Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

# Polymerization of Acrylamide with Permanganate/Mercaptosuccinic Acid Initiator System

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**To cite this Article** Misra, G. S. and Bhattacharya, S. N.(1980) 'Polymerization of Acrylamide with Permanganate/Mercaptosuccinic Acid Initiator System', Journal of Macromolecular Science, Part A, 14: 6, 907 — 914

**To link to this Article: DOI:** 10.1080/00222338008068120

**URL:** http://dx.doi.org/10.1080/00222338008068120

J. MACROMOL. SCI.–CHEM., A14(6), pp. 907-914 (1980)

# Polymerization of Acrylamide with Permanganate/Mercaptosuccinic Acid Initiator System

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## ABSTRACT

The aqueous polymerization of acrylamide initiated by the acidified potassium permanganate/mercaptosuccinic acid redox system was studied at 35 ± 0.2°C in nitrogen. In the studied range of activator concentration ($2.0 \times 10^{-3}$ to $6.25 \times 10^{-3}$ mole/liter) the polymerization rate remains unaffected. The initial rate of polymerization varies linearly with $KMnO_4$ and acrylamide concentrations in the studied range. The activation energy was found to be 6.61 kcal/mole (27.63 kJ/mole) in the temperature range of 30-50°C. The molecular weight of polyacrylamide was found to be independent of $[KMnO_4]$ but increased with increasing monomer concentration. The effect of DMF on polymerization rate and molecular weight was also investigated.

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## INTRODUCTION

Thiols have recently been used as the redox component to initiate the aqueous polymerization of acrylamide [1-3] and methacrylamide [4]. The present study deals with the kinetics of aqueous polymerization of acrylamide initiated by the acidified permanganate/mercaptosuccinic acid redox system. The effect of catalyst and monomer concentrations on the molecular weight of the polymer formed has also been investigated.

## EXPERIMENTAL

Acrylamide was crystallized twice from methanol (GR) and dried under vacuum. Mercaptosuccinic acid was used without further purification. All other reagents were of AR or equivalent grade. Doubly distilled water was used as solvent in all experiments.

The polymerization was followed by quantitative estimation of the double bonds in acrylamide as described by Wallace et al. [5]. The technique adopted was similar to that of Misra et al. [6]. The percentage conversion was calculated by using the formula given by Misra et al. [7]. The viscosities were determined in water at 30°C. Molecular weights were calculated from viscosity measurements by using the relationship of Dainton et al. [8].

## RESULTS AND DISCUSSION

Formamidine disulfide is produced by oxidation of thiourea with acid permanganate by intermediate isothiocarbamide radical formation [9]. Mercaptosuccinic acid (I) is known to oxidize to dithiodisuccinic acid (III) [10]. A two-step reaction scheme [Eqs. (1) and (2)] may be proposed for the oxidation of I by acid permanganate in light of the suggestions made by Palit et al. [11].

$$\underset{\mathrm{I}}{(\mathrm{COOH})_2\mathrm{CH}_2(\mathrm{COOH})_2} \xrightarrow{[\mathrm{O}]} \underset{\mathrm{II}}{(\mathrm{COOH})_2\mathrm{CH}_2\mathrm{CH}\dot{\mathrm{S}}} \qquad (1)$$

$$\mathrm{II} \longrightarrow (\mathrm{COOH})_2\mathrm{CH}_2\cdot\mathrm{CHS}\cdot\mathrm{SHC}\,\mathrm{CH}_2(\mathrm{COOH})_2 \qquad (2)$$

In the presence of a polymerizable monomer (acrylamide) reaction (1) is rapidly followed by the addition reaction (3):

$$(\mathrm{COOH})_2\mathrm{CH}_2\mathrm{CH}\dot{\mathrm{S}} + \mathrm{M} \longrightarrow \dot{\mathrm{M}} \qquad (3)$$

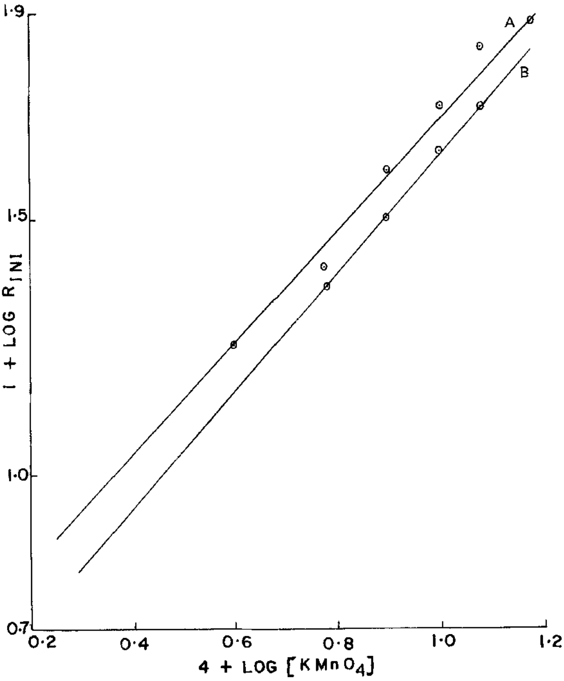

FIG. 1. Double logarithmic plot of the initial rate of polymerization $R_{INI}$ (in % conversion/min) vs. concentration of catalyst (potassium permanganate) (mole/liter): (A) in aqueous medium; (B) in presence of 5% DMF (v/v). [TMA] = $3.0 \times 10^{-3}$ mole/liter; [acrylamide] = $5.0 \times 10^{-2}$ mole/liter; [$H_2SO_4$] = $5.0 \times 10^{-2}$ mole/liter; 35 ± 0.2°C.

The rate of polymerization was independent of the activator concentration in the range $2.0\text{-}6.25 \times 10^{-3}$ mole/liter at fixed concentrations of catalyst ($6.0 \times 10^{-4}$ mole/liter) and monomer ($5.0 \times 10^{-2}$ mole/liter). When the concentration of activator (I) is several times the catalyst concentration, the population of free radicals would be independent of activator concentration. Hence the rate of polymerization, being dependent only on the concentration of the reactive species, would be independent of the concentration of I.

The initial rate of polymerization and the percentage conversion increased with increasing concentration of the catalyst at a fixed concentration of activator ($3.0 \times 10^{-3}$ mole/liter) and monomer ($5.0 \times 10^{-2}$ mole/liter). Since acidic potassium permanganate oxidizes I to II, on increasing initial catalyst concentration in the system more of I gets oxidized which subsequently raises the concentration of

TABLE 1. Dependence of Molecular Weight on the Initial Concentration of Catalyst[a]

| Expt. no. | $[KMnO_4] \times 10^4$ (mole/liter) | $R_{INI}$ (% conversion/min) | Molecular weight | Degree of polymerization |
|---|---|---|---|---|
| 1 | 8.0 | 2.64 | 4192 | 58.98 |
| 2 | 10.0 | 3.60 | 4086 | 57.48 |
| 3 | 12.0 | 4.68 | 3910 | 55.00 |
| 4 | 15.0 | 5.51 | 3708 | 52.17 |

[a] $[AA] = 1.5 \times 10^{-1}$ mole/liter; $[TMA] = 3.0 \times 10^{-3}$ mole/liter; $[H_2SO_4] = 5.0 \times 10^{-2}$ mole/liter; 35 ± 0.2°C.

sulfhydryl radicals, thereby increasing the rate of polymerization and the percentage conversion. The catalyst exponent, obtained from the slope of the double logarithmic plot of initial rate versus concentration of catalyst (Fig. 1), is almost unity. This indicates a first-order dependence of the polymerization rate on the catalyst concentration as well as the unimolecular termination of the growing chain probably due to dissolved metal ions or degradative chain transfer reaction [12-14].

With decrease in the initial concentration of the catalyst the molecular weight of the polymer formed should increase because of the low concentration of propagating polymer radicals. From Table 1 it seems that with decreasing catalyst concentration the increase in molecular weight is not very appreciable and the latter may be considered as almost independent of catalyst concentration. This may be attributed to the termination of a growing polymer radical by chain transfer reaction mainly with mercaptosuccinic acid (RSH) present in the system

$$\dot{M}n + RSH \longrightarrow Mn\text{-}H + R\dot{S} \qquad (4)$$

The initial polymerization rate and the conversion were found to increase with increasing monomer concentration at a fixed concentration of catalyst and activator (Fig. 2). The rate of polymerization (conversion in mole/liter-min) is directly proportional to the first power of the initial concentration of the monomer in the studied range (Fig. 3). Similar results have also been reported for the polymerization of acrylamide by using persulfate/thiomalic acid redox pair [15].

With the increase in the initial monomer concentration, the molecular weight of the resulting polymer is increased (Table 2). This

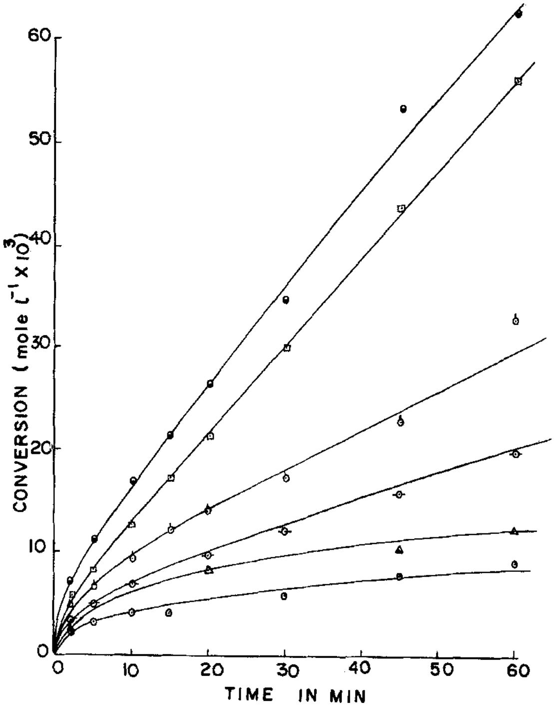

FIG. 2. Plot of initial course of polymerization for various initial concentration of monomer: ( ⊙ ) [AA] = 5.0 × $10^{-2}$ mole/liter; ( △ ) [AA] = 7.5 × $10^{-2}$ mole/liter; (-⊙-) [AA] = 10.0 × $10^{-2}$ mole/liter; ( ϕ ) [AA] = 15.0 × $10^{-2}$ mole/liter; ( ⊡ ) [AA] = 20.0 × $10^{-2}$ mole/liter; ( ● ) [AA] = 25.0 × $10^{-2}$ mole/liter. [$KMnO_4$] = 6.0 × $10^{-4}$ mole/liter; [TMA] = 3.0 × $10^{-3}$ mole/liter; 35 ± 0.2°C.

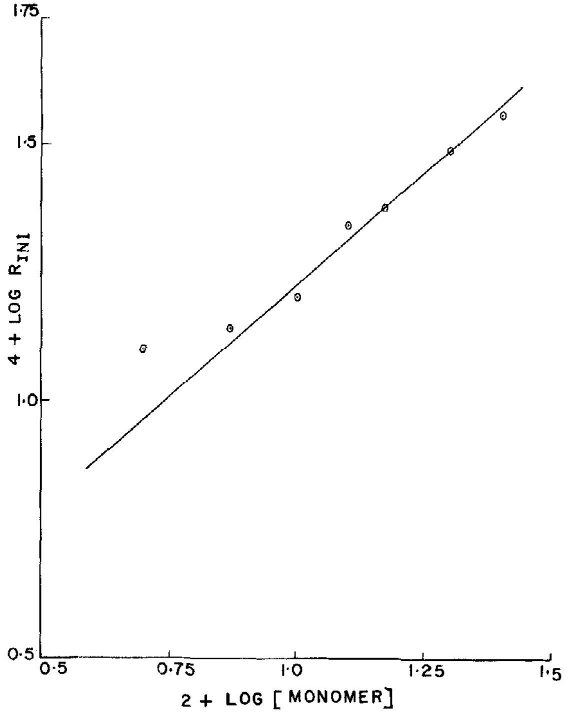

FIG. 3. Double logarithmic plot of the initial rate of polymerization $R_{INI}$ (mole/liter-min) vs. concentration of monomer (mole/liter). [$KMnO_4$] = 6.0 × $10^{-4}$ mole/liter; [TMA] = 3.0 × $10^{-3}$ mole/liter; [$H_2SO_4$] = 5.0 × $10^{-2}$ mole/liter; 35 ± 0.2°C.

TABLE 2. Dependence of Molecular Weight on the Initial Concentration of Monomer[a]

| Expt. no. | [Acrylamide] × $10^2$ (mole/liter) | $R_{INI}$ × $10^4$ (mole/liter-min) | Molecular weight | Degree of polymerization |
|---|---|---|---|---|
| 1 | 12.5 | 21.5 | 3385 | 47.62 |
| 2 | 15.0 | 23.5 | 4488 | 63.14 |
| 3 | 20.0 | 30.5 | 6231 | 87.66 |
| 4 | 25.0 | 36.0 | 7474 | 105.15 |

[a] [$KMnO_4$] = 6.0 × $10^{-4}$ mole/liter; [TMA] = 3.0 × $10^{-3}$ mole/liter; [$H_2SO_4$] = 5.0 × $10^{-2}$ mole/liter; 35 ± 0.2°C.

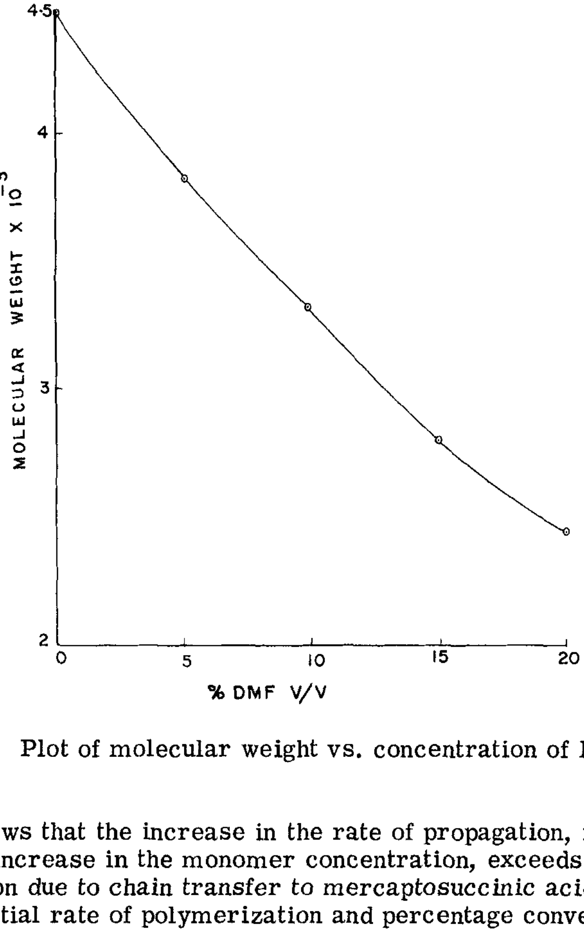

FIG. 4. Plot of molecular weight vs. concentration of DMF.

result shows that the increase in the rate of propagation, resulting from the increase in the monomer concentration, exceeds the rate of termination due to chain transfer to mercaptosuccinic acid.

The initial rate of polymerization and percentage conversion rise with an increase in polymerization temperature. High temperature favors the generation of free radicals by the oxidation of I, with the result that the concentration of sulfhydryl radicals increases, thus increasing the initial rate as well as percentage conversion. The overall energy of activation as calculated from the Arrhenius plot is 6.61 kcal/deg-mole (27.63 kJ/mole) in the temperature range 30-50°C.

Dimethylformamide (DMF) depresses both the initial rate and the percentage conversion. The dependence of the polymerization rate on catalyst concentration remains unity in presence of 5% DMF (Fig. 1). This shows that no change in the mode of termination takes place on addition of DMF. The molecular weight of the resulting polymer decreases with increasing initial DMF concentration. The decrease in the molecular weight is probably due to premature termination of the growing polymer chains by transfer to DMF, and the molecular weight of the polymer is regulated by the initial DMF concentration (Fig. 4).

## ACKNOWLEDGMENT

The authors thank the University Grants Commission (India) for financial assistance to one of them (S. N. B.).

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Accepted by editor April 9, 1979
Received for publication May 14, 1979