

Graft Copolymerization to Cellulose. Effect of Sodium Thiosulfate on Hydrogen Peroxide Initiator System

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Synopsis

The effect of sodium thiosulfate on the graft copolymerization of methyl methacrylate to cellulose in the hydrogen peroxide initiator system was investigated. The addition of sodium thiosulfate in general was effective for decreasing the per cent grafting and the average molecular weight of grafts and increasing the formation of homopolymer, and the effects became pronounced with increasing hydrogen peroxide concentration. Moreover, the addition of sodium thiosulfate slightly suppressed the formation of grafts at a hydrogen peroxide concentration of 3 mmole/l., but greatly promoted it at 20 mmole/l. Traces of metallic ions present in cellulose could not be eliminated sufficiently by treatment with 3*N* hydrochloric acid. Such ions were found to interact with hydrogen peroxide and thus participate directly in the initiation and termination of the polymerization reaction. EDTA, the chelating agent, was highly effective for suppressing such participation of metallic ions. In the hydrogen peroxide initiator system applied to the EDTA-treated samples, sodium thiosulfate caused an effective initiation of graft formation.

INTRODUCTION

In graft copolymerization of vinyl monomers to cellulose in the presence of hydrogen peroxide as an initiator, a variety of metallic ions are often added to raise the polymerization activity.¹⁻³ Metallic ions, however, are generally adsorbed readily on cellulose⁴ and the ions added may remain in the copolymers formed and affect the properties and stability of such copolymers. On the other hand, sodium thiosulfate is known to form an effective redox initiator system with persulfate, and a number of studies are known on the polymerization of vinyl monomers using such redox initiators.⁵⁻⁸ Hydrogen peroxide as an oxidizing agent in place of persulfate would be expected to show a similar initiation effect.

In this paper, graft copolymerization of methyl methacrylate to cellulose was attempted in the hydrogen peroxide-sodium thiosulfate initiator system for the purpose of eliminating the defects seen in the co-presence of metallic ions, and the effect of sodium thiosulfate on the graft copolymerization was primarily investigated.

EXPERIMENTAL

Cellulose Samples

Bleached semichemical pulp (SCP), dissolving pulp (DP), and bleached sulfite pulp (SP) for paper making, all commercial commodities, were used. Each cellulose sample was immersed in an aqueous EDTA solution of the concentration of 10 mmole/l. (liquid ratio 80) at room temperature for 30 min, filtered, and washed with water to furnish the EDTA-treated sample. On the other hand, the cellulose sample was packed in a column, treated with 3*N* hydrochloric acid for 1–2 hr, and washed repeatedly with water to give the hydrochloric acid-treated sample.

Graft Copolymerization

The cellulose sample (0.50 g, oven dry), 2.5 ml methyl methacrylate, and 30 ml aqueous sodium thiosulfate solution of a given concentration were charged into a polymerization tube, the system was placed under nitrogen, 10 ml aqueous hydrogen peroxide solution of a given concentration was injected to make the total liquid volume 42.5 ml, and the polymerization was allowed to proceed. The polymerization product was extracted with acetone to remove homopolymer, and the percentage increase in weight over the original cellulose sample was taken as the per cent grafting. The per cent homopolymer was expressed as the percentage of homopolymer formed based on the original cellulose sample similarly to the per cent grafting. The average molecular weight of the grafted poly(methyl methacrylate) which had been removed from the copolymer by means of 72% sulfuric acid was determined from the viscosity of the acetone solution at 25°C according to the following equation⁹:

$$[\eta] = 0.96 \times 10^{-4} M^{0.68}$$

The number of grafts of the copolymer was determined from the per cent grafting and the average molecular weight of the grafts and was expressed as the number of mmoles of grafts per 100 g of cellulose.

RESULTS AND DISCUSSION

Effect of Sodium Thiosulfate

The effect of sodium thiosulfate was examined on the system containing 3 mmole of hydrogen peroxide per liter, and the results are shown in Figure 1. As the addition of sodium thiosulfate increased, the rate of graft copolymerization tended to decrease but the formation of homopolymer was accelerated in contrast. The results obtained in the case of 20 mmole of hydrogen peroxide per liter are shown in Figure 2. They turned out a little complicated, but it may be said, when a comparison is made at a polymerization time of 70 min or more, that the per cent grafting is lowered by the addition of sodium thiosulfate. The formation of homopolymer shows

the same tendency as in the case of 3 mmole of hydrogen peroxide per liter, and this phenomenon seems to support the view that the addition of sodium thiosulfate promotes the formation of radicals in water. At higher concentrations of hydrogen peroxide, the induction period was present in the polymerization in the absence of sodium thiosulfate, but it disappeared in the presence of sodium thiosulfate.

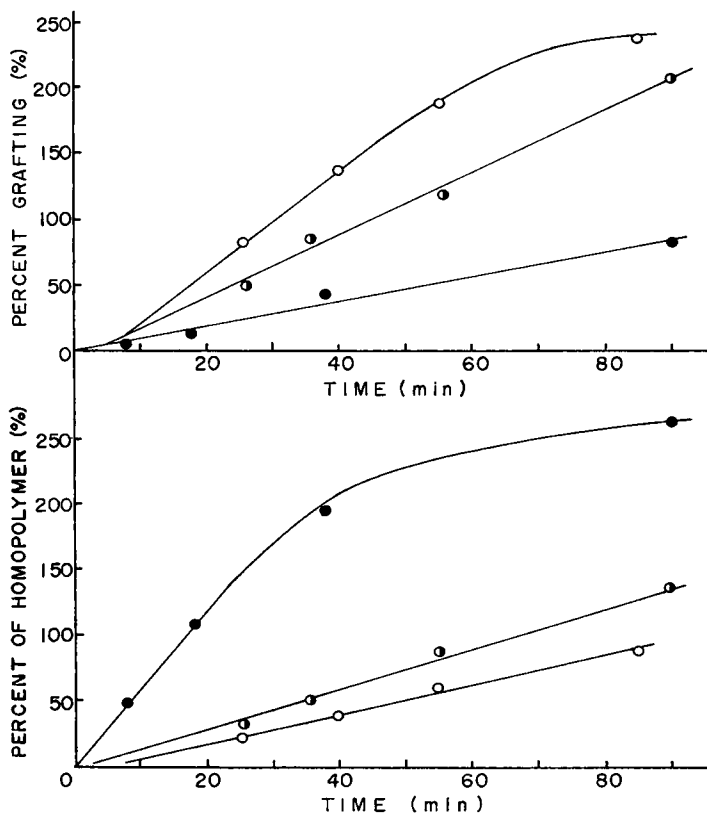


Fig. 1. Effects of sodium thiosulfate on per cent grafting and per cent homopolymer. Polymerization temperature 60°C. Concentration of hydrogen peroxide 3 mmole/l., concentration of sodium thiosulfate (mmole/l.): (O) 0; (◐) 1.0; (●) 5.0.

The average molecular weights of grafts of the copolymers obtained in the presence of the hydrogen peroxide–sodium thiosulfate initiator can be divided into two groups in relation to the hydrogen peroxide and sodium thiosulfate concentrations, as shown in Figure 3. They were in the range of 4 to 6 millions with or without addition of sodium thiosulfate in the case of 3 mmole of hydrogen peroxide per liter. In the case of 20 mmole of hydrogen peroxide per liter, the average molecular weight decreased below 2 millions with addition of sodium thiosulfate. Thus it is seen that sodium thiosulfate does not affect the molecular weight appreciably at low concen-

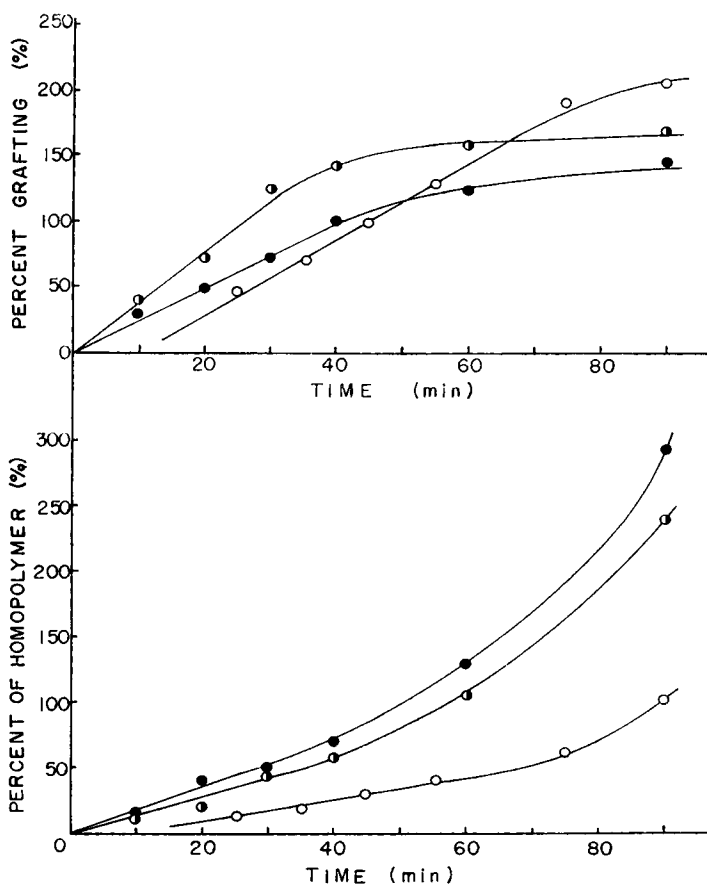


Fig. 2. Effects of sodium thiosulfate on per cent grafting and per cent homopolymer. Polymerization temperature 60°C. Concentration of hydrogen peroxide 20 mmole/l., concentration of sodium thiosulfate (mmole/l.): (O) 0; (◐) 1.0; (●) 3.0.

trations of hydrogen peroxide, but acts to reduce the molecular weight of grafts to a considerable extent at high concentrations of hydrogen peroxide.

Changes in the number of grafts with time are shown in Figure 4. The effect of sodium thiosulfate on the formation of grafts is seen to vary with the concentration of hydrogen peroxide. The number of grafts decreased upon addition of sodium thiosulfate in the case of 3 mmole of hydrogen peroxide per liter, whereas it increased in the case of 20 mmole of hydrogen peroxide per liter. It is inferred that, in the redox system where radicals are mainly formed in water, increasing amounts of sodium thiosulfate become more and more effective in the formation of homopolymer and consequently suppresses the formation of grafts. However, this inference is not satisfactory for a system with high concentration of hydrogen peroxide. In such a system, many factors seem to participate in the formation of grafts to yield complicated results.

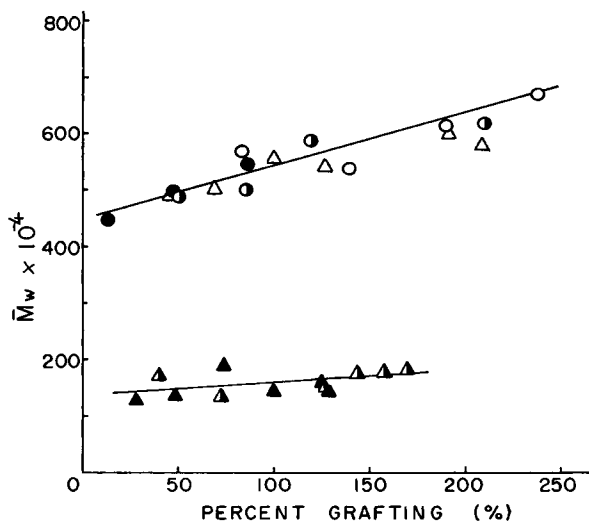


Fig. 3. Relationship between average molecular weight of grafts and per cent grafting. Concentration of hydrogen peroxide 3 mmole/l., concentration of sodium thiosulfate (mmole/l.): (○) 0; (●) 1.0; (●) 5.0. Concentration of hydrogen peroxide 20 mmole/l., concentration of sodium thiosulfate (mmole/l.): (△) 0; (▲) 1.0; (▲) 3.0.

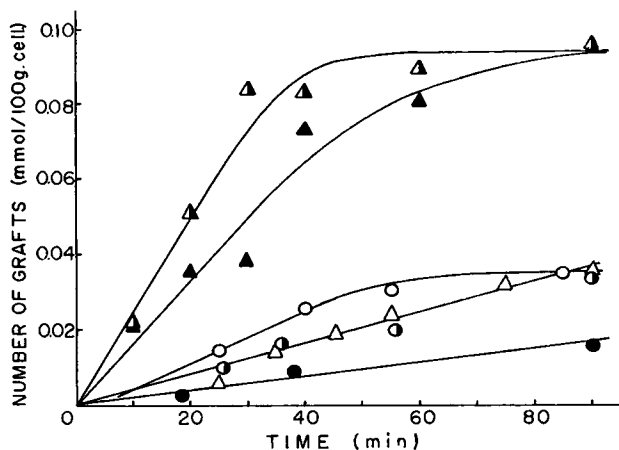


Fig. 4. Effect of sodium thiosulfate on number of grafts. Concentration of hydrogen peroxide 3 mmole/l., concentration of sodium thiosulfate (mmole/l.): (○) 0; (●) 1.0; (●) 5.0. Concentration of hydrogen peroxide 20 mmole/l., concentration of sodium thiosulfate (mmole/l.): (△) 0; (▲) 1.0; (▲) 3.0.

Graft Copolymerization of EDTA-Treated Samples

As mentioned above, hydrogen peroxide alone is fairly effective for initiating the graft copolymerization of the SCP sample even without the addition of sodium thiosulfate, and participation of traces of metals present in the cellulose sample is suspected. To eliminate such effects, the SCP

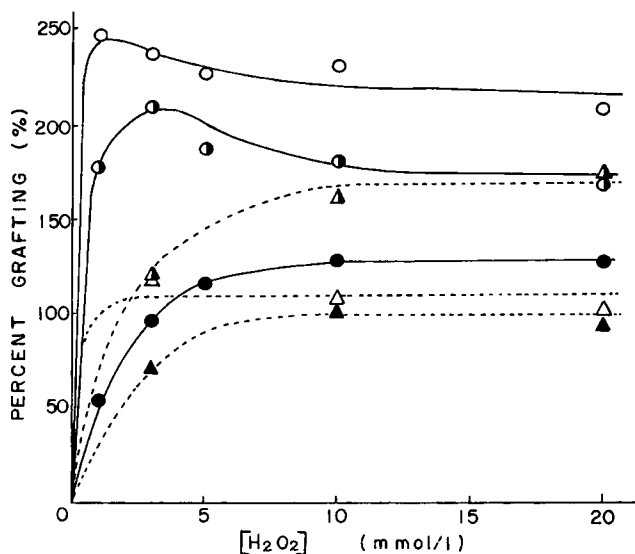


Fig. 5. Changes in per cent grafting due to EDTA treatment and addition of sodium thiosulfate. Polymerization temperature 60°C. Polymerization time 90 min. Untreated SCP (solid lines), concentration of sodium thiosulfate (mmole/l.): (○) 0; (●) 1.0; (●) 3.0. EDTA-treated SCP (dotted lines), concentration of sodium thiosulfate (mmole/l.): (△) 0; (△) 1.0; (▲) 3.0.

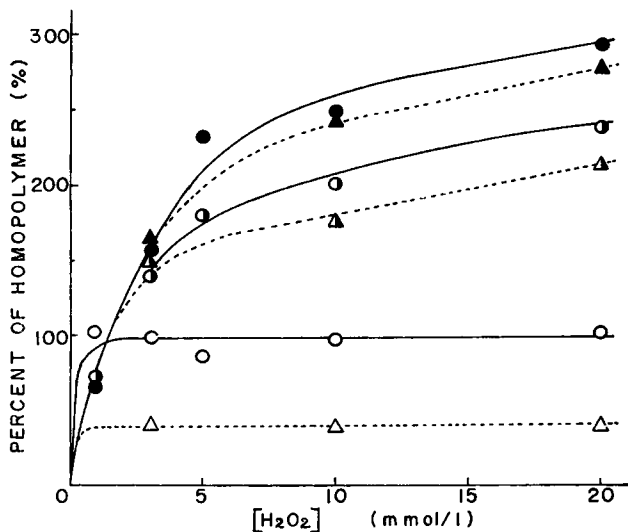


Fig. 6. Changes in per cent of homopolymer due to EDTA treatment and addition of sodium thiosulfate. Polymerization temperature 60°C. Polymerization time 90 min. Untreated SCP (solid lines), concentration of sodium thiosulfate (mmole/l.): (○) 0; (●) 1.0; (●) 3.0. EDTA-treated SCP (dotted lines), concentration of sodium thiosulfate (mmole/l.): (△) 0; (△) 1.0; (▲) 3.0.

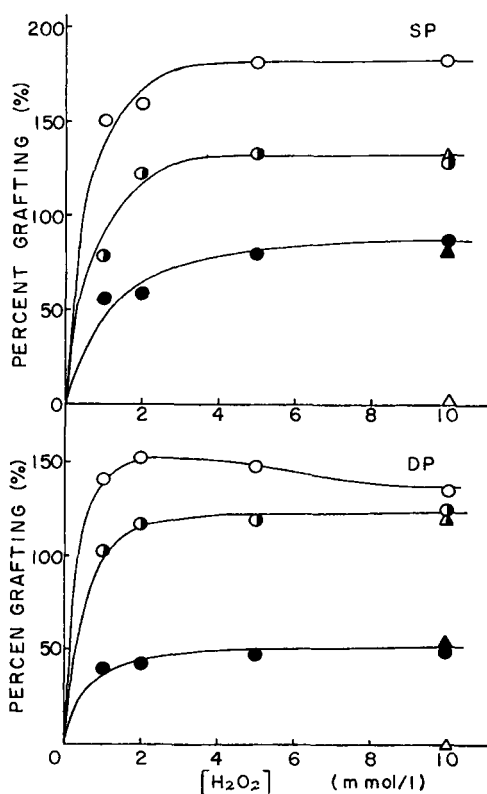


Fig. 7. Effects of sodium thiosulfate on per cent grafting on SP and DP samples with or without treatment of EDTA. Polymerization temperature 60°C. Polymerization time 90 min. Untreated sample (solid lines), concentration of sodium thiosulfate (mmole/l.): (○) 0; (◐) 1.0; (●) 3.0. EDTA-treated sample, concentration of sodium thiosulfate (mmole/l.): (△) 0; (◒) 1.0; (▲) 3.0.

sample which had been treated with aqueous EDTA solution to mask the characteristics of metallic ions was used and the behavior during the graft copolymerization was investigated. The results are shown in Figures 5 and 6. The polymerization temperature and time were maintained at 60°C and 90 min, respectively. The per cent grafting decreased upon treatment with EDTA as a whole, but the effect of the addition of sodium thiosulfate was entirely different from that in the case of the untreated sample. The formation of homopolymer tended to increase with increasing addition of sodium thiosulfate regardless of the EDTA treatment, and the EDTA treatment worked toward suppressing, albeit slightly, the formation of homopolymer as a whole.

Similar relationships are shown in Figure 7 for the SP and DP samples. Both samples gave lower per cent grafting at larger additions of sodium thiosulfate, and the EDTA-treated samples gave nearly 0% grafting. However, upon addition of 1 or 3 mmole of sodium thiosulfate per liter to

these samples, the per cent grafting again increased, thus making the effect of sodium thiosulfate on the graft copolymerization evident.

The average molecular weights of grafts of each copolymer are shown in Figure 8. The higher the concentration of hydrogen peroxide and the larger the addition of sodium thiosulfate, the lower the average molecular weight became. However, the EDTA treatment slightly increased the

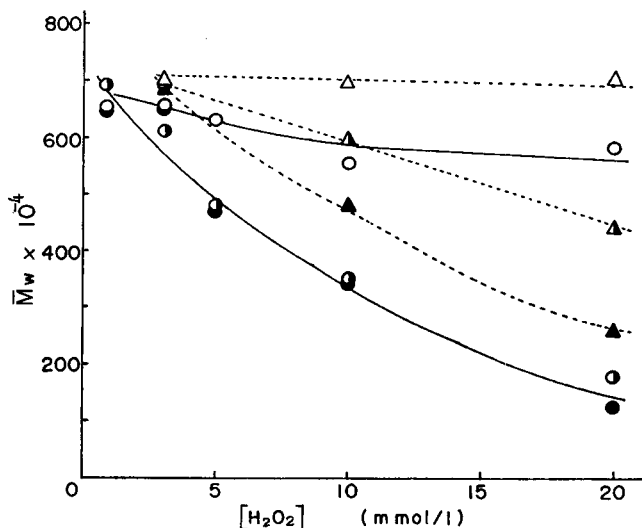


Fig. 8. Changes in average molecular weight of grafts related to concentration of hydrogen peroxide and EDTA treatment. Untreated SCP (solid lines), concentration of sodium thiosulfate (mmole/l.): (○) 0; (◐) 1.0; (●) 3.0. EDTA-treated SCP (dotted lines), concentration of sodium thiosulfate (mmole/l.): (Δ) 0; (◒) 1.0; (▲) 3.0.

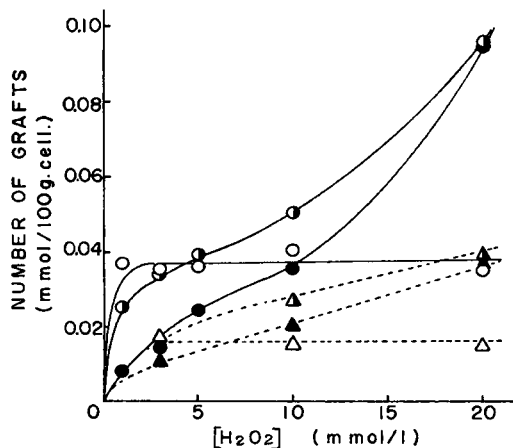


Fig. 9. Effects of concentration of hydrogen peroxide and EDTA treatment on number of grafts. Untreated SCP (solid lines), concentration of sodium thiosulfate (mmole/l.): (○) 0; (◐) 1.0; (●) 3.0. EDTA-treated SCP (dotted lines), concentration of sodium thiosulfate (mmole/l.): (Δ) 0; (◒) 1.0; (▲) 3.0.

average molecular weight on the whole. That is, in this polymerization system, both traces of metallic ions in cellulose and sodium thiosulfate in combination with hydrogen peroxide would presumably participate in the termination of graft polymer radicals.

The formation of grafts in the EDTA-treated sample is shown in Figure 9. The number of grafts in general decreased upon treatment with EDTA as in the case of the per cent grafting. Moreover, the effect of the concentration of hydrogen peroxide on the number of grafts was hardly noticeable in the absence of sodium thiosulfate, but it was extremely remarkable in the presence of sodium thiosulfate. The decrease in the number of grafts observed in the EDTA-treated system in the absence of sodium thiosulfate is probably caused by suppression of the formation of radicals as a result of masking of metallic ions in cellulose; an effective redox initiator system with hydrogen peroxide would be formed upon addition of sodium thiosulfate to this system and the formation of grafts would become active again. Thus, it may be said that both metallic ions and sodium thiosulfate in combination with hydrogen peroxide also participate in the formation of grafts.

The cellulose samples were treated with 3*N* hydrochloric acid to eliminate metallic ions contained therein, and the behavior during the formation of grafts was observed on such treated samples. The results obtained were similar to those shown in Figure 9. This indicates that the treatment with hydrochloric acid hardly affected the polymerization reaction and the elimination of metallic ions did not occur sufficiently. The mechanism of adsorption of metallic ions on cellulose is reported elsewhere.⁴

With the hydrogen peroxide-sodium thiosulfate initiator system, the graft copolymerization is considered to be initiated mainly upon attack of cellulose by radicals formed in water and is affected considerably by a combination of the sodium thiosulfate and hydrogen peroxide concentrations to be used. The polymerization reaction would become further complicated by the presence of traces of metallic ions in cellulose since they participate not a little in the decomposition of hydrogen peroxide.

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