JOURNAL OF APPLIED POLYMER SCIENCE VOL. 14, PP. 2611–2618 (1970)

Graft Copolymerization onto Cellulose by Ceric Ion Initiator System: Effects of Kind of Acid and Irradiation with Ultraviolet Light

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Synopsis

The effects of kind of acid and irradiation of ultraviolet light on the graft copolymerization of methyl methacrylate onto cellulose with adsorbed ceric ion were investigated. Irrespective of ultraviolet light irradiation, the amount of reduced ceric ion in the reaction systems was increased in the order $HCl > HClO_4 > HNO_3 > H_2SO_4$, and the number of grafts formed was increased in the order $HClO_4 > HNO_3 > HCl > H_2SO_4$. Thus, it was definitely observed that the graft copolymerization is affected by the kind of acid. Ultraviolet light remarkably accelerated the reduction of ceric ion adsorbed on cellulose in the various acid mediums, but decreased the efficiency of graft formation. The most favorable results for the formation of grafts were obtained in the system in which $HClO_4$ and ultraviolet irradiation was employed. A combination of H_2SO_4 and ultraviolet irradiation resulted in the lowest per cent grafting and average molecular weight of grafts. It was found that H_2SO_4 characteristically dissolves out ceric ion adsorbed into an aqueous solution and accelerates the formation of homopolymer.

INTRODUCTION

In our previous paper[1] it was observed that the amount of ceric ion adsorbed on cellulose with chelate formation[2] is reduced with cellulose, that the amount of the adsorbed ceric ion decreases gradually, and that the rate of reduction is remarkably accelerated by irradiation with ultraviolet light. It was also observed that the reaction of graft formation is fairly accelerated when the graft copolymerization of methyl methacrylate is carried out in this system. The initiation with ceric ion in the graft copolymerization depends very much on the pH value of the system[3] and a weakly acidic system is usually used. Saldick[4] and Ananthanarayanan and Santappa[5] carried out the polymerization of vinyl monomers by ceric ion in several acidic mediums and observed that the rate of polymerization varies with the kind of acid used. Reyes et al.[6] reported that ceric ion obtained from ceric nitrate is better than that from ceric sulfate as an initiator in the graft copolymerization onto starch by ceric ion. In our study the effect of the kind of inorganic acid and of irradiation with ultraviolet light on the rate of reduction of ceric ion and the formation reaction of grafts in the graft copolymerization of methyl methacrylate with cellulose-adsorbing ceric ion were investigated.

EXPERIMENTAL

Cellulose Sample Adsorbing Ceric Ion

Bleached sulfite pulp from softwoods (SP) was immersed in an aqueous solution of 10 mmole/l. of ceric ammonium nitrate at 45°C for 60 min to give sample-adsorbing ceric ion. After the ionically bonded ceric ion was removed by treatment with 0.1*N* HCl (liquid-to-solid ratio 150:1), the sample was washed with water and then pressed to expel the water.

Determination of Adsorbed Ceric Ion

A given amount of ferrous sulfate was added to cellulose sample-adsorbing ceric ion and suspended in water. The ceric ion adsorbed was back-titrated with a known concentration of ceric sulfate solution with *o*-phenanthroline as an indicator.

Graft Copolymerization

A 200-ml hard-glass vessel of about 1 mm thickness was used. The total content of 42.5 ml consisted of 0.50 g of cellulose sample with adsorbed ceric ion, 10 ml of a given concentration of acid ($HClO_4$, HNO_3, HCl, H_2SO_4), 2.5 ml of methyl methacrylate, and water. After the atmosphere was replaced by nitrogen, the graft polymerization was carried out by irradiation with ultraviolet light at 40°C for a given duration. The ultraviolet irradiation was conducted using a Toshiba high-pressure mercury lamp H-400P for photochemical use with a reaction system in a glass vessel about 11 cm distant from the light source. The per cent grafting, average molecular weight of grafts, and number of grafts were determined in accordance with the preceding paper.[7,8] The reduction of ceric ion adsorbed on cellulose was examined in the systems of the graft copolymerization conditions in which monomer was absent.

RESULTS AND DISCUSSION

Reduction of Ceric Ion Adsorbed on Cellulose

The changes of the total amount of ceric ion adsorbed on cellulose with time are shown in Figure 1 for the various kinds of acid used such as $HClO_4$, HNO_3, and H_2SO_4. It is known that consumption of ceric ion is due to the oxidation of cellulose.[1] It is observed that reduction of ceric ion without ultraviolet irradiation is very small for each acid, and ultraviolet light considerably accelerates the rate of reduction. The extent of acceleration depends on the kind of acid, the effect of the kind of acid on the rate of reduction being in the order $HClO_4 > HNO_3 > H_2SO_4$. The action of acid in the reduction of ceric ion clearly depends on the kind of acid used.

The effects of acid concentration on the reduction of ceric ion is shown in Figure 2 for each acid. This reduction was hardly affected by the acid concentration, but was considerably increased by ultraviolet light in gen-

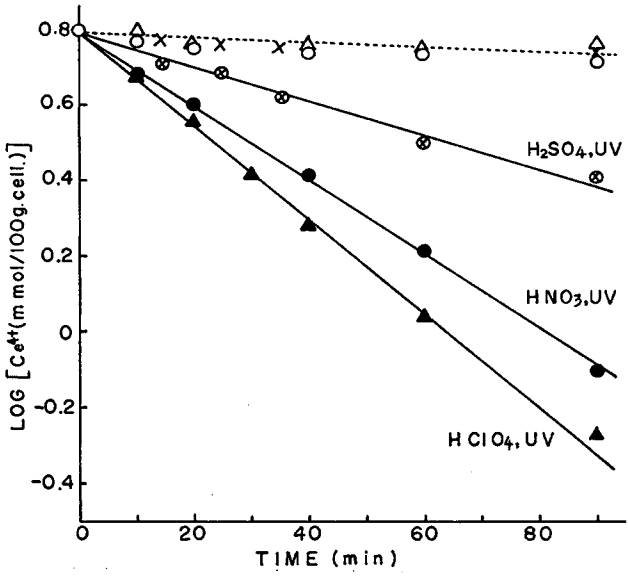

Fig. 1. Changes of total amount of ceric ion with time. Atmosphere, N_2; temperature, 40°C; amount of ceric ion adsorbed, 5.98 mmole/100 g cellulose; acid concentration; 0.47 mole/l. Dotted line represents the system without irradiation: (O) HNO_3; (△) $HClO_4$; (×) H_2SO_4.

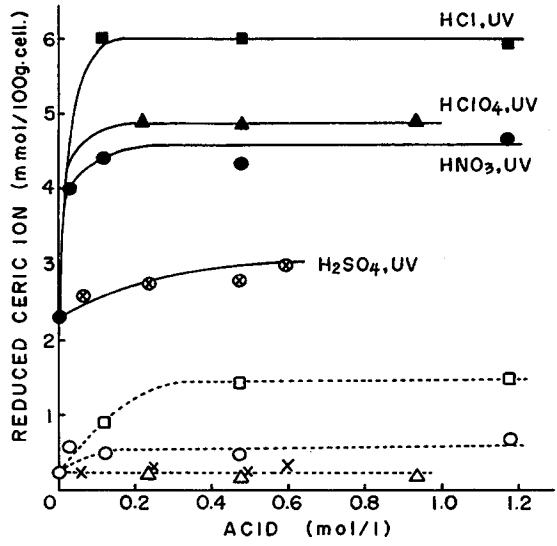

Fig. 2. Effects of kind of acid and acid concentration on reduction of ceric ion. Atmosphere, N_2; temperature, 40°C; time, 60 min; amount of ceric ion adsorbed, 5.98 mmole/100 g cellulose. Dotted lines represent the systems without irradiation: (O) HNO_3; (△) $HClO_4$; (×) H_2SO_4; (□) HCl.

TABLE I
Stability of Ceric Ion Adsorbed on Cellulose

Acid concn, mole/l.	Amount of ceric ion,[a] mmole/100 g cell.		Amount of ceric ion,[b] mmole/100 g cell.		Reduced amount of ceric ion, mmole/100 g cell.	
	No UV	With UV	No UV	With UV	No UV	With UV
H_2SO_4						
0.059	3.03	1.66	2.70	1.72	0.25	2.60
0.236	0.05	0.52	5.65	2.69	0.28	2.77
0.590	0	0	5.68	2.98	0.30	3.00
HCl						
0.120	5.12	0	0	0	0.86	5.98
0.470	4.60	0	0	0	1.38	5.98
1.180	4.48	0	0	0	1.50	5.98

[a] Ceric ion remaining in cellulose.
[b] Ceric ion remaining in solution. Reaction is carried out at 40°C for 60 min in N_2.

eral, the extent of which varied depending on the kind of acid. However, it was observed that the order remained the same irrespective of ultraviolet light irradiation: the reduction increased in the order $H_2SO_4 < HClO_4 < HNO_3 < HCl$.

It is generally thought that the metal ions adsorbed on cellulosic materials are easily isolated by inorganic acid, but ferric ion and ceric ion are known to be hard to isolate.[2,9] The stability of adsorbed ceric ion for H_2SO_4 and HCl is shown in Table I. The values indicate the amounts of remaining ceric ion in the filtrate and in cellulose and that consumed by reduction, after being treated under the same reaction condition as in Figure 2 and then filtered. When H_2SO_4 was used, ceric ion remaining in cellulose considerably decreased with increasing acid concentration, and the ceric ion in the filtrate increased. Accordingly, adsorbed ceric ion was clearly isolated from cellulose. This is explained by the assumption that ceric ion bonded to cellulose as a result of chelate formation easily produces a stable complex[10] with sulfate ion. For the system containing HCl, no ceric ion was detected in the filtrate for a wide range of acid concentrations and adsorbed ceric ion was not eluted. Neither was ceric ion eluted in the systems containing $HClO_4$ or HNO_3.

Graft Copolymerization of Cellulose on Which Ceric Ion is Adsorbed

In the graft copolymerization of vinyl monomers onto cellulose with initiator systems containing ceric ion, the systems are usually kept acidic with HNO_3, and many investigations have been carried out[11–13] on the effect of HNO_3 concentration on the graft copolymerization. Here, the effects of acid concentrations mainly on graft copolymerization were investigated using $HClO_4$, HNO_3, HCl, and H_2SO_4. As seen in Figure 3 per cent grafting increases at the initial stage with increasing acid concentration

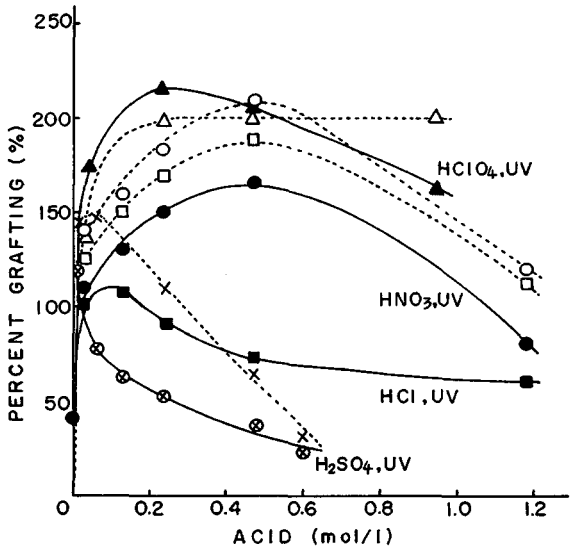

Fig. 3. Relation between per cent grafting and acid concentration. Temperature, 40°C; time, 60 min; amount of ceric ion adsorbed, 5.98 mmole/100 g cellulose. Dotted lines represent the systems without irradiation: (○) HNO_3; (△) $HClO_4$; (×) H_2SO_4; (□) HCl.

in each system containing these acids and gives a maximum at a certain acid concentration. These maxima are affected by the kind of acid and are increased in the order $HClO_4 > HNO_3 > HCl > H_2SO_4$. The amount of homopolymer was almost unaffected by acid concentration. The reverse order to per cent grafting was observed: $H_2SO_4 > HCl > HNO_3 > HClO_4$. Namely, it was found that irradiation with ultraviolet light decreased the per cent grafting, but the formation of homopolymer was accelerated.

The average molecular weight of the grafts of copolymers is decreased with increasing acid concentration and by irradiation with ultraviolet light, as shown in Figure 4. Ananthanarayanan and Santappa[5] have reported that the molecular weight of poly(methyl acrylate) obtained with ceric ion initiator system varies with the kind of acid and is increased in the order $H_2SO_4 > HNO_3 > HClO_4$. However, in the present experiment, no definite difference was observed among acids in the average molecular weight of the grafts.

The relations among the number of grafts as obtained from the per cent grafting, the average molecular weight of the grafts, and the acid concentration are shown in Figure 5. With the exception of the H_2SO_4-containing system, the number of grafts increased as the acid concentration became higher, and the equilibrium value was attained above a certain concentration for each acid. The formation of grafts was significantly accelerated by

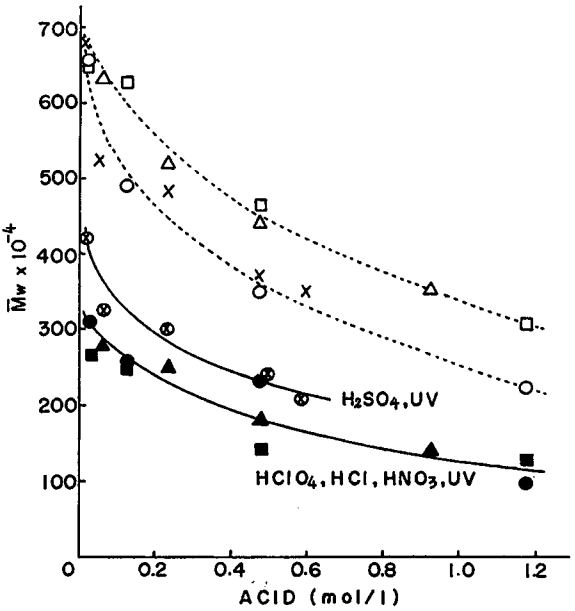

Fig. 4. Relation between average molecular weight of grafts and acid concentration. $\bar{M}_w$ was determined viscometrically after being isolated by hydrolysis of cellulose with 72% H_2SO_4. Dotted lines represent the systems without irradiation: (O) HNO_3; (△) $HClO_4$; (×) H_2SO_4; (□) HCl.

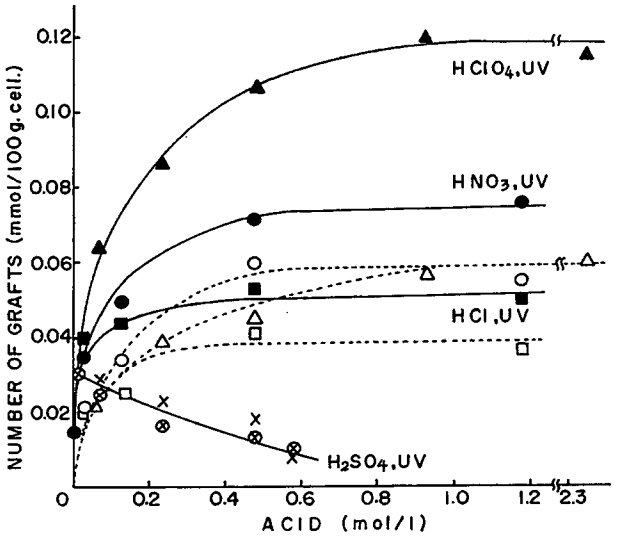

Fig. 5. Relation between number of grafts and acid concentration. Dotted lines represent the systems without irradiation: (O) HNO_3; (△) $HClO_4$; (×) H_2SO_4; (□) HCl.

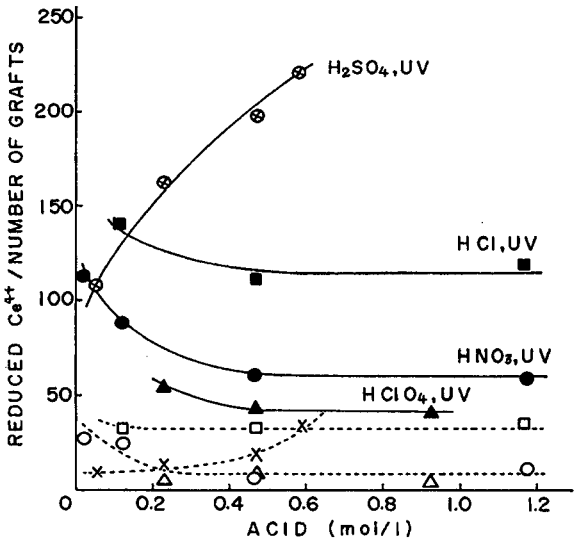

Fig. 6. Relation between molar ratio and acid concentration. Dotted lines represent the systems without irradiation: (○) HNO_3; (△) $HClO_4$; (×) H_2SO_4; (□) HCl.

irradiation with ultraviolet light. In the case of H_2SO_4, the number of grafts decreased as the acid concentration became higher, and ultraviolet light had no effect.

The molar ratio of the amount of reduced ceric ion (Fig. 2) to the number of grafts formed (Fig. 5) was calculated and is shown in Figure 6. In the systems containing $HClO_4$, HNO_3, and HCl, the molar ratio gradually decreases with increasing acid concentration, and is observed to participate in the increase of the efficiency of graft formation. In the H_2SO_4 system, an extraordinary change of molar ratio occurred, differing from other systems. As a result of ultraviolet irradiation, the molar ratio increased and the efficiency of graft formation decreased. $HClO_4$ was the most efficient acid for graft formation.

H_2SO_4 showed a different behavior from other acids, that is to say, the amount of reduced ceric ion was small, the number of grafts decreased as acid concentration became higher, and the molar ratio increased. Because H_2SO_4 easily isolates adsorbed ceric ion from cellulose, as already shown in Table I, not only the formation of grafts is suppressed but ceric ion in aqueous solution is excited by ultraviolet irradiation and accelerates the formation of homopolymer. Therefore, it is believed that unfavorable results for graft copolymerization persisted.

The authors wish to acknowledge the contribution of Mr. Hiroshi Yoshino for the experimental work.

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Received August 22, 1969
Revised December 15, 1969