Phase-Transfer-Agent-Aided Free Radical Polymerization of Methyl Methacrylate-A Kinetic Study

Victor Bulacovschi[a]; Camelia Mihilescu[a]; Silvia Ioan[b]; Bogdan C. Simionescu[a]

[a] Department of Organic and Macromolecular Chemistry, Polytechnic Institute of Jassy, Jassy, Romania [b] "P. Poni" Institute of Macromolecular Chemistry, Jassy, Romania

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PHASE-TRANSFER-AGENT-AIDED FREE RADICAL POLYMERIZATION OF METHYL METHACRYLATE—A KINETIC STUDY

VICTOR BULACOVSCHI and CAMELIA MIHĂILESCU

Department of Organic and Macromolecular Chemistry
Polytechnic Institute of Jassy
R-6600 Jassy, Romania

SILVIA IOAN

"P. Poni" Institute of Macromolecular Chemistry
R-6600 Jassy, Romania

BOGDAN C. SIMIONESCU

Department of Organic and Macromolecular Chemistry
Polytechnic Institute of Jassy
R-6600 Jassy, Romania

ABSTRACT

The kinetics of phase-transfer-agent-aided free radical polymerization of methyl methacrylate was investigated by using $K_2S_2O_8$ as the initiator and cetyltrimethyl ammonium chloride (Arquad) as the phase transfer agent. The rate of polymerization was found to be proportional to $[M]^{1.23}[K_2S_2O_8]^{0.8}[Arquad]^{0.25}$ and almost independent of the volume of water (V_w)/volume of organic solvent (V_o) (benzene) ratio for $V_w/V_o < 0.33$. A reaction mechanism is proposed.

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INTRODUCTION

The use of phase-transfer catalysis (PTC) in radical polymerization reactions has become commonplace in recent years by virtue of the rapid polymerization rates attained under milder conditions. This is compared to those required by the use of classical free radical initiators, such as AIBN or benzoyl peroxide [1–4]. In addition, PT agents (e.g., quaternary ammonium salts, crown ethers) may extend the use of lipophilic peroxydisulfate dianion to conduct free radical polymerization reactions in organic media (or in water–organic solvent mixtures) via complexation of its counterions.

Reports on mechanistic aspects of the polymerization in the presence of PT catalysts reveal that the initiating species is the sulfate anion radical appearing in the monomer containing the organic phase by decomposition of the peroxydisulfate transferred from the aqueous phase by PT agent [4–7]. However, the reaction conditions (volume ratio between aqueous and organic phases, nature of the PT agent, stirring of the system) may influence the first appearance of this primary free radical. It may either be generated in the organic phase or formed in the aqueous phase and subsequently transferred into the organic phase by the PT agent.

The present paper is concerned with kinetic studies on PT-agent-aided free radical polymerization of methyl methacrylate (MMA) with $K_2S_2O_8$ as initiator and cetyltrimethyl ammonium chloride (Arquad) as PT agent in unstirred water/benzene mixtures.

EXPERIMENTAL

Potassium peroxydisulfate was crystallized twice from distilled-deionized water and dried under vacuum before use. Commercially available quaternary ammonium salts were used without further purification. Reagent-grade organic solvents and MMA were purified according to standard procedures.

Polymerizations were carried out in a dilatometer, and the percent conversion and the rate of polymerization (R_p) were evaluated from the volume contraction. The two phase-reaction mixtures were equilibrated at room temperature prior to polymerization. The monomer was first dissolved in adequate organic solvent, purged with nitrogen, and injected into the dilatometer over the mixture of $K_2S_2O_8$ and quaternary salt (QX)

in water. When in contact, the two water solutions of $K_2S_2O_8$ and QX precipitated the $Q_2^+S_2O_8^{2-}$. The interface between the organic and aqueous phases was maintained constant in all polymerization experiments.

Finally, the dilatometer was immersed into a water bath thermostated at a preestablished temperature ($\pm 0.02\,°C$) for a predetermined time period. The reproducibility of the results was found to be within $\pm 2\%$.

Weight-average molecular weights were determined by light scattering (experimental error, $\pm 7\%$), while viscometry was used to determine the viscometric molecular weights by applying the relation $[\eta] = 6.27 \times 10^{-3} M^{0.76}$ [8].

RESULTS AND DISCUSSION

The polymerization of MMA under the mentioned conditions is influenced, as expected, by the nature of the quaternary ammonium salt (Table 1). The reactions carried out in a benzene/water mixture at $V_w/V_o = 0.1875$ (the subscripts refer to the aqueous phase and the organic phase, respectively) with $K_2S_2O_8$ as the initiating agent revealed that the

TABLE 1. Polymerization of MMA in Phase-Transfer Conditions. $[MMA] = 4.96\,M$; $[K_2S_2O_8] = 0.5\%$ on monomer; $[K_2S_2O_8]/[QX] = 1:2$ mol:mol; temperature, $50\,°C$; polymerization period, 5 h

Onium salt[a]	Yield, %	$\overline{M}_v \times 10^{-5}$	$\overline{M}_w \times 10^{-5}$
$(Me)_4N^+I^-$	Trace	—	—
$(Me)_4N^+Br^-$	2.18	4.03	—
$(Me)_4N^+Cl^-$	2.38	3.33	8.73
$(Et)_4N^+Cl^-$	2.41	3.13	9.07
$Bz(Me)_3N^+Cl^-$	2.13	4.37	9.07
$Bz(Et)_3N^+Cl^-$	2.17	3.16	—
$Cet(Me)_3N^+Cl^-$	22.54	5.86	8.26
$CetPyN^+Br^-$	29.43	5.41	9.52
$Me(Ph)_3P^+Br^-$	1.44	5.23	11.08
$Bz(Ph)_3P^+Cl^-$	5.36	9.51	13.84
None	Trace	—	—

[a]Me = methyl, Et = ethyl, Bz = benzyl, Cet = cetyl, Py = pyridil, Ph = phenyl.

most efficient catalysts were Arquad and cetylpyridyl ammonium bromide, so subsequent reactions were performed by using only Arquad as the PT catalyst.

Modification of the nature of the organic solvent resulted in significant changes of the polymer yield for the same initiating system (Table 2). A correlation has been observed between the dielectric constant of the solvent and the polymer yield.

The rate of polymerization for the PT-agent-aided free radical polymerization process was found to be dependent on the V_w/V_o ratio (Fig. 1). Two domains of V_w/V_o values were observed in which the contribution of the V_w/V_o ratio to the reaction rate was different, suggesting the possible existence of two initiation mechanisms [6].

According to the experimental data presented in Figs. 2–4 for V_w/V_o < 0.33, R_p is given by

$$R_p = K[M]^{1.23}[K_2S_2O_8]^{0.5}[Arquad]^{0.25}(V_w/V_o)^{0.004}$$

Comparison of the correlation coefficients (r) showed that the reaction order with respect to monomer was correct ($r = 0.99$), while the precision in determining the order with respect to persulfate and Arquad was lower ($r = 0.97$ and $r = 0.90$, respectively).

TABLE 2. Influence of Solvent on the Polymerization of MMA in Phase-Transfer Conditions. MMA = 5 mL; $[K_2S_2O_8]$ = 0.5% on monomer; $[K_2S_2O_8]/[Arquad]$ = 1:2 mol:mol; temperature, 40°C; polymerization period, 6 h; V_w/V_o = 0.23

Organic solvent	Dielectric constant	Polymer yield, %
Dioxane[a]	2.21 (25°C)	32.58
Acetone[a]	20.70 (25°C)	36.52
Benzene[b]	2.28	2.66
Methyl ethyl ketone[b]	18.50	31.49
Chloroform[b]	4.80	16.13
Ethyl acetate[b]	6.02 (25°C)	15.20
Methylene chloride[b]	9.08	18.13
Cyclohexanone[b]	18.30	55.78

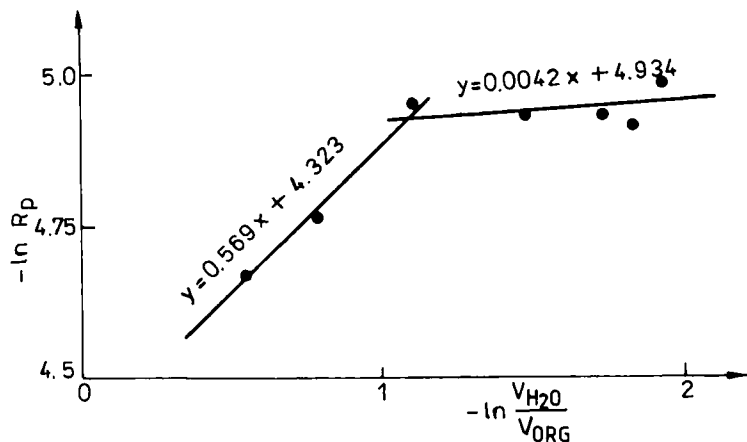[a]Homogeneous system.
[b]Heterogeneous system.

FIG. 1. Influence of V_w/V_o ratio on polymerization rate. [MMA] = 4.71 M; $[K_2S_2O_8]$ = 6.56 × 10^{-3} M; $[K_2S_2O_8]$/[Arquad] = 1:2 mol:mol; 50°C.
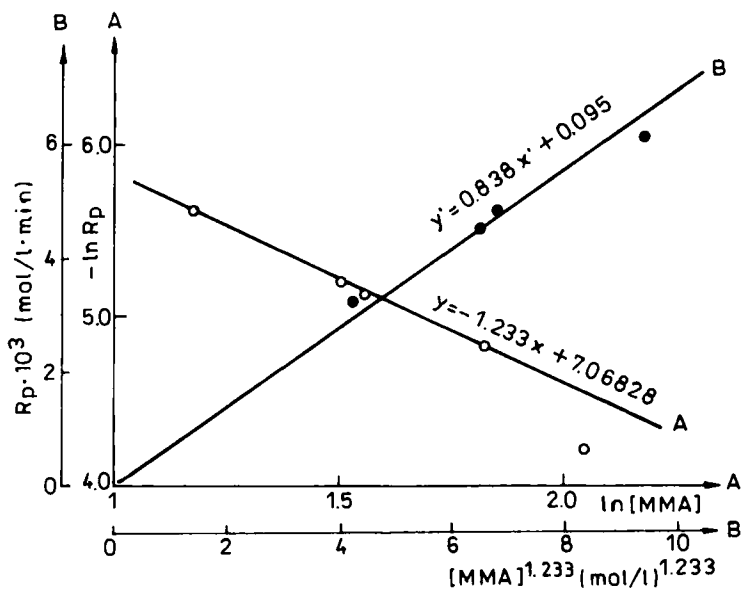

FIG. 2. Reaction order with respect to monomer. $[K_2S_2O_8]$ = 6.56 × 10^{-3} M; $[K_2S_2O_8]$/[Arquad] = 1:2 mol:mol; 50°C.
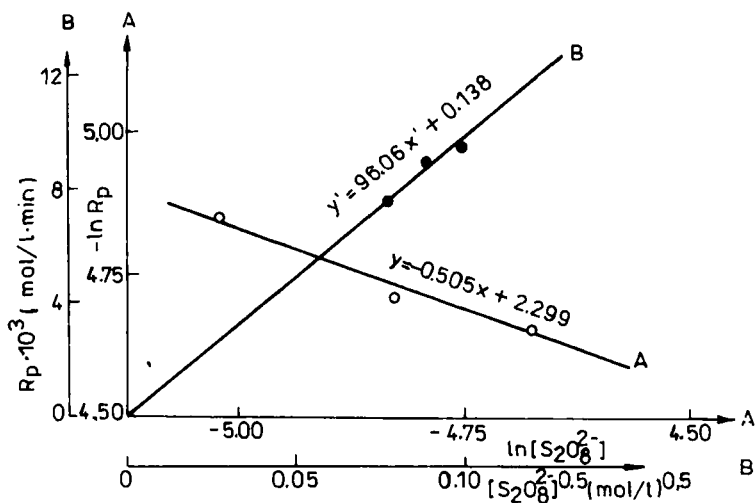
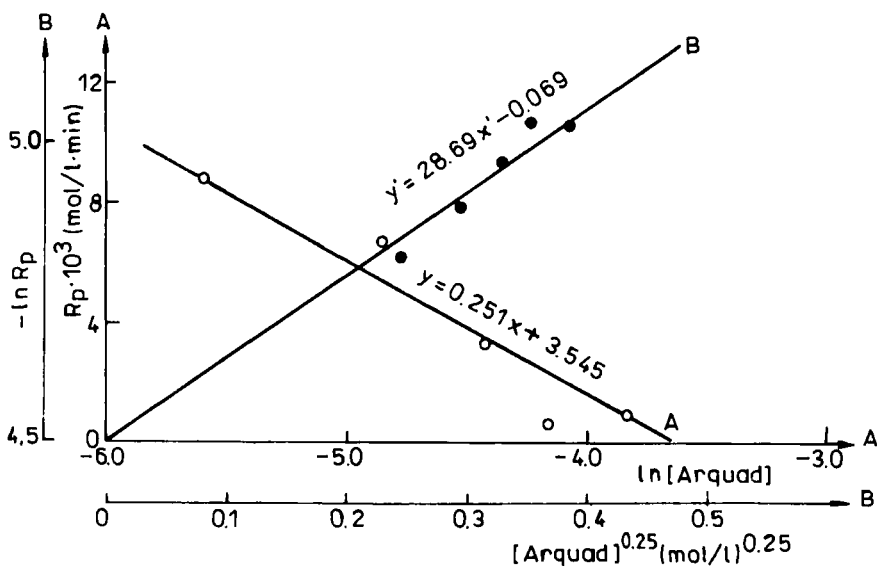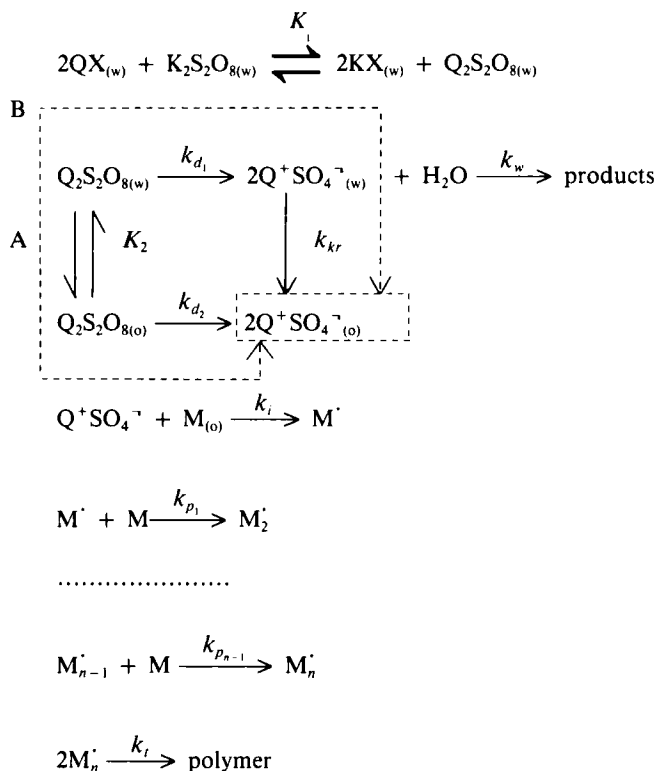FIG. 3. Influence of $[K_2S_2O_8]$ on polymerization rate. $[MMA] = 7.66\ M$; $[Arquad] = 1.975 \times 10^{-2}\ M$; 50°C.

FIG. 4. Influence of [Arquad] on polymerization rate. $[MMA] = 7.66\ M$; $[K_2S_2O_8] = 9.58 \times 10^{-3}\ M$; 50°C.

The Arrhenius plot of $\ln R_p$ vs $1/T$ is a straight line and yields an activation energy of 22.52 kcal/mol, comparable to the values usually found in common free radical polymerizations. Since $E_a = E_p + (E_i - E_t)/2$, and $E_p - E_t/2 = 5.15$ kcal/mol [9], E_i should be 34.74 kcal/mol (145.2 kJ/mol) (for $K_2S_2O_8$ decomposition in water, a value of $E_d = 140.2$ kJ/mol has been reported [10]).

The value found for E_i equals the decomposition energy of the peroxidic bond in $K_2S_2O_8$, which may argue for Mechanism A (see Scheme 1). Mechanism B, which supposes the formation of the SO_4^- ion radical in water and its subsequent transfer to the organic phase, should be associated with higher values of the initiating energies.

$$2QX_{(w)} + K_2S_2O_{8(w)} \underset{}{\overset{K_1}{\rightleftharpoons}} 2KX_{(w)} + Q_2S_2O_{8(w)}$$

$$Q^+SO_4^- + M_{(o)} \xrightarrow{k_i} M^\cdot$$

$$M^\cdot + M \xrightarrow{k_{p_1}} M_2^\cdot$$

$$\cdots\cdots\cdots\cdots\cdots$$

$$M_{n-1}^\cdot + M \xrightarrow{k_{p_{n-1}}} M_n^\cdot$$

$$2M_n^\cdot \xrightarrow{k_t} \text{polymer}$$

SCHEME 1.

Scheme 1 presents the reactions characterizing the polymerization process; it is assumed that termination is bimolecular.

According to the first initiation mechanism (Mechanism A), the rate of initiation is

$$R_i^{(A)} = \frac{2k_{d_2}K_1K_2^2[Q^+]_t^2[KX]_w^2[K_2S_2O_8]}{\{K_2[KX]^2 + 2K_1[QX]_w[K_2S_2O_8](1 + K_2)\}^2}$$

where $[Q^+]_t$ is the total concentration of the Q^+ species.

If initiation occurs according to Mechanism B, the initiation rate is given by

$$R_i^{(B)} = \frac{2k_{d_1}k_{tr}K_1[Q^+]_t^2[KX]_w^2[K_2S_2O_8]}{\{[KX]_w^2 + 2K_1[QX]_w[K_2S_2O_8]\}^2(k_w + k_{tr})}$$

For a bimolecular termination, the rates of polymerization corresponding to the two possible mechanisms will be

$$R_p^{(A)} = \frac{k_pK_2}{k_t^{1/2}} \frac{(2k_{d_2}K_1)^{1/2}[Q^+]_t[KX]_w[K_2S_2O_8]^{1/2}}{K_2[KX]_w^2 + 2K_1[QX]_w[K_2S_2O_8])(1 + K_2)} [M]$$

and

$$R_p^{(B)} = \frac{k_p}{k_t^{1/2}} \frac{(2k_{d_1}k_{tr}K_1)^{1/2}[Q^+]_t[KX]_w[K_2S_2O_8]^{1/2}}{([KX]_w^2 + 2K_1[QX]_w[K_2S_2O_8])(k_w + k_{tr})} [M]$$

Two distinct situations can be envisioned:

1) For high K_1 values and $[Q^+]_t \simeq [KX]$, the polymerization rates may be simplified to

$$R_p^{(A)} = \frac{k_p(2k_{d_2}K_1)^{1/2}}{k_t^{1/2}} [K_2S_2O_8]^{1/2}[M]$$

and

$$R_p^{(B)} = \frac{k_p}{k_t^{1/2}} \frac{(2k_{d_1}k_{tr}K_1)^{1/2}}{k_w + k_{tr}} [K_2S_2O_8]^{1/2}[M]$$

which means that for both mechanisms the following dependence is valid:

$$R_p^{(A,B)} \approx [K_2S_2O_8]^{1/2}[M]$$

2) For small K_1 values, it can be accepted that $[Q^+] \simeq [QX]_w$, and the polymerization rate becomes

$$R_p^{(A,B)} \approx \frac{[KX]_w}{[K_2S_2O_8]^{1/2}} [M]$$

In this last case the polymerization rate is very small due to both the reduced values of $[KX]_w$ and the inverse proportionality of R_p toward $[K_2S_2O_8]$.

The first case (high K_1 values) seems to fit the present experimental results better and justifies the half-order dependence of R_p with respect to peroxydisulfate and the absence of the influence of the concentration of the quaternary ammonium salt.

CONCLUSIONS

The polymerization of methyl methacrylate under the PT conditions studied should obey a first-order law with respect to monomer and a half-order law with respect to persulfate.

Deviation from first-order dependence with respect to monomer may be ascribed to the dependence of the rate of initiation on monomer concentration. The independence of R_p on the V_w/V_o ratio for $V_w/V_o < 0.33$ suggests that in the chosen experimental conditions, Mechanism B does not take place.

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