Grafting of Methyl Acrylate onto Cellulose by Ceric Ion

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ABSTRACT

Methyl acrylate was grafted onto dissolving pulp by ceric ion in aqueous sulfuric acid under oxygen-free argon. At a low Ce(IV) concentration (up to 1 mmol/L), the rate of polymerization (R_p) is proportional to $[Ce]^{0.5} [MA]^1 [cellulose]^1$. At higher concentrations of ceric ion (1-20 mmol/L), R_p is proportional to $[Ce]^0 [M]^{1.5} [cellulose]^1$. The mechanism of grafting is consistent with a kinetic scheme involving initiation by primary radicals and termination by growing polymer radicals. Above 20 mmol/L of ceric salt, the data are consistent with the linear termination mode.

INTRODUCTION

The use of ceric ions to initiate graft copolymerization was first proposed by Mino and Kaizerman in 1958 [1]. The method has attracted much attention during the last three decades because of its relative ease of application and high grafting efficiency. An excellent review of ceric salt initiated grafting of vinyl monomers onto cellulose has been recently published by Stannett et al. [2].

The heterogeneous nature of the reaction has made it difficult to ascertain its exact kinetics and mechanism. A number of papers [3-10] have been published on grafting of vinyl monomers onto cellulosic materials by ceric salts.

However, the data were mostly semiquantitative, and they were often obtained in the presence of traces of oxygen. Reliable data published are limited to soluble monomers (acrylamide) and polymers (dextran [11], yellow dextrin [12], and poly(vinyl alcohol) [13]). Unfortunately, the kinetics of these were studied over a limited range of reagent concentration.

Graczyk and Hornof [14] recently studied the dependence of the consumption of ceric ion in graft copolymerization of vinyl monomers onto cellulose on the reaction conditions. In the presence of oxygen-free argon, the Ce(IV) consumption is lower for the grafting reaction than for cellulose oxidation. The difference is dependent on the types of monomer and ceric salt. Also, Graczyk recently reported [15] that the reaction of oxidation of dissolving pulp was dependent on the concentration of cellulose to the second power.

In this work, graft copolymerization of methyl acrylate (a monomer completely soluble under the experimental conditions) onto dissolving pulp (about 80% crystalline cellulose) was studied in aqueous sulfuric acid under oxygen-free argon. The reaction was investigated over a broad range of reagents concentration. The ceric sulfate was chosen because the rate of polymerization was moderate at ambient temperature.

EXPERIMENTAL

The experimental procedure was described previously [14]. All reactions were initiated by ceric ammonium sulfate, and they were carried out at 25°C in aqueous 1% sulfuric acid. Grafting efficiency was determined by Soxhlet extraction with acetone and calculated as follows:

$$\text{Grafting efficiency} = \frac{(A - B)}{(D - B)} \cdot 100,$$

where A = weight of products after copolymerization and extraction
B = weight of cellulosic substrate charged
D = weight of products after copolymerization (i.e., including the homopolymer)

RESULTS AND DISCUSSION

Typical dependence of monomer conversion, consumption of ceric ion, and grafting efficiency on time are shown in Fig. 1. Complete conversion of
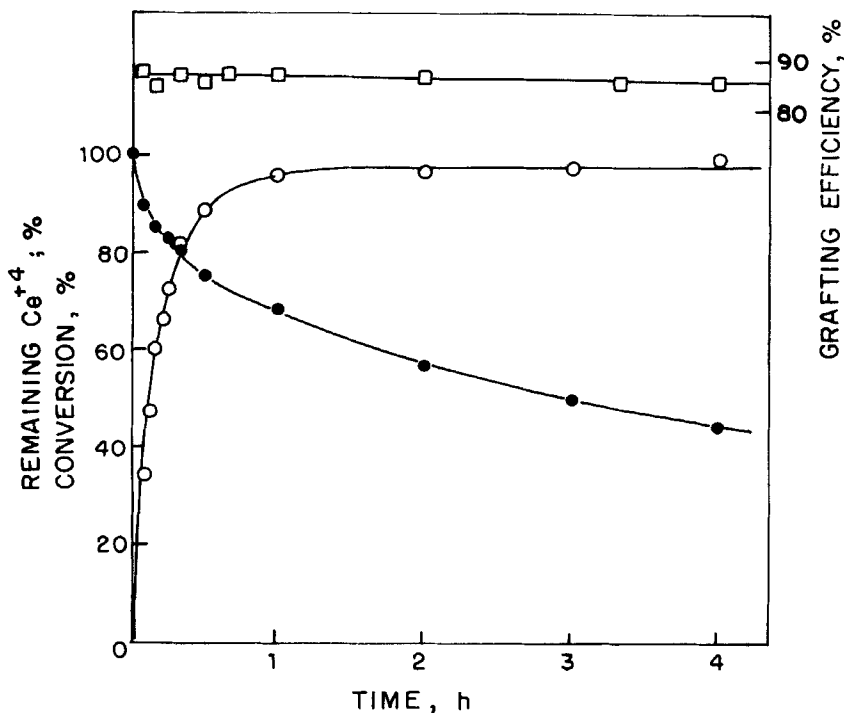
FIG. 1. Conversion to polymer, consumption of Ce(IV), and grafting efficiency as functions of time; [cellulose] = 10 g/L; [MA] = 0.128 mol/L; [Ce(IV)] = 0.25 mmol/L; (○) polymer; (●) Ce(IV); (□) grafting efficiency.

monomer was observed in most experiments after 1 h. The experiments were carried out so that the remaining amount of ceric ion at the end of reaction was not lower than 30-50%.

Rate of Polymerization

Concentration of Ce(IV). A plot of initial rate of polymerization (R_p) vs ceric ion concentration is shown in Fig. 2. The rate of polymerization is proportional to the square root of ceric ion concentration up to 1 mmol/L. In the middle range of Ce(IV) concentration (1-20 mmol/L), the rate of polymerization is independent of initiator concentration. Above 20 mmol/L Ce(IV) the rate of polymerization declines slightly with increasing Ce(IV) concentra-
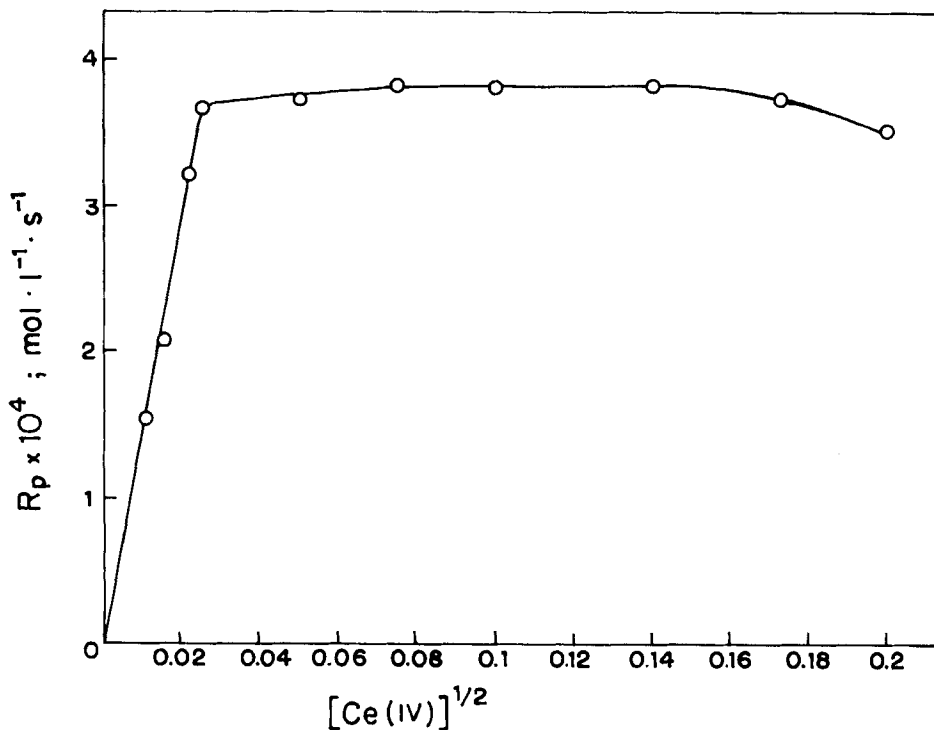
FIG. 2. Rate of polymerization (R_p) as a function of Ce(IV) concentration; [cellulose] = 10 g/L; [MA] = 0.128 mol/L.

tion. Several authors [16-18] reported that, in the polymerization of vinyl monomers by alcohol/mercaptan-Ce(IV) redox systems, the rate of polymerization was independent of Ce(IV) in the middle region of Ce(IV) concentration. The rate of polymerization at a low concentration of Ce(IV) was one-half order with respect to Ce(IV). The one-half order of polymerization with respect to Ce(IV) was also reported by others [19-24]. Thus, the results presented above are in good agreement with published data. The first-order reaction with respect to ceric ion at low concentration of Ce(IV) in graft polymerization onto poly(vinyl alcohol) is the only exception [13]. Plots of R_p vs Ce(IV) to the first power deviate considerably from straight lines.

This complex dependence of R_p on ceric ion rules out the possibility of a linear mode of termination, as was generally accepted for graft copolymeriza-

tion onto cellulose. Termination occurs by mutual interaction of polymer radicals, at least up to [Ce(IV)] = 20 mmol/L.

Monomer Concentration. The external and internal orders of reaction with respect to monomer are influenced by ceric ion concentration. The external orders are determined from the initial rate of polymerization (R_p). At low Ce(IV) concentration ([Ce(IV)] = 0.25 mmol/L), R_p increases linearly with increasing monomer concentration, and hence the order with respect to MA is unity (Fig. 3). In the middle range of Ce(IV) concentration (7.5 mmol/L), a 1.5 order in monomer is observed.

Plots of log $[M]_0/[M]$ vs time are shown in Fig. 4. The linearity of these plots means that the internal order is also unity. Thus, excellent agreement between external and internal orders is obtained. The fact that the plots are linear and pass through the origin also indicates that the concentration of propagating radicals is constant within the range studied.

At higher Ce(IV) concentration the experimental data deviate from the linear dependence of log $[M]_0/[M]$ with time and follow a 1.5 order. Once again the external and internal orders are the same.

Cellulose Concentration. The rate of polymerization R_p is a linear function of cellulose concentration at low Ce(IV) concentration. The intercept seen in Fig. 5 is related to the rate of reaction initiated by the complex of ceric ion with monomer. As will be calculated later, at 25°C the rate of polymerization by the Ce(IV)-MA complex is about 15% of the rate of the grafting reaction in the presence of 1% cellulose. However, in the absence of cellulose, under otherwise the same reaction conditions, only 2-3% of monomer is converted to polymer. This means that cellulose itself must be taking part in the production of homopolymer.

Rate of Ceric Ion Disappearance

Monomer Concentration. Semilogarithmic plots of Ce(IV) consumption versus time for three different concentrations of MA are shown in Fig. 6. The consumption of Ce(IV) was independent of monomer concentration under our experimental conditions. Once again, these data show that the amount of ceric ion consumed in the initiation reaction of the type M + Ce(IV) is relatively low although the authors have demonstrated in a previous paper [14] that a complex is indeed formed.

Ceric Ion Concentration. It is possible to observe two regions in the plot of log [Ce(IV)] versus time (Fig. 6). The initial fast reaction is caused by the
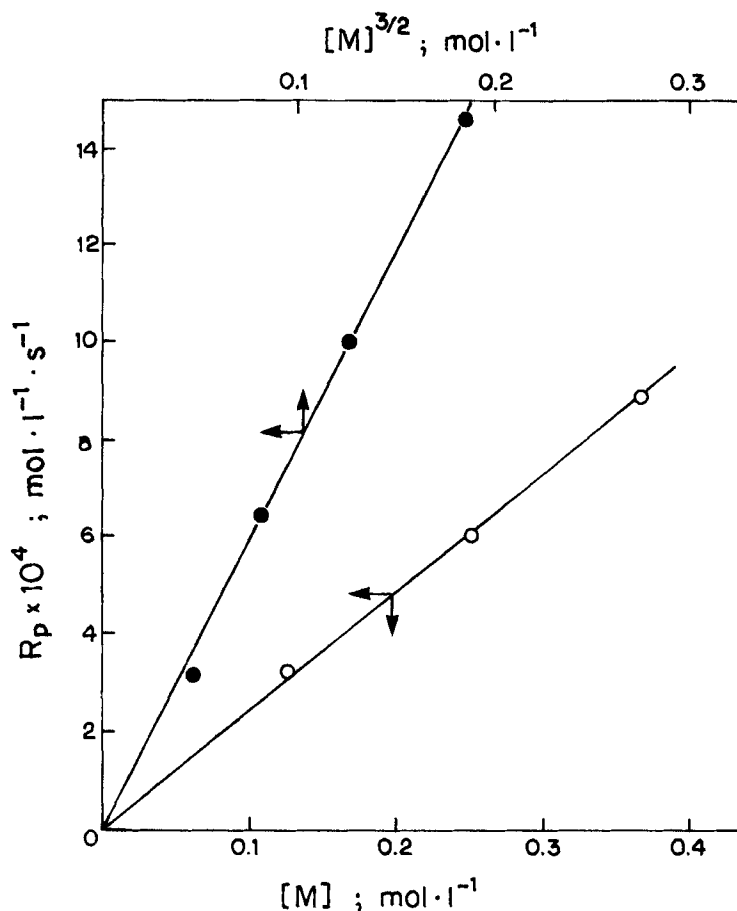
FIG. 3. Rate of polymerization as a function of MA concentration; [cellulose] = 10 g/L; (○) [Ce(IV)] = 0.5 mmol/L; (●) [Ce(IV)] = 7.5 mmol/L.

oxidation of the more reactive hemiacetal groups of cellulose [2]. This is followed by a first-order dependence.

A plot of ceric ion disappearance ($-R_{Ce}$) versus ceric ion concentration is shown in Fig. 7. The R_{Ce} at the beginning of the first-order consumption region levels off with increasing ceric ion concentration. Similar behavior is observed in the oxidation of cellulose [15].
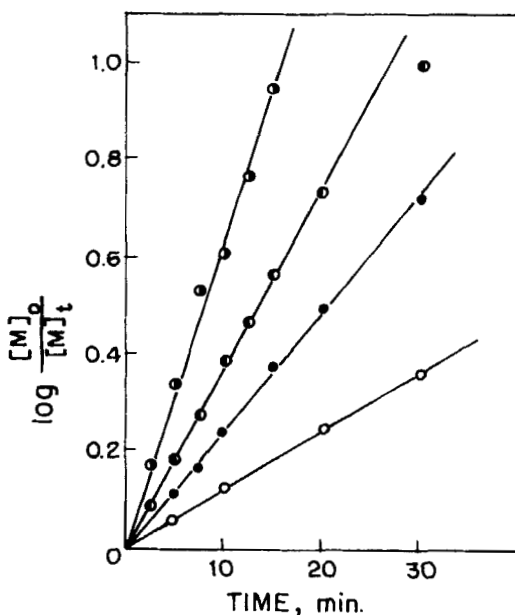
FIG. 4. Log $[M]_0/[M]$ as a function of time for different concentrations of cellulose; $[MA] = 0.128$ mol/L; $[Ce(IV)] = 0.25$ mmol/L; cellulose: (O) 0.25%; (●) 0.5%; (◐) 1%; (◑) 2%.

Cellulose Concentration. Figure 8 shows a semilogarithmic dependence of ceric ion disappearance on time for several concentrations of cellulose. Plotting log $[Ce(IV)]/dt$ as a function of cellulose concentration to the second power results in a straight line with a small intercept (Fig. 9). The same linear dependence has been observed for the oxidation of cellulose alone by ceric ion, although that plot passed through the origin. The intercept is related to the rate of consumption of Ce(IV) in the reaction initiated by the MA-Ce(IV) complex. As will be shown later, only about 4% of the total amount of ceric ion consumed is used in the initiation of homopolymerization, although as much as 15% of homopolymer is created. These results are in agreement with studies conducted on the ceric ion-alcohol redox system, Katai et al. [25], in studying the reaction of the polymerization of acrylonitrile by the pinacol-Ce(IV) redox system, found that the rate of the direct reaction AN-Ce(IV) represented nearly 1/3 of the overall reaction, yet the consumption of Ce(IV) due to this reaction was less than 9%.
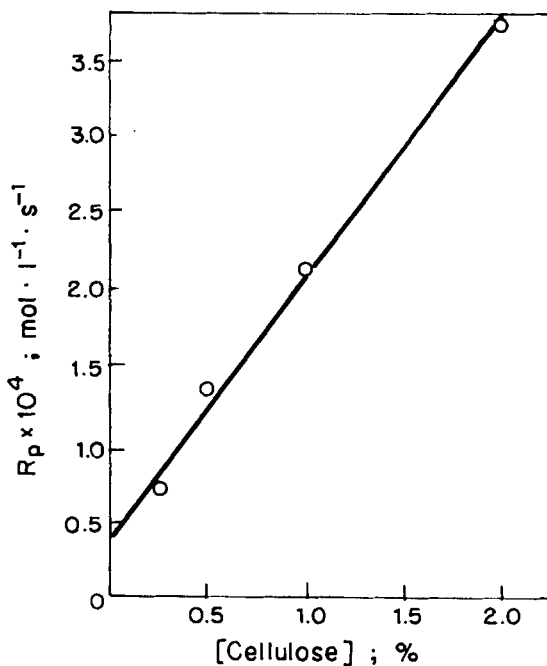
FIG. 5. Rate of polymerization as a function of cellulose concentration; [MA] = 0.128 mol/L; [Ce(IV)] = 0.25 mmol/L.
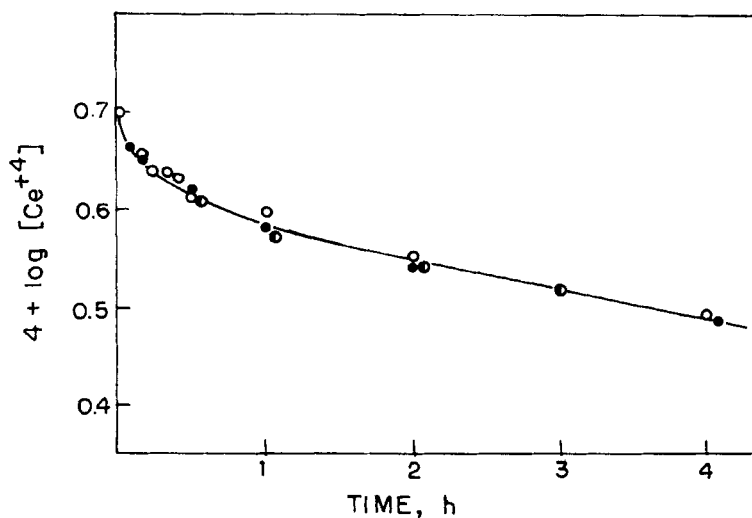

FIG. 6. Consumption of Ce(IV) as a function of time for different concentrations of monomer; [MA] : (○) 0.128 mol/L; (●) 0.25 mol/L; (◐) 0.55 mol/L.
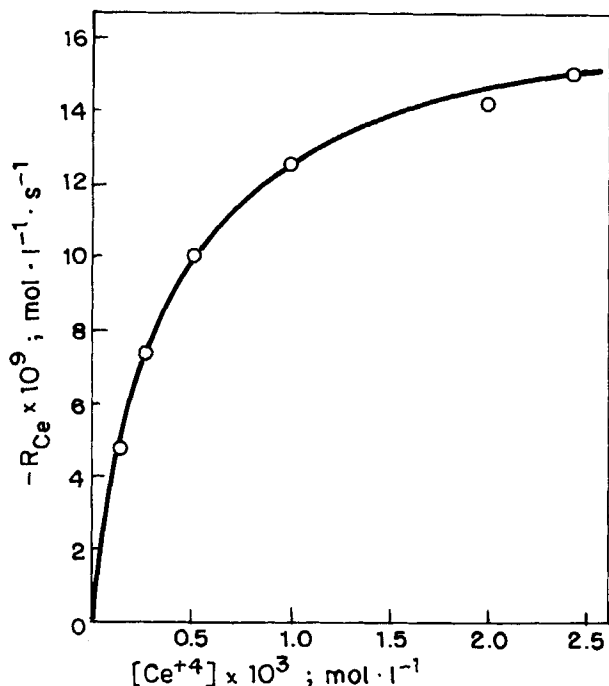
FIG. 7. Rate of Ce(IV) consumption ($-R_{Ce}$) as a function of Ce(IV) concentration; [MA] = 0.128 mol/L; [cellulose] = 1%.

Oxidation of alcohols by ceric ion in sulfuric acid medium is a direct bimolecular reaction without the creation of a complex. When the concentration of alcohol is much higher than that of ceric ion, the reaction becomes pseudo-first order. The dependence of ceric ion consumption on cellulose to the second power in cellulose oxidation and now in grafting is probably caused by reduced accessibility due to the high degree of cellulose crystallinity. Graczyk [15] suggested that when the effect of surface area is eliminated, the reaction becomes first order in respect to cellulose. This would mean that the formation of radicals in the grafting of MA onto cellulose by ceric ion in aqueous sulfuric acid proceeds via a direct reaction between cellulose and ceric ion, without the creation of a complex. This possible mechanism is only speculative at this time, and more evidence is required.
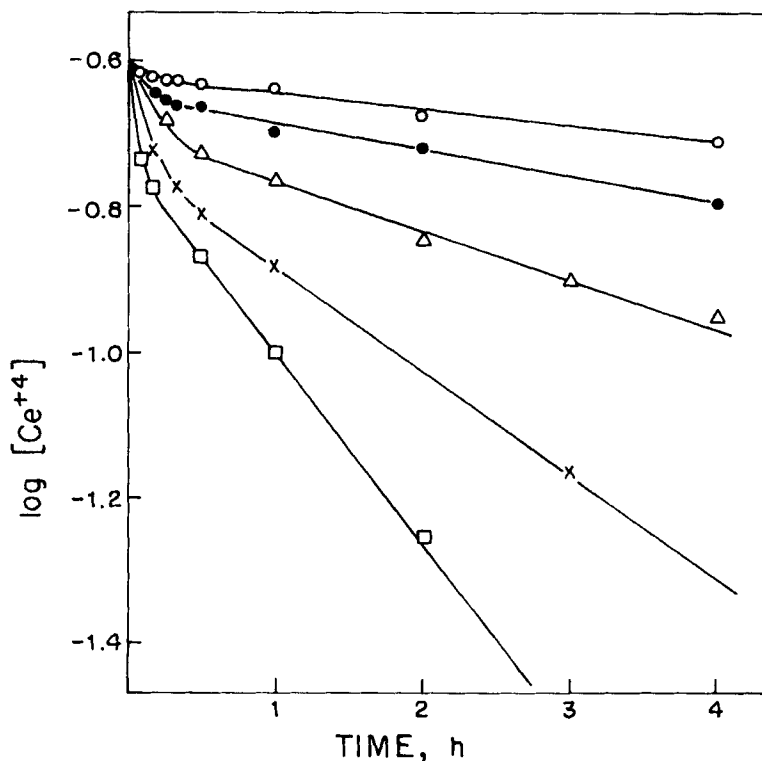
FIG. 8. Consumption of Ce(IV) as a function of time for different concentrations of cellulose; [MA] = 0.128 mol/L; [Ce(IV)] = 0.25 mmol/L; [cellulose] : (○) 0.25%; (●) 0.5%; (△) 1%; (X) 1.5%; (□) 2%.

Grafting Efficiency

Table 1 and Figs. 1 and 5 show how the grafting efficiency is dependent on reaction conditions. The grafting efficiency decreases with increasing ceric ion and monomer concentrations. It is especially evident in the latter case. The grafting efficiency is a function of cellulose concentration, and it is not dependent on the conversion, as shown in Fig. 1. However, at high monomer concentrations, a slightly higher grafting efficiency is observed at the beginning of the reaction.

The higher amount of homopolymer produced in grafting than by a direct reaction between Ce(IV) and MA in the absence of cellulose indicates that a
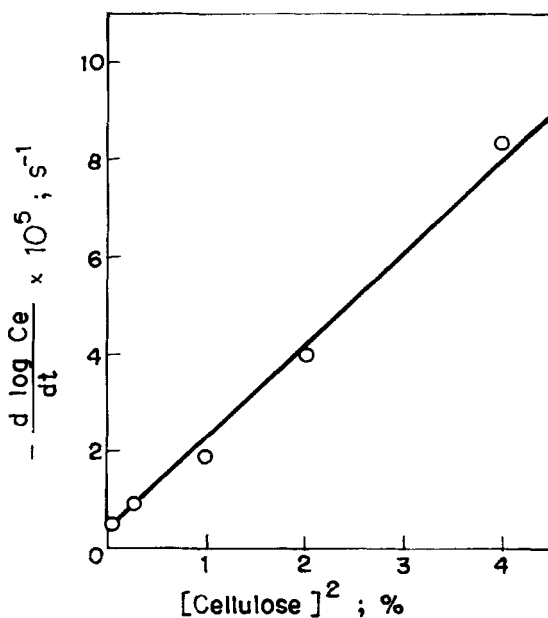
FIG. 9. Rate of ceric ion consumption as a function of cellulose concentration; [MA] = 0.128 mol/L; [Ce(IV)] = 0.25 mmol/L.

specific mechanism for transferring radicals from the cellulose backbone to the monomer probably exists. Chain transfer by monomer and by impurities present in the cellulose are probably responsible.

Reaction Mechanism and Rate Law

The following scheme is proposed to explain the experimental results obtained in this work. It is based on the mechanism of the polymerization of acrylonitrile initiated by the mannitol/cerium(IV) redox system recently published by Mohanty and coworkers [16].

Formation of primary radicals:

$$Ce(IV) + R \xrightarrow{k_r} Ce(III) + R^* + H^+, \qquad (1)$$
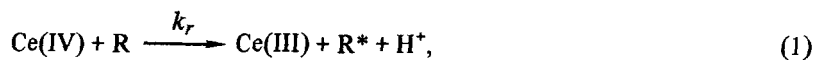
where R denotes cellulose.

TABLE 1. Grafting Efficiency in the Reaction of Grafting MA onto Cellulose by Ceric Ion in Sulfuric Acid

[Ce(IV)] = 0.25 mmol/L; [MA] = 0.125 mol/L		[Cellulose] = 1%; [MA] = 0.125 mol/L		[Cellulose] = 1%; [Ce(IV)] = 0.5 mmol/L	
Cellulose, %	Grafting efficiency, %	[Ce(IV)], mmol/L	Grafting efficiency, %	[MA], mol/L	Grafting efficiency, %
2	92.0	0.125	88.3	0.125	81.0
1	85.5	0.25	85.5	0.250	60.0
0.5	81.0	0.5	82.0		
0.25	79.7	1.0	80.8		
		7.5	67.0		

Initiation:
  (a) By primary radicals:

$$R^* + M \xrightarrow{k_i} R-M^*, \tag{2}$$
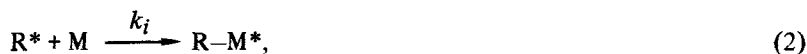
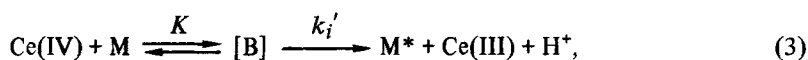where M is the monomer and $R-M^*$ is the radical formed by the reaction of a cellulose-bound primary radical with monomer.
  (b) By ceric ion (homopolymer):

$$Ce(IV) + M \underset{K}{\rightleftharpoons} [B] \xrightarrow{k_i'} M^* + Ce(III) + H^+, \tag{3}$$

where B is a complex between Ce(IV) and monomer.

Propagation:

$$R-M_n^* + M \xrightarrow{k_p} R-M_{n+1}^*, \tag{4}$$

$$M_m^* + M \xrightarrow{k_p} M_{m+1}^*. \tag{5}$$

Termination:
  (a) Mutual, by recombination:

$$R-M_m^* + R-M_n^* \xrightarrow{k_{tc}} polymer. \tag{6}$$

  (b) By primary radicals:

$$M_n^* + R^* \xrightarrow{k_{tp}} polymer. \tag{7}$$
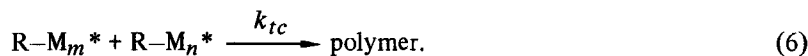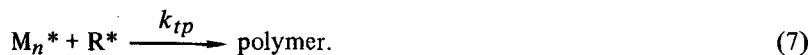
  (c) Linear, by ceric ions:

$$R-M_n^* + Ce(IV) \xrightarrow{k_{td}} polymer. \tag{8}$$
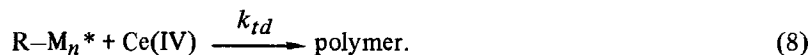
Primary radical reaction:
  (a) With ceric ion:

$$R^* + Ce(IV) \xrightarrow{k_0} products + Ce(III) + H^+. \tag{9}$$
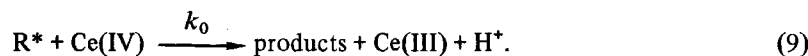
Assuming steady-state concentrations for primary and chain radicals and that R_p is dependent on cellulose concentration to the second power, the following expression for R_p and $-R_{Ce}$ are obtained for the three different types of termination:

(a) Mutual termination:

$$R_p = \frac{k_p [M]^{3/2} [Ce(IV)]^{1/2}}{k_{tc}^{1/2}} \left\{ Kk_i' + \frac{k_r [R]^2}{[M] + (k_0/k_i)[Ce(IV)]} \right\}^{1/2}, \quad (10)$$

$$-R_{Ce} = k_r [Ce(IV)] [R]^2 \left\{ 1 + \frac{(k_0/k_r)[Ce(IV)]}{[M] + (k^0/k_i)[Ce(IV)]} \right\}$$

$$+ Kk_i' [M] [Ce(IV)]. \quad (11)$$

(b) Linear termination:

$$R_p = \frac{k_p [M]^2}{k_{td}} \left\{ Kk_i' + \frac{k_r [R]^2}{[M] + (k_0/k_i)[Ce(IV)]} \right\}, \quad (12)$$

$$-R_{Ce} = 2(k_r [Ce(IV)] [R]^2) + Kk_i' [M] [Ce(IV)]. \quad (13)$$

(c) Primary radical termination:

$$R_p = \frac{k_p k_i [M]^2}{k_{tp}}, \quad (14)$$

$$-R_{Ce} = k_r [Ce(IV)] [R]^2. \quad (15)$$

The results presented above rule out the possibility of the linear mode of termination up to 20 mmol/L. Generally, the independence of R_p of metal ion concentration was explained by the metal ion oxidation of primary radicals. The independence of R_p on Ce(IV), however, in polymerization initiated by the alcohol-Ce(IV) redox systems is well explained on the basis of mutual termination [18]. This assumption is supported by experimental data for the graft copolymerization of butyl methacrylate [26]. Discarding linear and primary radical termination, Eq. (10) can be simplified for the two specific cases presented below.

(a) Low $[Ce(IV)]$, $R_p \sim [Ce(IV)]$

At a very low concentration of $Ce(IV)$ (<1 mmol/L), it is possible to suppose that $(k_0/k_i)[Ce(IV)] \ll [M]$. When k_i' is very small, Eq. (10) reduces to

$$R_p = k_p \left(\frac{k_r}{k_{tc}} \right)^{1/2} [R] [Ce(IV)]^{1/2} [M].$$

(16)

Similarly, Eq. (11) for ceric ion consumption simplifies to

$$-R_{Ce} = k_r [Ce(IV)] [R]^2 + Kk_i' [M] [Ce(IV)].$$

(17)

Equation (16) explains the linear plots of R_p vs $[M]$ and vs $[R]$, as well as the linear plots of R_p vs $[Ce]^{0.5}$ at low $[Ce(IV)]$.

(b) Intermediate $[Ce(IV)]$, R_p independent of $[Ce(IV)]$

At higher concentrations of $Ce(IV)$ (1-20 mmol/L), it is possible to assume that $k_0/k_i [Ce(IV)] \gg [M]$. Then Eq. (10) reduces to

$$R_p = k_p \left(\frac{k_r k_i}{k_0 k_{tc}} \right)^{1/2} [M]^{3/2} [R].$$

(18)

This equation explains why, in the region where the reaction is independent of the concentration of ceric ion, a linear plot of R_p vs $[M]^{1.5}$ is obtained.

At a very high concentration of ceric salt (20 mmol/L), termination by $Ce(IV)$ is possible. The downward trend of the curve of R_p vs $[Ce(IV)]^{0.5}$ for $Ce(IV) > 20$ mmol/L can be explained by assuming termination of polymer by $Ce(IV)$ alone.

Evaluation of Rate Constants

The initial slope of Fig. 9 is equal to k_r, while Kk_i' can be evaluated from the intercept. Furthermore, from the slope of Fig. 5 and the intercept, $k_p/k_{tc}^{1/2}$ can be evaluated by taking into account the above rate constants.

By taking the square of both sides of Eq. (10), taking reciprocals, and rearranging, the following expression is obtained:

$$\frac{[M]^2}{R_p^2} = \frac{k_t}{k_p^2 k_r [R]^2 [Ce(IV)]} + \frac{k_0 k_t}{k_p^2 k_r k_i [R]^2 [M]}.$$

(19)

The ratio k_0/k_i can be calculated from the intercept, while $k_p/k_{tc}^{1/2}$ can be obtained from the slope.

The calculated value of k_r represents the first-order dependence without taking into account the initial fast reaction. Furthermore, k_r is dependent on the concentration of ceric ion due to the effect of the saturation of cellulose. The initial fast oxidation reaction also influences k_0/k_i. Since oxidation is fastest at the beginning of the reaction, k_0/k_i will change with the time of reaction. The initial value will also be dependent on the relative concentration of cellulose. Consequently, the rate constants which have been evaluated and listed in Table 2 are only approximate values and refer to limited ranges of reaction conditions.

Although the individual rate constants are dependent on the method of determination, they are in reasonable agreement with data found in the litera-

TABLE 2. Rate Parameters for Graft Copolymerization of MA onto Cellulose Initiated by Ceric Ion

Rate parameter	Value
Kk_i', L/(mol·s)	9.6×10^{-5}
k_r, L/(g·s)	5.1×10^{-7}
$k_p/k_{tc}^{1/2}$:	
From slope R_p vs [cellulose]	3.9
From intercept R_p vs [cellulose]	8.7
From slope $[M]^2/R_p^2$ vs $[Ce(IV)]^{-1}$	10.7
k_0/k_i:	
From intercept $[M]^2/R_p^2$ vs $[Ce(IV)]^{-1}$	60
From R_p vs $[M]^{3/2}$	29

From Ref. 22 for polymerization of MA by the malonic acid-Ce(IV) redox system:

k_0/k_i	70
$k_p/k_t^{1/2}$	1.5

ture for the polymerization of MA initiated by the malonic acid-Ce(IV) redox system in sulfuric acid [24]. These are also listed in Table 2 for comparison.

ACKNOWLEDGMENT

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