Polymerization of Methyl Acrylate in the Presence of Ultrasound and Peroxodisulfate

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ABSTRACT: A systematic polymerization kinetic study of methyl acrylate with an added initiator, peroxodisulfate, in the presence of low-power ultrasound was done. The polymerization experiments were conducted at various concentrations of monomer and initiator at different temperatures (303–323 K). The polymerization was found to proceed without an induction period, and the steady state was attained in a fairly short time. The rate of monomer disappearance showed a second-order dependence on monomer concentration. The chain lengths of the polymer were calculated, and we found that the chain length increased with increasing monomer concentration and decreased with increasing initiator concentration. The reaction scheme proposed is based on the kinetic studies that indicated linear termination by sulfate-ion-radical-incorporating direct reaction between the monomer and the initiator. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1545–1549, 2008

Key words: activation energy; addition polymerization; kinetics (polym.)

INTRODUCTION

The polymerization of vinyl monomers is well-known and interesting with peroxo salt initiated polymerization. Isoelectronic peroxo salts, namely, peroxodisulfate (PDS) and peroxomonosulfate, have been used for the polymerization of vinyl monomers, acrylamide,[1] and methacrylamide[2] in inert atmospheres. Ultrasound was used to decompose PDS,[3] and this provided a scope for polymerization under this atmosphere with a faster rate of production of primary radicals. With this advantage, we carried out vinyl polymerization with PDS[4,5] and peroxomonosulfate[6,7] in the presence of ultrasound with a frequency of 1 MHz and a 5.5-W/cm² power output. The process involved here was free-radical addition polymerization. In continuation of our polymerization studies on vinyl monomers, in this study, we took methyl acrylate (MA), a methyl ester of acrylic acid, again a vinyl monomer, and studied the polymerization reaction kinetics under the influence of ultrasound with a frequency of 1 MHz and a 5.5-W/cm² power output and analyzed.

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EXPERIMENTAL

PDS of potassium salt was a guaranteed reagent (E-Merck, Mumbai, India) and was used after recrystallization in water. The monomer MA and initiator PDS were estimated by bromometry and iodometry. Water, doubly distilled over alkaline permanganate in an all-glass apparatus, was used to prepare all of the solutions. All other reagents used were Analar grade (E-Merck).

An ultrasonic interferometer, which could impart a constant ultrasonic power of 5.5 W/cm² at a 1-MHz frequency into a solution kept in a 12-mL thermostatic cell (M/S Mittal Enterprises, New Delhi, India), was used for the polymerization study. The required amount of an aqueous solution of MA was placed in the thermostatic cell and maintained at a predetermined temperature with a constant-temperature water bath (M/S Toshniwal Brothers, Delhi, India). A preequilibrated PDS solution was added to the cell, and the time of switching on the power supply of the ultrasonic interferometer was taken as the starting time for polymerization. The total volume of the polymerization reaction was kept as 10 mL in all experiments. We determined the rate of monomer disappearance ($R_p = -d[\text{MA}]/dt$ [t = 30 min]) by following the concentration of remaining monomer at the end of the polymerization time by bromometry to estimate the double bonds present in the monomer, and the rate of PDS disappearance ($-d[\text{PDS}]/dt$) was followed for the polymerization conditions
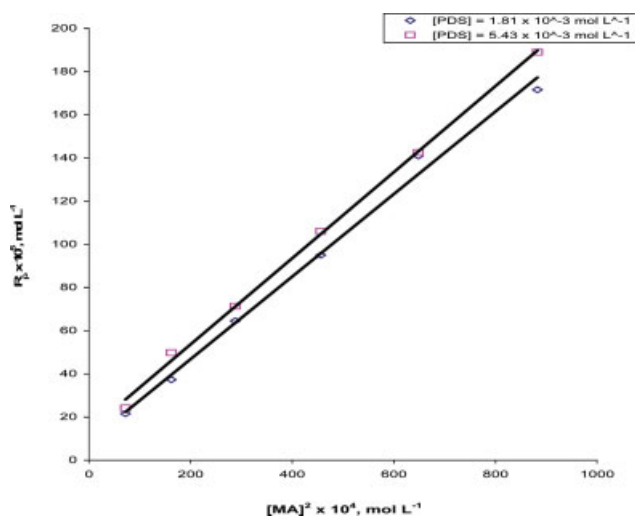
Figure 1 Variation of R_p with $[MA]^2$ for [PDS] = 1.81 × 10^{-3} mol/L and [PDS] = 5.43 × 10^{-3} mol/L at T = 303 K. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

separately by estimation of the concentration of the unreacted PDS by iodometry. Duplicate runs were performed, and the results were obtained within experimental error (± 3%).

RESULTS AND DISCUSSION

Polymerization conditions were so chosen in such a way that polymerization did not occur in the presence of MA alone or with both initiator and monomer in the absence of ultrasound. However, polymerization did occur in the presence of ultrasound and the initiator, and all the polymerization studies were carried out under those conditions, with the range of monomer (MA) equal to 4.0–26.0 × 10^{-2} mol/L and the range of initiator (PDS) equal to 4.0–12.0 × 10^{-3} mol/L in the presence of ultrasound of a constant frequency of 1 MHz in the temperature range 303–323 K.

The polymerization took place without an induction period, and a steady state rate was obtained within a short period.

The rate of monomer disappearance (R_p = $-d[MA]/dt$) was followed for various [MA] values with [PDS], temperature, and frequency of ultrasound kept constant. R_p showed an increasing trend with increasing [MA] but a square dependence on monomer disappearance (Fig. 1). The linear nature of this clearly indicated the second-order dependence on MA but gave a small intercept on the y axis. An additional set of experiments under different experimental conditions also obeyed this trend and confirmed the order with respect to the monomer as 2 (Fig. 1).
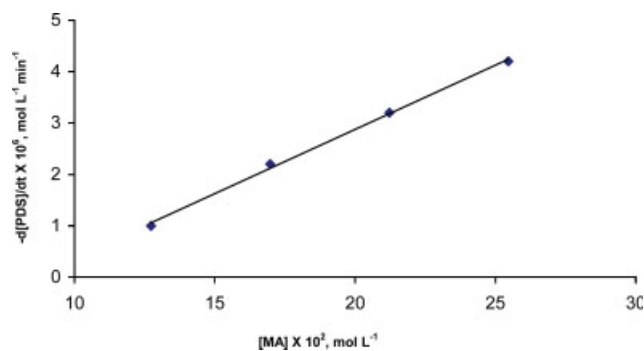

Figure 2 Variation of $-d[PDS]/dt$ with [MA] for [PDS] = 1.81 × 10^{-3} mol/L at T = 303 K. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

The rate of PDS disappearance ($-d[PDS]/dt$) was followed for various monomer concentrations separately at a fixed frequency in the presence of ultrasound and PDS. The $-d[PDS]/dt$ values increased linearly with increasing [MA]. The plot of $-d[PDS]/dt$ versus [MA] (Fig. 2) was linear, which suggested a first-order dependence on the monomer.

For a range of [PDS] values, the rate of monomer disappearance (R_p) was followed and was found to be independent of initial [PDS]. This observation was further supported from the results of a different set of experiments.

The rate of disappearance of PDS was also followed for the changes in [PDS] at a fixed monomer concentration separately in the presence of ultrasound of fixed frequency. The ($-d[PDS]/dt$) values increased linearly with increasing [PDS]. A first-order dependence was inferred from the linear plot of $-d[PDS]/dt$ versus [PDS] (Fig. 3).

The polymerization of MA was also carried out at different temperatures with all other conditions kept constant. R_p showed an increasing trend with increasing temperature (Table I).
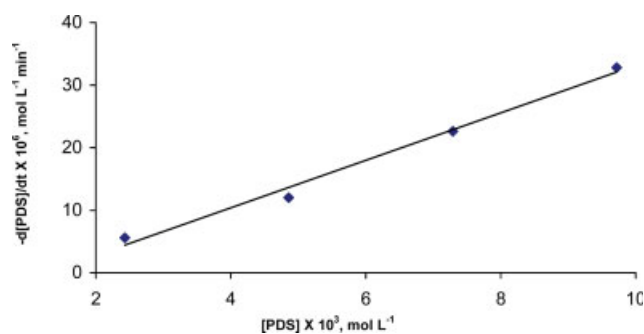

Figure 3 Variation of $-d[PDS]/dt$ with [PDS] for [MA] = 21.22 × 10^{-2} mol/L at T = 303 K. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

TABLE I
Rate of Polymerization for Two Different Experimental Conditions in the Presence of Ultrasound (1 MHz) and PDS

Temperature (K)	[MA] = 16.97×10^{-2} mol/L [PDS] = 5.31×10^{-3} mol/L $R_p \times 10^5$ (mol L min^{-1})	[MA] = 21.2×10^{-2} mol/L [PDS] = 3.54×10^{-3} mol/L $R_p \times 10^5$ (mol L min^{-1})
303	65.0	84.5
308	75.0	112.0
313	94.7	127.8
318	109.6	154.9
323	128.7	164.7

In the case of vinyl polymerization, the initiation step involved the formation of primary radicals and/or the involvement of direct interactions between the initiator and monomer for initiation followed by propagation. The termination of the growing chains may have been affected in general by mutual type. If the initiation was by primary radicals with mutual termination, the first-order dependence of monomer should have been observed, and if the initiation step involved a direct interaction between the initiator and monomer with mutual termination, three-halfth-order dependence on the monomer should have been obtained. The observed second-order dependence on the monomer ruled out the mutual type of termination. Again, the independence of [PDS] on the rate of monomer disappearance observed was also not supportive of the mutual type of termination.

A clear unusual second-order dependence on [MA] independent of initial [PDS] was of great significance because it completely ruled out the case of termination in our system by mutual type, which would have required either a first- or three-halfth order for the monomer disappearance but with linear-type termination. Furthermore, the intercept on the y axis may have been due to simultaneous initiation by hydroxyl radicals and/or a side reaction involving the monomer, as observed in our earlier studies.[4,5]
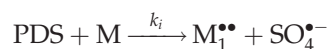
We used a plausible mechanism to attempt to account for the previous experimental results. In this study, the clear first-order dependence of $-d[\text{PDS}]/dt$ on [MA] (Fig. 2) indicated the direct involvement of the monomer in initiation. This obviously indicated the following type of reaction as initiation:
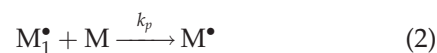
$$\text{PDS} + \text{M} \xrightarrow{k_i} \text{M}_1^{\bullet\bullet} + \text{SO}_4^{\bullet-} \quad (1)$$

where M is monomer, k_i is the individual rate constant for initiation. This type of initiation was also observed earlier in an aqueous thermal vinyl polymerization. However, this same reaction with a different rate (8.52×10^{-3} mol^{-1} L min^{-1}) was observed in our earlier study[4] with a 1-MHz frequency. If this was a case of

initiation and usual mutual termination, the system should have shown a three-halfth-order dependence of the monomer and a square-root-order dependence of PDS. The rate of monomer disappearance in this study followed square order on the monomer MA, which ruled out the mutual type of termination. With this and also the observed second-order dependence of the monomer in view, the following mechanistic scheme in the presence of ultrasound and PDS is proposed.

Initiation

$$\text{PDS} + \text{M} \xrightarrow{k_i} \text{M}_1^{\bullet\bullet} + \text{SO}_4^{\bullet-}$$

Propagation

$$\text{M}_1^{\bullet} + \text{M} \xrightarrow{k_p} \text{M}^{\bullet} \quad (2)$$

$$\text{M}_{n-1}^{\bullet} + \text{M} \xrightarrow{k_p} \text{M}_n^{\bullet} \quad (3)$$

Termination

$$\text{M}_n^{\bullet} + \text{SO}_4^{\bullet} \xrightarrow{k_t} \text{Polymer} \quad (4)$$

where k_i, k_p, and k_t refer to the rate of initiation, propagation, and termination, respectively.

With a steady state assumption of all the radicals present, we arrive at eqs. (5)–(7) for the rate of monomer disappearance, initiator disappearance, and chain length (n), respectively

$$-d[\text{MA}]/dt = R_p = (k_p/k_t) \times k_i[\text{MA}]^2 \quad (5)$$

$$-d[\text{PDS}]/dt = k_i[\text{PDS}][\text{MA}] \quad (6)$$

$$n = \{(k_p/k_t) \times k_i[\text{MA}]^2\}/(k_i[\text{PDS}][\text{MA}])$$

$$n = (k_p/k_t)[\text{MA}]/[\text{PDS}] \quad (7)$$

The derived eqs. (5) and (6) were consistent with the observed experimental results, namely, the square dependence of R_p on the monomer (Fig. 1) and the first-order dependence of the monomer and initiator on the rate of initiator disappearance (Figs. 2 and 3).

Evaluation of the rate constants

The validity of eqs. (5) and (6) could be tested individually by the evaluation of rate parameters. The slope of the plot R_p versus [MA]^2 at 303 K was used to evaluate the composite rate constant for two different experimental conditions (Fig. 1). The composite rate constants were found to be 18.5×10^{-3} and

TABLE II
Effect of the Monomer Concentration on n at 303 K

[PDS] = 5.43×10^{-3} mol/L		[PDS] = 1.81×10^{-3} mol/L
[MA] $\times 10^2$ (mol/L)	n	n
8.48	17.47	52.53
12.73	26.21	78.74
16.97	35.06	105.06
21.22	43.79	131.26
25.46	52.53	157.58
29.71	61.26	183.79

20.0×10^{-3} mol^{-1} L min^{-1}, and the average value was 19.3×10^{-3} mol^{-1} L min^{-1}. Such composite rate constants could also be calculated from the PDS variation, and they were found to be 18.5×10^{-3} and 16.3×10^{-3} mol^{-1} L min^{-1}. The average value turned out to be 17.4×10^{-3} mol^{-1} L min^{-1} at 303 K. The consistency of the values of the composite rate constant obtained through R_p and $-d$[PDS]$/dt$ supported the proposed reaction scheme.

The plot R_p versus [MA]^2 resulted in a small positive intercept. This intercept may have been caused by the initiation of the hydroxyl radical. Such a positive intercept for vinyl polymerization with metal ions was also reported,[8] and it was suggested that the intercept may have been due to hydroxyl radical initiation and/or side reactions in addition to linear termination by the sulfate ion radical.

k_i could be obtained from the plots $-d$[PDS]$/dt$ versus [MA] (Fig. 2) and $-d$[PDS]$/dt$ versus [PDS] (Fig. 3). The values of k_i from the monomer variation were found to be 13.3×10^{-3} and 17.9×10^{-3} mol^{-1} L min^{-1} from the PDS variation. The average k_i value was found to be 15.6×10^{-3} mol^{-1} L min^{-1} at 303 K.

The consistent composite rate constant ($k_i k_p/k_t$) value 17.4×10^{-3} mol^{-1} L min^{-1} and k_i value 15.6×10^{-3} mol^{-1} L min^{-1}, obtained independently, supported the proposed reaction scheme. From these values, k_p/k_t was calculated and was found to be 1.12 at 303 K.

This k_p/k_t value (1.12) at 303 K in the presence of ultrasound was lower than the reported[8] values (1.70 in HClO$_4$ at 308 K and 1.11 at 308 K in nitric acid medium). This kind of lower value was also noticed in this laboratory when acrylamide[4] and methacrylamide[5] were polymerized in the presence of ultrasound and peroxo salts. This observed lower k_p/k_t value pointed out the possibility of other reactions. The initiation by hydroxyl radical in addition to sulfate ion radical may have been the possible reason. Furthermore, the lower k_p/k_t value indicated that k_i may have been higher.

k_i in this study was 15.6×10^{-3} mol^{-1} L min^{-1}. This higher value was quite different from the k_i obtained[5] when methacrylamide was used as a monomer (3.18×10^{-3} mol^{-1} L min^{-1}), wherein the

decomposed PDS alone was involved in the initiation, whereas in the case of acrylamide[4] polymerization (8.53×10^{-3} mol^{-1} L min^{-1}), the initiation was the decomposition of PDS along with the direct reaction between the monomer and PDS, but for these two cases, the termination was mutual one. However, in this study, higher and different k_i and k_p/k_t values suggested that the termination may have been different from the mutual one we expected. Hence, we conclude and propose a reaction scheme with linear termination by sulfate-ion-radical-incorporating initiation by a direct reaction between the monomer and PDS. Furthermore, the observed unusual second-order dependence of R_p on the monomer and independent of PDS concentration also supports our proposal.

The higher k_i value (15.6×10^{-3} mol^{-1} L min^{-1}), in this case in combination with the linear nature of the plot of R_p versus [MA],[2] ruled out the initiation by sulfate ion radical, namely

$$S_2O_8^{2-} \text{(PDS)} \longrightarrow 2SO_4^{\bullet -}$$
$$SO_4^{\bullet -} + M \longrightarrow M_1^{\bullet -}$$
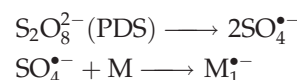
where $M_1^{\bullet -}$ = SO$_4$—CH$_2$—CHCOOCH$_3$. The rate of monomer disappearance (R_p) was followed at different temperatures (303–323 K), and they are presented in Table I. From the Arrhenius plot (log R_p vs $1/T$ [T = absolute temperature]), the activation energy (E_a) for the overall polymerization was calculated. The E_a values for two different experimental conditions were 6.4 and 7.4 kcal/mol. Similarly, the enthalpy and entropy of activation were calculated from the Eyring plot [log (R_p/T) vs $1/T$]. The slope gave enthalpy values, which were found to be 6.4 and 7.0 kcal/mol for these two different sets of experiments. From the intercept, entropy were calculated and were found to be -72.3 and -71.6 cal deg^{-1} mol^{-1}.

The observed E_a lower (7 kcal/mol) than the thermal polymerization[8] of MA (17 kcal/mol) again indicated that the ultrasound enhanced R_p and initiation in a combined way.

n study

As expected, n was calculated from eqs. (5) and (6). Knowing the k_p/k_t value at 30°C and from the

TABLE III
Effect of the Initiator Concentration on n at 303 K

[MA] = 18.7×10^{-2} mol/L		[MA] = 21.2×10^{-2} mol/L	
[PDS] $\times 10^3$ (mol/L)	n	[PDS] $\times 10^3$ (mol/L)	n
4.82	43.46	2.43	97.66
7.23	29.73	4.86	48.63
9.64	21.73	7.29	32.59
12.10	17.36	9.29	24.42
		12.16	19.49

monomer variation at the particular [PDS], we calculated n. We found that the obtained length increased as the monomer concentration increased. To determine reliability, a second set of experiments was also carried out, and we found the same trend (Table II). Similarly, from the initiator variation, n was calculated, and we found that n decreased with increasing initiator concentration (Table III). These findings were in agreement with the requirements of the kinetic scheme.

CONCLUSIONS

The polymerization reaction in the presence of ultrasound with MA and PDS occurred with linear termination with a sulfate-ion-radical-incorporating direct reaction between MA and PDS in the initiation steps. The unusual second-order dependence on the monomer concentration independent of the PDS concentration was the novel feature of the use of ultrasound for polymerization.

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