

PHOTOPOLYMERIZATION INITIATED BY DIMETHYLAMINOCHALCONE/DIPHENYL- IODONIUM SALT COMBINATION SYSTEM SENSITIVE TO VISIBLE LIGHT

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ABSTRACT

Several dimethylamino-substituted chalcone (i.e. dimethylaminobenzal acetophenone) (DBA) derivatives with intramolecular charge transfer transition character were used as visible light sensitizers for radical photopolymerization initiated by iodonium salt (DPIO). Initiating radical species is produced from DBA sensitized photolysis of DPIO through the single electron transfer, accompanying the bleaching of DBA. The activity of DBA decreases as a function of substituent attached to phenyl ring in the order: DBA-2 (OCH₃) > DBA-1 (H) > DBA-3 (Cl). The kinetic study on photopolymerization of MMA was carried out in CH₃CN solution at 30 °C by dilatometry. The polymerization rate was determined to be proportional to the concentration with exponents of 0.42, 0.25 and 0.86 for DPIO, DBA-1 and MMA, respectively.

INTRODUCTION

Onium salts, especially diaryliodonium and triarylsulphonium salts, with complex metal halide anions, such as BF₄⁻, AsF₆⁻, SbF₆⁻ etc., are thermally stable cationic photoinitiators^[1]. The low nucleophilicity of the anion reduces termination process and allows cationic polymerization to proceed under ambient conditions, which is more suitable to utilize in photoinduced curing^[2], imaging^[3] applications. However, the practical application of onium salts as initiators for technologically useful photopolymerization is severely hampered, as themselves absorb light significantly below 300nm, and require to broaden the spectral response into 300 — 400 nm and until visible range. The photoinduced electron transfer mechanism is usually proposed for this sensitization. As it is well known, triarylsulphonium salts and especially diaryliodonium salts possess low redox potentials with $E_{1/2}$ (On/On⁺) equal to -1.2V and -0.2V, respectively and may be employed as effective electron acceptors for composition of new photoinduced redox initiation system. Recently, various polynuclear compounds, such as arene, perylene, phenothiazine, thioxanthone etc., have been proposed as photosensitizers for onium salts^[2]. Since many of these compounds are known as carcinogenic substances, they have scarcely been used in practice. Other kind of suitable photosensitizers for this purpose are amines, which usually act as excellent

electron donors in electron transfer photochemistry. In the previous paper we have reported using small molecular amines as photosensitizers for radical vinyl photopolymerization through the formation of ground state CT complex with arylodonium salts^[4, 10]. In this work several tertiary amino-substituted chalcone derivatives were proposed as electron donors sensitive to visible light, which might be expected to occur single electron transfer reactions with arylodonium under irradiation.

EXPERIMENTAL

Materials and methods

Diphenyliodonium tetrafluoroborate (DPIO) was prepared and purified according to literature^[5], m.p. 135 °C, (lit. 136 °C). All p-dimethylamino benzalacetophenone derivatives (DBA) were prepared according to the method of Olomucki^[6] and Ichimura^[7] and recrystallized from methanol. The structures were confirmed by MS, NMR, IR and elementary analysis.

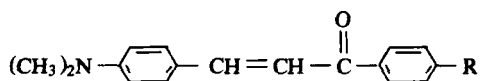
Photopolymerization procedure

Photopolymerization of MMA was carried out in dilatometer ($\varnothing$ 10mm) at 30 °C. The sample tubes were rotated around the light source. A Xenon lamp (400W) was used and short wavelength light ($<300\text{nm}$) was removed by Pyrex glass filter. The solutions were deaerated by bubbling highly pure nitrogen for 15 min. The monomers and solvents were redistilled before use.

Photoreaction The solutions for reaction were irradiated with a 400 W Xenon lamp in a manner similar to that of photopolymerization under N_2 . Reaction processes were monitored by measuring the absorption spectra.

RESULTS AND DISCUSSION

Several dimethylamino-substituted chalcone derivatives, i.e. dimethylaminobenzalacetophenone compounds (DBA) used in this work are listed below.



R	H	OCH ₃	Cl
Abbr.	DBA-1	DBA-2	DBA-3

1. Absorption spectra

The absorption spectra and molar extinction coefficients (ϵ_{max}) of some DBA derivatives in acetonitrile solution are listed in Table 1.

Table 1. Absorption properties of DBA derivatives

Compound	λ_{max}	$\epsilon_{\text{max}} (\text{M}^{-1} \cdot \text{cm}^{-1})$
DBA-1	406	3.8×10^4
DBA-2	402	4.0×10^4
DBA-3	416	3.5×10^4

* In acetonitrile solution.

These DBA derivatives have a common molecular structure in which dimethyl

amine group, as electron donor, substituted on phenyl ring is conjugated with carbonyl group as electron acceptor, which display an intramolecular charge transfer (CT) in polar solvents. Two absorption maxima, one at about 400 nm and the other at about 295 nm, can be observed. The longer wavelength peak with high molar extinction coefficient ($>10^4 M^{-1} \cdot \text{cm}^{-1}$) is characteristic of intramolecular CT transition. Introduction of an electron-withdrawing group ($-\text{Cl}$) to the phenyl ring at the other side of DBA molecule makes CT absorption band further red-shifted. The second absorption maximum at about 295 nm is of $\pi \cdot \pi^*$ transition character.

By adding fluoroboric acid to the DBA-1 solution, the absorption spectra of DBA-1 vary obviously as shown in Fig.1. The intensity of short wavelength maximum increases, along with a decrease in intensity of absorption band at long wavelength, and an isobestic point appears at 330nm. This spectral change can be explained by the acidification of DBA-1 to a protonated form, which destroys the original CT structure of DBA-1.

2. Radical photogeneration

Photolysis of diphenyliodonium salt (DPIO) when coupled with p-dimethylaminobenzalacetophenone compound (DBA) as electron donor proceeds readily through single electron transfer, leads both to bleaching of DBA and decomposition of DPIO to produce phenyl radical and cation radical species derived from DBA^[8], as depicted below:

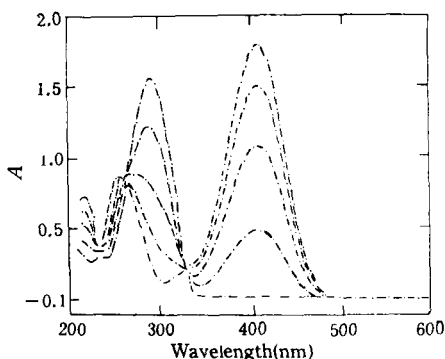
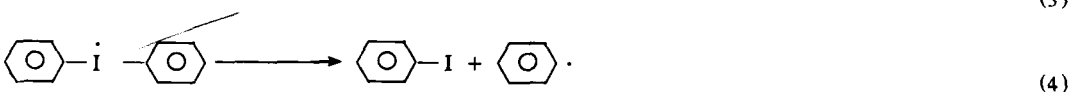
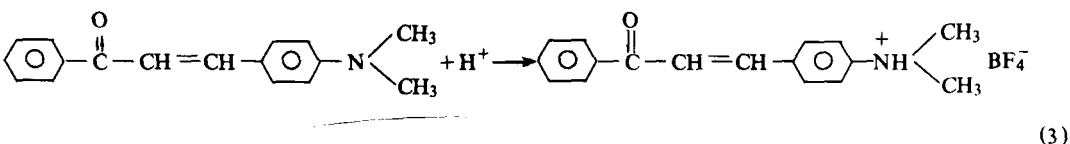
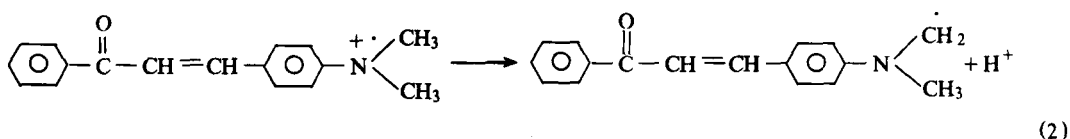
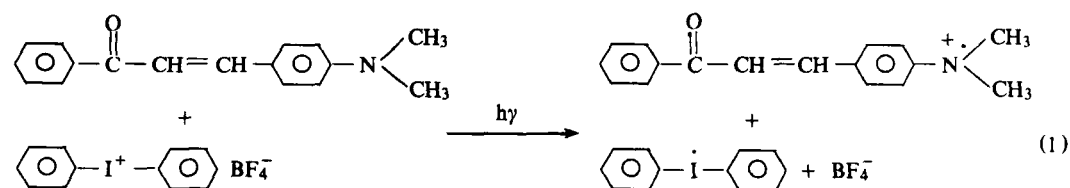


Fig.1 Change of spectrum of DBA-1 in acetonitrile by adding HBF_4 .
[DBA-1] = $4.2 \times 10^{-5} M$



Generally, the phenyl radical formed usually acts as effective initiating species and amine radical derived from chalcone DBA plays an important role in termination by the steric influence.

Two methods were useful to follow the DBA sensitized photolysis of DPIO in acetonitrile solution: (a) fluorescence quenching of DBA by DPIO; (b) disappearance of sensitizer DBA in reaction process. Both could be performed spectrophotometrically.

As shown in Fig. 2, the fluorescence of DBA-1 is quenched by iodonium salt which indicates that the photosensitization of DBA/DPIO system may easily occur via single excited electron transfer pathway. The iodonium concentration dependence of the relative fluorescence intensity (I_0/I) was plotted in inset of Fig. 2. The quenching constant K_q calculated from Stern-Volmer equation is $1.44 \times 10^{10} M^{-1} \cdot s^{-1}$ (singlet lifetime τ , 2.8 ns). It means that the photoinduced electron transfer from singlet excited DBA to ground state DPIO is nearly a diffusion controlled process^[9].

Photobleaching studies of DBA sensitized photolysis of DPIO could be followed from the changes in optical density at long wavelength band. The results of DBA-1 were illustrated in Fig. 3. Under irradiation the solution of DBA bleached gradually from yellow to colorless. The spectral change was similar to that observed upon the addition of acid to system as present in Fig. 1. The bleaching rates for these DBA decrease as a function of the nature of substituent in the order: DBA-2 > DBA-1 > DBA-3.

The results indicate that the electron-donating substituted group exhibits rate-enhancement, while electron-withdrawing group displays negative effect. The

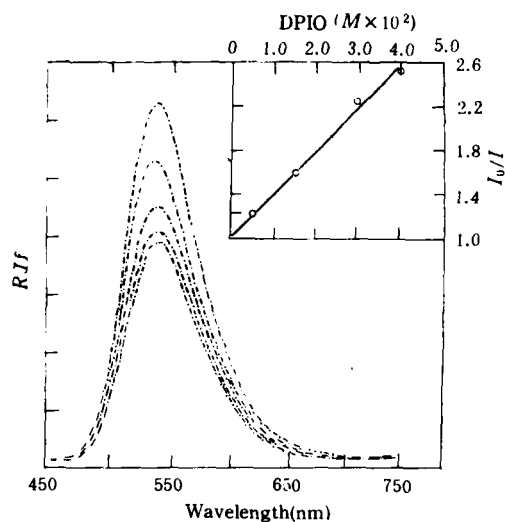


Fig.2 The fluorescence quenching of DBA-1 in acetonitrile by DPIO.
[DBA-1] = $5.0 \times 10^{-5} M$; λ_{ex} = 402 nm; λ_{em} = 534 nm

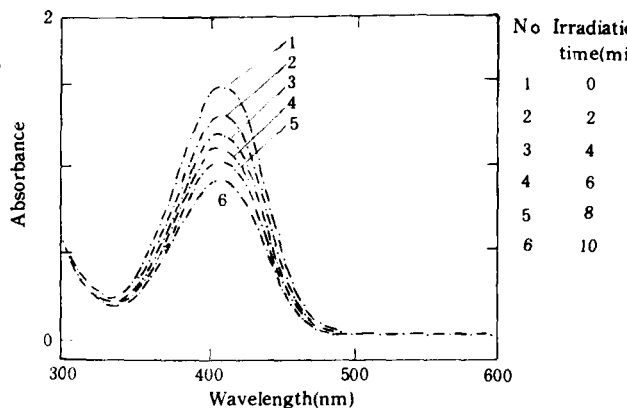


Fig.3 Spectrum change of DBA-1/DPIO system with irradiation time in acetonitrile solution.
[DBA-1] = $4.0 \times 10^{-5} M$; [DPIO] = $4.0 \times 10^{-5} M$

photobleaching rate constants (K_b) of different photosensitized systems were obtained which are listed in Table 2.

Table 2 Photobleaching rate constant (K_b) of DBA/DPIO system in acetonitrile solution

Reaction system	DBA-1 (H)	DBA-2 (OCH ₃)	DBA-3 (Cl)
K_b (M ⁻¹ · s ⁻¹)	30.30	72.32	22.75

3. Photopolymerization of MMA

Photopolymerization of MMA initiated with DBA/DPIO combination system was carried out in acetonitrile solution under N₂. The polymerization rate was determined from the conversion vs. time plot, and the experimental data were treated with the least square method.

(1) Photoinitiation by DPIO/DBA combination system

Fig.4 shows the relationships between percentage conversion of MMA and reaction time for polymerization initiated by different DPIO/DBA systems under the same concentration. It can be seen that DPIO alone cannot induce polymerization of MMA upon irradiation with visible light under the experimental condition (see curve 1). However, the polymerization proceeds readily with DPIO/DBA combination systems. The sensitization ability was found to vary with the substituent group attached to the phenyl ring of DBA derivatives (see curve 2—4). DBA with electron donating group showed higher activity than that of electron withdrawing group. As shown in Fig. 4, the polymerization rates decrease in the order: DBA-2 > DBA-1 > DBA-3, which agree well with the order of primary photoreaction.

(2) Effect of concentration

The effects of iodonium salt and dimethylaminobenzalacetophenone derivatives were examined by changing the concentration in the range of $1.0 - 8.0 \times 10^{-4}M$ (DPIO) and $0.4 - 4.0 \times 10^{-4}M$ (DBA-1), respectively at a fixed monomer concentration of $2.85M$. The polymerization rate in either case increases with increasing initiator concentration as shown in Fig. 5 and Fig. 6 for DPIO and DBA-1, respectively.

The reaction orders with respect to concentration of DPIO and DBA-1 obtained from the slopes of corresponding plots were 0.42 (DPIO) and 0.25 (DBA-1). The low DBA-1 exponent related to the value of DPIO is considered to be due to that a large part of DBA-1 transform to the inactive protonated DBA compounds by acid generated in primary photochemical process

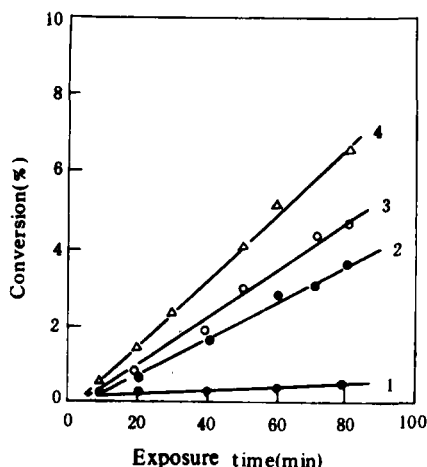


Fig.4 Monomer conversion with exposure time of photopolymerization initiated by several DBA/DPIO systems at the same concentration. [DPIO] = $3.0 \times 10^{-4}M$; [DBA] = $2.5 \times 10^{-4}M$; [MMA] = $2.85M$
 1. Alone DPIO; 2. DBA-3/DPIO;
 3. DBA-1/DPIO; 4. DBA-2/DPIO

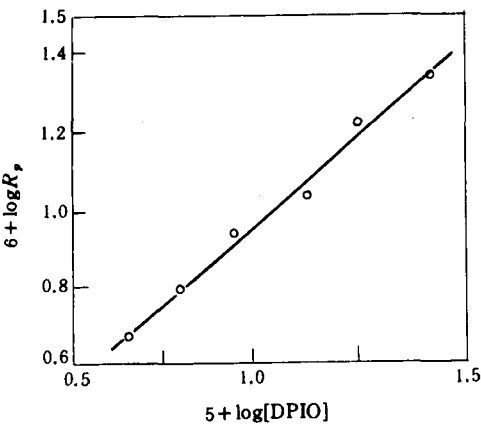


Fig.5 Relationship between R_p and DPIO concentration .
[DBA-1] = $2.5 \times 10^{-4} M$; [MMA] = $2.85 M$

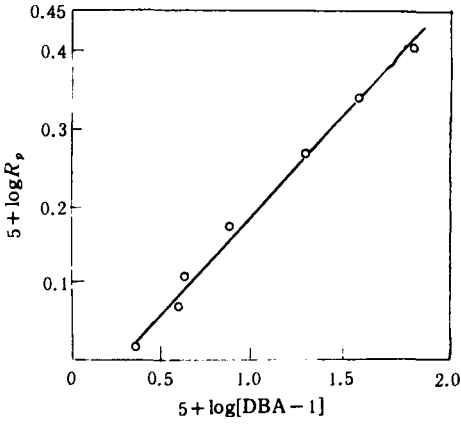


Fig.6 Relationship between R_p and DBA-1 concentration .
[DPIO] = $2.0 \times 10^{-4} M$; [MMA] = $2.85 M$

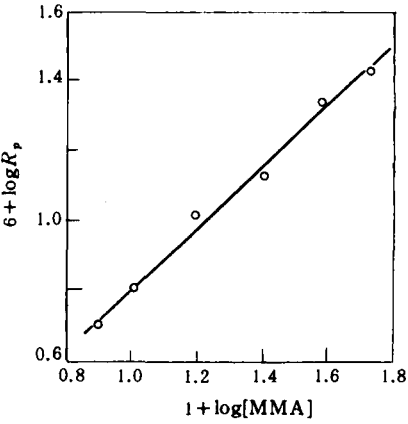


Fig.7 Dependence of R_p on monomer concentration.
[DPIO] = $3.0 \times 10^{-4} M$; [DBA-1] = $2.5 \times 10^{-4} M$

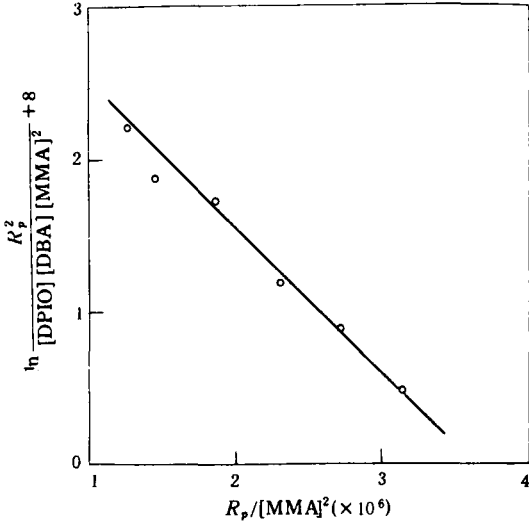


Fig.8 The relationship between $\ln \frac{R_p^2}{[\text{DPIO}][\text{DBA}][\text{MMA}]^2}$ and $\frac{R_p}{[\text{MMA}]^2}$

(eq.3) , which may be detected spectrophotometrically by following the spectral changes of reaction system .

Fig. 7 shows the dependence of R_p on concentration of MMA at constant concentration of DPIO and DBA-1 . Polymerization rate increases linearly with increasing monomer concentration from 1.0M to 5.5M with a slope of 0.86 . The exponent value of MMA somewhat deviates from the theoretical value of unity . It may be considered as a result of the decrease in the polarity of solution with increasing concentration of MMA . From the results obtained above , the R_p was formulated as follows :

$$R_p = k [\text{DPIO}]^{0.42} [\text{DBA}]^{0.25} [\text{MMA}]^{0.86}$$

The lower initiator exponent compared with theoretical value of 0.5 points

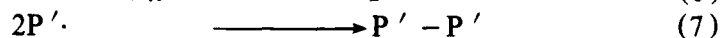
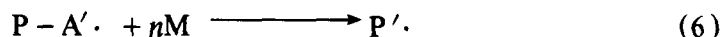
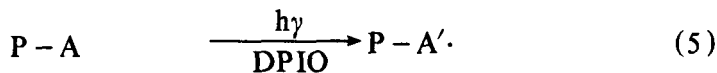
to the existence of some initiator dependent chain termination process along with the bimolecular termination. Primary radical termination (K_{pt}) is likely to be of some consequence in the present photopolymerization. The equation of Deb and Meyerhoff^[11] may be used to detect the effect of primary radical termination.

$$\ln \frac{R_p^2}{[\text{DPIO}][\text{DBA}][\text{MMA}]^2} = \ln \frac{f \cdot K_b \cdot K_p^2}{K_i} - \frac{2K_{pt}}{K_i \cdot K_p} \times \frac{R_p}{[\text{MMA}]^2}$$

Fig. 8 shows a plot of the left hand side of eq.(4) vs. $R_p/[\text{MMA}]^2$. Linearity of the plot with a negative slope provides evidence for primary radical termination. Chain initiation (K_i) is likely to be mainly due to the radical from DPIO decomposition and primary radical termination appears to take place mainly due to the radical derived from DBA, which may be detected by polymer end group analysis spectrophotometrically.

(3) Molecular weight distribution

An anomalous molecular weight distribution (*MWD*) with dual peaks (one at M_w 2.4×10^6 and the other at M_w 1.7×10^5) was observed in bulk polymerization of MMA with DBA/DPIO combination as photoinitiator. The high M_w peak grows with increasing irradiation time, along with a decrease in the intensity of low M_w peak. Similar result was also reported when the photopolymerization of MMA was initiated with benzophenone/tertiary amine system. It is reasonable to consider that a sequential polymerization occurs by the DBA moiety at polymer end which photochemically forms a polymer chain radical upon irradiation. These results lead to producing the high M_w polymer and broadening the *MWD* to the value of about 5.5. The sequential polymerization processes can be expressed below :



where P and A denote polymer chain and DBA moiety, respectively. These results may be useful as potential chain-extending backbone polymers, applied to photochemical synthesis of high molecular weight polymers and block copolymers.

Keywords:

Photopolymerization; Visible light sensitizer; Chalcone derivative; Iodonium salt

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