

A SENSITIZED PHOTOINITIATION SYSTEM — BIS(7-DIETHYLAMINO COUMARIN) KETONE-3 AND DIPHENYLIODONIUM SALT COMBINATION

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ABSTRACT

Bis(7-diethylaminocoumarin) ketone-3(DACK) and diphenyliodonium salt(DPIO) combination as an effective photoinitiation system for radical polymerization has been investigated. The sensitized photolysis of DACK/DPIO leads to bleaching of DACK and decomposition of DPIO to generate initiating radical species. The electron transfer sensitization occurs mainly from the triplet state of DACK. The photobleaching obeyed a second-order kinetics and the rate constant was evaluated to be $31.3 \text{ mol}^{-1} \cdot \text{l} \cdot \text{s}^{-1}$. Photopolymerization of MMA initiated by DACK/DPIO was carried out in acetonitrile solution. The polymerization rate was found to be proportional to the concentration of DACK, DPIO and MMA with the exponents of 0.34, 0.40 and 1.0 respectively. The initiated efficiency is comparable to those of small molecular ketones. The sensitized photoinitiation mechanism has been discussed.

INTRODUCTION

Ketones, particularly diacryl ketones, such as benzophenone, thioxanthone, are known to have relative high triplet yields and are utilized as triplet sensitizers for photochemical reactions. For practical application, high molar extinction coefficient is expected in the desired spectral region. Certain derivatives of 3-ketocoumarins with electron-donating substituents in the 7-position, such as bis(7-diethylaminocoumarin) ketone-3(DACK), are such a kind of promising triplet sensitizers^[1-3].

Ketocoumarins are used for photoinitiation polymerization, mainly in combination with activators. Williams had reported that the use of amines as activators gave quantum yield of initiated polymerization comparable to that of benzophenone/amine combination^[4]. Yamaoka studied a variety of ketocoumarins with 3,3,4,4-tetrakis(t-butylperoxycarbonyl)benzophenone to form high sensitive initiation systems for laser curing polymerization^[5].

In this paper, we recommend a new photoinitiation system in which DACK and diphenyliodonium salt were used as electron-donor and electron-acceptor respectively for free radical polymerization.

EXPERIMENTAL

Materials Bis(7-diethylamino coumarin)ketone-3, an orange red colour crystal,

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was obtained from Nippon Kankoh Shikiso Kenkyusho Co. Ltd. Diphenyliodonium tetrafluoroborate (DPIO) was prepared according to literature[6]. Methylmethacrylate (MMA) and all solvents were purified by conventional methods.

Methods Polymerization was carried out in a dilatometer ($\phi 10\text{mm}$) at 30°C . A Xenon lamp (400w) was used as the light source. The light below 300 nm was cut off by a Pyrex glass filter. UV/Vis absorption spectra and fluorescence spectra were recorded on a Diode Array 8451 A Spectrophotometer and a Hitachi MPF-4 Spectrofluorometer respectively. Fluorescence lifetime was determined in ariel acetonitrile using a ns time-resolved single photon counter (Horiba NAES-1100).

The oxidation potential was measured using a 79-1 Cyclic Voltameter (Jinan, China).

RESULTS AND DISCUSSION

I. Spectral characteristics

The absorption spectrum of DACK in acetonitrile shows a maximum at 456 nm with $9.12 \times 10^4 \text{ mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}$ of molar extinction coefficient. DPIO absorbs the light only below 300 nm with maximum at 228 nm ($\epsilon = 1.71 \times 10^4 \text{ mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}$). Evidently, in the DACK/DPIO combination, DACK is the only component sensitive to near UV and visible light (Fig. 1 a.). The typical fluorescence spectrum of DACK in acetonitrile is shown in Fig. 1 b. The intense fluorescence band at 493 nm was resulted from the excitation at 386 nm. The fluorescence lifetime of DACK was measured to be 1.88 ns. The short singlet lifetime may be attributed to the high $S \rightarrow T$ intersystem crossing efficiency ($\phi_{isc} = 0.94$).

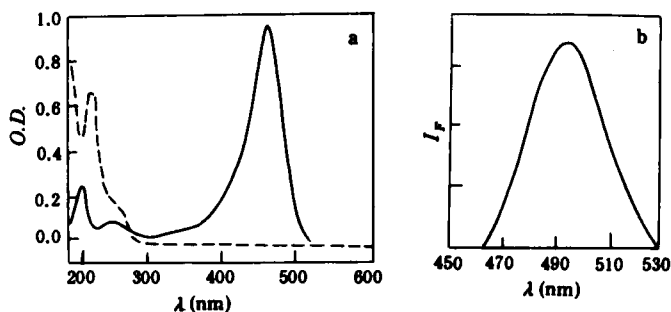


Fig. 1 a) Absorption spectra of DACK, (—) and DPIO, (---) in acetonitrile;
b) fluorescene spectrum of DACK in acetonitrile

2. Photolysis of DACK/DPIO combination

Photolysis of DACK in acetonitrile in the presence of DPIO led to bleaching of DACK and decomposition of DPIO to generate initiating radical species. The rate constant of DACK disappearance was estimated to be $31.3 \text{ mol}^{-1} \cdot \text{l} \cdot \text{s}^{-1}$ based on the observation of the change in optical density at 456nm (Fig. 2). The bleaching reaction obeys a second-order kinetics (see inset in Fig. 2). On the contrary, in the case of the absence of DPIO the bleaching of

DACK could not occur.

On account of the high intersystem crossing efficiency of DACK, it may be considered that the coumarins sensitized photolysis of onium salt proceeds mainly from the excited triplet state. Considering the triplet energy of DACK ($52 \text{ kcal} \cdot \text{mol}^{-1}$) is far lower than the triplet energy of DPIO ($74 \text{ kcal} \cdot \text{mol}^{-1}$)^[7], the sensitization could undergo only through electron transfer pathway. According to Weller equation^[8],

$$\Delta G = E^{\text{ox}} - E^{\text{red}} - E^* \quad (1)$$

where E^{ox} represents oxidation potential of DACK that was determined to be 1.1V by cyclic voltammetry method, E^{red} is reduction potential of DPIO (-0.2 V)^[9] and E^* is the triplet energy of DACK. The free energy change for the photoinduced electron transfer reaction of DACK/DPIO (ΔG) can be calculated to be $-22 \text{ kcal} \cdot \text{mol}^{-1}$. The high negative value of ΔG means that the electron transfer process in acetonitrile is diffusion-controlled ($k_{\text{dif}} = 2.7 \times 10^{10} \text{ mol}^{-1} \cdot \text{s}^{-1}$).

3. Photoinitiated polymerization

In our experimental condition, polymerization of MMA initiated by DACK/DPIO combination occurred more readily, but hardly when only using either DACK or DPIO alone. The polymerization rates were estimated from the slopes of conversion vs. time plots. The effects of initiator concentration and oxygen on polymerization rate are discussed separately.

(1) Initiator concentration

The polymerization was carried out at constant monomer concentration ($2.85 \text{ mol} \cdot \text{l}^{-1}$) in nitrogen purged acetonitrile. As shown in Fig.3, the polymerization rate is directly dependent on the concentrations of both DACK and DPIO up to $6 \times 10^{-4} \text{ mol} \cdot \text{l}^{-1}$, and then deviates with increasing concentration of DACK. Such a negative concentration effect can be attributed to that self-quenching of excited state and deactivation of intermediate become significant at high concentration range. The reaction orders with respect to DACK and DPIO concentrations are 0.34 and 0.40. These values, near that of benzophenone/tertiary amine^[10], indicate that the initiation efficiency of DACK/DPIO is comparable to those of small molecular ketones.

(2) Monomer concentration

A good linear correlation between polymerization rate and monomer concentration has been found when MMA concentrations varied from 1.0 to 7.0 $\text{mol} \cdot \text{l}^{-1}$ (Fig.3c). The reaction order with respect to MMA concentration is 1.0 in good agreement with the theoretical value. As a result, the total kinetic formula for the polymerization of MMA initiated by DACK/DPIO system can be expressed as follows:

$$R_p = k \cdot [\text{DACK}]^{0.34} \cdot [\text{DPIO}]^{0.40} \cdot [\text{MMA}]^{1.0} \quad (2)$$

where the concentration ranges are limited to $[\text{DACK}], [\text{DPIO}] \leq 6.0 \times 10^{-4} \text{ mol} \cdot \text{l}^{-1}$ and $[\text{MMA}] = 1.0 - 7.0 \text{ mol} \cdot \text{l}^{-1}$.

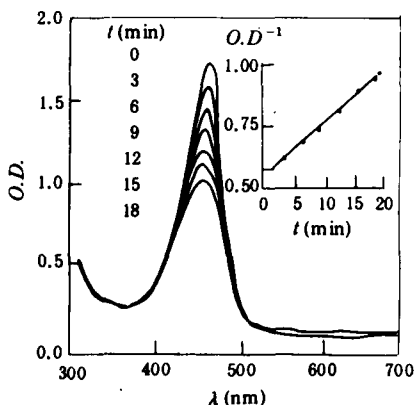


Fig. 2 Spectral change of DACK/DPIO with irradiation time
[DACK]=[DPIO]= $2.0 \times 10^{-5} \text{ M}$

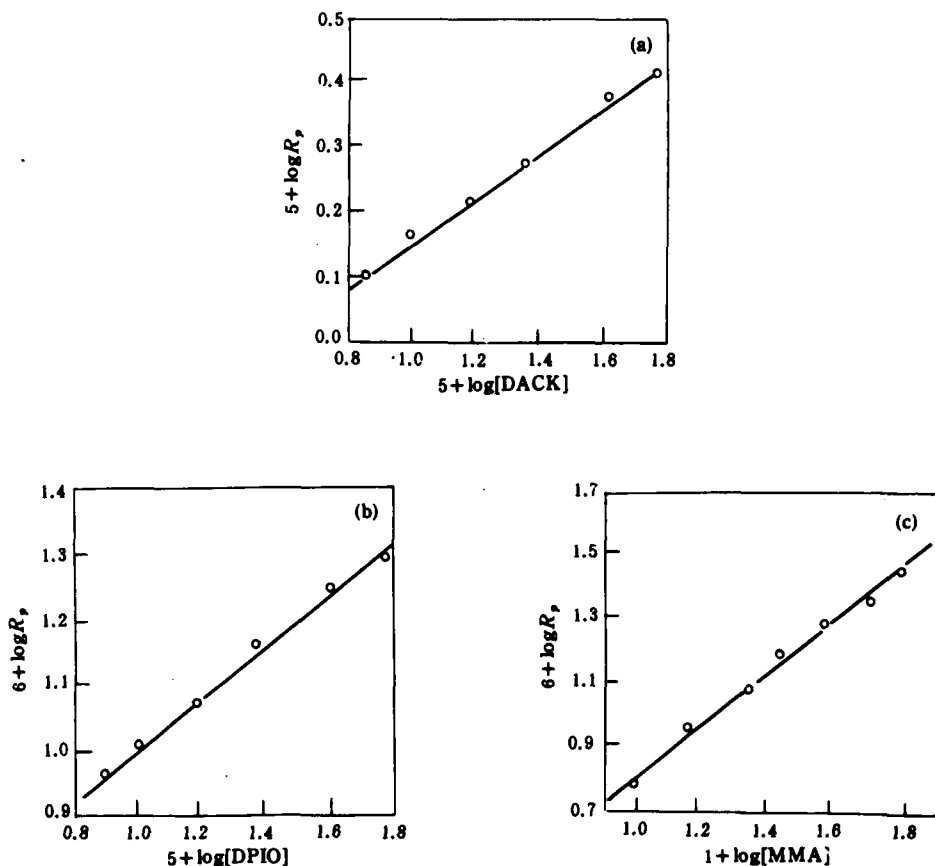


Fig. 3 Plots of R_p vs. a) [DACK], b) [DPIO] and c) [MMA]

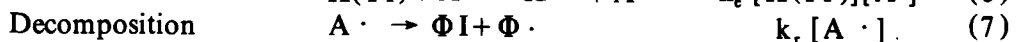
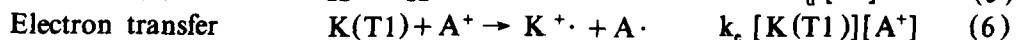
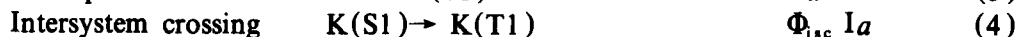
(3) Oxygen

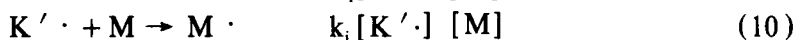
Table 1 shows the dependence of polymerization rate and inductive period on oxygen concentration. Comparing these data obtained both in nitrogen and in air, it can be seen that the polymerization rate decreases and inductive period increases in the presence of oxygen. The considerable inhibition of oxygen implies that the quenching of excited triplet state plays an important role as well as the commonly known inhibition of oxygen for free radical chain reaction.

Table 1 Oxygen effect on polymerization of MMA initiated by DACK/DPIO system

	Nitrogen	Air	Oxygen
$R_p (\times 10^5 \text{ mol} \cdot \text{l}^{-1} \cdot \text{s}^{-1})$	1.65	1.41	1.35
Inductive period (s)	60	360	900

Summarily, the sensitized photoinitiation induced by DACK/DPIO can be expressed as follows:





where K , A^+ , Φ and M represent DACK, DPIO, phenyl group and monomer, respectively. S_1 , T_1 and $*$ represent singlet, triplet and total excited states.

The overall efficiency of the initiation process includes a few factors,

$$\Phi_i = \Phi_{isc} \cdot \Phi_e \cdot \Phi_r \cdot f = \Phi_{isc} \cdot f \cdot \Phi_r \cdot \frac{k_e [A^+]}{\tau_0^{-1} + k_e [A^+]} \quad (11)$$

here ϕ_{isc} is the yield of intersystem crossing, Φ_e ; Φ_r are the efficiencies for electron transfer and decomposition of DPIO radical f represents the fraction of initiation of MMA. The decomposition of DPIO radical occurred much quickly ($k_r = 10^{10} \text{s}^{-1}$) and produced PhI and phenyl radical in acetonitrile exclusively^[11].

The polymerization rate can be expressed as eq. 12.

$$R_p = k_p \cdot k_i^{-\frac{1}{2}} \cdot [M] \cdot \Phi_i^{\frac{1}{2}} \cdot I_a^{\frac{1}{2}} = K_1^{\frac{1}{2}} \cdot k_p \cdot k_i^{-\frac{1}{2}} \cdot I_a^{\frac{1}{2}} [M] \cdot \left(\frac{k_e [A^+]}{\tau_0^{-1} + k_e [A^+]} \right)^{\frac{1}{2}} \quad (12)$$

$$R_p^{-2} = K_1^{-1} \cdot k_p^{-2} \cdot k_i \cdot I_a^{-1} \cdot [M]^{-2} \cdot (1 + \tau_0^{-1} \cdot k_e^{-1} \cdot [A^+]^{-1}) \\ = K_1^{-1} \cdot K_2 \cdot I_a^{-1} \cdot [M]^{-2} \cdot (1 + K_3 [A^+]^{-1}) \quad (13)$$

where $K_1 = \Phi_{isc} \cdot f \cdot \Phi_r$; $K_2 = k_p^{-2} \cdot k_i$; $K_3 = \tau_0^{-1} \cdot k_e^{-1}$

According to the eq. 13, for constant concentrations of both DACK and MMA, R_p^{-2} should correlate linearly with reciprocal concentration of DPIO. As shown in Fig 4, we observed the linear relationship within the limit of experimental error. Thus our experimental result is in agreement with the above mechanism proposed.

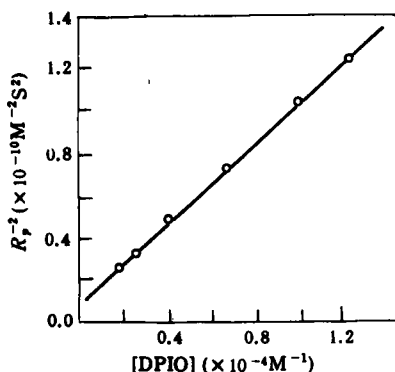


Fig. 4 Relationship between R_p^{-2} and $[DPIO]^{-1}$

Keywords:

Bis (7- diethylaminocoumarin) ketone -3 (DACK); Diphenyliodonium tetrafluoroborate (DPIO); Sensitive photoinitiation system; Triplet sensitizers

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