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

Photopolymerization of Acrylonitrile with the Isopropanol-Ag(I) System as Initiator

T. partha Sarathy[a]; K. Nageswar Rao[a]; B. Sethuram[a]; T. Navaneeth Rao[a]
[a] Department of Chemistry, Osmania University, Hyderabad, India

To cite this Article Sarathy, T. partha , Rao, K. Nageswar , Sethuram, B. and Rao, T. Navaneeth(1986) 'Photopolymerization of Acrylonitrile with the Isopropanol-Ag(I) System as Initiator', Journal of Macromolecular Science, Part A, 23: 8, 955 — 961

To link to this Article: DOI: 10.1080/00222338608081103

URL: http://dx.doi.org/10.1080/00222338608081103

J. MACROMOL. SCI.–CHEM., A23(8), pp. 955-961 (1986)

Photopolymerization of Acrylonitrile with the Isopropanol-Ag(I) System as Initiator

T. PARTHA SARATHY, K. NAGESWAR RAO, B. SETHURAM, and
T. NAVANEETH RAO

Department of Chemistry
Osmania University
Hyderabad 500007, India

ABSTRACT

Photopolymerization of acrylonitrile was studied with the isopropanol-Ag(I) system as initiator in aqueous medium. The rate of polymerization increased with time and reached a steady state within 10 min. The rate of polymerization was found to be proportional to $[\text{acrylonitrile}]^{1.5}$, $[\text{Ag(I)}]^{0.5}$, and $[\text{isopropanol}]^{0.5}$. A probable mechanism consistent with the observed results is proposed and discussed.

INTRODUCTION

Nitrates of Ag, K, Na, Li, Pb, Co, and Cu have been reported to act as photoinitiators for the polymerization of vinyl monomers [1, 2]. Delzenne [3] reported that photographic silver halide emulsion initiates the photopolymerization of acrylamide. Hydroxyl radicals formed by the reaction of halogen atoms with water were found to initiate polymerization. A preliminary study on photopolymerization of acrylonitrile with $AgNO_3$ in bulk and in solution was reported by Schnecko [4]. He

0022-233X/86/2308-0955$3.50/0

found that NO_3 radicals, formed by the decomposition of $AgNO_3$, are responsible for the polymerization. Recently Rajan et al. [5] reported the photochemical oxidation of alcohols by Ag(I), Cu(II), and Fe(III) by a free-radical pathway in aqueous medium. It should, therefore, be possible to initiate polymerization more effectively with the Ag(I)-isopropanol system. To investigate such a possibility, we carried out a systematic kinetic study of photochemical polymerization of acrylonitrile with $AgNO_3$-isopropanol as photoinitiator in aqueous medium.

EXPERIMENTAL

All reagents used were of AnalaR grade. Stabilized acrylonitrile was purified by washing with dilute acid and alkali followed by water. This was then dried over anhydrous calcium chloride and distilled under reduced pressure. Doubly distilled deionized water was used for the preparation of stock solutions. Isopropanol was purified by the method described by Wells and Davies [6]. Photolysis was carried out using a medium-pressure mercury lamp (UVS 500 Hanovia). Pyrex glass vessels were used in a semicircular stand and arranged in such a way that the distance of each vessel from the lamp was the same. Standard ferrioxalate actionometry was employed for measuring the light intensity. Before irradiation, the sample solution was deaerated by bubbling with oxygen-free nitrogen for 15 min. After irradiation, the reaction mixture was filtered through a G_4 sintered glass crucible, dried at 30°C for 1 day, and weighed. Any atomic silver adsorbed on the polymer surface during polymerization was removed by washing with 1 N HNO_3. The crucible was then dried and weighed.

RESULTS AND DISCUSSION

Polymer was not obtained when AN alone or AN and ISP was exposed to light. Polymer was observed only after 2 h of irradiation in the presence of Ag(I) + AN. However, when ISP + Ag(I) + AN was exposed to light, polymer was obtained with an induction period of only 0.20 min (Table 1).

Effect of Ag(I) Concentration

An increase in Ag(I) from 0.02 to 0.10 mol/L increased the rate, and the plot of log R_p vs log [Ag(I)] indicated the order in [Ag(I)] to be 0.5 (Fig. 1A). This indicates termination by mutual combination of two growing polymer radicals. If the termination had been affected by Ag(I), the order in [Ag(I)] should have been zero or negative. The

TABLE 1[a]

Time, min	% Conversion	$R_p \times 10^5$ mol/(L·s)
30	3.86	1.62
40	5.67	1.79
60	9.59	2.02
80	12.0	1.89
100	12.7	1.60

[a] [Ag(I)] = 0.080 mol/L; [ISP] = 0.200 mol/L; [AN] = 0.760 mol/L; 298 K.

fractional order also indicates that Ag(I) may be involved in complex formation either with the monomer or with ISP. Earlier workers [1, 2, 4] have proposed formation of a complex between Ag(I) and AN which decomposed to give atomic silver and NO_3 radical. The latter thus formed was assumed to initiate the polymerization, but the rates were found to be very low when it was repeated in aqueous medium. However, in the present work, in the presence of ISP, the rates were found to be relatively high. Ag(I) is also known to form colorless complexes with oxygen-containing compounds [7, 8]. Though there is a possibility of formation of two types of complexes, viz., $(Ag\text{-}AN)^+$ and $(Ag\text{-}ISP)^+$, we assume the decomposition of $(Ag\text{-}ISP)^+$ complex to be faster since, in the absence of ISP, polymer was obtained only after 2 h as compared to less than 20 min in its presence. IR spectra of the polymer show a broad peak at 3 600 cm^{-1}, corresponding to the –OH group, and indicating the presence of the ketyl group which initiates polymerization. This indicates that $(Ag\text{-}ISP)^+$ is dissociating faster to give ketyl radicals and that decomposition of the $(Ag\text{-}AN)^+$ complex to give monomer and nitrate radical is negligible.

Effect of ISP Concentration

The rate of polymerization increased with an increase in [ISP], and the order in [ISP] was found to be 0.5 (Fig. 1B). This fractional order in [ISP] supports both formation of an $(Ag\text{-}ISP)^+$ complex and mutual type of termination. If the termination step were affected by Ag(I), the order in [ISP] would have to be unity.

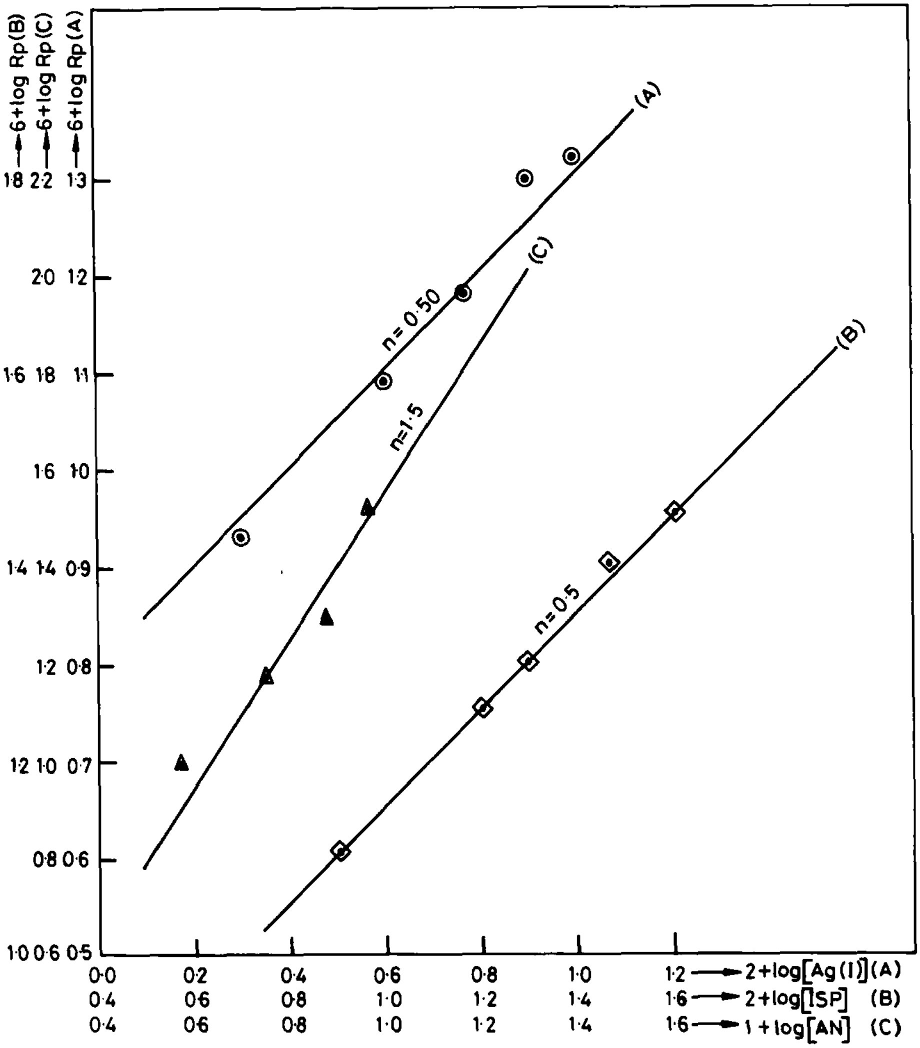

FIG. 1. (A) Plot of log R_p vs 2 + log [Ag(I)]. [AN] = 0.760 mol/L; [ISP] = 0.200 mol/L; temperature, 298 K. (B) Plot of log R_p vs 2 + log [ISP]. [Ag(I)] = 0.080 mol/L; other conditions are the same as in A. (C) Plot of log R_p vs 1 + log [AN]. Conditions are the same as in A and B.

TABLE 2

Intensity of light, $I_a \times 10^{-15}$, quanta/s	$R_p \times 10^6$ mol/(L·s)	$R_p/(I_a)^{1/2}$
5.40	20.2	8.69
5.05	18.7	8.32
3.65	16.6	8.68
1.95	11.6	8.30

Effect of Monomer Concentration

Increasing the monomer concentration increased the rate of polymerization, and the order in [M] was found to be 1.5 (Fig. 1C).

Effect of Intensity (I_a)

Increasing the intensity increased the rate, and the rate of polymerization was found to be proportional to $(I_a)^{1/2}$ (Table 2).

The following mechanism is proposed to explain the results:

$$\mathrm{Ag(I)} + (\mathrm{ISP}) \xrightleftharpoons{K_1} (\mathrm{complex})_1. \tag{1}$$

$$\mathrm{Ag(I)} + \mathrm{M} \xrightleftharpoons{K_1'} (\mathrm{complex})_2. \tag{2}$$

$$(\mathrm{Complex})_1 \xrightleftharpoons{I_a} (\mathrm{complex})_1^*. \tag{3}$$

$$(\mathrm{Complex})_2 \xrightleftharpoons{I_a'} (\mathrm{complex})_2^*. \tag{4}$$

$$(\mathrm{Complex})_1^* \xrightleftharpoons{k_1} \mathrm{Ag(O)} + \dot{\mathrm{R}} + \mathrm{H}^+. \tag{5}$$

$$(\mathrm{Complex})_2^* \xrightarrow{k_1'} \mathrm{Ag(O)} + \mathrm{N\dot{O}_3} + \mathrm{M}. \tag{6}$$

$$\mathrm{R}^{\cdot} + \mathrm{Ag(I)} \xrightarrow{k_0} \text{products}. \tag{7}$$

Initiation:

$$M + R^{\bullet} \xrightarrow{k_i} M_1^{\bullet}. \tag{8}$$

Propagation:

$$M_1^{\bullet} + M \xrightarrow{k_p} M_2^{\bullet}. \tag{9}$$

$$M_n^{\bullet} + M \xrightarrow{k_p} M_{n+1}^{\bullet}. \tag{10}$$

Termination:

$$(M_n^{\bullet}) + (M_m^{\bullet}) \xrightarrow{k_t} M_{n+m} \text{ (polymer)}. \tag{11}$$

Applying the steady-state principle to reactive intermediates, the rate law becomes

$$R_p = k_p \left\{ \frac{I_a k_i [\text{ISP}] [\text{Ag(I)}] [M]}{k_t (k_i [M] + K_0 [\text{Ag(I)}]} \right\}^{1/2} [M]$$

The above rate law explains well all the experimental results obtained. For the above mechanism, the decomposition of $(\text{complex})_2$ to give atomic silver and $NO_3^{\bullet}$ followed by initiation with $NO_3^{\bullet}$ is discounted on the basis that the polymer was obtained only after 2 h in the absence of ISP.

ACKNOWLEDGMENT

One of the authors (T.P.S.) is grateful to CSIR, India, for the award of a junior research fellowship.

REFERENCES

[1] H. Schnecko, Makromol. Chem., 111, 146, 158 (1968).
[2] H. Schnecko, Chimia (Aarau), 19, 113 (1965).
[3] G. A. Delzenne, Photogr. Sci. Eng., 7, 335 (1963).
[4] H. W. Schnecko, Makromol. Chem., 66, 19 (1963).

[5] S. Rajan and D. Ramesh, J. Org. Chem., 44, 138 (1979).
[6] C. F. Wells and G. Davies, Trans. Faraday Soc., 63, 2737 (1967).
[7] N. V. Sidgwick, The Chemical Elements and Their Compounds, Oxford University Press, Oxford, England, 1950, p. 141.
[8] A. D. E. Pullin and J. McPullock, Trans. Faraday Soc., 54, 11 (1958).

Received April 18, 1985
Revision received July 16, 1985