

# Polymerization of Methacrylamide in the Presence of Ultrasound and Peroxomonosulphate

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**ABSTRACT:** Polymerization of methacrylamide has been carried out in the presence of ultrasound and peroxomonosulphate for the first time. The rate of polymerization and the rate of disappearance of peroxomonosulphate were followed simultaneously. A first order dependence on monomer and half order dependence with respect to peroxomonosulphate were found towards rate of polymerization. However, a first-order dependence on peroxomonosulphate was noted with rate of peroxomonosulphate disappearance. A suitable reaction scheme is suggested to fit with the experimental results. The composite rate constants for the polymerization were evaluated and compared for acrylamide and methacrylamide polymerization in the presence of ultrasound. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 524–529, 2000

## INTRODUCTION

Peroxo salts-initiated polymerization of vinyl monomers is well known and interesting. This led our earlier research team to study the vinyl polymerization of acrylamide<sup>1</sup> and methacrylamide<sup>2</sup> with peroxodisulphate (PDS) as initiator in the inert atmosphere. An acid salt of PDS, namely peroxomonosulphate (PMS), was also used for the polymerization of acrylamide<sup>3</sup> by this research group. Recently Price<sup>4</sup> used ultrasound to decompose peroxodisulphate at ambient temperature and also provided scope for performing polymerization under these conditions, with a faster rate of production of primary radicals. Taking this into account, we have carried out polymerization of acrylamide with PMS,<sup>5</sup> acrylamide with PDS,<sup>6</sup> and methacrylamide with PDS<sup>7</sup> in the presence of an ultrasound of frequency 1 MHz. It would be interesting to compare the kinetic results of the above studies with the one obtained for methacrylamide polymerization and analyzed.

## EXPERIMENTAL

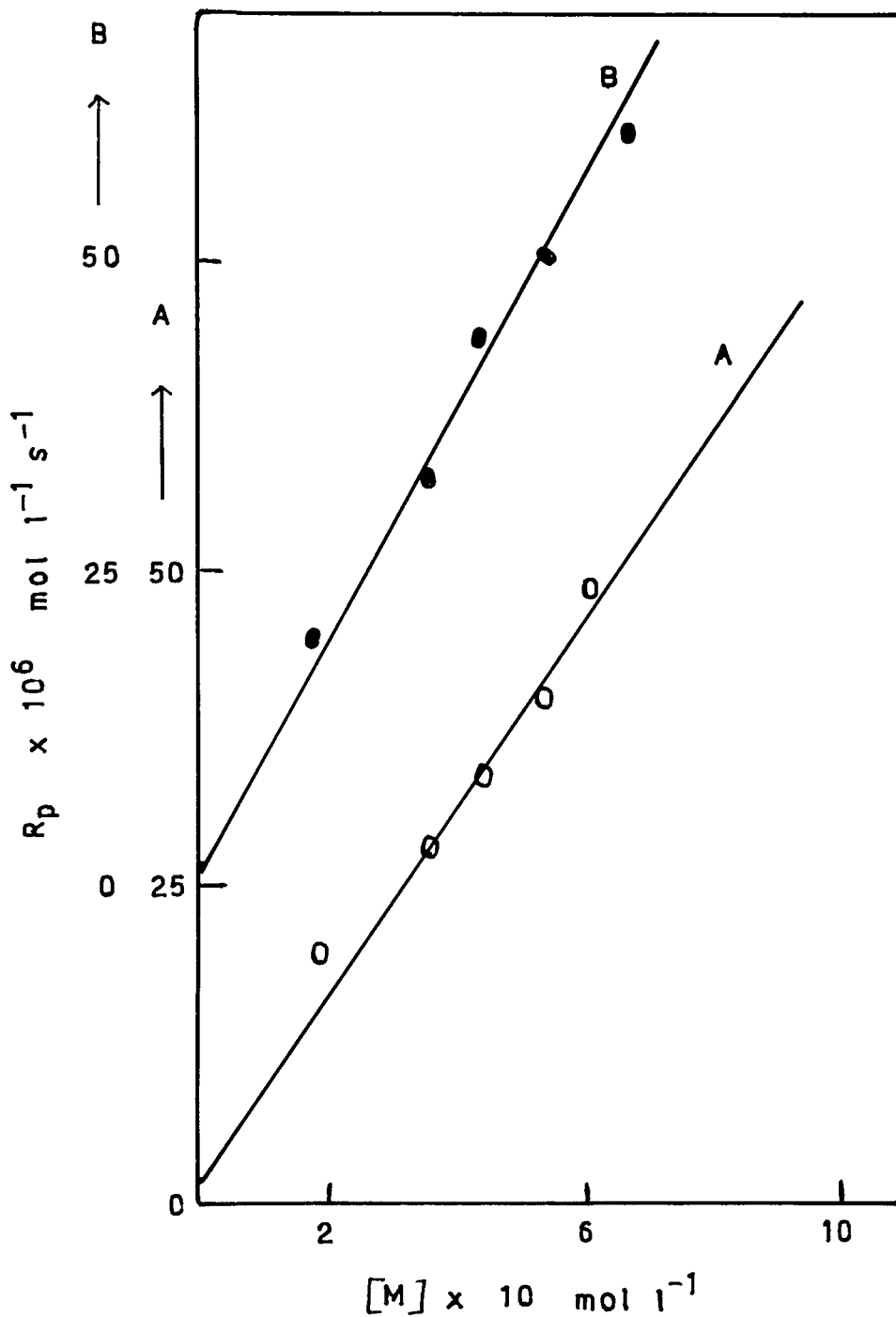
Peroxomonosulphate (Oxone) was a gift sample from Du Pont Co. and was used as obtained. Methacrylamide (E. Merck, Germany) was recrystallized from a mixture of benzene and ethanol (4 : 1). The monomer and the initiator were estimated by bromometry and iodometry as usual. Water, doubly distilled over alkaline permanganate in an all glass apparatus, was used for preparing all the solutions. Other reagents used were of AnalaR grade.

Ultrasonic interferometer (M/s. Mittal Enterprises, Delhi, India) can impart a constant ultrasonic frequency of 1 MHz (intensity was measured as 0.7 mW/cm<sup>2</sup>), and a 12-mL thermostatic cell supplied by this firm was used for the polymerization study. The required amount of the solution of methacrylamide (M) was placed in the cell and maintained at a predetermined temperature using a constant temperature water bath (M/s. Toshniwal Brothers, India). A pre-equilibrated solution of peroxomonosulphate was added into the cell, and the time of passing the sound was taken as the starting time for polymerization. The total volume for the polymerization reaction was kept as 10 mL in all experiments. The rate of polymerization,  $R_p$  ( $-d[M]/dt$ ) was determined by following the concentrations of unreacted

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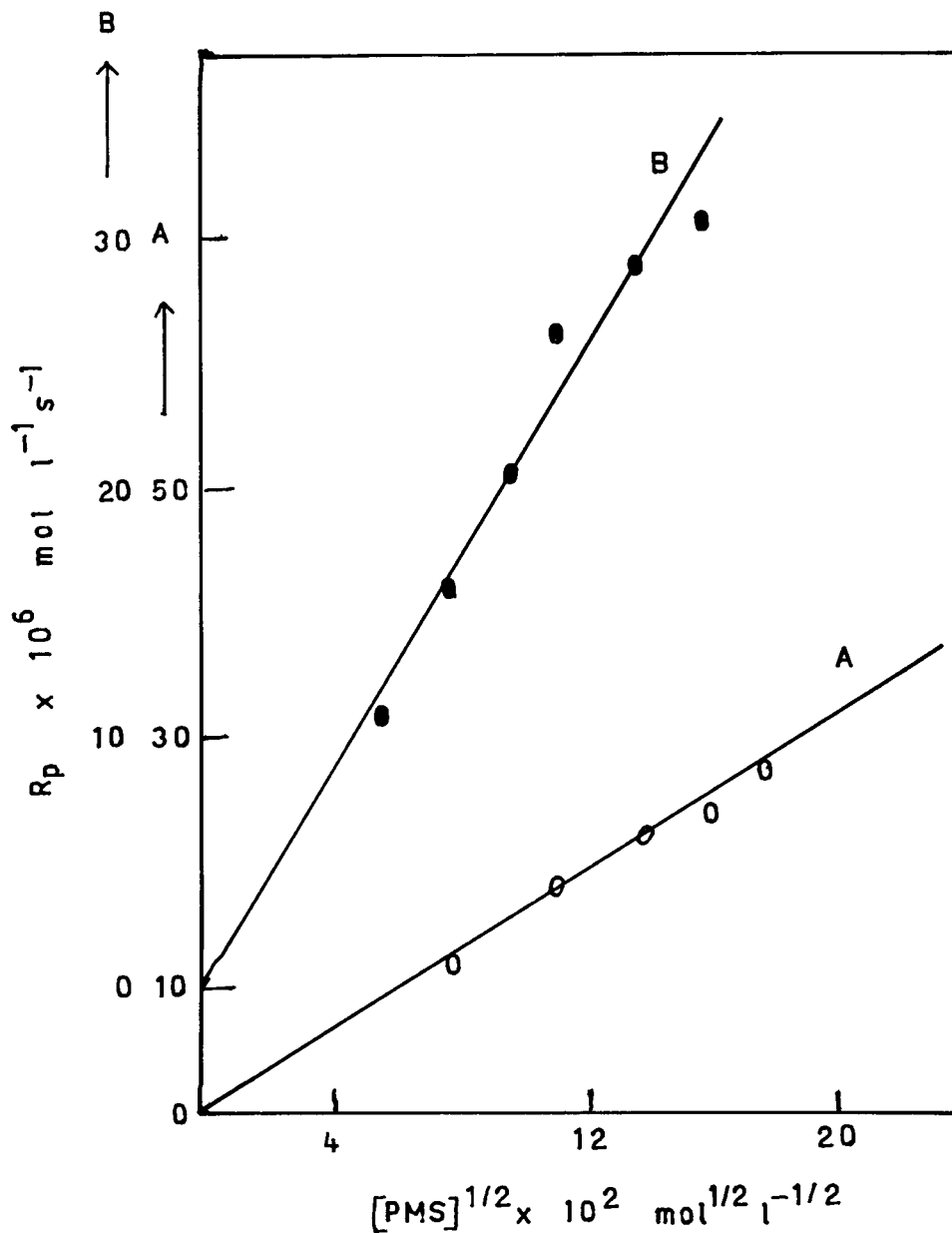


**Figure 1** Dependence of  $R_p$  on  $[M]$  at  $50^\circ\text{C}$  and in the presence of a constant ultrasound frequency of 1 MHz. (A)  $[\text{PMS}] = 12.3 \times 10^{-3} \text{ mol L}^{-1}$ ; (B)  $[\text{PMS}] = 24.7 \times 10^{-3} \text{ mol L}^{-1}$ .

monomer at the end of polymerization time by using bromometry to estimate the double bonds present in it. Rate of disappearance of PMS ( $-d[\text{PMS}]/dt$ ) was also followed simultaneously by estimating the unreacted PMS by iodometry under the same polymerization conditions.

## RESULTS AND DISCUSSION

Polymerization conditions were chosen in such a way that polymerization did not occur in the presence of methacrylamide alone or with both initiator and monomer in the absence of ultrasound.



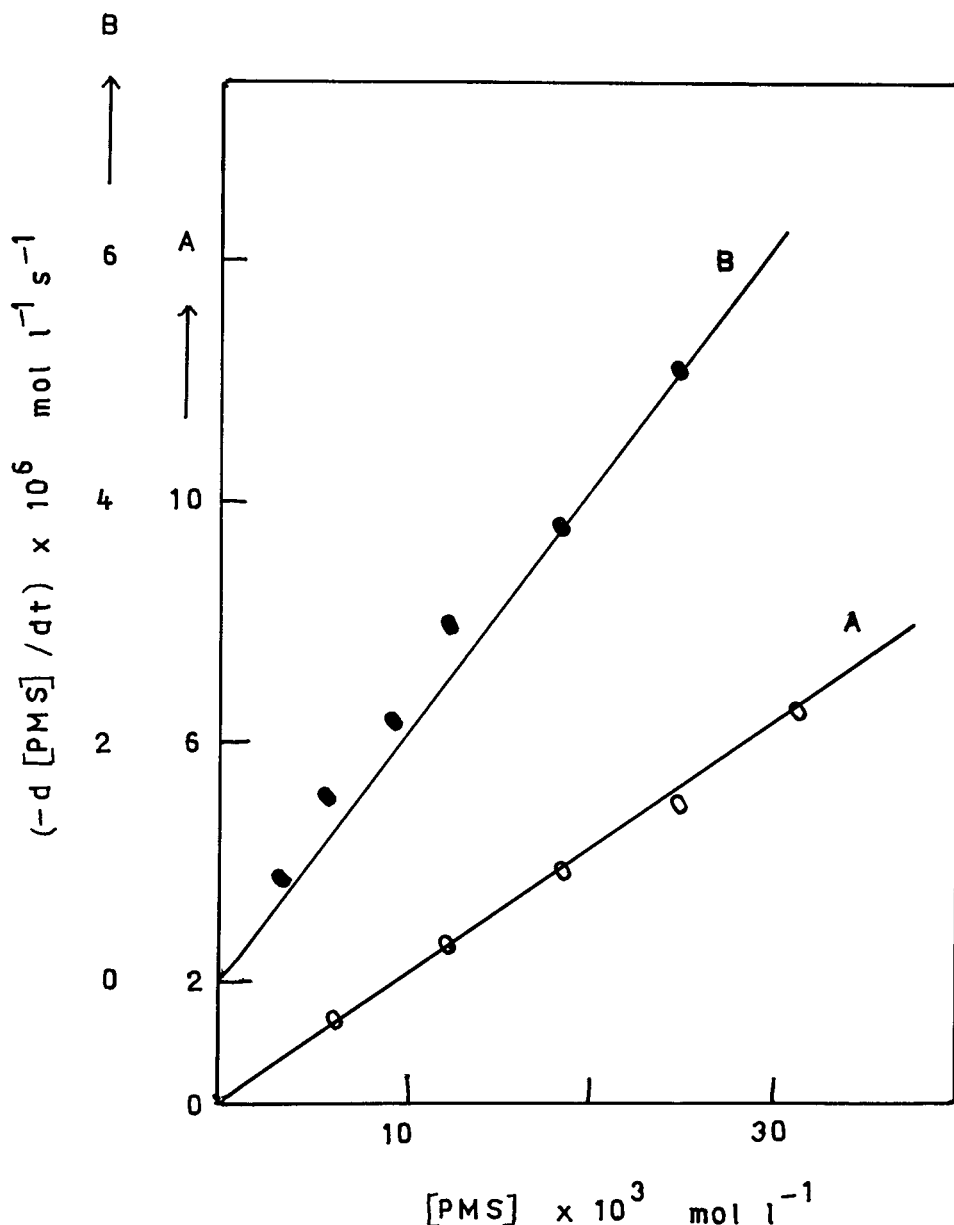
**Figure 2** Dependence of  $R_p$  on  $[PMS]^{1/2}$  at  $50^\circ\text{C}$  and in the presence of a constant ultrasound frequency of 1 MHz. (A)  $[M] = 0.266 \text{ mol L}^{-1}$ ; (B)  $[M] = 0.354 \text{ mol L}^{-1}$ .

However, polymerization did occur in the presence of ultrasound and initiator, and all the polymerization studies were carried out in those conditions, with the range of monomer ( $0.2\text{--}0.6 \text{ mol L}^{-1}$ ) and the initiator PMS ( $6\text{--}30 \times 10^{-3} \text{ mol L}^{-1}$ ) concentration in the presence of ultrasound of a constant frequency 1 MHz at various temperature ( $40\text{--}55^\circ\text{C}$ ).

Rate of polymerization,  $R_p$  was followed for changes in  $[M]$  while keeping  $[PMS]$ , temperature, and frequency of ultrasound constant.  $R_p$  showed an increasing trend with a increase in  $[M]$

(Fig. 1, Plot A). The linear nature of  $R_p$  versus  $[M]$  plot revealed a first-order dependence of  $[M]$  on  $R_p$ . An additional set of experiments under different experimental conditions also obeyed this trend (Fig. 1, Plot B) and confirmed the order with respect to monomer as one. Under the above conditions,  $(-d[PMS]/dt)$  also was followed simultaneously and found to be independent of the change in  $[M]$ , and this was observed in both conditions.

For a range of  $[PMS]$  ( $6\text{--}30 \times 10^{-3} \text{ mol L}^{-1}$ ), the rate of polymerization and the rate of disap-



**Figure 3** The rate of disappearance of PMS at a frequency of 1 MHz and at 50°C. (A)  $[M] = 0.266 \text{ mol L}^{-1}$ ; (B)  $[M] = 0.354 \text{ mol L}^{-1}$ .

pearance of PMS were followed.  $R_p$  was found to show a square root order dependence with  $[PMS]$ , and this was evident from the linear plot  $R_p$  versus  $[PMS]^{1/2}$  (Fig. 2, Plot A). This observation was further supported from a different set of experiments (Fig. 2, Plot B).  $(-d[PMS]/dt)$  was found to increase with  $[PMS]$  in both the above experimental conditions. A first-order dependence was noticed from the direct plot of  $-d[PMS]/dt$  versus  $[PMS]$  (Fig. 3, Plots A and B).

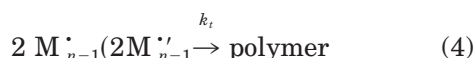
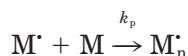
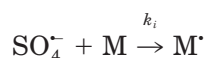
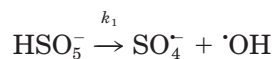
Polymerization also was carried out in the presence of ultrasound with different tempera-

tures.  $R_p$  showed an increasing trend with temperature. The energy of activation for polymerization was found to be  $\approx 4.2 \text{ kcal/mol}$ . However,  $(-d[PMS]/dt)$  did not have much influence with the changes in temperature.

A suitable mechanism for the methacrylamide polymerization in the presence of ultrasound is proposed here on the basis of the results obtained. The decomposition of PMS and consequent production and reaction of hydroxyl radical with monomer was proposed as initiation. This type of initiation was already proposed in our earlier

works for thermal polymerization.<sup>3</sup> However, in this case, the PMS decomposition occurs in the presence of ultrasound. The square root order dependence of [PMS] on  $R_p$  indicates mutual type of termination. The proposed scheme includes the normal propagation path of vinyl polymerization.

### Polymerization Mechanisms



where  $\text{M}^{\cdot} = \text{SO}_4^{\cdot-}\text{CH}_2\text{C}(\text{CH}_3)\text{CONH}_2$  and  $\text{M}'^{\cdot} = \text{HOCH}_2\text{C}(\text{CH}_3)\text{CONH}_2$ .

While proposing the above scheme, the reflection of our results through trial experiments in which no polymerization was observed in the absence of ultrasound also was considered. For the above scheme, assuming steady-state conditions for all the radicals, expressions for  $R_p$  and  $(-d[\text{PMS}]/dt)$  are arrived as

$$R_p = \sqrt{2(k_p/k_t^{1/2})k_1^{1/2}[\text{M}][\text{PMS}]^{1/2}} \quad (5)$$

$$(-d[\text{PMS}]/dt) = k_1[\text{PMS}] \quad (6)$$

The above derived eqs. (5) and (6) are in good agreement with our observed experimental results, such as first-order dependence of  $R_p$  on [M] (Fig. 1), square root order dependence of  $R_p$  on  $[\text{PMS}]^{1/2}$  (Fig. 2), and first-order dependence of [PMS] on  $(-d[\text{PMS}]/dt)$  (Fig. 3). The above two equations are used to evaluate the composite and individual rate constants for further analysis.

### Evaluation of Rate Constants

The validity of expressions (5) and (6) for  $R_p$  and  $(-d[\text{PMS}]/dt)$  can be tested by evaluation of rate parameters. For this purpose, the slope of the linear plots  $R_p$  versus [M] (Fig. 1),  $R_p$  versus  $[\text{PMS}]^{1/2}$  (Fig. 2), and  $(-d[\text{PMS}]/dt)$  versus [PMS] (Fig. 3) were used. The slopes are used to evaluate the composite rate constant  $(k_p/k_t^{1/2})k_1^{1/2}$

**Table I** Evaluation of Composite Rate Constants for the Polymerization of Methacrylamide in the Presence of Ultrasound (1 MHz) and Peroxomonosulphate at 50°C

[M] (mol L <sup>-1</sup> )	[PDS] × 10 <sup>3</sup> (mol L <sup>-1</sup> )	Slope	$k^*$ (mol <sup>-1/2</sup> L <sup>1/2</sup> s <sup>-1</sup> ) <sup>a</sup>	$k_1$ (s <sup>-1</sup> )	$(k_p/k_t^{1/2})$ (mol <sup>-1/2</sup> L <sup>1/2</sup> s <sup>-1/2</sup> )
Varied over a range of 0.2–0.6	12.3	$7.40 \times 10^{-5} \text{ s}^{-1}$	$5.23 \times 10^{-4}$	—	0.03
	12.3	$2.70 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$	—	$2.18 \times 10^{-4}$	—
	24.7	$9.25 \times 10^{-5} \text{ s}^{-1}$	$4.17 \times 10^{-4}$	—	0.03
	24.7	$5.00 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$	—	$2.03 \times 10^{-4}$	—
0.266	Varied over a range (6–30)	$1.60 \times 10^4 \text{ mol}^{-1/2} \text{ L}^{1/2} \text{ s}^{-1}$	$4.26 \times 10^{-4}$	—	0.03
		$2.15 \times 10^{-4} \text{ s}^{-1}$	—	$2.15 \times 10^{-4}$	—
0.354		$2.05 \times 10^{-4} \text{ mol}^{-1/2} \text{ L}^{1/2} \text{ s}^{-1}$	$4.09 \times 10^{-4}$	—	0.03
		$2.20 \times 10^{-4} \text{ s}^{-1}$	—	$2.20 \times 10^{-4}$	—

<sup>a</sup> Where  $k^* = (k_p/k_t^{1/2})k_1^{1/2}$ .

**Table II Composite and Individual Rate Constants for Vinyl Monomers in the Presence of Ultrasound and Peroxo Salts**

	Acrylamide and PMS	Methacrylamide and PMS	Methacrylamide and PDS
$k_1$ ( $s^{-1}$ )	$2.02 \times 10^{-4}$ at 40°C	$2.14 \times 10^{-4}$ at 50°C	$6.24 \times 10^{-5}$ at 50°C
$(k_p/k_t^{1/2})^a$ ( $mol^{-1/2} L^{1/2} s^{-1/2}$ )	0.12 (4.73)	0.03 (0.2)	0.05

<sup>a</sup>  $k_p/k_t^{1/2}$  values in parentheses are taken from Ref. 8.

and  $k_1$  by properly substituting the other experimental quantities maintained during polymerization (Table I). The consistency of the values of the composite rate constant  $(k_p/k_t^{1/2})k_1^{1/2}$  and  $k_1$  obtained through  $R_p$  and  $(-d[PMS]/dt)$  measurements independently supports the proposed reaction scheme. The average value of this composite rate constant was found to be  $4.44 \times 10^{-4} mol^{-1/2} L^{1/2} s^{-1}$ , and the average  $k_1$  value was found to be  $2.14 \times 10^{-4} s^{-1}$ . This  $k_1$  value is not only higher than the rate constant for the simple decomposition of peroxosalts<sup>1</sup> but coincides ( $2.02 \times 10^{-4} s^{-1}$ ) with acrylamide polymerization<sup>5</sup> with PMS. This  $k_1$ , on the other hand, when compared with methacrylamide polymerization<sup>7</sup> with PDS ( $0.63 \times 10^{-4} s^{-1}$ ) was found to be higher. This points out that PMS decomposes more effectively than PDS to produce primary radicals in the presence of ultrasound.

Upon substitution of  $k_1$  value in the composite rate constant  $(k_p/k_t^{1/2})k_1^{1/2}$ , the value of  $(k_p/k_t^{1/2})$  for the polymerization of methacrylamide in the presence of ultrasound and PMS was evaluated and presented in Table I.

This observed lower value for  $(k_p/k_t^{1/2})$  in comparison with the literature value<sup>8</sup> and Dainton<sup>9</sup> value points out the possibility of reaction such as



Remy et al.<sup>10</sup> have also reported the reaction between sulphate ion radical and the amide group of the growing radical, which results in the formation of a branched structure for the polymer. This

kind of observation was also noticed recently in this laboratory when acrylamide<sup>5,6</sup> and methacrylamide<sup>7</sup> were polymerized in the presence of ultrasound and peroxy salts. Further, the lowering of  $(k_p/k_t^{1/2})$  for acrylamide polymerization was greater (nearly 40 times) compared with that for methacrylamide (7 times). This obviously means that similar types of reactions were more facile in the case of the acrylamide–PMS system than that in the methacrylamide–PMS system in the presence of ultrasound (Table II).

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