

## Graft Copolymerization to Cellulose in the Presence of Hydrogen Peroxide with Ultraviolet Irradiation

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### Synopsis

The decomposition of hydrogen peroxide in the presence of cellulose with ultraviolet irradiation and graft copolymerization occurring upon addition of methyl methacrylate to this system was investigated. Graft copolymerization barely began in the hydrogen peroxide system without ultraviolet irradiation, but was markedly accelerated by ultraviolet irradiation. Ultraviolet light is capable of initiating the graft copolymerization even without addition of hydrogen peroxide, and this capability is enhanced further with the use of hydrogen peroxide. However, an increase in the hydrogen peroxide concentration was observed to exercise a zero or negative effect on the number of grafts. Such a phenomenon is absent in the ceric ion initiator system and, in the present study, is believed to be brought about by a characteristic enhancement of the stabilization of grafting sites effected by hydroxyl radicals. The number of grafts of copolymers obtained in the present initiator system is only approximately 0.085 mmole/100 g of cellulose at its maximum and is within the range of results obtained for the hydrogen peroxide initiator system in general.

### INTRODUCTION

In the graft copolymerization of vinyl monomers to cellulose initiated by the hydrogen peroxide system, the polymerizability of pure cellulose is extremely low, but it becomes remarkably enhanced by the addition of metallic ions. One explanation for this is that such metallic ions promote the decomposition of hydrogen peroxide<sup>1</sup> and cause an increase in the activity of graft copolymerization. On the other hand, hydrogen peroxide is also decomposed by ultraviolet light<sup>2-4</sup> and the resultant hydroxyl radicals are known to initiate the polymerization of vinyl monomers. A large number of studies have been undertaken on such an initiation system.<sup>5-7</sup> Thus, both metallic ions and ultraviolet light are effective in promoting the decomposition of hydrogen peroxide. Consequently, it is expected that ultraviolet irradiation of a graft copolymerization system with hydrogen peroxide initiator will promote the graft copolymerization in the same fashion as the addition of metallic ions.

The effect of ultraviolet irradiation on a ceric ion initiator system has already been reported;<sup>8,9</sup> in the present study, the effects of ultraviolet irradiation on the decomposition of hydrogen peroxide in the presence of

cellulose and on the graft copolymerization of methyl methacrylate to cellulose with hydrogen peroxide initiator are examined.

## EXPERIMENTAL

### Decomposition of Hydrogen Peroxide

Bleached sulfite pulp (SP) and bleached semichemical pulp (SCP), both commercial commodities, were used as cellulose samples. The cellulose sample (0.50 g, oven dry) was allowed to react with 42.5 ml of an aqueous hydrogen peroxide solution of varying concentrations under nitrogen at 40°C for a given reaction time. The cellulose sample was then filtered off and the concentration of hydrogen peroxide in the filtrate was determined by 0.1*N* KMnO<sub>4</sub>. The degree of polymerization of the cellulose sample after the reaction was determined from the viscosity of its cupriethylenediamine solution at 25°C.<sup>1</sup>

### Graft Copolymerization

The cellulose sample (0.50 g, oven dry), 2.5 ml of methyl methacrylate, and 30 ml of water were placed in a polymerization tube, 10 ml of an aqueous hydrogen peroxide solution of a given concentration was added, and the resultant mixture was kept under nitrogen at 40°C. The polymerization product was washed with water and then extracted with acetone for 24 hr to remove homopolymer. The percent grafting, the average molecular weight of grafts, and the number of grafts were determined in the manner given previously<sup>1</sup> and the graft efficiency was obtained according to the following equation:

$$\text{Graft efficiency (\%)} = \frac{\text{weight of grafts}}{\text{total weight of homopolymer and grafts}} \times 100$$

### Ultraviolet Irradiation

Irradiation with ultraviolet light was carried out with a Toshiba high-pressure mercury lamp H-400P for photochemical use while placing the polymerization system enclosed in a hard glass tube of about 1 mm thickness at a distance approximately 11 cm from the light source.

## RESULTS AND DISCUSSION

### Decomposition of Hydrogen Peroxide

The decomposition of hydrogen peroxide with ultraviolet irradiation in the system wherein the cellulose sample is present is shown in Figure 1. The decomposition was extremely small at the initial stage of the reaction, but it tended to become extensive rapidly with the passage of time. With the same cellulose sample, the higher the hydrogen peroxide concentration, the more extensive the decomposition became. Such an increase in the

decomposition of hydrogen peroxide may be explained as follows: Hydroxyl radicals are formed by the decomposition of hydrogen peroxide as a result of ultraviolet irradiation and they in turn decompose hydrogen

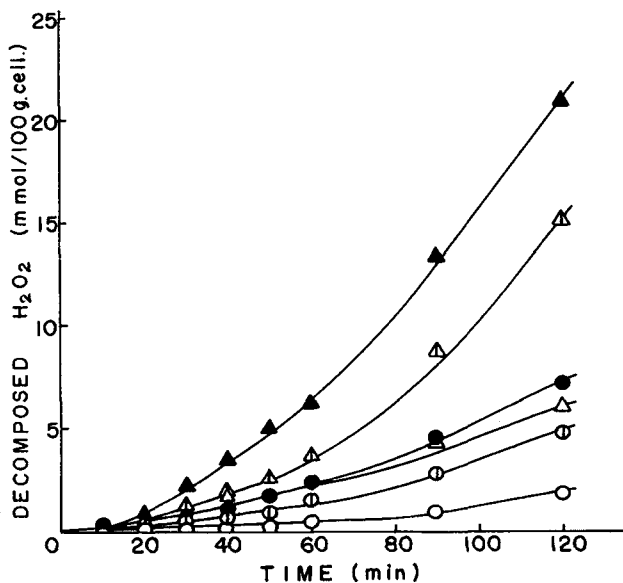


Fig. 1. Decomposition of hydrogen peroxide with ultraviolet irradiation in the system where cellulose sample is present. Reaction temperature 40°C. Concentration of hydrogen peroxide (mmole/l.): (O) SP, 1.10; (⊕) SP, 4.50; (●) SP, 9.00; (Δ) SCP, 1.10; (Δ) SCP, 5.20; (▲) SCP, 10.5.

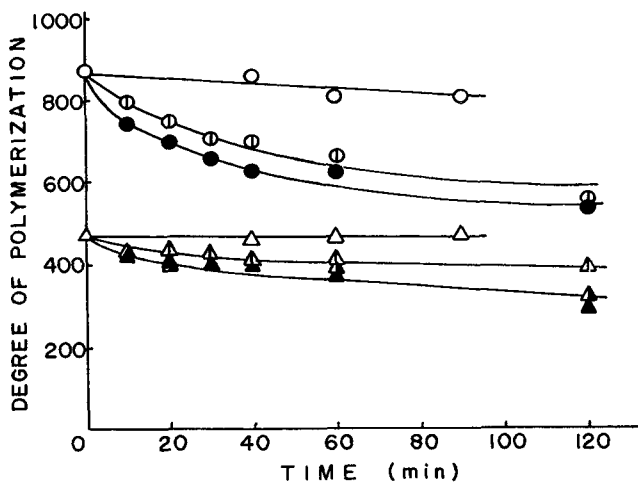


Fig. 2. Changes in degree of polymerization of cellulose with advancing decomposition of hydrogen peroxide under irradiation of ultraviolet light. Reaction temperature 40°C. Concentration of hydrogen peroxide (mmole/l.): (O) SP, 0; (⊕) SP, 1.10; (●) SP, 9.00; (Δ) SCP, 0; (Δ) SCP, 1.10; (Δ) SCP, 5.20; (▲) SCP, 10.5.

peroxide in a manner of a chain reaction.<sup>2-4</sup> The decomposition of hydrogen peroxide varied with the cellulose sample in the system and was in general larger for SCP than for SP.

Changes in the degree of polymerization of cellulose with advancing decomposition of hydrogen peroxide are shown in Figure 2. It is generally known that the degree of polymerization of cellulose is reduced by ultraviolet irradiation<sup>10,11</sup> but the reduction observed was extremely small in the system without hydrogen peroxide. Likewise, the reduction in the degree of polymerization was negligibly small in the hydrogen peroxide system without ultraviolet irradiation. The degree of polymerization of cellulose suffered reduction by hydrogen peroxide with ultraviolet irradiation, and the higher the hydrogen peroxide concentration, the larger the reduction became. As mentioned above, this phenomenon is probably caused by the attack of cellulose by the hydroxyl radicals which are formed upon decomposition of hydrogen peroxide. A similar phenomenon has been observed in the ferrous or ferric ion-hydrogen peroxide initiator system,<sup>1,12</sup> and the larger the amount of the metallic ions, the more exten-

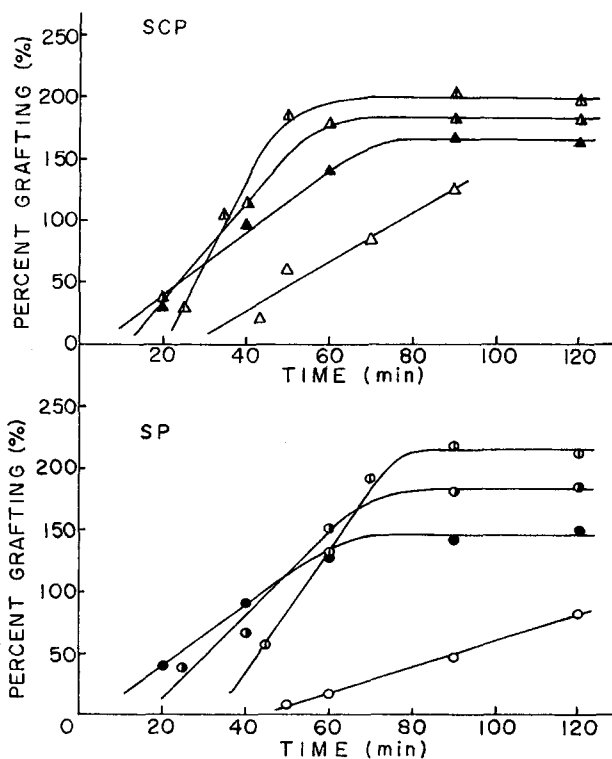


Fig. 3. Changes in per cent grafting of SP and SCP samples with time under various concentrations of hydrogen peroxide with ultraviolet irradiation. Polymerization temperature 40°C. Concentration of hydrogen peroxide (mmole/l.): (○) 0; (⊙) 1.10; (◌) 4.50; (●) 9.00; (△) 0; (▲) 1.10; (▲) 5.20; (▲) 10.5.

sive the decomposition of hydrogen peroxide and the larger the reduction in the degree of polymerization of cellulose became.

### Graft Copolymerization

Under the conditions of hydrogen peroxide concentration of 10 mmole/liter, polymerization temperature of 40°C, and polymerization time of 90 min, no initiation of graft copolymerization was observed for either SP or SCP without ultraviolet irradiation. As seen in Figure 3, however, the copolymerization began upon irradiation with ultraviolet light even in the absence of hydrogen peroxide, and the polymerization was promoted further by the addition of hydrogen peroxide. Moreover, the induction period was present in graft copolymerizations of both samples; it became shorter with increasing hydrogen peroxide concentration, and SCP generally showed a shorter induction period than SP.

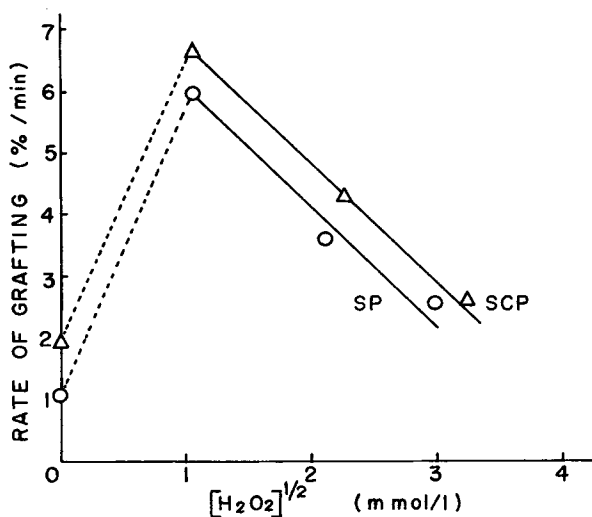


Fig. 4. Relation between initial reaction rate of graft copolymerization and concentration of hydrogen peroxide.

The initial reaction rate of graft copolymerization was determined from the slope of the straight line portion in Figure 3, and the relationship between such a rate and the hydrogen peroxide concentration is shown in Figure 4. The rate of copolymerization initially showed a considerable increase upon addition of hydrogen peroxide, but it thereafter tended to decrease with increasing hydrogen peroxide concentration. Such a decrease in the rate may be accounted for as follows: Hydroxyl radicals stabilize the grafting sites once formed on the cellulose and also actively participate in the termination reaction of graft polymer radicals. In fact, as will be described later, the higher the hydrogen peroxide concentration, the larger the reduction in the average molecular weight of grafts becomes.

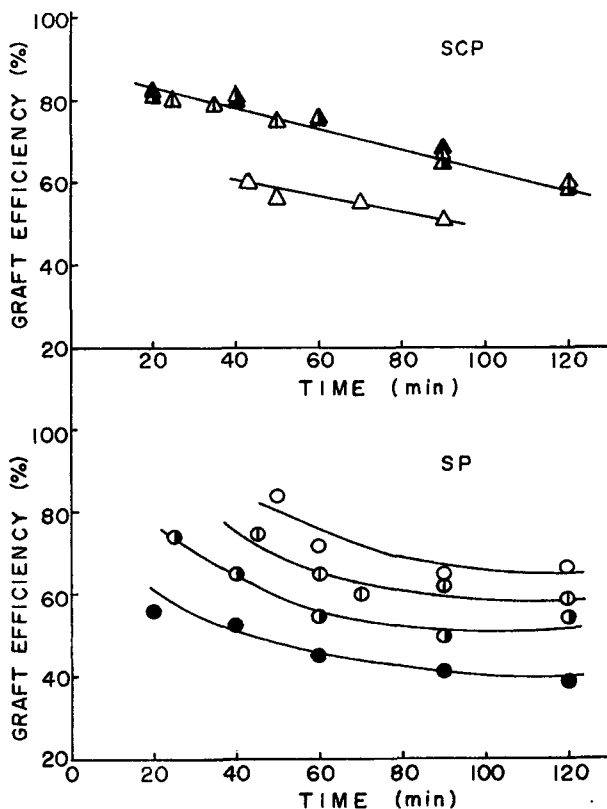


Fig. 5. Changes in graft efficiency with time. Polymerization temperature 40°C. Concentration of hydrogen peroxide (mmole/l.): (○) 0; (⊖) 1.10; (⊙) 4.50; (●) 9.00; (△) 0; (▲) 1.10; (▲) 5.20; (▲) 10.5.

The reaction rate of graft copolymerization varied with the kind of cellulose, and SCP gave a higher rate than SP.

Changes in the graft efficiency with time are shown in Figure 5. The graft efficiencies fell greatly as the reaction times increased for both cellulose samples, and this indicates that the formation of homopolymer by hydroxyl radicals lasts over a long period of time. It was observed that the graft efficiency rose with the use of hydrogen peroxide in the case of SCP, whereas it fell in contrast in the case of SP. Thus, the graft copolymerizability was affected greatly by the kind of cellulose sample used.

The graft copolymers were treated with 72%  $H_2SO_4$  to isolate grafted poly(methyl methacrylate). The average molecular weights of such grafts were determined from the viscosity of their acetone solution at 25°C and plotted against time in Figure 6. The average molecular weight is in the order of several millions without the use of hydrogen peroxide, but it is lower than this value with the use of hydrogen peroxide. In each system, the curve was extrapolated to the time at which the graft copolymerization

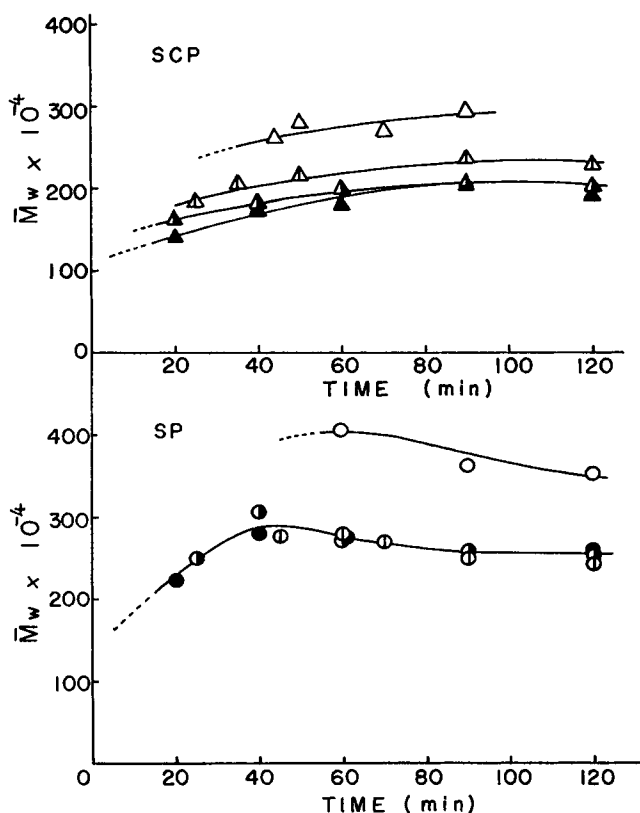


Fig. 6. Effect of hydrogen peroxide on average molecular weight of grafts. Concentration of hydrogen peroxide (mmole/l.): (○) 0; (◐) 1.10; (◑) 4.50; (●) 9.00; (△) 0; (◔) 1.10; (▲) 5.20; (▲) 10.5.

began, that is, to the end of the induction period (shown by a broken line in the figure), and the average molecular weight at the initial stage was determined. The relationship between this value and the hydrogen peroxide concentration is shown in Figure 7. The higher the hydrogen peroxide concentration, the larger the reduction in the molecular weight of grafts became; this indicates that the termination reaction of graft polymer radicals became active under influence of hydroxyl radicals. The molecular weight of grafts on SCP was much smaller than that on SP.

The number of grafts of copolymers is given in Table I. The number of grafts in the presence of hydrogen peroxide is definitely greater than that in the absence of hydrogen peroxide, but an increase in the hydrogen peroxide concentration exerts a zero effect on the number of grafts in the case of SCP and a negative effect in the case of SP. Such a phenomenon has already been noted in studies on the metallic ion-hydrogen peroxide initiator system<sup>1,13</sup> and may be explained by the accelerated stabilization of the grafting sites once formed on cellulose. Consequently, it is undoubtedly

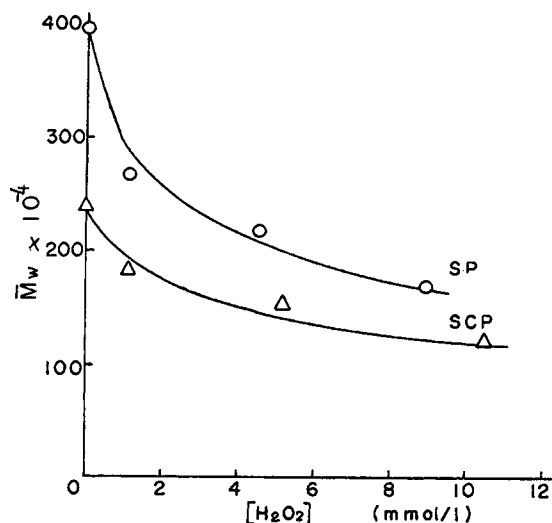


Fig. 7. Relationship between average molecular weight of grafts and concentration of hydrogen peroxide.

preferable to use a fairly low concentration of hydrogen peroxide for graft formation in the system such as this, and the maximum value experimentally observed was roughly the same for both SP and SCP, that is, 0.085 mmole/100 g of cellulose. However, this value falls in the range obtained for the hydrogen peroxide initiator system in general,<sup>1,12-15</sup> and is not particularly worthy of attention.

Thus, it is obvious that ultraviolet irradiation promotes the decomposition of hydrogen peroxide, activates the graft copolymerization reaction, and affects the molecular weight of grafts. However, the effect of such irradiation is similar to the catalytic action of ferrous ion,<sup>12,13</sup> ferric ion,<sup>1,12</sup> sodium thiosulfate,<sup>15</sup> and the like, and the accelerated formation of hydroxyl radicals appears to be the main cause. It was found in the present system that the higher the hydrogen peroxide concentration, the larger the reduction in the number of grafts tended to become. Such a phenomenon

TABLE I  
Number of Grafts of Graft Copolymer<sup>a</sup>

H <sub>2</sub> O <sub>2</sub> concn., mmole/liter		Number of grafts (×10 <sup>3</sup> ), mmole/100 g cellulose	
SP	SCP	SP	SCP
0	0	1.20	4.31
1.10	1.10	8.65	8.48
4.50	5.20	7.00	8.95
9.00	10.50	5.47	8.47

<sup>a</sup> The results of 90 min polymerization time and 40°C polymerization temperature are shown.



is not common in the ceric ion initiator system and seems to be characterized by the formation of hydroxyl radicals and their behavior.

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