Graft Copolymerization of Methyl Acrylate by Ceric Ion in the Presence of a Controlled Amount of Oxygen

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ABSTRACT

Methyl acrylate (MA) was grafted onto dissolving pulp by ceric sulfate in the presence of a controlled amount of oxygen. The magnitude and location of the maximum on the conversion vs the agitation speed curve are dependent on reaction conditions. The concentration of ceric sulfate and the reaction time are the most important determinants. The type of stirrer has only limited influence. The Ce(IV) consumption rises with increasing stirring speed due to higher diffusion of oxygen to active centers and is higher than for the oxidation of cellulose. The difference in Ce(IV) consumption for grafting and oxidation is not directly related to the amount of homopolymer because the grafting efficiency is independent of agitator speed. The rate of grafting is proportional to the amount of monomer to the second power, as a result of reaction of primary radicals with oxygen. Adding the MA later than the ceric sulfate causes a considerable increase in the induction period but no increase in the conversion. Hypothetical conversion curves are presented.

INTRODUCTION

Graczyk and Hornof, in a series of articles [1-4], studied the influence of the solubility of acrylic monomers on the consumption of ceric salt

both under oxygen-free argon and in the presence of oxygen, and a mechanism of grafting under oxygen-free argon was reported.

They found that the equation expressing the overall rate of polymerization for the graft copolymerization of methyl acrylate (MA) (completely soluble under experimental conditions) onto dissolving pulp in aqueous sulfuric acid under oxygen-free argon was nearly the same as the equation for the reaction of vinyl monomers initiated by the alcohols/mercaptans–Ce(IV) redox systems in the same medium. The initiation reaction was a direct reaction between cellulose and ceric ion, without the creation of a complex, as was generally accepted for the sulfuric acid medium. The order of the reaction with respect to Ce(IV) and monomer was identical and dependent on reaction conditions. The order of the reaction with respect to cellulose was the only exception. The rate of ceric ion disappearance was second order with respect to cellulose, while for alcohols it was first order. The unusual second-order kinetics were explained by the high degree of cellulose crystallinity. The reaction rate was dependent on the second power of the surface available for the reaction [2].

Slightly more Ce(IV) was consumed during cellulose oxidation in the presence of oxygen. Under oxygen-free conditions, the consumption of Ce(IV) was much lower than during cellulose oxidation. The opposite was observed in the presence of oxygen. The difference depended on the type of monomer, i.e., its water solubility and the ceric salt.

The purpose of this paper is to study the consumption of ceric ion and the mechanism of grafting of a soluble monomer (MA) onto cellulose in the presence of oxygen in more detail. These results are compared with graft copolymerization under oxygen-free argon and with the oxidation of cellulose, which is treated as a standard.

EXPERIMENTAL

Materials

A dissolving pulp supplied by Zaklady Celulozy i Papieru, Swiecie, Poland, was used as the grafting substrate. The pulp was preserved in a freezer and thawed before use. Methyl acrylate (MA) was purified by vacuum distillation. Ceric sulfate, ferrous sulfate, and sulfuric acid were reagent grade.

Graft Copolymerization

Graft copolymerization was carried out in a 1-L resin flask according to the experimental procedure described previously [6]. The reactions were carried out under a positive pressure of gases, which were purged at the rate of 12–15 L/h. Different methods of adding ceric salt and different purging times were applied.

Unless otherwise specified, the MA monomer was added first, and the reaction was started by an addition of ceric salt. In some experiments, ceric salt was added first, and the reaction was started by an addition of methyl acrylate.

Method 1: Ceric salt was added after 60 min of purging with oxygen-free argon without opening the reactor.

Method 2: Ceric salt was added after 15 min of purging with 99.99% nitrogen.

Method 3: Ceric salt was added after 15 min of purging with 99% nitrogen.

Method 4: Ceric salt was added first and, after a suitable time, the reaction was started by addition of MA (99% nitrogen).

Two types of stirrer were used, a Teflon paddle stirrer and an anchor stirrer. Details of the geometry of the stirrers were described previously [5].

Determination of Ceric Ion

The amount of ceric ion in the polymerization recipes (an aqueous solution) was determined volumetrically by adding a given amount of ferrous sulfate and back-titrating with ceric sulfate with o-phenantroline as an indicator. The ferrous salt was standardized daily with potassium permanganate, and the ceric sulfate was standardized against the ferrous salt.

RESULTS AND DISCUSSION

Effect of Monomer and Cellulose Concentration

Graczyk [6] and Hornof [7] recently reported that graft copolymerization of methyl acrylate (MA) and methyl methacrylate (MMA) onto
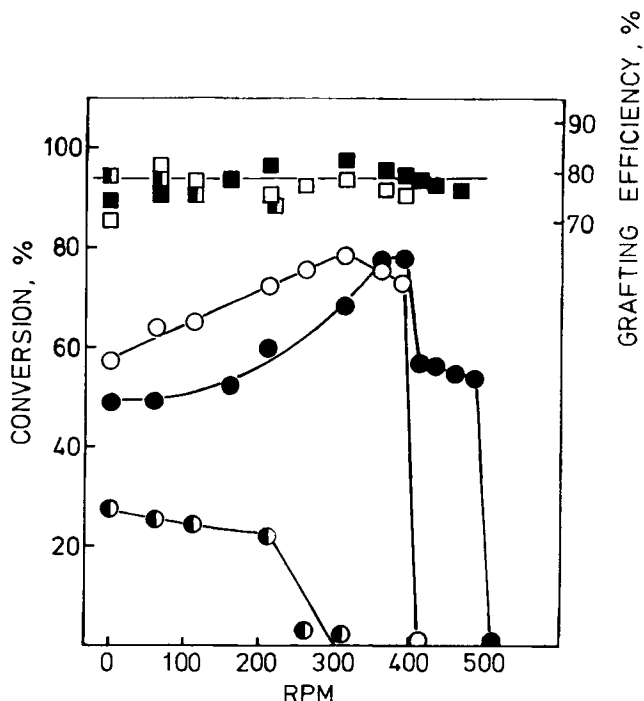
FIG. 1. Conversion and grafting efficiency as a function of agitator speed for different concentrations of ceric ion: temperature = 65°C; reaction time = 30 min; [cellulose] = 10 g/L; [MA] = 0.133 mol/L; (O) polymer; (□) grafting efficiency; (O, □) [Ce(IV)] = 10 mmol/L; (●, ■) [Ce(IV)] = 2.5 mmol/L; (◐, ◧) [Ce(IV)] = 0.5 mmol/L.

cellulose initiated by ceric ion was influenced by agitation. A maximum in the conversion vs stirring speed curve was observed followed by a drop in conversion to zero in most cases. The increase in conversion at low agitation speeds was caused by an increase in the diffusion of monomer from monomer droplets into cellulose fibers. On the other hand, the decline in conversion at high rates of stirring was caused by deactivation of growing polymer radicals and primary radicals by oxygen.

Although the purging nitrogen was purified in the author's recent paper [6], it still contained traces of oxygen, and its purity was roughly 99.99% (Method 2). The effect of stirring was observed for a low and a high concentration of the reagents. An example of these results at low cellulose and MA concentrations is presented in Fig. 1. It is seen that the shape of the
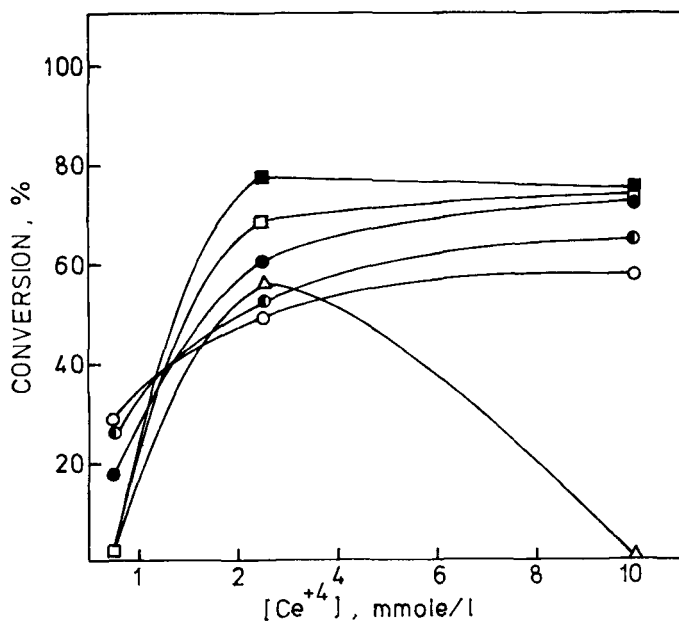
FIG. 2. Conversion as a function of Ce(IV) concentration at different stirring speeds: temperature = 65°C; reaction time = 30 min; [cellulose] = 10 g/L; [MA] = 0.133 mol/L; (O) 0 rpm; (●) 110 rpm; (◑) 210 rpm; (□) 310 rpm; (■) 360 rpm; (△) 410 rpm.

conversion curves is dependent on the reaction conditions. A more or less broad maximum is observed, which is followed by a drop of conversion to zero. However, in some cases the maximum does not appear, and conversion decreases steadily with increasing agitation speed.

Effect of Ceric Ion Concentration

The effect of ceric ion concentration on the conversion of monomers has been studied by a number of authors [8]. It has been well established, on the basis of graft copolymerization of several monomers in $HClO_4$, HNO_3, and H_2SO_4 that the grafting increases up to a narrow maximum with increasing ceric ion concentration, beyond which grafting decreases. Unfortunately, all these experiments were carried out in the presence of traces of oxygen [9-13].

Graft copolymerization under oxygen-free argon was found to be independent of Ce(IV) concentration over a broad concentration range (1–20 mmol/L) [3]. It is reasonable to expect that the breadth of the maximum should decrease with increasing oxygen concentration.

Diffusion of oxygen from the purging gas to active centers is governed by the stirring speed if other parameters remain unchanged. Thus, the influence of oxygen on the mechanism and kinetics of grafting can be studied by increasing the concentration of oxygen in the reaction mixture or changing the stirring speed. The latter approach was used primarily in this paper, especially because the reaction is heterogeneous and should also be influenced by the method of mixing.

It can be seen from Fig. 2, in which the results from Fig. 1 are replotted, that the effect of ceric ion on conversion depends strongly on the stirring rate. At low agitator speeds (0–110 rpm), the conversion rises steadily with increasing [Ce] without reaching a maximum in the studied range. At intermediate stirring rates, the same pattern is observed but the conversion is dependent to a higher degree on [Ce]. At high stirring rates, the maximum appears.

These observations suggest that the maximum becomes smaller and shifts to a lower concentration of ceric ion with increasing oxygen concentration.

Effect of Type of Stirrer

In a heterogeneous reaction, such as grafting, the type of stirrer and the reactor size can greatly influence the magnitude and location of the maximum in the conversion vs agitator speed curve [5]. The effect of the type of stirrer for graft copolymerization of MA above its solubility in water is shown in Fig. 3.

An anchor stirrer shifts the maximum to lower agitation speed compared to a Teflon paddle stirrer. However, the drop in conversion from 80–90% to zero is nearly independent of the type of stirrer used, as is the grafting efficiency. The disappearance rate of Ce(IV) occurs at a faster rate with an anchor stirrer than with a Teflon paddle stirrer. Above 350 rpm, differences disappear.

Effect of Reaction Time on Conversion

The effect of traces of oxygen on conversion in the presence of 99% nitrogen (Method 3) was studied at 310 and 810 rpm, i.e., above 300 rpm,
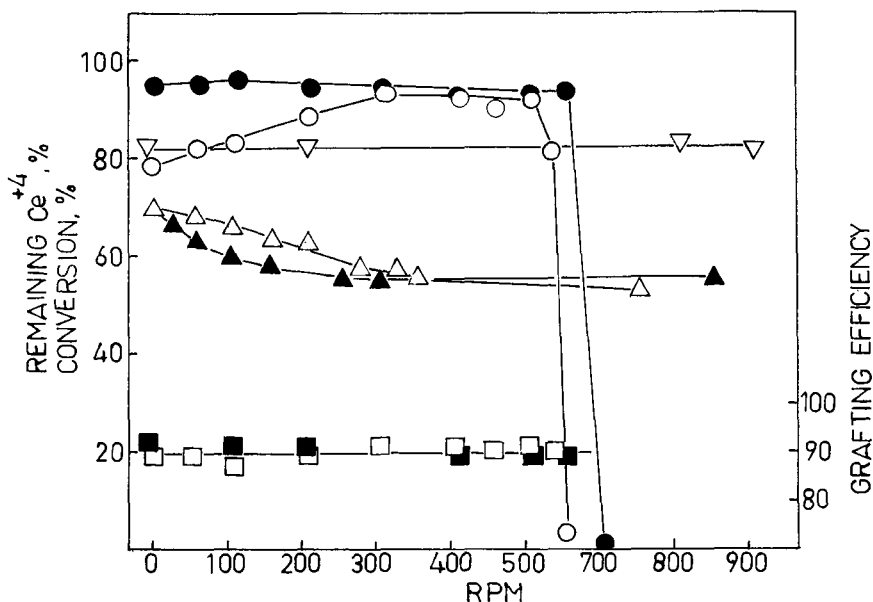
FIG. 3. Conversion, grafting efficiency, and consumption of ceric ion as a function of agitator speed for two types of agitator: temperature = 25°C; reaction time = 30 min; [cellulose] = 30 g/L; [MA] = 0.399 mol/L; [Ce(IV)] = 2.5 mmol/L; (O, □, △) Teflon paddle stirrer at 110 rpm; (●, ■, ▲) anchor stirrer at 310 rpm; (O, ●) polymer; (□, ■) grafting efficiency; (△, ▲) consumption of ceric ion in grafting; (▽) reaction of Ce(IV) with cellulose.

where the influence of monomer diffusion to active centers can be neglected [14]. The latter was arbitrarily chosen as being high enough for comparison while low enough to prevent significant shearing. Figure 4 shows that, at 310 rpm, only a short induction period (2.5 min) is seen and the conversion reaches a plateau after 30–40 min. At 810 rpm, a longer induction period (~45 min) is observed, but the shape of the curve is nearly the same as at 310 rpm. These results once again confirm those of previous reports [1, 6] that grafting efficiency in graft copolymerization of MA is independent of stirring speed.

The linearity of the plot in Fig. 5 means that the internal order is 2. The similarity of the conversion curves at both stirring speeds demonstrates that the order of the reaction is independent of agitation speed; in other words, the amount of oxygen.
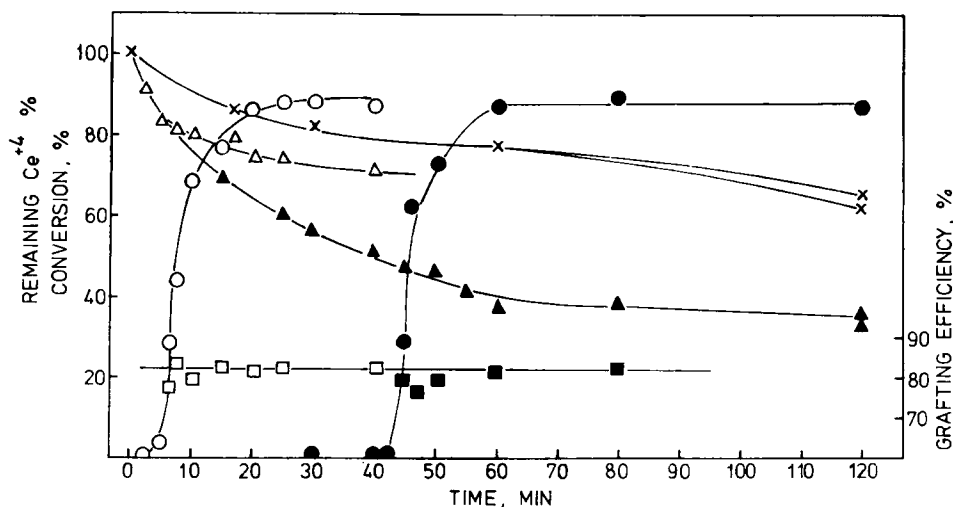
FIG. 4. Conversion, grafting efficiency, and consumption of ceric ion as a function of agitator speed: temperature = 35°C; [cellulose] = 20 g/L; [MA] = 0.266 mol/L; [Ce(IV)] = 2.5 mmol/L; (○, □, △) 310 rpm; (●, ■, ▲) 810 rpm; (○, ●) polymer; (□, ■) grafting efficiency; (△, ▲) consumption of ceric ion in grafting; (✕) reaction of Ce(IV) with cellulose.

Under oxygen-free argon at intermediate [Ce], 1–20 mmol/L, the reaction was independent of [Ce] and the order of reaction with respect to monomer was 1.5 [3]. Figure 6 shows that the external order changes from 1.5 to 2 in the presence of oxygen. Thus, excellent agreement between internal and external orders was observed. Furthermore, the order of reaction changes in the presence of even a small amount of oxygen.

Effect of Reaction Time on Ce(IV) Consumption

It was shown in Fig. 4 that Ce(IV) consumption at 310 rpm is nearly complete after 40 min, although only about 30% of the total Ce(IV) was used in this reaction. Consumption of Ce(IV) at 810 rpm still increases at that time and stabilizes after 80 min at 35% of its initial concentration. The stabilization of the Ce(IV) consumption is probably caused by steric hindrance. Thus, these data are in agreement with the results of Mansour and
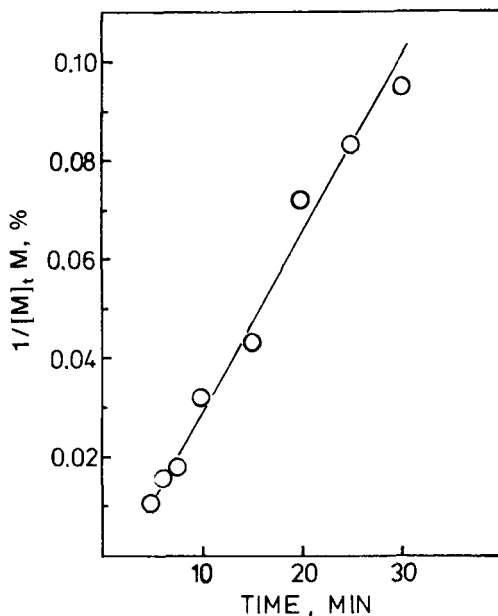
FIG. 5. Rate of polymerization $(1/[M]_t)$ as a function of time: temperature = 35°C; [cellulose] = 20 g/L; [MA] = 0.266 mol/L; [Ce(IV)] = 2.5 mmol/L; stirring rate = 310 rpm (date from Fig. 4).

Nagaty [15], who found first-order dependence and much faster consumption of Ce(IV) under intense agitation than with light hand shaking.

Although Ce(IV) consumption depends on stirring speed, the grafting efficiency is constant at 82%, i.e., the amount of homopolymer is the same at 310 as at 810 rpm. Thus, the difference in consumption of Ce(IV) in grafting and oxidation is not directly related to the amount of homopolymer, as was postulated by Hebeish and Mehta [10].

Ce(IV) consumption in graft copolymerization and in cellulose oxidation is plotted semilogarithmically in Figure 7. In the presence of oxygen, the fast reaction period is extended by increasing stirring speed. The slower range of Ce(IV) consumption starts before the onset of polymerization. This means that Ce(IV) was primarily consumed in the removal of radical polymerization inhibitor, i.e., oxygen.
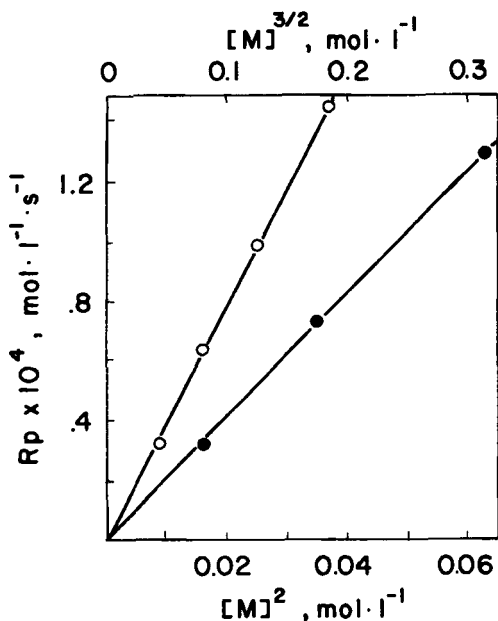
FIG. 6. Rate of polymerization (R_p) as a function of MA concentration: [cellulose] = 10 g/L; [Ce(IV)] = 7.5 mmol/L (O) oxygen-free argon; (●) 99% nitrogen.

The Order of Addition of the Reactants

Mansour and Schurz [17] indicated that, at least for some monomers, higher grafting levels and efficiency were obtained when the monomer was added last. However, other authors have found opposite results.

A set of experiments was carried out to elucidate how changing the order of reagent addition in connection with stirring speed influences conversion and ceric ion consumption. They were done in the presence of oxygen (Method 4) in order to generate data comparable to those of Mansour and Schurz.

Figure 8 shows that the smaller the time between addition of ceric salt and of MA, the higher the maximum and the higher the agitator speed at which the maximum is located.

Figure 9 shows that the induction period increases considerably when the time of addition of the reactants is changed. When ceric sulfate and
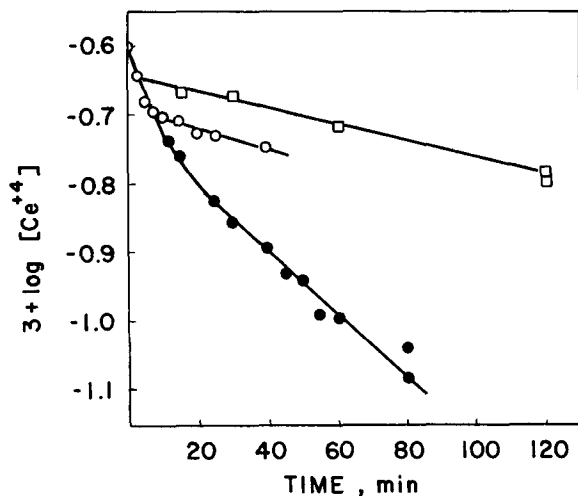
FIG. 7. Rate of Ce(IV) consumption ($-R_{Ce}$) as a function of Ce(IV) concentration: temperature = 35°C; [cellulose] = 20 g/L; [MA] = 0.266 mol/L; [Ce(IV)] = 2.5 mmol/L; (O) 310 rpm; (●) 810 rpm; (□) reaction of Ce(IV) with cellulose. Data from Fig. 4.

MA are added 5 min apart, the induction time is 15–20 min, while at 30 min it is 30 min. The level of conversion is only slightly lower than for graft copolymerization with MA added first. However, the conversion is not higher for any of these cases.

The long induction period when the order of addition is changed confirms the importance of the swelling period in this reaction. One could expect that for MA, a partly water-soluble monomer, the swelling period is not important due to its high ability to penetrate cellulose fibers compared to hydrophobic monomers.

Hypothetical Curves of Conversion vs Stirring Speed

It was mentioned above that, in the presence of oxygen, the shape of the plot of conversion vs stirring rate is dependent on reaction conditions. At constant concentration of oxygen in the purge gas, the most important variables are concentration of ceric ion and time of reaction. Figure 10 presents hypothetical curves for the graft copolymerization of MA onto cellulose initiated by ceric ion. It is possible to observe all five curve
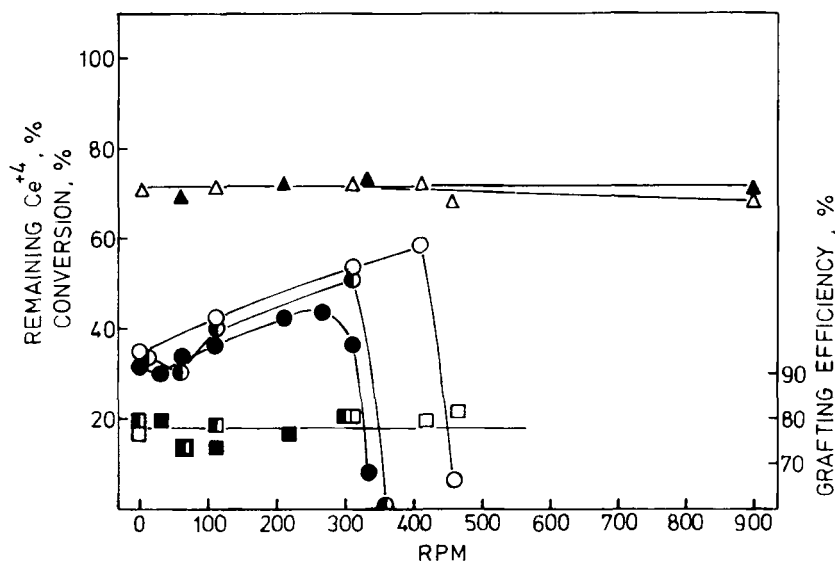
FIG. 8. Conversion, grafting efficiency, and consumption of Ce(IV) as a function of agitator speed for copolymerization started by the addition of MA: temperature = 45°C; [cellulose] = 10 g/L; [MA] = 0.133 mol/L; [Ce(IV)] = 25 mmol/L; (O) polymer; (□) grafting efficiency; (△) Ce(IV) remaining; (O, □, △) Ce(IV) added 5 min earlier; (◐, ◫, ▲) Ce(IV) added 15 min earlier; (●, ■, ▲) Ce(IV) added 30 min earlier.

shapes either by altering the concentration of ceric ion or by increasing the reaction time or by changing both factors at the same time.

Reaction Mechanism

Graczyk and Hornof [3] found that, in graft copolymerization onto cellulose under oxygen-free argon in sulfuric acid, the initiation is a direct reaction between cellulose and ceric ion without the creation of a complex. On the other hand, they also showed that a complex is created between ceric ion and monomer. Consumption of Ce(IV) in the direct reaction between MA and Ce(IV) was less than 2% of the total Ce(IV) consumed. However, nearly 15% homopolymer was created from the beginning of the reaction. It is reasonable to assume that at the same time, a complex is formed between cellulose and the soluble monomer (MA), as
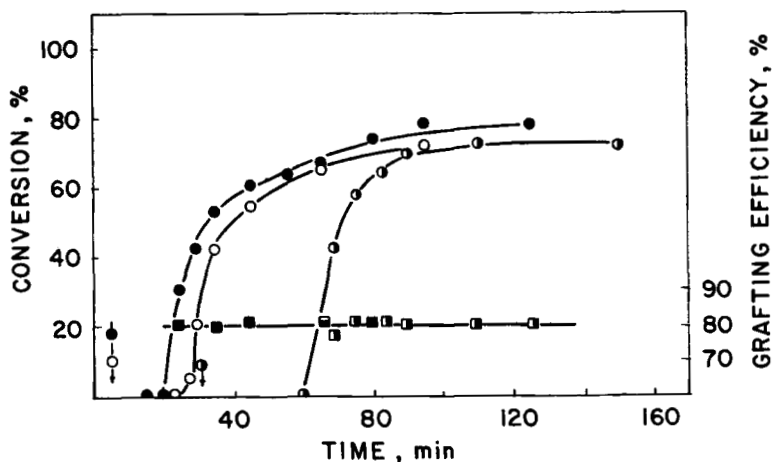
FIG. 9. Conversion and grafting efficiency as a function of agitator speed for copolymerization started by the addition of MA: temperature = 45°C; [cellulose] = 10 g/L; [MA] = 0.133 mol/L; [Ce(IV)] = 2.5 mol/L; (○) polymer; (□) grafting efficiency; (○, ●) Ce(IV) added 5 min earlier; (◐) Ce(IV) added 30 min earlier; (○, □) 110 rpm; (●, ■) 310 rpm; (◐, ◧) 310 rpm.
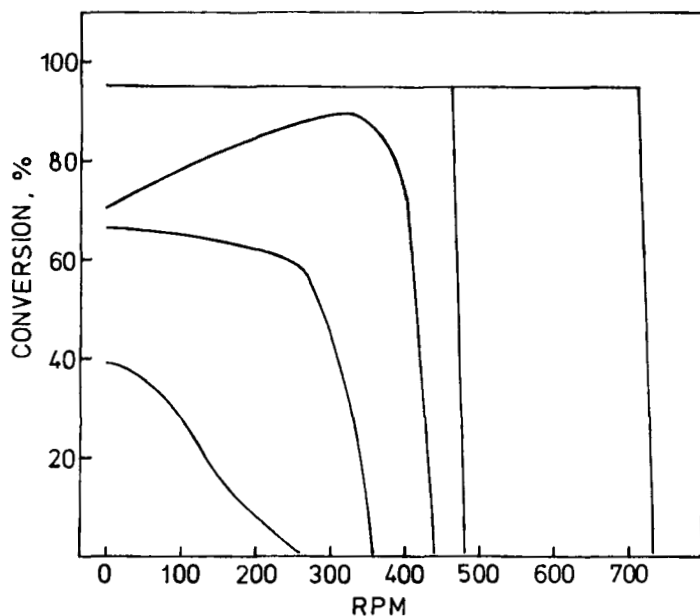

FIG. 10. Hypothetical curves for conversion vs stirring speed for different reaction conditions.

was postulated by Gaylord [18–20]. Both complexes can create six-membered rings which are stable due to charge delocalization (Fig. 11). In the presence of a large amount of water, hydrogen bonds in the complex are very weak, and the creation of radicals onto cellulose is still a direct bimolecular reaction.

When radicals are created on cellulose, the electric charge is delocalized in the ring, and the radicals are easily transferred to oxygen molecules, which leads to inhibition. This complex accelerates the consumption of ceric ion while oxidation of cellulose in the presence of only ceric ion depends slightly on the concentration of oxygen.

BMA does not form a complex with ceric ion. Thus, a six-membered complex with cellulose also cannot be formed. Consequently, consumption of ceric ion does not increase in the presence of oxygen. In the case of ceric ammonium nitrate in nitric acid, a complex forms between BMA and ceric ion, and the same effect is observed as for MA, but on a smaller scale [1].

Although primary radicals are scavenged by oxygen, the concentration of oxygen does not drop to zero, as was observed in graft copolymerization onto xanthated cellulose [14]. When nitrogen of 99.9% purity is purged at a rate of 15 L/h, the oxygen concentration stabilizes at the level of 0.1–0.2 ppm. A dynamic equilibrium is created, and copolymerization starts after the induction period.

The homopolymer is formed partly by chain transfer (to monomer and impurities of cellulose) and partly by direct reaction between monomer
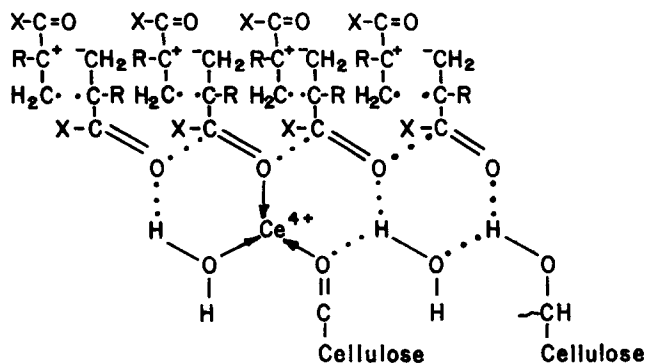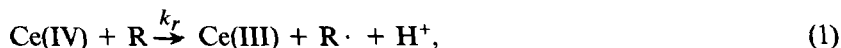

FIG. 11. The complex between cellulose, monomer, and ceric ion.

and Ce(IV). The contribution of the complex decreases with increasing monomer hydrophobility. In the case of BMA, the copolymer is created by chain transfer only.

The following mechanism is proposed to explain the experimental results.

Primary radical formation:

$$Ce(IV) + R \xrightarrow{k_r} Ce(III) + R\cdot + H^+, \tag{1}$$

where R is cellulose.

Initiation:
(a) by primary radicals:

$$R\cdot + M \xrightarrow{k_i} R-M\cdot, \tag{2}$$

(b) by ceric ion (homopolymer):

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

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

Propagation:

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

$$M_m\cdot + M \xrightarrow{k_p'} M_{m+1}\cdot. \tag{5}$$
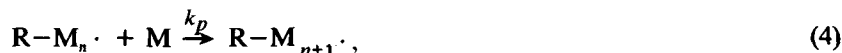
Termination:
(a) mutual by combination:

$$R-M_m\cdot + R-M_n\cdot \xrightarrow{k_{tc}} polymer, \tag{6}$$
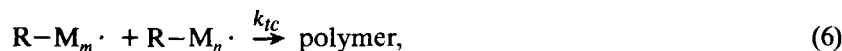
(b) linear by ceric ions:

$$R-M_n\cdot + Ce(IV) \xrightarrow{k_{td}} polymer, \tag{7}$$

(c) termination by oxygen:

$$R-M_n\cdot + O_2 \xrightarrow{k_{tO}} polymer, \tag{8}$$

Primary radical reaction:
(a) with ceric ion:

$$R\cdot + Ce(IV) \xrightarrow{k_{Ce}} \text{products} + Ce(III) + H^+, \tag{9}$$

(b) with oxygen:

$$R\cdot + O_2 \xrightarrow{k_{O_2}} \text{products}, \tag{10}$$

or

$$R\cdot + M + Ce(IV) \rightleftharpoons [C] \tag{11}$$

$$[C] + O_2 \rightarrow R-O_2\cdot + Ce(III) + M + H^+ \tag{12}$$
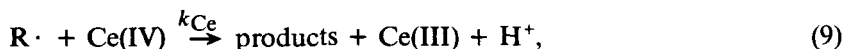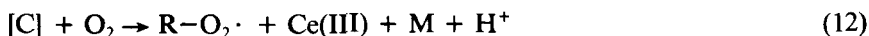
By assuming steady-state concentrations for primary and chain radicals and that R_p depends on the concentration of cellulose to the second power, the following expression for R_p and $-R_{Ce}$ can be derived for mutual and linear terminations. Primary radical termination can be ruled out, as was shown previously [3].

(a) Mutual termination:

$$R_p = \frac{k_p[M]^{3/2}[Ce(IV)]^{1/2}}{k_{tc}^{1/2}} \left\{ Kk_i' + \frac{k_r[R]^2}{[M] + (k_{Ce}/k_i)[Ce(IV)] + k_{O_2}/k_i[O_2]} \right\}^{1/2},$$

$$-R_{Ce} = k_r[Ce(IV)][R]^2 \left(1 + \frac{k_{Ce}/k_r[Ce(IV)]}{[M] + k_{Ce}/k_i'[Ce(IV)] + k_{O_2}[O]}\right)$$
$$+ Kk_i'[M][Ce(IV)].$$

(b) Linear termination:

$$R_p = \frac{k_p[M]^2}{k_{td}} \left(Kk_i' + \frac{k_r[R]^2}{[M] + (k_{Ce}/k_i)[Ce(IV)] + k_{O_2}/k_i[O_2]}\right),$$

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

Oxygen, if present, competes with ceric ion in linear termination and termination of primary radicals. The reaction maximum or plateau is located at lower ceric ion concentrations than with oxygen-free argon as purge gas. Consequently, the percentage of grafting also starts to decrease with increasing [Ce] at lower [Ce(IV)]. For example, in the presence of oxygen in the middle concentration range of ceric ion, second-power instead of 1.5-power dependence is observed, as was shown in Fig. 8.

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