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

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To cite this Article Misra, G. S. and Dubey, G. P.(1981) 'Aqueous Polymerization of Acrylamide Initiated by Ce(lV)-Thioglycolic Acid Redox System', Journal of Macromolecular Science, Part A, 16: 3, 601 — 613
To link to this Article: DOI: 10.1080/00222338108056808
URL: http://dx.doi.org/10.1080/00222338108056808

J. MACROMOL. SCI.–CHEM., A16(3), pp. 601-613 (1981)

Aqueous Polymerization of Acrylamide Initiated by Ce(IV)-Thioglycolic Acid Redox System

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ABSTRACT

The aqueous polymerization of acrylamide initiated by the redox system Ce(IV)-thioglycolic acid has been studied at 35 ± 0.2°C. The pH measurement shows that a 1:1 metal:ligand complex is formed between Ce(IV) and thioglycolic acid (TGA). The rate of polymerization is given by

$$R_p = K[M]^{1.08}[Ce^{4+}]^{0.65}[TGA]^0$$

The overall energy of activation has been found to be 4.56 kcal/deg/mol (19.06 kJ/mol). The number-average molecular weight ($\overline{M}_n$) of the polymer is directly proportional to the rate of polymerization. The $\overline{M}_n$ of the polymer decreases with increasing concentration of both Ce^{4+} and DMF.

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INTRODUCTION

Thiols have been used as molecular weight modifiers in industrial emulsion polymerization. The use of thiols as components of redox systems for the polymerization of vinyl monomer is of recent origin.

Ce(IV) has been used as an oxidant with various reducing agents such as alcohols [1, 2], aldehydes [3, 4], amines [5, 6], glycerol [7, 8], and thiols [9, 10] by various workers. In the present investigation, thioglycolic acid in combination with Ce(IV) has been used for the aqueous polymerization of acrylamide.

EXPERIMENTAL

Materials

Acrylamide was crystallized twice from methanol and dried in vacuum. Thioglycolic acid (S. Merck) was used without further purification. Ceric ammonium sulfate and all other reagents were of AR or equivalent grade. All solutions were prepared in double distilled water.

Technique

The polymerization was followed by quantitative estimation of the double bonds in acrylamide as described by Wallace et al. [11]. The technique adopted was similar to that used by Misra et al. [12, 13]. The number-average molecular weights ($\overline{M}_n$) of the polymers were determined by viscosity measurement at 30°C in aqueous medium using the relationship of Dainton et al. [14]:

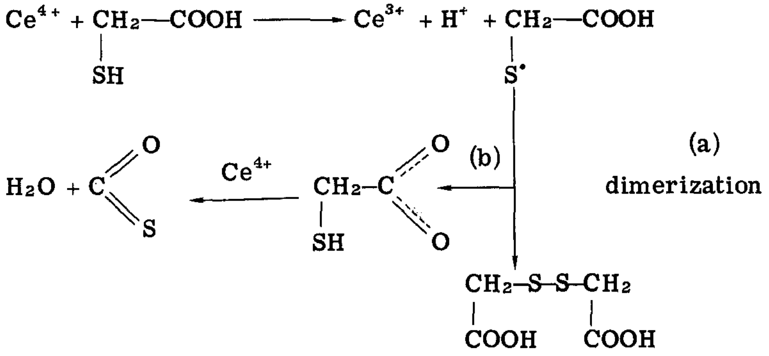
$$[\eta]_{30^\circ} = 6.8 \times 10^{-4}\ \overline{M}_n^{\,0.66}$$

where $[\eta]$ is the intrinsic viscosity of the polymer solution and $\overline{M}_n$ is the number-average molecular weight of the sample.

RESULTS AND DISCUSSION

Mechanism

McAuley et al. [15] have studied the oxidation of thioglycolic acid by Ce(IV), and have suggested the following reaction mechanism:



(1)

From the above reaction scheme it has been concluded that, in the presence of vinyl monomer, the carboxymethylthio free radicals ($\underset{\dot{S}}{\underset{|}{CH_2-COOH}}$ or $R\dot{S}$) initiate the polymerization reaction rather than Reactions (a) and (b). The formation of a similar type of 1:1 metal: ligand complex has also been observed in this system, as found in other similar systems [9].

The chain transfer constant of thioglycolic acid (mercaptoacetic acid) for methyl methacrylate is 0.63 and for styrene is > 14.0. Hence it is presumed that termination also takes place by transfer reaction to TGA. On the basis of the above facts, a plausible mechanism is

$$Ce^{4+} + RSH \overset{fast}{\rightleftharpoons} [complex] \xrightarrow[H_2SO_4]{slow} R\dot{S} + Ce^{3+} + H^+ \qquad (2)$$

Initiation:

$$M + R\dot{S} \longrightarrow \dot{M} \qquad (3)$$

Propagation:

$$M + \dot{M} \longrightarrow \dot{M}_2 \qquad (4)$$

$$M_{(n-1)} + \dot{M} \longrightarrow \dot{M}_n \qquad (5)$$

Termination by coupling:

$$\dot{M}_n + \dot{M}_m \longrightarrow M_{(n+m)} \qquad (6)$$

Termination by Ce^{4+}:

$$\dot{M}_n + Ce^{4+} \longrightarrow Ce^{3+} + H^+ + \text{dead polymer} \qquad (7)$$

Chain transfer:

$$\dot{M}_n + RSH \longrightarrow M_nH + R\dot{S} \qquad (8)$$

Dimerization:

$$R\dot{S} + \dot{S}R \longrightarrow R{-}S{-}S{-}R \qquad (9)$$

where RSH represents thioglycolic acid, $R\dot{S}$ is carboxymethylthio free radical, M and $\dot{M}$ are the monomer and monomer free radicals, respectively, and $\dot{M}_2$ and M_n represent growing polymer chains.

Study of the Complex

The yellowish complex which is formed between cerium(IV) and thioglycolic acid is insoluble in water and most of the organic solvents but it is easily decomposed in strong acidic medium (pH 1.2). It does not melt up to 300°C. The high conductance (0.625×10^{-2} mhos) of the complex indicates it to be an electrolyte. pH measurements show that at an equimolar concentration of metal and ligand (TGA), a sudden break in the pH is observed, confirming a 1:1 metal:ligand complex has been formed.

The IR spectroscopy further confirmed the complex formation. IR of the complex and ligand were recorded in the region of 4000-200 cm^{-1} (Table 1). A sharp absorption peak of the –SH group was observed at 2550 cm^{-1} in the ligand and disappeared in the complex. This shows involvement of the –SH group in the complex formation. The peak of $>C{=}O$ observed at 1720 cm^{-1} in the ligand shows a shift to 1630 cm^{-1} in the complex. Also, the peak of C–O stretching observed at 1400 cm^{-1} in the ligand shows a shift to 1210 cm^{-1} in the complex. These shifts indicate involvement of the carboxyl group in the complex formation.

The metal-oxygen and metal-sulfur bondings are further confirmed in the far-IR region. The two peaks obtained in the complex at 560 and 480 cm^{-1}, which were absent in the ligand, correspond to metal-oxygen and metal-sulfur bondings, respectively. A similar type of complex formation has also been observed in a similar system studied earlier [9].

TABLE 1. Important Infrared Spectral Bands of Thioglycolic Acid and Its Complex[a]

Compound	–SH	$>C=O$	–C–O str.	M–O	M–S
TGA	2550 cm^{-1}	1720 cm^{-1}	1400 cm^{-1}	-	-
Complex	-	1630 cm^{-1}	1210 cm^{-1}	560 cm^{-1}	480 cm^{-1}

[a] M represents cerium.

Catalyst Effect

The initial rate of polymerization and the maximum conversion have both been observed to increase with increasing catalyst concentration (Fig. 1).

Two sets of experiments were carried out at monomer concentrations of 5.0×10^{-2} and 15.0×10^{-2} mol/L and at fixed concentrations of TGA and sulfuric acid. The concentration ranges of the catalyst in both sets of experiments were the same (5.0×10^{-4} to 25.0×10^{-4} mol/L). At a higher concentration of ceric ions ($> 20.0 \times 10^{-4}$ mol/L), the initial rate and the maximum conversion have both been observed to decrease.

The catalyst exponent was found to be 0.65, which indicates approximately a half-order dependence of the rate of polymerization on the catalyst concentration. The half-order dependence indicates that the termination of the growing polymer chains takes place by coupling. The deviation of the catalyst exponent from 0.5 to 0.65 may be due to termination of the growing polymer chains by ceric ions.

The number-average molecular weight ($\overline{M}_n$) of the polymers was found to decrease with increasing ceric ion concentration (Table 2).

Activator Effect

The initial rate of polymerization has been found to be independent of thioglycolic acid concentration in the range 3.75×10^{-3} to 8.75×10^{-3} mol/L. A marginal increase in the rate is observed, however, in a small concentration range of TGA (2.5×10^{-3} to 3.75×10^{-3} mol/L) and at a fixed concentration of catalyst (1.0×10^{-3} mol/L) and monomer (5.0×10^{-2} mol/L). Above 7.5×10^{-3} mol/L of TGA, the maximum conversion was found to decrease, possibly due to the dimerization reaction of $R\dot{S}$ radicals (Table 3).

The independence of the initial rate of polymerization on the activator concentration is possibly due to a balance existing between the

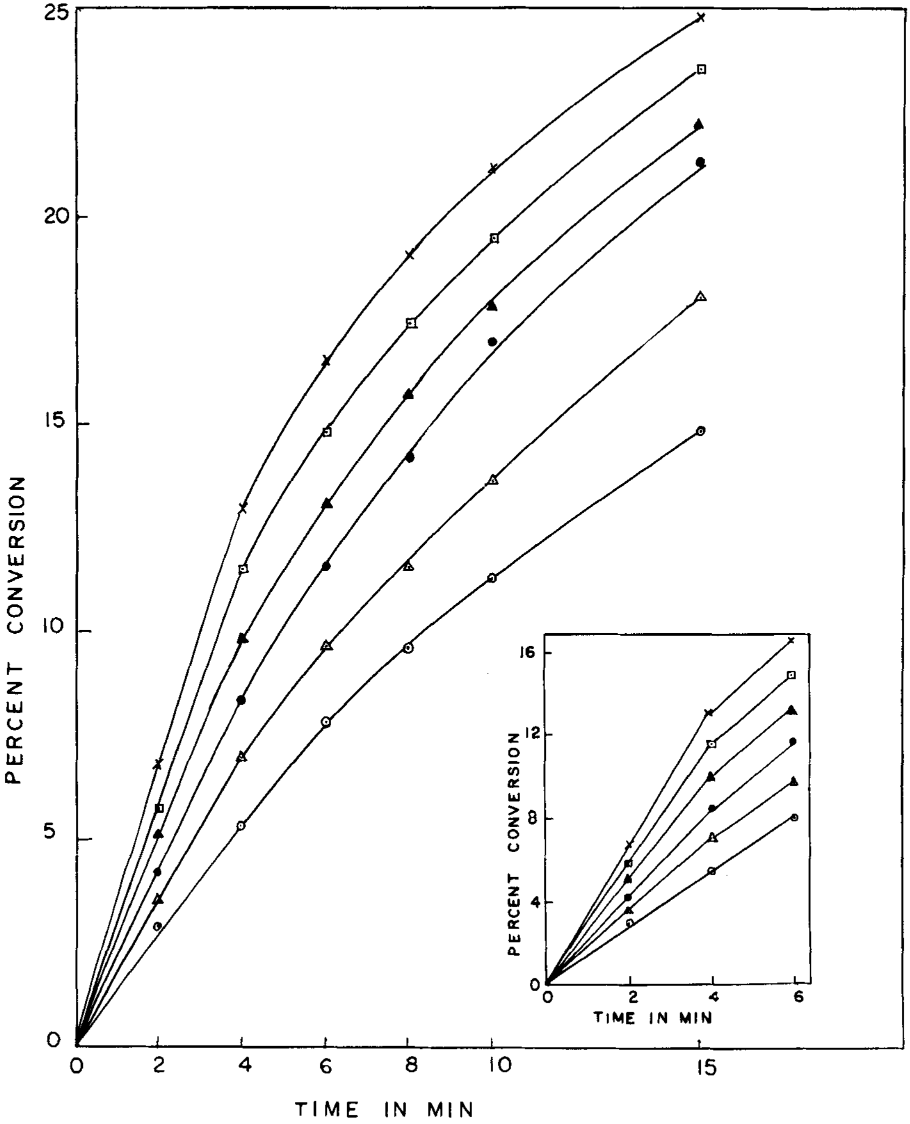


FIG. 1. Time vs % conversion curves for the aqueous polymerization of acrylamide with varying initial concentrations of ceric ammonium sulfate. [Acrylamide] = 5.0×10^{-2} mol/L, [TGA] = 5.0×10^{-3} mol/L, [H_2SO_4] = 0.25 mol/L, temperature = 35 ± 0.2°C, (⊙) [Ce^{4+}] = 5.0×10^{-4} mol/L, (△) [Ce^{4+}] = 7.5×10^{-4} mol/L, (•) [Ce^{4+}] = 1.0×10^{-3} mol/L, (▲) [Ce^{4+}] = 1.25×10^{-3} mol/L, (⊡) [Ce^{4+}] = 1.5×10^{-3} mol/L, (x) [Ce^{4+}] = 2.0×10^{-3} mol/L. Inset: Plot of conversion curves up to 6 min.

TABLE 2. Effect of Catalyst on Molecular Weight of the Polymer[a]

Expt. no.	$[Ce^{4+}] \times 10^4$ mol/L	Molecular weight	$\bar{p}$
1	5.0	3377	47.56
2	10.0	3214	45.21
3	15.0	3042	42.79
4	20.0	2673	37.60
5	25.0	2580	36.32

[a] [Acrylamide] = 15.0×10^{-2} mol/L, [TGA] = 5.0×10^{-3} mol/L, $[H_2SO_4]$ = 0.25 mol/L, temperature = 35 ± 0.2°C.

rate of generation of the primary free radicals and the rate of the side reactions.

Below a certain concentration (2.5×10^{-3} mol/L) of TGA, no polymerization has been found to occur, perhaps due to the low production of primary free radicals.

Low molecular weight polymers have been obtained because TGA acts as a chain transfer agent (Step 8):

$$\dot{M}_n + RSH \longrightarrow M_nH + R\dot{S}$$

It has been concluded from the above reaction that no reduction in the rate of polymerization is expected because, during the process of chain transfer, one radical is terminated and another is formed, which can take part in the propagation reaction.

The independence of the initial rate of polymerization on activator concentration has also been observed by Hussain et al. [16] in the polymerization of acrylamide by the acidified potassium permanganate-thioglycolic acid redox system.

Monomer Effect

The initial rate of polymerization and maximum conversion (in mol/L) both increase with increasing monomer concentration in the concentration range studied (5.0×10^{-2} to 15.0×10^{-2} mol/L). The concentrations of catalyst (1.0×10^{-3} mol/L) and activator (5.0×10^{-3} mol/L) were kept constant in the study of the monomer effect.

The monomer exponent was found to be 1.08 (Fig. 2), confirming the first power dependence of the rate of polymerization on monomer concentration.

TABLE 3. Aqueous Polymerization of Acrylamide with Varying Initial Concentration of Thioglycolic Acid[a]

Expt. no.	[TGA] × 10^3 mol/L	% conversion with reaction time in min							
		2	3	5	10	15	20	25	30
1	2.5	2.05	4.0	6.68	12.3	15.93	19.53	23.13	24.4
2	3.75	4.11	5.4	7.71	13.4	18.01	22.10	24.15	25.3
3	5.0	4.2	6.0	10.01	17.04	21.33	24.88	26.3	27.65
4	6.25	4.2	6.2	10.4	17.2	21.7	25.0	27.24	29.29
5	7.5	4.2	6.2	10.79	17.47	23.13	26.7	29.29	31.86
6	8.75	4.2	5.6	8.73	14.9	19.01	22.61	25.18	26.21

[a] [Acrylamide] = 5.0×10^{-2} mol/L, [Ce^{4+}] = 1.0×10^{-3} mol/L, [H_2SO_4] = 0.25 mol/L, temperature = 35 ± 0.2°C.

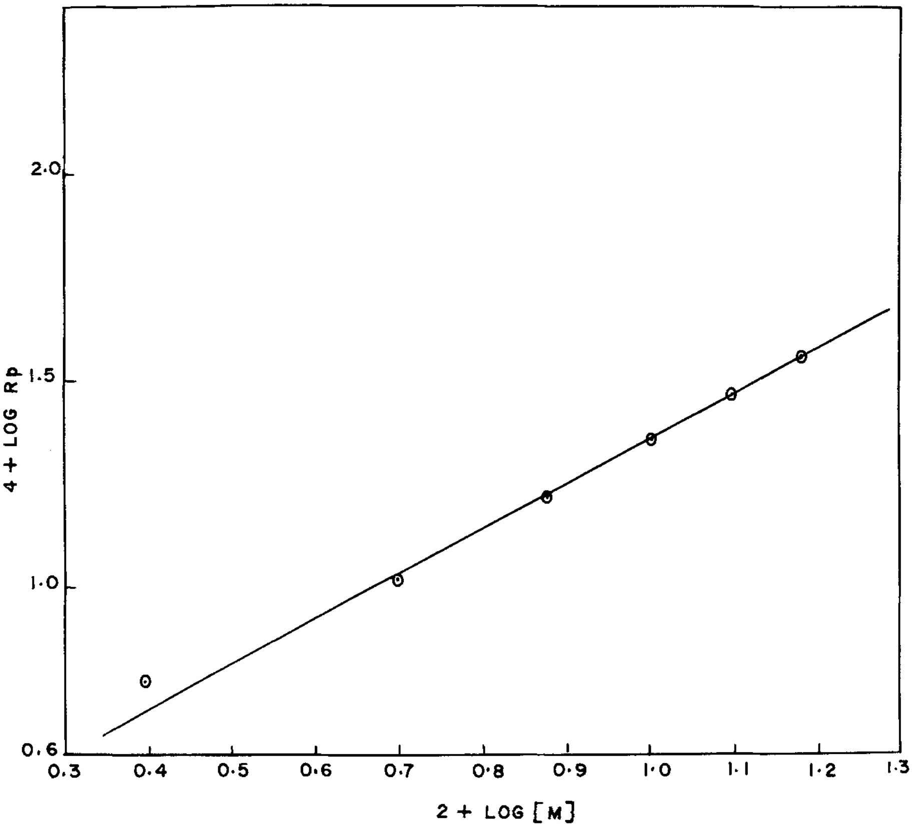


FIG. 2. Double logarithmic plot of the initial rate of polymerization vs the concentration of monomer. [Ce^{4+}] = 1.0×10^{-3} mol/L, [TGA] = 5.0×10^{-3} mol/L, [H_2SO_4] = 0.25 mol/L, temperature = 35 ± 0.2°C.

The $\overline{M}_n$ of the polymers increases with increasing monomer concentration. The plot of the number-average molecular weight vs the initial rate of polymerization gives a straight line, showing that the rate of polymerization is directly proportional to the $\overline{M}_n$ (Fig. 3). Low molecular weight polymers have been obtained. A similar result has been observed in a previous system [9].

Temperature Effect

The effect of temperature was studied in the range 25 to 45°C. The initial rate of polymerization and the maximum conversion

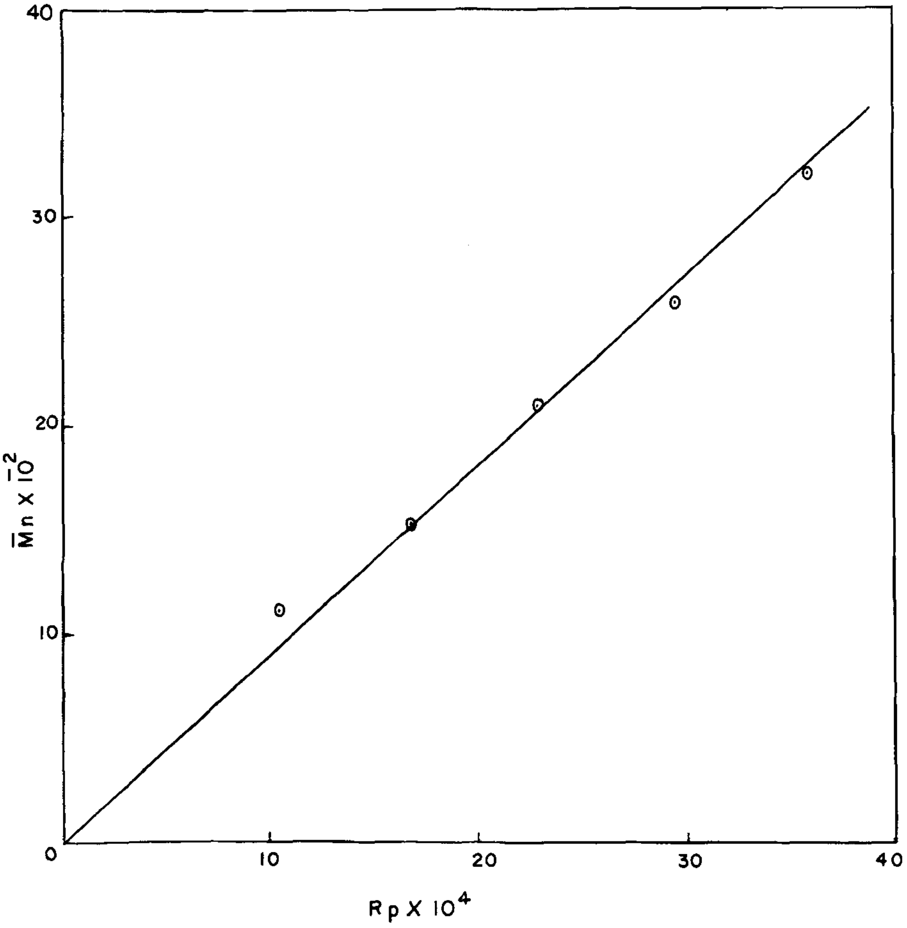


FIG. 3. Plot of the number-average molecular weight ($\overline{M}_n$) vs the rate of polymerization. [TGA] = 5.0×10^{-3} mol/L, [Ce^{4+}] = 1.0×10^{-3} mol/L, [H_2SO_4] = 0.25 mol/L, temperature = 35 ± 0.2°C.

increase with an increase in temperature from 25 to 35°C. Above this temperature the initial rate of polymerization increases but the maximum conversion decreases. High temperature favors the formation of primary free radicals ($R\dot{S}$) and the dimerization reaction in which the $R\dot{S}$ free radicals are consumed and the maximum conversion decreases.

The overall energy of activation calculated by the Arrhenius plot was found to be 4.56 kcal/deg/mol (19.06 kJ/mol) in the temperature

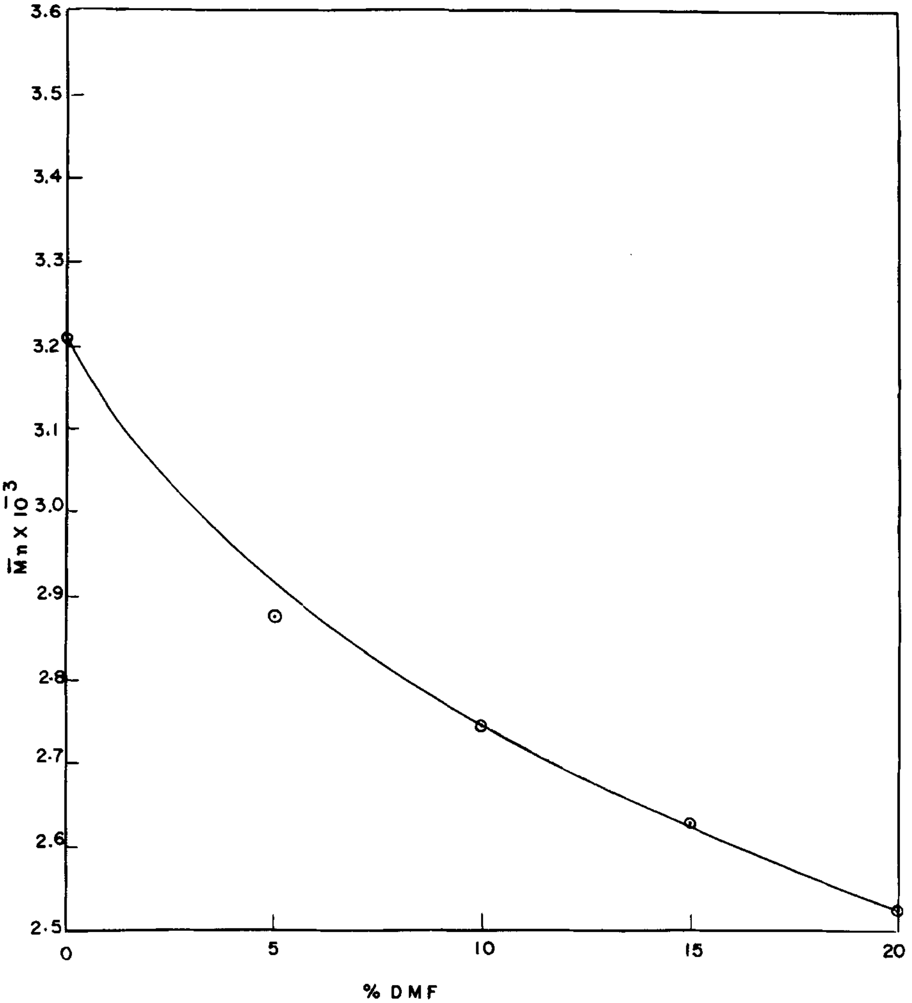


FIG. 4. Plot of the number-average molecular weight of the polymer ($\bar{M}_n$) vs % DMF. [TGA] = 5.0×10^{-3} mol/L, [acrylamide] = 15.0×10^{-2} mol/L, [Ce^{4+}] = 1.0×10^{-3} mol/L, [H_2SO_4] = 0.25 mol/L, temperature = 35 ± 0.2°C.

range 25-45°C. The energy of activation, 4.6 kcal/deg/mol, was also observed by Nayak et al. [17] in the polymerization of acrylonitrile initiated by dipotassium peroxidisulfate-citric acid catalyzed by Ag^+ system.

Effect of N,N-Dimethylformamide on $\overline{M}_n$ of the Polymer

The effect of DMF on the molecular weight of the polymer has also been studied. The range studied of DMF was 5 to 20% v/v. The $\overline{M}_n$ of the polymer decreases with an increase in DMF percentage (Fig. 4).

ACKNOWLEDGMENT

The authors desire to thank the Council of Scientific and Industrial Research (India) for financial assistance to one of them (G.P.D.).

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Accepted by editor March 3, 1980
Received for publication April 22, 1980