

# Graft Copolymerization of Vinyl Monomers on Cellulose Using Peroxyacetic Acid–Ferrous Ion Redox Initiator System

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## Synopsis

Graft copolymerization of vinyl monomers such as methacrylate, acrylamide, and acrylic acid on cellulose using the peroxyacetic acid–ferrous ion redox initiator system was studied. Filter paper was chosen as cellulosic material. The effect of the experimental conditions on grafting ratio, grafting efficiency, total conversion and number of branches, and other factors was studied by varying the concentration ratio of peroxyacetic acid to ferrous salt, reaction time, reaction temperature, the addition of disodium ethylenediaminetetraacetate (EDTA), pH, and so on. It was found that there is an optimum range of initiator concentration, that at a higher temperature the copolymerization proceeds more rapidly and more efficiently, and that the addition of EDTA enables the copolymerization to proceed at a higher pH.

## INTRODUCTION

Grafting methods of vinyl monomers on cellulosic materials by radical initiators have been studied by many research groups. Among these initiators, the ceric ion method is an excellent method and has been studied by researchers from various viewpoints since Mino and Kaizerman<sup>1</sup> reported the method in 1958.

There also have been many attempts to use peroxides as initiators for grafting vinyl monomers on cellulosic materials because peroxides have O—O bonds which are easily disrupted by heat or a reductant and form free radicals. For example, Sakurada and Sakaguchi<sup>2,3</sup> studied the graft copolymerization of styrene on cotton imbibing solutions of catalysts and on dry cotton imbibing catalysts such as peroxysulfates or hydrogen peroxide. They reported that potassium peroxysulfate was a suitable catalyst and that graft copolymerization proceeded smoothly under appropriate conditions. The redox system consisting of peroxysulfate and  $\text{Ag}^+$  was also used as an initiator for grafting methyl methacrylate onto cellulose.<sup>4</sup> There have been several detailed studies<sup>5,6</sup> on graft copolymerization using the hydrogen peroxide–ferrous ion redox system, known as Fenton's reagent. For example, Richards<sup>7</sup> has proved the formation of grafted cellulose, and Arthur et al.<sup>8</sup> have reported on the reaction site of cellulose with hydroxyl radical by ESR measurements. Ogiwara and Kubota<sup>9,10</sup> studied graft copolymerization initiated by the hydrogen peroxide–ferrous or ferric ion.

On the other hand, there have been only few reports on graft copolymerization on cellulosic materials using organic peroxides as initiators, although peroxides such as hydroperoxide, peroxyester, acyl peroxide, and so on, have been used for polymerization of vinyl monomers. For example, recently, Misra et al.<sup>11</sup> reported the graft copolymerization of vinyl acetate onto cellulose using benzoyl peroxide or azobisisobutyronitrile and obtained results which supported the chain-transfer mechanism.

Good results<sup>12</sup> were obtained from graft copolymerization of vinyl monomers onto dissolving pulp and ground pulp using a system consisting of acetic acid and hydrogen peroxide in the presence of trace amounts of sulfuric acid to form peroxyacetic acid. They also investigated the redox system consisting of peroxyacetic acid and a reductant because such a redox system was expected to form the primary radical from the initiator more easily. They accurately found that a system consisting of peroxyacetic acid and ferrous or ferric ion was effective for grafting onto pulp and lignin.<sup>13</sup>

Recently, we estimated that peroxyacetic acid, which is an organic peroxide, could be an effective initiator for grafting onto cellulosic materials because it has already been shown that the reaction to peroxyacetic acid with polysaccharide and lignin seems to involve radical reactions.

In this investigation, we studied the graft copolymerization of vinyl monomers, mainly methyl methacrylate, onto cellulose by using the peroxyacetic acid-ferrous ion redox system, and disodium ethylenediaminetetraacetate (EDTA) was also added to this system.

The reaction conditions such as concentration of the initiator, reaction time, reaction temperature, pH, and so on, were varied to know how these conditions affect the grafting ratio, the grafting efficiency, the total conversion, the number of branches, and other factors.

## EXPERIMENTAL

### Materials Used

Quantitative filter paper, No. 5C from Toyo Roshi Kaisha, Ltd., was used as cellulose sample. The degree of polymerization of cellulose determined by viscometry on Cadoxen solution<sup>14</sup> was 802. The filter paper was made into a suspension in water by a mixer and then dried. A peroxyacetic acid solution (42%) from Mitsubishi Gas Chemical Industries, Ltd.,  $\text{FeCl}_2 \cdot x\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , and disodium ethylenediaminetetraacetate (EDTA) from Wako Pure Chemical Industries, Ltd., were used. Commercially obtained methyl methacrylate (MMA), acrylamide (AAM), and acrylic acid (AAc) from Wako Pure Chemical Industries, Ltd., were used as monomers. MMA and AAc were purified by distillation under reduced pressure on an atmosphere of nitrogen. AAM was purified by recrystallization from benzene. All monomers were stored at about  $-15^\circ\text{C}$  before use.

### Polymerization Procedure

Generally, amounts of cellulose and vinyl monomer affect the grafting ratio and other factors. In this experiment, the amounts of cellulose and monomer were maintained constant, and a large excess of monomer was used according to the process reported elsewhere.<sup>9,12</sup>

A typical polymerization procedure was as follows: 0.2 g cellulose, 1.88 g MMA, 50 mL water containing 0.023 g (0.12 mmol) ferrous salt, and 0.1 ml 0.1N sulfuric acid were placed in a polymerization tube. Oxygen had been removed previously in the water by bubbling nitrogen. The reaction mixture was cooled to about  $0^\circ\text{C}$  in an ice water bath before addition of peroxyacetic acid. The

contents of the polymerization tube were immediately frozen with liquid nitrogen, degassed, and sealed after adding 0.2 mL 4.2% peroxyacetic acid (0.12 mmol).

Polymerization was carried out by shaking the sealed tube in a water bath at a fixed temperature for a predetermined time. After the reaction, the contents of the tube were cooled rapidly and hydroquinone was added to the reaction mixture. The mixture was then transferred to a Soxhlet extraction thimble and the reaction product was washed well with water and/or solvent (acetone for MMA, water for AAm, and methanol for AAc). Extraction was carried out with solvents to remove homopolymers. The grafted cellulose obtained as residue of the Soxhlet extraction was dried in a dryer at 105°C for 6 h and weighed.

### Fractionation of Polymerization Products

The grafted cellulose was transferred to a tared Soxhlet extraction thimble to remove the homopolymer (acetone for MMA, water for AAm, and methanol for AAc), and then extracted for 48 h with the solvent to remove any remaining homopolymer. The soluble fraction in the solvent was collected, concentrated under reduced pressure, and then added to a nonsolvent (methanol for MMA, methanol for AAm, and acetone for AAc) to precipitate the homopolymer.

The total conversion, the grafting ratio, and the grafting efficiency were calculated as follows:

$$\text{total conversion, \%} = \frac{\text{total weight of vinyl polymer formed}}{\text{weight of vinyl monomer used}} \times 100$$

$$\text{grafting ratio, \%} = \frac{\text{weight of vinyl polymer in grafts}}{\text{weight of cellulose}} \times 100$$

$$\text{grafting efficiency, \%} = \frac{\text{weight of vinyl polymer in grafts}}{\text{total weight of vinyl polymer formed}} \times 100$$

### Separation of PMMA Branches from Cellulose

For the purpose of characterization of the branches, the residue after extraction was directly transferred into a glass filter and then dried in air at room temperature and weighed. Half of the residue was dried in a dryer at 105°C for 6 h and weighed; the other half was used for characterization of the branches.

The separation of PMMA branches from cellulose was carried out by Ide's procedure.<sup>15</sup> Grafted cellulose was dissolved in 8 mL 72% sulfuric acid solution for 2 h, and then the solution was diluted with water, followed by boiling for 40 min. The residue was washed well with water and purified by reprecipitation with acetone-methanol. The molecular weight of PMMA branches was determined by viscometry. The intrinsic viscosity  $[\eta]$  was obtained by measurement at 25°C in acetone. The equation<sup>16</sup> used was as follows:

$$[\eta] = 9.6 \times 10^{-5} M_w^{0.69}$$

TABLE I  
 Effect of Concentration of Peroxyacetic Acid<sup>a</sup>

Ratio [CH <sub>3</sub> CO <sub>3</sub> H]/[Fe <sup>2+</sup> ]	GR, %	TC, %	$\bar{M}_w$ of grafted PMMA ×10 <sup>6</sup>	Number of branches, mmol/mol cellulose
0.5	38.0	14.1	9.60	5.2
1	112.3	58.3	7.68	19.0
2	119.7	66.3	4.82	32.3
3	139.4	68.8	4.02	45.2
4	72.4	49.8	3.70	26.3
5	45.1	23.6	4.11	15.6
8	4.7	5.1	3.55	1.7

<sup>a</sup> GR: Grafting ratio; TC: total conversion. Experimental conditions: 60°C, 90 min, [Fe<sup>2+</sup>] = 2.4 mmol/L, 0.2 g cellulose and 1.88 g MMA. Degree of polymerization of cellulose: 802.

## RESULTS AND DISCUSSION

### Peroxyacetic Acid–Ferrous Ion System

Table I shows the results of the graft copolymerization of MMA by the initiator system which had different ratios of peroxyacetic acid and ferrous salt by setting the concentration of ferrous salt at 2.4 mmol/L. As shown in the table, the grafting ratio increases with the concentration of peroxyacetic acid at ratios from 0.5 to 3. At ratios above 4, the grafting ratio becomes low again, suggesting that there is an optimum range for the ratio in this system.

The average molecular weight of grafted PMMA is summarized in Table I. The number of branches was calculated on the basis of the results of the blank tests which in the absence of monomer indicated no change in the molecular weight of cellulose. The molecular weight of grafted PMMA tends to decrease with increase in the ratio. On the other hand, the number of branches increases with the concentration of peroxyacetic acid at ratios from 0.5 to 3 and then becomes low again at ratios over 4.

Grafting at ratios over 4 seems to lead to extraordinary results compared with lower ratios. In the case of ratios over 4, despite the higher concentration of

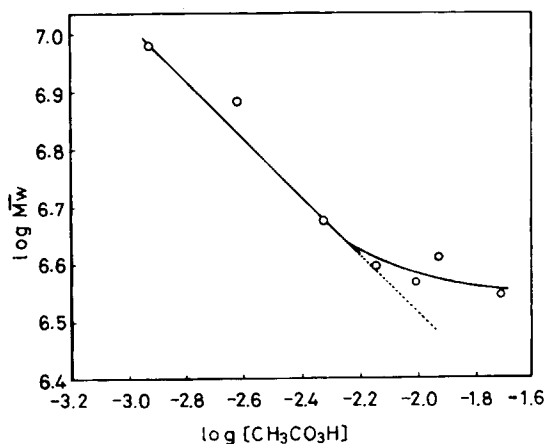


Fig. 1. Relationship between log [CH<sub>3</sub>CO<sub>3</sub>H] and log  $\bar{M}_w$ . Experimental conditions: 60°C, 90 min, [Fe<sup>2+</sup>] = 2.4 mmol/L, 0.2 g cellulose, and 1.88 g methyl methacrylate.

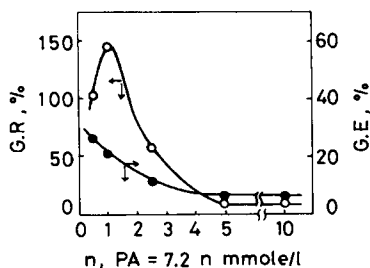


Fig. 2. Effect of concentration of initiator,  $[\text{CH}_3\text{CO}_3\text{H}]/[\text{Fe}^{2+}] = 3$ , on grafting ratio and grafting efficiency. The concentration of the initiator is shown in the concentration of peroxyacetic acid: (O) grafting ratio; (●) grafting efficiency. Experimental conditions:  $60^\circ\text{C}$ , 90 min,  $[\text{CH}_3\text{CO}_3\text{H}]/[\text{Fe}^{2+}] = 3$ , 0.2 g cellulose, and 1.88 g methyl methacrylate.

peroxyacetic acid, not only the grafting ratio but also the total conversion are low. This indicates that the primary radicals from peroxyacetic acid react with each other or with peroxyacetic acid; that is, some kind of reaction occurs which does not allow the primary radical to be consumed efficiently.

Figure 1 shows the plots of  $\log [\text{CH}_3\text{CO}_3\text{H}]$  vs.  $\log \bar{M}_w$ . The slope of the straight line is about  $-0.5$ . In conventional polymerization, as is well known,  $1/\bar{M}_n$  is proportional to  $[I]^{0.5}$ . If  $\bar{M}_n$  is proportional to  $\bar{M}_w$  in this copolymerization, the relationship of  $1/\bar{M}_w \propto [\text{CH}_3\text{CO}_3\text{H}]^{0.5}$  suggests that the copolymerization seems to proceed similarly to conventional radical polymerization at ratios below 4.

Copolymerization was carried out under various concentrations with the initiator at a constant ratio of  $[\text{PA}]/[\text{FeCl}_2] = 3.0$ . The results are shown in Figure 2. The grafting ratio depends on the concentration of the initiator, and there is an optimum range of initiator concentration. The grafting efficiency decreases with the initiator concentration. Similar results were obtained when the ratio of the concentration of peroxyacetic acid and ferrous salt was varied.

### Relation Between Copolymerization and Reaction Time

As shown in Figure 3, the grafting ratio increases with reaction time; after the first 2 h it gradually approaches a constant value. The grafting efficiency decreases gradually with the reaction time, approaching a constant value after 4 h. In addition, the average molecular weight of grafted PMMA was measured. The results are summarized in Table II. The molecular weight seems to be independent of the reaction time although the values are somewhat scattered.

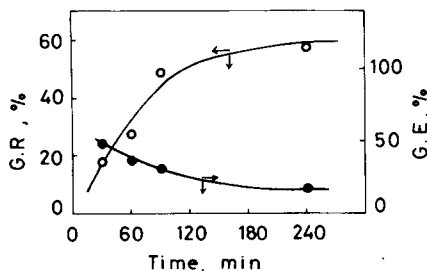


Fig. 3. Time course of grafting ratio and grafting efficiency: (O) grafting ratio; (●) grafting efficiency. Experimental conditions:  $60^\circ\text{C}$ ,  $[\text{CH}_3\text{CO}_3\text{H}] = 7.2$  mmol,  $[\text{Fe}^{2+}] = 2.4$  mmol, 0.2 g cellulose, and 0.94 g methyl methacrylate.

TABLE II  
Time Course of Molecular Weight of Grafted PMMA<sup>a</sup>

Time, min	$\bar{M}_w$ of grafted PMMA $\times 10^6$
60	2.30
90	2.34
240	2.26

<sup>a</sup> Experimental conditions: 60°C, [CH<sub>3</sub>CO<sub>3</sub>H] = 7.2 mmol/L, [Fe<sup>2+</sup>] = 2.4 mmol/L, 0.2 g cellulose and 0.94 g MMA.

### Effect of Reaction Temperature

Copolymerization was carried out at 45, 60 and 75°C (Table III). Figure 4 shows that the rate of copolymerization increases with the reaction temperature. The grafting efficiency changes with the reaction time at each temperature. As shown in Figure 5, the grafting efficiency was plotted against the grafting ratio. In comparing the grafting efficiency at 45, 60, and 75°C at a grafting ratio of about 40%, the grafting efficiencies are ca. 15, 30, and 50% for 45, 60 and 75°C, respectively. From Figure 4, it can be said that the graft copolymerization occurs more efficiently at a higher temperature. This fact is reasonable from the viewpoint that a higher temperature will advantageously affect the hydrogen abstracting reaction from cellulose and the diffusion of initiator and monomer into the cellulose matrix.

TABLE III  
Effect of Reaction Temperature<sup>a</sup>

Temperature, °C	Time, min	GR, %	GE, %	TC, %
45	90	6.8	15.2	9.4
	180	17.9	13.7	27.8
	360	35.3	11.8	63.4
60	30	18.2	51.5	7.5
	60	27.6	38.5	15.3
	90	48.3	32.7	31.4
	240	57.7	17.6	70.0
75	30	46.1	45.7	21.5
	60	53.3	29.3	44.6
	90	65.4	26.9	51.8

<sup>a</sup> GR: Grafting ratio; GE: grafting efficiency; TC: total conversion. Experimental conditions: [CH<sub>3</sub>CO<sub>3</sub>H] = 7.2 mmol/L, [Fe<sup>2+</sup>] = 2.4 mmol/L, 0.2 g cellulose, and 0.94 g MMA.

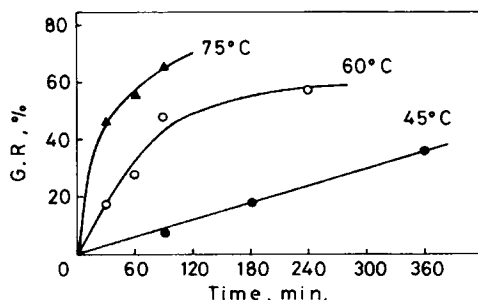


Fig. 4. Time course of grafting ratio at various temperatures: (●) 45°C; (○) 60°C; (▲) 75°C. Experimental conditions: [CH<sub>3</sub>CO<sub>3</sub>H] = 7.2 mmol/L, [Fe<sup>2+</sup>] = 2.4 mmol/L, 0.2 g cellulose, and 0.94 g methyl methacrylate.

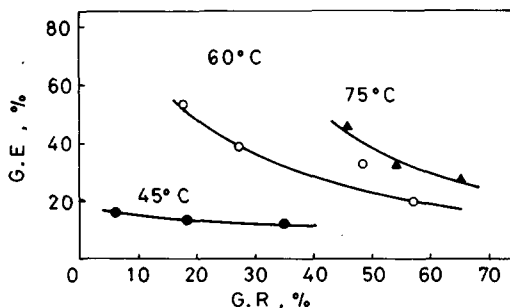


Fig. 5. Effect of reaction temperature on grafting efficiency (G.E): (●) 45°C; (○) 60°C; (▲) 75°C. Experimental conditions:  $[\text{CH}_3\text{CO}_3\text{H}] = 7.2 \text{ mmol/L}$ ,  $[\text{Fe}^{2+}] = 2.4 \text{ mmol/L}$ , 0.2 g cellulose, and 0.94 g methyl methacrylate. G.R.: Grafting ratio.

### System with EDTA

We also studied the copolymerization in various pH values of the reaction media. In this case EDTA was added to the initiator system to prevent ferrous or ferric compounds to precipitate during the polymerization. We first attempted polymerization by adding sodium pyrophosphate at various pH values to the initiator system. However, polymer was not formed. On the other hand, with the addition of EDTA, grafted cellulose could be obtained.

### Effect of Addition of EDTA

Generally, the pH of a polymerization medium affects the dispersion of monomers and the other factors of the initiation reaction in aqueous polymerization. A transition metal compound is ordinarily used as a reductant of a redox system at a higher pH; and a reagent such as EDTA, which can form a complex with the transition metal ion, is added to avoid precipitation of the transition metal compound.

We carried out copolymerization initiated by the following four systems: peroxyacetic acid–ferrous ion–EDTA; peroxyacetic acid–ferric ion–EDTA; peroxyacetic acid–EDTA; and peroxyacetic acid. As reported in Table IV, system 1 leads to greater yields than the other system. Systems 2 and 3 were better than system 4. This suggests that there could be some kind of interaction between peroxyacetic acid and ferric ion–EDTA or EDTA.

TABLE IV  
Effect of Addition of EDTA to Initiator System<sup>a</sup>

System No.	Initiator system	GR, %	TC, %
1	$\text{CH}_3\text{CO}_3\text{H}-\text{FeCl}_2-\text{EDTA}$	90.9	41.4
2	$\text{CH}_3\text{CO}_3\text{H}-\text{FeCl}_3-\text{EDTA}$	33.2	6.6
3	$\text{CH}_3\text{CO}_3\text{H}-\text{EDTA}$	21.5	4.4
4	$\text{CH}_3\text{CO}_3\text{H}$	7.9	1.6

<sup>a</sup> GR: Grafting ratio; TC: total conversion. Experimental conditions: pH 4, 60°C, 90 min,  $[\text{I}] = 2.4 \text{ mmol/L}$ , 0.2 g cellulose, 1.88 g MMA.

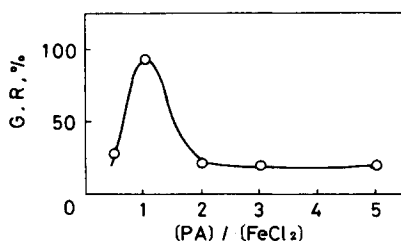


Fig. 6. Effect of concentration of peroxyacetic acid on grafting ratio (G.R). Experimental conditions: pH 4, 60°C, 90 min,  $[\text{Fe}^{2+}]$  and  $[\text{EDTA}] = 2.4 \text{ mmol/L}$ , 0.2 g cellulose, and 1.88 g methyl methacrylate.

### Effect of Concentration of Initiator

Copolymerization was carried out initially with various ratios of peroxyacetic acid and ferrous ion-EDTA at pH 4. Figure 6 shows grafting ratio vs. ratio of the concentration of peroxyacetic acid and ferrous ion-EDTA. As shown in Table I and Figure 6, there is an optimum range of peroxyacetic acid concentration. In comparing systems with EDTA and without EDTA, it can be seen that the grafting ratio of the system with EDTA is more strongly dependent on the concentration of peroxyacetic acid than that of the system without EDTA. Table 5 shows the results of copolymerization initiated by the system without EDTA (at pH 2) and with EDTA (at pH 4). There is little difference between the two systems.

### Effect of pH

MMA was copolymerized at various pH values using an initiator system consisting of equimolar amounts of peroxyacetic acid and ferrous ion-EDTA. The results are summarized in Table VI. As shown in Figure 7, the grafting ratio is maximal at around pH 4–5. The total conversion was maximal at around pH 4, and the grafting efficiency was minimal at around pH 3 (Table VI).

Table VII summarizes results of copolymerization of AAm and AAc using a system consisting of 7.2 mmol/L peroxyacetic acid and 2.4 mmol/L ferrous ion-EDTA. In AAm, which is soluble in water, the grafting ratio and the grafting efficiency were low and reached 15.4 and 4.5%, respectively at around pH 4.5. On the other hand, a great amount of homopolymer was obtained. In AAc, the grafting ratio and the grafting efficiency were low but they increased with pH.

TABLE V  
Effect of Addition of EDTA to Ferrous Ion System

System		GR, %	$M_w$ of branch $\times 10^6$	Number of branches, mmol/mol cellulose
$\text{CH}_3\text{CO}_3\text{H}-\text{Fe}^{2+}-\text{EDTA}$	(pH 4)	89.9	7.51	15.6
$\text{CH}_3\text{CO}_3\text{H}-\text{Fe}^{2+}$	(pH 2)	112.3	7.68	18.2



TABLE VI  
Effect of pH on Copolymerization of Methyl Methacrylate (MMA)<sup>a</sup>

pH	GR, %	GE, %	TC, %
2	36.4	21.2	18.4
3	38.4	19.7	20.2
4	90.9	23.3	41.4
5	87.2	31.7	29.1
6	38.5	40.1	10.2

<sup>a</sup> GR: Grafting ratio; GE: grafting efficiency; TC: total conversion. Experimental conditions: 60°C, 90 min, [CH<sub>3</sub>CO<sub>3</sub>H], [Fe<sup>2+</sup>], and [EDTA] = 2.4 mmol/L, 0.2 g cellulose, and 1.88 g MMA.

### Effect of Reaction Temperature

Table VIII shows the copolymerization of MMA at 48, 60, and 75°C. These results tend to be similar to those for the copolymerization initiated by the system without EDTA. The grafting ratio increased with reaction time, while the grafting efficiency decreased with reaction time. The grafting efficiency was plotted against grafting ratio in Figure 8 for different temperatures. Apparently a higher temperature is more efficient for the copolymerization.

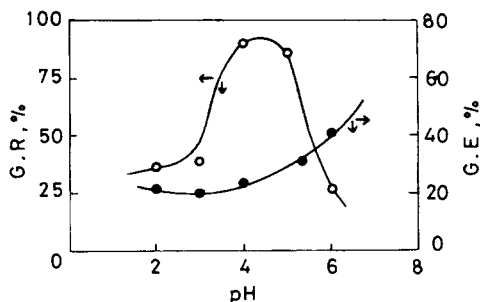


Fig. 7. Effect of pH on copolymerization of methyl methacrylate. (○) grafting ratio; (●) grafting efficiency. Experimental conditions: 60°C, 90 min, [CH<sub>3</sub>CO<sub>3</sub>H], [Fe<sup>2+</sup>], and [EDTA] = 2.4 mmol/L, 0.2 g cellulose, and 1.88 g methyl methacrylate.

TABLE VII  
Effect of pH on Copolymerization of Acrylamide (AAM) and Acrylic Acid (AAc)<sup>a</sup>

Monomer	pH	GR, %	GE, %	TC, %
AAM	2	0.6	0.4	37.6
	3	7.3	2.0	35.7
	4.5	15.4	4.5	34.0
	5.5	5.7	1.5	38.9
	7	7.4	1.6	45.0
AAc	2	7.1	2.4	29.9
	3.5	8.2	3.5	22.9
	4.5	10.5	4.8	21.7
	5.5	14.7	6.7	22.0
	7	20.7	8.8	23.7

<sup>a</sup> GR: Grafting ratio; GE: grafting efficiency; and TC: total conversion. Experimental conditions: 60°C, 90 min, [CH<sub>3</sub>CO<sub>3</sub>H] = 7.2 mmol/L, [Fe<sup>2+</sup>-EDTA] = 2.4 mmol/L, 0.2 g cellulose, and 2.0 g monomer.

TABLE VIII  
 Effect of Reaction Temperature<sup>a</sup>

Temperature, °C	Time, min	GR, %	GE, %	TC, %
48	60	19.0	29.0	7.0
	120	35.9	24.0	15.9
	270	87.9	19.0	50.0
60	30	34.4	51.0	7.2
	60	57.6	34.7	17.7
	90	90.9	23.3	41.4
	180	111.2	21.9	53.9
75	30	110.0	47.4	24.7
	60	168.9	40.2	47.3
	90	187.6	34.0	58.7

<sup>a</sup> GR: Grafting ratio; GE: grafting efficiency; TC: total conversion. Experimental conditions: pH 4, [CH<sub>3</sub>CO<sub>3</sub>H], [Fe<sup>2+</sup>], and [EDTA] = 2.4 mmol/L, 0.2 g cellulose, 1.88 g MMA.

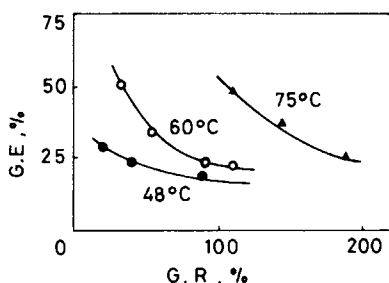


Fig. 8. Effect of reaction temperature on grafting efficiency (G.E.): (●) 48°C; (○) 60°C; (▲) 75°C. Experimental conditions: pH 4, [CH<sub>3</sub>CO<sub>3</sub>H], [Fe<sup>2+</sup>], and [EDTA] = 2.4 mmol/L, 0.2 g cellulose, and 1.88 g methyl methacrylate.

## CONCLUSIONS

The following conclusions were obtained from the graft copolymerization of MMA, AAm, and AAC (mainly MMA) on cellulose by using the peroxyacetic acid-ferrous ion redox system:

- (1) The concentration of the initiator system affects the graft copolymerization; there is an optimum the concentration range.
- (2) At higher temperatures, the graft copolymerization proceeds more rapidly and more efficiently.
- (3) The addition of EDTA leads to results similar to those obtained by the peroxyacetic acid-ferrous ion system and enables the graft copolymerization to be carried out at a higher pH.

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