Phase-Transfer-Catalyzed Free-Radical Polymerization: Kinetics of Polymerization of Methyl Methacrylate Using Ammonium Peroxydisulfate/Hexadecyl Pyridinium Chloride in Ethyl Acetate/Water

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Synopsis

The kinetics of phase-transfer-catalyzed free-radical polymerization of methyl methacrylate using the system ammonium peroxydisulfate/hexadecyl pyridinium chloride have been investigated in the temperature range of 50–60°C in ethyl acetate/water two-phase systems. The superior efficiency of the phase-transfer-catalyzed reaction in comparison with polymerization initiated by oil soluble initiators such as 2,2′-azobisisobutyronitrile and benzoylperoxide has been demonstrated. Rate of polymerization increased with increase in concentration of the quaternary salt but showed a tendency to level off at higher concentrations. Increase in the peroxydisulfate concentration also resulted in an increase in the rate at lower concentrations, but was found to decrease at higher concentrations. The order with respect to the monomer was found to be approximately unity. The title reaction has been found to be not truly phase-transfer catalyzed in character as claimed by previous workers. A suitable kinetic scheme has been proposed to account for the experimental data and its significance discussed.

INTRODUCTION

Phase-transfer-catalyzed reactions have received considerable attention in recent years.[1] A wide variety of reactions such as anion displacement reactions, alkylation, arylation, oxidation, reduction, elimination, hydrolysis, etc., could be successfully accelerated using phase-transfer catalysts. Macrocylic ethers and quaternary salts find extensive application as phase-transfer catalysts. Although phase-transfer catalysts have been successfully employed for anionic polymerization, their use for free-radical polymerization is recent. Rasmussen and Smith[2,3] recently reported that the peroxydisulfate anion could be transferred into the organic phase using crown ethers and quaternary salts as phase-transfer agents. In the case of $K_2S_2O_8$/hexadecyl pyridinium chloride and $K_2S_2O_8$/methyl trioctylammonium chloride, they postulated that the formation of the quaternary peroxydisulfate which is soluble in the organic medium (ethyl acetate/butyl acrylate) was responsible for the rapid polymerization of butyl acrylate by decomposition to sulfate anion radicals. The kinetics and mechanism of these reactions have not been understood. In view of the fact that the quaternary salt–alkali peroxydisulfate can function as an effective initiator for vinyl polymerization, it was felt worthwhile to investigate the kinetics of polymerization of methyl methacrylate using ammonium peroxydisulfate/hexadecyl pyridinium chloride in ethyl acetate/water two-phase systems.

EXPERIMENTAL

Fisher certified grade methyl methacrylate (MMA) containing 25 ± 5 ppm hydroquinone inhibitor was used without further purification. 2,2′-Azobisisobutyronitrile (AIBN, Eastman Kodak), benzoyl peroxide (Bz_2O_2 Fisher), ammonium peroxydisulfate (Fisher, AnalaR), and hexadecyl pyridinium chloride 1 H_2O (HPC, K & K Laboratories, Inc.) were used as received. Reagent grade ethyl acetate was used after distillation. Distilled water was employed throughout. Stock solutions of HPC and $(NH_4)_2S_2O_8$ were prepared in distilled water. Stock solutions of Bz_2O_2 and AIBN were prepared in ethyl acetate. Unless otherwise specified, all the reaction mixtures contained 9 mL of the organic phase and 2 mL of the aqueous phase. Polymerization reactions were carried out in thick-walled Pyrex glass tubes fitted with screw caps. The polymerization reactions were conducted by the batch-type method. After pipetting out the reaction mixture into each tube, it was sparged with oxygen-free nitrogen for 5 min, screw capped, shaken vigorously, and left in the thermostat at the desired temperature. On mixing aqueous solutions of HPC and $(NH_4)_2S_2O_8$ in ethyl acetate/water containing methyl methacrylate, the quaternary persulfate was found to be precipitated, but it went into solution on shaking or when heated above 50°C. The system remained clear during polymerization. The percent conversions at various times were obtained by quenching the reaction at various times by the addition of a large volume of methanol containing 1% hydroquinone. The precipitated polymer was filtered through a sintered medium porosity glass crucible (ASTM 10–15), washed several times with water and methanol, and dried *in vacuo* at 60°C to constant weight. Percent conversions were computed from the weight of the polymer obtained. For determining the rate of polymerization with changes in the concentration of various reactants, the polymerization was carried out for 60 min. At the end of 60 min (conversions <15–20%), the reactions were quenched as before and the rates were calculated from the weight of the polymer obtained. Thus the rates reported are not initial rates but time average rates for 60 min reaction where the conversions were always less than 20%. Viscosity measurements were made using a Cannon Fenske viscometer at 30°C in benzene solution. The following equation was employed to obtain the average degree of polymerization from viscosity data:

$$\log \overline{P}n = 1.316 \log [\eta] + 3.636$$

where $[\eta]$ refers to the intrinsic viscosity.[4]

RESULTS AND DISCUSSION

In the absence of added quaternary salt, ammonium peroxydisulfate alone did not induce polymerization of MMA in ethyl acetate (Fig. 1). In the presence of 0.0128 mol dm^{-3} HPC, the conversion reached 90% in 10 h (Fig. 1). The time versus percent conversion plots for the polymerization of MMA using initiators such as AIBN and Bz_2O_2 are also shown in Figure 1 for comparison. Thus, it can be seen that the alkali peroxydisulfate coupled with HPC in a two-phase system functions as a better initiator for polymerization of MMA under identical conditions. Changing the cation from NH_4^+ to K^+ did not alter the rate of polymerization as illustrated in Figure 1. This observation is typical of almost
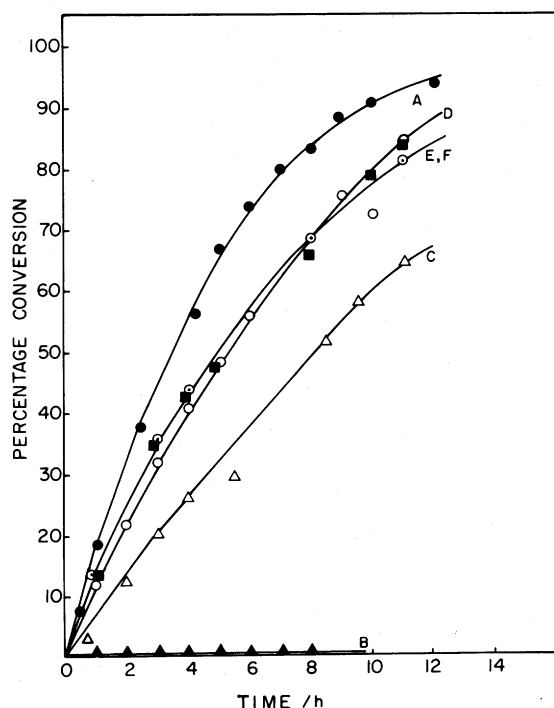
Fig. 1. Percent conversion versus time plots for polymerization of MMA using various initiators at 60°C. Line A: [MMA] = 3.74, [(NH$_4$)$_2$S$_2$O$_8$] = 0.025 and [HPC] = 0.0128 mol dm^{-3}. Volume of organic phase-9 mL, volume of aqueous phase-1 mL. Line B: [MMA] = 3.74 and [(NH$_4$)$_2$S$_2$O$_8$] = 0.025 mol dm^{-3}, no HPC. Volume of organic phase-9 mL, volume of aqueous phase-1 mL. Line C: [MMA] = 3.74 and [Bz$_2$O$_2$] = 0.025 mol dm^{-3}. Volume of reaction mixture = 10 mL, no aqueous phase. Line D: [MMA] = 3.74 and [AIBN] = 0.025 mol dm^{-3}. Volume of reaction mixture = 10 mL, no aqueous phase. Line E: [MMA] = 3.40, [(NH$_4$)$_2$S$_2$O$_8$] = 0.0151, and [HPC] = 0.0047 mol dm^{-3}. Volume of organic phase-9 mL, volume of aqueous phase-2 mL. Line F: [MMA] = 3.40, [K$_2$S$_2$O$_8$] = 0.0151, and [HPC] = 0.0047 mol dm^{-3}. Volume of organic phase-9 mL, volume of aqueous phase-2 mL.

all phase-transfer-catalyzed reactions since the ease of transfer of anion depends only on the organic nature of the catalyst cation.

Polymerization rates for MMA increased with an increase in concentration of the quaternary salt but showed a tendency to level off at high concentrations (Fig. 2). It was pointed out by a referee that whether this trend observed could probably be owing to the presence of the small amount of inhibitor present in the monomer, but later we found that purified monomer also showed the same trend. With an increase in concentrations of (NH$_4$)$_2$S$_2$O$_8$, these rates increased, reached a maximum, and then fell off at large concentrations, a phenomenon which was not observed with homogeneous polymerization initiated with oil soluble initiators (Fig. 3). With respect to the monomer, the order of the reaction was almost unity (Fig. 4). Based on these observations, the following mechanism could be written for the phase-transfer-catalyzed polymerization of MMA initiated by (NH$_4$)$_2$S$_2$O$_8$/HPC in ethyl acetate/water two-phase systems:
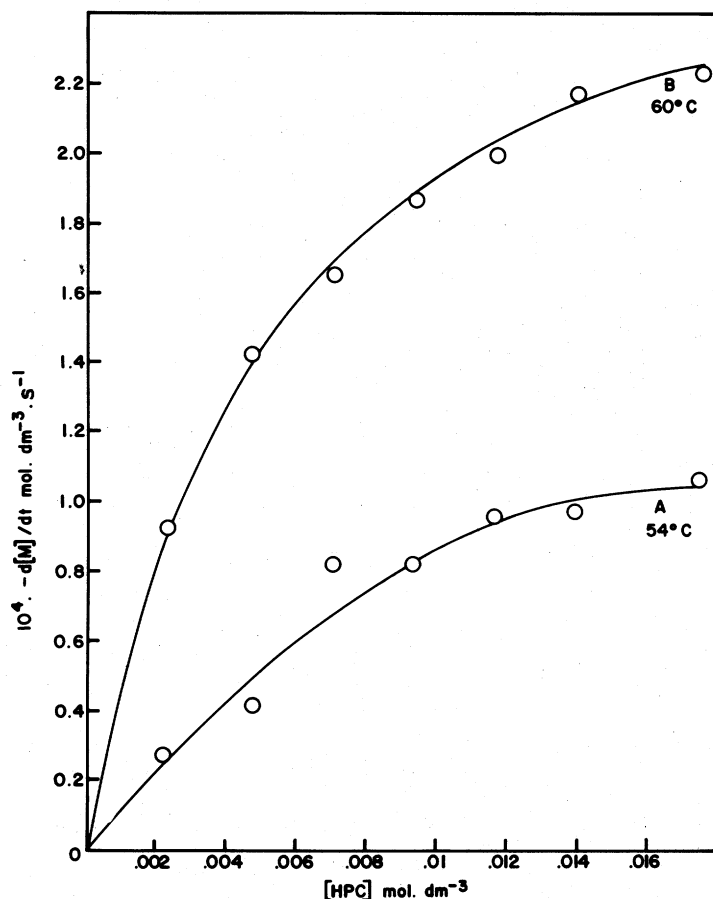
$$2Q^+ + S_2O_8^{2-} \overset{K}{\rightleftharpoons} (Q^+)_2S_2O_8^{2-} \tag{1}$$
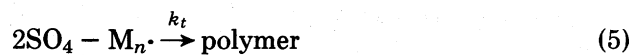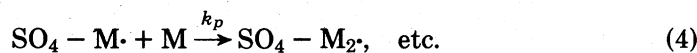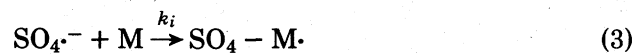
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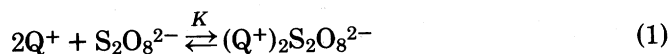
Fig. 2. Plot of polymerization rate versus [HPC] at 54 and 60°C. [MMA] = 3.40 and [(NH$_4$)$_2$S$_2$O$_8$] = 0.0227 mol dm^{-3}.

where Q$^+$ represents the hexadecyl pyridinium cation.

$$(Q^+)_2S_2O_8{}^{2-} \xrightarrow{k_d} 2SO_4\cdot{}^- + 2Q^+ \tag{2}$$

$$SO_4\cdot{}^- + M \xrightarrow{k_i} SO_4 - M\cdot \tag{3}$$

$$SO_4 - M\cdot + M \xrightarrow{k_p} SO_4 - M_2\cdot, \quad \text{etc.} \tag{4}$$

$$2SO_4 - M_n\cdot \xrightarrow{k_t} \text{polymer} \tag{5}$$
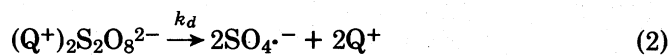
Applying the steady-state approximations to the species SO$_4\cdot{}^-$ and SO$_4$ − M$_n\cdot$, one can derive the following expression for the rate of polymerization:

$$-\frac{d[M]}{dt} = \frac{k_p(2k_dK)^{1/2}}{k_t^{1/2}} \frac{[Q^+]_{\text{tot}}[S_2O_8{}^{2-}]^{1/2}[M]}{1 + 2K[Q^+]_{\text{eq}}[S_2O_8{}^{2-}]} \tag{6}$$
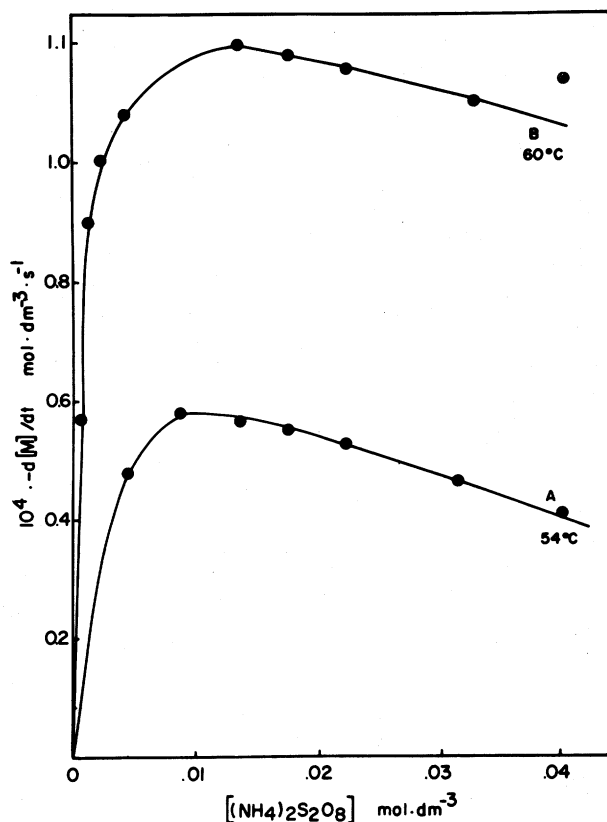
Fig. 3. Plot of polymerization rate versus $[(NH_4)_2S_2O_8]$ at 54 and 60°C. [MMA] = 3.40 and [HPC] = 0.0023 mol dm^{-3}.

where $[Q^+]_{eq}$ represents the equilibrium concentration of the quaternary salt.

Equation (6) explains the most of the observed kinetic data. If $1 \gg 2K[Q^+]_{eq}[S_2O_8{}^{2-}]$, we have

$$-\frac{d[M]}{dt} = k_p \left(\frac{2k_dK}{k_t}\right)^{1/2} [Q^+]_{tot}[S_2O_8{}^{2-}]^{1/2}[M] \qquad (7)$$

Thus, at very low concentrations of HPC and $(NH_4)_2S_2O_8$, the rate of polymerization may obey the above rate law. On the other hand, if $2K[Q^+]_{eq}[S_2O_8{}^{2-}] \gg 1$, we have

$$-\frac{d[M]}{dt} \propto \frac{[Q^+]_{tot}[M]}{[Q^+]_{eq}[S_2O_8{}^{2-}]^{1/2}} \qquad (8)$$

Thus, it appears that neither term in the denominator of eq. (6) could be neglected in comparison with the other to satisfactorily explain the observed kinetics.

It has been reported[5] that the distribution ratio α of anions such as $SO_4{}^{2-}$ and $S_2O_3{}^{2-}$ between water and chloroform is of the order of 1×10^{-3}. Although Rasmussen and Smith[3] reported that, in the case of HPC and potassium peroxydisulfate in ethyl acetate/water, the quaternary peroxydisulfate formed *in*
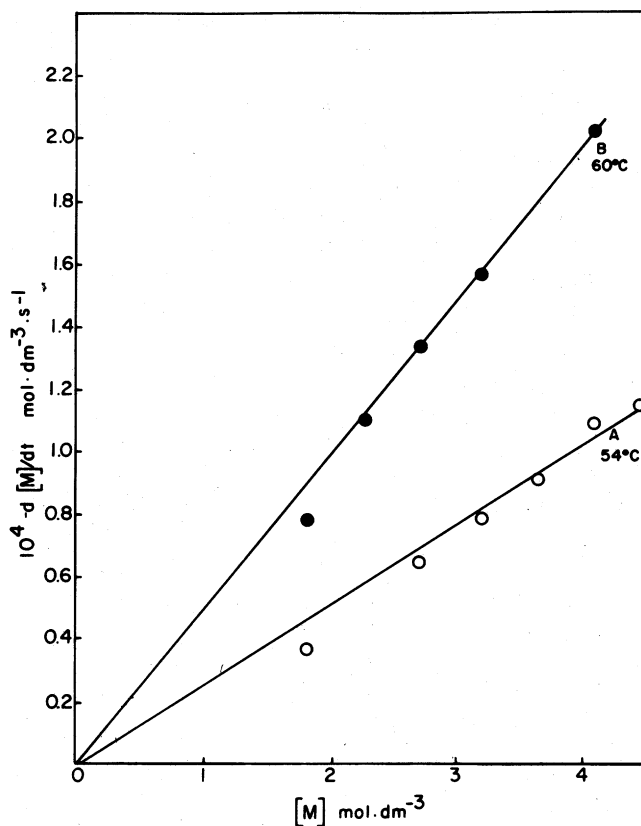
Fig. 4. Plot of polymerization rate versus [MMA]. $[(NH_4)_2S_2O_8] = 0.0455$ and [HPC] = 0.0116 mol dm^{-3}.

situ was soluble in the organic medium, our observations point out that this was not indeed the case. This was demonstrated as follows: the hexadecyl pyridinium peroxydisulfate could be isolated in the solid form by simply mixing an aqueous solution of HPC with a saturated solution of ammonium peroxydisulfate. The solid insoluble quaternary peroxydisulfate formed was filtered, washed several times with water, and dried *in vacuo*. The quaternary peroxydisulfate was not found to be soluble to any appreciable extent in ethyl acetate, MMA, or in a mixture of the two. Qualitative determinations of the extent of solubility showed that the solubility was less than 0.25 mg/mL. Using this solid quaternary peroxydisulfate, the reaction was performed in the presence and absence of water. There was a sevenfold increase in conversion when water was present in the system as compared to when no water was employed (Table I). The question as to whether the small percentage of conversion observed when no water was incorporated in the system was entirely due to the decomposition of the peroxydisulfate solubilized on a microscale in the organic phase or owing to the trace amount of water present in the reactants used were intriguing and were checked further. MMA and ethyl acetate were purified, distilled, and dried, and introduced into an ampule, the quaternary persulfate was added, and the contents degassed and sealed. The reaction was allowed to proceed for 4 h at 60°C. It

TABLE I
Comparison of the Rates of Polymerization of MMA in Ethyl Acetate Using Hexadecyl Pyridinium Peroxydisulfate in the Presence and Absence of Water at 60°C

Reaction mixture		Percentage conversion in 4 h
Ethyl acetate	5 mL	
MMA	4 mL	9.6
Hexadecyl pyridinium peroxydisulfate	0.05 g	
Ethyl acetate	5 mL	
MMA	4 mL	
Hexadecyl pyridinium peroxydisulfate	0.05 g	64.9
Water	2 mL	

was found that even with 0.1% (wt/vol) of the quaternary persulfate, no polymerization took place. This suggests that the small percent conversion observed could be owing to the presence of trace amounts of moisture present initially in the reactants.

Thus it appears that the high charge on the $S_2O_8^{2-}$ ion is unfavorable for its partition into the organic phase at least when hexadecyl pyridinium ion was the cation. It must therefore be construed that most of the catalyst is present in environments where the hydrophilic ($S_2O_8^{2-}$) and oleophilic (Q^+) parts of the molecule could be properly solvated. Thus the catalyst would tend to concentrate at the liquid/liquid interface as well as in the oil solubilized in the water phase and water solubilized in the oil phase. A possible involvement of normal or reverse micelles could not be ruled out, and the results shown in Figure 3 could be owing to their removal at high $S_2O_8^{2-}$ concentrations since hexadecyl pyridinium peroxydisulfate was soluble only on a microscale in both the organic and aqueous media.

Whether the sulfate radical ion or a secondary radical produced by the oxidation of the monomer is the chain-carrying species is not evident, since the possibility of oxidation of the monomer could not be excluded in view of the fact that the peroxydisulfate anion is one of the strongest oxidizing agents known in aqueous solution and has been known to oxidize a variety of organic and inorganic compounds.[6] However, the quaternary peroxydisulfate was not found to oxidize the solvent ethyl acetate. The UV spectra of ethyl acetate in water and that treated with the quarternary peroxydisulfate at 60°C for 1 h were found

TABLE II
Viscosity Average Degree of Polymerization of PMMA Obtained Using Various Initiators at 60°C

System	$\overline{P}n$
HPC/$(NH_4)_2S_2O_8$[a]	1459
Bz_2O_2[b]	2564
AIBN[c]	1594

[a] Recipe corresponds to curve A of Figure 1.
[b] Recipe corresponds to curve C of Figure 1.
[c] Recipe corresponds to curve D of Figure 1.

to be identical. However, it could be shown that such distinctions as to whether the primary $SO_4 \cdot^-$ or secondary $(R \cdot)$ radical produced by a reaction such as

$$SO_4 \cdot^- + M \rightarrow R \cdot + SO_4^{2-}$$
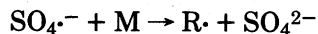
is the chain-carrying species makes little difference in the overall kinetics of the process. The molecular weight of the polymer obtained by using various initiators was found to be in the same range as demonstrated by viscosity measurements (Table II).

In conclusion, it may be said that the quaternary salts coupled with alkali peroxydisulfates are better initiators for vinyl polymerization in two-phase systems than conventional initiators such as AIBN or Bz_2O_2. But, whether the peroxydisulfate anion is actually phase transferred or not is disputable, at least, it does not appear to be transferred as demonstrated by our experimental observations when hexadecyl pyridinium chloride was coupled with ammonium peroxydisulfate in ethyl acetate/water two-phase systems.

References

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