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### A Kinetic Study of the Photosensitized Cyclopolymerization of *N,N'*-Methylenebisacrylamide

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## NOTE

# A KINETIC STUDY OF THE PHOTSENSITIZED CYCLOPOLYMERIZATION OF *N,N'*-METHYLENEBISACRYLAMIDE

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### INTRODUCTION

Polymerization of nonconjugated diolefins is of recent interest. *N,N'*-Methylenebisacrylamide (MBA), a nonconjugated diolefin, is generally used as a crosslinking agent. It can also be polymerized under certain conditions without crosslinking [1]. Butler and Inglely [2] proposed a novel chain propagation mechanism for such reactions in which the radical produced undergoes cyclization before the propagation step. Subbaratnam et al. reported the polymerization of MBA under thermal conditions [1, 3, 4]. Recently, polymerization of MBA with the vanadium(V)-cyclohexanone redox system was reported from our laboratory [5]. The present work on the photopolymerization of this monomer using uranyl ion as photosensitizer was undertaken with a view to find out whether cyclization of the radical occurs under these conditions or not, and also to establish the mechanism.

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## EXPERIMENTAL

The MBA used was from Aldrich and recrystallized from water just before use. Uranyl ion was in the form of uranyl sulfate ( $\text{UO}_2\text{SO}_4$ ). A medium-pressure mercury vapor lamp (UVS-500 Hanovia make) was used as the source of light. Polymerization reactions were conducted under  $\text{N}_2$ , and the kinetics were followed gravimetrically. The detailed procedure for following the rates are discussed elsewhere [5].

Polymerization of MBA initiated by uranyl ion was carried out at 298 K, and polymer was observed soon after exposure to light. The steady state was attained within 8 min.

## RESULTS AND DISCUSSION

### Effect of $[\text{UO}_2^{2+}]$ on Polymerization Rate

Increasing the concentration of uranyl ions increased the rate of polymerization ( $R_p$ ), and a plot of  $\log [\text{UO}_2^{2+}]$  vs  $\log R_p$  is a straight line with a slope of 0.60 (Fig. 1B). This indicates that  $\text{UO}_2^{2+}$  is not participating in the termination step, otherwise the rate of polymerization would have decreased with increasing  $[\text{UO}_2^{2+}]$ . The order in  $[\text{UO}_2^{2+}]$  would then have been zero or negative.

### Effect of [MBA] on Polymerization Rate

Increasing the concentration of MBA increased the rate, and the order with respect to [MBA] was found to be 1.5 (Fig. 1A). This also strongly supports that the termination is of the mutual type. The order in [MBA] would have been 2.0 if the polymerization were terminated by  $\text{UO}_2^{2+}$  ions.

### Effect of Intensity

Increasing the light intensity increased the rate, and the order with respect to intensity was found to be 0.5 (Fig. 1C). A similar observation was made by Dainton et al. [6] for the photopolymerization of vinyl monomers.

Excited uranyl ions are known to be reduced by abstracting an electron from the substrate. With MBA as substrate, the resulting radical can be shown as

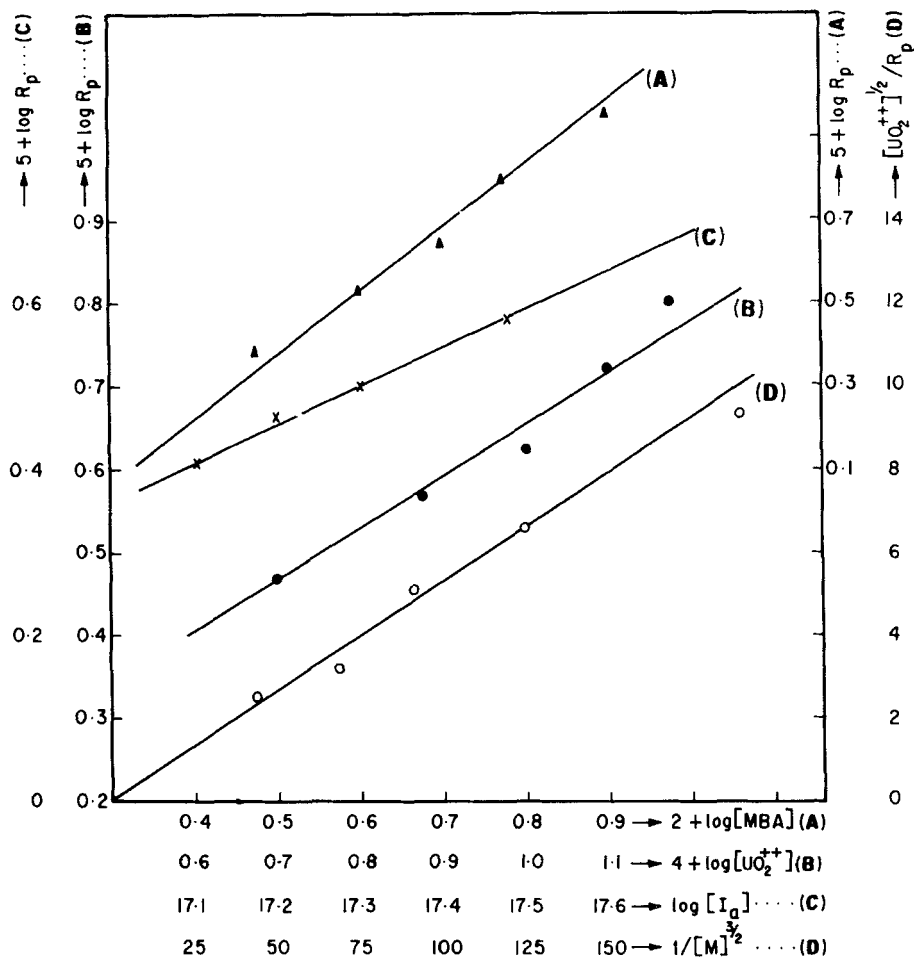


FIG. 1. Rate plots. (A) Plot of  $5 + \log R_p$  vs  $2 + \log [MBA]$ :  $[UO_2^{2+}]$  1.0 mmol/L,  $I_a = 3.00 \times 10^{17}$  quanta/s, temperature = 298 K. (B) Plot of  $5 + \log R_p$  vs  $4 + \log [UO_2^{2+}]$ :  $[MBA] = 0.05$  mol/L,  $I_a = 3.00 \times 10^{17}$  quanta/s, temperature = 298 K. (C) Plot of  $5 + \log R_p$  vs  $\log [I_a]$ :  $[MBA] = 0.05$  mmol/L,  $[UO_2^{2+}] = 1.0$  mol/L, temperature = 298 K. (D) Plot of  $[UO_2^{2+}]^{1/2} / R_p$  vs  $1/[M]^{3/2}$ :  $[UO_2^{2+}] = 1$  mmol/L,  $I_a = 3.00 \times 10^{17}$  quanta/s, temperature = 298 K.



Here  $M_c^{\cdot+}$  is the cyclized growing polymer radical ion.

Applying the steady-state hypothesis to the various radicals, the expression for the rate of polymerization becomes

$$R_p = k_p \left( \frac{k_i}{k_t} I_a [\text{UO}_2^{2+}] \right)^{1/2} [\text{M}]^{3/2}. \quad (6)$$

The above rate law explains well all the experimentally observed results, viz., 0.5 order with respect to both  $[\text{UO}_2^{2+}]$  and  $I_a$  and 1.5 order with respect to  $[\text{M}]$ . As predicted by Eq. (6), a plot of  $[\text{UO}_2^{2+}]^{1/2}/R_p$  against  $1/[\text{M}]^{3/2}$  is linear (Fig. 1D), supporting the suggested mechanism.

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### REFERENCES

- [1] (a) A. Gopalan, P. Venuvanalngam, S. P. Manickam, K. Venkatarao, and N. R. Subbarathnam, *Eur. Polym. J.*, **18**, 531 (1982); (b) K. C. Gupta, G. D. Raja, and K. Behari, *J. Macromol. Sci.—Chem.*, **A24**, 587 (1987); (c) S. Rathnasabapathy, N. Marisami, S. P. Manickam, and N. R. Subbarathnam, *Ibid.*, **A25**, 97 (1988).
- [2] G. B. Butler and F. L. Ingley, *J. Am. Chem. Soc.*, **73**, 894 (1951).
- [3] A. Gopalan, S. Paulrajan, K. Venkatarao, and N. R. Subbarathnam, *Eur. Polym. J.*, **19**, 817 (1983).
- [4] N. R. Subbarathnam, S. P. Manickam, P. Venuvanalngam, and A. Gopalan, *J. Macromol. Sci.—Chem.*, **A23**, 117 (1986).
- [5] T. Parthasarathy, K. Nageswar Rao, B. Sethuram, and T. Navaneeth Rao, *J. Polym. Mater.*, **3**, 191 (1986).
- [6] E. Collison, F. S. Dainton, and G. S. McNaughton, *J. Chem. Phys.*, **52**, 556 (1955); *Ibid.*, **54**, 476 (1957).

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