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NOTE

DYE-SENSITIZED PHOTOPOLYMERIZATION OF ACRYLONITRILE WITH THE EOSIN-PERIODATE INITIATING SYSTEM

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ABSTRACT

A new photoinitiating system (eosin-periodate) was employed for the polymerization of acrylonitrile in which dye acts as both sensitizer and reducing agent. The rate of polymerization was found to be proportional to monomer concentration, dye concentration, and light intensity, but independent of periodate concentration. A mechanism involving initiation by OH radicals and termination by periodate is proposed to explain the results.

INTRODUCTION

Generally, in a photoinitiating system consisting of a dye and a reducing agent, the excited-triplet-state dye acts as the oxidizing agent [1, 2]. In a system consisting of eosin dye and a reducing agent, the excited dye abstracts a hydrogen atom from the reducing agent to form a semiquinone dye and the semioxidized product of the reducing agent. However, it is possible to reverse this reaction if the reducing agent is replaced by a suitable oxidizing agent. In such a case the dye acts as a reducing agent [3-6]. Formation of semioxidized dye species by electron transfer between ground-state oxidant and excited-triplet-state dye was confirmed by flash photolysis [3]. Recently, McNally et al. [7] reported that a system containing a dye and a reducing agent is an effective initiator when periodate is present. This is attributed to a net increase in the production of initiating free radicals. A preliminary study showed that, even in the absence of a reducing agent, the above system is capable of initiating the polymerization. In order to elucidate the mechanism of this initiating system, the polymerization of acrylonitrile with eosin as a dye and periodate as an oxidant has been studied.

EXPERIMENTAL

All the reagents used were of AnalaR grade. Stabilized acrylonitrile was purified by washing with dilute acid and alkali followed by water. It was then dried over anhydrous calcium chloride and distilled under reduced pressure. KIO_4 and eosin supplied by BDH were used as received. Photolysis used a 500-W tungsten lamp, and its output was stabilized by an automatic line-voltage corrector (Instruments Techniques Limited, Hyderabad, India). Standard ferrioxalate actinometry was employed for measuring the light intensity. The procedure employed for following the rate of polymerization is described elsewhere [8].

RESULTS AND DISCUSSION

The polymerization was conducted at 298 K in an inert atmosphere. A steady state was attained within 15 min, and conversion was proportional to the time (Table 1). Polymerization was not observed in the absence of eosin or periodate or both. The following conclusions can be drawn from the results in Fig. 1.

Effect of Eosin Concentration on Rate of Polymerization. The rate of polymerization increased with [eosin], and the order in [eosin] was found to be unity (Fig. 1).

Effect of KIO_4 Concentration on Polymerization Rate. Polymerization was not observed when $[KIO_4]$ was less than 0.5 mmol/L. At higher concentrations, however, the rate was found to be independent of $[IO_4^-]$. The order in $[KIO_4]$ would have been 0.5 if mutual termination occurred. The zero-order dependence of rate on $[KIO_4]$ suggests a linear type of termination.

TABLE 1. Rate of Polymerization[a]

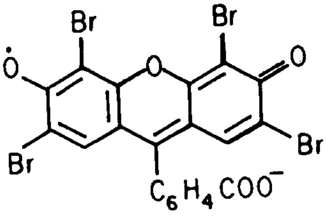
Time, min	Conversion, %	$R_p \times 10^4$, mol/(L·s)
8.00	4.76	0.904
12.0	9.72	1.23
15.0	15.1	1.53
20.0	20.0	1.52
25.0	23.7	1.45

[a] $[KIO_4]$ = 3.00 mmol/L, [eosin] = 0.50 mmol/L, [AN] = 912 mmol/L, $I_a = 6.30 \times 10^7$ quanta/(L·s), temperature = 298 K.

Effect of AN Concentration on Polymerization Rate. R_p increased with [AN], and the order in [AN] was found to be unity (Fig. 1).

Effect of Light Intensity on Polymerization Rate. R_p increased with increasing light intensity, and the order with respect to I_a was found to be unity (Fig. 1).

It is reported [3] that a highly stabilized radical is produced during the photooxidation of dyes such as eosin and erythroeosins, by a suitable oxidant. In the case of eosin the semioxidized form was shown [3] to have the following structure:



The above radical is highly resonance stabilized and incapable of initiating polymerization [9] in the present case. The hydrated form of periodate $[H_2IO_6^-]$ is known to decompose to give hydroxyl radicals when exposed to light at 220-290 nm [10-12]. Since the reaction was carried out in Pyrex glass vessels, direct absorption of UV light by periodate is ruled out, so that, in the present case, the photochemical activity of KIO_4 is probably due to sensitization by the dye. The rate of dye fading was very slow when eosin-

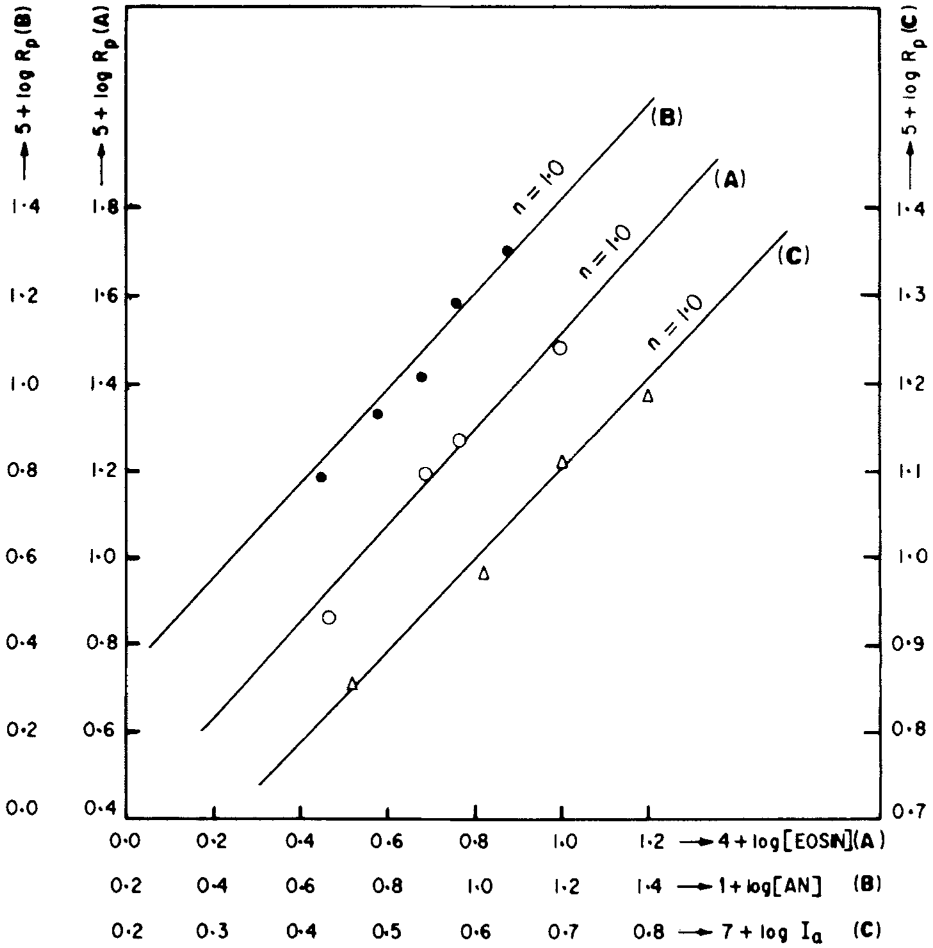


FIG. 1. Plot of (A) log [eosin] ; (B) log [AN], and (C) log I_a vs log R_p. [Periodate] = 3.00 mmol/L; [AN] = 912 mmol/L; [eosin] = 0.50 mmol/L; I_a = 6.30 X 10^7 quanta/(L·s); temperature, 298 K.

KIO_4 was exposed to light. However, the dye fading rate increased rapidly when AN was added to the system, possibly due to the interaction of AN with eosin or periodate. There was a shift in λ_{max} of the periodate solution from 220 to 280 nm when AN was added, suggesting complex formation between AN and periodate.

The triplet state of the dye was assumed to react with the complex to give hydroxyl radicals, which probably initiate the polymerization. This assumption receives support from the IR spectra of the polymer, which show the characteristic O–H stretching frequency at 3600 cm^{-1}.

On the basis of the above experimental results and discussion, the following mechanism is suggested.

$$D \xrightarrow{I_a} {}^1D \rightsquigarrow {}^3D, \tag{1}$$

$$M + H_4IO_6^- \overset{K}{\rightleftharpoons} \text{complex}. \tag{2}$$

Initiation:

$$\text{Complex} + {}^3D \xrightarrow{k_i} HO{-}M^{\bullet} + D^{\bullet} + H_2IO_4^- + H_2O. \tag{3}$$

Propagation:

$$M_1^{\bullet} + M \xrightarrow{k_p} M_2^{\bullet}, \tag{4}$$

$$M_n^{\bullet} + M \xrightarrow{k_p} M_{n+1}^{\bullet}. \tag{5}$$

Termination:

$$M_n^{\bullet} + \text{complex} \xrightarrow{k_t} \text{polymer} + H_3IO_5^- + H_2O, \tag{6}$$

$$2D^{\bullet} \xrightarrow{k_0} \text{dimer}. \tag{7}$$

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

$$R_p = \frac{k_p k_i I_a [D]\,[M]}{k_t}, \tag{8}$$

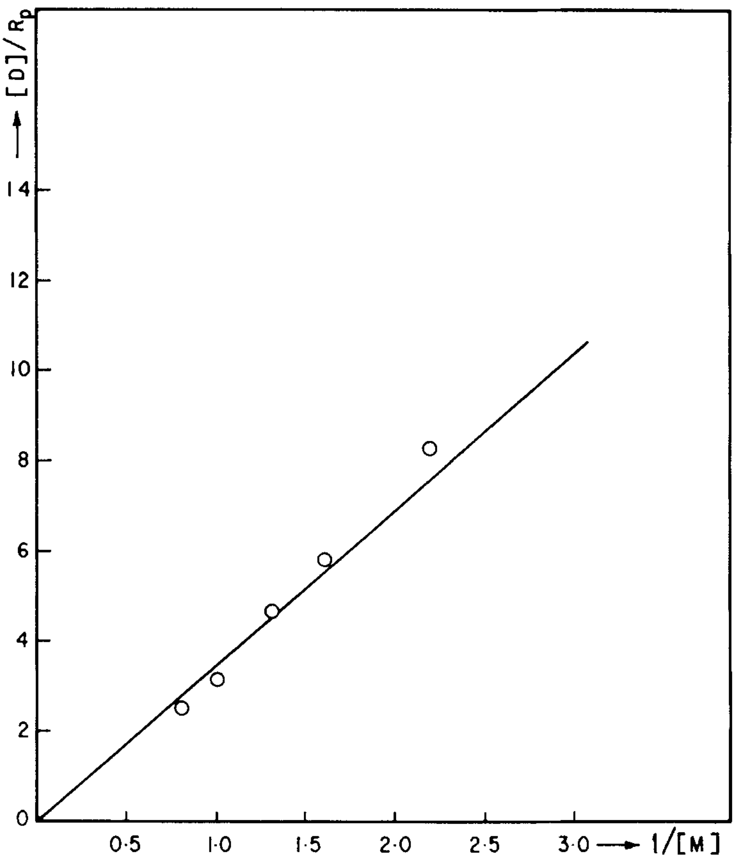


FIG. 2. A plot of $[D]/R_p$ vs $1/[M]$. [Periodate] = 3.00 mmol/L; [AN] = 912 mmol/L; $I_a = 6.30 \times 10^7$ quanta/(L•s); [eosin] = 0.50 mmol/L; temperature, 298 K.

which is consistent with all the observed results. Rearrangement of Eq. (8) gives

$$\frac{[D]}{R_p} = \frac{k_t}{k_p k_i I_a} \frac{1}{[M]} \tag{9}$$

A plot of $[D]/R_p$ vs $1/[M]$ was linear, passing through the origin according to Eq. (9), supporting the mechanism suggested (Fig. 2).

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