

Phase-Transfer Polymerization of Methyl Methacrylate with Tetrabutylammonium Chloride– $\text{Na}_2\text{S}_2\text{O}_4$ – CCl_4 in an Aqueous-Organic Two-Phase System

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ABSTRACT: The phase-transfer polymerization of methyl methacrylate with tetrabutylammonium chloride (TBACl)– $\text{Na}_2\text{S}_2\text{O}_4$ – CCl_4 initiator system was investigated in an aqueous-organic two-phase system. The initial rate of polymerization (R_p) was found to be proportional to the fed quantity of TBACl and square root of the fed quantity of $\text{Na}_2\text{S}_2\text{O}_4$ and CCl_4 . A cyclic phase-transfer initiation mechanism has been proposed to account for the experimental data.

KEY WORDS Phase-Transfer Polymerization / Methyl Methacrylate / Tetrabutylammonium Chloride / Sodium Dithionite / Carbon Tetrachloride /

Many studies have been made on the phase-transfer-catalyzed reaction because of its preparative usefulness. A wide variety of reactions such as anionic displacement, alkylation, arylation, oxidation, reduction, and hydrolysis could be effectively accelerated by phase transfer catalysts. As for the applications of polymerization reactions, they have been successfully employed in condensation polymerization¹ and anionic polymerization.² Recently several authors reported the use of phase transfer catalysts for free-radical polymerizations of hydrophobic vinyl monomers in aqueous-organic two-phase.³ In most cases, peroxydisulfate was used as a water-soluble initiator with a phase-transfer catalyst such as crown ethers or quaternary ammonium salts. During the course of our investigation on aqueous-organic two-phase polymerization⁴ we found that the addition of tetrabutylammonium chloride (TBACl) as a phase-trans-

fer catalyst to $\text{Na}_2\text{S}_2\text{O}_4$ – CCl_4 initiator system induced radical polymerization of methyl methacrylate (MMA) under mild condition. On the basis of kinetic studies an initiation mechanism is suggested for the polymerization of MMA with TBACl– $\text{Na}_2\text{S}_2\text{O}_4$ – CCl_4 in aqueous-organic two-phase system.

EXPERIMENTAL

Materials

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

Polymerization

Polymerization was carried out with stirring in a four-necked flask under nitrogen atmo-

sphere at 303 K. In a 300 cm³, four-necked round-bottomed flask equipped with a mechanical stirrer, an inlet-tube of N₂, a Dimroth condenser with an outlet-tube of N₂, and a dropping funnel were placed 15 mmol of Na₂S₂O₄ and 1 mmol of TBACl and then 80 cm³ of water and 20 cm³ of MMA containing 1 mmol of CCl₄ were added in this order through the dropping funnel under a stream of N₂. The mixture was stirred at a constant rate for an hour 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 the TBACl–Na₂S₂O₄–CCl₄ initiator was carried out in an aqueous-organic two-phase system. The polymerization of MMA proceeded fast even at 303 K, but the polymer was not detected in every case when one of these three components was excluded (Table I). These results suggest that S₂O₄²⁻ paired with TBA⁺ in the aqueous-phase and transferred to the organic phase to induce the polymerization of MMA.

The polymerization of MMA was thus carried out in the aqueous-organic two-phase system with changing feed ratios of TBACl, Na₂S₂O₄, and CCl₄ and the conversions of MMA were plotted against time. A linear

Table I. Polymerization of MMA using TBACl, Na₂S₂O₄, and CCl₄ in the aqueous-organic two-phase system^a

TBACl	Na ₂ S ₂ O ₄	CCl ₄	Conversion
mmol	mmol	mmol	%
—	15	1	1.1
0.1	—	1	0
0.1	15	—	0
0.1	15	1	23.7

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

relation was obtained for the polymerization at higher concentrations of Na₂S₂O₄. At fixed concentrations of Na₂S₂O₄ and CCl₄, the initial rate of polymerization (R_p) was proportional to the fed quantity of TBACl as shown in Figure 1. R_p was also proportional to the square root of the fed quantity of Na₂S₂O₄ and CCl₄, (Figures 2 and 3). From

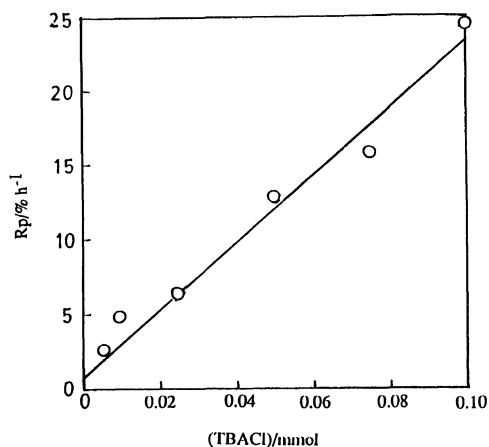


Figure 1. R_p vs. (TBACl) for the polymerization of MMA using TBACl, Na₂S₂O₄, and CCl₄ in the aqueous-organic two-phase system: MMA, 20 cm³; H₂O, 80 cm³; Na₂S₂O₄, 15 mmol; CCl₄ 1 mmol; temp, 303 K; time 1 h.

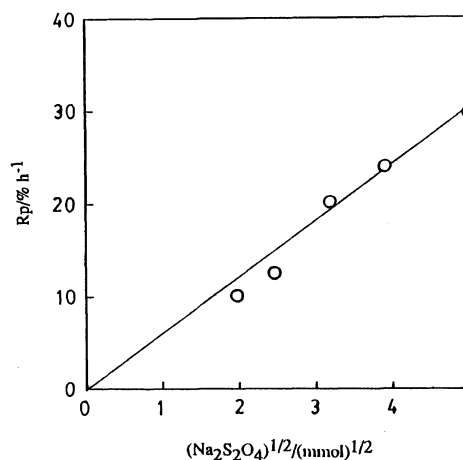


Figure 2. R_p vs. (Na₂S₂O₄)^{1/2} for the polymerization of MMA by the use of TBACl, Na₂S₂O₄, and CCl₄ in the aqueous-organic two-phase system: MMA, 20 cm³; H₂O, 80 cm³; TBACl, 0.1 mmol; CCl₄, 1 mmol; temp, 303 K; time, 1 h.

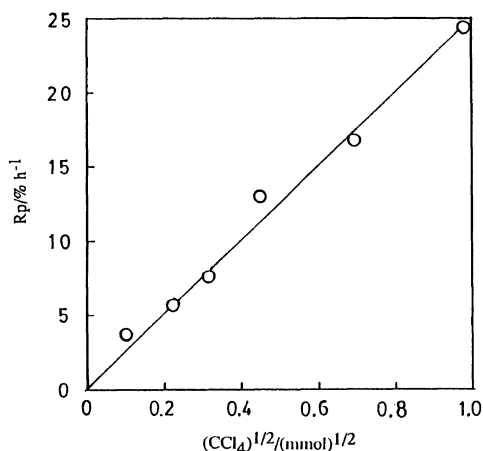
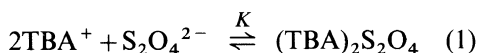


Figure 3. R_p vs. $(\text{CCl}_4)^{1/2}$ for the polymerization of MMA by the use of TBACl, $\text{Na}_2\text{S}_2\text{O}_4$, and CCl_4 in the aqueous-organic two-phase system: MMA, 20 cm^3 ; H_2O , 80 cm^3 ; TBACl, 0.1 mmol ; $\text{Na}_2\text{S}_2\text{O}_4$, 15 mmol ; temp, 303 K ; time, 1 h .

these observations, we postulate the following mechanism for the polymerization of MMA with TBACl– $\text{Na}_2\text{S}_2\text{O}_4$ – CCl_4 in MMA–water two-phase system. In the aqueous phase $(\text{TBA})_2\text{S}_2\text{O}_4$ is formed as in eq 1 with an equilibrium constant K .

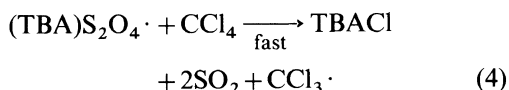
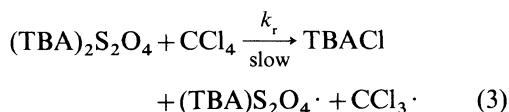


The partition coefficient (k) of $(\text{TBA})_2\text{S}_2\text{O}_4$ between the two phases is expressed by eq 2,

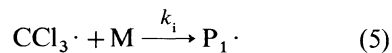
$$k = \frac{[(\text{TBA})_2\text{S}_2\text{O}_4]_o}{[(\text{TBA})_2\text{S}_2\text{O}_4]_w} \quad (2)$$

where the subscripts o and w refer to the organic and aqueous phases, respectively.

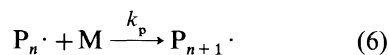
In the organic phase $(\text{TBA})_2\text{S}_2\text{O}_4$ would react with CCl_4 according to eq 3 and 4, where the former would be rate-determining. $\text{CCl}_3\cdot$ radicals thus formed initiate the polymerization as shown in eq 5, 6, 7.



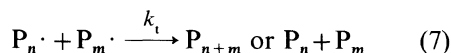
Initiation:



Propagation:



Termination:



From eq 1 and 2, $[(\text{TBA})_2\text{S}_2\text{O}_4]_o$ is expressed by eq 8 on the assumption that $[\text{TBA}^+]_w$ and $[\text{S}_2\text{O}_4^{2-}]_w$ are equal approximately to the initial fed quantities of TBACl and $\text{Na}_2\text{S}_2\text{O}_4$, respectively.

$$[(\text{TBA})_2\text{S}_2\text{O}_4]_o = kK[\text{TBA}^+]_w^2[\text{S}_2\text{O}_4^{2-}]_w = kK[\text{TBACl}]^2[\text{Na}_2\text{S}_2\text{O}_4] \quad (8)$$

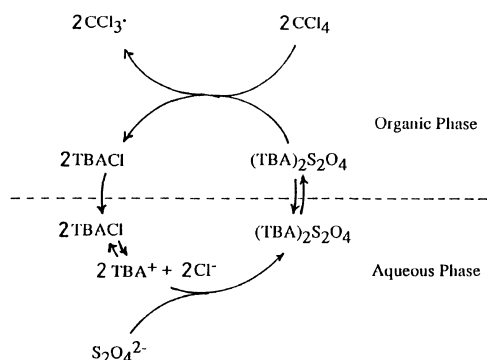
The rate of $\text{CCl}_3\cdot$ formation is expressed as eq 9 from eq 3, 4, and 8.

$$\begin{aligned} d(\text{CCl}_3\cdot)/dt &= 2k_r[(\text{TBA})_2\text{S}_2\text{O}_4]_o[\text{CCl}_4]_o \\ &= 2k_r kK[\text{TBACl}]^2[\text{Na}_2\text{S}_2\text{O}_4][\text{CCl}_4]_o \end{aligned}$$

Applying the steady-state approximation to the species $\text{CCl}_3\cdot$ and $\text{P}_n\cdot$ or $\text{P}_m\cdot$, the rate of polymerization is expressed as eq 10.

$$R_p = (2fk_r kKk_p^2/k_t)^{1/2} [\text{TBACl}] [\text{Na}_2\text{S}_2\text{O}_4]^{1/2} [\text{CCl}_4]_o^{1/2} [\text{MMA}]_o \quad (10)$$

Where f is the initiator efficiency and k_p and k_t are the rate constants of the propagation and termination of the polymer radicals, respectively. Equation 10 is in good agreement with the observed kinetic data. These results allow us to propose a radical initiation mechanism as shown in Scheme 1. At the interface between the aqueous and organic phases an ion pair, butylammonium dithionite $(\text{TBA})_2^{2+} \text{S}_2\text{O}_4^{2-}$, is formed and a small amount of $(\text{TBA})_2\text{S}_2\text{O}_4$ transfers to the organic phase. In the organic phase, $(\text{TBA})_2\text{S}_2\text{O}_4$ reduces CCl_4 to $\text{CCl}_3\cdot$ and TBACl. The former initiates the polymerization of MMA and the latter is transferred to the aqueous phase.



Scheme 1. Polymerization of MMA with TBACl- $\text{Na}_2\text{S}_2\text{O}_4$ - CCl_4 in the aqueous-organic two-phase system.

Quantitative analysis of sulfur in the organic phase was made by a total sulfur autoanalyzer, when MMA was polymerized with or without TBACl under the experimental conditions shown in Table I. A small difference in sulfur content of the organic phase was ascertained in the two cases whether TBACl was added to the system or not. The content of $\text{S}_2\text{O}_4^{2-}$ in the organic phase was calculated as about 2% of the added $\text{S}_2\text{O}_4^{2-}$. Beside these experimental results, Table 1 shows that MMA does not polymerize without TBACl. These results support our suggestion in Scheme 1, where TBACl acts as a cyclic phase transfer catalyst. As another reductant, NaHSO_3 or Na_2SO_3 was used instead of $\text{Na}_2\text{S}_2\text{O}_4$, but no polymerization occurred as expected from their redox potentials (Table II).⁵⁾ It seems that the important characteristic of the initiation mechanism is in the reduction of CCl_4 with dithionite transferred to the organic phase.

Polymerization was carried out with some other halides with CCl_3 -group (Table III). C_2Cl_6 was as effective as CCl_4 , but *p*- and *m*-hexachloroxylylene were less effective, possibly due to the small electron acceptability of CCl_3 -group on the aromatic ring.

The effects of organic solvents on the rate of polymerization were also studied by addition of organic solvents such as benzene, ethyl acetate, chloroform, and 1,2-dichloroethane to the two-phase polymerization system (Table

Table II. Polymerization of MMA using TBACl, reductant and CCl_4 in the aqueous-organic two-phase system^a

Reductant	Conversion
	%
$\text{Na}_2\text{S}_2\text{O}_4$	23.7
Na_2SO_3	0
NaHSO_3	0

^a MMA, 20 cm³; H₂O, 80 cm³; TBACl, 0.1 mmol; reductant, 15 mmol; CCl_4 , 1 mmol; temp, 303K; time, 1 h.

Table III. Polymerization of MMA using TBACl, $\text{Na}_2\text{S}_2\text{O}_4$, and organic halide in the aqueous-organic two-phase system^a

Organic halide	Conversion
	%
CCl_4	23.7
C_2Cl_6	23.1
<i>p</i> -Ph(CCl_3) ₂	9.6
<i>m</i> -Ph(CCl_3) ₂	9.7

^a MMA, 20 cm³; H₂O, 80 cm³; TBACl, 0.1 mmol; $\text{Na}_2\text{S}_2\text{O}_4$, 15 mmol; organic halide, 1 mmol; temp, 303 K; time, 1 h.

Table IV. Effects of organic solvent on the polymerization of MMA using TBACl, $\text{Na}_2\text{S}_2\text{O}_4$, and CCl_4 , and CCl_4 in the aqueous-organic two-phase system^a

Organic solvent (Dielectric constant)	Conversion
	%
Benzene (2.27)	6.2
Ethyl Acetate (6.03)	11.9
Chloroform (4.70)	11.4
1,2-Dichloroethane (10.37)	23.2

^a MMA, 20 cm³; organic solvent, 10 cm³; H₂O, 80 cm³; TBACl, 0.1 mmol; $\text{Na}_2\text{S}_2\text{O}_4$, 15 mmol; CCl_4 , 1 mmol; temp, 303K; time, 1 h.

IV). The rate of polymerization increased with increasing polarity (dielectric constant, *D*) of the solvents.

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