

Studies on the Ability of Cellulosic Materials to Initiate Graft Copolymerization

YOSHITAKA OGIWARA, KIKUJI IGETA, and HITOSHI KUBOTA,
*Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu,
Gunma 376, Japan*

Synopsis

The activity to initiate graft copolymerization was investigated for various cellulose samples. Oxidation of the sample with hydrogen peroxide or sodium hypochlorite indicated a remarkable increase in the per cent grafting as well as the number of grafts. This phenomenon must be attributed to the formation of special reactive groups in cellulosic materials. However, the treatment with hot water caused a definite decrease in the per cent grafting or the number of grafts for the graft copolymerization on the sample, indicating a lower activity to initiate graft copolymerization. Accordingly, the reactive groups, once formed on the sample by oxidation, seemed to be easily decomposed by hot water. The ferric ion adsorbed on cellulose increased the per cent grafting and accelerated the formation of grafts, and the contribution of metallic ions to the initiation was recognized as one of the important factors of graft copolymerization.

INTRODUCTION

It has been observed that cellulosic materials can initiate polymerization when they are heated with vinyl monomer and water and that, if cellulose samples are treated with hot water beforehand, the ability to initiate polymerization is decreased drastically.¹ This is attributed to the destruction by hot water of reactive groups existing in cellulosic materials. The effects of carbon tetrachloride and metallic salts on this system have been thoroughly investigated by Imoto and co-workers.²⁻⁴ The kinetics of a similar polymerization system using oligomeric poly(vinyl alcohol) have also been examined.⁵

However, it seems that many problems still remain unsolved concerning the characteristics of cellulosic materials that contribute to this initiation reaction. The oxidation state of cellulosic materials is considered to be one of the factors affecting their reactivity. Namely, cellulosic materials pass through various oxidation states during the course of preparation, and, if any metallic ions exist in cellulosic materials and act as catalyst, the specific reactivity of these celluloses in polymerization initiation seems to be further affected.

In the present study, graft copolymerization of methyl methacrylate onto oxidized and metallic ion-adsorbing cellulose samples was carried out in

order to determine how the state of the cellulosic materials affects the graft copolymerization.

EXPERIMENTAL

Cellulose Samples

Dissolved pulp from hardwoods was used as cellulose. The air-dried pulp was tumbled in a blender and designated as untreated sample. This sample was treated according to the following conditions and used for grafting.

Treatment with Hot Water. A given amount of untreated sample was weighed and dispersed in water to a 1% concentration. After dispersion, the sample was refluxed with water for 2 hr, washed with water, and used for further experiments in wet or dry state.

Oxidation by Sodium Hypochlorite and Hydrogen Peroxide. After being treated with hot water, the wet sample was dispersed in water to a 1% concentration, oxidized by a given concentration of sodium hypochlorite at 45°C for 120 min or by hydrogen peroxide at 60°C for 90 min, washed with cold water, and used for further experiments in wet or dry state.

Ferric Ion-Adsorbing Cellulose. The above-mentioned sample was treated with a given concentration of ferric chloride aqueous solution at 45°C for 60 min, washed with water, and treated with 0.1*N* HCl (volume ratio of liquid to material, 150:1). After being washed with water to neutral, the material was used for further experiments.

Graft Copolymerization

A mixture of 0.50 g cellulose (oven dry) and 40 ml water was placed in a 100-ml polymerization tube. After evacuation and replacement with nitrogen, 2.5 ml methyl methacrylate was charged, and the polymerization was carried out at 85°C for a given duration. After the polymerization was stopped by adding a small amount of hydroquinone, the polymerization product was washed with water and then dried. Homopolymer was separated by acetone extraction for 30 hr. Weight increase of the graft copolymer after extraction, represented by percentage of cellulose, was indicated as per cent grafting.

Weight-Average Molecular Weight of Grafts and Number of Grafts

After the grafted poly(methyl methacrylate) was isolated with 72% H₂SO₄, its weight-average molecular weight was obtained from the intrinsic viscosity in acetone at 25°C by means of the following equation:⁶

$$[\eta] = 0.96 \times 10^{-4} M^{0.69}.$$

The molar number of grafts per 100 g cellulose was calculated from the weight-average molecular weight and per cent grafting and was indicated as the number of grafts.

RESULTS AND DISCUSSION

The results of the graft copolymerization for various cellulosic materials are shown in Figure 1. Although the relation between per cent grafting and polymerization time varied with each cellulose sample, the per cent grafting peculiar to each sample appeared to be almost attained after 5 hr. The untreated sample itself showed its own activity to initiate copolymerization to some extent. When this sample was treated with hot water, however, an appreciable decrease in per cent grafting was observed. Imoto and co-workers¹ also observed a similar tendency when cellulose was treated with hot water or ethyl alcohol extraction. It can be easily assumed that the ability of a sample to initiate copolymerization might be affected by such actions as that of air when a wet sample which has been treated with hot water is dried.

This possibility was examined, and a slight difference was observed in the initial increase of the per cent grafting; however, the effect was found to be negligible. The oxidation of a sample whose activity was decreased by treating it with hot water was also examined, and it was found that the per cent grafting for the sample oxidized with 4.70 mmole/l. solution of sodium

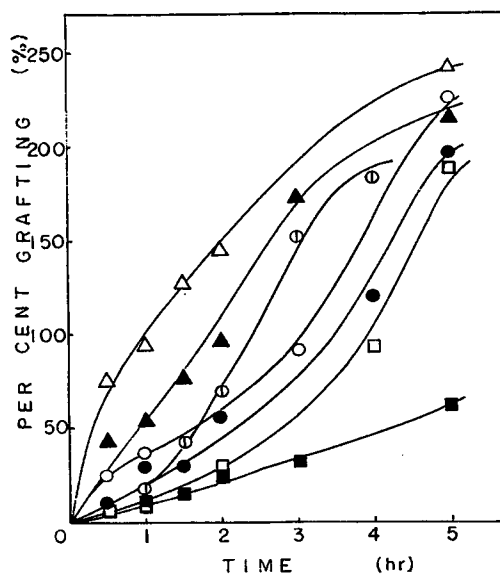


Fig. 1. Relationship between per cent grafting and polymerization time for various cellulose samples: (○) untreated cellulose sample. Cellulose sample treated with hot water: (■) dry; (□) wet. Cellulose sample oxidized with sodium hypochlorite: (●) dry; (○) wet. Cellulose sample oxidized with hydrogen peroxide: (▲) dry; (△) wet.

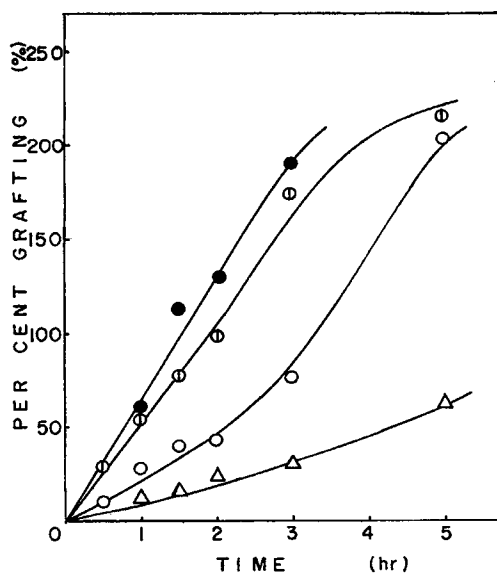


Fig. 2. Effect of oxidation with hydrogen peroxide on per cent grafting. Concentration of hydrogen peroxide: (Δ) 0 mmole/l.; (\circ) 5.0 mmoles/l.; (\odot) 11.7 mmoles/l.; (\bullet) 20.0 mmoles/l.

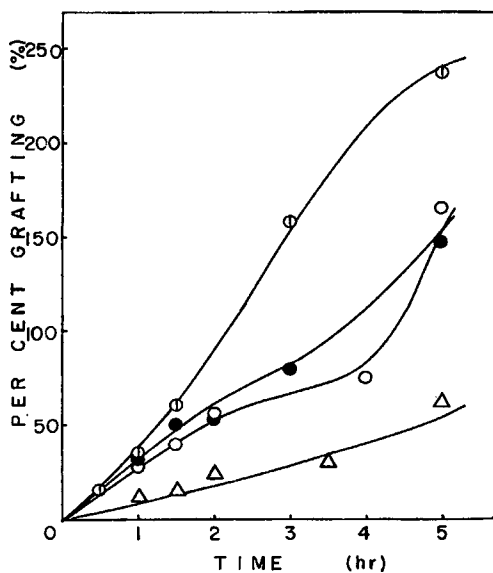


Fig. 3. Effect of oxidation with sodium hypochlorite on per cent grafting. Concentration of sodium hypochlorite: (Δ); 0 mmole/l.; (\circ) 4.7 mmoles/l.; (\bullet) 10.0 mmoles/l.; (\odot) 20.0 mmoles/l.

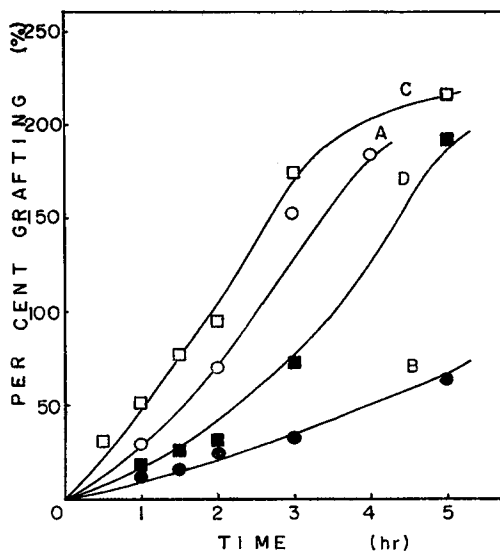


Fig. 4. Effect of hot-water treatment on per cent grafting: (O) untreated sample (A); (●) A treated with hot water (B); (□) B oxidized with hydrogen peroxide (C); (■) C treated with hot water (D).

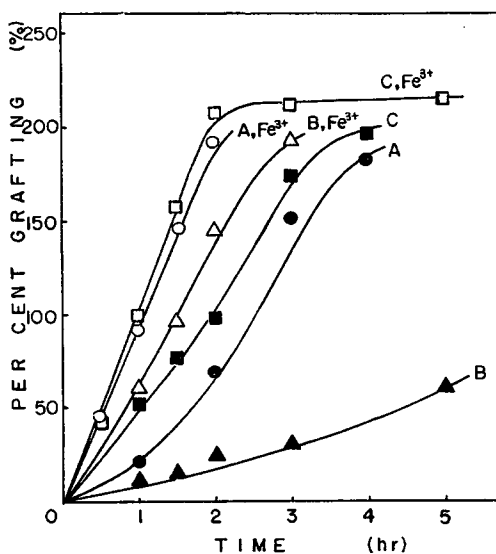


Fig. 5. Effect of ferric ion adsorption on cellulose samples on per cent grafting. Cellulose samples not adsorbing ferric ion: (●) untreated sample (A); (▲) A treated with hot water (B); (■) B oxidized with hydrogen peroxide (C). Cellulose samples adsorbing ferric ion: (O) A; (Δ) B; (□) C.

hypochlorite was increased remarkably. The sample oxidized with a 11.7 mmole/l. solution of hydrogen peroxide showed a higher per cent grafting, as seen in Figure 1. From this significant increase in the per cent grafting brought about by oxidation, the assumption can be made that the special oxidized state of cellulose has a close relation to its ability to initiate graft copolymerization.

Similar examination was also carried out on the samples oxidized to different extents, and the results are shown in Figures 2 and 3. As seen in Figure 2, the per cent grafting was increased with a higher concentration of hydrogen peroxide. The results for sodium hypochlorite are shown in Figure 3, and a higher per cent grafting was observed with a higher concentration of oxidizing agent as well as for hydrogen peroxide. Thus, it was found for both oxidizing agents that the activities of samples to initiate graft copolymerization were increased by severer oxidizing conditions. This might indicate that the oxidation of samples contributes directly to the activity to initiate graft copolymerization.

The formation of unstable peroxides is naturally expected in the oxidation of cellulosic materials. Therefore, detection of peroxides was attempted by estimating iodine isolated from the reaction between potassium iodide⁷ and the sample, or by spectrophotometric measurement using phenolphthalein.⁸ Each sample reacted only slightly, indicating that the formation of peroxide groups was very slight. However, the authors⁹ have observed the formation of functional groups which are very active after oxidation of cellulose. It might be supposed that these active groups suffer in the course of heating with water and that this type of reaction has a close relation to the initiation of copolymerization.

The effect of hot water treatment of cellulose on graft copolymerization was examined, and the results are shown in Figure 4. As in Figure 1, the activity to initiate graft copolymerization decreased significantly by treatment of the untreated samples with hot water. The samples whose activity to initiate graft copolymerization was first increased by oxidizing them with 11.7 mmole/l. hydrogen peroxide also showed a remarkable decrease in activity of copolymerization initiation in a similar manner as the untreated samples. However, in this case, the per cent grafting did not reach the low value observed in untreated samples after hot water treatment. This result indicates that the oxidation increases the ability of limitation of the sample after hot water treatment.

The effect of adsorbed ferric ion on cellulose on graft copolymerization was examined, and results are shown in Figure 5. Untreated, hot water-treated, and hot water-treated and then hydrogen peroxide-oxidized cellulose samples were treated with a 0.1 mmole/l. aqueous solution of ferric chloride at 45°C for 60 min. The adsorption of ferric ion definitely increase the activity to initiate graft copolymerization for each cellulose sample. The same effects of metallic salts have been observed by Takeda and Takemoto³ in the nylon 6-H₂O-vinyl monomer-carbon tetrachloride system, and by Iki and co-workers⁴ in the cellulose-H₂O-vinyl monomer-

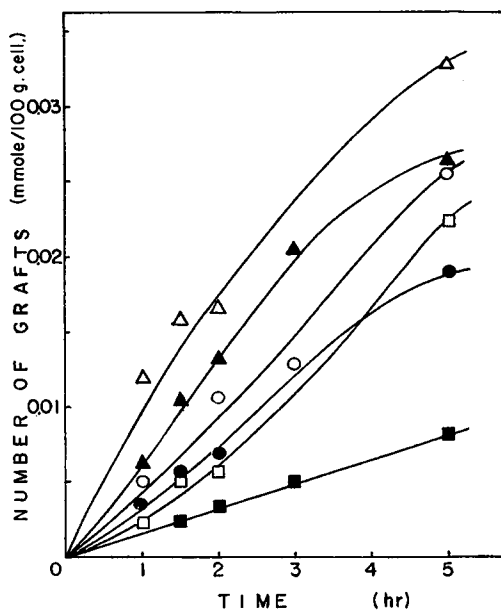


Fig. 6. Relationship between number of grafts and polymerization time for various cellulose samples. Cellulose sample treated with hot water: (■) dry; (□) wet. Cellulose sample oxidized with sodium hypochlorite: (●) dry; (○) wet. Cellulose sample oxidized with hydrogen peroxide: (▲) dry; (△) wet.

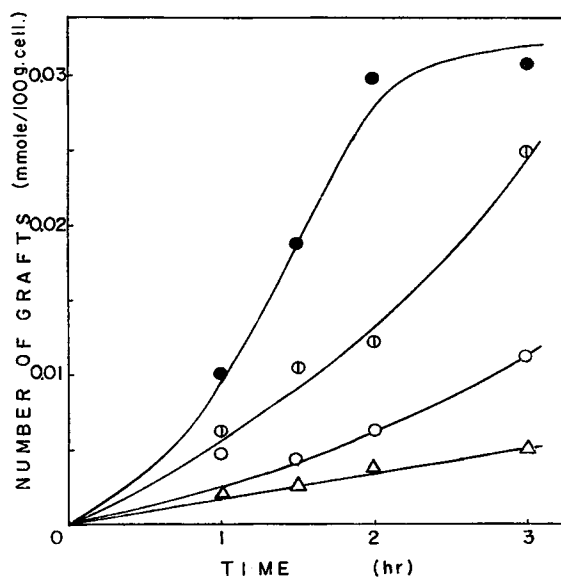


Fig. 7. Effect of oxidation with hydrogen peroxide on rate of formation of grafts. Concentration of hydrogen peroxide: (△) 0 mmole/l.; (○) 5.0 mmoles/l., (⊙) 11.7 mmoles/l.; (●) 20.0 mmoles/l.

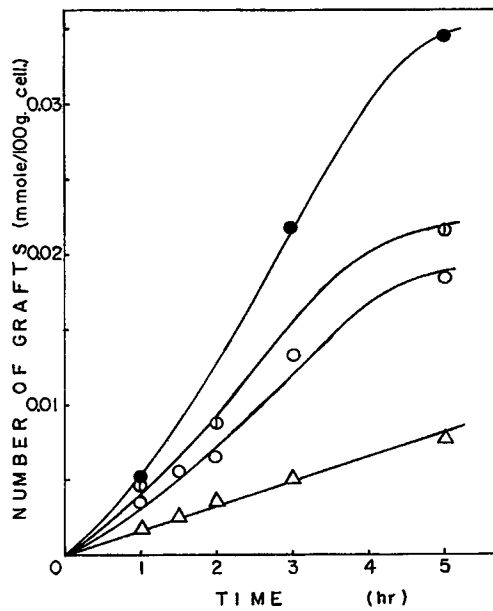


Fig. 8. Effect of oxidation with sodium hypochlorite on rate of formation of grafts. Concentration of sodium hypochlorite: (Δ) 0 mmole/L; (\circ) 4.7 mmoles/L; (\odot) 10.0 mmoles/L; (\bullet) 20.0 mmoles/L.

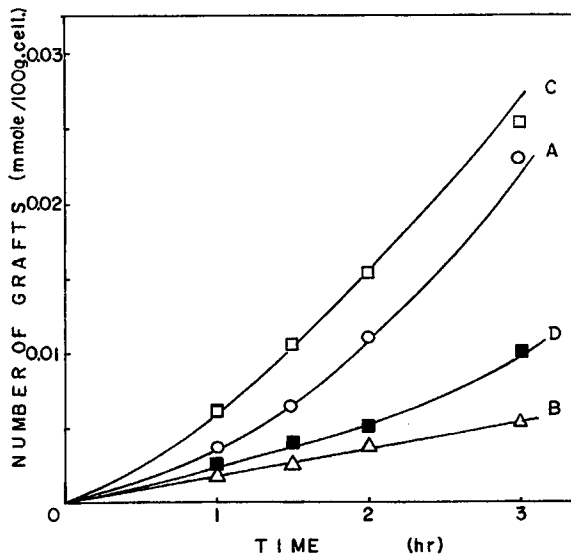


Fig. 9. Effect of hot water treatment on the rate of formation of grafts: (\circ) untreated samples (A); (Δ) A treated with hot water (B); (\square) B oxidized with hydrogen peroxide (C); (\blacksquare) C treated with hot water (D).

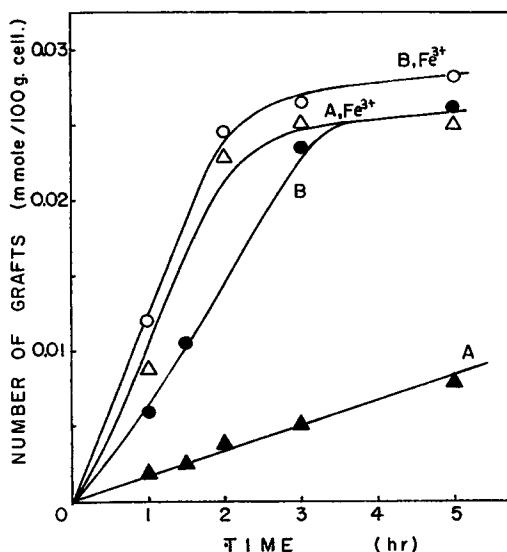


Fig. 10. Effect of ferric ion adsorbed on various cellulose samples on rate of formation of grafts. Cellulose samples unadsorbing ferric ion: (▲) cellulose samples treated with hot water (A); (●) A oxidized with hydrogen peroxide (B). Cellulose samples adsorbing ferric ion: (△) A; (○) B.

carbon tetrachloride system; in this polymerization system, it was also confirmed that ferric ion can accelerate graft copolymerization.

In order to investigate the activity of cellulosic materials to initiate graft copolymerization in more detail, the number of grafts of the copolymer was obtained and the formation reaction of the grafts was examined. In Figure 6, the changes in number of grafts with polymerization time are shown for oxidized samples after hot-water treatment. The rate of formation of grafts for the samples whose activity to initiate was decreased by hot water was observed to increase remarkably by oxidation with sodium hypochloride and further with hydrogen peroxide. The state of the cellulose (whether wet or dry) had little if any influence on the formation of grafts or on the per cent grafting.

Figure 7 shows the effect of hydrogen peroxide concentration. The rate of formation of grafts definitely increased with higher concentration of hydrogen peroxide, and in the comparison at the same polymerization time, the number of grafts increased also with higher concentration of oxidizing agent. In case of sodium hypochlorite (Fig. 8), the formation of grafts was also accelerated with a higher concentration of oxidizing agent. Thus, it can be concluded that oxidation provides cellulose with special reactive groups, and these act as site of formation of grafts.

The results for hot-water treatment are shown in Figure 9. The sample treated with hot water indicates a remarkable decrease in the rate of formation of grafts. However, the oxidation of this sample by hydrogen per-

oxide increased the rate of formation of grafts as well as the number of grafts, again to values rather larger than those of untreated samples. As might be expected, the sample subjected to further treatment with hot water after oxidation indicated a fairly low rate of formation of grafts, but the value did not reach the low value for the untreated sample after treatment with hot water.

The effect of ferric ion on the formation of grafts is shown in Figure 10. Ferric ion definitely accelerated the rate of formation of grafts for each cellulose sample. Sakamoto and co-workers¹⁰ reported that ferric ion initiates polymerization with methyl methacrylate via the formation of a complex. Though the action of ferric ion in this polymerization system is not clear, the effect on the formation of grafts must be taken into consideration, and it can be safely said that ferric ion directly contributes to the initiation reaction of graft copolymerization.

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