

PHOTOPOLYMERIZATION IN THE MICELLAR SYSTEMS II THE CATALYSIS OF PKT FUNCTIONAL MICELLE*

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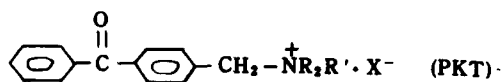
ABSTRACT

A kind of cationic compounds, having benzophenone end group and various length chain (PKT) ($\text{BP-CH}_2\text{N}^+\text{R}_2\text{R}'\text{X}^-$, R&R' different chain length alkyl group) were used as photosensitizers. Various BP/TEA systems have been used for study. The efficiency of MMA photopolymerization initiated by them shows $\text{PKT} > \text{BP}$ in homogeneous water solution and $\text{PKT} > \text{BP/CTAB}$ in micellar water solution. The results obtained indicate that catalytic effects of PKT type functional micelles are far greater than that of common micelle with the enhancement of polymerization rate over 10 times compared with BP in water solution. The catalytic role, reaction character of PKT, effect of counter ions and retarding effect of oxygen have also been discussed.

A particularly attractive aspect of photochemical studies in micellar systems is the possibility of organizing the reactants at molecular level. The quite large enhancements of the reaction rate and efficiency have been observed in many cases of micellar systems^[1]. The micellar aggregates may influence photophysical and photochemical properties of solutes in interesting ways as a result of the local concentration effect, the restricted space, the microviscosities and the local electric field etc. that are compartment-alized in a micellar aggregate. For example, photoreduction of benzophenone may be greatly accelerated both by the high local concentration and by proximate polar environment in sodium dodecyl-sulfate (SDS) micelle^[2]. The encouraging feature with the simple surfactant micelle stimulated our effort to search more developed molecular organization suited for photochemical reactions. Recently, a significant development in the micellar systems is the design of novel structural micelles with expected properties, where the functional group is chemically linked to the surfactant and itself participates in the photophysical or/and photochemical process. For this purpose, a series of benzophenone cationic derivatives, having tetraalkyl-ammonium group in the para-position and with various length alkyl chain (PKT) were prepared and used as photosensitizers and surfactants in this paper. The common structure of PKT compounds is shown as follows: Unusual reaction efficiency was found by Tazuke when the cationic BP derivatives in analogy to the PKT were used as photosensitizers for photooxidation of Leuco Crystal Violet in acetonitrile in air^[3]. To enhance the solubility of BP in aqueous solution, Guthrie utilized BP compound with quaternary ammonium as a hydrophilic group for photografting modification of celluloses^[4]. But these reactions only took place in the homogeneous solution, so the phenomenon and cooperative effects of molecular self-assembly would not display in these systems.

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PKT	1	2	3	4	5	6
R	C ₂ H ₅	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃
R'	C ₂ H ₅	n-C ₆ H ₁₃	n-C ₁₂ H ₂₅	n-C ₁₄ H ₂₉	n-C ₁₆ H ₃₃	n-C ₁₂ H ₂₅
X ⁻	Br ⁻	Br ⁻	Br ⁻	Br ⁻	Br ⁻	Cl ⁻
CMC(M)	non	non	1.12 × 10 ⁻³	1.66 × 10 ⁻⁴	3.47 × 10 ⁻⁵	1.1 × 10 ⁻³

EXPERIMENTAL

The preparation of PKT compounds: 4-methylbenzophenone was brominated by N-bromosuccinimide (NBS) to yield 4-bromomethyl benzophenone, then tertiary amines with different length alkyl chain was added respectively and the mixture was heated to reflux. The reaction product was separated and purified by recrystallization to give PKT compounds respectively. For the details of the synthetic method refer to other paper^[5].

Benzophenone (BP), triethylamine (TEA) and cetyltrimethylammonium bromide (CTAB) were commercially available and purified by the usual methods. Methylmethacrylate (MMA) was distilled under vacuum prior to use.

Photopolymerization procedure: photosensitized polymerization was carried out in the glass tubes at 30°C using high pressure mercury lamp as light source. The light wavelength less than 300 nm were removed by glass filter and the light intensity at near ultraviolet was measured to be 4.5×10^{15} photons/cm² · s. The reaction solution was prepared with twice-distilled water and kept transperence through the reaction period. The monomer content in the solution was determined with bromination method^[6].

The values of critical micellar concentration (CMC) of surfactants were measured by the surface tension method^[7].

The UV-spectra and ¹HNMR spectra were performed with Hitach-340 spectrophotometer and Varian EM-360 spectrometer, respectively.

RESULTS AND DISCUSSION

The UV absorption spectral properties of PKT compounds are listed in Table 1.

It is obvious that the BP group linked to the molecular head of PKT remains its original photophysical properties due to existence of methylene as isolating group between BP and ammonium group. All PKT homologues show the lowest excited states to be a n-π* transition which more favors photoreduction of BP^[8]. Their n-π* absorption peak (λ_{max}) and molar extinction coefficient (ε) locate at the values between BP and 4-methyl BP. The lowest triplet energies (E_T) of PKT compounds is slightly lower than that of BP.

In order to evaluate the catalytic effect of PKT micelle, a comparison study of photopolymerization with the same BP/TEA initiation system was carried out in the micellar system

Table 1 Spectral properties of BP and PKT compounds*

Characteristics	BP	4-Me-BP	PKT-1	PKT-2	PKT-3	PKT-4	PKT-5
$\lambda_{\max}(\text{nm})$	340	329	337	334	336	333	333
$\varepsilon(\text{M}^{-1}\cdot\text{cm}^{-1})$	133	244	159	150	156	165	156
$E_{T1}(\text{kcal/mol.})$	69.2	69.2	68.4	68.4	68.4	68.1	67.9

* ethanol solution

and in the homogeneous solution. The conversion plot of MMA photopolymerization initiated by BP, BP/CTAB and PKT respectively are shown in Fig.1. The polymerization rate (R_p) is shown as in the following order PKT-3(> CMC) > PKT-3(< CMC) > BP/CTAB (> CMC) > BP. These results indicate that the capability of initiating photopolymerization is PKT > BP and the catalytic efficiency of micelles is PKT micelle > CTAB micelle.

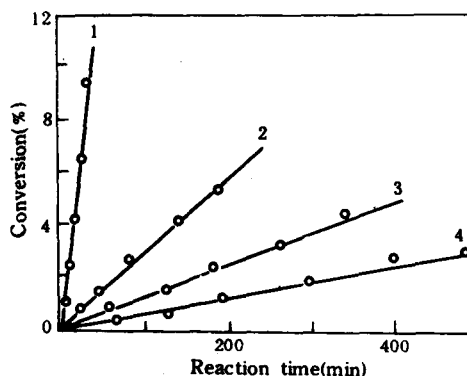


Fig.1 Photopolymerization of MMA with various initiation systems in aqueous solution

1. PKT-3 $2.0 \times 10^{-3}(\text{M})(> \text{CMC})$; 2. PKT-3 $3.2 \times 10^{-4}(\text{M})(< \text{CMC})$;3. BP/CTAB $3.4 \times 10^{-4}/1.9 \times 10^{-3}(\text{M})(> \text{CMC})$; 4. BP $3.4 \times 10^{-4}(\text{M})$ Under N_2 $[\text{MMA}] = 1.4 \times 10^{-1} \text{M}$ $[\text{TEA}] = 2.1 \times 10^{-2} \text{M}$ at 30°C

Obviously, the significant catalytic effect of PKT micelles is related not only to the molecular structure but also to the molecular assembly and arrangement in the reaction system. To further clarify the different contributions of various rate-accelerating effects, these factors are discussed as follows:

1. The role of molecular aggregation

In order to evaluate the catalytic effect of PKT molecular aggregation on reaction in this system, the PKT-3 compound was used as photosensitizer to observe the dependence of polymerization rate on the concentration of PKT-3 in the range above and below CMC. As can be seen in Fig.2, the polymerization rate increases smoothly with concentration below CMC. In this case

it is a homogeneous solution and PKT-3 molecules exist in the free state. On the contrary, an abrupt rate-enhancement of polymerization occurs at CMC and above that R_p increases with concentration remarkably. It indicates clearly that the PKT micelle effect play an important role in promoting the polymerization.

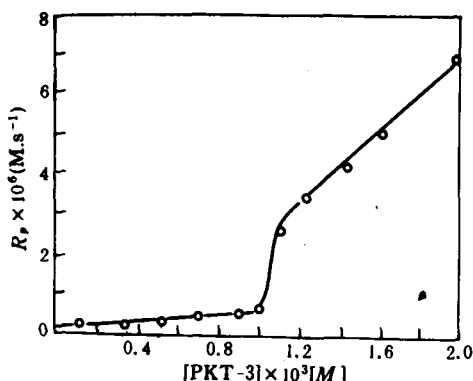
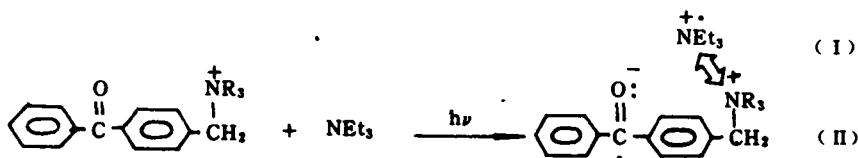


Fig.2 The relationship between polymerization rate and concentration of PKT-3

Exp. condition ibid Fig.1

2. Nature of active head group

The promoting effect of photoactive head group of PKT, a kind of positive charged benzophenone ($\text{BP}-\text{CH}_2-\overset{+}{\text{N}}\text{R}_3$), on the photoinitiation of MMA polymerization with BP/TEA is shown in Fig.1. The polymerization rate (R_p) of PKT is much larger than that of BP or BP/CTAB systems both in the homogeneous solution and in the micelles under the same concentration condition. This observation may be attributed to the fact that the cationic intermediate (I) produced from photoreduction of BP/TEA is repulsed by the positive charge of ammonium group in PKT and prevented from approaching the semipinacol anion (II) formed. It leads to reducing the back electron transfer process and increase greatly in a quantum yield of photoreduction, giving an excellent radical initiation efficiency.



To analyze the contributions of the active head group and the functional micelle of PKT-3 respectively for accelerating the polymerization, comparison study of a series of PKT analogy in the same experimental condition was performed. The results obtained (as seen from Fig.3) show that the polymerization rate of PKT-1 and PKT-2 are far lower than that of PKT-3, owing to that the former two are unable to form the micelle. Apparently, it demonstrates that the promoting effect of active head group of PKT is amplified after the PKT molecular aggregation to form micelle.

3. Influence of alkyl chain length

The molecular association abilities of the different PKT compounds mainly depend on their chain length. In order to observe the influence of chain length on the rate (R_p), various PKT

compounds with different chain length were used to photoinitiate MMA polymerization. The results obtained as shown in Fig.4 illustrate that the curve of the polymerization rate as a function of the chain length has two distinct sections. When the chain length is less than 8 carbon atoms these PKT are unable to form micelle and exhibit a relative low rate. When the carbon number of alkyl chain is greater than 8, these PKT display a high rate due to the molecular self-association. Based on the comparison of above results, it may confirm once again that the PKT micellar action take an active part in this reaction system related to other factors.

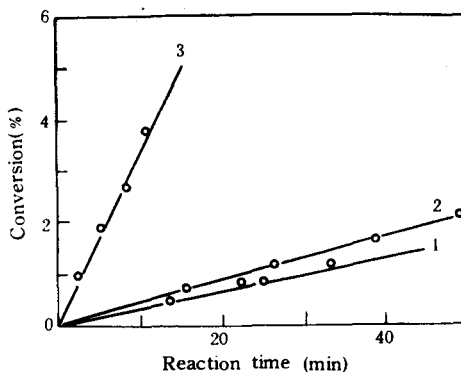


Fig.3 Photopolymerization of MMA with PKT-1, PKT-2 and PKT-3

1. PKT-1; 2. PKT-2; 3. PKT-3

[PKT] $2.0 \times 10^{-3} M$

Exp. condition ibid Fig.1

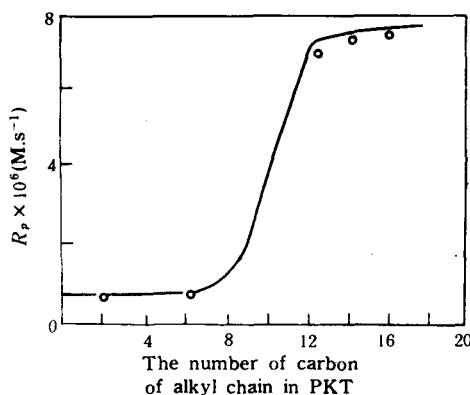


Fig.4 Dependence of R_p on chain length of PKT

[PKT] $2 \times 10^{-3} M$

Exp. condition ibid Fig.1

4. Effect of counter ion

The correlation between polymerization rate and different counter ions is shown in Fig.5. The polymerization rate obtained is in the order $Cl^- > Ac^- > Br^-$. On account of the very weak influence of counter ions with one valence on the surface activity of surfactants, here obviously the other factors should play an important role. As reported the Br^- ion is able to quench triplet BP markedly and causes to decrease in photoreaction rate^[9], so that the PKT micellar catalysis is the

lowest in the presence of Br^- ion. It was also found from ^1H NMR spectra that proton chemical shift of isolating methylene group in PKT compound is affected by the counter ion. The value of their chemical shifts (δ_{ppm}) is to be Ac^- (4.9), Cl^- (5.2) and Br^- (5.3). It demonstrates that the difference in interaction between counterion and positively charged nitrogen atom is existed in this system. The Ac^- ion, due to the solubilization action of C_2 carbon chain, locates at more near the ammonium ion, that causes to weaken the surface electrostatic effect and to decrease in the micellar catalysis. So that the selection of appropriate counterion is worthy of notice in the case of utilizing micellar solution as reaction system.

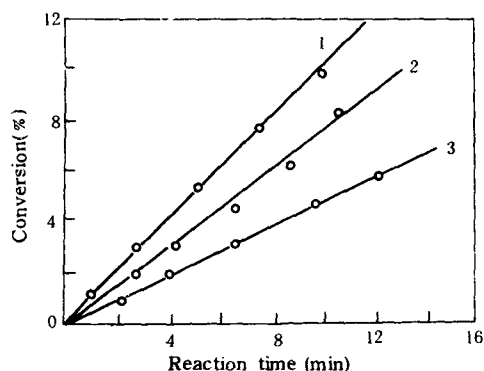


Fig.5 Effect of different counterions in PKT micellar system

1. Cl^- ; 2. Ac^- ; 3. Br^-

Exp. condition ibid Fig.1

Table 2 Influence of O_2 on various BP/TEA systems

Reaction system	$R_p \times 10^6 (\text{M}\cdot\text{S}^{-1})$		Relative quantum yield	
	N_2	air	$\phi_{\text{N}_2} / \phi_{\text{N}_2}$	$\phi_{\text{N}_2} / \phi_{\text{air}}$
BP	1.3	0.18	1.0	7.2
PKT-1	8	8*	1.1	10
PKT-2	9	11*	1.2	8.2
PKT-3	70	160*	9.5	4.3
PKT-4	74		10.0	
PKT-5	75		10.1	
BP/CTAB	3		2.3	

[PKT] $2.0 \times 10^{-3} \text{M}$ [BP] $3.3 \times 10^{-4} \text{M}$ [CTAB] $1.9 \times 10^{-3} \text{M}$

* Incident light intensity increases 10 times

5. Action of oxygen

As known, the quenching of triplet BP and the inhibition of radical polymerization propagating chain by oxygen contained in the system, usually lead to a decrease of polymerization rate. Table 2 shows that when polymerization of MMA undergoes in the presence of air or oxygen, the inhibition by oxygen in PKT micellar system is quite low compared with that in neat water solution, that is

similar to the reaction in the ordinary micelles. This observation can be interpreted by fact that the oxygen in the system mainly solubilizes into micellar core because the solubility of oxygen in water is very low ($\sim 10^{-4}M$). On the other hand, the very high microviscosity of micelle interior restricts the diffusion of oxygen in micelle, so that the inhibition by O_2 is suppressed.

CONCLUSION

As mentioned above, it has shown clearly that the photosensitive functional PKT micelle exhibits a good catalytic efficiency. The much high polymerization rate-enhancement of PKT micelle compared with ordinary micelle (e.g. CTAB) may be attributed to the following factors.

1. The BP local concentration in the PKT micellar reaction system is far higher than that in ordinary micellar solution. It is due to that in PKT compounds BP is chemically linked to the surfactant and in PKT micelle the BP number is equal to the aggregation number of PKT molecules. The local concentration of BP in the PKT micelle, obtained by experimental method, is up to 3.3(M).

2. The PKT compounds possess much high reactivity and quite suit for electron transfer photoreaction, these effects are further more intensified by the molecular aggregation to form a micelle.

3. The orientation degree of BP group in the interface of PKT micelle is much higher than that of the ordinary micelles as a result of fact that the BP moieties are assembled with self-association of surfactant molecules according to the certain order and degree to form micelles, that leading to a decrease in the self-quenching of triplet BP and enhancing the quantum yield of reaction to one order of magnitude, as shown in Table 2.

The above results have much great significance not only due to that they lead to a great promotion of photopolymerization but also that demonstrate a large effect of molecular assembly and orientation on reactive ability. This information should be applicable as a model to the investigation of more complex assemblies of biological interest such as enzymes and membranes.

Keywords:

Photopolymerization; Functional micelle; Benzophenone

REFERENCES

- [1] Fendler, J. H. and Fendler, E. J., *Catalysis in Micellar and Macromolecular Systems*, Academic Press, New York, **1975**.
- [2] 王尔锺, 朱德英, 常志英, 冯新德, *分子科学与化学研究 (Molecular Science and Chemical Research)*, **1983**, (3) 47.
- [3] Tazuke, S.; Kawasaki, Y.; Kitamura, N. and Lnoe, T., *Chemistry Letters*, **1980**, 251.
- [4] Guthrie, J.T. and Green, P.N., *Polym. Photochem.*, **1985**, 6, 59.
- [5] 方培基, 王尔锺, *感光科学与光化学 (Photographic Science and Photochemistry)*, in press, **1988**.
- [6] Stanley, E.I., *Analytical Chemistry of Polymer*, G.M. Kline ed., New York, **1959**.
- [7] 朱玮瑶, *化学通报 (Chemistry)*, **1981**, (6), 21.
- [8] Turro, N.J., *Modern Molecular Photochemistry*, Benjamin/Cummings, Menlo part, **1978**, 375.
- [9] Treinin, A. and Hayon, E., *J. Am. Chem. Soc.*, **1976**, 98, 3884.