

PHOTOINITIATED POLYMERIZATION BY ARYLIODONIUM SALT/BENZOPHENONE/ TERTIARY AMINE BINARY PHOTOSENSITIZATION SYSTEM

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ABSTRACT

A novel binary photosensitization system composed of benzophenone (BP) /diphenyliodonium chloride (DPIOC) /triethylamine (TEA), exhibiting a good photoresponse at near UV and visible light regions, was used as the initiator for photopolymerization of MMA. The radical photogeneration in the binary system consists mainly of two parallel reactions, i. e., BP/TEA photohydrogen-abstraction and DPIOC/TEA complex photodecomposition, but the latter is more active than the former. The results of comparative study indicate that the rate of polymerization induced by the binary system (BDT) is remarkably higher than those by the corresponding single systems. The polymerization rates are proportional to $[BP]^{0.16}$, $[DPIOC]^{0.32}$, $[TEA]^{0.45}$ and $[MMA]$. The mechanism is also discussed.

In our previous work^[1], a kinetic study on the polymerization of MMA using the aryliodonium salt /tertiary amine complex system as the photoinitiator was reported in detail. The results obtained indicated that this complex system exhibits a stronger absorbability at the visible region with absorption peak at 507 nm compared with single onium salt, but therein a minimum absorption exists at near UV region. For the sake of improving the photoresponse capability of this complex system at near UV region, benzophenone, having absorption band at 340nm, is selected as a second photosensitizer in this work. Hence the binary photosensitization system composed of aryliodonium salt, benzophenone and tertiary amine exhibits an effective absorbability at both UV and visible regions and may be considered as a kind of sunlight type photosensitization system. In this paper, we present details of the kinetic mechanism and of the efficiency of MMA polymerization initiated by this binary photosensitization system.

EXPERIMENTAL

Diphenyliodonium chloride (DPIOC) was prepared as described in a previous article^[2]. Methyl methacrylate (MMA) and others were purified by conventional procedures and were redistilled before use, the middle fractions were used.

The photopolymerization was carried out in dilatometers at 30 °C. The irradiation was conducted in a rotary photochemical reactor with a high pressure mercury lamp (375W), around which the sample tubes were rotated, conversion was kept less than 10% and the experimental data were treated with the least square method, for details refer to the previous papers.

Absorption spectra were recorded with Hitach spectrophotometer 330 type.

RESULTS AND DISCUSSION

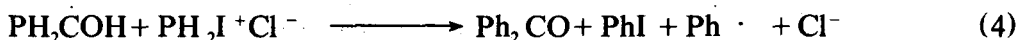
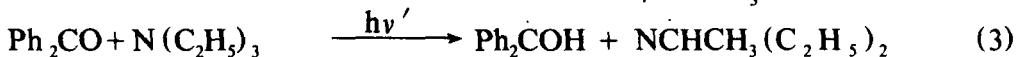
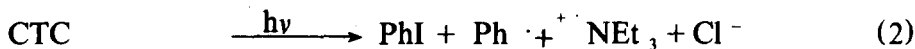
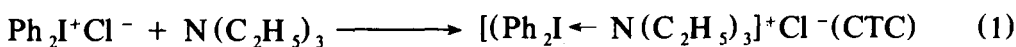
Photopolymerization of MMA initiated by BP/DPIOC/TEA binary photosensitization system was carried out in the $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (14:1, v/v) mixture solution. The samples were freed from oxygen by bubbling with nitrogen.

1. Characteristics of spectra

The absorption spectrum of benzophenone /diphenyliodonium salt/triethylamine combination system is given in Fig. 1. As can be seen from this plot, a characteristic absorption band of DPIOC/TEA (CTC) complex is located at wavelength 507 nm with a minimum at about 400nm (curve 1). When adding BP to the DPIOC/TEA system, a new absorption band appears at wavelength 340nm characteristic of $n\pi^*$ transition of BP, indicating that the benzophenone molecule in the system possesses its original photophysical and photochemical properties. As a result of the addition of the second photosensitizer, the spectral photoresponse of the complex initiation system well overlaps the emission bands of light source, which is more favorable to an increase in polymerization rate and light energy utilizing efficiency.

2. Mechanism of initiation.

Under irradiation, the BP/DPIOC/TEA binary photosensitization system undergoes several photochemical reactions, including the following main reactions [4, 5, 6, 7]: (1) photolysis of diphenyliodonium chloride (eq. 1, 2), (2) photoreduction of BP with TEA through electron transfer and proton transfer processes (eq. 3), (3) electron transfer reaction between electron donor radical $\text{Ph}_2\dot{\text{C}}\text{OH}$ and onium salt (eq. 4):



In order to evaluate the contribution of each of the above reactions to the initiation of vinyl polymerization when BP/DPIOC/TEA system is used as photoinitiator, the comparative studies of photopolymerization were carried out with the following various photoinitiation systems:

- (1) DPIOC (D), (2) BP + DPIOC (BD), (3) BP + TEA (BT),
(4) DPIOC + TEA (DT), (5) BP + DPIOC + TEA (BDT)

The experimental results obtained are presented in Fig. 2. The polymerization rate R_p of MMA decreases in the order: $\text{BDT} > \text{DT} > \text{D} > \text{BD} > \text{BT}$. Here it is worth noticing that the polymerization rate (R_p (BDT) $3.6 \times 10^{-5} \text{ mol} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$) induced by BP/DPIOC/TEA binary photosensitization system is equal to the sum of those with the single photosensitization systems of DPIOC/TEA (R_p (DT) $2.5 \times 10^{-5} \text{ mol} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$) and BP/TEA (R_p (BT) $1.0 \times 10^{-5} \text{ mol} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$) respectively. This means that the two photosensitization components (i. e.,

DPIOC/TEA and BP/TEA) in the binary system undergo photoreactions independently following eqs (2) and (3) respectively. It was also found that the polymerization rate R_p (BD) induced by BP/DPIOC combination system is slower than that R_p (D) by DPIOC alone. This result demonstrated that the photosensitization by BP is absent in the BP/DPIOC system, due to that the excited state energies of DPIOC (E_s 92 Kcal $\cdot$ mol $^{-1}$, E_T 74 Kcal $\cdot$ mol $^{-1}$) are higher than those of BP (E_s 76 Kcal $\cdot$ mol $^{-1}$, E_T 69 Kcal $\cdot$ mol $^{-1}$). On the contrary, herein the quenching by BP may take effect. In the case of relatively high concentration of BP and TEA, as shown in Fig. 3 (curve 1), a broken relationship between percentage conversion and irradiation time for polymerization of MMA with BP/DPIOC/TEA binary system was observed. This indicates that there exist

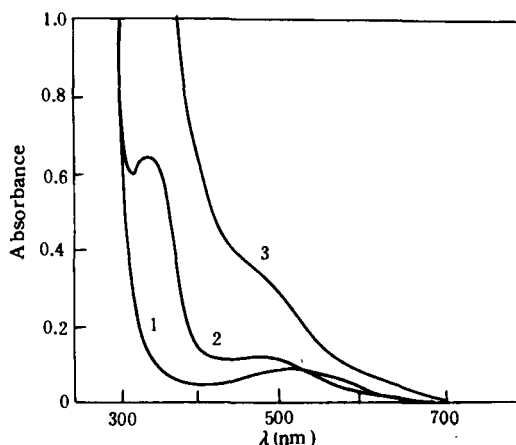


Fig. 1 Absorption spectra of DPIOC/TEA (DT) (1) and BP/DPIOC/TEA (2, 3) systems
DT 1, [DPIOC] 1.0×10^{-2} M, [TEA] 5.0×10^{-3} M; BDT (2, 3); 2. [DPIOC] 5×10^{-3} M, 3. [DPIOC] 1×10^{-3} M, [TEA] 2.0×10^{-1} M, [BP] 5.0×10^{-3} M

two different polymerization rates R_{p1} and R_{p2} at the earlier and later reaction stages. It also can be seen from Fig. 3 that the rate R_{p1} obtained from the slope of curve 1 at the first stage is just as the sum of polymerization rates of R_p (DT) (curve 2) and R_p (BT) (curve 3) induced by the single systems DPIOC/TEA and BP/TEA respectively. Whereas the rate R_{p2} calculated from the slope of curve 1 at the second reaction stage is only equal to R_p (BT). These results obtained above show clearly that when BP/DPIOC/TEA binary system used as photoinitiator, at the first reaction stage both the DPIOC/TEA and BP/TEA components initiate photopolymerization of MMA, but at the second reaction stage the photopolymerization is induced only by BP/TEA component. It can be explained as that since the DPIOC is more active than BP in the photoinitiation process, which can be estimated from the slopes of curves 2 and 3, at the later stage the DPIOC has been exhausted and BP is retained in reaction system. The observation above was further confirmed by the change in absorption spectra of BP/DPIOC/TEA system with irradiation time.

From the above results, we can calculate the total rate of polymerization R_{p1} induced by BP/DPIOC/TEA binary system (BDT) as well as the partial rates R_{p2}

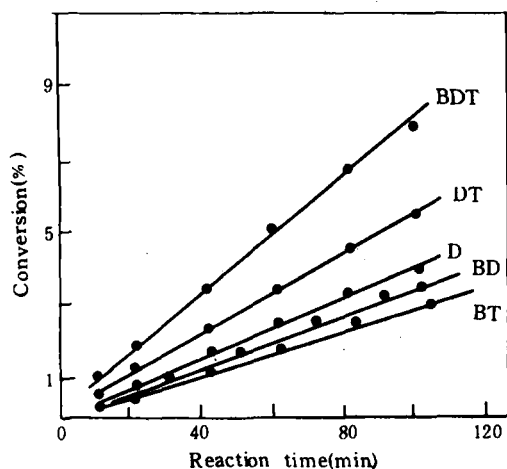


Fig. 2. Photopolymerization of MMA initiated by various initiator systems
 $[BP] 5.0 \times 10^{-3} M$, $[DPIOC] 5.0 \times 10^{-3} M$,
 $[TEA] 5.0 \times 10^{-3} M$, $[MMA] 2.8 M$

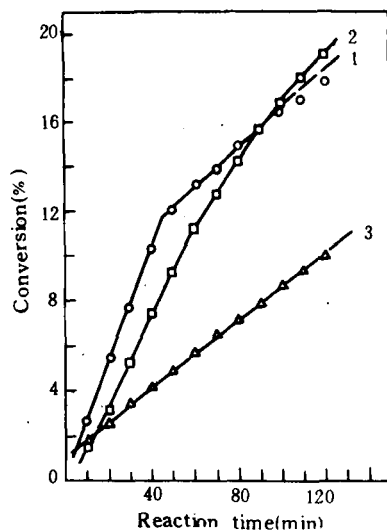


Fig. 3. Photopolymerization of MMA initiated by various initiator systems
 BP/DPIOC/TEA (1), DPIOC/TEA (2),
 BP/TEA (3) $[BP] 1.0 \times 10^{-2} M$, $[DPIOC] 3.4 \times 10^{-3} M$, $[TEA] 1.0 \times 10^{-1} M$, $[MMA] 3.76 M$

and R_{p3} (i.e., $R_{p1} - R_{p2}$) corresponding to the polymerization initiated by the components BP/TEA and DPIOC/TEA respectively.

3. Influencing factors of polymerization

(1) Effect of onium salt concentration

The relationship between polymerization rate and DPIOC concentration is given in Fig. 4. The results obtained indicated that the rate of polymerization R_{p1} with

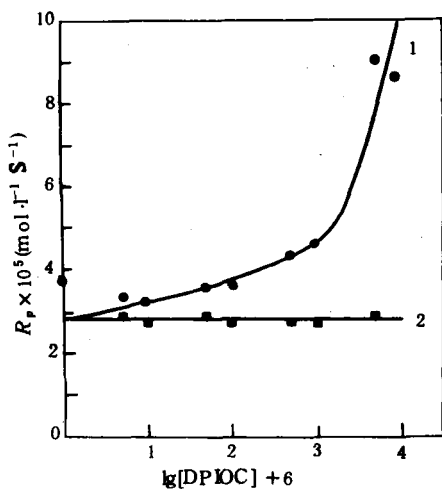


Fig. 4. Dependence of photopolymerization rates: R_{p1} (1) and R_{p2} (2) on concentration of DPIOC
 $[BP] 5.0 \times 10^{-3} M$, $[TEA] 1.0 \times 10^{-3} M$,
 $[MMA] 2.8 M$

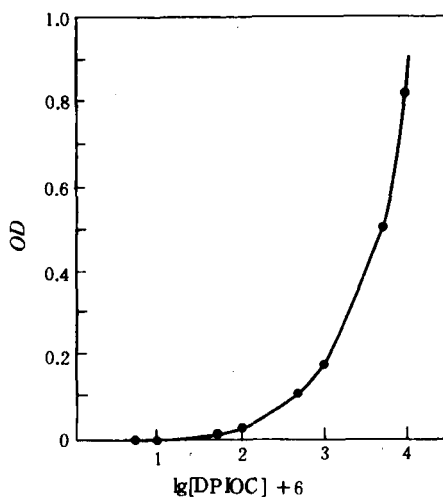


Fig. 5. Dependence of optical density of complex on concentration of DPIOC

the binary system (BDT) increases with increasing onium salt concentration to a certain extent of the concentration, and then rises sharply (curve 1) while the rate R_{p2} measured keeps constant (curve 2). It demonstrates that R_{p1} rate enhancement is caused by the action of onium salt /amine (DT) component, as a result of the increasing formation of CTC complex between onium salt and amine in ground state. The corresponding change in absorption ($\lambda_{\max}$ 507nm) of the CT complex with varying DPIOC concentration in excess of TEA concentration was obtained which is given in Fig. 5. To further evaluate the contribution of DT component in binary system (BDT) to the photoinitiation of polymerization of MMA, the dependence of R_{p3} calculated from $(R_{p1} - R_{p2})$ on DPIOC concentration was depicted in Fig. 6, and a similar broken relationship was observed. From the slopes of this plot, the concentration exponents were estimated to be 0.32 and 1.2 at low concentration range and high concentration range of DPIOC respectively.

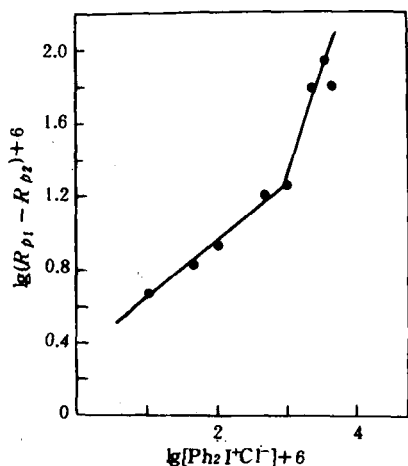


Fig. 6 Plot of $\log(R_{p1} - R_{p2})$ vs. $\log[\text{DPIOC}]$

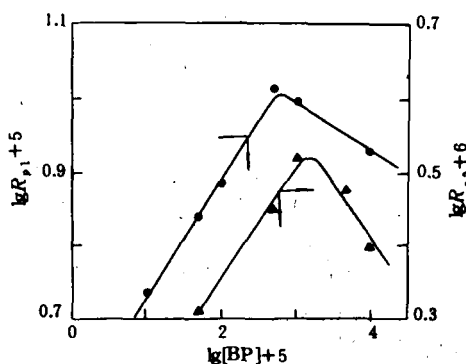


Fig. 7 Dependence of polymerization rate on concentration of BP [DPIOC] $2.5 \times 10^{-3} \text{ M}$, [TEA] $1.0 \times 10^{-1} \text{ M}$, [TEA] 2.8M

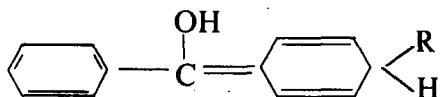
(2) Effect of BP concentration

The influence of BP concentration on the rate of polymerization initiated by the binary system (BDT) is presented in Fig. 7. The polymerization rates R_{p1} and R_{p2} both increase linearly with BP concentration, reach a maximum and then drop down. This rate-decreasing effect at the high concentration range may be considered as the fact that as BP concentration increases the reaction system becomes more inhomogeneous, the photoreaction zone diminishes and moves to the near surface due to the internal light screening effect by BP chromophore. Thus the large local concentration formed from the excited BP and its active intermediates, such as radical species, causes dramatic enhancement of cage deactivation, leading to reduction of polymerization rate. The BP concentration exponents obtained from the slopes of linear plots of $\log R_{p1}$ and $\log R_{p2}$ vs. $\log [\text{BP}]$ respectively are the same, equal to 0.16 at the relatively low BP concentrations. These parallel results show

that R_{p1} is directly dependent on R_{p2} and independent of R_{p3} , since as the concentration of BP varies, the rate of polymerization R_{p2} initiated by BP/TEA varies with the concentration, while the rate of polymerization R_{p3} induced by DPIOC/TEA remains constant.

(3) Effect of TEA concentration

The relationship between polymerization rate and concentration of amine has also been studied. The results obtained, as given in Fig. 8, show that the polymerization rates R_{p1} and R_{p2} both increase linearly with increasing amine concentration up to a certain extent and then decrease. In general, in the higher concentration of TEA the intermediate by-products in the photoreduction of BP with TEA become relatively important [3], such as a radical combination compound,



which absorbs light at wavelength 300–700nm^[8] and acts as an internal light screening agent, resulting in a decrease of photoreaction considerably. The tertiary amine concentration exponents for R_{p1} and R_{p2} were estimated to be 0.45 and 0.43 respectively.

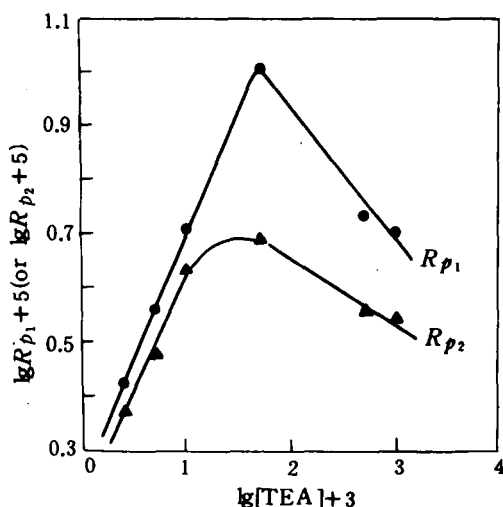


Fig. 8 Dependence of polymerization rate on concentration of TEA [DPIOC] $2.5 \times 10^{-3} M$, [BP] $5.0 \times 10^{-3} M$, [MMA] $2.8 M$

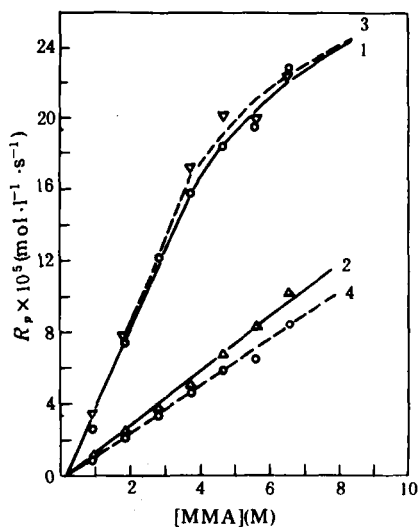


Fig. 9 Dependence of polymerization rate on concentration of MMA [DPIOC] $3.4 \times 10^{-3} M$, [BP] $1.0 \times 10^{-2} M$, [TEA] $1.0 \times 10^{-1} M$

4. Effect of MMA concentration

When photopolymerization of MMA is initiated by BP/DPIOC/TEA binary photosensitization system, the polymerization rate R_{p1} increases directly with the concentration of MMA and then levels out at the high concentration range (see curve 1), whereas the rate R_{p2} increases linearly over a wide range of concentration (see curve 2). These observations may be due to that with adding MMA to

the reaction system the polarity of solution decreases, which is unfavorable to the formation of CTC complex between DPIOC and TEA. Therefore when the MMA concentration reaches a certain extent, the negative effect of MMA concentration becomes important and the rate R_{p1} starts decreasing. In order to further verify that discussed above, the polymerizations of MMA by using the corresponding single systems DPIOC/TEA(DT) and BP/TEA(BT) as the photoinitiators were carried out in the same experimental conditions and the polymerization rates R_p (DT) and R_p (BT) were measured. The correlations of R_p (BDT)(i.e., R_p (DT) + R_p (BT)) and R_p (BT) with the concentration of MMA are given in Fig. 9, corresponding to curves 3 and 4. It can be found that the curves 1 and 2 are well coincident with the curves 3 and 4 respectively. Therefore it may be considered that the rate-decreasing effect of R_{p1} at high MMA concentration is directly related to the change of the rate R_{p3} and is independent of the rate R_{p2} .

From the results mentioned above, the kinetic equation of photopolymerization of MMA initiated by BP/DPIOC/TEA binary photosensitization system can be expressed as follows:

$$R_p = k [\text{DPIOC}]^{0.32} [\text{BP}]^{0.16} [\text{TEA}]^{0.45} [\text{MMA}]$$

where the concentration ranges of components of the initiation system are:

$[\text{DPIOC}] \leq 1.00 \times 10^{-3} \text{M}$, $[\text{BP}] \leq 5.00 \times 10^{-3} \text{M}$, $[\text{TEA}] \leq 5.02 \times 10^{-2} \text{M}$, $[\text{MMA}] \leq 3.76 \text{M}$. Obviously, the spectral photoresponse capability, photosensitization selectivity of the binary photosensitization system are much higher than those of the corresponding single photosensitization systems, thus it leads to an increase in polymerization rate effectively.

Keywords:

Photopolymerization; Binary Initiation System; Onium Salt; Benzophenone

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