

RADICAL PHOTOPOLYMERIZATION USING ARYLIODONIUM SALT/TERTIARY AMINE COMPLEX SYSTEM AS THE PHOTOINITIATOR

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ABSTRACT

The diphenyliodonium salt (DPIOC) /triethylamine (TEA) is used as photoinitiator for radical photopolymerization. It was found that a ground state CT complex formed between DPIOC as electron acceptor and TEA as electron donor, which results in extending the photosensitivity range of DPIOC/TEA system up to above 500nm compared with DPIOC alone. The kinetic studies on photopolymerization of methyl methacrylate (MMA) were carried out in $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (14:1, v/v) mixture solution at 30 °C by dilatometer. The results obtained show that the polymerization rate (R_p) increases with increasing concentrations of DPIOC and TEA with exponent 0.65 and 0.62 respectively. The activation energy E_a and $k_p/k_t^{1/2}$ value were determined to be 4.1 Kcal $\cdot$ mol $^{-1}$ and 0.045 respectively. The other influence factors and reaction mechanism were also discussed.

For the practical utilization of photopolymerization, how to extend the spectral photoresponse and how to increase the reactivity of photoinitiation systems are of more importance. For this purpose the organic complex compounds are potentially useful to participate in a great number of photoreactions induced by near UV and visible light^[1]. But complex compounds used as photoinitiators do not meet these demands for photoinitiation of radical polymerization^[2], hence they have scarcely been used as photoinitiators in practice. It spurs us on to search for a novel effective complex photoinitiator. Recently aryl onium salts, such as triarylsulfonium and diaryliodonium salts, used as photoinitiators for the cationic polymerization have attracted significant attention. Actually, using these onium salts as cationic photoinitiators are strongly hampered by their low absorptivity at wavelengths above 300nm, where medium and high pressure mercury arcs provide substantial emission^[3]. It has, however, been found possible to increase photoresponse of some onium salts to a certain extent at near UV region through the use of photosensitizers^[4,5] or by an increase in conjugation degree of onium salt molecule itself^[6]. But they are difficult to reach to the visible light region. In this paper, we suggest formation of a novel ground state complex compound from aryl onium salts as electron acceptors with suitable electron donor which absorbs light effectively at wavelength near UV or even into the visible region. For this reason, we have undertaken study on the vinyl radical photopolymerization using diphenyliodonium salt /triethylamine complex system as the photoinitiator.

EXPERIMENTAL

Diphenyliodonium chloride $\text{Ph}_2\text{I}^+\text{Cl}^-$ (DPIOC) was prepared according to the literature^[7], m. p. 231–233 °C.

Methyl methacrylate (MMA), acrylonitrile (AN), and other reagents were purified by conventional procedures and were redistilled prior to be used for polymerization.

Photopolymerization was carried out in dilatometer (ϕ 10 mm) at 30 °C. The sample tubes were rotated around the light source in a merry-go-round apparatus with a high pressure mercury lamp (HPK-2M, 375W) placed at the center. The short wavelength light ($< 300\text{nm}$) was removed by the Pyrex glass filter. The incident light intensity was determined using the benzophenone/benzophenol actinometer to be 2.2×10^{16} photons/min. $\cdot \text{cm}^2$.^[8]

UV-visible absorption spectra were measured by Hitach 330 spectrophotometer.

RESULTS AND DISCUSSION

1. Spectroscopic studies

When electron donor TEA is added to the DPIOC solution, the absorption is shifted to the red considerably and a new absorption band appears clearly at wavelength 507nm as shown in Fig. 1.

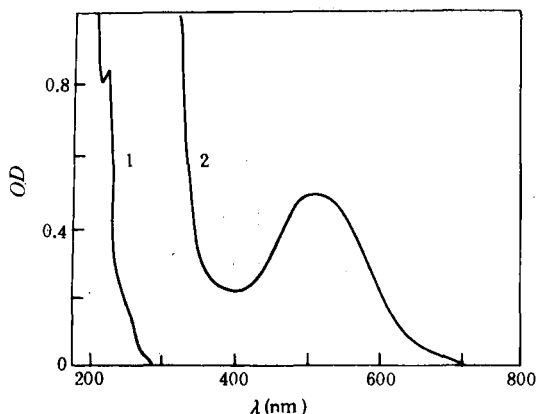


Fig. 1 Absorption spectra of DPIOC and DPIOC/TEA system
 1. DPIOC alone [DPIOC] 4.8×10^{-5} M, 2. DPIOC/TEA system
 [DPIOC] 3.4×10^{-3} M, [TEA] 2.5×10^{-2} , Solution $\text{CH}_3\text{CN}/\text{H}_2\text{O}$
 (14:1, v/v)

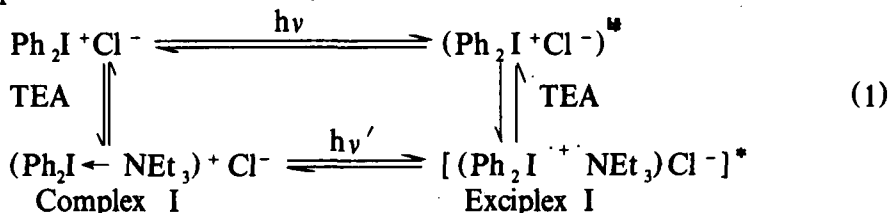
This observation is attributed to a CT interaction between the iodonium salt (DPIOC) and tertiaryamine (TEA) to form a CT complex in the ground state, resulting in extending the spectral response up to 700nm. The structure of the ground state CT complex I formed has been estimated by using the Benesi-Hildebrand method^[9] to be a one-to-one molar ratio complex. In the fluorescence spectra of DPIOC/TEA system, a new emission band produced from the excited complex I was also observed. Some photophysical properties of DPIOC and DPIOC/TEA complex are listed in Table 1.

Based on the results above, it may be considered that the intermolecular

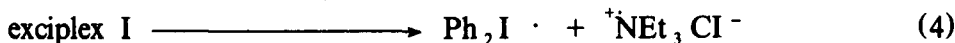
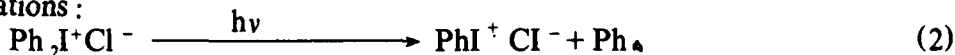
Table 1 Physical properties of DPIOC and DPIOC /TEA complex

Properties	DPIOC	DPIOC /TEA
Max . absorption λ_{ab} (nm)	228	507
Max . emission λ_{em} (nm)	288	568
Singlet energy E_s (Kcal $\cdot$ mol $^{-1}$)	99.3	50.4
Association constant K (mol $^{-1}$)	---	21
Extinction coefficient ε (M $^{-1} \cdot$ cm $^{-1}$)	1.7×10^4	2.8×10^3

interactions of DPIOC /TEA system in the ground state and in the excited state occur in the polar solution as follows :



Under irradiation the diphenyliodonium salt undergoes direct photolysis (eq. 2)^[3,4] and the complex I occurs photocleavage through electron transfer process^[10, 11] (eq. 3 — 5) both to produce radical and cation-radical species as depicted in the following equations :



Where RH represents H-donor (e.g. solvents, monomers)

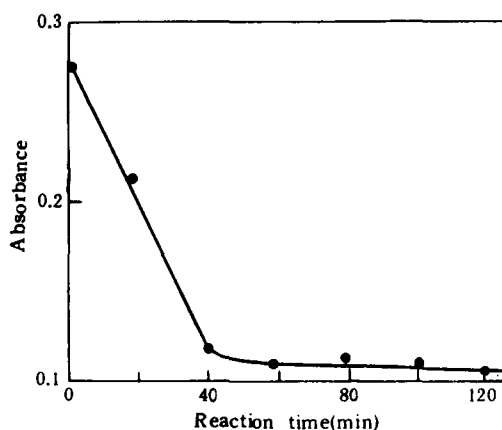


Fig. 2 Variation in the absorption band (λ_{max} 506.3 nm) of DPIOC /TEA complex with irradiation time in reaction system

[DPIOC] 3.4×10^{-3} M, [TEA] 2.5×10^{-2} M, [MMA] 3.8 M.

These radicals formed in this photolysis process were detected using radical scavenge

technique with stable radical, such as 2,2,6,6-tetramethylpiperidinoxyl radical^[12]. The photodecomposition rate of complex I was determined by means of absorption spectrophotometry. The maximum absorption of complex I was found to vary linearly with the irradiation time, which is shown in Fig. 2. From the slope of this plot, the photodecomposition rate constant k_d was obtained to be $7.9 \times 10^{-4} \text{ s}^{-1}$.

In despite of diaryliodonium salt, as known, being an effective cationic photoinitiator, in the case of DPIOC/TEA system, they only could function as radical initiator due to the strong termination effects of the nucleophilic anion Cl^- and the electron donor NEt_3 .

2. Kinetic studies

Photopolymerization was carried out in the $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (14:1, v/v) mixture solution at 30°C . The solutions were bubbled with nitrogen for 20min. The polymerization rates were established from the percentage conversion vs. time plots by treatment with the least square method. Effects of various factors on photopolymerization rate are discussed as follows.

(1) Photoinitiation by DPIOC/TEA complex system

Fig. 3 shows the relationships between conversion and reaction time for photopolymerization of MMA initiated by DPIOC/TEA complex system and DPIOC alone respectively at the same concentration. The polymerization rate R_p of complex I system ($9.0 \times 10^{-5} \text{ mol} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$) is far larger than that of DPIOC alone ($1.1 \times 10^{-5} \text{ mol} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$). Obviously, the weak absorption of DPIOC at above 300 nm results in its very low polymerization rate. On the contrary, DPIOC/TEA complex system exhibits strong absorption at near UV and visible region and overlaps excellently with the emission bands of the light source, which made the polymerization rate much high.

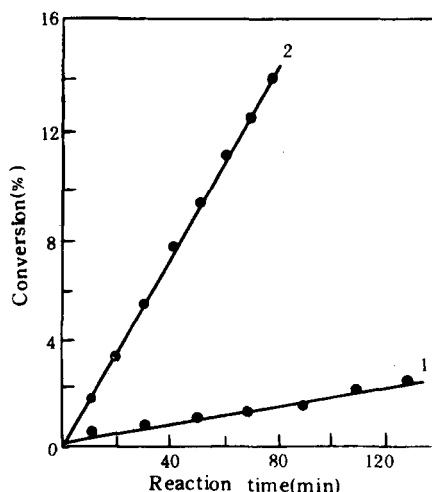


Fig. 3 Photopolymerization of MMA induced by DPIOC alone and DPIOC/TEA system
1. DPIOC alone, 2. DPIOC/TEA system [DPIOC] $3.4 \times 10^{-3} \text{ M}$,
[TEA] $1.0 \times 10^{-1} \text{ M}$, [MMA] 2.8 M.

(2) Effect of concentration

In Fig. 4 and 5, the polymerization rate of MMA is plotted vs. the concentra-

tion of iodonium salt and tertiary amine respectively. It can be seen that with enhancing the concentration of DPIOC the polymerization rate R_p increases linearly and then levels out. The analogous results were obtained for the concentration effect of amine on polymerization rate. The rate R_p increases directly with the increase of concentration of amine and then decreases sharply. These rate-reducing effects at high concentration may be attributed to several reasons. In fact, as the absorption density of reaction system rises near to unity, the distribution of absorbed dose in the system becomes inhomogeneous due to the internal screening effect by chromophore. It results in forming a high local concentration of excited molecule and intermediate at surface region, leading to a dramatic increase in the deactivations of both above. From the initial line slopes of the plots at low concentration, the concentration exponents were calculated to be 0.65 and 0.62 for DPIOC and TEA respectively.

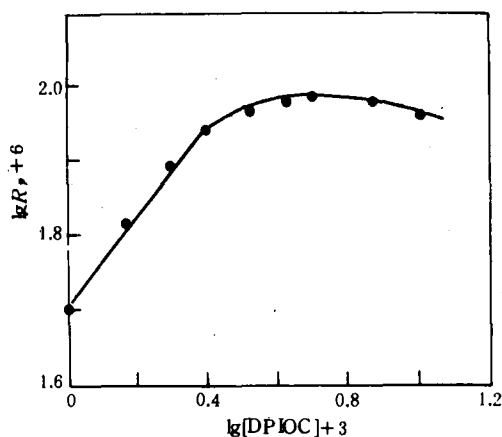


Fig. 4 Relationship between R_p and DPIOC concentration
[TEA] 1.0×10^{-1} , [MMA] 2.8M, in N_2

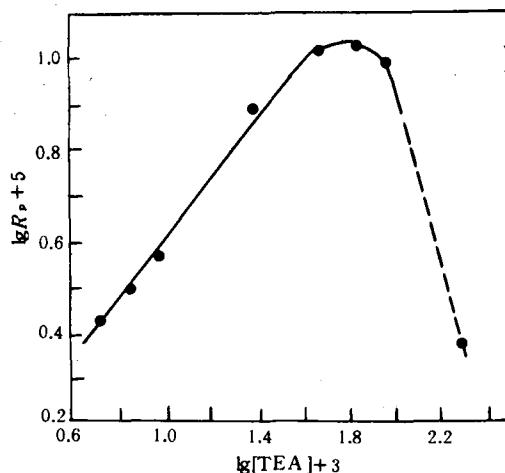


Fig. 5 Relationship between R_p and TEA concentration
[DPIOC] 3.4×10^{-3} M, [MMA] 2.8M, in N_2

The relationship between rate of polymerization R_p and concentration of MMA is given in Fig. 6. R_p varies directly with the concentration of monomer and then levels out at high concentration range due to lowering the polarity of solution which is unfavorable to the formation of CT complex, thus leading to decrease in R_p . Fig. 7 demonstrates the change in absorption of complex I band with varying MMA concentration in system. It is evident that the formation of CT complex between DPIOC and TEA drops down by the addition of MMA. On the contrary, in the case of more polar monomers, such as acrylonitrile (AN), the result of Fig. 8 indicates that the rate of polymerization of AN is varied directly with increasing the concentration of monomer in system over a wide range of concentration in the same experimental conditions.

The kinetic equation of photopolymerization of MMA initiated by DPIOC/TEA system at 30 °C may be written as follows:

$$R_p = K [\text{DPIOC}]^{0.65} [\text{TEA}]^{0.62} [\text{MMA}]$$

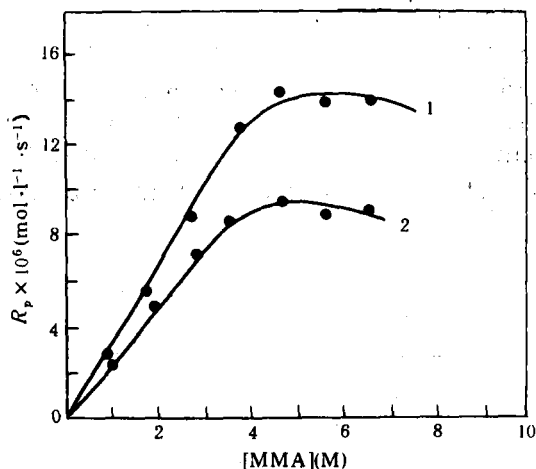


Fig. 6 Dependence of R_p on monomer concentration
1. [TEA] $1.0 \times 10^{-1} M$, 2. [TEA] $2.5 \times 10^{-2} M$; in N_2 , [DPIOC] $3.4 \times 10^{-3} M$.

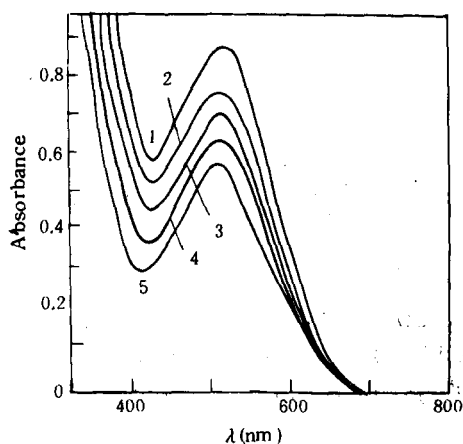


Fig. 7 Change in the absorption of the CT band of DPIOC/TEA with increasing concentration of MMA [MMA]: 1. 0.94M, 2. 1.9M, 3. 3.8M, 4. 5.6M, 5. 6.6M, Solvent CH_3CN/H_2O (14:1, v/v).

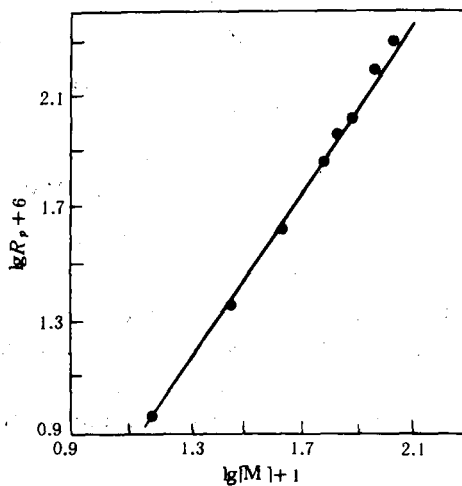


Fig. 8 Relationship between R_p and acrylonitrile concentration [DPIOC] $3.4 \times 10^{-3} M$, [TEA] $2.5 \times 10^{-2} M$.

where the concentration ranges of components of the initiation system are :
[DPIOC] $\leq 2.5 \times 10^{-3} M$, [TEA] $\leq 5.02 \times 10^{-2} M$, [MMA] $\leq 3.76 M$.

3. Effect of oxygen

Influence of oxygen on the polymerization is shown in Fig. 9. The induction period for polymerization appeared in the presence of oxygen in system, arising from the excited state quenching and the radical termination by oxygen. It is in good agreement with the radical polymerization mechanism. The rate-enhancing effect by oxygen was also observed in the DPIOC/TEA system. It may be considered that oxygen in system transforms into an active peroxide through photooxidation with tertiary amine and then undergoes photolysis to produce new initiating radicals as described early^[13].

(4) Effect of polarity of solvents

Polarity effect of solvents was examined by varying the mixture ratio of CH_3CN to H_2O . The results of Fig. 10 indicate that the polymerization rate of MMA is directly proportional to the content of H_2O in system, giving the exponent of 0.25. Since the formation of CT complex between DPIOC/TEA is strongly dependent on the polarity of reaction medium as mentioned above, the phenomenon is reasonable.

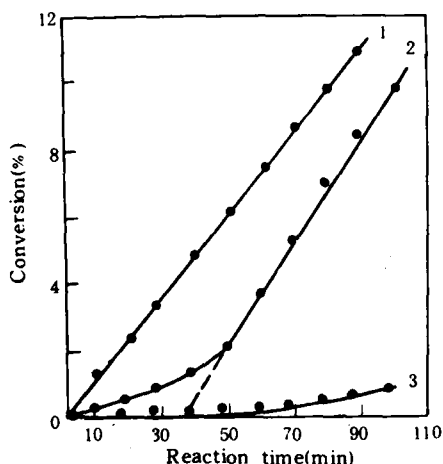


Fig. 9 Effect of oxygen on polymerization of MMA
1- N_2 , 2-Air, 3- O_2
[DPIOC] $3.4 \times 10^{-3} \text{M}$, [TEA] $2.5 \times 10^{-2} \text{M}$,
[MMA] 3.8M .

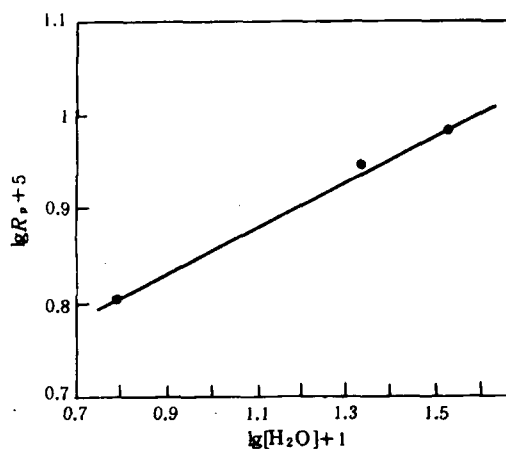


Fig. 10 Influence of solvent polarity on R_p
[DPIOC] $3.4 \times 10^{-3} \text{M}$, [TEA] $2.5 \times 10^{-2} \text{M}$,
[MMA] 3.8M , Solvent $\text{CH}_3\text{CN}/\text{H}_2\text{O}$
(14:1, v/v).

(6) The value of $k_p/k_t^{1/2}$ and E_a

A plot of $1/\bar{P}_n$ vs. R_p with data for photopolymerization of MMA practically passes through the origin, indicating negligible chain transfer as shown in Fig. 11, $\bar{P}_n$ being the number-average degree of polymerization. Assuming normal

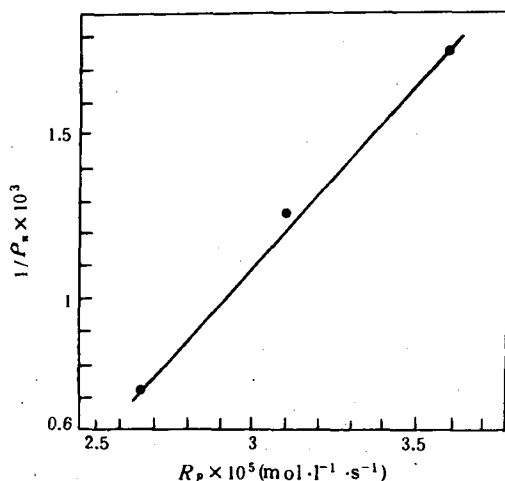


Fig. 11 Correlation of reciprocal average degree of polymerization $1/\bar{P}_n$ with R_p
[DPIOC] $3.4 \times 10^{-3} \text{M}$, [MMA] 2.8M .

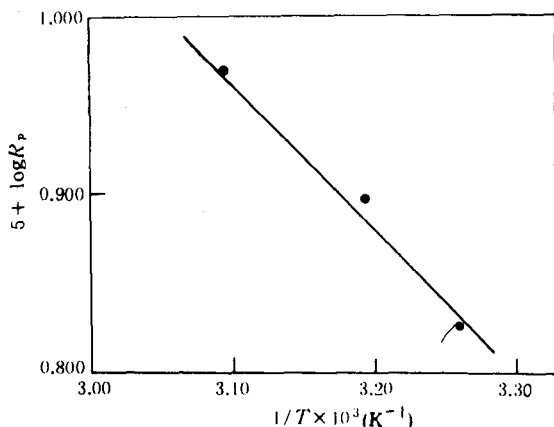


Fig. 12 Plot of R_p vs. $1/T$
 $[DPIOC] 3.4 \times 10^{-3} M$, $[TEA] 2.5 \times 10^{-2} M$, $[MMA] 3.8 M$

bimolecular termination with disproportionation outweighing combination by a factor of 85:15, the apparent $k_p/k_t^{1/2}$ value at 30 °C obtained from its slope is 0.045, which is somewhat lower than the datum for benzoin ether^[14].

The apparent activation energy (E_a) of photopolymerization induced by DPIOC/TEA complex system was determined by the Arrhenius formula from the relationship between $\lg R_p$ vs. $1/T$. The E_a value was 4.1 Kcal · mol⁻¹ which coincides with reported values for general photoinitiated polymerization.

Keywords:

Photopolymerization; Initiation System; CT Complex; Onium Salt

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