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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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Phase-Transfer Catalysis: Free-Radical Polymerization of Methyl Methacrylate using $K_2S_2O_8$ -Quaternary Ammonium Salt Catalyst System. A Kinetic Study

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To cite this Article Balakrishnan, T. and Jayachandramani, N.(1994) 'Phase-Transfer Catalysis: Free-Radical Polymerization of Methyl Methacrylate using $K_2S_2O_8$ -Quaternary Ammonium Salt Catalyst System. A Kinetic Study', Journal of Macromolecular Science, Part A, 31: 7, 847 – 857

To link to this Article: DOI: 10.1080/10601329409349762

URL: <http://dx.doi.org/10.1080/10601329409349762>

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PHASE-TRANSFER CATALYSIS: FREE-RADICAL POLYMERIZATION OF METHYL METHACRYLATE USING $K_2S_2O_8$ -QUATERNARY AMMONIUM SALT CATALYST SYSTEM. A KINETIC STUDY

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ABSTRACT

The kinetics of phase-transfer-agent-assisted free-radical polymerization of methyl methacrylate using $K_2S_2O_8$ as the water-soluble initiator and triethylbenzylammonium chloride (TEBA) as the phase-transfer catalyst (PTC) was investigated in toluene–water biphasic media at 60°C. The effect of varying $[MMA]$, $[K_2S_2O_8]$, $[TEBA]$, $[H^+]$, the ionic strength of the medium, and the temperature on the rate of polymerization (R_p) was studied. R_p was found to be proportional to $[MMA]^2$, $[K_2S_2O_8]^1$, and $[TEBA]^{0.5}$. Based on the kinetic results, a mechanism involving initiation of polymerization by phase-transferred $S_2O_8^{2-}$ and termination by Q^+ (quaternary ammonium ion) is proposed.

INTRODUCTION

The free-radical polymerization of water-soluble monomers with peroxydisulfate as the initiator has been studied extensively in aqueous media [1]. But similar studies with water-insoluble monomers could not be carried out in organic solvents since $K_2S_2O_8$ is insoluble in organic solvents and thus its utility is severely restricted for solution or bulk polymerization. Rasmussen and Smith reported for the first time that water-soluble initiators could be effectively used for bulk or solution polymerization if they were used in conjunction with certain phase-transfer agents like quaternary ammonium salts (QX) or crown ethers [2, 3]. In the presence of a phase-transfer catalyst (PTC), the monomer in the organic phase is reacted with the initiator in the aqueous phase. The reaction is achieved by means of the PTC which complexes and solubilizes the water-soluble initiator into the organic phase. Rasmussen et al. showed that polymerization with PTC could be conducted at low temperatures with high reaction rates for some monomer systems [4].

Kunieda et al. used cyclodextrins as the PTC to investigate the transfer of initiators soluble in organic solvents into aqueous media for the polymerization of water-soluble monomers [5, 6]. Jayakrishnan and Shah studied the polymerization of methyl methacrylate (MMA) and acrylonitrile (AN) in the presence of ammonium peroxydisulfate and hexadecylpyridinium chloride in ethyl acetate-water media [7, 8]. It was shown that quaternary salts coupled with peroxydisulfates are better initiators for vinyl polymerizations in biphasic systems than are common organic initiators like AIBN or benzoyl peroxide. Mandal and coworkers investigated the free-radical polymerization of styrene and MMA using $K_2S_2O_8$ as the initiator and Bu_4NBr as the PTC [9, 10]. Choi and Lee reported the kinetics of bulk (free-radical) polymerization of MMA with the $K_2S_2O_8$ -18-crown-6 catalyst system [11]. Bulacovschi et al. studied the kinetics of polymerization of MMA using the $K_2S_2O_8$ -Arquad catalyst system in benzene-water media [12].

A survey of the literature reveals that no systematic investigation of the kinetics and mechanism of polymerization of MMA with $K_2S_2O_8$ and TEBA as the phase-transfer catalyst has been carried out. This prompted us to undertake the present study which deals with the kinetics and mechanism of free-radical polymerization of MMA in unstirred toluene-water mixtures using $K_2S_2O_8$ as the initiator and triethylbenzylammonium chloride as the phase-transfer catalyst.

EXPERIMENTAL

Potassium peroxydisulfate (E. Merck) was crystallized twice from deionized water and dried under vacuum before use. Commercially available triethylbenzylammonium chloride (Fluka) was used without further purification. AnalaR-grade organic solvents were used after distillation. Methyl methacrylate was freed from the inhibitor by washing with 5% NaOH solution, followed by 3% H_3PO_4 and then with water, dried over anhydrous $CaCl_2$, and distilled under reduced pressure. The middle fraction of the distillate was collected and used in our polymerization studies.

Polymerization was carried out in a Pyrex glass polymerization tube in a nitrogen atmosphere at 60°C without stirring. The reaction mixture comprised 8

mL of the organic phase (e.g., 6 mL MMA + 2 mL toluene) and 12 mL of the aqueous phase containing $K_2S_2O_8$, the quaternary ammonium salt, H_2SO_4 , and $KHSO_4$. H_2SO_4 and $KHSO_4$ were used to maintain the acid and ionic strengths, respectively. A typical polymerization reaction mixture consisted of $[MMA] = 3.0$ M, $[K_2S_2O_8] = 0.04$ M, $[QX] = 0.05$ M, $[H^+] = 0.5$ M, and $\mu = 1.0$ M. At the end of the predetermined reaction time, the polymerization was arrested by pouring the reaction mixture into ice-cold methanol (containing traces of hydroquinone). The polymer formed was coagulated by the controlled addition of a few drops of concentrated HCl. The polymer yield was determined gravimetrically. The rate of polymerization (R_p) was calculated from the weight of the polymer formed by using the equation

$$R_p = 1000W/vtM$$

where W = weight of the polymer in grams

v = volume of the reaction mixture in milliliters

t = reaction time in seconds

M = molecular weight of the monomer

RESULTS AND DISCUSSION

The steady-state rate of polymerization was first arrived at by determining R_p at different time intervals, and it was attained in ~ 90 minutes. There was no significant induction period (Fig. 1). To determine the rate of polymerization with variations in concentrations of various species, the polymerization was carried out for 90 minutes (conversion $< 10\%$).

Effect of Initiator Concentration on R_p

At fixed concentrations of monomer, QX, acid strength, and ionic strength, the effect of $[K_2S_2O_8]$ on R_p was studied by varying the concentration of $K_2S_2O_8$ in the 0.02–0.05 M range. R_p increases with the concentration of $K_2S_2O_8$. A plot of $\log R_p$ vs $\log [K_2S_2O_8]$ is linear with a slope of 0.9, indicating nearly a first-order dependence of R_p on $[K_2S_2O_8]$. The plot of R_p vs $[K_2S_2O_8]$ is a straight line with a zero intercept, confirming the above observation (Fig. 2).

Generally, the order with respect to initiator is 0.5 when termination is bimolecular in free-radical polymerization processes, and it drops to nearly zero when primary radical termination predominates. The high initiator rate exponent of 0.9 observed in the present investigation precludes such possibilities. The experimental observation can be explained on the basis of a "gel effect" [13, 14]. It is believed that the termination step in vinyl polymerization is diffusion controlled under most conditions. North et al. reported that the termination in radical polymerization of MMA was diffusion controlled even in the initial stages of polymerization [15]. In heterogeneous polymerization conditions, the polymer is in a state of incipient precipitation, and the radicals suffer severe coiling and immobilization which entails a significantly reduced possibility of bimolecular terminations. This leads to a considerable decrease in the termination rate constant. In such cases termination becomes nearly first order. The weight-average and number-average molecular weights

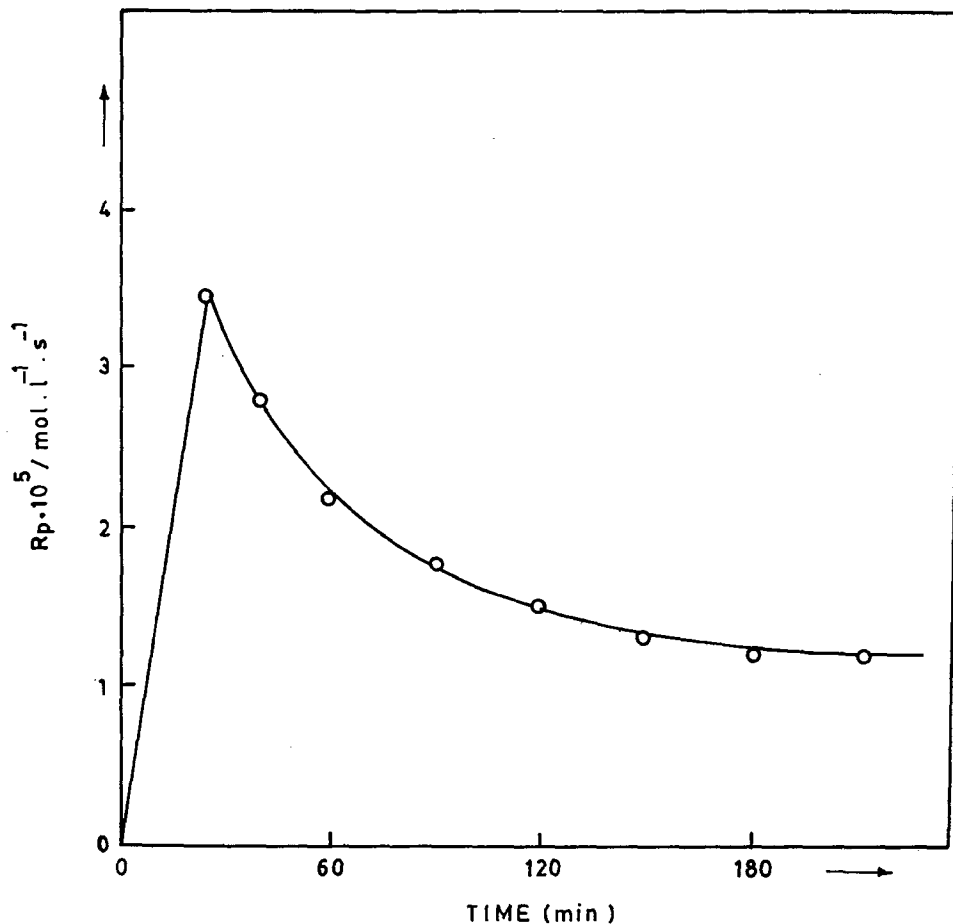


FIG. 1. Steady-state rate of polymerization. $[\text{MMA}] = 3.2 \text{ M}$, $[\text{K}_2\text{S}_2\text{O}_8] = 0.04 \text{ M}$, $[\text{QX}] = 0.05 \text{ M}$, $[\text{H}^+] = 0.5 \text{ M}$, $\mu = 1.0 \text{ M}$, 60°C .

of the polymer determined by GPC analysis are of the order of 1.14×10^6 and 6.98×10^4 , respectively, and the ratio of the weight-average degree of polymerization to the number-average degree of polymerization (\bar{X}_w/\bar{X}_n) ≈ 16 . Such a high value for \bar{X}_w/\bar{X}_n also lends strong support to the occurrence of a gel effect.

Effect of Monomer Concentration on R_p

The effect of monomer concentration on the rate of polymerization was studied by varying $[\text{MMA}]$ in the 2.5–3.5 M range at fixed concentrations of $\text{K}_2\text{S}_2\text{O}_8$ (0.04 M), QX (0.05 M), H^+ (0.5 M), and ionic strength (1.0 M). A plot of $\log R_p$ vs $\log [\text{MMA}]$ is linear with a slope of 1.9, indicating a ~ 2 order dependence of R_p on $[\text{monomer}]$ (Fig. 3).

A reaction order greater than unity with respect to monomer may be ascribed to a dependence of the initiation rate on monomer concentration, primary radical

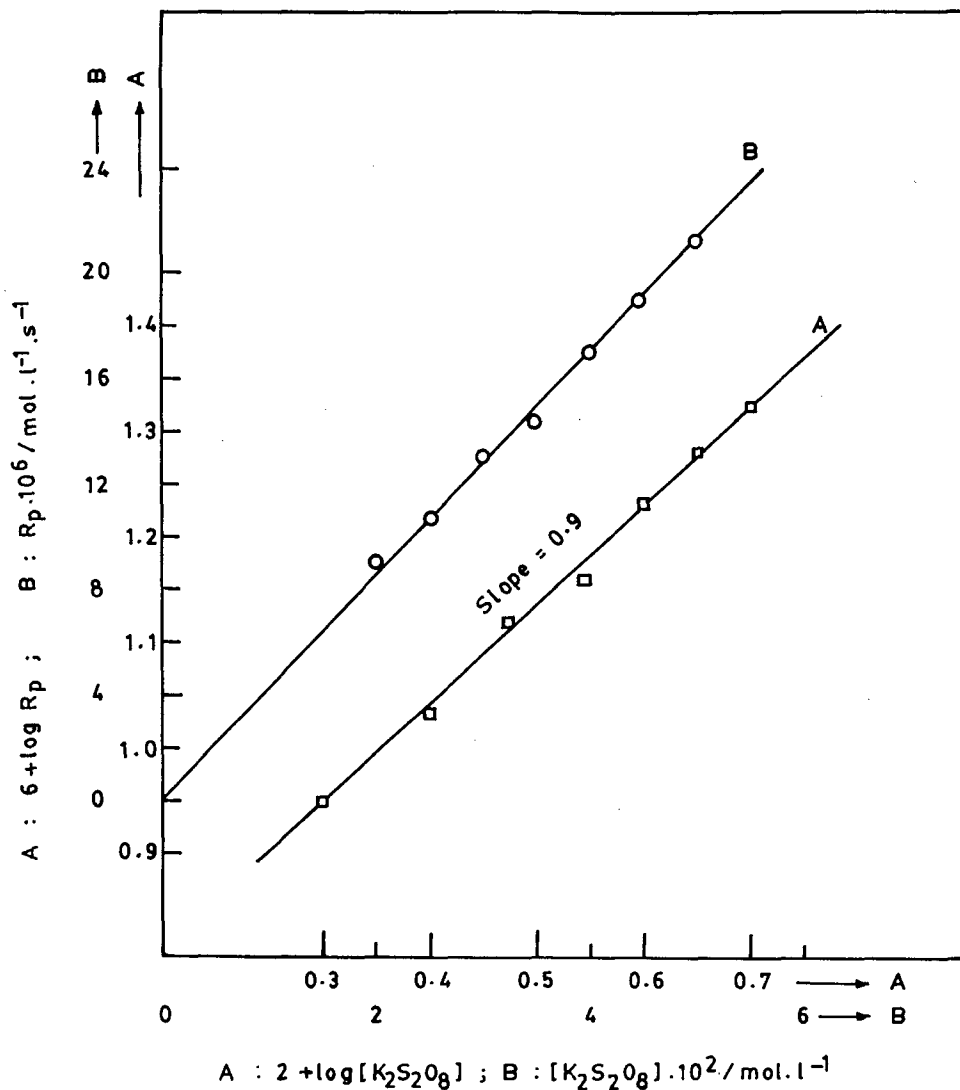


FIG. 2. Influence of [K₂S₂O₈] on R_p. [MMA] = 3.2 M, [QX] = 0.05 M, [H⁺] = 0.5 M, μ = 1.0 M, 60°C.

termination, occlusion phenomena, and/or a gel effect. At temperatures of ~60°C, the incidence of occlusion is negligible [16] and an order as high as 0.9 with respect to initiator dismisses the possibility of primary radical termination. Hence, the high monomer order in the present study can be attributed to the dependence of initiation rate on [monomer]. It is also to be borne in mind that variations in the diffusion-controlled termination rate constant, usually traceable to viscosity factors, significantly affect the monomer order even at very small polymer conversions [17]. Either or both of these factors could contribute to the monomer order of ~2 observed in the present work.

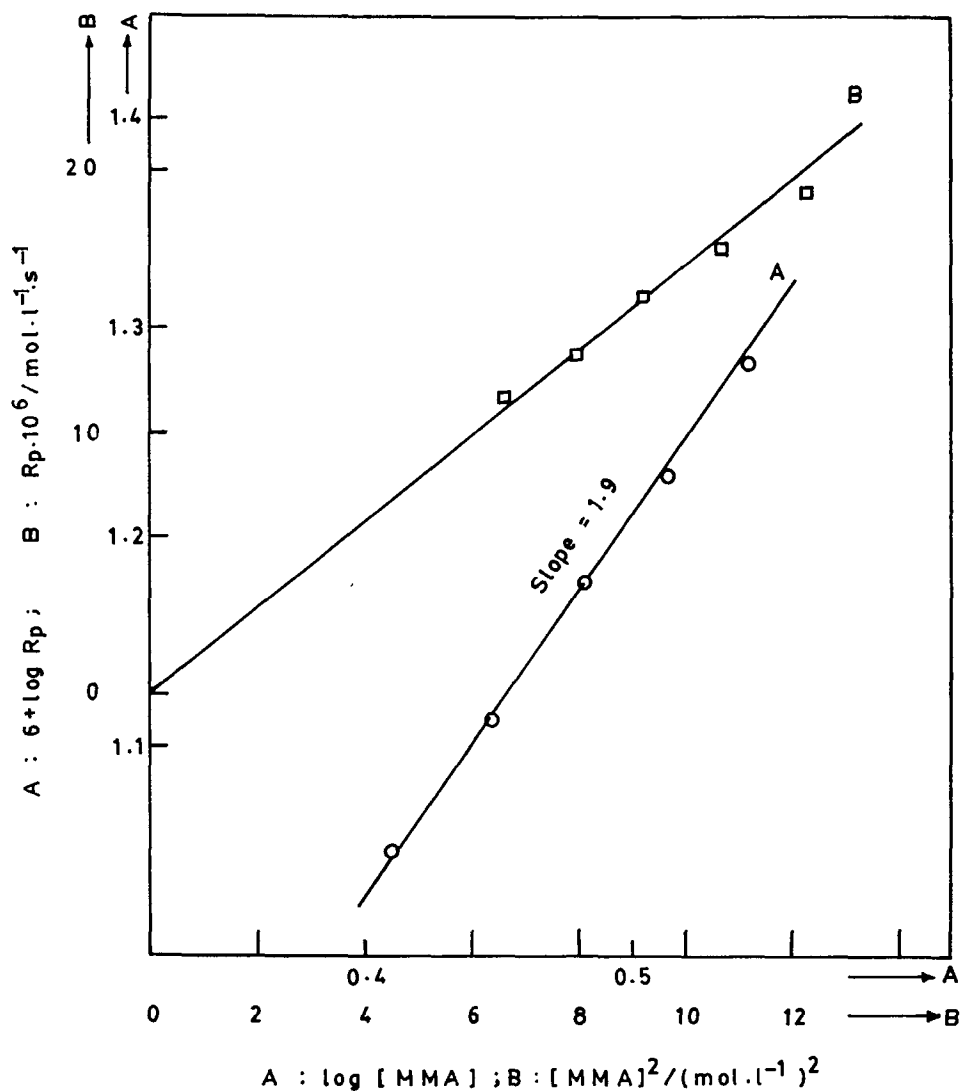


FIG. 3. Influence of [MMA] on R_p . $[K_2S_2O_8] = 0.04$ M, $[QX] = 0.05$ M, $[H^+] = 0.5$ M, $\mu = 1.0$ M, 60°C .

Effect of QX Concentration on R_p

R_p increases with an increase in the concentration of TEBA. A plot of $\log R_p$ vs $\log [\text{TEBA}]$ is linear with a slope of 0.5, and a plot of R_p vs $[\text{TEBA}]^{0.5}$ is a straight line passing through the origin, thereby confirming the above inference (Fig. 4).

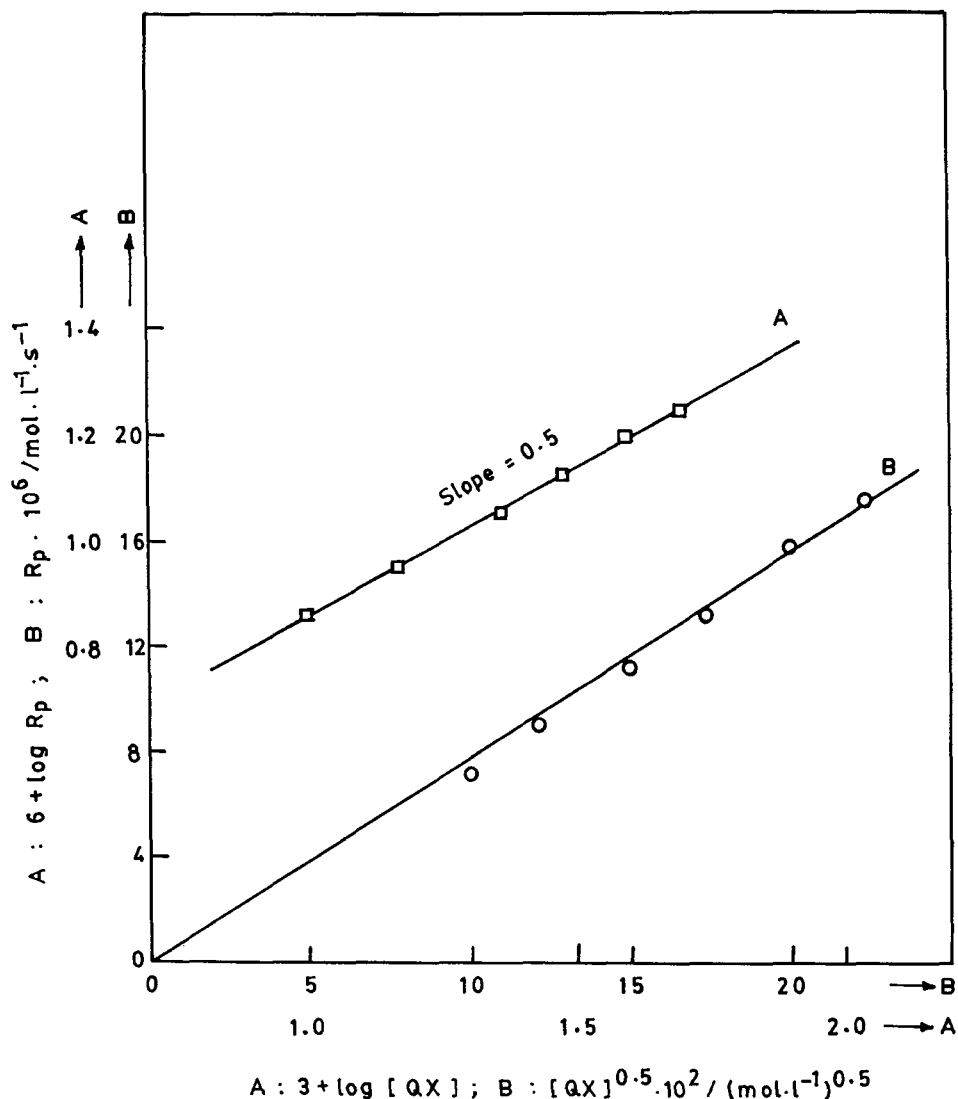


FIG. 4. Influence of $[QX]$ on R_p . $[MMA] = 3.2 \text{ M}$, $[K_2S_2O_8] = 0.04 \text{ M}$, $[H^+] = 0.5 \text{ M}$, $\mu = 1.0 \text{ M}$, 60°C .

Effect of $[H^+]$ and μ on R_p

The influence of H^+ ion concentration and ionic strength on the rate of polymerization was studied by varying $[H^+]$ in the 0.25–1.00 M range and μ in the 0.5–1.25 M range independently at definite concentrations of monomer, $K_2S_2O_8$, and QX . Variations in either $[H^+]$ or μ of the medium have no discernible effect on R_p .

Effect of Temperature on R_p

The rate of polymerization increased with temperature. The activation energy for the overall rate of polymerization computed from the Arrhenius plot (Fig. 5) of $\log R_p$ vs $1/T$ was $58.3 \text{ kJ}\cdot\text{mol}^{-1}$. The thermodynamic parameters were also evaluated. They are $\Delta H^\ddagger = 55.4 \text{ kJ/mol}$, $\Delta S^\ddagger = -170.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and $\Delta G^\ddagger = 112.3 \text{ kJ}\cdot\text{mol}^{-1}$.

The following mechanism is proposed to explain the above observations.

Phase transfer:

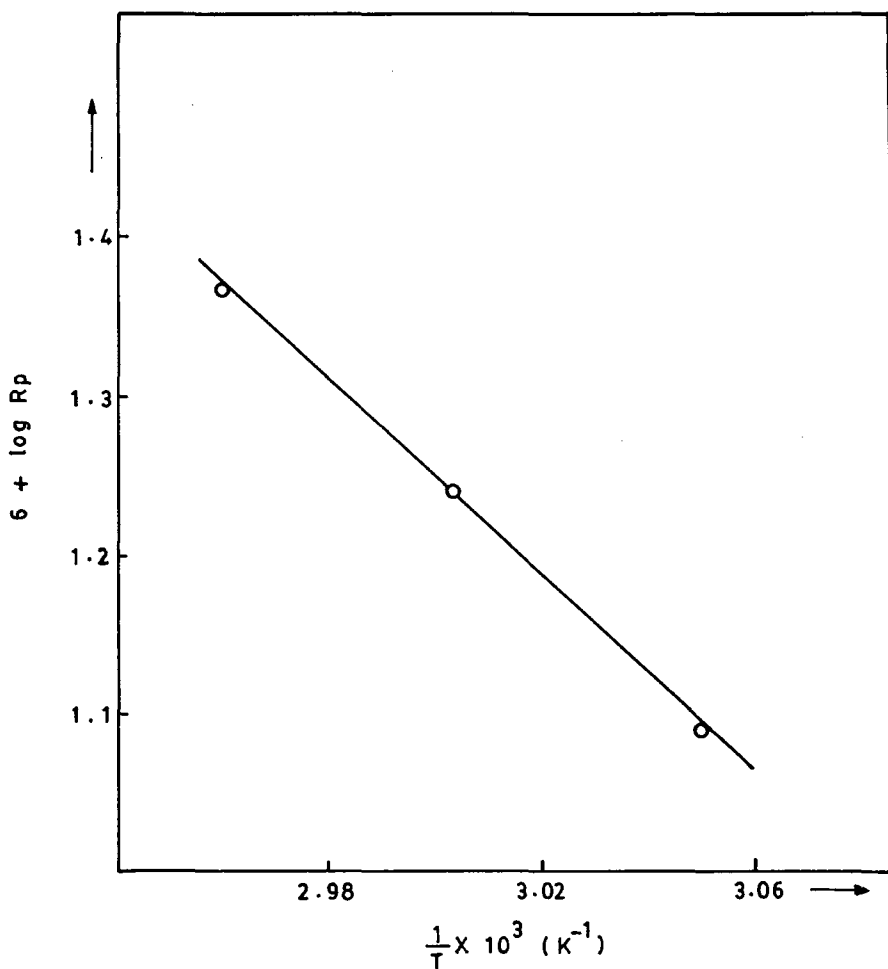
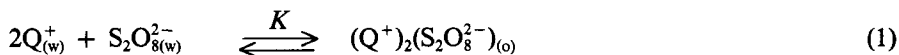
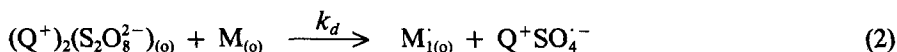
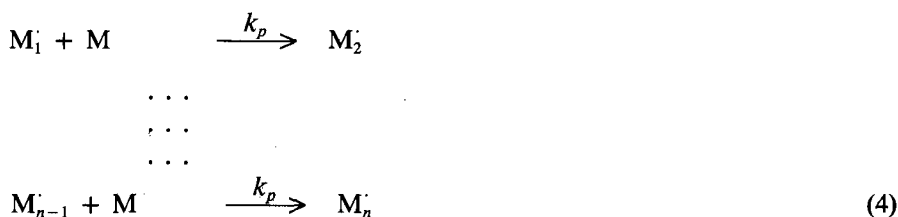


FIG. 5. Temperature variation. $[\text{MMA}] = 3.2 \text{ M}$, $[\text{K}_2\text{S}_2\text{O}_8] = 0.04 \text{ M}$, $[\text{QX}] = 0.05 \text{ M}$, $\mu = 1.0 \text{ M}$, $[\text{H}^+] = 0.5 \text{ M}$.

Initiation:



Propagation:

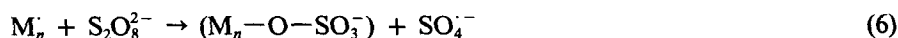


Termination:



The subscripts (o) and (w) refer to the organic phase and the aqueous phase, respectively. The mechanism involves the phase transfer of $S_2O_8^{2-}$ ion from the aqueous phase to the organic phase containing the monomer, facilitated by the quaternary ammonium salt (PTC), where the former initiates polymerization following its decomposition to SO_4^- . It was observed that there was little polymerization in the absence of PTC, and the polymerization rate increased with an increase in the concentration of QX.

Considering the termination reaction, the quaternary ammonium ion (Q^+) may exist as the ion pairs Q^+X^- , $(Q^+)_2S_2O_8^{2-}$, or $Q^+SO_4^-$. Interaction between M_n and X^- (halide ion) seems unlikely. A reaction of the following pattern,



is shown to be negligible compared to reactions of the type [18]:



As regards the possible interaction between M_n and SO_4^- , it could be reasonably argued that since the stationary state concentration of primary radicals, SO_4^- , is believed to be very low, and lower still in the presence of monomer, the reaction between M_n and SO_4^- is assumed to be unimportant. The negatively charged polymer radicals M_n (due to sulfate end groups) would possibly repel the sulfate anion radicals (SO_4^-), so that the interaction between M_n and SO_4^- radicals (i.e., primary radical termination) is likely to be insignificant. Hence, the termination process given above seems to be more feasible than any of the interactions of M_n with the counteranions of Q^+ .

Applying the general principles of free-radical polymerization and stationary-state hypothesis to the radical species, the rate law for this mechanism can be derived as

$$R_p = \frac{2k_p k_d K}{k_t} \frac{[M]^2 [S_2O_8^{2-}]_w [Q^+]_{total}}{\{1 + K[Q^+]_w [S_2O_8^{2-}]_w\}} \quad (9)$$

where

$$[Q^+]_{total} = [Q^+]_w + [(Q^+)_2 S_2O_8^{2-}]_o$$

This equation satisfactorily explains the experimental observations.

CONCLUSIONS

The phase-transfer-catalyzed free-radical polymerization of MMA using the $K_2S_2O_8$ -quaternary ammonium salt catalyst system follows a first-order kinetics with respect to monomer and a half-order with respect to peroxydisulfate. The observed deviation from first-order dependence with respect to monomer may be ascribed to the dependence of the rate of initiation on monomer concentration and also to the "gel effect." The high initiator rate exponent may be attributed to the gel effect. We propose a mechanism involving initiation by the phase-transferred peroxydisulfate anion and termination by the quaternary ammonium ion.

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Received July 21, 1993

Revision received October 22, 1993