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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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Online publication date: 22 June 2000

To cite this Article Balakrishnan, T. and Kumar, S. Damodar(2000) 'PHASE TRANSFER CATALYZED FREE RADICAL POLYMERIZATION: KINETICS OF POLYMERIZATION OF ALKYL METHACRYLATES USING POTASSIUM PEROXOMONOSULPHATE/TETRABUTYL PHOSPHONIUM CHLORIDE CATALYST SYSTEM', *Journal of Macromolecular Science, Part A*, 37: 7, 719 – 733

To link to this Article: DOI: 10.1081/MA-100101120

URL: <http://dx.doi.org/10.1081/MA-100101120>

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PHASE TRANSFER CATALYZED FREE RADICAL POLYMERIZATION: KINETICS OF POLYMERIZATION OF ALKYL METHACRYLATES USING POTASSIUM PEROXOMONOSULPHATE/TETRABUTYL PHOSPHONIUM CHLORIDE CATALYST SYSTEM

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Key Words: Polymerization, Phase Transfer Catalyst, and Potassium Peroxomonosulphate

ABSTRACT

The kinetics of phase transfer catalyzed free radical polymerization of alkyl methacrylates (MMA and EMA) using potassium peroxomonosulphate (water-soluble initiator) coupled with phase transfer catalyst viz., tetrabutylphosphonium chloride (TBPC) have been investigated in ethylacetate-water biphasic system at $50 \pm 0.1^\circ\text{C}$. The rate of polymerization increased with an increase in the quaternary salt concentration, but showed a tendency to level off at a higher concentration. An increase in peroxomonosulphate concentration also increased the rate of polymerization (R_p). The order with respect to monomer was found to be in unity. A square root order was observed for both peroxomonosulphate and phase transfer catalyst. A suitable

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kinetic scheme has been proposed to account for the experimental data and its significance is discussed.

INTRODUCTION

The free radical polymerization of water soluble monomers, acrylic monomers with potassium peroxydisulphate and peroxomonosulphate as initiators has been studied extensively in aqueous media [1]. Since potassium peroxomonosulphate and potassium peroxydisulphate are insoluble in organic solvents, their utility is severely restricted for solution or bulk polymerization. The phase transfer catalyst assisted polymerization reactions have received considerable attention in recent years [2]. 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 conjugation with certain phase transfer agents like quaternary ammonium salts $[Q^+X^-]$ [3, 4].

In the presence of phase transfer catalyst (PTC), the monomer in the organic phase reacted with the initiator in the aqueous phase. The reaction was achieved by means of PTC which complexes and solubilizes the water soluble initiator in the organic phase. Rasmussen *et al.* showed that polymerization with PTC could be conducted at low temperature with high reaction rates for some monomer systems [5].

Jayakrishnan and Shah studied the polymerization of methyl methacrylate (MMA) and acrylonitrile (AN) in the presence of ammonium peroxydisulphate and hexadecylpyridinium chloride in ethylacetate-water media [6, 7]. Choi and Lee reported the kinetics of bulk free radical polymerization of MMA with the $K_2S_2O_8$ -18-crown-6 catalyst system [8]. Balakrishnan *et al.* reported the kinetics of free radical polymerization of AN, with potassium peroxomonosulphate and Tetrabutyl ammonium chloride/Tetrabutylbenzylammonium chloride (TBAC/TBBAC) Toluene-water biphasic system [9]. Mandal *et al.* [10] studied the kinetics and mechanism of phase transfer catalyst assisted free radical polymerization of styrene at 60°C. Balakrishnan *et al.* reported the kinetics of the free radical polymerization of MMA- $K_2S_2O_8$ coupled with Benzyltriethylammonium chloride (BTEAC) in ethylacetate-water biphasic system under unstirred condition [11]. They have also reported a kinetic investigation of PTC catalyzed free radical polymerization of Acrylonitrile using $K_2S_2O_8$ as water soluble initiator in the presence of TMAB, TEAB, and TBAB as the phase transfer catalysts [12]. A survey of the literature reveals that no systematic investigation of the



kinetics and mechanism of polymerization of alkyl methacrylates coupled with tetrabutylphosphonium chloride (TBPC) and potassium peroxomonosulphate (PMS).

EXPERIMENTAL

Potassium peroxomonosulphate was obtained from E. I. Dupont-De Nemours & Co., (USA) and used as received [13] (Trade name "Oxone"). The commercially available phase transfer catalyst viz., tetrabutylphosphonium chloride was used without further purification. Methyl methacrylate (CDH, Bombay, India), and Ethyl methacrylate (Merck, Bombay, India), were used. Analar grade KHSO_4 , acetic acid, sodium acetate, ethylacetate and methanol were also used.

Polymerization experiments were carried out in a pyrex glass polymerization tube in a nitrogen atmosphere at $50 \pm 0.1^\circ\text{C}$ without stirring. The reaction mixture consists of 10 ml aqueous phase and 10 ml of organic phase (ethyl acetate). The reaction mixture was deaerated for 45 minutes. When PMS was added to the reaction mixture polymerization occurred and polyalkylmethacrylates are precipitated continuously during polymerization. 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 yield was determined gravimetrically. The rate of polymerization (R_p) was calculated from the weight of the polymer formed by using the equation.

$$R_p = \frac{1000 \times W}{V t M}$$

where

- W = Weight of the polymer in grams
- V = Volume of the reaction mixture
- t = Reaction time in seconds
- M = Molecular weight of the monomer

The viscosity of the polymer samples were determined using a Ubbelohde viscometer. The solvents benzene (E. Merck, India), and ethylacetate (Qualigens, India) were taken for viscosity samples of MMA and EMA poly-



mers. The intrinsic viscosity was determined experimentally using the extrapolation method of Kraemer. The molecular weights were calculated using the appropriate Mark-Houwink relationships [14].

$$[\eta] = K \bar{M}_v^a$$

where K and 'a' are constants for the polymers and solvents used at a specified temperature. From the molecular weight of the polymers, the degree of polymerization \bar{X}_n values were calculated using the following relationship.

$$\bar{M}_v = \bar{M}_0 \cdot \bar{X}_n$$

assuming $\bar{M}_n = \bar{M}_v$

where

- \bar{M}_0 = molecular weight of the monomer
- \bar{M}_n = number average molecular weight of the polymer
- \bar{M}_v = viscosity average molecular weight of the polymer
- \bar{X}_n = degree of polymerization

RESULTS AND DISCUSSION

Polymerization reactions have been carried out at $50 \pm 0.1^\circ\text{C}$ in ethyl acetate, the induction period is found to be negligible. The steady state rate of polymerization was attained after 120 minutes for MMA and EMA (Figure 1). The reaction time was fixed at 120 minutes to carry out the experiments with variations in other parameters. All the polymerization reactions were carried out at $50 \pm 0.1^\circ\text{C}$ up to the conversion of <15%.

Rate of Polymerization R_p and Monomer Effect

The effect of monomer concentration on the rate of polymerization was studied by varying the monomer concentration range MMA: $1.80\text{--}2.80 \text{ mol}\cdot\text{dm}^{-3}$, EMA: $1.19\text{--}3.01 \text{ mol}\cdot\text{dm}^{-3}$, at fixed concentration of Potassium peroxomonosulphate: $0.02 \text{ mol}\cdot\text{dm}^{-3}$, phase transfer catalyst: $0.02 \text{ mol}\cdot\text{dm}^{-3}$. A plot of R_p vs. \log [alkyl methacrylate] was found to be linear (Figure 2) with slope MMA:1.1 and EMA:1.0, clearly indicating the dependence of R_p on [alkyl methacrylates] [1]. A similar order on monomer concentration was reported by Jayakrishnan



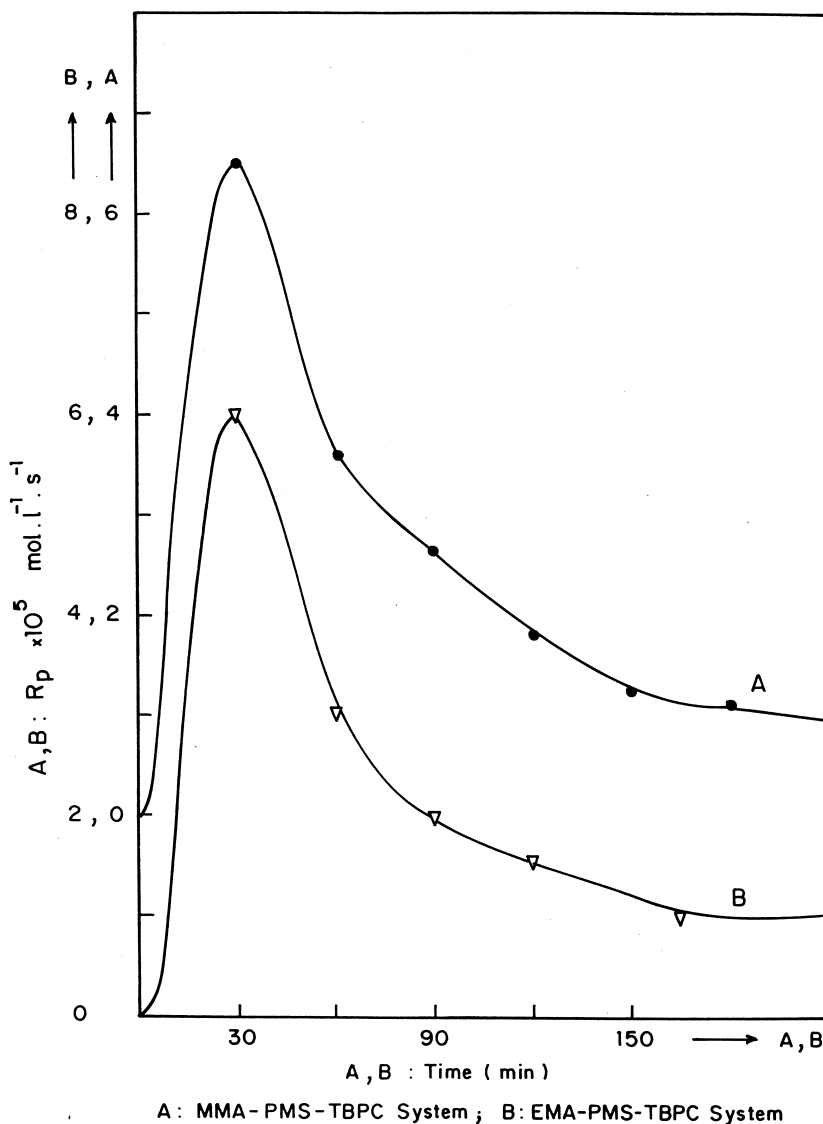


Figure 1. Steady state rate of polymerization. Line A : $R_p \times 10^5, \text{ mol.l}^{-1}.\text{s}^{-1}$, Time in minutes (MMA). Line B : $R_p \times 10^5, \text{ mol.l}^{-1}.\text{s}^{-1}$, Time in minutes (EMA). [monomer] = 2.0M, [TBPC] = 0.02M, [PMS] = 0.02M, $\mu = 0.05\text{M}$, Temp. = 50°C .

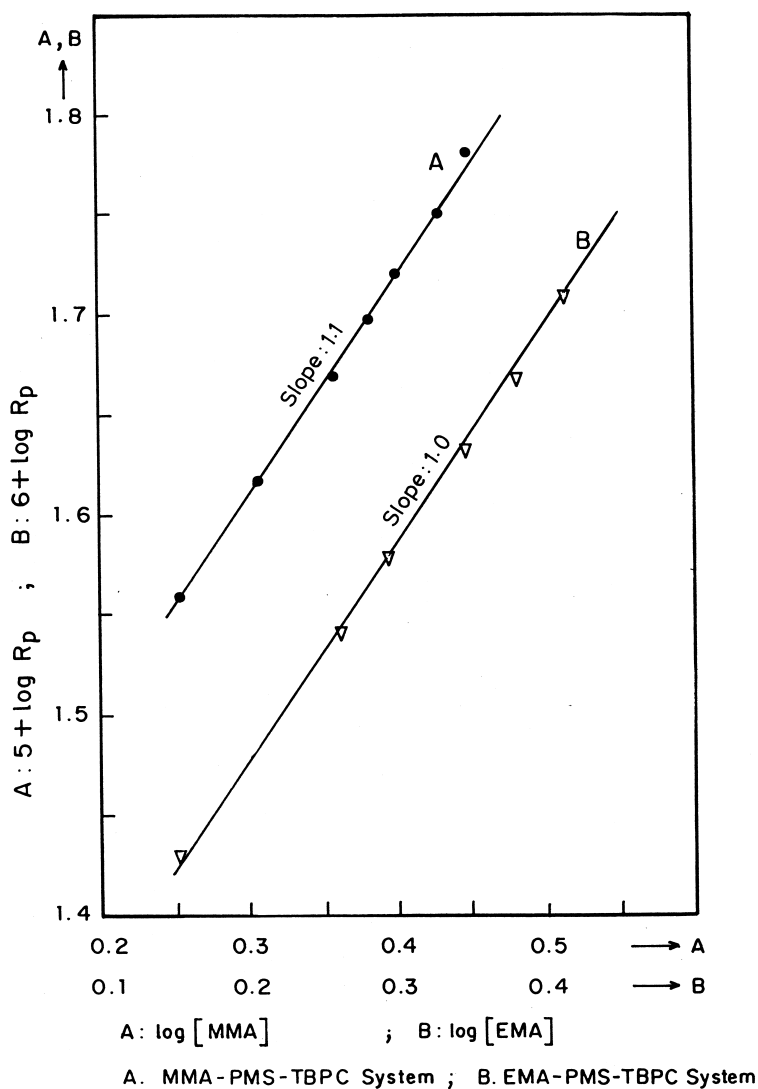


Figure 2. Influence of [monomer] on R_p . Line A : $5 + \log R_p$ vs. $\log[\text{MMA}]$. Line B : $6 + \log R_p$ vs. $\log[\text{EMA}]$. $[\text{PMS}] = 0.02\text{M}$, $[\text{TBPC}] = 0.02\text{M}$, $\mu = 0.05\text{M}$, Temp = 50°C .

et al. [6] in the phase transfer catalyzed polymerization of MMA using ammonium peroxydisulphate/hexadecylpyridinium chloride in ethylac-etate-water system. The kinetics of polymerization of AN initiated by PMS and catalyzed by Ag(I) was investigated in aqueous medium over the temperature range $35\text{-}50^\circ\text{C}$

by Samal *et al.* [15] and reported the order with respect to [AN] to be unity. Ghosh *et al.* [10] reported the first order dependence on [monomer] in tetrabutylammonium bromide assisted free radical polymerization of styrene initiated by potassium peroxydisulphate at 60°C. A similar order on monomer concentration was reported by Balakrishnan *et al.* [16] for MMA polymerization initiated by K₂S₂O₈/tributylbenzylammonium chloride, respectively.

Rate of Polymerization and Effect of Initiator [PMS]

At a fixed monomer concentration, EMA: 1.98 mol.dm⁻³, MMA: 2.04 mol.dm⁻³, PTC: 0.02 mol.dm⁻³ and constant ionic strength (0.05M), the effect of PMS concentration on R_p was studied by varying the concentration range 0.06-0.024 mol.dm⁻³ for EMA and 0.012-0.024 mol.dm⁻³ for MMA. The plot of R_p vs log [PMS] was found to be linear with slope equal to 0.5 indicating the half order dependence on [PMS] (Figure 3). A plot of R_p Vs [PMS]^{0.5} was also found to be linear passing through the origin supporting the half order dependence on [PMS]. A similar order was observed in the homogeneous polymerization of AN using PMS as initiator [15]. The order with respect to initiator 0.5 was reported by Ghosh *et al.* [10] in the polymerization of styrene using K₂S₂O₈-tetrabutylammonium bromide system at 60°C. Wherever termination is bimolecular in the free radical polymerization process, it suggests that the monomer induced decomposition of PMS was absent.

Effect of Phase Transfer Catalyst [PTC] on R_p

At a fixed concentration of monomer and potassium peroxomonosulphate, and constant ionic strength (0.05 M), the effect of TBPC concentration on R_p was studied by varying [TBPC] in the concentration range 0.006-0.02 M for MMA and 0.006-0.02 M for EMA. The plot of log R_p vs. log [TBPC] was found to be linear with a slope equal to 0.5 inferring that half order dependence on [TBPC] (Figure 4). A plot of R_p vs [TBPC]^{0.5} was also found to be linear, passing through the origin supporting the half order dependence on TBPC concentration. A similar order was observed by Jayakrishnan *et al.* [6]. The rate of polymerization was found to be proportional to the square root of phase transfer catalyst concentration by Choi and Lee [8] in the bulk polymerization of MMA initiated by K₂S₂O₈-18-crown-6 catalyst system. Balakrishnan *et al.* [12] had observed the phase transfer catalyst exponent to be 0.5 in the polymerization of AN with K₂S₂O₈ - TEAB, K₂S₂O₈ - TMAB and K₂S₂O₈ - TEBAC systems.



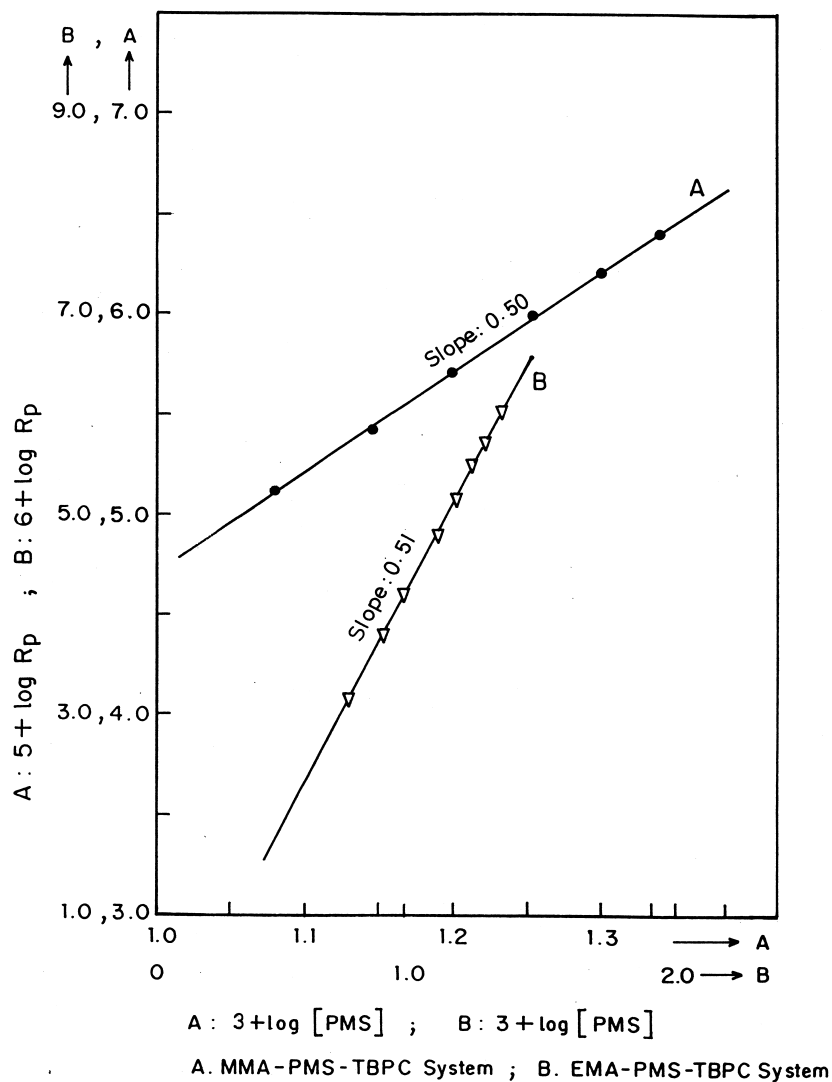


Figure 3. Influence of [PMS] on R_p . Line A : $5 + \log R_p$ vs. $3 + \log [PMS]$. Line B : $6 + \log R_p$ vs. $3 + \log [PMS]$. [monomer] = 2.0 M, [TBPC] = 0.02M, μ = 0.05M, Temp = 50°C.

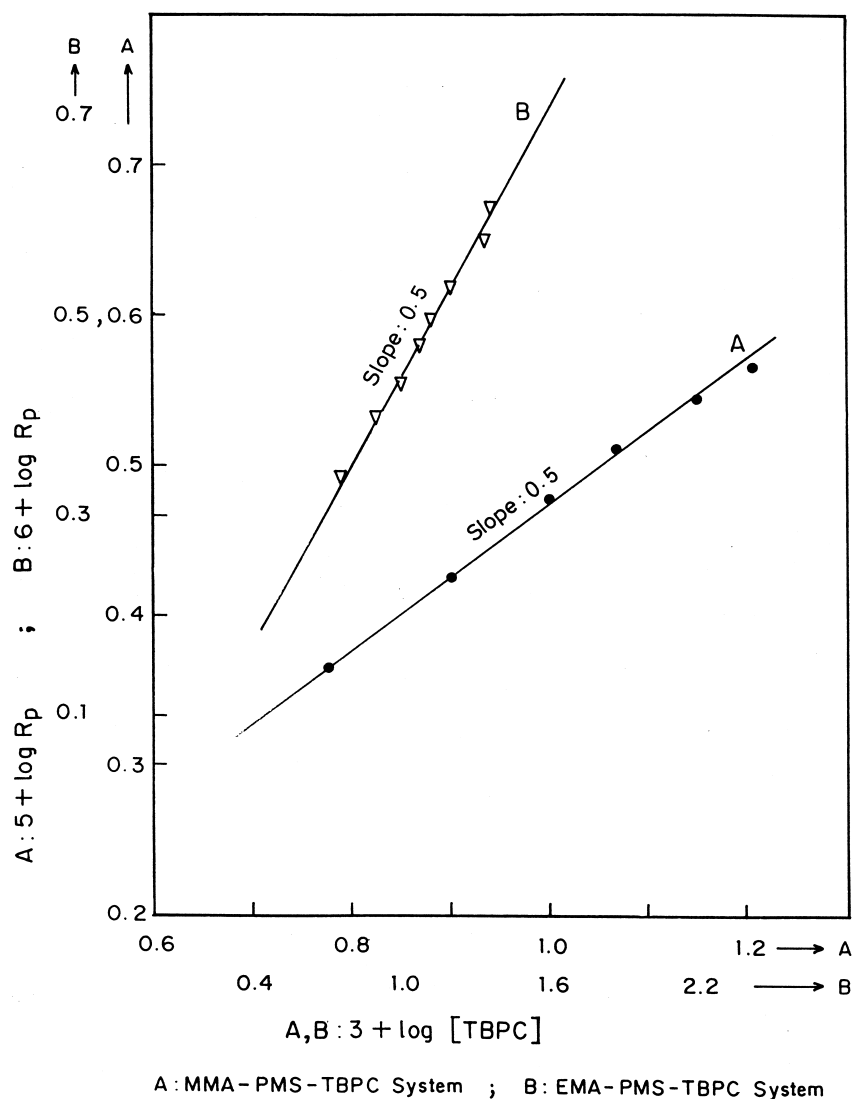


Figure 4. Influence of [TBPC] on R_p . Line A : $5 + \log R_p$ vs. $3 + \log [TBPC]$. Line B : $6 + \log R_p$ vs. $3 + \log [TBPC]$. [monomer] = 2.0 M, [PMS] = 0.02M, $\mu = 0.05M$, Temp = 50°C.

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Dependence of R_p on Ionic Strength

The effect of ionic strength was observed in the range of 0.03-0.07 M[KHSO₄] at a fixed monomer concentration, potassium peroxomonosulphate 0.02 mol.dm⁻³ and tetrabutylphosphonium chloride 0.02 mol.dm⁻³. The variation of ionic strength was found to exert no significant change in the R_p in the present investigation.

Effect of Temperature on R_p

When increasing the temperature from 45-55°C, the percentage conversion and R_p increased steadily and reached a steady state for 120 minutes. The activation energy was calculated from the Arrhenius plot of log R_p vs 1/T in the above temperature range. From the Arrhenius plot, the thermodynamic parameters are calculated and listed in Table 1.

Mechanism and Rate Law

Peroxomonosulphate exists as HSO₅⁻ in aqueous solution in the absence of high acidity and alkalinity [17] (First pK_a of PMS is in the high acidity region and second pK_a is equal to 9.4) unlike symmetrical peroxide, S₂O₈²⁻ which gives rise to two sulphate radicals on homolytic scission as shown in Equation 1 and PMS by a similar process, generates SO₄^{•-} and OH[•] radicals as in Equation 2.

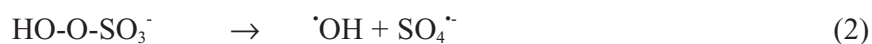
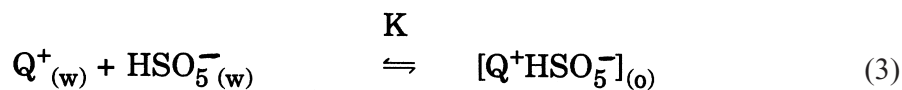


TABLE 1. Activation Parameters for the Polymerization of MMA and EMA Using KHSO₅-tetrabutylphosphonium Chloride

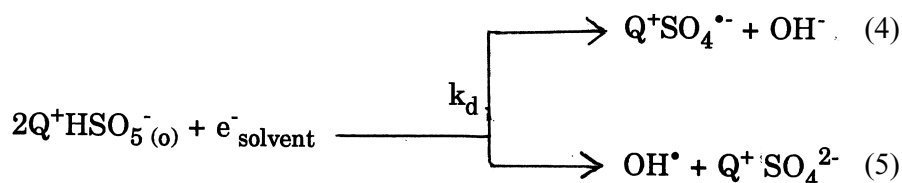
Monomer	A (mol.dm ⁻³ .sec ⁻¹)	E _a (kj.mol ⁻¹)	ΔH [#] (kj.mol ⁻¹)	ΔS [#] (j.k ⁻¹ . mol ⁻¹)	ΔG [#] (kj.mol ⁻¹)
MMA	7.65 x 10 ⁷	40.5	40.1	- 739.3	99.6
EMA	2.35 x 10 ⁵	51.0	46.4	- 192.0	105.4



Phase Transfer



Decomposition

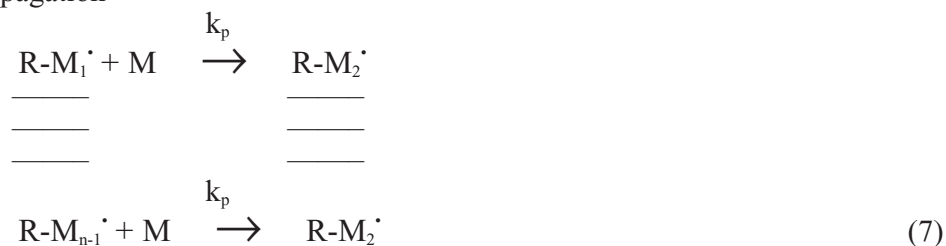


Initiation

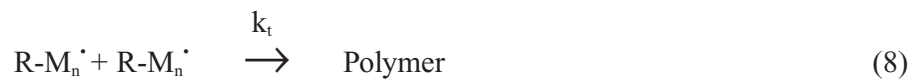


Where $R^\bullet = HO^\bullet$ (or) $Q^+SO_4^{\bullet-}$.

Propagation



Termination



Applying the general principles of free radical polymerization and steady state hypothesis to the radical species, the rate equation to the present kinetic data can be derived considering the above reaction steps (3-14).



Rate of Initiation

$$R_i = k_i [R^\bullet] [M] \quad (9)$$

$$\frac{d[R^\bullet]}{dt} = 2k_d [Q^+ HSO_5^-]_{(o)} - k_i [R^\bullet] [M] = 0.$$

$$[R^\bullet] = \frac{2k_d [Q^+ HSO_5^-]_{(o)}}{k_i [M]} \quad (10)$$

Substituting the value of $[Q^+ HSO_5^-]_{(o)}$ from Equation 3 into (10) and substituting $[R^\bullet]$ in Equation 9 becomes:

$$R_i = 2 k_d K [Q^+]_{(w)} [HSO_5^-]_{(w)} \quad (11)$$

Rate of termination

$$R_t = 2 k_t [R - M_n^\bullet]^2 \quad (12)$$

At a steady state, the rate of initiation is equal to the rate of termination in the free radical polymerization.

$$\begin{aligned}
 R_i &= R_t \\
 2k_d K [Q^+]_{(w)} [HSO_5^-]_{(w)} &= 2k_t [R - M_n^\bullet]^2 \\
 [R - M_n^\bullet] &= \left(\frac{K k_d}{k_t} \right)^{0.5} [Q^+]_{(w)}^{0.5} [HSO_5^-]_{(w)}^{0.5} \quad (13)
 \end{aligned}$$

The rate of polymerization is

$$R_p = d[M]/dt = k_p [M] [R - M_n^\bullet] \quad (14)$$

substituting the above value $[R - M_n^\bullet]$ from Equation 13 in Equation 14:

$$-d[M]/dt = R_p = k_p \left(\frac{k_d K}{k_t} \right)^{0.5} [Q^+]_{(w)}^{0.5} [HSO_5^-]_{(w)}^{0.5} [M]^{1.0} \quad (15)$$



The derived rate Equation 15 agrees well with the experimental results observed. The kinetic results are supplemented with viscosity studies. The degree of polymerization (\bar{X}_n) was evaluated from the intrinsic viscosity data of the polymer solution. The expression for the degree of the polymerization is given by ratio of rate of propagation to rate of termination.

$$\bar{X}_n = \frac{R_p}{R_t} = \frac{\text{rate of propagation}}{\text{rate of termination}}$$

$$R_p = k_p \left(\frac{Kk_d}{k_t} \right)^{0.5} [Q^+]_w^{0.5} [HSO_5^-]_w^{0.5} [M]^{1.0} \quad (16)$$

$$R_t = 2k_t \left(\frac{Kk_d}{k_t} \right) [Q^+]_w [HSO_5^-]_w \quad (17)$$

$$\bar{X}_n = \frac{R_p}{R_t} = \frac{k_p[M]^{1.0}}{2(k_d K/k_t)^{0.5} [Q^+]_w^{0.5} [HSO_5^-]_w^{0.5}} \quad (18)$$

This equation requires that the degree of polymerization should be proportional to $[M]^{1.0}$ and inversely proportional to $[\text{initiator}]^{0.5}$. It was found that a plot of \bar{X}_n Vs $[\text{monomer}]^{1.0}$ was linear with zero intercept (Figure 5). This observation lends strong support to the mechanism proposed.

CONCLUSION

Polymerization kinetics of alkyl methacrylates using potassium peroxo monosulphate was studied under Phase transfer conditions using tetrabutyl phosphonium chloride as a phase transfer catalyst. The phase transfer catalyzed polymerization of MMA and EMA system follows a first order dependence with respect to monomer and a half-order with respect to both peroxomonosulphate and phase transfer catalyst. We propose a mechanism involving initiation by the phase transfer peroxomonosulphate radicalanion and termination by the combination of radicals. The results suggested that MMA and EMA polymerization follows similar type of mechanism, although MMA is around 1.2 times (with



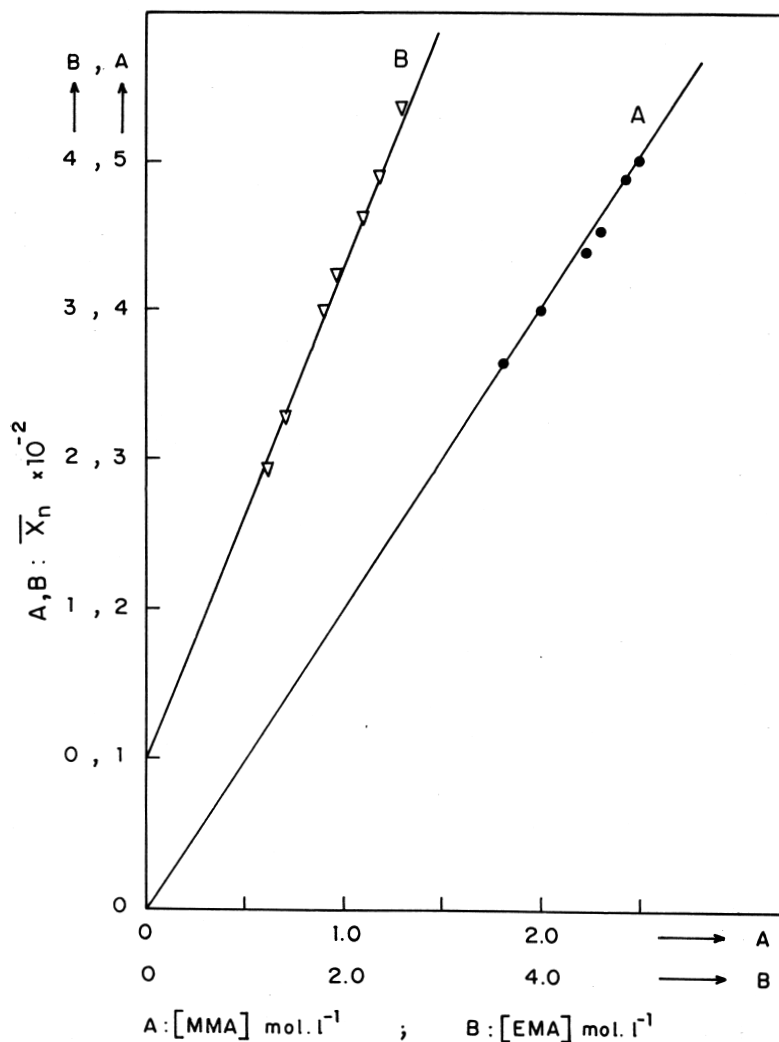


Figure 5. Degree of polymerization. Line A: $\bar{X}_n \times 10^{-2}$ Vs [MMA], mol.l⁻¹. Line B: $\bar{X}_n \times 10^{-2}$ Vs [EMA], mol.l⁻¹.

respect to E_a) more reactive than EMA. The possible reason for the above observation is due to the steric hinderance of the additional methylene group present in EMA hampering the collision with other free radicals in the propagation step of the polymerization.



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Received October 25, 1999

Revision received February 16, 2000



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