Photopolymerizations of Methyl Methacrylate with N-Cetylpyridinium Bromide and N-Cetylpyridinium Chloride in Aqueous System

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ABSTRACT: The photopolymerizations of methyl methacrylate (MMA) with N-cetylpyridinium bromide (CPB) and N-cetylpyridinium chloride (CPC) were investigated in aqueous system. With CPB alone, photopolymerization did not proceed, but by the addition of a small quantity of CCl_4, it was significantly accelerated. The rate of the photopolymerization of MMA with CPB in the presence of CCl_4 showed a linear relationship with the square root of CPB concentration, but was little affected by the concentration of CCl_4. With CPC MMA also photopolymerized in the presence of CCl_4, and especially at more than a critical micelle concentration (CMC) of CPC, the time-conversion curve showed a characteristic feature of emulsion polymerization, where R_p was proportional to the 0.75 power of the fed quantity of CPC, but almost independent of CCl_4 concentration. The above photopolymerizations with CPB and CPC in the presence of CCl_4 were, however, remarkably accelerated by the addition of KBr.
KEY WORDS   Photo-Emulsion Polymerization / Photo-Suspension Polymerization / Methyl Methacrylate / N-Cetylpyridinium Chloride / N-Cetylpyridinium Bromide / Carbon Tetrachloride /

In a series of studies[1,2,3] we reported that N-benzylpyridinium bromide (BPB) sensitized the photopolymerization of MMA in methanol and especially in the presence of CCl_4 the polymerization was well induced. In methanol solution, BPB may exist in an equilibrium among free ions, an ion pair and a charge transfer (CT) complex as shown in the following.
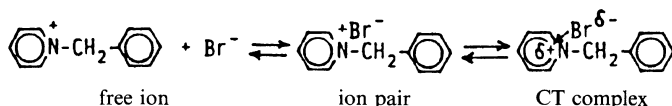
The CT complex photodecomposed to form both bromine atom and N-benzylpyridinyl radical. The former initiated the photopolymerization and the latter reacted with a growing radical to terminate the polymerization. By the addition of CCl_4 to this system, the rate of photopolymerization (R_p) was significantly accelarated. CCl_4 captured by N-benzylpyridinyl radical would produce N-benzylpyridinium chloride (BPC) and also the trichloromethyl radical which initiated the polymerization of MMA.

In the present study, the photopolymerizations of MMA with N-cetylpyridinium bromide (CPB) and N-cetylpyridinium chloride (CPC) in aqueous system were carried out in the presence of CCl_4, where CPB or CPC could be expected to act as an emulsifier and

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photosensitizer like BPB. The profiles of the photo-suspension polymerization of MMA with CPB and the photo-emulsion polymerization with CPC are discussed along with their kinetic properties.

EXPERIMENTAL

Materials

MMA was purified by the usual method just before use. Water was deionized. CPB and CPC of reagent grade (Tokyo Kasei Kogyo) were used without further purification. All other chemicals were of reagent grade.

Electronic Spectra

Electronic spectra were recorded on a Japan Spectroscopic Company Model Ubest-35 spectrophotometer and measured in a quartz cell having a 10 mm path length.

Polymerization

Photopolymerizations in aqueous system were performed by the use of photochemical reaction apparatus described in detail in the previous paper[3]. A 150 cm³ reaction vessel was charged with 20 cm³ of MMA solution containing CCl₄ and 80 cm³ of aqueous solution containing CPC. The contents in the reaction vessel were bubbled by blowing pure nitrogen at constant temprature (303 K) and flow rate (1 cm³ s⁻¹) through a glass filter from the bottom of the reaction vessel and irradiated by a Fuji Glass High Pressure Mercury Lamp HL-100 (100W). After irradiation, the reaction mixture was poured into a large quantity of methanol and the precipitated polymer was filtered, washed with methanol, and dried *in vacuo*. Photopolymerizations with CPB were performed by the same procedure.

The molecular weight of poly(methyl methacrylate) (PMMA) obtained was measured by viscometry and calculated by the following equation.[4]

$$[\eta] = 8.69 \times 10^{-5} \, M^{0.76} \text{ (benzene, 303 K)}$$

RESULTS AND DISCUSSION

Photopolymerization of MMA with CPB in Aqueous System

The photopolymerization of MMA with CPB was carried out in the aqueous system. The photopolymerization proceeded rapidly in the presence of CCl₄ as shown in Table I, and seemed to proceed by suspension polymerization mode, since CPB was used at less concentration than its critical mecelle concentration (CMC) because of its small solubility.

The photopolymerizations with CPB in the presence of CCl₄ were also carried out changing the feed ratios of CPB to CCl₄. All

Table I. Photopolymerization of MMA with CPB in the presence of CCl₄ in aqueous system[a]

CPB	CCl₄	Conversion
mmol	mmol	%
—	—	0.9
—	1	1.6
0.05	—	1.2
0.05	1	17.6

[a] MMA, 20 cm³; H₂O, 80 cm³; temp, 303 K; time, 1 h.
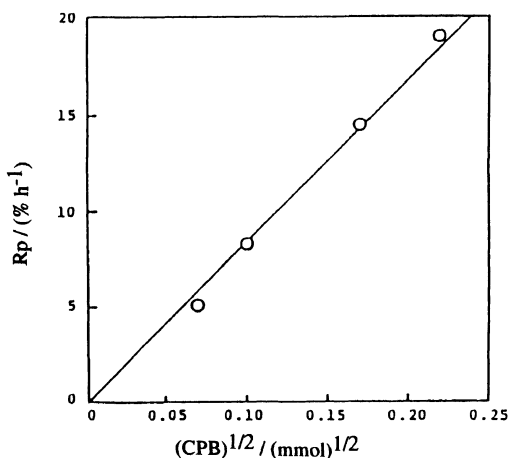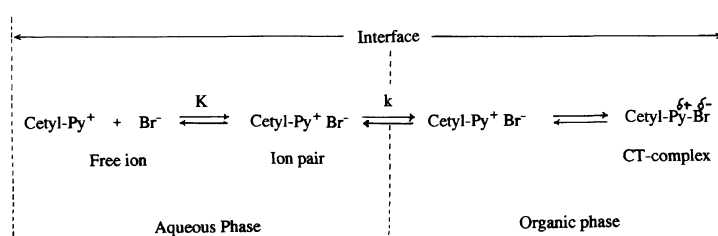

Figure 1. Relation of R_p *vs.* (CPB)$^{1/2}$ for the photopolymerization of MMA with CPB–CCl₄ in aqueous system: MMA, 20 cm³; H₂O, 80 cm³; CCl₄, 1 mmol; temp, 303 K.

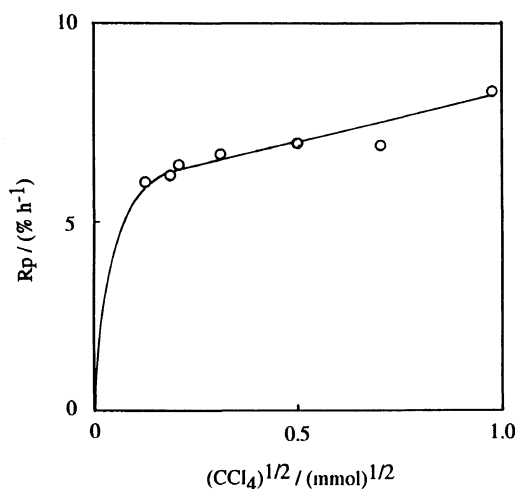Scheme 1. A equilibrium model of the CPB at aqueous–organic interface of a MMA droplet.

Figure 2. Relation of R_p vs. $(CCl_4)^{1/2}$ for the photopolymerization of MMA with CPB–CCl$_4$ in aqueous system: MMA, 20 cm^2; H$_2$O, 80 cm^3; CPB, 0.01 mmol; temp, 303 K.
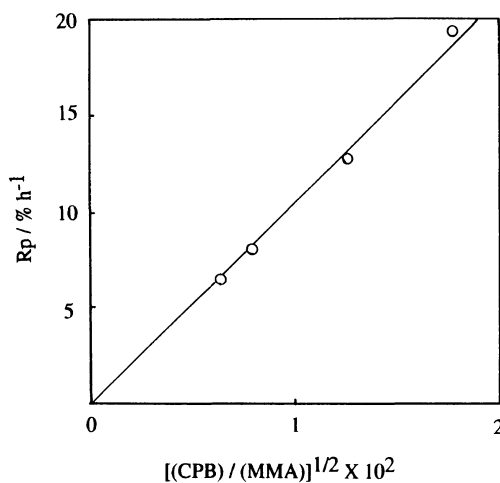
Figure 3. Relation of R_p vs. $[(CPB)/(MMA)]^{1/2}$ for the photopolymerization of MMA with CPB–CCl$_4$ in the aqueous system.

conversion-time relations were linear. The initial rate of polymerization (R_p) was plotted against the square root of the fed quantity of CPB and CCl$_4$, respectively. A linear relationship was observed between R_p and the quantity of CPB as shown in Figure 1. This implies that the equilibrium of CPB in the aqueous phase (Scheme 1) shifts extremely to ion pair side, because if it shifted to free ions, R_p should be linearly proportional to the fed quantity of CPB. R_p, however, little increased with increase of the fed quantity of CCl$_4$ in spite of the remarkable effect of CCl$_4$ (Figure 2). This implies that the reaction participated by CCl$_4$ is very fast and that it is not a rate-determining step.

In another series of experiments, the pho-

topolymerizations of MMA with CPB in the presence of CCl$_4$ were carried out at various volume ratios of MMA/water. R_p increased with decrease of volume % of MMA. Assuming that most molecules of CPB were aligned at the interface between aqueous and organic phases, the apparent concentration of CPB in the organic phase would increase with decrease of the fed quantity of MMA. The linear relation of R_p vs. $[(CPB)/(MMA)]^{1/2}$ plotted in Figure 3 may be explained according to the above-assumption.

The accelerating effect of KBr for this photopolymerization system is shown in Figure 4. This effect suggests that even in the equilibrium of CPB shifted to the ion pair side as described above, a small portion of the free ion in the aqueous phase could not be negligible

and therefore the equilibrium shifts more to the ion pair side by the addition of KBr. These results make possible for us to propose a cyclic radical initiation mechanism where CPB acts as a sort of phase transfer photosensitizer or catalyst as shown in Scheme 2. The CT complex in the organic phase photodecomposes into bromine atom and N-cetylpyridinyl radical. The former initiates the photopolymerization and the latter reacts with CCl_4 to yield CPC
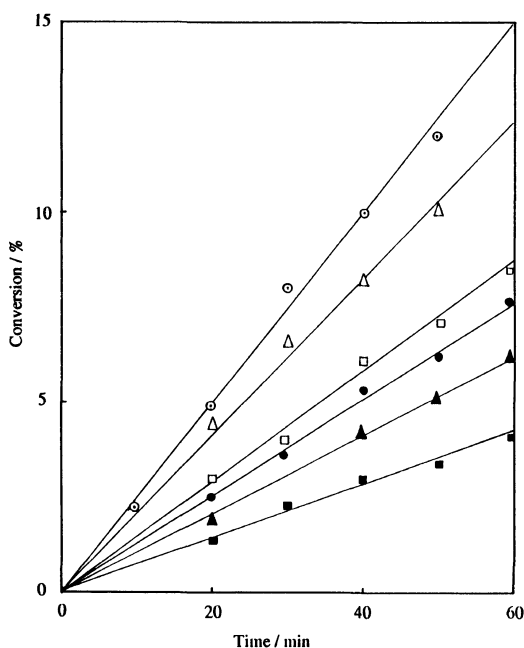
which is transferred into the aqueous phase and also $CCl_3 \cdot$ which initiates the polymerization of MMA. N-Cetylpyridinium ion in the aqueous phase may make an ion pair with bromide ion which is transferred into the organic phase due to the smaller electronegativity of bromide ion.
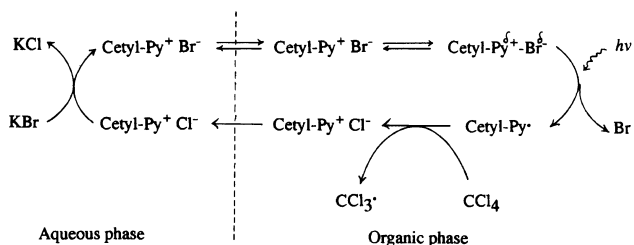
The photopolymerizatin of MMA with CPC in Aqueous System

The photopolymerization of MMA with CPC in the presence of CCl_4 was also carried out in aqueous system, where CPC was used at higher concentration than its CMC.[5] The number-average molecular weight of PMMA obtained by CPC–CCl_4 was larger than that by CPB–CCl_4 as shown in Table II. This suggests that the polymerization proceeded by emulsion polymerization mode. Without CCl_4 the conversion of the photopolymerization did not exceed 2% for an hour, but by the addition of CCl_4 the rate of polymerization was remarkably accelerated.

Figure 4. Effects of KBr on the photopolymerization of MMA with CPB–CCl_4 in aqueous system: MMA, $20\,cm^3$; H_2O, $80\,cm^3$; CPB, $0.001\,mmol$; CCl_4, $0.5\,mmol$; KBr (mmol), (⊙), 1.00; (△), 0.50; (□), 0.10; (●), 0.05; (▲), 0.01; (■), 0.00; temp, 303 K.

Table II. Photopolymerization of MMA with CPC in the presence of CCl_4 in aqueous system[a]

	Surfactant	CCl_4	Conversion	M_n
	mmol	mmol	%	
CPC	0.50	—	1.4	
	0.50	1.0	13.4	1.5×10^6
	0.05	1.0	3.8	
CPB	0.05	1.0	17.6	
	0.05	0.5	15.2	8.1×10^5

[a] MMA, $20\,cm^3$; H_2O, $80\,cm^3$; temp, 303 K; time, 1 h.

Scheme 2. Photo-radical initiation mechanism with the CPB–CCl_4–KBr system at an interface of aqueous–organic two-phase.
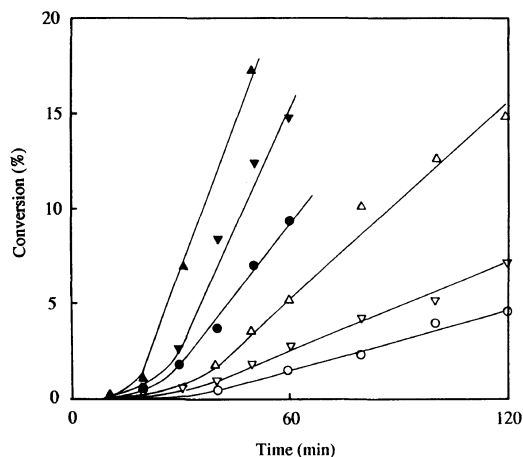
Figure 5. Effects of CPC concentration on the photo-emulsion polymerization of MMA with CPC–CCl$_4$: MMA, 20 cm^3; H$_2$O, 80 cm^3; CCl$_4$, 0.01 mmol; temp, 303 K; CPC (mmol), (▲), 1.5; (▼), 1.0; (●), 0.50; (△), 0.30; (▽), 0.10; (○), 0.05.

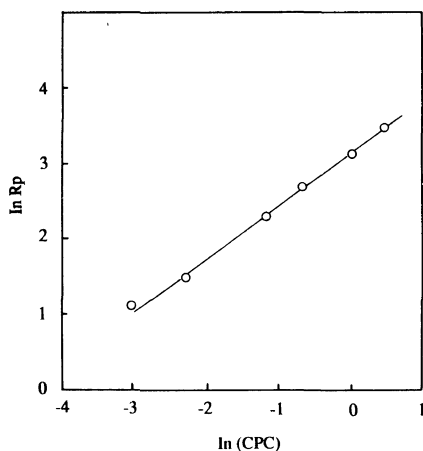**Figure 7.** Relation of ln R_p vs. ln(CCl$_4$) for the photo-emulsion polymerization of MMA with CPC–CCl$_4$.

Figure 6. Relation of ln R_p vs. ln(CPC) for the photo-emulsion polymerization of MMA with CPC–CCl$_4$.

The photopolymerizations of MMA with CPC in the presence of CCl$_4$ were also carried out by varing the fed quantity of CPC, and the conversion-time relations were typical of emulsion polymerization as shown in Figure 5. The rates of photopolymerization (R_p) were estimated from the slope of the straight line after the initial curvatures in Figure 5. Logarithmic plots of R_p against CPC concentration ga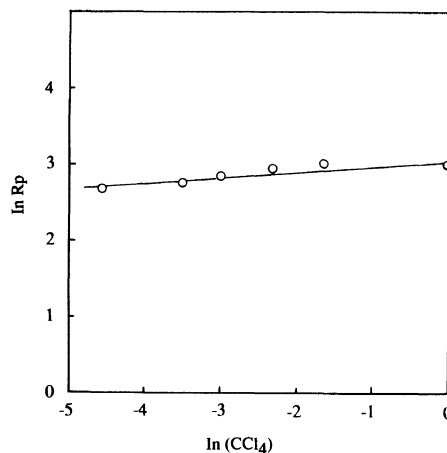ve a straight line with an exponent of 0.75 (Figure 6). By Smith and Ewart,[6] R_p was related to [emulsifier]$^{0.6}$[initiator]$^{0.4}$ for a typical emulsion polymerization. This relation is closely borne out by experimental data for water-insoluble monomers such as styrene and butadiene-styrene and for initiators generating free radicals in the aqueous phase.[7] The 0.75 power of the CPC concentration suggests that CPC acts not only as an emulsifier but also a photosensitizer in the photo-polymerization under the experimental condition.

The photopolymerizations of MMA with a definite quantity of CPC were carried out in the presence of the various quantities of CCl$_4$. The conversion-time relation was linear. The logarithmic plots of R_ps against CCl$_4$ suggest that R_p is scarcely affected by the quantities of CCl$_4$ (Figure 7). These results imply that the rate of the reaction participated by CCl$_4$ is very fast and that the reaction is not a rate-determining step. The photopolymerization of MMA with CPC in the presence of CCl$_4$ seems to proceed by the same polymerization mode as that of typical emulsion polymerizations,[8] whereas CPC serves as an emulsifier as well as a photosensitizer. The initiation mechanism seems similar to that of the photo-suspension polymerization of MMA with CPB–CCl$_4$ as
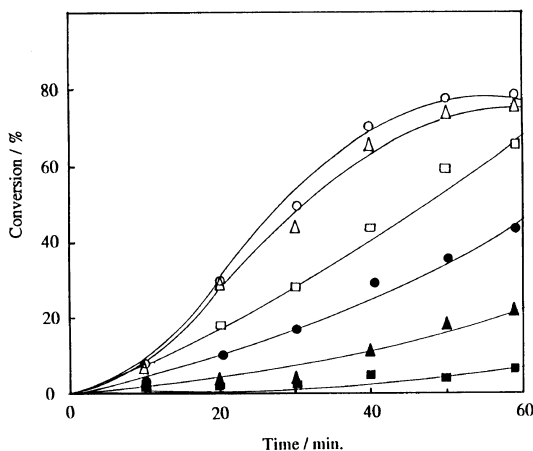
Figure 8. Effects of KBr on the photo-emulsion polymerization of MMA with CPC–CCl$_4$: MMA, 20 cm^3; H$_2$O, 80 cm^3; CPC, 0.5 mmol; CCl$_4$, 0.5 mmol; KBr (mmol); (○), 1.00; (△), 0.50; (□), 0.10; (●), 0.05; (▲), 0.01; (■), 0.005; temp, 303 K.
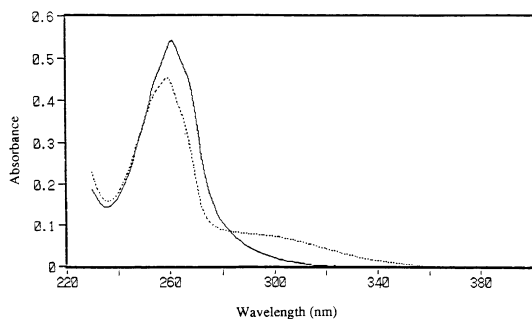

Figure 9. UV spectra of CPC (—) and CPB (---) in CH$_2$Cl$_2$.

mentioned above. The CT complex of CPC at the interface of the micelles photodecomposes into *N*-cetylpyridinyl radical and Cl·. *N*-Cetylpyridinyl radical reacts with CCl$_4$ to yield CPC and CCl$_3$·. Cl· and CCl$_3$· initiate the polymerization of MMA dissolved therein, yielding latex particles. Their radicals also initiate the polymerizaton of MMA diffusing

into the internal part of latex particles.

The effect of added KBr on the photopolymerization reaction is shown in Figure 8. Remarkable acceleration of the photopolymerization might be due to CPC being transformed into CPB to some extent by ion exchange, and CPB may act as a more effective photosensitizer than CPC. Measurements of UV spectra of CPB and CPC in the emulsion systems were very difficult and therefore performed in methylene chloride to draw an analogy (Figure 9). In the case of CPB, the CT absorption band appeared clearly in the region from 280 nm to 340 nm slightly behind the large pyridinium ring absorption around 258 nm. These are analogous to UV spectra of BPB and BPC reported in our previous papers.[1,2] In this case, however, a convenient rate equation for KBr addition effect could not obtained, as neither in the case of CPB.

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