

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Note: Gel-Free Polymerization of *N, N'*-Methylenebisacrylamide by Persulfate/Ascorbic Acid in Aqueous Medium

K. C. Gupta^a; G. D. Raja^a; K. Behari^a

^a Department of Chemistry, University of Allahabad, Allahabad, India

To cite this Article Gupta, K. C. , Raja, G. D. and Behari, K.(1987) 'Note: Gel-Free Polymerization of *N, N'*-Methylenebisacrylamide by Persulfate/Ascorbic Acid in Aqueous Medium', *Journal of Macromolecular Science, Part A*, 24: 5, 587 – 592

To link to this Article: DOI: 10.1080/00222338708068143

URL: <http://dx.doi.org/10.1080/00222338708068143>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

NOTE

GEL-FREE POLYMERIZATION OF *N,N'*-METHYLENEBISACRYLAMIDE BY PERSULFATE/ASCORBIC ACID IN AQUEOUS MEDIUM

K. C. GUPTA, G. D. RAJA, and K. BEHARI*

Department of Chemistry
University of Allahabad
Allahabad 211002, India

INTRODUCTION

N,N'-Methylenebisacrylamide has been used in graft copolymerization as a crosslinking agent to increase the quality of naturally occurring fibers [1]. Recently Venkatarao et al. [2, 3] studied the kinetics of polymerization of *N,N'*-methylenebisacrylamide and proposed cyclopolymerization chain propagation as suggested by Butler and Engley [4]. Such studies prompted us to study the kinetics of polymerization of this monomer with the present redox system.

EXPERIMENTAL

All the chemicals used were either of E. Merck or AnalaR Grade B.D.H. products. The rate of polymerization was determined as reported previously [5], and the percent conversion was calculated by the modified equation of Wallace and Young [6].

*To whom correspondence should be addressed.

RESULTS AND DISCUSSION

Since preliminary experiments clearly indicated that gel formation takes place even at low conversion at higher concentration of monomer (Table 1), we kept the monomer concentration below 10 mmol/L. The interaction of persulfate ion with the monomer generates primary free radicals and sulfate ion radical ($\text{SO}_4^{\cdot-}$). The reactions were carried out in an inert atmosphere to exclude the possibility of autoxidation of ascorbic acid. Ascorbic acid accelerates the rate of polymerization and maximum conversion. The information of ascorbate radicals is presumed to take place by interaction of sulfate ion radical and ascorbic acid [7]. Monomer units which are activated either by sulfate ion radical or by ascorbate radicals form seven-membered rings on reacting with other monomer molecules. The higher rate of polymerization compared to acrylamide was ascribed to an intra-intermolecular mechanism [9-11].

EFFECT OF PERSULFATE ION CONCENTRATION

The initial rate of polymerization (R_p) and maximum conversion increased (1.66-5.0 mmol/L), which can be assumed to be due to the formation of pri-

TABLE 1. Dependence of Gel Point on Monomer Concentration^a

[Monomer], mmol/L	Time of appearance of gel, min.	% Conversion at appearance of gel
5.55	b	
6.25	b	
7.14	78	93.2
8.33	62	83.6
10.00	45	76.2
20.00	18	17.5
40.00	7	8.3

^a[$\text{K}_2\text{S}_2\text{O}_8$] = 2.0 mmol/l, [ascorbic acid] = 5.0 mmol/L.

^bNo gel formation.

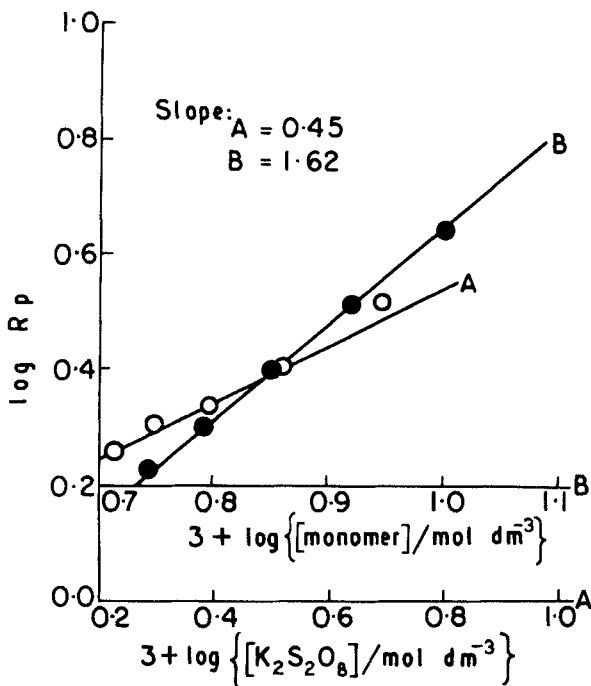


FIG. 1. A. Double logarithmic plot of initial polymerization rate vs initial persulfate concentration. [*N,N'*-Methylenebisacrylamide], 6.25 mmol/L; [ascorbic acid], 5.0 mmol/L. 40°C. B. Double logarithmic plot of propagation rate vs initial *N,N'*-methylenebisacrylamide concentration. [$K_2S_2O_8$], 2.0 mmol/L; [ascorbic acid], 5.0 mmol/L. 40°C.

many free radicals. The order of reaction with respect to persulfate was found to be 0.45 (Fig. 1A), which indicates the bimolecular mode of termination of growing chain radicals.

EFFECT OF ASCORBIC ACID CONCENTRATION

The initial rate of polymerization remains more or less constant up to 4.55 mmol/L, but the initial rate and maximum conversion decrease appreciably at higher concentrations (Fig. 2). At lower concentration of ascorbic acid, the

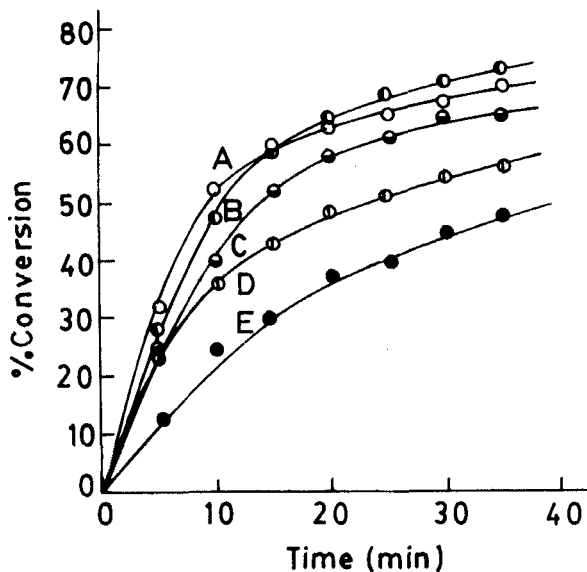


FIG. 2. Effect of ascorbic acid on the rate of polymerization. [*N,N'*-Methylenebisacrylamide], 6.25 mmol/L; [$K_2S_2O_8$], 2.0 mmol/L; [ascorbic acid]: (A) 2.85, (B) 3.33, (C) 4.0, (D) 4.55, (E) 5.0 mmol/L. 40°C.

rate of formation of primary radicals is more or less equal to the rate of degradative termination of growing chain radicals, but at higher concentration of ascorbic acid, the degradative termination [7] of growing chain radicals predominates. The rate of polymerization therefore becomes inversely proportional to the square root of the acid concentration. The decrease in initial rate of polymerization at ascorbic acid concentration above 4.55 mmol/L can also be assumed to be due to the hydrogen-ion-catalyzed decomposition of $S_2O_8^{2-}$ ions to predominantly polar SO_4^{2-} ions rather than $SO_4^{\cdot-}$ ion radicals [11].

EFFECT OF MONOMER CONCENTRATION

At low monomer concentration the propagation goes by intra-intermolecular linear propagation, but gel is formed at higher concentration due to the active participation of *N,N'*-methylenebisacrylamide molecules in crosslinking

of growing chains, and the chances of linear propagation through the chain cyclization process are reduced. The order of reaction with respect to *N,N'*-methylenebisacrylamide was found to be 1.62 (Fig. 1B), which indicates the occurrence of the cage effect. This was also found by earlier workers [13-15] and is a characteristic of the solvent and initiator. The energy of activation was found to be 40 ± 2 kJ/mol.

EFFECT OF ADDITIVES

The addition of alcohols (Fig. 3) increased the initial rate of polymerization and maximum conversion appreciably, which can be ascribed to the formation of additional radicals. The addition of sodium oleate or sodium lauryl-

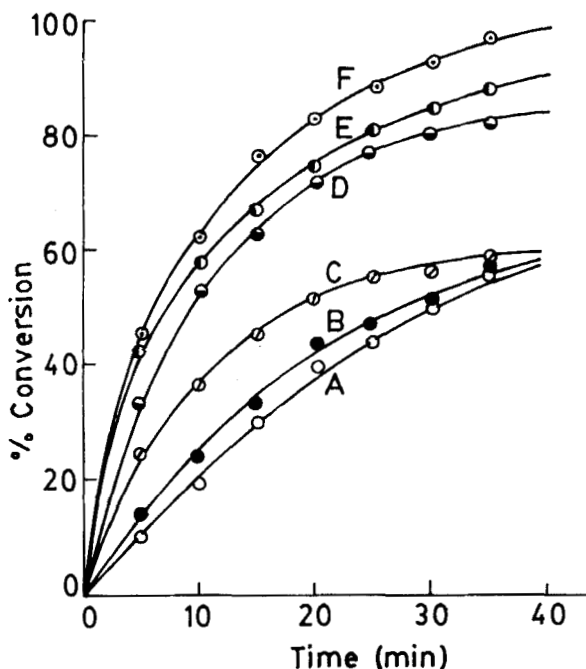


FIG. 3. Effect of water-miscible organic solvents. [*N,N'*-Methylenebisacrylamide], 5.0 mmol/L; [$K_2S_2O_8$], 2.0 mmol/L; [ascorbic acid], 5.0 mmol/L. [Solvents] (50.0 mmol/L): (A) blank, (B) acetone, (C) methanol, (D) ethanol, (E) propanol, (F) butanol. 40°C .

sulfate lowered the polymerization rate since they formed negatively charged ionic micelles which reduced cyclization due to their repelling action on the growing chain radicals. But the micelles formed by the addition of the cationic detergent, cetyltrimethylammonium bromide (CTAB), were found to be helpful in catalyzing the cyclization, as indicated by the observed increase of the polymerization rate. Addition of inorganic salts like LiCl, KCl, NaCl, NH_4Cl , Na_2SO_4 , or MnSO_4 was found to decrease the rate of polymerization, while lower pH was found to have a retarding effect [12].

The following rate expression was derived from the experimental results:

$$R_p = \frac{k_p(k_t)^{1/2} [M]^{3/2} [\text{S}_2\text{O}_8^{2-}]^{1/2}}{(k_{tc} + k_{dt}[\text{AH}_2])^{1/2}}, \quad (1)$$

where AH_2 is ascorbic acid.

ACKNOWLEDGMENT

One of the authors (K.C.G.) is thankful to CSIR, New Delhi, for the award of a Senior Research Fellowship.

REFERENCES

- [1] L. A. Miller and R. E. Whitefield, *Text. Res. J.*, **31**, 451 (1961).
- [2] A. Gopalan, S. Paulrajan, K. Venkatarao, and N. R. Subbaratnam, *Eur. Polym. J.*, **19**, 817 (1983).
- [3] A. Gopalan, P. Venuvanalingam, S. P. Manickam, K. Venkatarao, and N. R. Subbaratnam, *Ibid.*, **18**, 531 (1982).
- [4] G. B. Butler and F. L. Engley, *J. Am. Chem. Soc.*, **73**, 894 (1961).
- [5] K. Behari, K. C. Gupta, and M. Verma, *Angew. Makromol. Chem.*, **130**, 67 (1985).
- [6] R. A. Wallace and D. G. Young, *J. Polym. Sci., Part A-1*, **4**, 1179 (1966).
- [7] H. Narain, S. M. Jagdale, and N. D. Ghatge, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 1225 (1981).
- [8] U. S. Mehrotra and S. P. Mushran, *J. Indian Chem. Soc.*, **47**, 41 (1970).
- [9] C. S. Marvel, *J. Polym. Sci.*, **48**, 101 (1960).
- [10] G. B. Butler, A. Cranshaw, and W. L. Miller, *J. Am. Chem. Soc.*, **80**, 3615 (1958).