Ceric Salt-Initiated Graft Copolymerization of Methyl Methacrylate on Preoxidized Cellulose Samples

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Synopsis

The effects of preoxidation of cellulose samples on graft copolymerization in the presence of ceric salt (Ce^{4+}) as an initiator were investigated. The use of Ce^{4+} as oxidizing agent inhibited the formation of grafts, and the number of grafts decreased as the concentration of Ce^{4+} in the pretreatment rose. In contrast, the samples oxidized with periodic acid (HIO_4) or hydrogen peroxide (H_2O_2) tended to show improved initiation characteristics and gave a larger number of grafts than the unoxidized samples. The reactivity of oxidized samples toward Ce^{4+} was examined and the following results were obtained: The part of easy reactivity decreased in the Ce^{4+}-oxidized samples but it increased in the HIO_4-oxidized samples; on the other hand, it did not vary greatly in the H_2O_2-oxidized samples. Cellulose is probably oxidized to different states by different oxidizing agents, and the reactivity of Ce^{4+} toward these oxidized samples, as one index, seems to be reflected in the graft copolymerization. It was consequently recognized that the graft copolymerization characteristics of cellulose samples could be improved significantly by proper selection of oxidation conditions.

INTRODUCTION

It is known that graft copolymerization of cellulosic materials with ceric salt (Ce^{4+}) as initiator is initiated by the oxidation of the cellulosic materials.[1] A number of points, however, still remain unclear about the relationship between the initiating action and the character of the cellulose samples. Cumberbirch and Holker[2] studied the effects of pretreating samples with ceric sulfate and sodium periodate in graft copolymerization of acrylic acid on viscose rayon in the presence of ceric sulfate and reported that the graft copolymerization was not affected appreciably by such pretreatments. Takahashi and Takahashi,[3] Toda,[4] and Ishizu et al.[5] reported on graft copolymerization characteristics of the cellulose samples oxidized with periodic acid. Toda observed a lower initiating ability for the oxidized samples in the sodium periodate initiator system, presuming that the growing polymer radicals undergo terminations with the aldehyde groups formed by the oxidation. On the other hand, others observed an increased per cent grafting in the Ce^{4+} initiator system for samples preoxidized with the agent at proper conditions.

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In our previous study[6] on graft copolymerization of methyl methacrylate (MMA) to several oxidized cellulose samples in the presence of Ce^{4+}, we observed that the vigorous initiation reaction of copolymerization lasted only as long as the portion of cellulose showing a high reactivity with Ce^{4+} (the reactive part) underwent oxidation and pointed out that the copolymerization reaction was closely related to the properties of cellulose toward oxidation. In this study, cellulosic materials were oxidized with various oxidizing agents, generally known also as initiators, such as Ce^{4+}, periodic acid[4] (HIO_4), and hydrogen peroxide (H_2O_2), and the preoxidized cellulose samples were subjected to graft copolymerization with MMA in the presence of Ce^{4+} as initiator to see how the properties of the cellulose affect graft copolymerization.

EXPERIMENTAL

Preparation of Oxidized Cellulose Samples

Commercial dissolving sulfite pulp was used as the cellulose sample. Ceric ammonium nitrate, HIO_4, and 30% H_2O_2, all commercially available materials, were used as oxidizing agents. The reaction conditions for each oxidizing agent are shown in Table I. The oxidation with Ce^{4+} was carried out in a system containing nitric acid at a concentration of 0.47 mmole/l. A certain amount of Ce^{4+} was adsorbed on the oxidized sample, and this amount was determined by the method reported previously.[7] Two kinds of samples were prepared for the Ce^{4+}-oxidized samples. Ce^{4+} was contained as adsorbed in one sample (Ce^{4+}-adsorbing sample) and the

TABLE I
Oxidiation Conditions of Cellulose Samples[a]

Oxidizing agent	Concn. of oxidizing agent, mmole/l.	Time, min	Temperature, °C	Total C=O, mmole/100g of cell.	COOH, mmole/100g of cell.
Absence	—	—	—	12.0	1.86
Ceric ammonium	5[b]	60	45	—	—
nitrate	10[c]	60	45	—	—
	30[d]	60	45	—	—
	10[e]	60	45	11.7	1.75
	30[e]	60	45	10.8	1.86
Hydrogen peroxide	10	90	60	15.5	2.20
	20	90	60	12.4	2.25
Periodic acid	10	60	45	23.4	1.76
	30	60	45	55.6	1.51

[a] Liquor ratio, 100.
[b] Amount of adsorbed Ce^{4+}, 9.9 mmole/100 g cellulose.
[c] Amount of adsorbed Ce^{4+}, 13.5 mmole/100 g cellulose.
[d] Amount of adsorbed Ce^{4+}, 18.3 mmole/100 g cellulose.
[e] Ce^{4+}-nonadsorbing sample.

adsorbed Ce^{4+} was removed completely in the other (Ce^{4+}-nonadsorbing sample). The sample treated with the oxidizing agent was washed successively with water, $0.1N$ hydrochloric acid, and water, and dried under vacuum. Analysis of each sample for total carbonyl, carboxyl, and adsorbed Ce^{4+} is shown in Table I. The amount of total carbonyl groups determined by the hydroxylamine method[8] varies somewhat from one oxidized sample to another, but the amount of carboxyl groups determined by the calcium acetate method[9] does not vary so much.

Graft Copolymerization

The reaction system consisting of 0.50 g cellulose (dry weight), 2.5 ml MMA, and 25 ml water was flushed with nitrogen, a solution of Ce^{4+} in 15 ml $0.1N$ nitric acid was injected, and the reaction was allowed to proceed at 45°C for a given duration. The concentration of Ce^{4+} in the polymerization system was set at 3 mmole/l. The polymers formed were washed with water and then extracted with acetone for 24 hr to remove homopolymers. Weight increase of the graft copolymer, represented by percentage of cellulose, was indicated as per cent grafting. Average molecular weight of grafts was determined viscometrically as reported previously.[6,10] The molar number of grafts per 100 g cellulose was calculated from the average molecular weight and the per cent grafting and was indicated as number of grafts.

Reactions of Cellulose Samples with Ce^{4+}

The consumption of Ce^{4+} was investigated in the systems excluding only the monomer from the graft copolymerization compositions. After reaction for a given length of time at 45°C at a Ce^{4+} concentration of 3 mmole/l., the amount of residual Ce^{4+} in the system was determined by adding ferrous sulfate to the system and titrating the excess of ferrous sulfate with Ce^{4+} using o-phenanthroline as an indicator.

RESULTS AND DISCUSSION

Graft Copolymerization Characteristics of Oxidized Cellulose Samples

The relationship between the average molecular weight of grafts and the per cent grafting is shown in Figure 1 for the samples oxidized with Ce^{4+}. In each sample, the average molecular weight increases linearly as the per cent grafting increases. At the same time, a tendency for the average molecular weight to increase as the oxidation conditions become increasingly stronger has been observed. Thus, there is an indication that the oxidation of the sample has caused changes in the termination reaction of growing polymers, and this phenomenon is more pronounced in the Ce^{4+}-adsorbing samples. Here, the preoxidation of cellulose samples in effect acted to reduce the number of functional groups[6] participating in the termination reaction of polymerization.
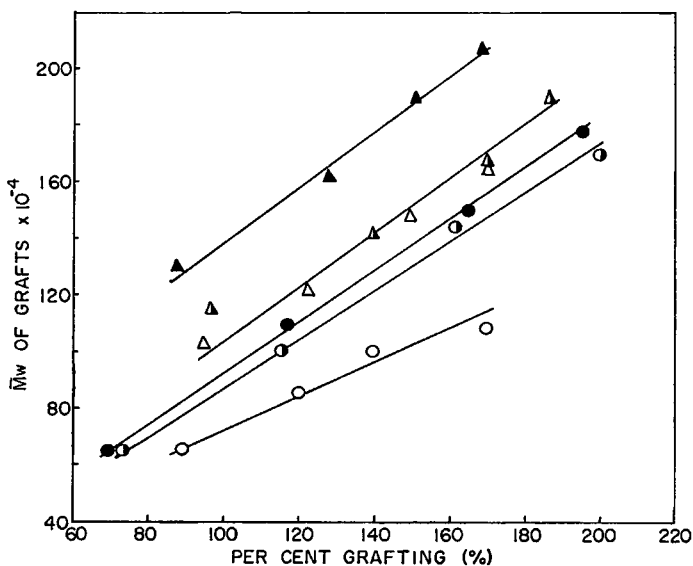
Fig. 1. Relationships between average molecular weight of grafts and per cent grafting in Ce⁴⁺-oxidized samples: (O) unoxidized sample; Ce⁴⁺-adsorbing sample: (Δ) $[Ce^{4+}]$ = 5 mmole/l.; ($\blacktriangle$) $[Ce^{4+}]$ = 10 mmole/l.; ($\blacktriangle$) $[Ce^{4+}]$ = 30 mmole/l.: Ce⁴⁺-nonadsorbing sample: (◗) $[Ce^{4+}]$ = 10 mmole/l.; (●) $[Ce^{4+}]$ = 30 mmole/l.

The behavior of the number of grafts in graft copolymers is shown in Figure 2. The number of grafts reaches a roughly constant value in about 10 min after initiation of the polymerization, and increases extremely slowly thereafter. This constant value becomes smaller as the oxidation conditions
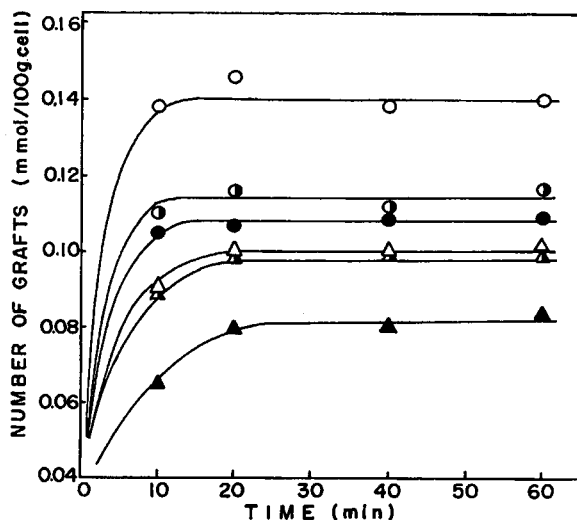

Fig. 2. Change in number of grafts with time in Ce⁴⁺-oxidized samples. Samples are same as those used in Fig. 1.

of samples become stronger, and is lowest for the Ce^{4+}-adsorbing samples. Thus, it has become clear that the initiation characteristics of the cellulose samples deteriorate markedly by preoxidation with Ce^{4+}. The Ce^{4+}-adsorbing samples are those which have been subjected to sufficient oxidation with Ce^{4+} and still coexist with the oxidizing agent in question; hence, they show an extremely small possibility of being attacked freshly by Ce^{4+} and retain only a weak initiating capability.

The behavior of the number of grafts in copolymerization on the samples oxidized by H_2O_2 or HIO_4 is shown in Figure 3. As with the samples oxidized with Ce^{4+}, the number of grafts here reaches a constant value in
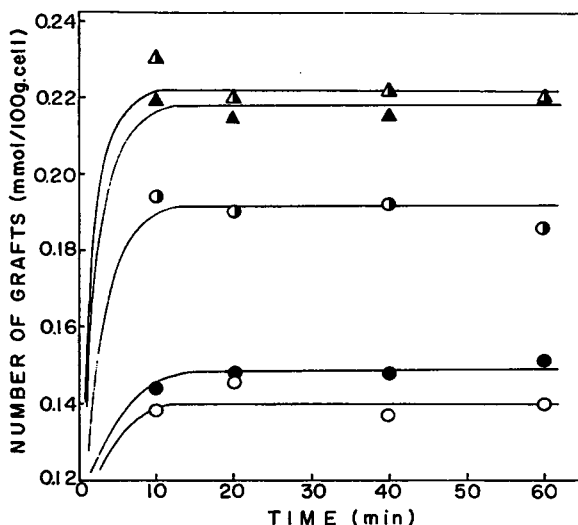

Fig. 3. Change in number of grafts with time in H_2O_2- or HIO_4-oxidized samples: (O) unoxidized sample; H_2O_2-oxidized sample: (◑) $[H_2O_2]$ = 10 mmole/l.; (●) $[H_2O_2]$ = 20 mmole/l.; HIO_4-oxidized sample: (▲) $[HIO_4]$ = 10 mmole/l.; (▲) $[HIO_4]$ = 30 mmole/l.

about 10 min. In contrast to the samples oxidized with Ce^{4+}, however, the samples oxidized with H_2O_2 or HIO_4 gave a slightly larger number of grafts than the unoxidized samples. It is suggested that oxidation by H_2O_2 or HIO_4 caused rather an increase in the number of functional groups effective for graft copolymerization on cellulose samples. A comparison of H_2O_2 and HIO_4 indicates that HIO_4 gives graft copolymers with a much larger number of grafts, but the number of grafts tends to decrease gradually with both oxidizing agents when the oxidation conditions exceed a certain limit in severity.

As described above, the number of grafts decreases with Ce^{4+}, whereas it increases with HIO_4. On the other hand, the oxidizing effect of H_2O_2 is sensitively dependent upon the concentration. From this fact, it is understandable that the oxidized state of cellulose varies widely with the oxidizing agent used, and such variation is probably responsible for the characteristic behavior of each sample during polymerization.
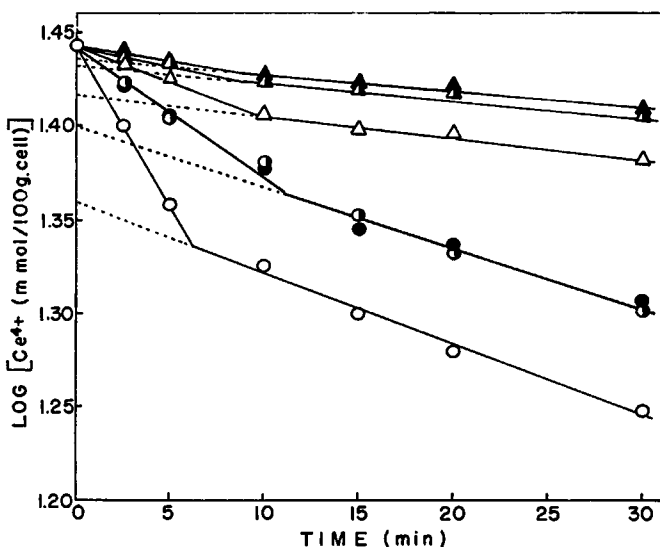
Fig. 4. Reactivities of Ce^{4+}-oxidized samples toward Ce^{4+}. Samples are same as those used in Fig. 1.

Reactivity of Oxidized Cellulose Samples Toward Ce^{4+}

To find distinguishing features of the oxidized state of each oxidized sample, the reactions of cellulose samples with Ce^{4+} were investigated under the conditions similar to those for graft copolymerization. The results obtained on the Ce^{4+}-oxidized samples are presented in Figure 4, and the logarithm of the Ce^{4+} concentration in the reaction system is plotted on the vertical axis. It is seen from Figure 4 that the more severe the pre-oxidation conditions, the more the reactivity toward Ce^{4+} declines. Common to all the samples, however, the consumption of Ce^{4+} proceeds fastest in the first 10 min of the reaction, and the length of this time roughly agrees with that of the period in which the formation of grafts takes place vigorously. Hence, it seems reasonable to assume that the Ce^{4+} consumed in this period contributes effectively to the formation of grafts. Moreover, it is clear that the Ce^{4+}-adsorbing samples exhibit a lower reactivity toward Ce^{4+} than the Ce^{4+}-nonadsorbing samples.

Similar relationships for the samples oxidized with H_2O_2 and HIO_4 are shown in Figure 5. The reactivity of the samples toward Ce^{4+} increases considerably upon oxidation with HIO_4, but it does not change very much by oxidation with H_2O_2 in a wide range of the H_2O_2 concentration. Kulkarni and Mehta[11,12] also reported that the cellulose samples oxidized with HIO_4 showed an increased reactivity toward Ce^{4+}.

The reaction of cellulose with Ce^{4+} can be divided into two parts, a reaction with a higher rate followed by a reaction with a lower rate. The straight line representing the lower rate reaction is extended to the vertical axis, and the amount of Ce^{4+} participating in the higher rate reaction is obtained from this intercept. Now, it is assumed here that a part of easy
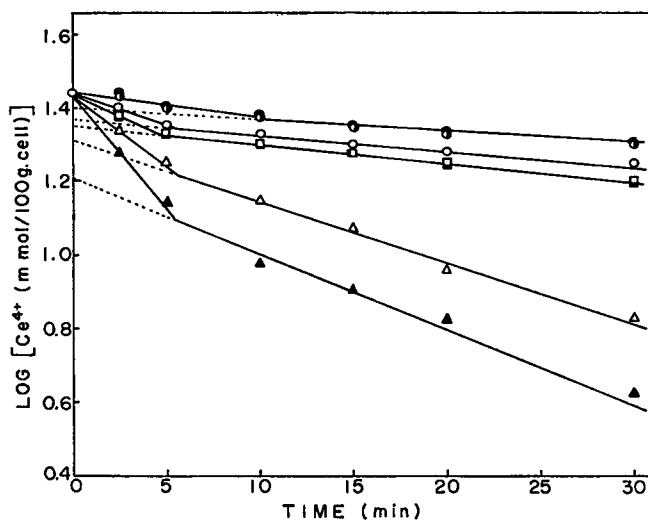
Fig. 5. Reactivities of H₂O₂- or HIO₄-oxidized samples toward Ce⁴⁺: (O) unoxidized sample; Ce⁴⁺-oxidized sample: (◑) [Ce⁴] = 10 mmole/l.; (●) [Ce⁴⁺] = 30 mmole/l.; H₂O₂-oxidized sample: (□) [H₂O₂] = 10 mmole/l.; (■) [H₂O₂] = 20 mmole/l.; HIO₄ oxidized sample: (△) [HIO₄] = 10 mmole/l.; (▲) [HIO]₄ = 30 mmole/l.

reactivity corresponding to this amount is present in the cellulose sample. Compared with the unoxidized samples, this amount decreases upon oxidation with Ce⁴⁺, but it increases upon oxidation with HIO₄; on the other hand, it changes only slightly with H₂O₂.   The constant number of grafts
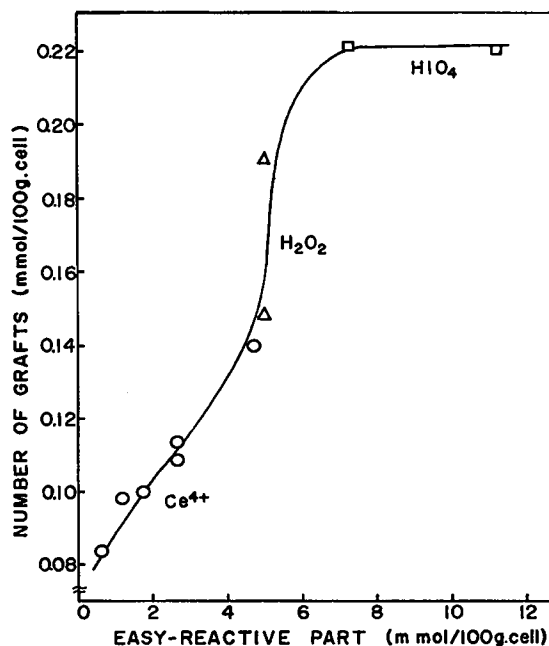

Fig. 6. Relationship between number of grafts and the reactive part of cellulose.

obtained for each sample in Figures 2 and 3 is again shown in Figure 6 in comparison with the amount of the easily reactive part. It seems possible here to find a certain series of relationships throughout the samples unoxidized and oxidized with Ce^{4+}, H_2O_2, and HIO_4. The results indicate that a sample with a greater part of easy reactivity undergoes graft copolymerization more readily. In this study, the concentration of Ce^{4+} (3 mmole/l.) seems to be a little too low to demonstrate the above-mentioned feature. A further study, if undertaken at higher concentrations of Ce^{4+}, would prove this relationship more clearly.

It is thus possible to conclude that the oxidized state of a cellulose sample varies markedly with the oxidizing agent used, and the reactivity of the sample toward Ce^{4+} itself can be an important index in determining graft copolymerization characteristics of the oxidized samples. Hence, it is obvious that graft copolymerization characteristics of cellulose samples can be improved significantly by proper selection of preoxidation conditions.

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