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

Aqueous Polymerization of Acrylamide Initiated by Glycolic Acid/Ce⁴ Redox System

G. S. Misra[a]; B. D. Arya[a]
[a] Department of Chemistry, University of Jammu, Jammu, India

To cite this Article Misra, G. S. and Arya, B. D.(1983) 'Aqueous Polymerization of Acrylamide Initiated by Glycolic Acid/Ce⁴ Redox System', Journal of Macromolecular Science, Part A, 19: 2, 253 — 264
To link to this Article: DOI: 10.1080/00222338308069439
URL: http://dx.doi.org/10.1080/00222338308069439

J. MACROMOL. SCI.–CHEM., A19(2), pp. 253-264 (1983)

Aqueous Polymerization of Acrylamide Initiated by Glycolic Acid/Ce^{4+} Redox System

G. S. MISRA and B. D. ARYA

Department of Chemistry
University of Jammu
Jammu 180001, India

ABSTRACT

The aqueous polymerization of acrylamide initiated by the glycolic acid/Ce^{4+} redox system was studied in sulfuric acid medium at 35 ± 0.2°C under a nitrogen atmosphere. The initiation was carried out by the free radical generated in the decomposition of the complex formed between the oxidant and the reductant. The monomer disappearance was found to be proportional to $[GA]^{0.89}[Ce^{4+}]^{0.57}[M]^{1.0}$, and the rate of ceric ion disappearance was found to be directly proportional to $[Ce^{4+}]$ and $[GA]$ but independent of $[M]$. The activation energy of the system was found to be 7.21 kcal/deg/mol. The molecular weight of polyacrylamide increased with increasing [monomer] and decreased with increasing [catalyst]. The effect of pH was also studied in the pH range 2.22 to 1.44.

INTRODUCTION

Ceric ion forms an effective redox pair with various reducing agents like alcohols [1, 2], aldehydes [3], and amines [4] for the polymerization of vinyl monomers. Recently, hydroxy acids have been used with ceric ion for the polymerization of various monomers. In the present investigation the glycolic acid-ceric ammonium sulfate

0022-233X/83/1902-0253$3.50/0

redox pair has been used for the polymerization of acrylamide with a view to elucidate the mechanism involved in the process.

EXPERIMENTAL

Materials

Acrylamide (SD's) was recrystallized twice from methanol. Ceric ammonium sulfate (Sarabhai M.) and glycolic acid (Reidel) were used as such. The water used as solvent in all the experiments was prepared by the redistillation of distilled water containing a small amount of alkaline $KMnO_4$.

Polymerization Procedure

The polymerization was followed by quantitative estimation of double bonds in acrylamide as described by Wallace et al. [5]. The experimental procedure was similar to that used by Misra et al. [6].

The rate of disappearance of cerium was estimated by cerimetry. The polymerization reaction was quenched after a certain period of time by the addition of a known excess of standard ferrous ammonium sulfate solution, and the excess of Fe^{2+} was titrated with a standard Ce^{4+} solution using ferroin as indicator.

The molecular weight of polyacrylamide was determined using Schulz and Blaschke's [7] equation (Eq. 1) as well as the relationship of Dainton et al. [8] (Eq. 2):

$$[\eta]_{30^\circ} = \frac{\eta_{sp}/c}{1 + K'\eta_{sp}} \qquad \text{(where } K' = 0.28\text{)} \tag{1}$$

$$[\eta]_{g/mL} = 68 \times 10^{-3}\, \overline{M}_v^{\,0.66} \tag{2}$$

RESULT AND DISCUSSION

Rate of Monomer Disappearance (R_p)

Rate Dependence on Activator

The initial rate and the maximum conversion have been found to increase with increasing [glycolic acid] in the range studied (5.0 to 20) $\times 10^{-2}$ mol/L at fixed [M], [Ce^{4+}], and [H_2SO_4] (Fig. 1).

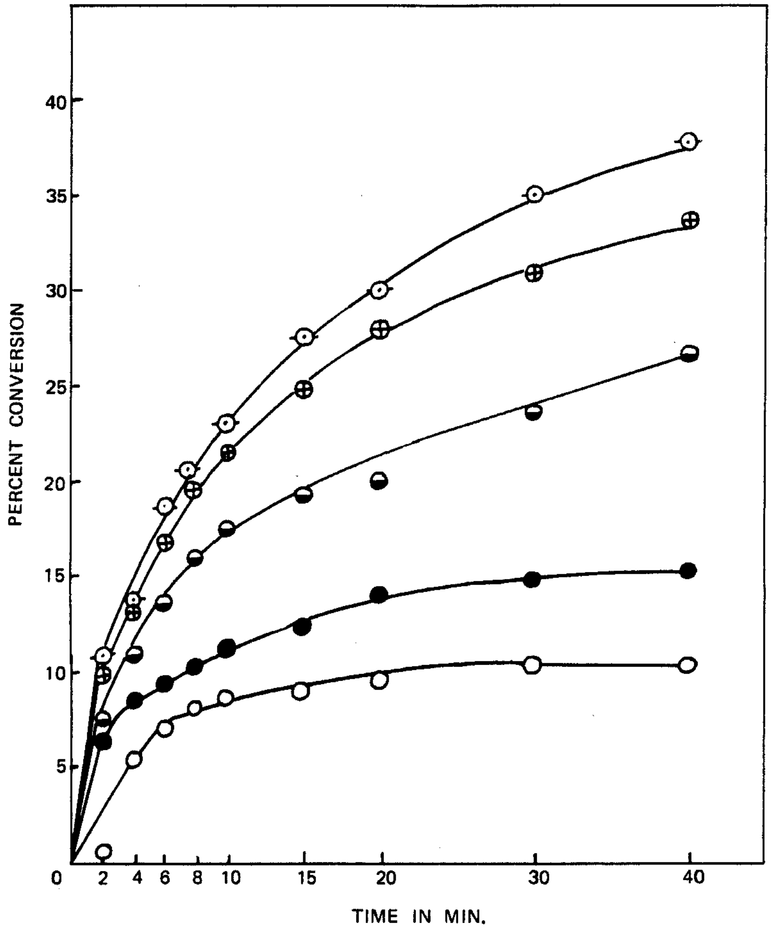

FIG. 1. Time versus conversion curves for the aqueous polymerization of acrylamide with varying initial concentrations of glycolic acid at constant $[M] = 5.0 \times 10^{-2}$ mol/L, $[Ce^{4+}] = 10.0 \times 10^{-4}$ mol/L, $[H_2SO_4] = 12.5 \times 10^{-3}$ mol/L. Temperature = 35 ± 0.2°C. ○ = 5.0×10^{-2} mol/L, ● = 10.0×10^{-2} mol/L, ◒ = 12.5×10^{-2} mol/L, ⊕ = 15.0×10^{-2} mol/L, -⊙- = 20×10^{-2} mol/L.

Increasing [activator] increases the concentration of active free radicals, hence the rate of polymerization increases. The activator exponent of 0.89 (Fig. 2) shows a first-order dependence of the rate of polymerization on the [activator].

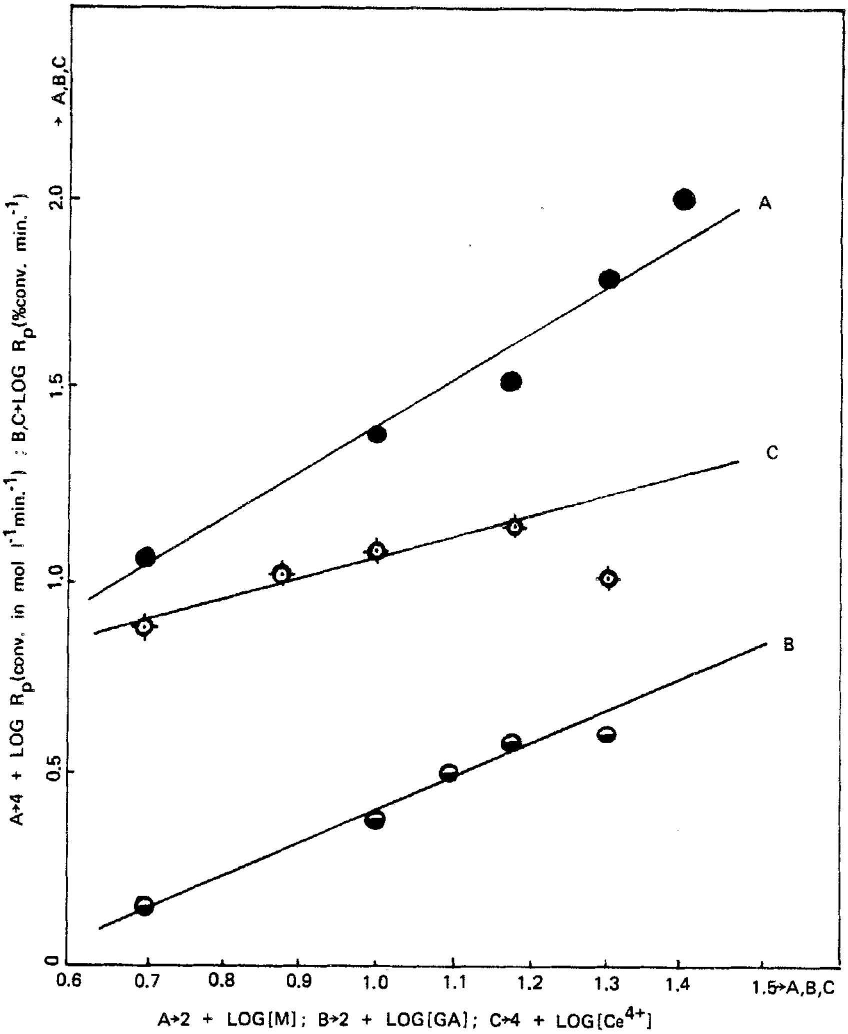

FIG. 2. Double logarithmic plots of A (●) R_p (in mol/L/min) versus [M] in mol/L; B (⊖) R_p (in % conversion/min) versus [GA] in mol/L; C (⌖) R_p (in % conversion/min) versus [Ce^{4+}] in mol/L.

Rate and Molecular Weight Dependence on Catalyst

The dependence of the rate of polymerization on the catalyst was studied in the range (5 to 20) × 10^{-4} mol/L at fixed [M], [H_2SO_4], and [glycolic acid]. The variation of [Ce^{4+}] showed an increase in initial rate up to a concentration of 15 × 10^{-4} mol/L and in maximum conversion up to a concentration of 10 × 10^{-4} mol/L. Above 15 × 10^{-4} mol/L, both showed a decline. Since the activator is always present in excess of the catalyst, an increase in the catalyst will increase the production of active free radicals. Hence the rate increased up to a concentration of 15 × 10^{-4} mol/L. Beyond this concentration, radicals are consumed in side reactions, thus decreasing the rate of polymerization. The catalyst exponent 0.57 (Fig. 2) indicates a bimolecular termination mechanism. Molecular weight determination (Table 1) showed a regular decrease with an increase in [catalyst].

Rate and Molecular Weight Dependence on Monomer

The initial rate as well as the maximum conversion were found to increase with increasing [monomer] in the range studied, (5 × 10^{-2} to 25 × 10^{-2} mol/L) at fixed [GA], [Ce^{4+}], and [H_2SO_4] (Fig. 3).

The rate of polymerization was found to be proportional to the first power of the monomer (Fig. 2), which rules out the possibility of premature chain transfer and primary radical termination. A similar behavior has been observed by Misra et al. [9] and Dainton et al. [8]. With the increase in monomer concentration the availability of monomer molecules in the propagation step increases, resulting in an increase in the rate of polymerization. Molecular weight determination showed a regular increase with increasing [monomer] in the range studied (Table 2).

Temperature Dependence

The dependence of the rate of polymerization has been studied in the temperature range 30 to 50°C at fixed [Ce^{4+}], [M], and [GA]. It was observed that the initial rate and the maximum conversion increased up to 35°C. Above 40°C, both showed a decline, which may be due to side reactions in which primary free radicals are consumed. The overall activation energy as calculated from an Arrhenius plot was found to be 7.21 kcal/deg/mol (30.21 kJ/deg/mol). Such lower activation energies have been reported by various workers [10-12].

Effect of pH

In the pH range studied (2.22 to 1.44), maximum conversion was obtained at pH 1.65, corresponding to [H_2SO_4] = 12.5 × 10^{-3} mol/L. This pH is sufficient to decompose the complex formed between the reductant (glycolic acid) and the oxidant (Ce^{4+}) to produce primary free radicals ($R^\bullet$).

TABLE 1. Dependence of Molecular Weight on Varying Initial $[Ce^{4+}]$ at Constant $[M] = 5 \times 10^{-2}$ mol/L, $[H_2SO_4] = 12.5 \times 10^{-3}$ mol/L, $[GA] = 15.0 \times 10^{-2}$ mol/L, 35 ± 0.2°C

Sample	$[Ce^{4+}]$ 10^{-4} mol/L	R_p (% conversion/ min)	Molecular weight $(\overline{M}_v)$	Degree of polymerization $(\overline{p})$	$1/\overline{p} \times 10^2$
1	5	2.4	15,260	214.69	0.4657
2	7.5	3.3	8,487	119.40	0.8375
3	10	3.8	5,613	78.97	1.266
4	15	4.4	3,855	54.23	1.844

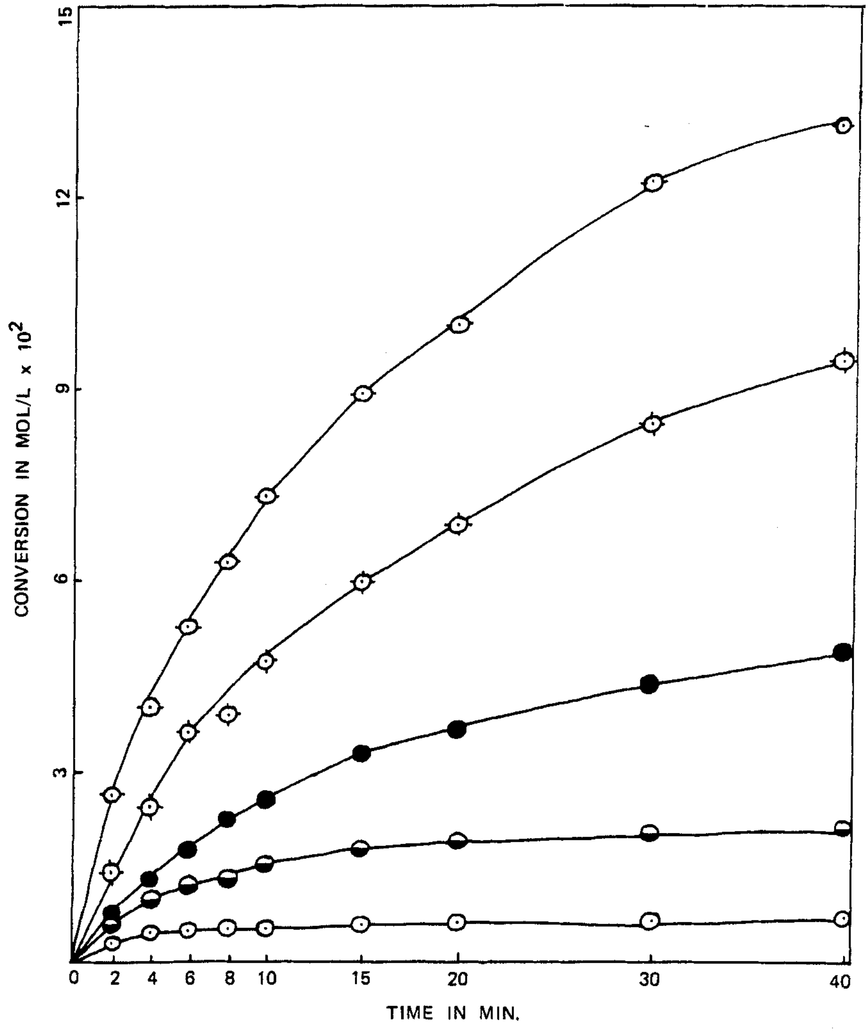

FIG. 3. Time versus conversion curves for the aqueous polymerization of acrylamide with varying initial concentrations of monomer at constant [GA] = 7.5×10^{-2} mol/L, [Ce^{4+}] = 5.0×10^{-4} mol/L, [H_2SO_4] = 12.5×10^{-3} mol/L. Temperature = 35 ± 0.2°C. ⊙ = 5, ◒ = 10, ● = 15, -⌽- = 20, -⊙- = 25; all $\times 10^{-2}$ mol/L.

TABLE 2. Dependence of Molecular Weight on Varying the Initial Concentration of Acrylamide at Constant [GA] = 7.5×10^{-2} mol/L, [Ce^{4+}] = 5.0×10^{-4} mol/L, [H_2SO_4] = 12.5×10^{-3} mol/L, 35 ± 0.2°C

Sample	[M] $\times 10^2$ mol/L	$R_p \times 10^3$ (conversion in mol/L/min)	Molecular weight ($\overline{M}_v$)	Degree of polymerization ($\overline{p}$)	$1/\sqrt{\overline{p}} \times 10^2$
1	10	2.50	20,320	285.875	0.34
2	15	3.29	22,740	319.921	0.31
3	20	6.15	27,300	384.074	0.26
4	25	10.03	31,330	440.770	0.22

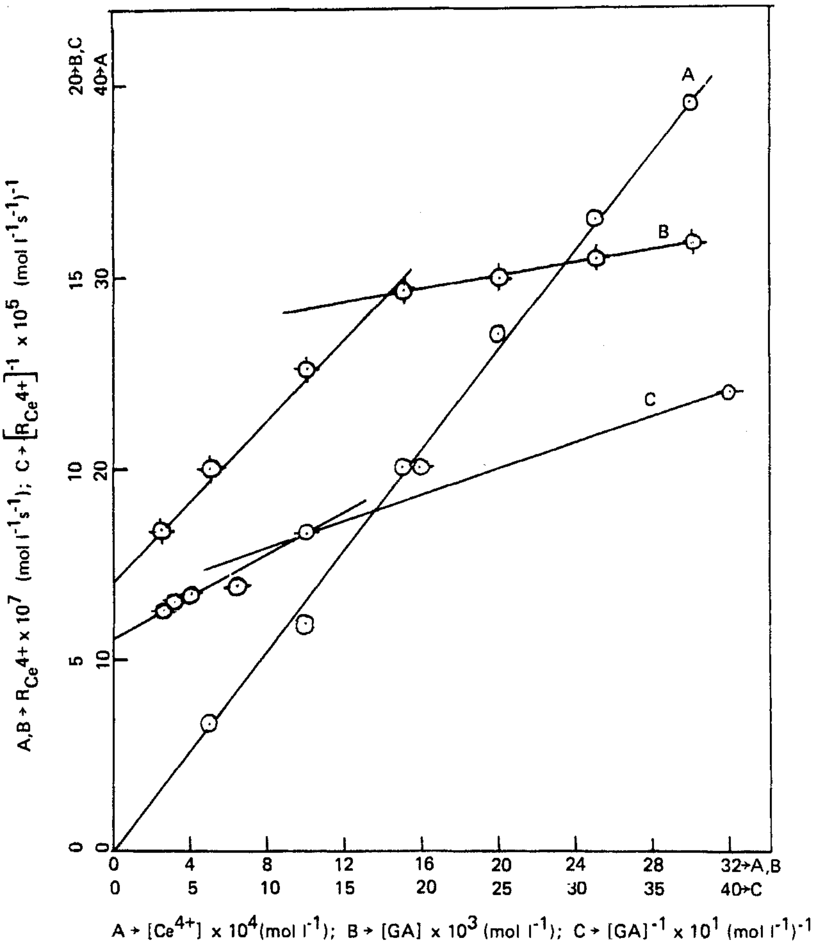

FIG. 4. Rate of ceric ion disappearance in mol/L/s versus (A) $[Ce^{4+}]$, (B) [GA], and (C) $[GA]^{-1}$. A (⊙): [M] = 5.0 × 10^{-2} mol/L, [GA] = 15.0 × 10^{-3} mol/L, $[H_2SO_4]$ = 7.5 × 10^{-2} mol/L, temperature = 35 ± 0.2°C. B (-⊕-) and C (-⊙-): [M] = 5 × 10^{-2} mol/L $[Ce^{4+}]$ = 9.5 × 10^{-4} mol/L, $[H_2SO_4]$ = 7.5 × 10^{-2} mol/L, temperature = 35 ± 0.2°C.

Rate of Ceric Ion Disappearance

The rate was found to be directly proportional to $[Ce^{4+}]$. The plot of $-d[Ce^{4+}]/dt$ versus $[Ce^{4+}]$ gave a straight line passing through the origin (Fig. 4), which confirmed that ceric ion was not involved in the initiation reaction by direct interaction with the monomer or in the process of termination. The rate increased linearly with [GA]. At higher [GA] the change in the rate of disappearance of Ce^{4+} was slightly lower. A plot of $-d[Ce^{4+}]/dt$ versus [GA] gave a straight line up to a certain range, leaving an intercept on the ordinate. The presence of an intercept in the plot $[\text{rate}]^{-1}$ versus $[\text{GA}]^{-1}$ shows complex formation between ceric ion and glycolic acid (Fig. 4). A yellowish complex has been isolated at room temperature. It was insoluble in all solvents but dissolved in sulfuric acid. IR spectral studies confirmed the formation of a complex. A carbonyl peak at 1730 cm^{-1} in the spectrum of glycolic acid was absent in the spectrum of the complex. C–O stretching showed a shift from 1400 to 1180 cm^{-1}. In addition to this, a peak at 560 cm^{-1} corresponding to a metal-oxygen bond was also obtained in the case of the complex. This shows that the carboxylic group participates in complex formation.

Kinetic Scheme

The following kinetic scheme is proposed as consonant with the experimental results.

Generation of primary free radicals:

$$Ce^{4+} + R \overset{K}{\rightleftharpoons} [\text{complex}] \xrightarrow[H_2SO_4]{k_a} R^{\bullet} + Ce^{3+} + CO_2 + H^{+} \qquad (3)$$

where R is the activator molecule and $R^{\bullet}$ is the primary free radical formed.

Reaction of primary free radical $R^{\bullet}$ with Ce^{4+}:

$$R^{\bullet} + Ce^{4+} \xrightarrow[\text{fast}]{k_0} \text{products} + Ce^{3+} + H^{+} \qquad (4)$$

Initiation of polymerization:

$$R^{\bullet} + M \xrightarrow{k_i} RM^{\bullet} \qquad (5)$$

Propagation:

$$RM^{\cdot} + M \xrightarrow{k_p} RM_2^{\cdot} \tag{6}$$

$$RM_{(n-1)} + M \xrightarrow{k_p} RM_n^{\cdot}$$

Termination:

$$RM_n^{\cdot} + RM_m^{\cdot} \xrightarrow{k_t} \text{polymer} \tag{7}$$

Reactions (3) and (4) can be illustrated by

$$CH_2(OH)COOH + Ce^{4+} \overset{K}{\rightleftharpoons} [\text{complex}] \to \left[\begin{array}{l} \dot{C}H(OH)COOH + H^+ + Ce^{3+} \\ (A) \\ CH_2(OH)CO\dot{O} + H^+ + Ce^{3+} \\ (B) \\ \dot{C}H_2(OH) + CO_2 + H^+ + Ce^{3+} \\ (C) \end{array}\right.$$

(A), (B) and (C) may then undergo fast reactions to generate stable species instead of initiating polymerization:

$$(A) + Ce^{4+} \xrightarrow{\text{fast}} HCOCOOH + Ce^{3+} + H^+$$

$$(B) \xrightarrow{\text{very fast}} (C) + CO_2$$

$$(C) + Ce^{4+} \xrightarrow{\text{fast}} HCHO + Ce^{3+} + H^+$$

Applying the steady-state assumption to both $[R^{\cdot}]$ and $[M^{\cdot}]$ separately and assuming that the concentration of the complex formed in Reaction (3) is smaller than both [GA] and $[Ce^{4+}]$, the rate equation for the rate of disappearance of monomer and ceric ion can be derived as:

$$-\frac{d[M]}{dt} = R_p = \frac{k_p[M][Ce^{4+}]^{1/2}}{K_t^{1/2}} \left\{ \frac{Kk_ik_a[R][M]}{k_0[Ce^{4+}] + k_i[M]} \right\}^{1/2} \tag{8}$$

and

$$-\frac{d[Ce^{4+}]}{dt} = Kk_a[R][Ce^{4+}] \qquad (9)$$

We have neglected the possibility of linear termination because the experimental results show a preponderance of bimolecular termination. In the initiation step Ce^{4+} does not attack the monomer. It reacts with glycolic acid to produce the complex (Eq. 4) which gives primary free radicals on dissociation that initiate the reaction.

ACKNOWLEDGMENT

The authors desire to thank the University Grants Commission (India) for the award of a Junior Research Fellowship to one of them (B.D.A.).

REFERENCES

[1] A. A. Katai, V. K. Kulshrestha, and R. H. Marchessault, J. Polym. Sci., C, 2, 403 (1963).

[2] S. P. Rout, A. Rout, N. Mallick, B. C. Singh, and M. Santappa, Makromol. Chem., 178, 1971 (1977).

[3] S. V. Subramanian and M. Santappa, Ibid., 112, 1 (1968).

[4] S. K. Saha and A. K. Chaudhuri, J. Polym. Sci., Polym. Chem. Ed., 10, 797 (1972).

[5] R. A. Wallace and D. G. Young, J. Polym. Sci., A-1, 4, 1179 (1966).

[6] G. S. Misra, J. S. Shukla, and H. Narain, Makromol. Chem., 119, 74 (1968).

[7] G. V. Schulz and F. Blaschke, J. Prakt. Chem., 158, 130 (1941).

[8] E. Collinson, F. S. Dainton, and G. S. McNaughton, Trans. Faraday Soc., 53, 489 (1957).

[9] G. S. Misra and S. N. Bhatacharya, J. Macromol. Sci.–Chem., A14(6), 907 (1980).

[10] A. K. Roy, S. Pattnaik, R. K. Samal, and P. L. Nayak, Ibid., A12, 1241 (1978).

[11] G. S. Misra and S. N. Bhattacharya, Colloid Polym. Sci., 258, 954 (1980).

[12] G. S. Misra and G. P. Dubey, J. Macromol. Sci.–Chem., A16(3), 601 (1981).

Accepted by editor April 5, 1982
Received for publication May 3, 1982