Pyronine G-sensitized Photopolymerization of Vinyl Monomers

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Kinetics of polymerization of methylmethacrylate sensitized by the system pyronine G + ascorbic acid + buffer (citric acid-Na$_2$HPO$_4$) in aqueous medium have been studied. A mechanism involving electron transfer from the excited complex, ascorbic acid-Na$_2$HPO$_4$, to the monomer resulting in the radicals of the latter has been suggested. Certain rate parameters have also been evaluated.

DYES alone or in conjunction with some electron donors have been used as sensitizers for polymerization of vinyl monomers[1-8]. So far, three types of mechanisms for the dye-sensitized photopolymerization of vinyl monomers were proposed. These involve: (a) direct energy transfer between the excited dye molecule and the vinyl monomer[1], (b) direct interaction of excited dye molecule and vinyl monomers[2-4,6,8], giving rise to radicals, and (c) production of the free radicals by the reaction of the excited dye with a third substance, like oxygen, OH$^-$ or the reducing agent[5,9-11]. Conflicting views have often been expressed with regard to not only the mechanism, but also the necessity or otherwise of oxygen and/or reducing agent in the system for polymerization to occur. Sherriff and Santappa[13] investigated the kinetics of uranine-ascorbic acid sensitized photopolymerization of vinyl monomers. Santappa and Anwaruddin[15] found that anthraquinone sulphonates alone did not initiate polymerization, but anthraquinone + Cl$^-$ initiated polymerization without induction period. In this paper kinetics of polymerization of methylmethacrylate sensitized by a xanthene dye, pyronine G, is described. Only a qualitative report on the initiating capacity of pyronine G was found in the literature[6].

In agreement with the finding of Watanabe[9] that xanthene type of dyes initiate polymerization in the presence of reducing agent, we found that pyronine G could initiate polymerization only in the presence of reducing agents such as ascorbic acid or phenyl hydrazine hydrochloride.

All the experiments were, however, conducted under deaerated conditions at 35° ± 0·1°C. The system with methyl methacrylate monomer buffered at pH 6 (citric acid-Na$_2$HPO$_4$) in aqueous medium was deaerated and then irradiated with monochromatic light of λ = 546 mμ, isolated[16,17] from a high pressure mercury vapour lamp (250 watts, supplied

by B.T.H. Co., UK) for 25 min. The polymerization got initiated within a few seconds of irradiation. After 25 min of irradiation the polymer was filtered off. Rate of monomer disappearance, −d[M]/dt, was computed from the weight of the dried polymer. The filtrate after removing the polymer was used for the determination of the dye concentration taking advantage of absorption of the latter at λ = 520 mμ, the optical measurements being made in a spectrophotometer (Hilger-Watts Uvispeck H-700). The rate of dye disappearance, −d[D]/dt, was thus computed. The chain length of the poly(methylmethacrylate) was determined viscometrically using the equation due to Bexandale *et al.*[14], $n = 2·81 \times 10^3(\eta)^{1·32}$, at 25°C in benzene. Rate measurements were made against variations in light absorption fraction k_e (effected by variations in dye concentration), light intensity, I, monomer concentration, [M], and reducing agent concentration, [AA] [(AA) = ascorbic acid].

The results are summarized below.

(a) Polymerization took place when the system, dye-ascorbic acid, buffered with citric acid-Na$_2$HPO$_4$ for pH 6, was irradiated both in the presence and the absence of oxygen. There was considerably high induction period (55 min) when the system was undeaerated.

(b) λ = 546 mμ, 365 mμ were found to be effective.

(c) The steady state curve for −d[M]/dt versus time indicated that the rate levelled off after 25 min. So, most of our experiments were confined to 25 min.

(d) −d[M]/dt was found to be proportional to [M]$^{3/2}$ (Fig. 1, curve A), [AA]$^{1/2}$ (Fig. 1, curve B), $k_e^{1/2}$ (Fig. 1, curve D) and I$^{1/2}$ (Fig. 1, curve C), and −d[D]/dt was found to be proportional to k_e (Fig. 2, curve C) and [AA] (Fig. 2, curve A), and I (Fig. 2, curve B).
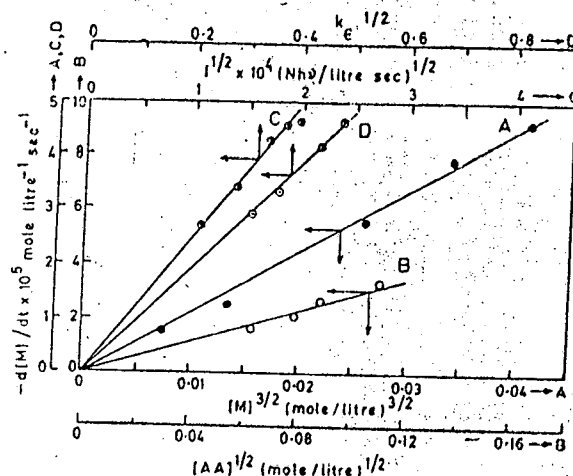

Fig. 1 — (A) Plot of −d[M]/dt × 10^5 mole litre^{-1} sec^{-1} versus [M]$^{3/2}$ (mole litre^{-1})$^{3/2}$. (B) Plot of −d[M]/dt × 10^5 versus [AA]$^{1/2}$ (mole litre^{-1})$^{1/2}$. (C) Plot of −d[M]/dt × 10^5 versus I$^{1/2}$ × 10^4 (Nhv)/(litre sec)$^{1/2}$. (D) Plot of −d[M]/dt × 10^5 versus $k_e^{1/2}$

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(e) The viscosity results showed that the chain length was inversely proportional to $[\text{ascorbic acid}]^{1/2}$, light intensity (I) and light absorption fraction (k_{ϵ}); plot of log n versus log $[AA]$ was linear (Fig. 3, curve A) with a slope equal to one half; plots of log n versus log I and log n versus k_r were linear (Fig. 3, curves C and B respectively) with slopes equal to unity in each case.

(f) Complex formation was observed[18] between ascorbic acid and disodium hydrogen orthophosphate and the composition was found to be 1:1 and the stability constant K was found to be 3.09×10^3.

Apart from the above, we also made the following observations: (i) No initiation was observed with dye alone. (ii) Initiation of polymerization was not noticed in the absence of ascorbic acid. (iii) The decrease in [ascorbic acid] was noticed after irradiation of the system. (iv) Polymerization was also found in the presence of ascorbic acid and buffer, but not in the presence of either alone and the rate was found to be lower than that observed with dye + ascorbic acid + buffer. (v) The complex Na_2HPO_4-ascorbic acid in the system was photo-active both in the presence and absence of oxygen. (vi) The presence of citric acid in the buffer had nothing to do with rate of polymerization since no change in the latter was observed in the presence or absence of the former. (vii) The rates were found to be very low when fructose and glucose were used in place of ascorbic acid.

A reaction scheme based on primary photochemical reaction being excitation of the complex Na_2HPO_4-ascorbic acid, followed by transfer of electron from the excited complex to monomer resulting in a radical from the latter, appears to be plausible. On the basis of such a scheme the rate expressions derived are:

$$-\frac{d[M]}{dt} = k_p/k_t^{1/2}[M]^{3/2}\left[\frac{k_r K[AA]k_{\epsilon(\text{total})}I[D]}{k_f}\right]^{1/2}$$

$$-\frac{d[D]}{dt} = \frac{k_r[M][D]K[AA]k_{\epsilon(\text{total})}I}{k_f}$$

$$n = \left[\frac{k_p[M]k_f k_t}{k_r k_{\epsilon(\text{total})}K[AA]I[D]}\right]^{1/2}$$

k_p and k_t are the usual propagation and termination rate constants, k_r is the rate constant for radical production, and k_f is the dark back rate constant for the primary photochemical step.

From the plots $-d[D]/dt$ versus I, k_{ϵ} (Fig. 2, curves B and C), $-d[M]/dt$ versus $[M]^{3/2}$, $I^{1/2}$, $k_{\epsilon}^{1/2}$, and $[AA]^{1/2}$ (Fig. 1, curves A, C, D and B) rate parameters $k_p/k_t^{1/2} = 1$ to 1.1 were evaluated. These values were comparable with values[19,20] reported earlier with other initiators.

Fig. 2 — (A) Plot of $-d[D]/dt \times 10^9$ mole litre^{-1} sec^{-1} versus $[AA] \times 10^3 M$. (B) Plot of $-d[D]/dt \times 10^9$ versus $I \times 10^8$ (Nhv)/litre sec. (C) Plot of $-d[D]/dt \times 10^9$ versus k_{ϵ}
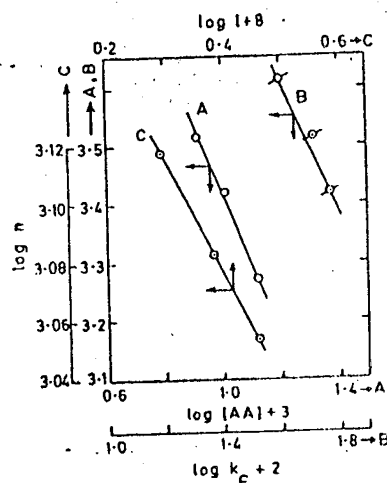
Fig. 3 — (A) Plot of log n versus log $[AA]+3$. (B) Plot of log n versus log $k_{\epsilon}+2$. (C) Plot of log n versus log $I+8$

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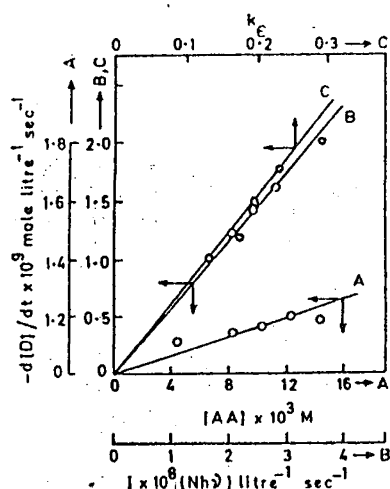20. NATARAJAN, L. V. & SANTAPPA, M., Polymer Lett., 5 (1967), 357.

POLYMERIZATION OF AQUEOUS ACRYLIC ACID PHOTO-INITIATED BY MONO- AND DI-AZIDO COBALT (III) AMINES

QUALITATIVE studies on the photolysis of azido-pentamine-cobalt (III) complexes by Linhard et al.[1] and Adamson et al.[2] followed by detailed kinetic studies by Natarajan and Santappa[3-5] on the polymerization of aqueous vinyl monomers photo-initiated by the complex established that N_3 radicals were the initiating species. In the present study it was found that irradiation of azidopentaminecobalt (III) complex as well as diazidotetraminecobalt (III) complexes at λ ≃ 365 mμ led to the evolution of nitrogen in the absence of any monomer, while in the presence of acrylic acid, monomer, initiation of the polymerization of the latter was observed under deaerated conditions. The kinetics of : (a) the decomposition of the complexes was followed both spectrophotometrically and by the volume of nitrogen evolved (for azidopentamine complex), (b) the rate of polymerization of the monomer was followed by determining the rate of disappearance of the monomer, $-d[M]/dt$, bromometrically, (c) the disappearance of the complex $-d[C]/dt$, was followed spectrophotometrically using a calibrated Beer's law curve (at λ = 300 mμ, ε = 8500 for monoazido[*] and at λ340 mμ, ε = 14,400 for the diazido complex), and (d) the chainlengths (n) of polyacrylic acid samples were determined viscometrically using the Mark-Houwink relationship.[6]

We have observed that : (i) initiation of polymerization under deaerated conditions was photochemical in nature and not thermal, (ii) steady state was attained in about 15 minutes with ≈ 30% conversion of the monomer, (iii) decomposition of the complex in the absence of the monomer was first order with respect to the former, (iv) the values of $-d[M]/dt$ were proportional to $[M]^{2/3}$, $k_e^{\frac{1}{2}}$ and $I^{\frac{1}{2}}$ in the case of azidopentamine complex and to $[M]^2$, k_e and I in the case of diazido-tetramine complex, (vi) the rate of polymerization was independent of $[H^+]$, (vii) $-d[C]/dt$ was proportional to k_e and I in both the cases, and (viii) n was proportional to $[M]^{\frac{1}{2}}$, $k_e^{-\frac{1}{2}}$ and $I^{-\frac{1}{2}}$ for the monoazido initiator and proportional to $[M]$ and $[C]^{-1}$ in the case of diazido initiator.

Our experimental observations of the polymerization reactions were explained by the reaction scheme consisting of : (a) photo-excitation of the complex, $(k_e I)$, (b) dark back reaction leading to the de-excitation of the complex (k_d), (c) redox decomposition of the excited complexes yielding the azide radical (k_r), (d) initiation of polymerization by the azide radical (k_i), (e) propagation of polymerization (k_p), (f) termination by mutual combination of the radicals $(k_{t,3})$ for mono-azido initiator, (g) termination by the complex molecules $(k_{t,1})$ for diazido initiator, and (h) radical scavenging by and the consequent reduction of the complex (k_2).
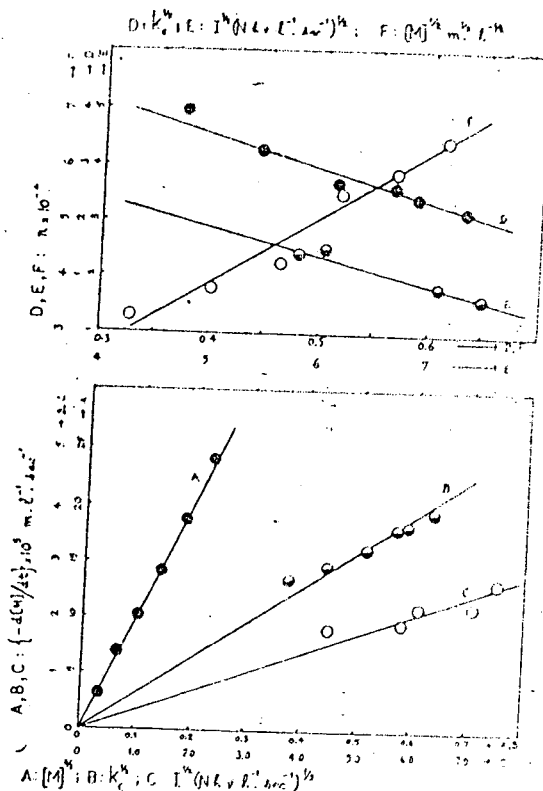

$$D : k_e^{\frac{1}{2}} I ; E : I^{\frac{1}{2}} (N_3 + C' \cdot \text{sec}^{-1})^{\frac{1}{2}} ; F : [M]^{\frac{1}{2}} m^{\frac{1}{2}} \ell^{-\frac{1}{2}}$$

$$A : [M]^{\frac{1}{2}} ; B : k_e^{\frac{1}{2}} ; C : I^{\frac{1}{2}} (N_3 + C' \cdot \text{sec}^{-1})^{\frac{1}{2}}$$

FIG. 1. Polymerization of Acrylic acid photo-initiated by azidopentamine cobalt (III) chloride at λ = 365 mμ.

Assuming stationary state concentrations for the reactive species, the rate expressions for monoazido initiator derived were :

$$-d[M]/dt$$
$$= \frac{k_p k_i^{1/2} k_r^{1/2} k_e^{1/2} I^{1/2} [M]^{3/2}}{k_{t_3}^{1/2} (k_r + k_d)^{1/2} (k_i [M] + k_2 [C])^{1/2}} \quad (1)$$

$$d[C]/dt$$
$$= \left\{ 1 + \frac{k_2 [C]}{k_i [M] + k_2 [C]} \right\} \frac{k_r}{k_r + k_d} k_e I \quad (2)$$

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and

$$\Pi = \frac{k_p [M]^{1/2} (k_r + k_d)^{1/2} (k_i [M] + k_2 [C])^{1/2}}{k_{t_i}^{1/2} k_r^{1/2} k_i^{1/2} k_e^{1/2} I^{1/2}}$$

(3)

Similarly, for the diazido complex:

$$\frac{d[M]/dt}{} = \frac{k_p k_i k_r k_e I [M]^2}{(k_{t_i} [C]) (k_d + k_r) \{(k_i [M] + k_2 [C])\}}$$

(4)

$$\frac{d[C]/dt}{} = \frac{2k_r}{(k_d + k_r)} k_e I$$

(5)

and

$$\Pi = \frac{k_p [M]}{k_{t_i} [C]}$$

(6)

Rate expressions derived on the basis of initiation by the excited complex, terminations by the primary radical or by the excited complex did not conform to experimental results.

ϕ_{net} for the disappearance of azidopentamine complex was found to be ~0·19 at $\lambda = 365$ mμ both in the presence and absence of the monomer while the value of $k_p/k_t^{1/2} = 3\cdot4$ (mole./l)$^{1/2}$ sec.$^{1/2}$ was obtained from plots of

$-d[M]/dt$ and $-d[C]/dt$ against the variables. ϕ_{net} for the disappearance of diazidotetramine complex was found to be ~0·27 at $\lambda = 365$ mμ both in the presence and absence of the monomer while the value of $k_p/k_t = \cdot14$ was obtained from plots of $-d[M]/dt$ against the variables. ϕ_{net} for diazidotetramine complex is reported for the first time and the $k_p/k_t^{1/2}$ and k_p/k_t values for acrylic acid polymerization are being reported for the first time by any initiator.

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