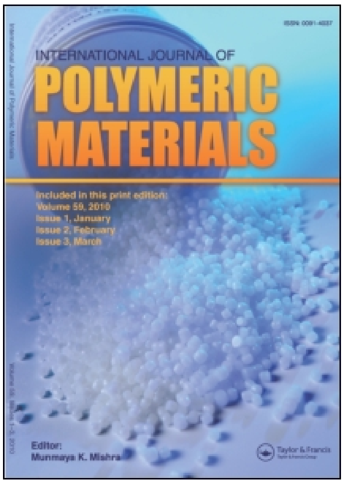

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Phase Transfer Catalysis: Polymerization Kinetics and Mechanism of Methyl Acrylate

H. Thajudeen[a]; V. S. Jamal Ahamed[a]; T. K. Shabeer[a]
[a] Post Graduate and Research Department of Chemistry, The New College, Chennai, Tamilnadu, India

To cite this Article Thajudeen, H. , Jamal Ahamed, V. S. and Shabeer, T. K.(2008) 'Phase Transfer Catalysis: Polymerization Kinetics and Mechanism of Methyl Acrylate', International Journal of Polymeric Materials, 57: 9, 904 — 917
To link to this Article: DOI: 10.1080/00914030802153264
URL: http://dx.doi.org/10.1080/00914030802153264

International Journal of Polymeric Materials, 57:904–917, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914030802153264

Phase Transfer Catalysis: Polymerization Kinetics and Mechanism of Methyl Acrylate

H. Thajudeen
V. S. Jamal Ahamed
T. K. Shabeer
Post Graduate and Research Department of Chemistry,
The New College, Chennai, Tamilnadu, India

Kinetics and mechanism of the free-radical polymerization of methyl acrylate (MA), using potassium peroxomonosulfate (PMS) as a water-soluble initiator in the presence of benzyltributylammonium chloride (BTBAC) as a phase-transfer catalyst (PTC), were studied. The polymerization reactions were carried out under inert and unstirred conditions at a constant temperature of 60 ± 1°C in ethyl acetate/water biphasic medium. The rate of polymerization (R_p) increased with an increase in the concentrations of MA, BTBAC and PMS. The order with respect to the monomer, initiator, and PTC was found to be 1.0, 0.5, and 0.5 respectively. R_p was independent of the ionic strength and pH of the medium. Based on the kinetic evidences a suitable mechanism is proposed.

Keywords: benzyltributylammonium chloride, kinetics, methyl acrylate (MA), phase transfer catalyst, potassium peroxomonosulfate, radical polymerization

INTRODUCTION

The chemistry of polymers is one of the most fascinating and spectacular branches of modern science. Macromolecules form the basis of a variety of major industries such as adhesives, paint, textile and plastic. Reactions between substances located partly in an organic phase and partly in an aqueous phase are frequently slow and ineffective. In order to achieve an efficient reaction in such cases, without the use of solvents that codissolve the reagents, the new technique of phase transfer catalysis was developed.

Received 25 March 2008; in final form 1 April 2008.

Address correspondence to T. K. Shabeer, Post-Graduate and Research Department of Chemistry, The New College, Chennai 600 014, Tamilnadu, India. E-mail: dr_tkshabeer@yahoo.com

Though the first report on phase transfer catalysis had appeared in 1965, the method has been employed by several research groups only after 1969 [1–6]. Owing to its simplicity and the low cost of most of the phase transfer catalysts (PTC), the method has found universal adoption. The literature on the theory and practical applications of phase transfer catalysis has grown very rapidly and has been periodically reviewed [7–12].

Rasmussen and Smith [13] investigated the kinetics of phase transfer catalyzed polymerization of acrylonitrile in the presence of peroxydisulfate (PDS) - Aliquat 336 system. The reaction order with respect to monomer, PTC and $S_2O_8^{2-}$ was 1.6, 0.2 and 0.6, respectively.

Balakrishnan and Jayachandramani [14] investigated the kinetics of phase transfer catalyzed polymerization of MMA in the presence of PDS and triethylbenzylammonium chloride system. Umapathy and Balakrishnan [15] investigated the kinetics of free radical polymerization of methyl methacrylate using $(NH_4)_2S_2O_8$ in the presence of tributylbenzylammonium chloride.

Here, we study the effect of variation in methyl acrylate concentration, peroxomonosulfate concentration, quaternary salt concentration, hydrogen ion concentration, ionic strength and temperature on the rate of polymerization. Based on the kinetic results, a suitable mechanism for the polymerization would be proposed.

EXPERIMENTAL

Polymerization studies were carried out in long Pyrex tubes (4 cm × 20 cm) of about 80 ml capacity with a B-24 quickfit socket fitted with a B-24 cone with a provision for inlet and outlet terminals in order to isolate the reaction mixture from atmospheric oxygen. All the experiments were conducted in a thermostat bath of 20 liter capacity. The temperature of the bath was controlled by a hot wire vacuum switch relay to an accuracy of ±0.10°C using a toluene regulator. Water in the bath was heated electrically and stirred well by a mechanical stirrer for maintaining constant temperature throughout the bath. Experiments were carried out in the temperature range 48–60°C. Nitrogen gas used for deaeration was freed from traces of oxygen and other impurities by passing through four vertical glass tubes containing separately (i) Fieser's solution, (ii) lead acetate solution, (iii) potassium hydroxide solution and (iv) distilled water. The monomer methyl acrylate (Qualigens, Mumbai), benzyltributylammonium chloride (Spectro Chem), potassium peroxomono sulfate (Merck, Mumbai) sulfuric acid (Qualigens, Mumbai) and potassium sulfate

(SD Fine, Mumbai) were used as received. Double-distilled water was used throughout the experiment for the preparation of reagents and solutions.

Polymerization Technique

Polymerization reactions were carried out in the reaction vessels thermostated at the desired temperature. A known amount of monomer, benzyltributylammonium chloride, sulfuric acid and potassium sulfate were taken in the reaction tube and flushed with purified nitrogen gas for about 30 min to ensure an inert atmosphere. A calculated amount of deaerated peroxomonosulfate solution thermostated at the experimental temperature was added to the reaction mixture and simultaneously a stop watch was started. The reaction tubes were then carefully sealed by rubber gaskets to ensure an inert atmosphere. The reaction was arrested by blowing air inside the tube and keeping the reaction vessel in ice cold water for some time.

The polymer was filtered out quantitatively through a crucible (G-3), washed several times with double-distilled water and dried at 50–60°C in a vacuum oven to constant weight. The rate of polymerization was computed from the weight of the polymer formed, using the following relationship:

$$R_p = 1000\,W/VtM$$

where, W = weight of the polymer, V = total volume of the reaction mixture, t = reaction time in seconds, and M = molecular weight of the monomer.

By separate experiments it was confirmed that neither PMS nor BTBAC alone initiated polymerization under the experimental conditions employed.

Analysis of the Results

In order to estimate the limits of consistency in the results, duplicate experiments were carried out under identical conditions and it was found that the R_p values were subjected to the error limits of ±5%. The accuracy of the results was tested by the method of least squares.

RESULTS

The present investigation deals with the kinetics and mechanism of phase transfer catalyst-assisted polymerization of methyl

TABLE 1 Steady State Rate of Polymerization

Time, minutes	$R_p \times 10^5$, $mol{\cdot}dm^{-3}{\cdot}s^{-1}$
15	0.3232
30	0.7012
45	1.3208
60	2.3104
75	3.7429
90	2.2512
105	0.8793
120	0.4132
135	0.2976
150	0.2575
165	0.3229

MA $= 1.1081\,mol{\cdot}dm^{-3}$; PMS $= 2 \times 10^{-2}\,mol{\cdot}dm^{-3}$; BTBAC $= 2 \times 10^{-2}\,mol{\cdot}dm^{-3}$; $H^+ = 0.2\,mol{\cdot}dm^{-3}$; $\mu = 0.66\,mol{\cdot}dm^{-3}$; Temp $= 333\,K$.

acrylate, initiated by benzyltributylammonium chloride–$KHSO_5$ initiator system. The polymerization reactions were carried out in ethyl acetate–water two-phase system under nitrogen atmosphere and unstirred conditions at 60°C. The dependence of the rate of polymerization (R_p) on MA, BTBAC, $KHSO_5$, H^+, ionic strength and temperature was studied.

The general observations made during this investigation are

1. The polymerization reactions were inhibited by the presence of air, oxygen and hydroquinone, showing the free radical nature of polymerization.
2. Photochemical initiation of polymerization by stray light was not observed.
3. Under the experimental conditions no discernible induction period and negligible oxidation of H_2O by $KHSO_5$ were noticed.
4. The polymerization of MA with the BTBAC–$KHSO_5$ initiator system proceeded fast, but in the absence of either BTBAC or $KHSO_5$ no polymer was detected.

The results obtained in this investigation are presented in the form of Tables 1–8 and Figures 1–9.

Steady State Rate of Polymerization

Polymerization reactions were carried out at different time intervals at fixed concentrations of MA, BTBAC, $KHSO_5$, H^+ and ionic strength

TABLE 2 Effect of Variation of [MA] on R_p

[MA], $mol{\cdot}dm^{-3}$	[MA] $mol{\cdot}dm^{-3}$	$R_p \times 10^6$, $mol{\cdot}dm^{-3}{\cdot}s^{-1}$	1 + log [MA]	6 + log R_p
0.7757	0.7757	2.1637	0.8897	0.3352
0.8866	0.8866	2.5433	0.9477	0.4054
0.9974	0.9974	2.8517	0.9989	0.4551
1.1081	1.1081	3.1261	1.0446	0.4950
1.2190	1.2190	3.4682	1.0860	0.5401
1.3298	1.3298	3.8054	1.1238	0.5804

PMS = 2×10^{-2} $mol{\cdot}dm^{-3}$; BTBAC = 2×10^{-2} $mol{\cdot}dm^{-3}$; H+ = 0.2 $mol{\cdot}dm^{-3}$; $\mu = 0.66$ $mol{\cdot}dm^{-3}$; Temp = 333 K.

to arrive at the steady state rate of polymerization. It has been found that at first the polymerization rate increases sharply with time, then decreases and, finally, attains a constant value. Steady state rate of polymerization was found to be attained at about 2 h and 15 min (Table 1, Figure 1). To study the effects of various reaction parameters on the rate of polymerization, the polymerization was conducted for the duration of 2 h and 15 min.

Effect of [MA] on R_p

To find the effect of MA on R_p, the concentration of MA was varied in the range of 0.7757–1.3298 $mol{\cdot}dm^{-3}$ at fixed concentration of the other components. R_p was found to increase with increase of [MA] (Table 2). The slope of the straight line obtained in the plot of log R_p vs log [MA] is equal to 1.0 (Figure 2). The reaction order of 1.0 with

TABLE 3 Effect of Variation of PMS on R_p

$[PMS] \times 10^2$, $mol{\cdot}dm^{-3}$	$[PMS]^{0.5}$ $(mol{\cdot}dm^{-3})^{0.5}$	$R_p \times 10^6$, $mol{\cdot}dm^{-3}.s^{-1}$	2 + log [PMS]	6 + log R_p
1.4	0.1465	2.7422	0.1461	0.4381s
1.6	0.1555	2.8609	0.2041	0.4565
1.8	0.1640	3.0655	0.2553	0.4865
2.0	0.1720	3.2621	0.3010	0.5135
2.2	0.1795	3.3121	0.3424	0.5201
2.4	0.1867	3.4738	0.3802	0.5408

MA = 1.1081 $mol{\cdot}dm^{-3}$; BTBAC = 2×10^{-2} $mol{\cdot}dm^{-3}$; H+ = 0.2 $mol{\cdot}dm^{-3}$; $\mu = 0.66$ $mol{\cdot}dm^{-3}$; Temp = 333 K.

TABLE 4 Effect of Variation of BTBAC on R_p

$[BTBAC] \times 10^2$, $mol \cdot dm^{-3}$	$[BTBAC]^{0.5}$, $(mol \cdot dm^{-3})^{0.5}$	$R_p \times 10^6$, $mol \cdot dm^{-3} \cdot s^{-1}$	2 + log [BTBAC]	6 + log R_p
1.4	0.1183	3.2584	0.1461	0.5130
1.6	0.1265	3.4946	0.2041	0.5434
1.8	0.1342	3.7171	0.2553	0.5702
2.0	0.1414	3.9210	0.3010	0.5934
2.2	0.1483	4.1002	0.3424	0.6128
2.4	0.1549	4.3053	0.3802	0.6340

$MA = 1.1081\,mol \cdot dm^{-3}$; $PMS = 2 \times 10^{-2}\,mol \cdot dm^{-3}$; $H+ = 0.2\,mol \cdot dm^{-3}$; $\mu = 0.66\,mol \cdot dm^{-3}$; Temp = 333 K.

respect to methyl acrylate is further confirmed from the straight line passing through the origin in the plot of R_p vs [MA] (Figure 3).

Effect of [PMS] on R_p

The effect on R_p of varying the $KHSO_5$ was examined by varying $KHSO_5$ in the range of 1.4×10^{-2}–2.4×10^{-2} $mol \cdot dm^{-3}$ at fixed MA, BTBAC, H^+ and ionic strength. R_p increases with increase in the $KHSO_5$ (Table 3). A plot of log R_p vs. log $KHSO_5$ is linear with a slope of 0.5, indicating the half order dependence of R_p on $KHSO_5$ (Figure 4). This is supported by a straight line passing through origin in the plot of R_p vs. $KHSO_5{}^{0.5}$ (Figure 5). The half order dependence of R_p on initiator concentration indicates that the termination is bimolecular [16]. An important characteristic of polymerization of MA is an auto-acceleration or the gel effect [17,18]. It is the autogenous increase in the rate of polymerization and molecular weight observed in media of high viscosity. This effect is more often seen in bulk and high concentration solution polymerization [19]. It is also observed in polymerization reactions involving high conversions [20]. In such

TABLE 5 Effect of Temperature on R_p

T, K	$1/T \times 10^3$, K^{-1}	$R_p \times 10^6$, $mol \cdot dm^{-3} . s^{-1}$	6 + log R_p	9 + log (R_p/T)
321	3.115	2.1869	0.3398	0.8333
325	3.077	2.6171	0.4178	0.9059
329	3.040	2.8609	0.4565	0.9393
333	3.003	3.2696	0.5145	0.9921

$MA = 1.1081\,mol \cdot dm^{-3}$; $PMS = 2 \times 10^{-2}\,mol \cdot dm^{-3}$; $BTBAC = 2 \times 10^{-2}\,mol \cdot dm^{-3}$; $H^+ = 0.2\,mol \cdot dm^{-3}$; $\mu = 0.66\,mol \cdot dm^{-3}$.

TABLE 6 Thermodynamic Parameters

Parameters	Value
Energy of activation, Ea	28.80 kJ.mol^{-1}
Entropy of activation, $\Delta S^{\neq}$	−100.26 EU
Enthalpy of activation, $\Delta H^{\neq}$	26.09 kJ.mol^{-1}
Free energy of activation, $\Delta G^{\neq}$	33.40 kJ.mol^{-1}

cases, the reaction order with respect to initiator was reported to be greater than 0.5. An initiator rate exponent of 0.5 in the present study shows that the gel effect is not observed in this case.

Effect of BTBAC on R_p

It has been observed that increasing BTBAC increases the values of R_p in the employed concentration range of 1.4×10^{-2}–2.4×10^{-2} mol·dm^{-3} [Table 4]. From the slope of bilogarithmic plot of R_p vs BTBAC, the rate exponent with respect to BTBAC was found to be 0.5 [Figure 6]. A straight line passing through the origin in the plot of R_p vs. BTBAC$^{0.5}$ confirms the observed order of 0.5 (Figure 7).

Effect of temperature on R_p

The polymerization was carried out at different temperatures, i.e., 321, 325, 329 and 333 K, at definite concentrations of MA, $KHSO_5$, BTBAC,

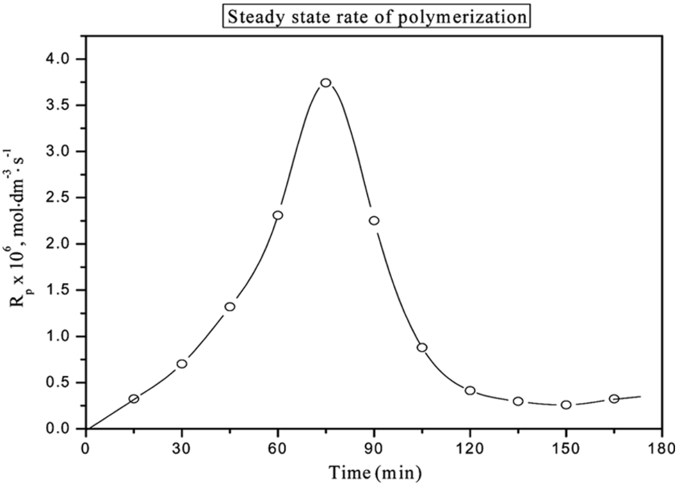

FIGURE 1 Steady state rate of polymerization.

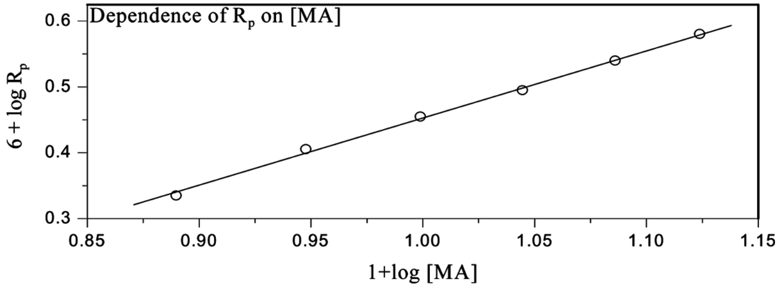

FIGURE 2 Dependence of R_p on [MA].

H^+ and ionic strength. The rate of polymerization increases with temperature (Table 5) (Figure 8). The activation energy for the overall rate of polymerization has been computed from the Arrhenius plot of log R_p vs. 1/T and it was found to be 28.80 kJ·mol^{-1}. The thermodynamic parameters such as $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ have also been calculated, from the Eyring plot of log R_p/T vs 1/T and are presented in Table 6.

Effect of H^+ and of ionic strength on R_p

Variation in either acid strength or ionic strength of the medium had no discernable effect on the rate of polymerization.

DISCUSSION

Reaction Mechanism and Rate Law

The following salient features were observed in the present kinetic investigation of the polymerization of methyl acrylate initiated by $KHSO_5$–BTBAC catalyst system:

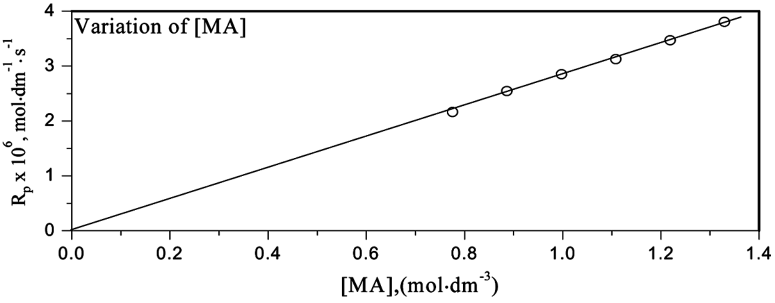

FIGURE 3 Variation of [MA].

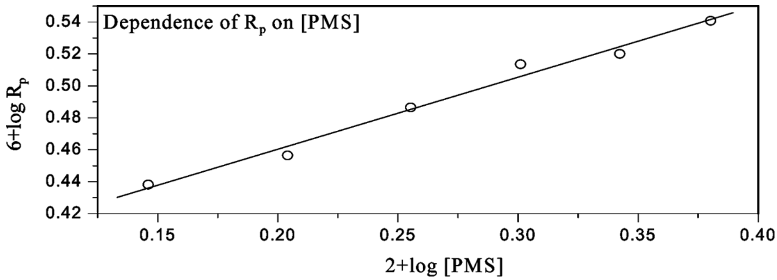

FIGURE 4 Dependence of R_p on PMS.

(i) The reaction exponent with respect to MA = 1.0
(ii) The reaction exponent with respect to $KHSO_5 = 0.5$
(iii) The reaction exponent with respect to BTBAC = 0.5
(iv) R_p is independent of H^+ and ionic strength of the medium.

In the polymerization of methyl acrylate initiated by the $KHSO_5$–BTBAC catalyst system, conducted under unstirred conditions employing equal volumes of aqueous and organic phases, ($V_w/V_o = 1$), the obtained results indicate the following notable points:

1. The mechanism involves a phase transfer of peroxomonosulfate ion from the aqueous phase to the monomer-containing organic phase, facilitated by the quaternary ammonium salt, benzyltrimethylammonium chloride (BTBAC).
2. The quarternary peroxomonosulfate ($QHSO_5$) formed is assumed to be present as ion-pair in the organic phase. The increase in R_p with an increase in $KHSO_5$ and BTBAC may be due to an increase in the amount of $QHSO_5$ transferred to the organic phase, which in turn increases the number of active SO_4^{-} radical ions.

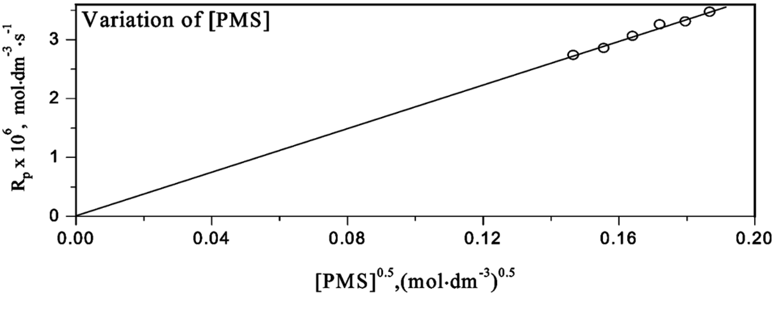

FIGURE 5 Variation of PMS.

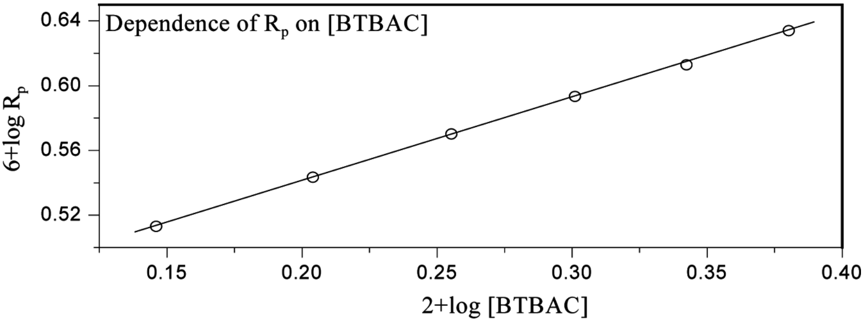

FIGURE 6 Dependence of R_p on [BTBAC].

From the aforementioned points, it is clear that the mechanism involves the formation of quaternary ammonium peroxomonosulfate ion-pair $Q^+HSO_5^-$ in the aqueous layer, and its subsequent transfer to the organic phase. The decomposition of the phase transferred ion-pair $Q^+HSO_5^-$ then results in the production of $Q^+SO_4^{\cdot-}$ that initiates polymerization.

Mechanism

(a) Phase Transfer

$$Q^+_{(w)} + HSO^-_{5(w)} \overset{K}{\rightleftharpoons} Q^+HSO^-_{5(o)} \tag{1}$$

(b) Initiation

$$Q^+HSO^-_{5(o)} \xrightarrow{k_d} Q^+SO^{\cdot-}_{4(o)} + OH^{\cdot} \tag{2}$$

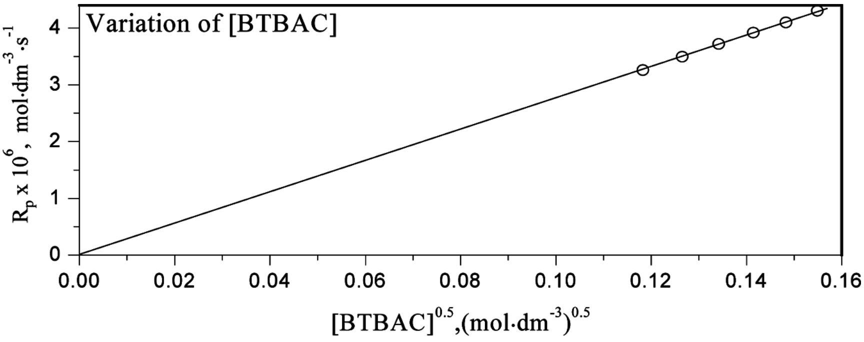

FIGURE 7 Variation of [BTBAC].

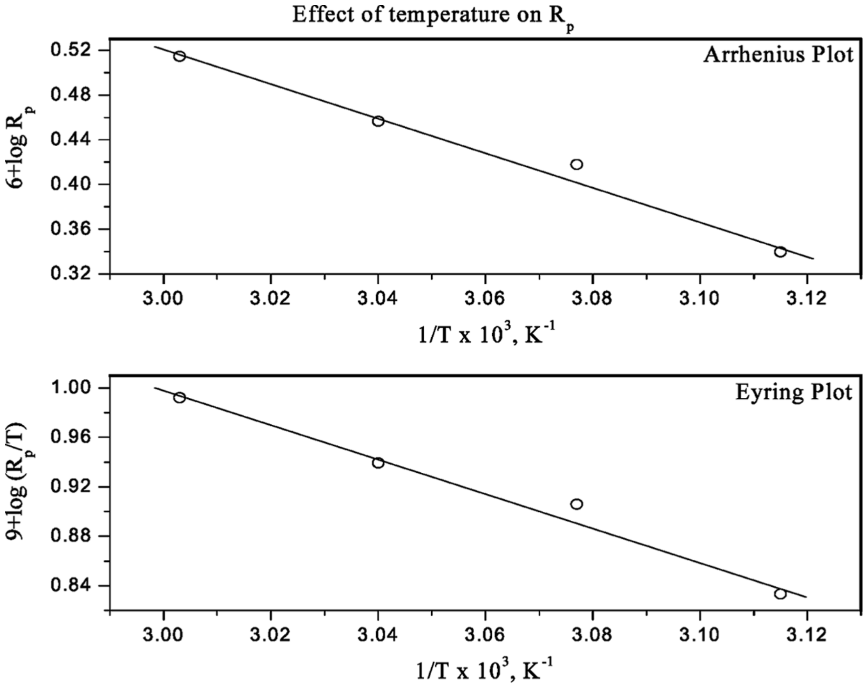

FIGURE 8 Effect of temperature on R_p.

$$Q^+SO_{4(o)}^{\cdot -} + M_o \xrightarrow{k_i} M_{1(o)}^{\cdot}\ (M{-}O{-}SO_3^- Q^+) \tag{3}$$

(c) Propagation

$$M_1^{\cdot} + M \xrightarrow{k_p} M_2^{\cdot}$$

$$\cdots$$

$$\cdots$$

$$M_{n-1}^{\cdot} + M \xrightarrow{k_p} M_n^{\cdot} \tag{4}$$

(e) Termination

$$2M_n^{\cdot} \xrightarrow{k_t} \text{Polymer} \tag{5}$$

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

The rate of initiation is given by

$$R_i = k_i[M][Q^+SO_4^{\cdot -}] \tag{6}$$

$$\frac{d[Q^+SO_4^{\cdot -}]}{dt} = 2k_d[Q^+HSO_5^-] - k_i[M][Q^+SO_4^{\cdot -}] = 0 \tag{7}$$

$$\therefore\ [Q^+SO_4^{\cdot -}] = \frac{2k_d[Q^+HSO_5^-]}{k_i[M]} \tag{8}$$

Considering the equilibrium (1),

$$[Q^+HSO_5^-]_o = k[Q^+]_w\ [HSO_5^-]_w \tag{9}$$

Substituting the value of $[Q^+HSO_5^-]_o$ in Eq. 8 we get,

$$[Q^+SO_4^{\cdot -}] = \frac{2k_dK[Q^+]_w[HSO_5^-]_w}{k_i[M]} \tag{10}$$

Inserting the value of $Q^+SO_4^{\cdot -}$ in Eq. 6,

$$R_i = 2k_d\ K[Q^+]_w[HSO_5^-]_w \tag{11}$$

Rate of termination is given by

$$R_t = 2k_t[M^{\cdot}]^2 \tag{12}$$

At steady-state,

$$R_i = R_t$$

$$2k_d\ K[Q^+]_w[HSO_5^-]_w = 2k_t[M]^2$$

$$\therefore\ [M^{\cdot}] = \frac{(k_d\ K)^{1/2}}{(k_t)^{1/2}} \quad [Q^+]_w^{1/2}[HSO_5^-]_w^{1/2} \tag{13}$$

The expression for the rate of polymerization is

$$R_p = \frac{-d[M]}{dt} = k_p[M][M^{\cdot}] \tag{14}$$

Substituting the value of $[M^{\cdot}]$ from Eq. 13 in Eq. 14,

$$R_p = k_p\frac{(k_d\ K)^{1/2}}{(k_t)^{1/2}} \quad [M][Q^+]_w^{1/2}[HSO_5^-]_w^{1/2} \tag{15}$$

The total concentration of quaternary ammonium ion, $[Q^{+}]_{Total}$ can be given as

$$[Q^{+}]_{Total} = [Q^{+}]_{w} + [Q^{+}HSO_5^{-}]_{o} \tag{16}$$

Substituting the value of $[Q^{+}HSO_5]$ from Eq. 9 gives,

$$[Q^{+}]_{Total} = [Q^{+}]_{w} + K[Q^{+}]_{w}[HSO_5^{-}]_{w} \tag{17}$$

$$[Q^{+}]_{w} = \frac{[Q^{+}]_{Total}}{1 + K[Q^{+}]_{w}[HSO_5^{-}]_{w}} \tag{18}$$

Substitution of the value of $[Q^{+}]_{w}$ in Eq. 15 gives,

$$R_p = k_p \frac{(k_d K)^{1/2}}{(k_t)^{1/2}} \frac{[M][HSO_5^{-}]^{1/2}[Q^{+}]_{Total}^{1/2}}{1 + K[Q^{+}]_{w}[HSO_5^{-}]_{w}} \tag{19}$$

The above expression for R_p explains satisfactorily the experimental observations.

CONCLUSION

The kinetic parameters, such as the rate of polymerization (R_p) of free radical polymerization of methyl methacrylate, increase with increasing concentration of monomer, initiator and catalyst. The hydrogen ion concentration and ionic strength of the medium do not show any appreciable effect on the (R_p). The reaction rate increases with increasing temperature.

REFERENCES

[1] Makosza, M., Serafinowa, B., and Urbanski, T., *Chemie et Industrie (Paris)* **93**, 537 (1965).

[2] Makosza, M. and Serafinowa, B., *Rocz. Chem., 122* **39**, 3 (1965).

[3] Gibson, N. A. and Hosking, J. W., *Aust. J. Chem.* **18**, 123 (1965).

[4] Makosza, M. and Wawrzyniewicz, W., *Tetrahedron Lett.* 4659 (1969).

[5] Makosza, M., *Tetrahedron Lett.* 673 & 677 (1969).

[6] Brandstron, A. and Junggren, U., *Acta Chem. Scand.* **23**, 2204 (1969).

[7] Weber, W. P. and Gokel, G. W. (1978). *Phase Transfer Catalysis in Organic Synthesis*, Springer-Verlag, Berlin.

[8] Starks, C. M. and Liotta, C. (1978). *Phase Transfer Catalysis: Principles and Techniques*, Academic Press, New York.

[9] Keller, W. E. (1979). *Compendium of Phase Transfer Reactions and Related Synthetic Methods*, Fluka, Switzerland.

[10] Dehmlow, E. V. and Dehmlow, S. S. (1980). *Phase Transfer Catalysis*, Springer-Verlag, Weinheim.

[11] Cocange, P., Elguero, J., and Gallo, R., *Heterocycles*, **20**, 1379 (1983).
[12] Freedman, H. H., *Pure & Appl. Chem.* **58**, 857 (1986).
[13] Rasmussen, J. K. and Smith II, H. K. (1984). In *Crown Ethers and Phase Transfer Catalysis in Polymer Science*. L. J. Mathias and C. E. Carraher Jr., Eds., Plenum, New York, pp. 105–119.
[14] Balakrishnan, T. and Jayachandramani, N., *Indian J. Chem.* **35A**, 201 (1996).
[15] Umapathy, M. J. and Balakrishnan, T., *J. Polym. Mater.* **15**, 275, (1998).
[16] George Odian (1981). *Principles of Polymerization*, 2nd Ed. Wiley – Interscience, New York, pp. 190–199.
[17] Schulz, G. V. and Harborth, G., *Makromol. Chem.* **1**, 106 (1947).
[18] Lee, S. I., *Adv. Chem. Ser.* **109**, 78 (1972).
[19] Swift, G. and Hughes, K. A. (1989). *Encyclopedia of Polymer Science and Engineering*, Wiley – Interscience, New York, Vol. 15, p. 409.
[20] Hayden, P. and Melville, H., *J. Polym. Sci.* **43**, 201, 215 (1960).