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Effect of Metallic Ions in Photo-Induced Graft Copolymerization onto Cellulose

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Synopsis

In photo-induced graft copolymerization of methyl methacrylate onto cellulose, the effect of metallic ions as sensitizer was investigated. Some metallic ions were effective in their adsorbed states and accelerated the formation of grafts in the order $Fe^{2+} > Ag^{+} > Fe^{3+}$. However, Cu^{2+} acted negatively, and little effect was observed for Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, and Cr^{3+}. In the systems in which aqueous metallic salt solutions were added, the formation of grafts was generally depressed, but Fe^{3+} was an exception. The effect of metallic ions on the scission reaction of cellulose main chains did not necessarily agree with the effect on the formation of grafts. This is attributed to the varied interaction between cellulose and the different active species produced by irradiation, depending on the type of metallic ions used.

INTRODUCTION

It is well known that various inorganic ions are effective in the photo-induced polymerization of vinyl monomers.[1–3] Especially, the effects of Fe^{2+}, Ag^{+}, Ce^{3+}, UO_2^{2+}, and Fe^{3+} in aqueous solutions were investigated.[4–12] We have already observed a remarkable accelerating effect[13,14] of Ce^{4+} in the graft copolymerization onto cellulose by irradiating with ultraviolet light. A similar effect was also reported by Cremonesi and Focher.[15] Ce^{4+} combines with cellulose by chelate formation,[16] and UV light accelerates not only the reduction of Ce^{4+} by cellulose but also the formation of grafts. It was also observed that Fe^{3+}, which shows a strong affinity for cellulose, as well as Ce^{4+} have a remarkable sensitizing effect on photo-induced graft copolymerization.[17,18]

The purpose of the present investigation is to find other metallic ions in addition to Ce^{4+} and Fe^{3+} which can accelerate photo-induced graft copolymerization onto cellulose. The graft copolymerization of methyl methacrylate (MMA) onto cellulose samples adsorbing various metallic ions was carried out under irradiation, and the effect of the metallic ions was examined mainly from the amounts of grafts formed.

EXPERIMENTAL

Cellulose Samples Adsorbing Metallic Ions

A commercial softwood pulp was immersed in 10 mmole/l. aqueous solution of each metallic salt at 45°C for 60 min (liquor ratio 80). The cellulose samples were then thoroughly washed with water. The amounts of metal ion absorbed by the cellulose samples were derived from the weight of ash; these amounts were in the range of 1–2 mmole/100 g of cellulose for each metal, except for adsorbed Fe^{3+}, which amounted to about 15 mmole/100 g of cellulose because of its higher affinity for cellulose.[16] The following commercial metallic salts were used: $AgNO_3$, $FeCl_3 \cdot 6H_2O$, $ZnSO_4 \cdot 5H_2O$, $CoSO_4 \cdot 7H_2O$, $MnSO_4 \cdot 4H_2O$, $NiSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, and $Cr(C_2H_3O_2)_3 \cdot H_2O$. For aqueous solution of ferrous sulfate, pure iron wire and dilute sulfuric acid were employed.

Graft Copolymerization

Graft copolymerization was carried out at 45°C under nitrogen by irradiating with UV light a system in a hard glass tube consisting of 0.50 g cellulose samples with or without adsorbed metallic ions, 2.5 ml MMA, and 40 ml distilled water. The addition of aqueous metallic salts to the system without adsorbed metallic ions was examined to elucidate the location of the sensitizer. As UV light source, a Toshiba mercury lamp for photochemical use (H-400 P) was used.

Polymerization products were extracted with acetone to remove homopolymers. The per cent grafting, the grafting efficiency, and the number of grafts were calculated as described in the previous papers.[19,20]

The weight-average molecular weight of grafts was determined from the viscosity of acetone solutions at 25°C.[21]

The effects of metallic ions on the degradation of cellulose were examined in systems in the absence of monomers, and the changes in the degree of polymerization (DP) of cellulose were determined viscometrically as described in the previous paper.[22]

RESULTS AND DISCUSSION

Graft Copolymerization on Metallic Ion-Adsorbing Cellulose

Table I gives the results for the samples adsorbing various metallic ions. The irradiation time was 120 min. With the use of metallic ions, the per cent grafting increased generally, but a distinct difference among metallic ions was observed in the formation of grafts. Namely, the number of grafts increased with Fe^{2+}, Ag^{+}, and Fe^{3+} compared to unadsorbed samples, but decreased with Cu^{2+}. The action of the other metallic ions was hardly noticeable. Grafting efficiency was in the range of 60% to 80% throughout for all metallic ions. Small effects of metallic ions were observed in the formation of homopolymers.

TABLE I
Effects of Metallic Ions on Graft Copolymerization[a]

Metallic ion	Per cent grafting, %	Grafting efficiency, %	Number of grafts × 10^2, mmoles per 100 g of cell
Fe^{2+}	251.3	67.1	6.75
Ag^{+}	251.4	72.4	6.31
Fe^{3+}	227.8	72.7	4.55
Zn^{2+}	204.2	75.5	3.52
Co^{2+}	180.0	68.1	4.04
Cr^{3+}	173.8	83.9	3.48
Mn^{2+}	171.4	78.4	3.33
Ni^{2+}	166.9	68.2	3.34
Cu^{2+}	151.6	60.0	2.82
None	148.8	61.5	3.57

[a] Irradiation time, 120 min; temperature, 45°C; amount of adsorbed metallic ion, 1–2 mmoles/100 g of cellulose.

The changes in the formation of grafts along with the reaction time are shown in Figure 1 for the metallic ions which showed characteristic effects in Table I. Throughout all systems, the formation of grafts fell after irradiation for 60 to 90 min. The initial rate of the formation of grafts was accelerated by some metallic ions in the order $Fe^{2+} > Ag^{+} > Fe^{3+}$, was depressed by Cu^{2+}, and was not affected by Co^{2+}. In the system without UV the authors[23] observed that a slight amount of adsorbed Fe^{3+} greatly increased the initiating activity in the graft copolymerization initiated by

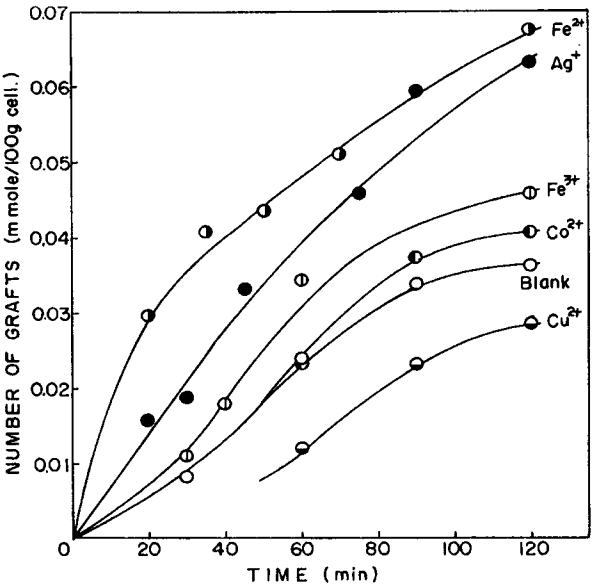

Fig. 1. Effects of adsorbed metallic ions on formation of grafts.

cellulose itself. Imoto and co-workers[24] also reported that the adsorbed Cu^{2+} accelerates the polymerization of MMA initiated by cellulose–water. However, in the photo-induced system, Cu^{2+} was found to depress the formation of grafts. In the photodegradation of cellulose[25,26] and silk fibers[27,28] it is observed that the photodegradation is prevented to some extent by using copper. It was therefore assumed that the absorption of UV light by copper is one of the causes for this effect. On the other hand, it is observed that Fe^{2+}, Ag^{+}, and Fe^{3+} absorb UV light in aqueous solution to produce protons,[3] nitric radicals,[6] and hydroxyl radicals,[11,12] respectively, and result in initiating species for photopolymerization.

The average molecular weights of copolymer grafts are shown in Figure 2. The molecular weights of grafts from Cu^{2+}- and Ag^{+}-adsorbing samples were rather higher than those of the unadsorbing samples, whereas Fe^{3+}-, Co^{2+}-, and Fe^{2+}-adsorbing samples resulted in lower molecular weights. The effect differed from metal to metal.

In a previous report,[22] it was observed that the effect of the wavelength region of light on graft copolymerization onto cellulose initiated by irradiation is considerable. Therefore, the effects of metallic ions were examined using light of shorter wavelength, and the results are given in Table II. By using a quartz reaction tube, which transmits shorter wavelengths, the per cent grafting, the grafting efficiency, and the average molecular weight of grafts obtained were all lowered. On the other hand, the number of grafts increased remarkably for the nonadsorbing samples; but for Ag^{+} and Fe^{3+}, the rate of increase was small and the number of grafts was smaller than that of the nonadsorbing sample. Accordingly, it seems that there is almost no possibility that by using a shorter wavelength metallic ions are effective in the formation of grafts.

TABLE II
Graft Copolymerization in Quartz Tube[a]

Sample	Per cent grafting, %		Grafting efficiency, %		$\bar{M}_w$ of grafts $\times 10^{-4}$		Number of grafts $\times 10^2$, mmoles per 100 g of cell	
	G	Q	G	Q	G	Q	G	Q
Unadsorbed sample	106.2	123.6	68.8	33.7	446	219	2.38	5.65
Adsorbed Ag^{+}	180.0	139.0	77.5	43.7	480	270	4.10	5.15
Adsorbed Fe^{3+}	148.6	142.3	74.3	51.8	436	288	3.41	4.94

[a] G, glass tube; Q, quartz tube; irradiation time, 60 min; temperature, 45°C; amount of adsorbed metallic ion (mmoles/100 g of cell): Ag^{+}; 1.3; Fe^{3+}, 15.

Effect of Addition of Metallic Salts on Photo-Induced Graft Copolymerization

Metallic salts at a concentration of 0.1 mmole/l. were added to the copolymerization system, and the results of polymerization were compared

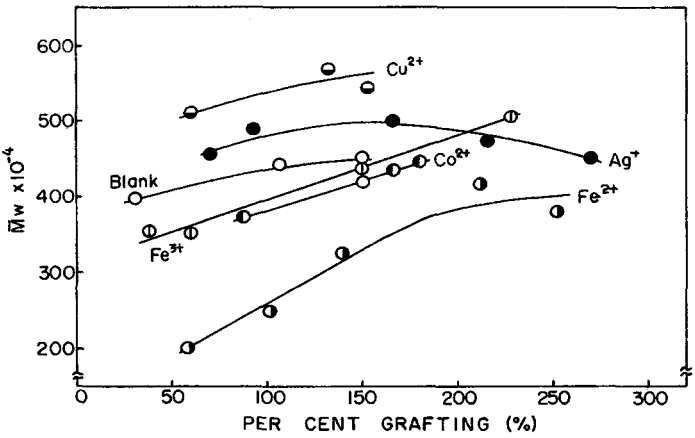

Fig. 2. Effects of adsorbed metallic ions on average molecular weight of grafts.

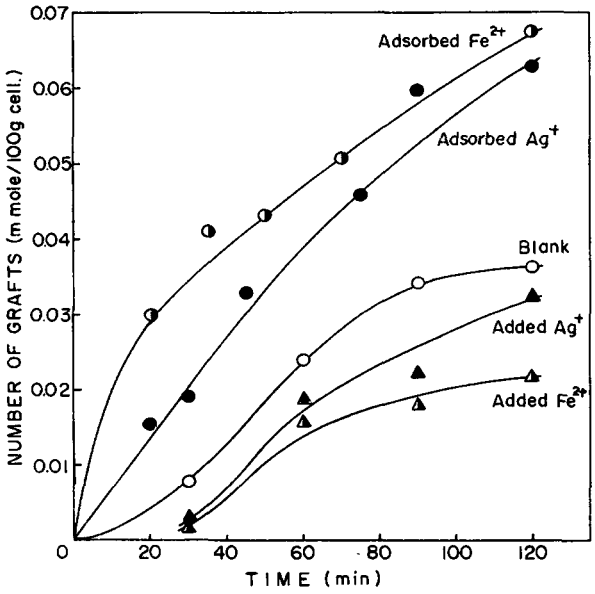

Fig. 3. Comparison of formation of grafts due to different methods of applying metallic ions. Concentration of metallic salt added, 0.1 mmole/l.

with those of the adsorbing system. As can be seen from Figure 3, the formation of grafts is considerably depressed and the number of grafts becomes lower in the Fe^{2+}- and Ag^{+}-added systems. A similar decrease was also observed for Cu^{2+}. Although the amounts of existing metallic ions are almost equal for both copolymerization systems, the rate of formation of grafts is affected remarkably by the distribution of metallic ions in the systems. It is thought that in the adsorbing system the sensitizing effect of metallic ions occurs in the close neighborhood of cellulose, and this difference affects also the formation of homopolymer. The grafting efficiency of the Fe^{2+}-added system shown in Figure 4 becomes extremely low

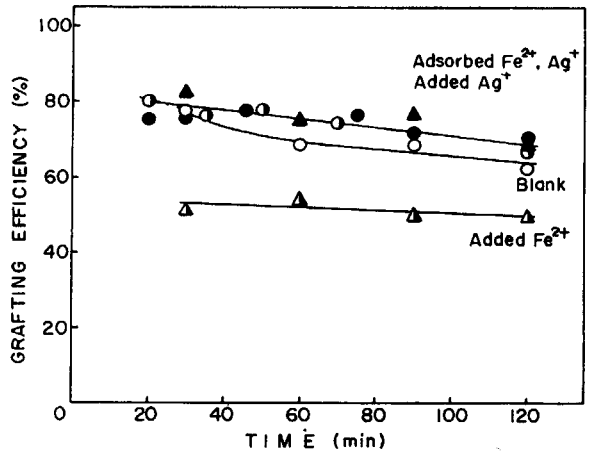

Fig. 4. Comparison of grafting efficiencies due to different methods of applying metallic ions. Concentration of metallic ions added, 0.1 mmole/l.

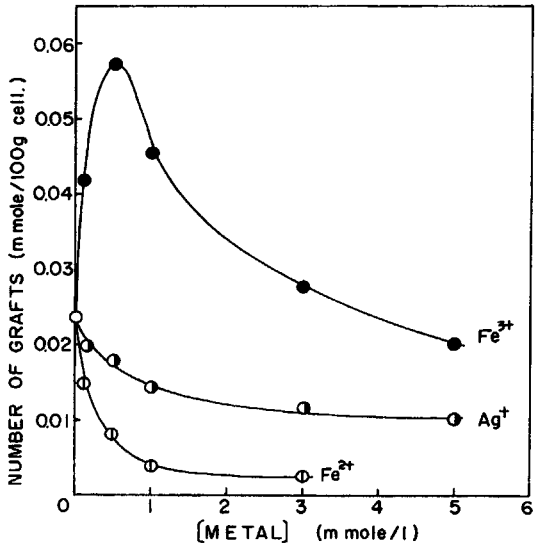

Fig. 5. Dependence of formation of grafts on concentration of metallic salts added. Irradiation time, 60 min.

compared to other systems, and it indicates that the formation of homopolymer is large. However, in contrast to the Fe^{2+} system, the grafting efficiency of the Ag^{+}-added system shows little difference from the adsorbing system. It is therefore assumed that the initiating activity depends on the metallic ion used.

The effect of the concentration of aqueous metallic salt solutions in the added system was further examined. The results are shown in Figure 5. For Fe^{2+} and Ag^{+}, the number of grafts decreased with increasing con-

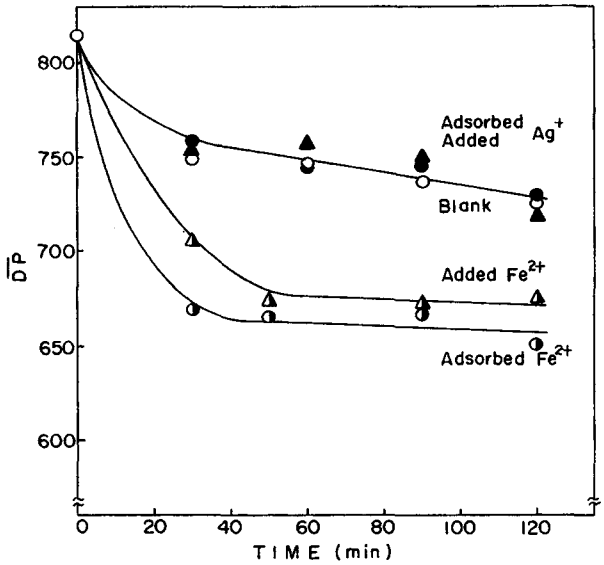

Fig. 6. Changes in average degree of polymerization of cellulose with time in various applications of metallic ions. Concentration of metallic salts added, 0.1 mmole/l.

centration of metallic salts. However, the maximum number of grafts was obtained at a certain concentration of Fe^{3+}. This value is higher than that of the unadsorbing sample and decreases at higher concentration. As the binding of Fe^{3+} with cellulose[16] is stronger than those of Fe^{2+} and Ag^{+}, it is supposed that even in the added system, the stronger binding effect acts in the close neighborhood of cellulose.

The effect of metallic ions on the change in average DP of cellulose by irradiation is shown in Figure 6. The effects were large for both Fe^{2+}-adsorbing and added systems, but almost no effect was observed for Ag^{+}. It is well known that the metals existing in cellulose as impurities have a remarkable effect on the photodegradation of cellulosic materials.[29] It is thought that Fe^{2+} acts also in a similar manner in the present systems. Both Fe^{2+} and Ag^{+} accelerated the formation of grafts, but it was observed that their action on the scission reaction of cellulose chains differed. This is attributed to the differences in reactivity to UV light and of the active species formed between these ions.

As mentioned above, it was observed that metallic ions depressed the formation of homopolymers and the scission of cellulosic main chains, and accelerated the formation of grafts by proper selections of the type and the state of metallic ions. In conclusion, such sensitizing actions of metallic ions might effectively be utilized in the photo-induced graft copolymerization on cellulose.

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