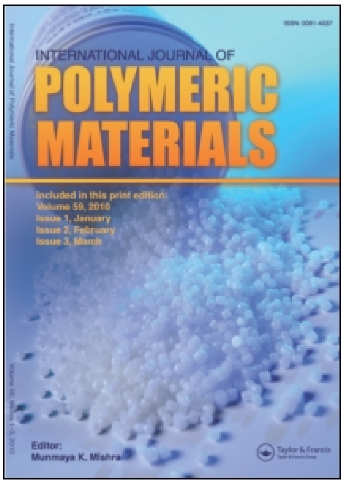

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Comparison of Redox Initiators Reactivities in the Grafting of Methyl Methacrylate onto Chitin

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Comparison of Redox Initiators Reactivities in the Grafting of Methyl Methacrylate onto Chitin

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Relative reactivities of potassium persulfate (KPS) and ferrous ammonium sulfate-potassium persulfate (FAS-KPS) systems, in aqueous medium, as initiators for grafting of methyl methacrylate (MMA) onto chitin, were studied. Evidence of grafting was obtained from IR spectroscopic measurements of the grafted and ungrafted chitin. To compare the efficiency of both redox initiators, a systematic study was carried out to optimize the grafting yield by varying reaction conditions such as initiator, monomer and chitin concentrations as well as reaction time and temperature. Under optimum polymerization conditions 94.5% grafting was obtained by using KPS while up to 352% grafting was reached when FAS-KPS redox system was used. The apparent activation energy, in the case of the FAS-KPS initiated grafting, was estimated to be 23 Kcal/mol. The grafted chitin is insoluble in most solvents, as chitin, but show enhanced affinity for some organic solvents.

KEY WORDS Chitin, redox initiators, graft copolymer, methylmethacrylate.

INTRODUCTION

Redox initiators are capable of initiating vinyl polymerization with few side reactions and often they are used instead of conventional radical initiators for grafting a variety of monomers onto natural polymers. Among redox initiators, KPS is frequently used in aqueous solution for this purpose.[1-5] Ion radical sulfate ($SO_4^{\cdot -}$) produced during thermal decomposition of persulfate is capable of initiating vinyl polymerization. On the other hand, the presence of a reducing agent, such as Fe^{2+}, results in obtaining higher grafting yield. For example, this effect has been observed by Misra and co-workers, when they grafted methyl acrylate and vinyl acetate onto wool,[6] reduced wool[7] and ethyl acrylate onto cellulose[8] by using (FAS-KPS) redox system. Morin and coworkers[9] have also employed the FAS-KPS combination as redox initiator to initiate graft copolymerization of water soluble monomers onto viscous fibers. Later on Graczyk and Hornof examined the use of KPS and FAS-KPS redox initiators in grafting of styrene onto cellulose.[3]

Chitin is a naturally occurring polysaccharide consisting of 2-acetoamido-2-deoxy-β-glucose repeating units, which forms principal component of the supporting structure of several living organisms such as fungi and crustacea. Chitin is structurally similar to cellulose but its chemical and physical properties are different. Although chitin is very abundant and widely distributed in nature, it has not found much application compared with other polysaccharides, probably due to its intractable characteristic. Many attempts have been made to modify chitin chemically to overcome this limitation.[10-21] The grafting technique has recently attracted growing interest.[22-30] Graft copolymerizations of MMA onto chitin using tributylborane as initiator,[22] styrene onto chitin by using gamma irradiation,[23,24] MMA onto chitin film by using a ceric salt,[25] γ-methyl-L-glutamate NCA onto chitin and water soluble chitin,[26] MMA onto chitin and oxy-chitin by a noncatalytic photo-induced and photo-sensitized method,[28] MMA,[29] acrylamide and acrylic acid[30] onto chitin using cerium ammonium nitrate as redox initiator has been reported. However, potassium persulfate alone or in combination with a reductor counterpart has not been used either to graft MMA or any other vinyl monomer onto chitin.

The present paper reports a quantitative study of the graft copolymerization of MMA onto chitin by using KPS and FAS-KPS systems. This was done in order to compare their relative efficiency as much between them as with the other reported initiators. Moreover the effect of different reaction variables were extensively studied.

EXPERIMENTAL

Material and Methods

Chitin was obtained from lobster shells and powdered (<100 mesh). It was purified by extraction with acetone in a Soxhlet apparatus for 24 h, washed with methanol and then with diethylether and finally dried under vacuum at room temperature. MMA from Fluka was washed with 5% NaOH, dried over $CaCl_2$, and finally distilled under vacuum. KPS from Alfa chemicals and FAS from Merck were used as received. All used solvents were reagent grade from Aldrich.

Graft Copolymerization

Graft copolymerizations were carried out in 50 cm^3 stoppered flasks by first dispersing an exact amount of dry chitin in the previously prepared initiator solution (KPS or FAS-KPS). The flask was then closed and placed in the thermostated bath at the desired reaction temperature (50, 60, 70 and 80°C) and shaken for one minute. The monomer was then added. Polymerization was started and continued for a predetermined period, between 15 and 150 min., during which time the reaction mixture was shaken occasionally. At the end of the polymerization, an small amount of hydroquinone was added to stop the reaction. The grafted chitin was separated by filtration, washed thoroughly with warm water to eliminate unreacted MMA and dried under vacuum at 50°C to constant weight. In order to remove poly(methyl methacrylate) (PMMA) homopolymer formed during the grafting reaction, the whole sample was extracted with acetone in a Soxhlet for 24 h.

Grafting percentage (%G) and efficiency (%E) were calculated, as described before[31] from the increase in weight of the original chitin after homopolymer extraction. The percentage of homopolymer (%H) was calculated from the weight difference between grafted chitin before and after acetone extraction.

The viscosity average molecular weights (M_v) of the homopolymers samples were determined by viscosity measurements in toluene at 25°C in an Ubbelohde type viscometer. The M_v values were calculated by using the Mark-Houwink-Sakurada constants given by Chinai *et al.*[32]

RESULTS AND DISCUSSION

Infrared spectroscopy was used to characterize chitin (Figure 1a) and MMA-grafted chitin (Figure 1b). The bands at 5.95–6.15 μ in Figure 1a is assigned to carbonyl absorption of chitin. In the spectrum of grafted chitin, in addition to the chitin characteristic bands, three new bands appear at 5.75, 11.9 and 13.3 μ. The first one corresponds to the carbonyl absorption from PMMA and the other two bands are characteristic of PMMA chains.

The M_v values of some of the PMMA homopolymer samples were determined by viscosity measurements and they were in the range from 190000 to 550000.

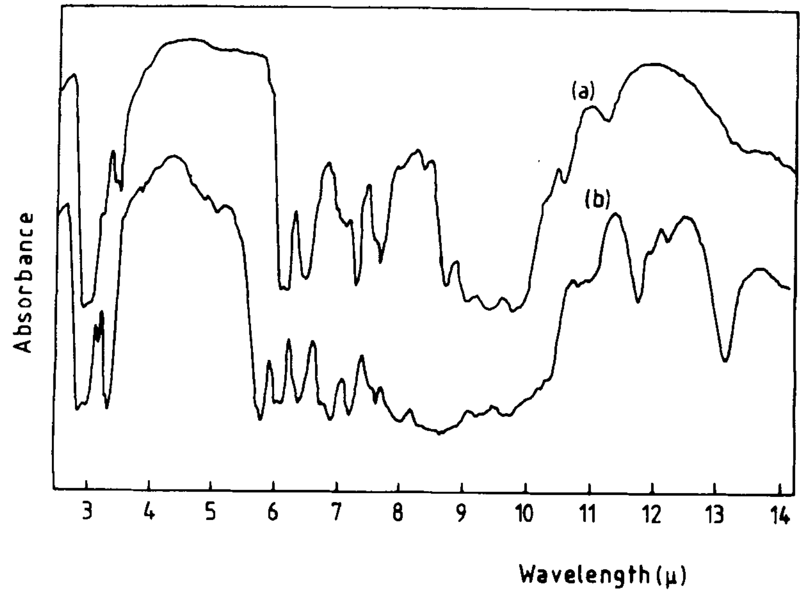

FIGURE 1 IR spectra of chitin (a) and chitin grafted PMMA (b).

Persulfate Role in Grafting

It has been shown by Kolthoff and Miller[33] that on heating KPS in aqueous solution, it decomposes to sulfate ion radicals ($SO_4^{\cdot -}$) These radicals may react with water to produce hydroxyl radicals (-$\dot{O}H$). The formation and participation of -$\dot{O}H$ radicals in KPS and FAS-KPS initiated grafting of vinyl monomers onto cellulose and wool have been reported by a number of investigators.[1-9,33] The possible mechanism for the formation of active sites on chitin could hence be postulated, by analogy with the cellulose, and by considering that chitin can act as a weak reducing agent. Therefore, the principal reactions (Equations 1-4) leading to grafting of MMA onto chitin, and the homopolymer formation, are:

$$SO_4^{\cdot -} + H_2O \rightarrow HSO_4 + \dot{O}H \tag{1}$$

$$\dot{O}H + \text{Chi-H} \rightarrow H_2O + \dot{\text{C}}\text{hi} \tag{2}$$

$$\dot{O}H + \text{MMA} \rightarrow \text{OH-MM}\dot{\text{A}} \xrightarrow{n(\text{MMA})} \text{OH-(MMA.)}_{n+1} \tag{3}$$

$$\dot{\text{C}}\text{hi} + \text{MMA} \rightarrow \text{Chi-MM}\dot{\text{A}} \xrightarrow{n(\text{MMA})} \text{Chi-(MMA.)}_{n+1} \tag{4}$$

The most important termination reactions could be written as follows:

$$\text{HO-(MM}\dot{\text{A}})_n\text{-} + \dot{R} \rightarrow \text{P(MMA)R} \tag{5}$$

$$\text{Chi-(MM}\dot{\text{A}})_n + \dot{R} \rightarrow \text{Chi-(MMA)}_n\text{R} \tag{6}$$

Where $\dot{R}$ could represent $\dot{O}H$, $SO_4^{\cdot -}$, MMA, and chitin or their corresponding radicals. When Fe^{2+} is present, the KPS decomposition is promoted according to:

$$Fe^{2-} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\cdot -} \tag{7}$$

However, an excess of Fe^{2+} consumes both $\dot{O}H$ and $SO_4^{\cdot -}$ radicals in the following manner:

$$\dot{O}H + Fe^{2+} \rightarrow \dot{O}H + Fe^{3+} \tag{8}$$

$$SO_4^{\cdot -} + Fe^{2+} \rightarrow SO_4^{2} + Fe^{3+} \tag{9}$$

The results obtained in this work by studying the effect of experimental variables on grafting reaction can be explained, by taking into account the above mechanisms, as described thereafter.

Effect of Total Amount of Chitin

The influence of total amount of chitin used on %G, %H and %E obtained on grafting MMA onto chitin, where concentration of monomer and initiator were kept constant, are shown in Figure 2 and Figure 3. When KPS alone is used (Figure 2) it can be seen that, for lower amounts of chitin, the percentages of grafting and homopolymer are very low. This suggests that the presence of a minimum amount of polysaccharide is necessary in order to generate sufficient number of radicals capable of initiating grafting and homopolymerization, since for higher concentration of chitin an abrupt increase in %G and %H was observed. This fact also indicates that the thermal homopolymerization of MMA does not take place under the reaction conditions used here. As the concentration of chitin increases, the %G, %H and %E also increases up to a maximum and then decrease with further increase in chitin concentration. This could probably be due to a limited number of free radicals that can be generated. Apparently the number of free radicals in

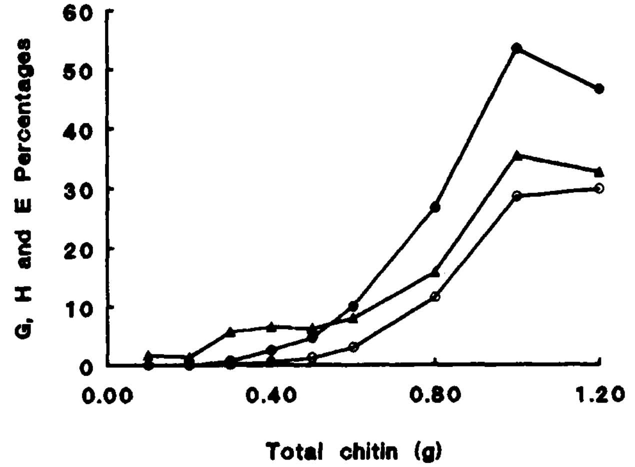

FIGURE 2 Effect of total amount of chitin on grafting parameters. ● %G; ▲ %H; ○ %E. Initiator KPS (10^{-2} M); MMA (2 ml); temp. (60°C); time (60 min); H_2O (10 ml).

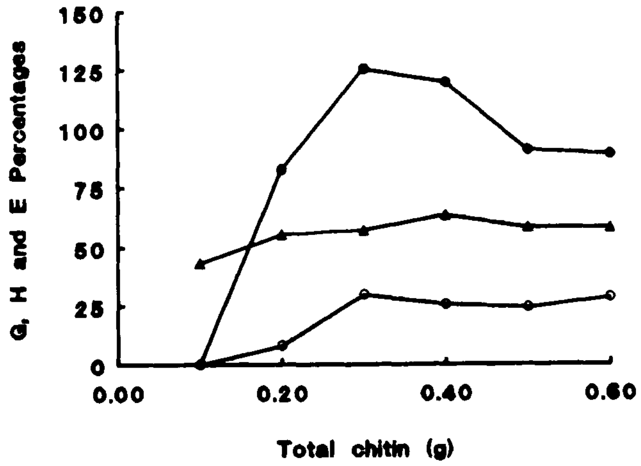

FIGURE 3 Effect of total amount of chitin on grafting parameters. ● %G; ▲ %H; ○ %E. Initiator FAS-KPS (10^{-3} M–10^{-2} M); MMA (2 ml); temp. (60°C); time (90 min); H_2O (10 ml).

the system does not increase with the same proportion as the concentration of the substrate since the existing relation of chitin/MMA and chitin/KPS are far from optimum conditions as was established in Figure 2.

Figure 3 shows the effect of the amount of chitin on grafting parameters for the FAS-KPS initiated grafting reactions. No grafting was occurred when the amount of chitin used was below 0.1 g as in the case of KPS initiated copolymerization. However, the percentage of homopolymer formed is substantial and increases slightly as the concentration of chitin is further increased. This means that an important number of $\dot{O}H$ radicals capable of initiating the homopolymerization of MMA are present in the reaction media (Equation 3). The rapid polymerization of the monomer in this case could be attributed to a much higher decomposition rate of the KPS induced by Fe^{2+} ions (Equation 7). For higher concentrations of chitin, an increase in %G and %E were observed. This indicates that an important number of active sites are formed on the chitin backbone which are capable of initiating grafting (Equation 4). It can be seen from Figure 3 that the maximum %G obtained in this case is notably higher when it is compared with the percentage obtained when KPS alone was used. This fact demonstrates the important role of Fe^{2+} in this reaction. Further increase in chitin concentration resulted in obtaining lower percentages of grafting probably due to similar reasons as was discussed for the KPS system.

Effect of MMA Concentration

The effect of MMA concentration on the grafting yield obtained with chitin is shown in Figure 4 (KPS) and Figure 5 (FAS-KPS). For both initiator systems the %G increases with increasing MMA concentration to a maximum and then decreases. This behavior could be explained by taking into account that the growth rate of the grafted PMMA chains (Equation 4) are higher than the rate of the attack of hydroxyl radicals to monomer to form homopolymer (Equation 3). The

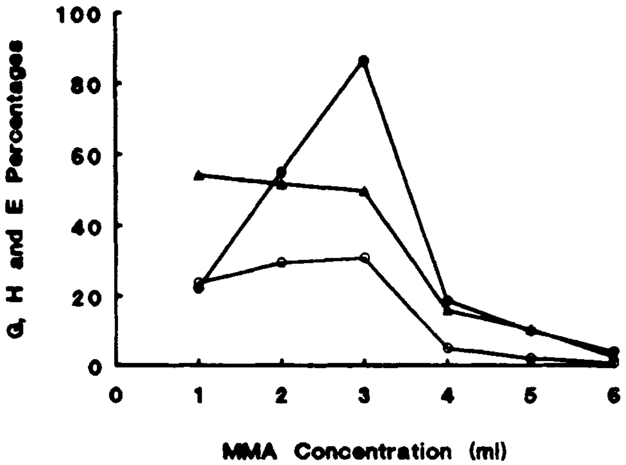

FIGURE 4 Effect of MMA concentration on grafting parameters. ● %G; ▲ %H; ○ %E. Initiator KPS ($3 \cdot 10^{-2}$ M); chitin (1 g); temp. (60°C); time (90 min); H_2O (10 ml).

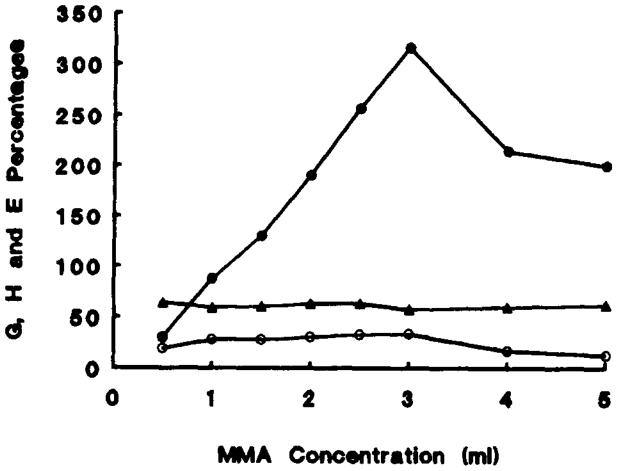

FIGURE 5 Effect of MMA concentration on grafting parameters. ● %G; ▲ %H; ○ %E. Initiator FAS-KPS (10^{-3} M–10^{-2} M); chitin (0.3 g); temp. (60°C); time (90 min); H_2O (10 ml).

%H formed during grafting reaction is relatively high for both initiator systems even at low concentration of MMA and does not increases with monomer concentration as it is evident from Figure 4 and Figure 5 where the %H decreases as the amount of MMA increases. This could be explained by assuming that when the concentration of MMA is low, this tends to react rapidly when $\dot{O}H$ radicals present in solution to form homopolymer. Consequently, the percentage of grafting is low due to the limited amount of monomer available that should diffuse toward chitin to initiate grafting. The decrease in %G observed for KPS and FAS-KPS initiated polymerizations with the further increase in MMA concentration indicates that chain transfer and other termination reactions involving the free radicals, present in solution, are possible (Equation 6).

By comparing the two initiator systems used in this study, it can be seen from Figure 4 that when KPS alone is used, the maximum grafting obtained corresponds to a molar ratio of MMA/chitin = 5.3.

In the case of FAS-KPS initiated grafting (Figure 5) the maximum grafting was attained for a molar ratio of MMA/chitin = 17.7. It is apparent that the molar ratio of MMA/chitin = 5.3 corresponds to approximately 1 ml of MMA. For this monomer concentration the %G and %H values are roughly the same as those found for optimum grafting yield obtained in the KPS initiated polymerization (see Figure 4). This fact suggests that an initial part of the monomer is converted to homo-and copolymer with the same amount and proportions through a similar mechanisms for both initiator systems. This common process is due to attack of the free radicals generated in solution to monomer and chitin molecules to form homopolymer and macroradicals respectively (Equation 3 and Equation 2). On the other hand, it is evident from Figure 5 that the amount of homopolymer formed during grafting reaction remains almost constant when FAS-KPS is used. %G increases considerably by increasing the relative amount of the monomer, only when Fe^{2+} ions are present in the reaction. Moreover the amount of homopolymer formed remains nearly constant in this case. The fact that the presence of Fe^{2+}

ions does not affect the amount of the homopolymer formed suggests that it should interact exclusively with chitin. This indicates that the Fe^{2+} ions are adsorbed by the chitin so that the KPS decomposition take place in close proximity to the polysaccharide chains. The free radicals thus generated react preferently with chitin (Equation 2) to produce active sites (macroradicals). In the case of grafting onto cellulose it has been shown by Ogiwara and Kubota that Fe^{2+} ions are adsorbed by polysaccharide chains.[34]

Influence of Fe II Concentration

From the results obtained in this work it is evident that the presence of Fe^{2+} in the reactions leading to the grafting of MMA onto chitin play an important role. The effect of the variation of Fe^{2+} concentration on the grafting parameters is shown in Figure 6. In this case the concentration of KPS was kept constant. It can be observed that the %G and %H increase with Fe^{2+} concentration due to an increase in the decomposition rate of KPS and hence the concentration of $\dot{O}H$ radicals increases. The maximum grafting was obtained when Fe^{2+} concentration was in the range from 10^{-3} to $3 \cdot 10^{-3}$ [M]. The effect on %G is notably greater than the effect on %H. This is due to the adsorption of the Fe^{2+} ions onto chitin as was already discussed. For higher concentrations, an slight decrease in grafting was observed. This is due to the consumption of $\dot{O}H$ radicals by reaction with the excess of Fe^{2+} (Equation 8). The optimum Fe^{2+} concentration was found to be near 10^{-2} M which corresponds to a ratio of KPS/FAS of about 10.

Effect of KPS Concentration

The influence of initiator (KPS) concentration on grafting parameters for KPS and FAS-KPS initiated polymerizations are shown in Figure 7 and Figure 8 respectively. For both systems %G increases sharply with the increase in initiator concentration reaching a maximum value and then decreases. The lowering of %G observed

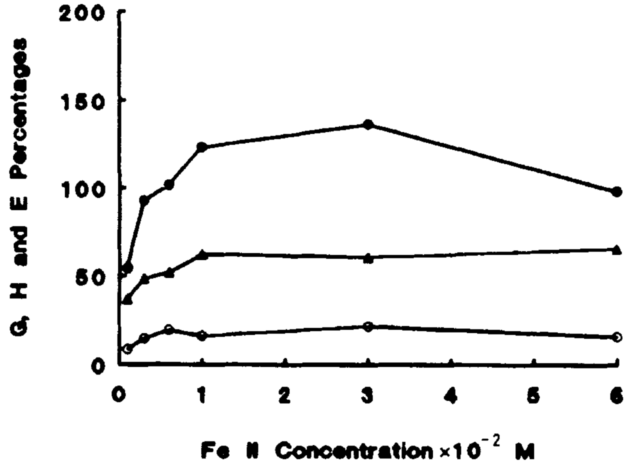

FIGURE 6 Effect of Fe^{2+} concentration on grafting parameters. ● %G; ▲ %H; ○ %E. Initiator FAS-KPS; chitin (0.3 g) MMA (2 ml); KPS (10^{-2} M); temp. (60°C); time (90 min); H_2O (10 ml).

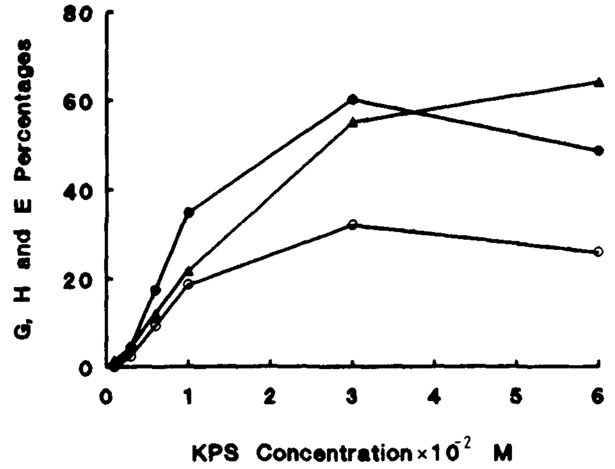

FIGURE 7 Effect of initiator concentration on grafting parameters. ● %G; ▲ %H; ○ %E. Initiator KPS. Chitin (1 g); MMA (2 ml); temp. (60°C); time (90 min); H_2O (10 ml).

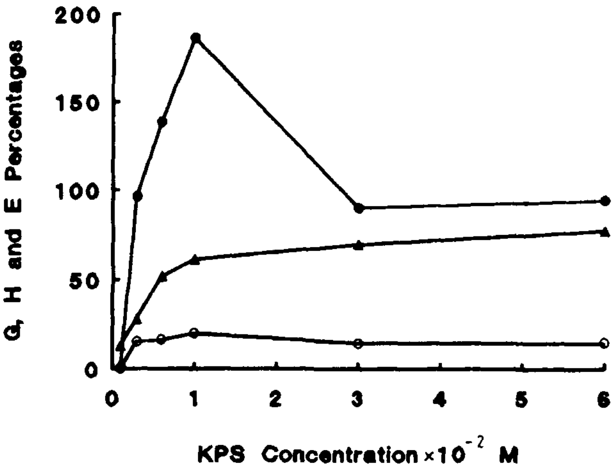

FIGURE 8 Effect of initiator concentration on grafting parameters. ● %G; ▲ %H; ○ %E. Initiator FAS-KPS. Chitin (0.3 g); MMA (2 ml); Fe^{2+} (10^{-3} M); temp. (60°C); time (90 min); H_2O (10 ml).

could be due to the possible combination of the chitin macroradicals with the existing excess of free radicals that are present in solution. When FAS-KPS is used, a sharp maximum in %G is observed (Figure 8) for an optimum ratio of KPS/FAS of about 10, which is the same value previously found for this system when the effect of Fe^{2+} ion concentration was studied.

The %H formed in both systems initially increases rapidly with KPS concentration due to the greater number of available free radicals. Therefore this begins to level off probably due to free radicals combination and termination reactions.

Effect of Temperature and Reaction Time

The results obtained from the study of the variation of temperature and reaction time on grafting parameters, for both used initiators systems, are shown in Table

TABLE I

Effect of temperature and reaction time on grafting of MMA onto chitin

№	Initiator	T°C	t(min)	%G	%H	%E
1	FAS-KPS	50	15	4.9	0.1	0.5
2			30	10.4	0.7	1.1
3			45	12.2	1.0	1.3
4			60	15.9	2.6	1.7
5			90	28.0	5.5	3.0
6			120	35.5	9.7	3.8
7			150	47.2	15.6	5.0
8	FAS-KPS	60	15	6.2	5.8	0.7
9			30	21.2	8.0	2.3
10			45	36.7	18.0	3.9
11			60	95.9	35.7	10.2
12			90	171.7	59.8	18.3
13			120	207.0	65.2	22.1
14			150	210.6	69.6	22.5
15	FAS-KPS	70	15	36.2	14.2	3.9
16			30	280.0	39.5	29.9
17			45	343.0	48.2	36.7
18			60	352.0	55.6	37.6
19			90	339.5	48.0	36.3
20			120	332.7	47.0	35.5
21			150	335.8	49.0	35.9
22	FAS-KPS	80	15	72.4	14.3	7.8
23			30	180.0	38.3	19.2
24			45	194.8	44.7	20.8
25			60	194.0	52.6	20.7
26			90	189.6	46.7	20.2
27			120	178.7	40.4	19.1
28			150	180.5	46.4	19.3
29	KPS	60	15	0.0	0.0	0.0
30			30	3.2	2.7	1.1
31			45	11.7	6.1	4.2
32			60	36.5	16.5	13.0
33			90	68.4	33.9	24.4
34			120	82.7	45.5	29.4
35			150	89.9	47.2	32.0
36	KPS	70	15	27.6	18.0	9.8
37			30	50.1	28.0	17.9
38			45	67.0	36.4	23.9
39			60	94.5	44.3	36.7
40			90	88.3	44.2	31.5
41			120	85.3	51.7	30.4
42			150	81.8	52.4	29.1

Reaction conditions

FAS-KPS: Chitin 0.3g;[$K_2S_2O_8$] 10^{-2}M;[Fe^{2+}] 3×10^{-3}M ;MMA 3 cm^3

KPS: Chitin 1g; [$K_2S_2O_8$] 3×10^{-2}M ;MMA 3cm^3

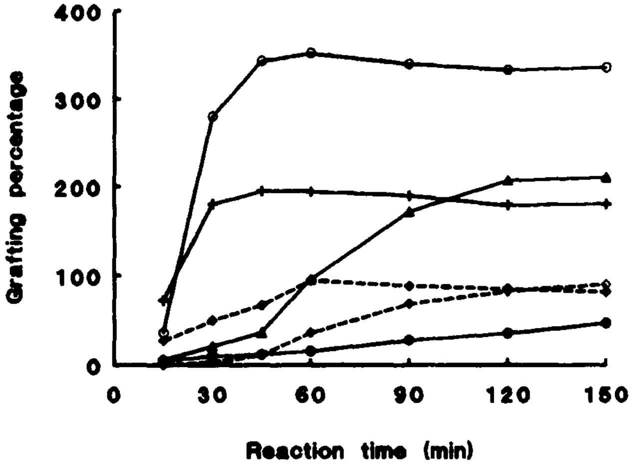

FIGURE 9 Influence of reaction time on grafting percentage at various temperatures. Initiator KPS ($3 \cdot 10^{-2}$ M); chitin (1 g); MMA (3 ml); H_2O (10 ml) ◇ 60°C, ◆ 70°C. Initiator FAS-KPS ($3 \cdot 10^{-3}$ M–10^{-2} M); chitin (0.3 g); MMA (3 ml); H_2O (10 ml) ● 50°C, ▲ 60°C, ○ 70°C, + 80°C.

I. These values were obtained from polymerizations performed under optimum reaction conditions as previously established. To illustrate clearly the grafting tendency, the %G data at various temperatures are plotted against reaction time in Figure 9. It can be seen that, after an initial period in which the amount of grafted polymer increases, a nearly constant value is reached. As expected, the maximum grafting is obtained in a shorter reaction period at higher temperatures. From this figure it is apparent that at 50°C (FAS-KPS) and at 60°C (KPS), even after 150 minutes, the grafting percentage has not attained its maximum value. For FAS-KPS initiated reaction the %G increases with temperature reaching its highest value of 70°C. At higher temperatures the grafting yield decreases rapidly. This could be due to chain transfer and termination reactions which are favored at higher temperatures and do not contribute to grafting.

It was found that 70°C is the optimum reaction temperature for both KPS and FAS-KPS initiated grafting reactions. To highlight the differences that exist between these systems the values of %G and %H under optimum reaction conditions are plotted against reaction time in Figure 10. From this figure it is evident that the maximum %G obtained in the case of FAS-KPS (352%) is several times higher than the maximum value obtained when KPS alone is used (94.5%). The reason for this behavior is undoubtedly due to the adsorption of Fe^{2+} ions onto chitin, and its role as promoter of KPS decomposition has been discussed before. It should be noted that the maximum %G attained in this work is higher than the published values for MMA and other grafted vinyl monomers onto chitin. The %H for both initiator systems are practically the same according to the reasons given when the effect of monomer concentration on grafting reaction was discussed.

The overall activation energy for the grafting process was estimated from the usual Arrhenius plot of the rate versus polymerization temperature. A value of 23.4 Kcal/mol (Figure 11) was obtained by using the data shown in Table I. A

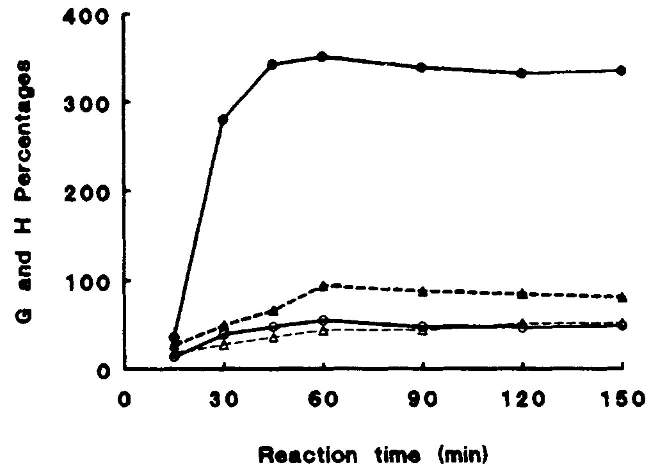

FIGURE 10 Comparison of initiator efficiency under optimum reaction conditions. Initiator KPS ($3 \cdot 10^{-2}$ M); chitin (1 g); MMA (3 ml); temp. (70°C); time (60 min); H_2O (10 ml) ▲ %G; △ %H. Initiator FAS-KPS ($3 \cdot 10^{-3}$ M–10^{-2} M); chitin (0.3 g); MMA (3 ml); temp. (70°C); time (60 min); H_2O (10 ml) ● %G, ○ %H.

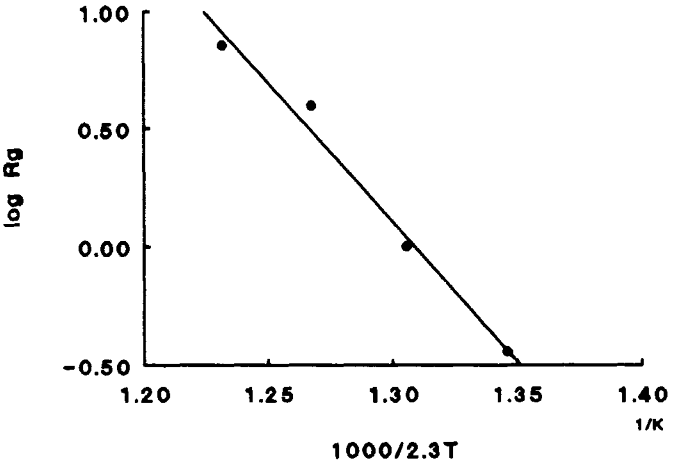

FIGURE 11 Relation between the rate of grafting (Rg) and temperature. Initiator FAS-KPS ($3 \cdot 10^{-3}$ M–10^{-2} M); chitin (0.3 g); MMA (3 ml); H_2O (10 ml).

similar value (22.8 Kcal/mol) has been reported by Kojima *et al.*[22] when they grafted MMA onto chitin by using tributylborane as initiator.

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