**A NEW ELECTRON TRANSFER SENSITIZED INITIATION SYSTEM
FOR VISIBLE LIGHT INDUCED PHOTOPOLYMERIZATION:
p-N,N-DIMETHYLAMINO BENZAL KETONE/DIPHENYLIODONIUM SALT SYSTEM**

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Abstract

Some p-N,N-dimethylamine substituted benzal ketone derivatives (ABK) are used as a new class of sensitizer for visible light induced radical photopolymerization of methylmethacrylate (MMA) by combination with diphenyliodonium salt (DPIO). The electron-transfer sensitized photolysis of DPIO-DABA system was studied by spectroscopy and rate of radical photogeneration was determined to be $94.59(\text{mol.l}^{-1}\text{s}^{-1})$. The relative efficiency of various ABK for polymerization of MMA is in the order DABA>DABP>ABA. The polymerization rate was proportional to $[\text{DPIO}]^{0.37}[\text{DABA}]^{0.16}$ and $[\text{MMA}]^{1.0}$. Photopolymerization was retarded by oxygen indicating a radical mechanism. Effect of several additives on the polymerization revealed that some heterocyclic thiol compounds exhibit significant role of rate acceleration.

Advances in laser imaging technology and photocuring materials require high performane photosensitive polymers having high sensitivity and broader spectral response until visible light. Onium salts, especially diaryl iodonium and triarylsulfonium are used as initiator for cationic photopolymerization[1]. However, since the onium salts themselves absorb light significantly only below ca.300 nm, so the practical utilization of onium salts for photopolymerization is necessary to extend the spectral sensitivity to longer wavelength region by suitable photosensitizer.

Photosensitization of the onium salts may take place through energy transfer or electron transfer mechanisms[2,3]. Considering the role of the iodonium salts as a stronger electron acceptor, a variety of donating dyes may be employed. In addition to aromatic hydrocarbons, bis(p-dialkyl-amino) benzophenone (Michler's ketone) is also an effective sensitizer as described in a patent literature[4]. This type

of sensitizer has the common molecular structure in which dialkylamine group substituted on phenyl ring is conjugated with electron-withdrawing carbonyl group to form intramolecular charge transfer structure. These compounds are possible to induce the photocleavage of diaryliodonium salts via the electron transfer process. In this paper the effectiveness of p-N,N-dimethylamine substituted benzal ketone derivatives (ABK) as sensitizer for the decomposition of iodonium salts and applicability to visible light to induced sensitive radical photopolymerization were studied kinetically.

Experiment

All p-N,N-dimethylamine substituted benzal ketone derivatives (ABK) were prepared according to the method of literature[5]. and recrystallized from toluene . The molecular structures were confirmed by IR, NMR and elementary analysis. Diphenyliodonium tetrafluoroborate (DPIO) was synthesized and purified by literature [3].mp.135°C.

Methylmethacrylate (MMA) was purified by standard procedure, and was redistilled before polymerization. Other reagents and solvents were purified by conventional methods.

Photopolymerization was carried out in dilatometers (ϕ 10mm) at 30°C. A Xenone lamp (400W) was used as the light source and short wavelength (<300nm) light was cutted out by Pyrex glass filter.

UV-visible absorption spectra were measured with Hewlett-Packard 8451A spectrophotometer.

Result and Discussion

I. Photosensitization of ABK derivatives.

Various p-N,N-dimethylamine substituted benzalketones (ABK) used as the sensitizers for photoinduced radical polymerization by combination with iodonium salts (DPIO) are shown as follows.

Abbrev.	Formula	Absorbtion peak(nm) (ϵ)
BA		322 (3.29X10 ⁴)
ABA		418 (3.21X10 ⁴)
DABA		432 (5.81X10 ⁴)
DABP		472 (6.10X10 ⁴)

The absorption spectra of various ABK compounds in acetonitrile solution are shown in Fig.1. Their absorption bands are located at blue light region, except for BA, removing considerably to the longer wavelength by conjugated

with dimethylamine group. When DPIO is added to the ABK solution, the longest wavelength of absorption bands of ABK suffered red shift, which is attributed to a formation of charge transfer complex[6].

Fig. 1. Absorption Spectra of ABK in acetonitrile. $[ABK] = 2.5 \times 10^{-5} M$.
BA(—); ABA(---); DABA(.....); DABP(-.-.).

Fig. 2. Monomer conversion with exposure time of photopolymerization initiated by different ABK-DPIO system at same concentration.
 $[MMA] = 2.85 M$; $[DPIO] = 2.0 \times 10^{-2} M$; $[ABK] = 1.0 \times 10^{-4} M$. At $30^\circ C$.

The photopolymerization of MMA initiated with different ABK/DPIO combination systems under the same concentration are demonstrated in Fig. 2. The Polymerization did not take place in the dark but occurs readily in visible light. The relative efficiency of various ABK as sensitizers is conveniently evaluated by measuring polymerization rate, which can be calculated from the conversion vs. time plots. It can be found that series ABK as sensitizers exhibit high photoinitiation efficiency and the polymerization rate of different ABK is in the order $DABA > DABP > DBP > ABA$. While the BA was practically inactive. These results obtained are evidence that the sensitizer having conjugated donor and acceptor structure is a kind of effective photoinitiation systems when coupled with DPIO.

Based on the above results, the DABA/DPIO initiated system is selected for further study of polymerization. The kinetic, mechanism and the effect of factor on photopolymerization are described as follows.

2. Primary reaction of DABA/DPIO system

Photolysis of DABA/DPIO system was carried out in acetonitrile solution with Xenone lamp, through single electron transfer from the excited DABA to DPIO with rapid rate to generate DPIO radical and DABA cation radical. They subsequently undergo decomposition to produce phenyl radical and radical species of DABA [6,7] respectively, as shown in eq. 1-4.

The photoreaction process of DABA/DPIO could be monitored spectrophotometrically (see Fig.3). It can be detected that a new absorption peak appears at 714nm, which is corresponding to the relative stable semi-quinonoid form of cation radical species of DABA (II), the radical photogeneration rate was obtained from the plot of the increasing absorption intensity at the 714nm against irradiation time that presented in the insert of Fig.3, its to be 94.59 (mol.l⁻¹.s⁻¹).

Fig.3. Spectral change by irradiation time for DPIO-DABA System in acetonitrile under N₂.

Although the new absorption band at 714nm did not appear in the vinyl monomer solution. It means that in this case the semi-quinonoid form is unstable and easily transform a radical intermediate.

3. Photosensitized polymerization of MMA

The Polymerization of MMA photoinitiated by DABA/DPIO system was proceeded in acetonitrile solution under N₂. Since the onium salts is poor soluble in MMA, a polar solvent is necessary to maintain the homogeity of reaction system.

Influence of initiators concentration

In Fig.4 and 5, the polymerization rate (R_p) of MMA is plotted against the concentration of di(p-N,N-dimethylamino benzal)-acetone (DABA) and diphenyliodonium salt (DPIO) respectively. It can be seen that the rate of polymerization R_p increases directly with increasing concentration of both DABA and DPIO. Some deviation from linear relationship was observed in the high concentration range of DABA, as a result of strong enhancing cage deactivation of intermedia formed and interior extinction of sensitizer as described previously [8]. Concentration exponent was 0.37 (DPIO) and 0.16(DABA) respectively. The lower DABA exponent was obtained compared to the value of DPIO may be considered due to that a large part of dimethylamine group of DABA is consumed to trap the acid generated in photochemical process (eq.1--3) to form a stable protonated DABA compound.

This result also indicates that the DABA-DPIO system is inactive practically to photoinduce cationic polymerization, inspite of DPIO as a good cationic polymeriztion photoinitiator.

Fig.4. Relationship between R_p and DABA concentration.
[DPIO] = 2.0×10^{-4} M; [MMA] = 2.85 M.

Fig.5. Relationship between R_p and DPIO concentration.
[DABA] = 1.0×10^{-4} M; [MMA] = 2.85 M.

Influence of MMA concentration

Fig.6 shows the relationship between polymerization rate and monomer concentration at a fixed content of DABA/DPIO. A linear dependence of R_p on MMA concentration was observed and the exponent has been calculated from the

slop of plot being unity, which is in good agreement with the theoretical value for normal photopolymerization of MMA.

From the above experimental results the R_p was formulated as follows:

$$R_p = K [DPIO]^{0.37} [DABA]^{0.16} [MMA]^{1.0}$$

Effect of oxygen

Table 1 shows that with increasing content of oxygen in system the polymerization rate reduced and introduction period increased. As known in free radical photopolymerization, oxygen acts as an effective quencher for excited sensitizer and as a inhibitor for radical chain, resulting in a larger introduction periods and slower polymerization rate .

Table 1. Influence of oxygen on th photopolymerization of MMA induced by DABA/DPIO system

Reaction Condition	Nitrogen	Air	Oxygen
Polymerization Rate (mol·L ⁻¹ ·S ⁻¹)	1.96X10 ⁻⁵	1.06X10 ⁻⁵	5.93X10 ⁻⁶
Introduction Period (min)	0.5	8	17

The rate accelerarating effect by oxygen which usually takes place in the photoinitiation system containing tetryary amine[9,10], was not detected in this system.

Fig.6. Dependence of R_p on monomer concentration.
[DABA] = 1.0X10⁻⁴ M; [DPIO] = 2.0X10⁻⁴ M.

Fig.7 Effect of mercaptan additives on photopolymerization of MMA.
[DPIO] = 2.0X10⁻⁴ M; [DABA] = 1.0X10⁻⁴ M;
[MMA] = 2.35 M.
● — No additive.
Δ — Trihydroxymethyl-propane-(mercapto) propionate.
○ — 3-SH-4-methyl-4H-1,2,4-triazol.

Effect of additives

Some H-donor, such as thiol, were used as chain transfer reagents for the radical polymerization by DABA/DPIO system as given in Fig.7. It was found that both thiols as H-donors facilitate polymerization obviously as a result of an increase in the activity of initiating radical species formed through the chain transfer from larger molecule radical (DABA). By adding 3-mercaptopotriazol (MTA), there is worthy of note that a significant rate-enhancement was appeared in Fig.7, curve 3. The large difference between MTA and conventional thiol as chain transfer reagents implies that the other acceleration mechanism may play an important role. As known from photographic chemistry some mercaptan substituted triazols act as effective antifoggants, and so it is reasonable to consider that a redox reaction of cation radical of DABA with MTA takes place in system to produce the more active initiating radicals derived from MTA, which promote polymerization effectively. It may be described as follows.

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