

PHOTOPOLYMERIZATION IN THE MICELLAR SYSTEMS IV THE PHOTSENSITIZATION EFFECTS OF THE BENZOPHENONES WITH DIFFERENT CHARGE IN IONIC MICELLAR SYSTEMS*

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ABSTRACT

The photosensitization effects of the benzophenone derivatives having different charges, such as cationic BP(BP—CH₂—N⁺(C₂H₅)₃Br⁻) (PKT-1), anionic BP(BP—COONa) and the neutral BP in the various ionic micellar systems were studied. From the photopolymerization of MMA initiated by the various BP/TEA in different micellar systems, the results obtained show that the polymerization rate is in the order of PKT-1 > BP > BP—COONa in the SDS anionic micelle. On the contrary, the order changes to BP—COONa > BP > PKT-1 in the CTAB cationic micelle, and to BP—COONa ≈ PKT-1 > BP in the PKT-3 functional micelle. It is noteworthy that the PKT-1/SDS system is more efficient with its quantum yield more than 50 times compared with that of simple BP/H₂O system.

In recent years, using the electrostatic effect of the ionic micelle to prevent the charge recombination, promoting or retarding the reactions has become an efficient method to control some reaction processes, particularly, for charge transfer ones. A new feature of interests in this field is the functionalization of the conventional model of micelles formed from commercial surfactants. Such functionalized micelles can easily be achieved by selecting different kind of counter ion or ionic compound with desired property incorporated into the boundaries of micelles. For example, Thomas^[1] exploited a functionalized sodium dodecyl-sulfate (SDS) micelle with "heavy atom effect" by use of Ag⁺ as the counterion, to allow the observation of phosphorescence of some aromatic hydrocarbons. Grätzel^[2] selected Ni²⁺ or Co²⁺ as counterions instead of Na⁺ for SDS and yield a functional micelle with photophysical active interface that lead to drastic increase in the quenching efficiency of N-methylphenothiazine triplet. Thus, through this way of molecular or ionic assembly the quenchers (or sensitizers) can be enriched in the interface of micelle, to produce high local concentration of quencher (or sensitizer) (3~5M) even in very dilute solutions. Apparently, it is more simple and convenient method to acquire the functional micelle from commercial surfactants. In this paper benzophenone (BP)/triethylamine (TEA) is still used as a photosensitized initiation system^[3]. A series of functional micelle with photosensitive action are obtained by functionalization of the ordinary ionic micelles formed from commercial surfactants utilizing the

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benzophenone having different charge. The catalytic effects of them on the vinyl photopolymerization are also studied.

EXPERIMENTAL

(4-benzoylbenzyl) triethylammonium bromide (PKT-1) ($\text{BP}-\text{CH}_2\text{N}^+(\text{C}_2\text{H}_5)_3\text{Br}^-$) was synthesized by reaction of 4-bromomethylbenzophenone with triethylamine under reflux for 8 hours. After separation and purification the yield of PKT-1 product was 60% and its melting point is $185 \sim 187^\circ\text{C}$.

4-Carboxyl benzophenone (BP-COOH) was purchased from Tokyo Kasei Co. Japan, and was purified by recrystallization, m.p. 202°C .

Benzophenone was recrystallized, m.p. $47\text{--}48^\circ\text{C}$.

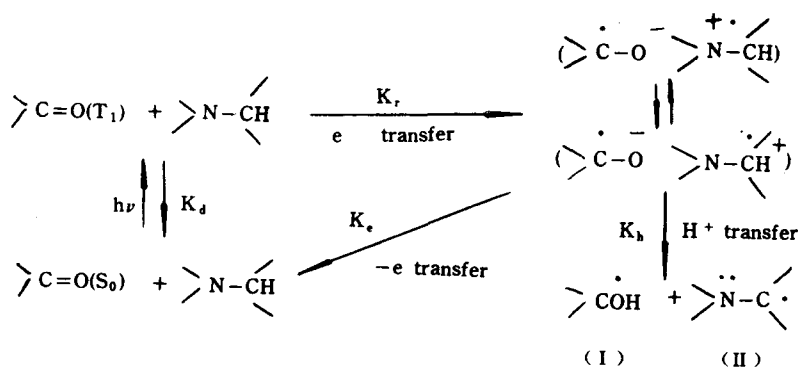
Cetyltrimethylammonium bromide (CTAB), sodium dodecylsulfate (SDS) were purified by recrystallization.

Other reagents all purified with common methods before use.

Photopolymerization was carried out in glass tubes with capillary branch at 30°C in thermostat. The reaction solutions freed from oxygen by bubbling with high pure nitrogen. The high pressure mercury lamp 300W was used as light source. The monomer concentration was determined by bromination method, for details may refer to the previous papers^[3,4].

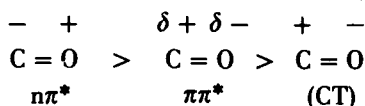
RESULTS AND DISCUSSION

Under UV irradiation the BP/TEA photoinitiation system undergoes charge transfer reaction, including electron transfer process to form an exciplex (CT) and following proton transfer process to yield semipinacol radical (I) and α -alkylamine radical (II). The energy and electron back transfer processes also occur simultaneously to result in deactivation of excited BP*^[5]. The scheme for the above reaction processes can be illustrated as follows:



In some literatures^[5,6] it has been indicated that the reaction environment and the properties of benzophenone derivatives have strong influence on both reaction rate and quantum yield of product. The enhancement of media polarity facilitates electron transfer process and leads to an increase in the reaction constant and quantum yield of product (ϕ_r). When the reaction carried out in the micellar environment the K_e/K_d value increases pronouncely. When the concentration of tertiary amine is up to the certain extent, the proton transfer process is accelerated and the K_h/K_e

+ K_e ratio value rises considerably^[7]. The electronic structure of the lowest excited state for different substituent benzophenones also plays an important role. The different reactivities toward photoreduction are dependent on the character of electronic structure of carbonyl oxygen in the lowest triplet state^[8].



where CT refers to charge transfer excitation.

The present work deals with reaction ability of the photoinitiation systems composed of benzophenones with different charge and tertiary amine, as well as the effects of micellar environment.

1. Photopolymerization in the neat water solution

The benzophenone derivatives having different charge, such as positive (PKT-1), negative (BP-COONa) and neutral BP respectively were used with TEA to compose various photosensitized initiation systems in this paper. Obviously, benzophenone with different charge exhibit different reactivity toward photoreduction with tertiary amine to generation of radicals. The results obtained show that the rate of methyl methacrylate (MMA) photopolymerization in the neat water solution under the same condition is in the order of PKT-1 > BP-COONa > BP. The rate of PKT-1, that has positive charge, is three times greater than that of the latter two. This observation can be attributed to that the cationic intermediate produced in the electron transfer process is repelled by the neighboring ammonium group and consequent charge recombination is suppressed, thus leading to raising the quantum yield of photoreduction.

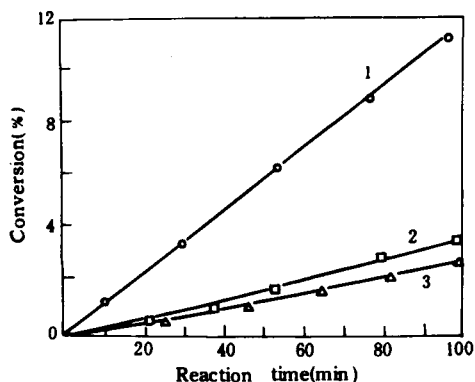
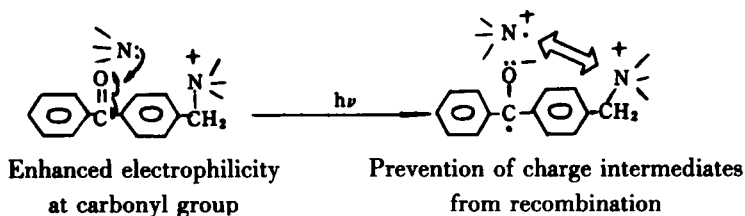


Fig. 1 Photopolymerization with BP derivatives having different charge in the aqueous solution

1. PKT-1; 2. BP-COONa; 3. BP

Neat water solution	PKT-1	BPCOONa	BP
$R_p \times 10^6 (\text{M}\cdot\text{S}^{-1})$	2.5	0.85	0.75

$[\text{MMA}] = 1.4 \times 10^{-1} \text{M}$ under N_2

$[\text{TEA}] = 2.1 \times 10^{-2} \text{M}$, $[\text{BP}] = [\text{PKT-1}] = [\text{BP-COONa}] = 1.0 \times 10^{-3} \text{M}$

at 30°C

The result of BP—COONa related to that of BP is quite approximate, because BP—COONa, that bearing negative charge, is not favorable to the separation of cationic intermediates formed.

2. Photopolymerization in the cationic CTAB micellar system

Fig. 2 shows the photopolymerization of MMA initiated by benzophenones with different charge in the CTAB micellar aqueous solution. The results obtained indicate the sequence of polymerization rate to be BP—COONa > BP > PKT-1. The rate of BP—COONa increases nearly a fold, but the rate of PKT-1 decreases about 4 times as compared with the rate of BP. This phenomenon may be considered as a result of electrostatic interaction in the ionic micellar system. When photopolymerization of BP/TEA/MMA system carried out in the CTAB micellar solution, the reactions occur at interface layer, that has been proved by UV absorption and ^1H NMR spectra^[3]. In this case the BP—COO[−] anion is attracted, on the contrary, the PKT-1 cation is repelled by the surface positive charge of micelles. This effect facilitates the solubilization of BP—COONa into the micelles to yield a very high local concentration with respect to that of neutral BP, resulting in an increase in reaction rate. In the PKT-1/CTAB system, the entry of the PKT-1 cation into micelles is suppressed, so that PKT-1 molecules are difficult to locate at reaction site (micellar interface). Such results make a difference in capability to initiate polymerization.

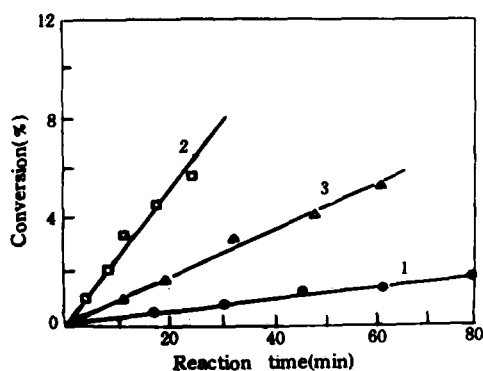


Fig. 2 Photopolymerization in the cationic CTAB micellar solution

Exp. condition ibid Fig. 1

1. PKT-1; 2. BP—COONa; 3. BP

CTAB micellar system	PKT-1	BP—COONa	BP
$R_p \times 10^6 (\text{M}\cdot\text{S}^{-1})$	0.6	4.0	2.3

3. Photopolymerization in the anionic SDS micellar system

As can be seen from Fig. 3, in the SDS micellar aqueous solution the polymerization rates of MMA initiated by BP derivatives with different charge are in sequence $PKT-1 > BP > BP-COONa$, as contrasted with that obtained in the cationic CTAB micelles. This observation may be explained by the effect of negative charge in SDS micelle surface which attracts PKT-1 cations and repels $BP-COO^-$ anions to produce a different local concentration of benzophenone in micelles, consequently leading to varying in polymerization rate. Here, it is notable that the reaction efficiency obtained in the SDS micelles is many times greater than that in the CTAB micelles under the same condition. These results demonstrate that the characteristic of PKT-1 and its promoting effect are further intensified after molecular aggregation. Moreover, the other important factor is the excellent solubilization of PMMA produced in the polymerization of MMA by SDS micelles. The limited conversion degree of monomer permissible to keep the solution transparent in the SDS micellar system is much higher than that in the CTAB system in this experiment.

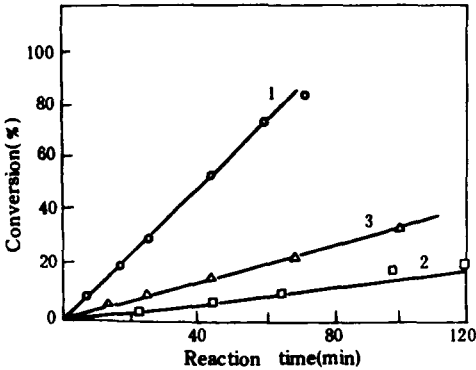


Fig. 3 Photopolymerization of MMA in the anionic SDS micellar solution Exp. condition ibid Fig. 1
1. PKT-1; 2. BP-COONa; 3. BP.

SDS micellar system	PKT-1	BP-COONa	BP
$R_p \times 10^6 (M S^{-1})$	40	3.8	9.5

4. Photopolymerization in the PKT-3 functional micellar aqueous solution

Both PKT-3 and PKT-1 exhibit the same cationic benzophenone as end group, but only PKT-3, having relative long alkyl chain, is able to form the micelle. Fig. 4 shows the photopolymerization of MMA in the PKT-3 micellar aqueous solution. The sequence of polymerization rate of MMA obtained is $BP-COONa \approx PKT-1 > BP > \text{no additive}$. Here, the influence of BP addition to the functional micelle is not very eminent. Perhaps, the molecular orientation degree of BP solubilized in the PKT-3 micelle reduces and the excited BP^* deactivation processes e.g. self-quenching become easy, leading to decrease of the reactivity. It seems that in PKT-3 micellar system the repulsion effect of such micelles on PKT-1 ions charged with the same kind of electricity appears not significant. The intermolecular distance between two surfactants at interface of PKT-3 micelle has been measured to be about $9\text{\AA}$, that is somewhat larger than that of ordinary ionic micelles. This result can be interpreted in terms of the steric hindering influence of the BP end group in PKT-3.

Therefore the molecular aggregation of PKT-3 become looser and its surface electric charge density of micelle lowers.

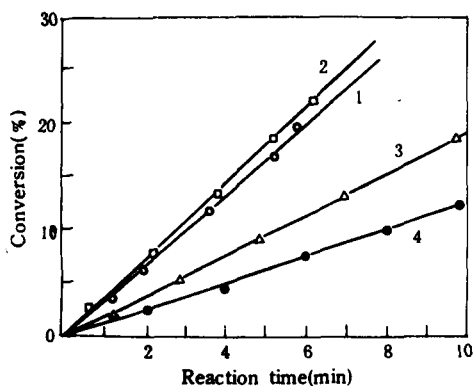


Fig. 4 Photopolymerization in PKT-3 functional micellar solution Exp. condition ibid Fig. 1

1. PKT-1; 2. BP—COONa; 3. BP; 4. no additive

PKT-3 micellar system	PKT-1	BP—COONa	BP	No additive
$R_p \times 10^6 (M \cdot S^{-1})$	68	70	33	22

CONCLUSION

On the basis of the experimental results, in order to evaluate the efficiency of various reaction system, the neat water solution system, in which the photopolymerization of MMA initiated by BP

Table 1 Photopolymerization of MMA initiated by the different BP derivative/micelle systems

Reaction system	Concentration of BP $\times 10^3 (M)$	Polymerization rate (R_p) $\times 10^6 (M \cdot S^{-1})$ at 30°C			Relative quantum yield (ϕ_{rel})		
		PKT-1	BP—COONa	BP	PKT-1	BP—COONa	BP
SDS system	1.0	40	3.8	9.5	53	5.1	13
CTAB system	1.0	0.6	4.0	2.3	0.8	0.53	3.1
PKT-1	2.8	68	70	33	32	33	16
neat water solution	1.0	2.5	0.85	0.75	3.3	1.1	1.0

Under N_2

$[MMA] = 1.4 \times 10^{-1} M$

$[PKT-1], [BP-COONa], [BP] = 1.0 \times 10^{-3} M$

$[PKT-3] = 1.8 \times 10^{-3} M$

$[TEA] = 2.1 \times 10^{-2} M$

$[SDS] = 1.2 \times 10^{-2} M$

$[CTAB] = 2.1 \times 10^{-3} M$

carried out, was used as criteria to calculate the relative quantum yield (ϕ_{rel}). In view of the fact that the experiments for various reaction systems proceed under the same condition, the light intensity is constant, and so the relative quantum yield (ϕ_{rel}) may be obtained by dividing the polymerization rate (R_p) by the concentration of photosensitizer BP, namely,

$$\phi_{\text{rel}} = R_p \times C_{\text{BP}}^0 / R_p^0 \times C_{\text{BP}}$$

(label 0 being criterion system)

The results obtained are listed in Table 1. From the data demonstrated in Table 1, the conclusions may be drawn as the following:

- (1) In the case of PKT-3 functional micellar reaction system, the addition of ionic or nonionic BP both give very high rate of polymerization, particularly, the ionic is much better one. These result in an increase in the quantum yield by about 30 folds. It may be ascribed to the very high local concentration (3.3M) as well as the uniform distribution of BP in the boundary layer of micelles.
- (2) In the case of the ordinary ionic micellar system, the electric charge property of BP-additives plays an important role. When addition of BP derivative having the same kind of electricity as appears in the micelle, the reaction efficiency decreases. On the contrary, when addition of BP with the charge different from the charge of micelles the reaction efficiency increases. Therefore the reaction quantum yield of the latter is higher than that of the former by 5~10 times.
- (3) As shown in Table 1, the micellar reaction system composed of PKT-1/SDS possesses attractive fine efficiency. Its polymerization rate is far greater than that in other ordinary ionic micellar system and closes to the values of PKT-3 functional micellar system.
- (4) In the case of neat water system, it is obvious that the BP with different charge exhibit different photochemical activity. The BP having positive charge, e.g. PKT-1, is the most active. Using PKT-1 to initiate polymerization both rate and quantum yield obtained are about 3 times higher than that by the simple neutral BP. Whereas the results of BP with negative charge, e.g. BP-COONa, is only slightly better compared with that of neutral BP.
- (5) Results listed in Table 1 indicate that the catalytic effect of PKT-3 functional micelles are far greater in respect to the ordinary ones. It may be considered that forming a photosensitive molecular assembly that has characteristics of the uniform distribution and high density of photosensitizers plays an important role. On the other hand, the functional micelles also can be acquired by functionalization of the conventional model of micelles, through the proper combination of the surfactant and photosensitizer with different charge, steric molecule arrangement, solubilized site etc. to allow displaying the same expectant effects. Evidently, the latter is a more simple and convenient method to gain the functional micelles.

Keywords:

Photopolymerization; Functionalization; Surfactant.

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