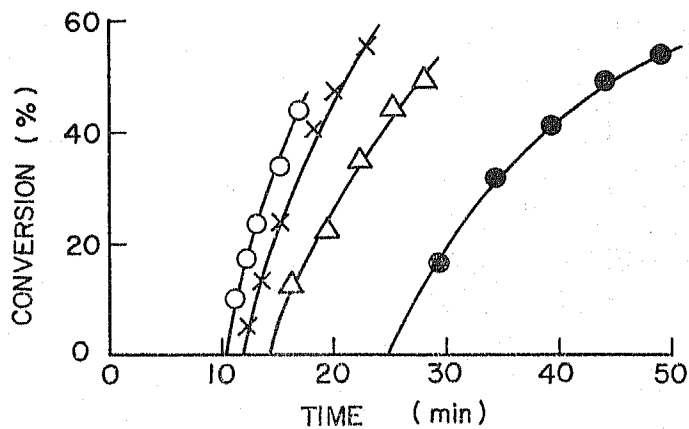


Fig. 1 Effect of initiator concentration. (Acrylamide : 0.353 mol/l, 10°C)
 KMnO_4 : \circ 6.33, \times 5.06, \triangle 2.53, \bullet 1.27×10^{-4} mol/l.

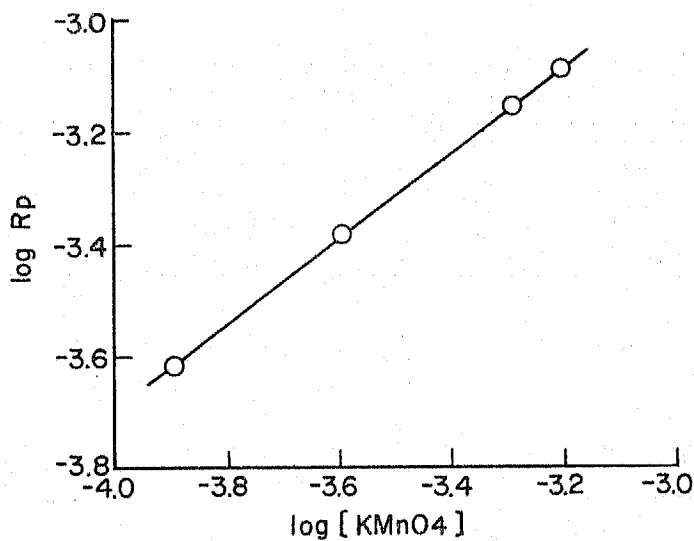


Fig. 2. Relation between the rate of polymerization and the initiator concentration. (Acrylamide : 0.353 mol/l, 10°C)

Table 2 Effect of monomer concentration
(Potassium permanganate; 1.27×10^{-4} mol/l, 10°C)

Acrylamide (mol/l)	Induction period (min)	$R_p \times 10^4$ (mol/l·sec)	DP
0.353(2.50%)	25	2.42	26000
0.706(5.00%)	8	5.89	31600
1.06 (7.50%)	10.5	11.0	44400
1.41 (10.0%)	0	—	—

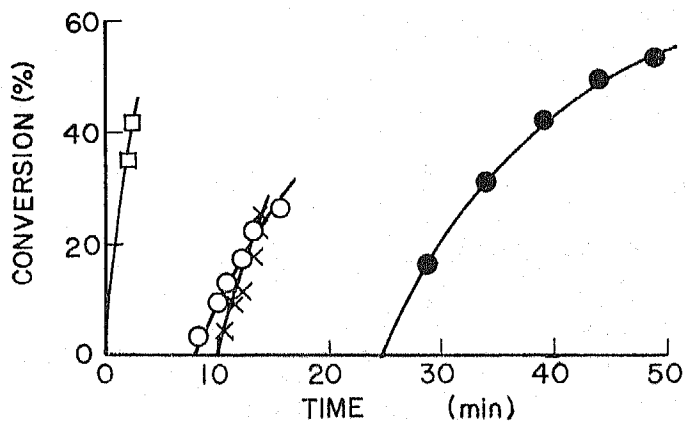


Fig. 3 Effect of monomer concentration. (KMnO_4 : 1.27×10^{-4} mol/l, 10°C)
Acrylamide : \square 1.41, \times 1.06, \circ 0.703, \bullet 0.353 mol/l

Table 3 Effect of temperature (Acrylamide : 0.353 mol/l,
potassium permanganate : 1.27×10^{-4} mol/l)

Temperature ($^\circ\text{C}$)	Induction period (min)	$R_p \times 10^4$ (mol/l \cdot sec)	DP
10	25	2.42	26000
20	13	4.35	11500
30	6	7.29	10100

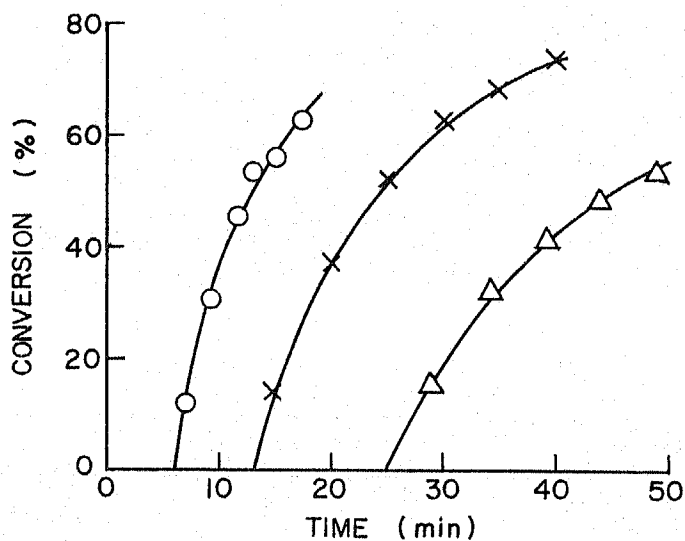


Fig. 4 Effect of temperature. (Acrylamide : 0.353 mol/l, KMnO_4 : 1.27×10^{-4} mol/l) \circ 30°C , \times 20°C , \triangle 10°C .

/1 (0.00200 %) and 10°C. The results are shown in Table 2 and Fig. 3. The polymerization started after an induction period at a monomer concentration below 1.06 mol/l, but the period was not observed at that of 1.41 mol/l. The induction period seems to decrease as the concentration of monomer increases. The rate of polymerization increased as the concentration of monomer increased and was found to be proportional to the 1.4 power of the monomer concentration from the log-log plot of the rate of polymerization versus the concentration of monomer. The polymerization proceeded rapidly at the concentration of monomer of 1.41 mol/l. The degree of polymerization increased as the concentration of monomer increased below the concentration of monomer of 1.06 mol/l.

3.3. Effect of temperature

The rates of polymerization were determined at 10, 20 and 30°C at the fixed concentrations of monomer of 0.353 mol/l and of potassium permanganate of 0.127 mmol/l. The rates and the degrees of polymerization are summarized in Table 3. The time-conversion curves are shown in Fig. 4. The induction period and the degree of polymerization decreased and the rate of polymerization increased as the temperature of polymerization increased.

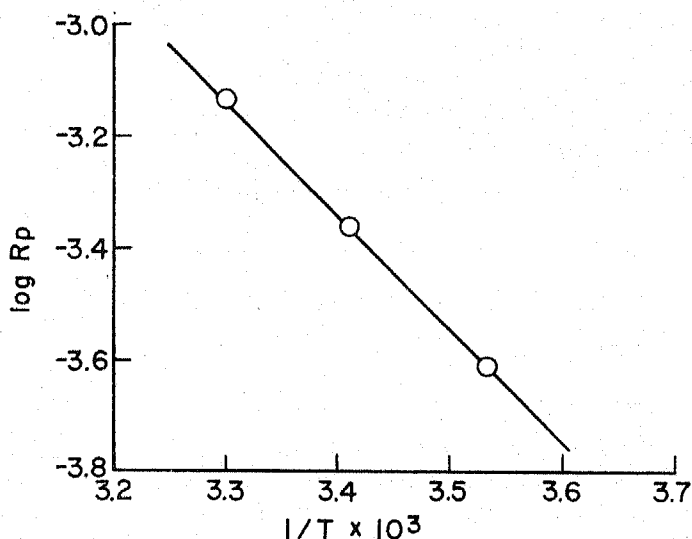


Fig. 5 Arrhenius plot of the rate of polymerization.
(Acrylamide : 0.353 mol/l, KMnO_4 : 1.27×10^{-4} mol/l)

Table 4 Relation between degree of polymerization DP and conversion
(Acrylamide : 0.353 mol/l, potassium permanganate : 1.27×10^{-4} mol/l, 10°C)

Conversion (%)	15.6	31.1	40.6	48.8	53.0
DP	26000	25300	25600	21700	22700

The Arrhenius plot of polymerization is shown in Fig. 5. The activation energy was 9.2 Kcal/mol.

3.4. Relation between the conversion and the degree of polymerization

The relation is shown in Table 4. The degree of polymerization keeps almost a constant value regardless the conversion up to 50 %.

IV DISCUSSION

4.1. Rate of polymerization

4.1.1. Effect of initiator concentration

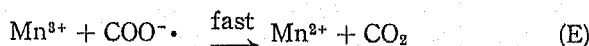
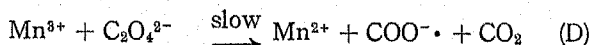
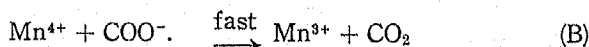
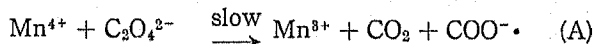
The rate of polymerization was found to be proportional to the 0.75 power of the concentration of potassium permanganate. Misra et al. have reported that the rate of polymerization was proportional to the 0.5–1.0 power of the concentration of potassium permanganate in the case of the polymerization of acrylic acid⁵⁾, methacrylic acid⁶⁾ and acrylamide⁷⁾ by potassium permanganate-oxalic acid redox system at 30°C and thus that the monomolecular termination with a dissolved metal ion occurred. It seems that the present result can be explained by the occurrence of the same termination as described above.

4.1.2. Overall activation energy

The overall activation energy was 9.2 Kcal/mol. Misra et al.⁷⁾ reported that it was 12 Kcal/mol. These values are identical with the activation energy of the redox polymerization.

4.2. Initiation mechanism and induction period

Launer et al.⁹⁾ proposed the following mechanism for the reaction of potassium permanganate with oxalic acid.



The ion radical $\text{COO}^{\cdot-}$ has been thought to initiate polymerization.^{2)-d5)6)7)} The induction period which decreased with an increase of the concentration of potassium permanganate or monomer was found in the present study. If we assume that Mn^{4+} ion changes into Mn^{3+} ion through its slow reaction with acrylamide instead of oxalate ion, and the Mn^{3+} ion reacts with oxalate ion to produce the ion radical $\text{COO}^{\cdot-}$, the presence of the induction period which depends on the concentration of monomer or potassium permanganate will be explained. Sakurada et al.¹⁰⁾ reported that the polymerization of acrylamide by periodic acid was initiated by the radical produced through the reaction between the two substances. Misra et al. did not observe the induction period. It is seemingly due to high polymerization temperature.

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V SUMMARY

Aqueous polymerization of acrylamide was initiated at 10°C by potassium permanganate-oxalic acid redox system. The polymerization proceeded smoothly in the case of the monomer concentration 0.353 mol/l (2.50%). The rate of polymerization was found to be proportional to the 0.75 power of the concentration of potassium permanganate in the concentration range of 0.127 to 0.633 mmol/l. The degree of polymerization of the polymer obtained ranged from 26000 to 8300. The results can be explained by the presence of both the monomolecular termination arising from the reaction of the growing chain with a dissolved metal ion and the bimolecular termination. The rate of polymerization was also found to increase with increasing concentration of acrylamide in the concentration range of 0.353 to 1.41 mol/l.

The overall activation energy of polymerization was 9.2 Kcal/mol in the temperature range of 10 to 30°C.

Induction periods were found in this polymerization. The period decreased as the concentration of potassium permanganate or that of acrylamide increased. This result seems to indicate that the reaction of Mn^{4+} ion with acrylamide occurs to produce Mn^{3+} ion and the ion radical $COO^{\cdot-}$ is produced by the reaction of the Mn^{3+} ion with oxalic acid.

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