Polymerization of Methyl Methacrylate with N-Benzyl Quinolinium Chloride–$Na_2S_2O_4$–CCl_4 in Aqueous-Organic Two-Phase System

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ABSTRACT: The polymerization of methyl methacrylate with N-benzyl quinolinium chloride (BQ^+Cl^-)–$Na_2S_2O_4$–CCl_4 initiator system was investigated in aqueous-organic two-phase system. The initial rate of polymerization (R_p) was proportional to the square root of fed quantity of initiator components, BQ^+Cl^-, $Na_2S_2O_4$, and CCl_4, respectively. R_p was also affected by the rate of stirring. A cyclic phase-transfer initiation mechanism is proposed to account for the experimental data.
    KEY WORDS   Polymerization / Methyl Methacrylate / N-Benzyl Quino-
linium Chloride / Sodium Dithionite / Carbon Tetrachloride /

In the previous paper,[1] the authors reported that methyl methacrylate (MMA) was photopolymerized with methyl viologen (MV^{2+})–$Na_2S_2O_4$–CCl_4 as an initiator system in MMA–water two-phase system and that the following cyclic phase-transfer photoinitiation mechanism was suggested for this polymerization. $MV^{\ddagger}$ produced by the reduction of MV^{2+} with $Na_2S_2O_4$ in the aqueous phase is transferred to the organic phase. $MV^{\ddagger}$ disproportionates to give 1,1′-dimethyl-4,4′-bipyridylidene (MV) and MV^{2+}. The fomer reacts with CCl_4 photochemically yielding $MV^{\ddagger}$ and $CCl_3{}^{\cdot}$ which initiates the polymerization of MMA, and the latter transfers to the aqueous phase. When N-benzyl quinolinium chloride was used instead of MV^{2+} in the initiator system for the polymerization of MMA, N-benzyl quinolinium chloride –$Na_2S_2O_4$–CCl_4 was found to act as an initiator system as MV^{2+}–$Na_2S_2O_4$–CCl_4 and polymerize MMA even without photoirra-

diation. In this paper, on the basis of kinetic studies an initiation scheme is proposed for the polymerization of MMA with this initiator system in an aqueous–organic system.

EXPERIMENTAL

Materials

MMA was purified by usual method just before use. Water was deionized. BQ^+Cl^- was prepared by the Menschutkin reaction. All other chemicals used in this study were of reagent grade.

Polymerization

Polymerization was carried out at a constant stirring rate in a four-necked flask under nitrogen atomosphere at 303 K. In a four-necked round-bottomed $100\,cm^3$ flask equipped with a mechanical stirrer, an inlet-tube of N_2, a Dimroth condenser with an outlet-tube of N_2, and a dropping funnel were placed

prescribed amounts of *N*-benzyl quionolinium chloride, $Na_2S_2O_4$, and Na_2CO_3. After completely dissolved in water degassed under N_2, degassed MMA containing CCl_4 was added through the dropping funnel. The mixture was stirred at a constant rate for an hour under stream of N_2 and the contents were poured into a large amount of aqueous methanol. The precipitated polymer was filtered, washed several times with water and methanol, and dried *in vacuo*.

RESULTS AND DISCUSSION

The polymerization of MMA with BQ^+Cl^-–$Na_2S_2O_4$–CCl_4 was carried out in an aqueous-organic two-phase system, where MMA polymerized even at 303 K. When one of these three components was excluded, however, polymerization was remarkably suppressed.

Table I. Polymerization of MMA with BQ^+Cl^-–$Na_2S_2O_4$–CCl_4 in the aqueous-organic, two-phase system[a]

BQ^+Cl^-	$Na_2S_2O_4$	CCl_4	Conversion
mmol	mmol	mmol	%
0.05	1	5	6.82
—	1	5	1.75
0.05	—	5	0
0.05	1	—	0

[a] MMA, $10\,cm^3$; H_2O, $40\,cm^3$; Na_2CO_3, 7.5 mmol; temp, 303 K; time, 1 h; stirring, 390 rpm.

Table II. Polymerization of MMA with BQ^+Cl^- reductant–CCl_4 in the aqueous-organic, two-phase system[a]

Reductant	Conversion
	%
$Na_2S_2O_4$	6.82
$NaHSO_3$	0
Na_2SO_3	0

[a] MMA, $10\,cm^3$; H_2O, $40\,cm^3$; BQ^+Cl^-, 0.5 mmol; reductant, 1 mmol; CCl_4, 5 mmol; $NaCO_3$, 7.5 mmol; temp, 303 K; time, 1 h; stirring speed, 390 rpm.

No polymerization was induced at all without either $Na_2S_2O_4$ or CCl_4 (Table I). This shows that these three components form one initiator system for the polymerization of MMA. When $NaHSO_3$ or Na_2SO_3 was used in place of $Na_2S_2O_4$, no polymerization occurred (Table II).

Little is known about the reactions of quinolinium salts with dithionites and unsuccessful attempts were made to characterize the products from the reaction of 1-substituted quinolinium salts with sodium dithionite.[2] However, the mechanism of reduction of pyridinium salts with dithionite has been elucidated to proceed *via* an intermediate sodium sulfinate, which is stable in alkaline solution and has been isolated.[3] Inoue *et al.*, reported the dehalogenation reaction by sodium 1-benzyl-1,4-dihydronicotinamide-4-sulfinate which was isolated in the course of the reduction of 1-benzylnicotiamide with $Na_2S_2O_4$ as an intermediate, and they also reported the usefulness of the sulfinate as a reducing agent.[4]
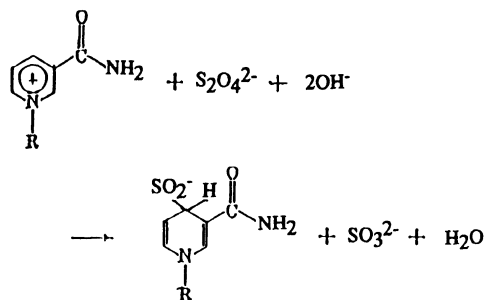
The polymerization of MMA was carried out in the aqueous-organic two-phase system with changing feed ratios of BQ^+Cl^-, $Na_2S_2O_4$, and CCl_4, and the conversions of MMA were plotted against time. Conversion-time relationships for varying BQ^+Cl^- concentrations are shown in Figure 1. The polymerizations proceeded fast at the beginning, but became gradually slow with reaction time. This suggests that the reaction of BQ^+Cl^- with $Na_2S_2O_4$ is more complicated than that of pyridinium salts with $Na_2S_2O_4$, and some other reaction products which do not take part in the

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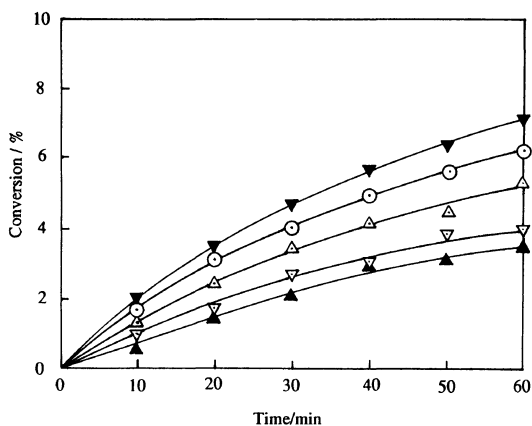**Figure 1.** Polymerization of MMA with BQ$^+$Cl$^-$–Na$_2$S$_2$O$_4$–CCl$_4$ in aqueous organic, two-phase system: MMA, 10 cm^3; H$_2$O, 40 cm^3; BQ$^+$Cl$^-$, 0.005 mmol (▲), 0.01 mmol (▽), 0.03 mmol (△), 0.05 mmol (⊙), 0.1 mmol (▼); Na$_2$S$_2$O$_4$, 1 mmol; CCl$_4$, 5 mmol; Na$_2$CO$_3$, 7.5 mmol; temp, 303 K; stirring rate, 390 rpm.
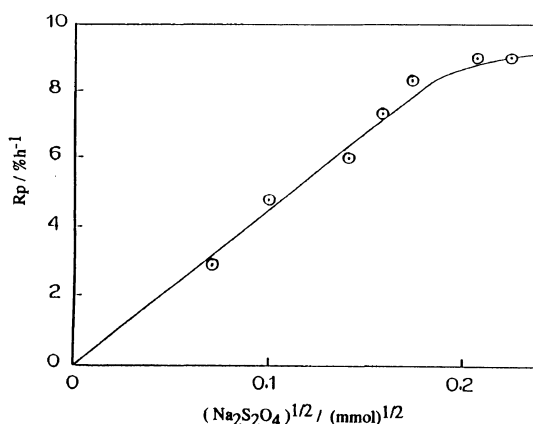
Figure 3. Relation of R_p *vs.* (N$_2$S$_2$O$_4$)$^{1/2}$ for polymerization of MMA with BQ$^+$Cl$^-$–Na$_2$S$_2$O$_4$–CCl$_4$ in aqueous organic, two-phase system: MMA, 10 cm^3; H$_2$O, 40 cm^3; BQ$^+$Cl$^-$, 0.05 mmol; CCl$_4$, 5 mmol; Na$_2$CO$_3$, 7.5 mmol; temp, 303 K; stirring speed, 390 rpm.
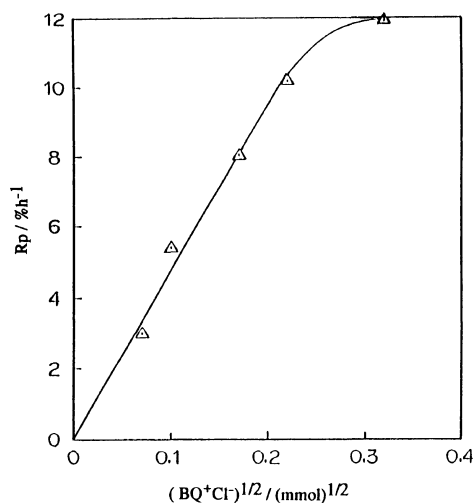

Figure 2. Relation of R_p *vs.* (BQ$^+$Cl$^-$)$^{1/2}$ for polymerization of MMA with BQ$^+$Cl$^-$–Na$_2$S$_2$O$_4$–CCl$_4$ in aqueous organic, two-phase system: MMA, 10 cm^3; H$_2$O, 40 cm^3; Na$_2$S$_2$O$_4$, 1 mmol; CCl$_4$, 5 mmol; Na$_2$CO$_3$, 7.5 mmol; temp, 303 K; stirring speed, 390 rpm.
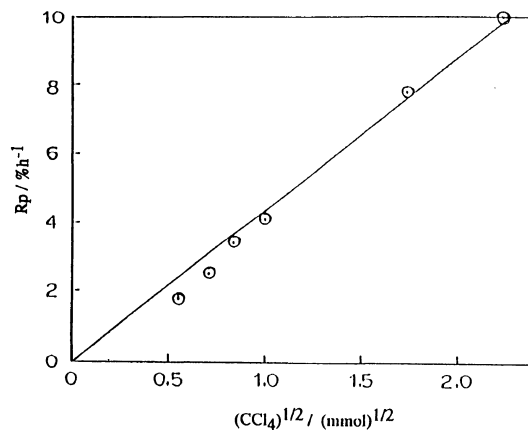
Figure 4. Relation of R_p *vs.* (CCl$_4$)$^{1/2}$ for polymerization of MMA with BQ$^+$Cl$^-$–Na$_2$S$_2$O$_4$–CCl$_4$ in aqueous organic, two-phase system: MMA, 10 cm^3; H$_2$O, 40 cm^3; BQ$^+$Cl$^-$, 0.05 mmol; Na$_2$S$_2$O$_4$, 1 mmol; Na$_2$CO$_3$, 7.5 mmol; temp, 303 K; stirring speed, 390 rpm.

polymerization are produced besides sodium *N*-benzyl-1,4-dihydro-qunoline-4-sulfinate (BQ-sulfinate) which is expected as the main product from analogy of the reaction of pyridinium salts with Na$_2$S$_2$O$_4$.

The initial rate of polymerization (R_p) was plotted against the square root of fed quantity of BQ$^+$Cl$^-$ and a linear relationship was observed as shown in Figure 2. The downward drift at a higher concentration of BQ$^+$Cl$^-$ can be explained by the following. White crystalline product, possibly BQ-sulfinate, precipitates from the reaction system at a high concentration before adding MMA, so that the concentration of BQ-sulfinate in the aqueous
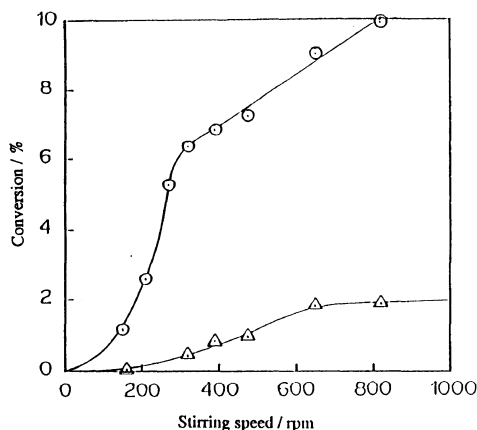
Figure 5. Relation of Conv. *vs.* stirring speed for polymerization of MMA with BQ^+Cl^-–$Na_2S_2O_4$–CCl_4 in aqueous organic, two-phase system: MMA, $10\,cm^3$; H_2O, $40\,cm^3$; BQ^+Cl^-, $0.05\,mmol$ ($\odot$), none ($\triangle$); $Na_2S_2O_4$, $1\,mmol$; CCl_4, $5\,mmol$; Na_2CO_3, $7.5\,mmol$; temp, $303\,K$; time, $1\,h$.

Figure 6. Scheme for the polymerization of MMA with BQ^+Cl^-–$Na_2S_2O_4$–CCl_4 in the aqueous-organic, two phase system.

phase does not increase over its solubility. BQ-Sulfinate, however, could not be isolated due to its unstability. The initial rates of polymerization were plotted against the square root of fed quantity of the other initator components, $Na_2S_2O_4$, and CCl_4. Linear relationships were also observed between them (Figures 3 and 4).

In the presence of an excess of $Na_2S_2O_4$, however, R_p gradually decreased and became constant. Figure 3 shows that R_p is proportional to the square root of the fed quantity of $Na_2S_2O_4$ when the concentration of $Na_2S_2O_4$ is less than equivalent of BQ^+Cl^-. These results suggest that the reaction between BQ^+Cl^- and $Na_2S_2O_4$ in aqueous phase is very fast.

The rate of polymerization in the aqueous-organic two phase was also affected by the rate of stirring as shown in Figure 5. Particularly around 200—300 rpm the conversion rapidly increased with stirring rate. This may be due to the remarkable increase in the intersurface area between the two phases with an increase in stirring speed, which facilitates the phase transfer of BQ-sulfinate. These results suggest the initiation mechanism shown in Figure 6.
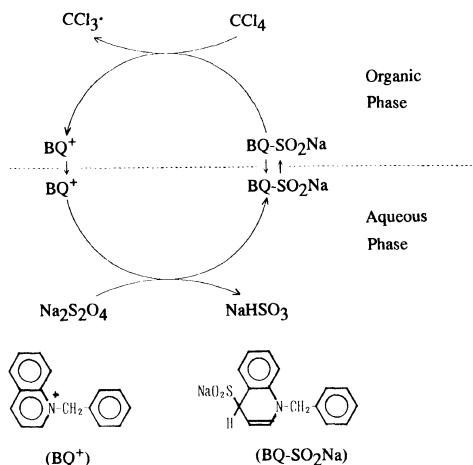
BQ^+Cl^- in the aqueous phase was reduced by $Na_2S_2O_4$ into sodium *N*-benzyl-1,4-dihydro-quinoline-4-sulfinate (BQ-sulfinate), which is transferred to the organic phase from the aqueous phase by vigorous stirring. BQ-sulfinate in the organic phase reacts with CCl_4 to yield BQ^+ and $CCl_3{}^{\bullet}$. The former is recycled to the aqueous phase and the latter initiates the polymerization of MMA.

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