

NOTES

Phase-Transfer Photopolymerization of Methyl Methacrylate with Tetrabutylammonium Chloride–KSCN–CCl₄ in an Aqueous–Organic Two-Phase System

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The previous paper¹ reported that methyl methacrylate (MMA) was photopolymerized with *N*-cetylpyridinium chloride (CPC)–KSCN–CCl₄ in an aqueous–organic two-phase system. The following photoinitiation mechanism was suggested for this photopolymerization. The charge transfer complex of *N*-cetylpyridinium thiocyanate (CPT) photodecomposes into thiocyno radical and *N*-cetylpyridinyl radical, and the latter reacts with CCl₄ to yield CPC and CCl₃· in the organic phase. The CPC transfers into the aqueous phase to regenerate CPT.

The thiocyno radical and CCl₃· initiate the polymerization of MMA. In this study, tetrabutylammonium chloride (TBACl), a commonly used phase transfer catalyst, was used in place of CPC which would act as a phase transfer catalyst as well as an electron acceptor in CPC–KSCN–CCl₄ initiator system. On the basis of kinetic studies, an initiation scheme was proposed for the photopolymerization of MMA with TBACl–KSCN–CCl₄ in an aqueous–organic two phase system.

EXPERIMENTAL

Materials

MMA was purified by the usual method and distilled in a nitrogen stream under reduced pressure just before use. Water was deionized. All other chemicals were of reagent grade and used without further purification.

Tetrabutylammonium Thiocyanate. Equimolar quantities of tetrabutylammonium chloride and potassium thiocyanate were mixed in acetone for 1 h at room temperature. After the precipitated potassium chloride was filtered off, the solution was evaporated under reduced pressure to dryness. Residual matter was recrystallized from benzene, mp 123–124°C (lit.² 123°C).

Polymerization

Photopolymerizations in aqueous–organic two-phase system were performed by using a photochemical reaction apparatus described in the previous paper.³ A 150 cm³ reaction vessel was charged with 20 cm³ of MMA containing CCl₄ and 80 cm³ of water containing prescribed amounts of TBACl and KSCN. The contents in the reaction vessel were bubbled with nitrogen at a con-

stant flow rate (1 cm³ s⁻¹) through a glass filter from the bottom of the vessel and irradiated with a 100 W high pressure mercury lamp (Fuji Glass HL-100) at 303 K. After irradiation, the reaction mixture was poured into excess methanol and the precipitated polymer was filtered, washed with methanol, and dried under reduced pressure. The rate of polymerization was determined by measuring the weight of the polymer obtained.

RESULTS AND DISCUSSION

The photopolymerizations of MMA with TBACl–KSCN–CCl₄ were carried out in aqueous–organic two-phase system, and the results are summarized in Table I. The polymerization of MMA proceeded in this system at 303 K, but only a very small amount of polymer was detected in any case when one of these three components was excluded. These results suggest that SCN⁻ paired with TBA⁺ in the aqueous-phase transferred to the organic phase containing CCl₄ and induced polymerization of MMA.

The photopolymerizations of MMA were thus carried out in an aqueous–organic two-phase system with changing feed ratios of TBACl, KSCN, and CCl₄, and percent conversions of MMA were plotted against time. Linear relations were obtained for the polymerizations

Table I. Phase-transfer photopolymerization of MMA with TBACl–KSCN–CCl₄ in the aqueous–organic two-phase systems^a

TBACl	KSCN	CCl ₄	Conversion
mmol	mmol	mmol	%
1.4	16.0	0.5	10.3
1.4	16.0	—	0.2
1.4	—	0.5	0.5
—	16.0	0.5	0.3
—	16.0	—	0.6
—	—	0.5	0.5
1.4	—	—	0.2
1.4	16.0	0.5	0.0 ^b

^a MMA, 20 cm³; H₂O, 80 cm³; temp, 303 K; time, 1 h. ^b Without UV-irradiation.

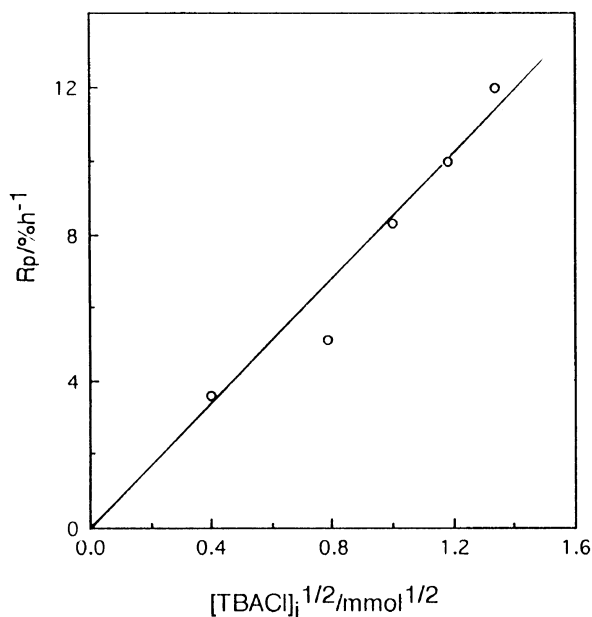


Figure 1. R_p vs. $[\text{TBACl}]_i^{1/2}$ for the photopolymerization of MMA with TBACl-KSCN- CCl_4 in the aqueous-organic two-phase system: MMA, 20 cm^3 ; H_2O , 80 cm^3 ; KSCN, 16 mmol; CCl_4 , 0.5 mmol; temp, 303 K; time, 1 h.

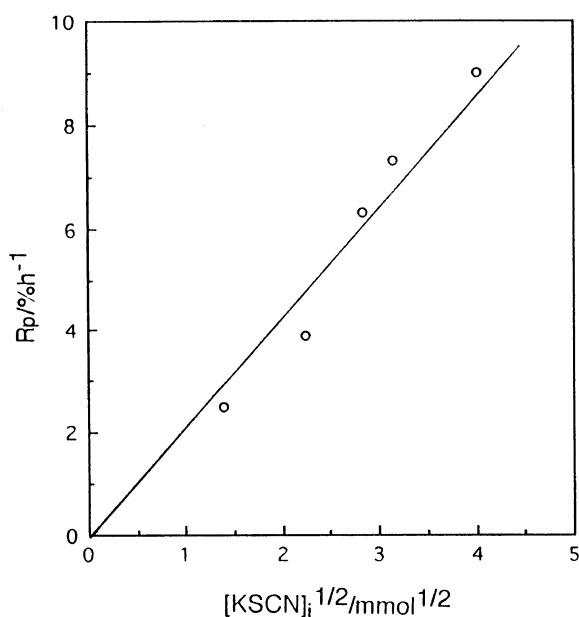


Figure 2. R_p vs. $[\text{KSCN}]_i^{1/2}$ for the photopolymerization of MMA with TBACl-KSCN- CCl_4 in the aqueous-organic two-phase system: MMA, 20 cm^3 ; H_2O , 80 cm^3 ; TBACl, 1.4 mmol; CCl_4 , 0.5 mmol; temp, 303 K; time, 1 h.

over the experimental range studied. At fixed concentrations of KSCN and CCl_4 , the initial rate of polymerization (R_p) was proportional to the square root of the initial quantity of TBACl, $[\text{TBACl}]_i$, as shown in Figure 1. R_p s were proportional to the square root of the initial quantities of KSCN and CCl_4 , respectively (Figures 2 and 3). These results show the similar dependency of polymerization rate on the concentrations of radical initiator and phase transfer catalyst as seen in the case of the polymerization of MMA with $\text{K}_2\text{S}_2\text{O}_8$ -[18-crown-6].⁴ From these observations, we postulate the following mechanism for the polymeriza-

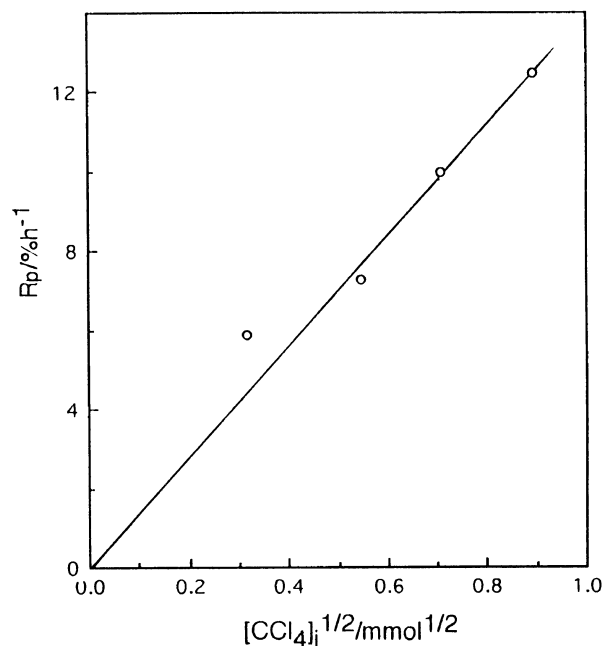


Figure 3. R_p vs. $[\text{CCl}_4]_i^{1/2}$ for the photopolymerization of MMA with TBACl-KSCN- CCl_4 in the aqueous-organic two-phase system: MMA, 20 cm^3 ; H_2O , 80 cm^3 ; TBACl, 1.4 mmol; KSCN, 16 mmol; temp, 303 K; time, 1 h.

tion of MMA with TBACl-KSCN- CCl_4 in the aqueous-organic two-phase system.

In aqueous phase TBA^+SCN^- is formed by eq 1 with equilibrium constant K_1 .



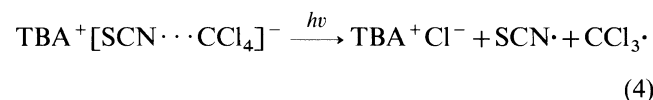
The partition coefficient of TBA^+SCN^- between two phases (k) is expressed by eq 2,

$$k = \frac{[\text{TBA}^+\text{SCN}^-]_o}{[\text{TBA}^+\text{SCN}^-]_w} \quad (2)$$

where the subscripts o and w refer to the organic and aqueous phases, respectively. TBA^+SCN^- transferred to the organic phase may form a complex with CCl_4 as eq 3 with equilibrium constant (K_2), which generates the radicals, $\text{SCN}\cdot$ and $\text{CCl}_3\cdot$, on UV irradiation as eq 4.

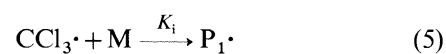


Complex



The radicals thus formed initiate the polymerization as shown in eq 5, 6, and 7.

Initiation:



Propagation:

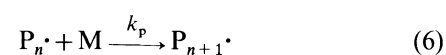


Table II. Phase-transfer photopolymerization of MMA with TBACl–KX–CCl₄ in the aqueous–organic two-phase systems^a

TBACl	KX	CCl ₄	Conversion
mmol		mmol	%
1.4	KSCN	0.5	10.3
1.4	KSCN	—	0.2
1.4	KCl	0.5	1.0
1.4	KCl	—	0.3
1.4	KBr	0.5	1.3
1.4	KBr	—	0.6
1.4	KI	0.5	1.1
1.4	KI	—	0.4

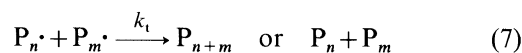
^a MMA, 20 cm³; H₂O, 80 cm³; KX, 16.0 mmol; temp, 303 K; time, 1 h.

Table III. Photopolymerization of MMA with TBA⁺SCN⁻–CCl₄ in nonaqueous solutions and aqueous solution^a

TBA ⁺ SCN ⁻	CCl ₄	Solvent	Conversion
mmol	mmol		%
4.0	0.5	CH ₂ Cl ₂	0.0
4.0	—	CH ₂ Cl ₂	0.0
4.0	0.5	MeOH	0.0
4.0	0.5	H ₂ O	6.7

^a MMA, 20 cm³; solvent, 80 cm³; temp, 303 K; time, 1 h.

Termination:



From eq 1 and 2, [TBA⁺SCN⁻]_w is expressed as eq 8 on the assumption that [TBA⁺]_w and [SCN⁻]_w are equal approximately to the initial quantities of TBACl and KSCN, [TBACl]_i and [KSCN]_i, respectively,

$$[\text{TBA}^+\text{SCN}^-]_w = K_1[\text{TBA}^+]_w[\text{SCN}^-]_w = fK_1[\text{TBACl}]_i[\text{KSCN}]_i \quad (8)$$

where f is the correlation coefficient between [TBA⁺]_w, [SCN⁻]_w and [TBACl]_i[KSCN]_i. Therefore, [TBA⁺SCN⁻]_o is expressed as eq 9.

$$[\text{TBA}^+\text{SCN}^-]_o = k[\text{TBA}^+\text{SCN}^-]_w = fK_1k[\text{TBACl}]_i[\text{KSCN}]_i \quad (9)$$

The concentration of the initiating complex in eq 3 is expressed as eq 10 from eq 3 and 9.

$$[\text{Complex}] = K_2[\text{TBA}^+\text{SCN}^-]_o[\text{CCl}_4]_i = fK_1K_2k[\text{TBACl}]_i[\text{KSCN}]_i[\text{CCl}_4]_i \quad (10)$$

In radical polymerization, the initial polymerization rate is proportional to the square root of the concentration of initiator.

$$R_p \propto [\text{Complex}]^{1/2} \quad (11)$$

Substituting eq 10 into eq 11, the photopolymerization rate as,

$$R_p \propto [\text{TBACl}]_i^{1/2}[\text{KSCN}]_i^{1/2}[\text{CCl}_4]_i^{1/2} \quad (12)$$

Equation 12 is in good agreement with the observed kinetic data, and suggests the radical initiation mechanism mentioned above for the photopolymerization of MMA with TBACl–KSCN–CCl₄.

Photopolymerizations of MMA were carried out with other potassium halides (KX) in place of KSCN in TBACl–KSCN–CCl₄. As shown in Table II only KSCN effectively initiates the photopolymerization.

Coetzee⁵ reported that thiocyanate ions which act like a pseudohalide had greater electron-donating ability than other halides, chloride or bromide. This also supports that thiocyanate ions form a complex with CCl₄.

Photopolymerizations of MMA were also performed in nonaqueous system with TBA⁺SCN⁻–CCl₄, and the results are summarized in Table III. TBA⁺SCN⁻ was prepared by mixing TBACl and KSCN in acetone and recrystallization from benzene described in the experimental section. In methanol and dichloroethane, no polymerization was induced with TBA⁺SCN⁻–CCl₄.

Jayakrishnan and Shah⁶ reported the phase-transfer-catalyzed free radical polymerization of MMA using ammonium peroxydisulfate {(NH₄)₂S₂O₈}/hexadecyl pyridinium chloride (HPC) in ethyl acetate–water two-phase system. Although Rasmussen and Smith⁷ reported, in the case of HPC and peroxydisulfate in ethyl acetate–water, the quaternary peroxydisulfate formed *in situ* was soluble in the organic medium, Jayakrishnan *et al.*, pointed out that this was not indeed the case because quaternary peroxydisulfate was not found soluble to any appreciable extent in ethyl acetate. They reported a seven-fold increase in conversion when water was present in the system compared to the case when no water was added, and that the low conversion observed without water derived from the presence of small quantities of water contaminated in MMA or ethyl acetate.⁶ In our polymerization system with TBA⁺SCN⁻–CCl₄, the presence of water may induce the dissociation of TBA⁺SCN⁻ into TBA⁺ and SCN⁻ which would be favorable to the formation of the initiating complex, [SCN⁻···CCl₄]⁻ TBA⁺. These findings also supports the above mechanism.

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