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(24) This level of contamination probably could be detected easily with the aid of modern analytical methods such as pulse Fourier transform NMR. However, we were unable to attempt the direct analysis of our AIBN samples for MAN, since these samples were no longer available when this analysis became desirable (i.e., at the time when the presence of copolymerized MAN units was discovered). As was noted above, other workers[8] have reported conclusive evidence for MAN formation during the recrystallization of AIBN, and it is relevant to point out here that their recrystallization procedure is similar to the one that we used.

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(28) In fact, after our paper had been submitted for publication, Dr. D. H. Solomon kindly informed us (private communication, May, 1984) that he and his associates had obtained some evidence for the presence of copolymerized MAN units in AIBN-initiated polystyrene. **Note Added in Proof.** This evidence has now been published: Moad, G.; Solomon, D. H.; Johns, S. R.; Willing, R. I. *Macromolecules* **1984**, *17*, 1094.

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Mechanism of Graft Copolymerization onto Polysaccharides Initiated by Metal Ion Oxidation Reactions of Model Compounds for Starch and Cellulose

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ABSTRACT: Oxidation of model compounds for starch and cellulose with Mn(III), Ce(IV), and V(V) ions has been studied by means of UV–vis absorption spectroscopy and ESR. The oxidation of diols proceeds via a stable complex and is almost first order with respect to proton concentration. Acyl radical spin adducts are detected as intermediates from aldehydes and diols by means of ESR trapping experiments. Reactivity studies reveal that cis-C1–C2 glycol groups are oxidized 4 times faster than cis-C3–C4 glycol groups. Trans glycol groups and C6 hydroxyl groups have negligible reactivities. Model compounds for reducing end groups of polysaccharides are oxidized 50 times faster than model compounds for nonreducing end groups. Considering the large number of repeating diol groups along the polysaccharide chain, it is concluded that both C1–C2 (end groups) and C2–C3 glycol groups are predominant sites for initiation of graft copolymerization.

Introduction

Oxidation of alcohol and glycol groups involving free radicals has been used to develop a technique of graft copolymerization onto starch and cellulose. The most widely used system is that initiated by ceric ions, in which high grafting efficiencies have been obtained with both hydrophobic and hydrophilic monomers.[1-6]

On the basis of studies of model compounds, the initiation is thought to involve the formation of a complex between the metal ion and hydroxyl groups in the polysaccharide followed by disproportionation of the complex to generate radicals. The formation of radicals in cellulose

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Table I

model compounds	model for
model compounds I	
ethanol	C6 alcohol group
propionaldehyde	aldehyde group generated by peroxidation of the C6 alcohol group or oxidation of the glycol group
2,3-butanediol and cyclohexanediol	C2–C3 glycol group
model compounds II	
monosaccharides	reducing end group and diol

has been demonstrated by means of ESR in the ceric ion system.[7] Several studies using model compounds have been carried out to seek the predominant grafting sites in polysaccharides in this system. The relative importance of C1–C2 glycol, C2–C3 glycol, C6 hydroxyl, carbonyl, and hemiacetal groups, respectively, for the initiation reaction has been proposed.[8-13] However, the relative roles of these groups depend on the experimental conditions and have not been established.

Recently, a manganic pyrophosphate ion for initiation has been developed in our laboratory for grafting of vinyl monomers onto starch and cellulose. High grafting efficiencies are obtained with hydrophobic monomers such as acrylonitrile and methyl methacrylate.[14-18] The purpose of the present study is to reveal the initiation mechanism in this system. Table I shows the model compounds (of low molecular weight) for starch and cellulose selected for this purpose. The initiation systems of starch and cellulose itself will be too complicated to study directly due to the possibility of multiple reactions, both simultaneous and consecutive. Because of crystalline regions (in cellulose) and molecular aggregation due to hydrogen bonds (in starch and cellulose), the accessibility of the polysaccharides is limited in the grafting systems used here.

Experimental Section

Materials. Chemicals used as model compounds are ethanol (AB Svensk Sprit, 95%), propionaldehyde (Merck, synth.), ethylene glycol (Merck), 2,3-butanediol, 2,3-dimethyl-2,3-butanediol (EGA Chemie), cyclohexanediol (Riedel-de Haen, pro synth.), D-ribose, D-galactose, 2-deoxy-D-glucose, 2-deoxy-D-ribose, 3-*O*-methyl-D-glucose (Aldrich), D-glucose (Mallinckrodt), α-methyl-D-glucoside (US Biochemical Corp.), and cellobiose (Merck).

Chemicals for the preparation of metal ion solutions are manganic sulfate monohydrate (Merck), potassium permanganate (Merck), ammonium cerium(IV) nitrate (KEBO, Sweden), sodium metavanadate (The British Drug House Ltd), copper sulfate (KEBO, Sweden), silver nitrate, potassium dichromate, tetrasodium pyrophosphate decahydrate, sulfuric acid (all from Merck), and sodium hydroxide (EKA, Sweden).

All chemicals without remarks are of analytical grade and used as received.

Preparation of Metal Ion Solutions. The solution of manganic pyrophosphate ion was prepared as described previously.[14-17] First, solutions of Mn(II), Mn(VII), and $P_2O_7^{4-}$ ions were prepared by dissolving 0.3 g of $MnSO_4{\cdot}H_2O$, 0.07 g of $KMnO_4$, and 0.4 g of $Na_4P_2O_7{\cdot}10H_2O$ in 100 mL of distilled water, respectively. The acidities of the solutions were adjusted to pH 6 by adding H_2SO_4 to the solutions of Mn(II) and $P_2O_7^{4-}$ ions and NaOH to that of Mn(VII) ion. The solution of manganic pyrophosphate ion was obtained by addition of 5 mL of Mn(VII) ion solution to the mixed solution of 5 mL of Mn(II) ion and 40 mL of $P_2O_7^{4-}$ ion.

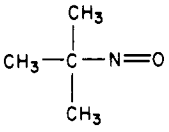
Ceric and vanadic ion solutions were prepared by dissolving 0.12 g of ammonium cerium(IV) nitrate and 0.027 g of sodium metavanadate in 100 mL of distilled water, respectively.

The acidities of the resulting solutions were adjusted to pH 1.5 by adding H_2SO_4 and using a pH meter.

Measurements of Oxidation Rates. Usually, the experiments were carried out at 25 °C in aqueous solutions of 2 mmol/L of metal ion and 20 mmol/L of substrate. For manganic pyrophosphate and ceric ions, the solutions of both metal ion and substrate were made oxygen-free by bubbling nitrogen gas through them for about 0.5 h and then mixed. The experiments for vanadic ion were carried out in solutions of 6 mmol/L of vanadic ion and 60 mmol/L of substrate without bubbling of nitrogen gas, because no noticeable effect of oxygen has been reported in this case.[19]

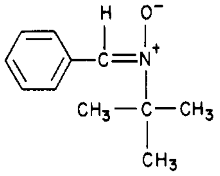
The concentration changes of manganic pyrophosphate, ceric, and vanadic ions were monitored at 510, 370, and 350 nm, respectively, using a UV–vis spectrophotometer, Perkin-Elmer Model 575/572.

Measurements of ESR Spectra. In the ESR spin trapping experiments, methanol (Merck) solutions containing **2-methyl-2-nitrosopropane** (I) or **α-phenyl-*N*-*tert*-butylnitrone** (II) (Aldrich) as spin traps (50 mmol/L), model compounds (100 mmol/L), and acidic aqueous solutions of metal ion (10 mmol/L) were evacuated separately by means of the freeze–pump–thaw technique and then mixed.



$(CH_3)_3C{-}N{=}O$

I



II

The ESR spectra were measured at room temperature immediately after mixing by means of an X-band Bruker ER-420 electron spin resonance spectrometer.

In the measurements of ESR without spin traps, the acidic aqueous solution of ceric ion (50 mmol/L) or manganic pyrophosphate ion (10 mmol/L) was poured onto the model compounds in the solid state after evacuation. The reactions were allowed to progress for 15 s at room temperature (ca. 298 K) and then the samples were frozen with liquid nitrogen and measured at 77 K. ESR spectra in air were measured after introduction of air into the samples and annealing at ca. 250 K.

Results and Discussion

1. Model Compounds I. A. Reactivities with Manganic Pyrophosphate Ion.

Manganic pyrophosphate ion in aqueous solution shows an optical absorption band with a maximum at 510 nm in the visible region. This absorption decreases gradually after addition of the substrate. The concentration changes of manganic pyrophosphate ion in the reaction with ethanol, propionaldehyde, 2,3-butanediol, and cyclohexanediol were monitored at 510 nm as shown in Figure 1. The manganic pyrophosphate ion in acidic aqueous solution (pH 1.5) is stable for a few hours in the absence of substrate or in the presence of ethanol and ethylene glycol. On the other hand, high reactivities were observed in the reactions of 2,3-butanediol and cyclohexanediol. Both oxidations deviated from first-order kinetics. A similar deviation has been reported in the cerium(IV) oxidation of cyclohexanediol in the presence of oxygen.[8] In the present study, the deviation was observed both in air and under vacuum in the system of 2,3-butanediol as shown in Figure 2, in which no obvious effect of oxygen was observed. In the system of cyclohexanediol, a new absorption band in the region of wavelength from 300 to 400 nm appeared immediately after mixing of manganic pyrophosphate ion solution with cyclohexanediol solution as shown in Figure 3. This absorption might be attributed to a complex between cyclohexanediol and manganic pyrophosphate ion. This phenomenon was clearly observed only in this system. Aldehyde was oxidized at zero-order kinetics with respect to the concentration of manganic pyrophosphate ion. This result suggests that the oxidation proceeds via enolization, which will be discussed in a later section.

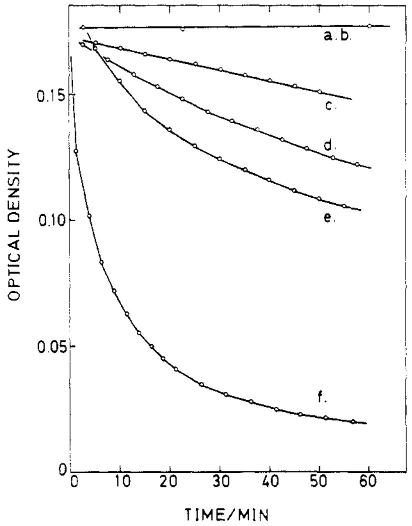


Figure 1. Concentration changes of manganic pyrophosphate ion reacting with model compounds I at 25 °C in sulfuric acid aqueous solution (pH 1.5). Initial concentration: metal ion, 2 mmol/L; substrates, 20 mmol/L. (a) Ethanol; (b) ethylene glycol; (c) propionaldehyde; (d) 2,3-dimethyl-2,3-butanediol; (e) cyclohexanediol; (f) 2,3-butanediol.

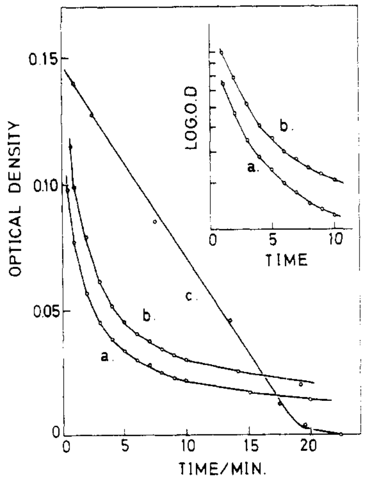
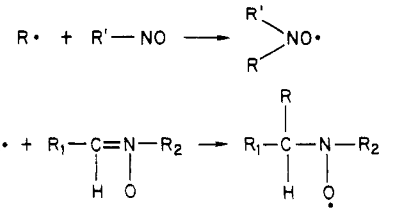


Figure 2. Concentration changes of manganic pyrophosphate ion reacting with 2,3-butanediol in air (a) and under vacuum (b) and propionaldehyde (c) at 25 °C in sulfuric acid aqueous solution (pH 0.5). Initial concentration: metal ion, 10 mmol/L; substrates, 100 mmol/L.

B. ESR Study of Oxidation by the Spin Trapping Technique. In order to reveal the oxidation mechanism, the short-lived free radicals in the oxidation were accumulated and studied by means of the ESR spin trapping technique. The short-lived free radicals were trapped by nitroso or nitrone compounds to generate nitroxyl radicals that were sufficiently stable to be measured by ESR.[20-22]



$$R\cdot + R'{-}NO \longrightarrow \overset{R'}{\underset{R}{>}}NO\cdot$$

$$R\cdot + R_1{-}\underset{H}{C}{=}\underset{O}{N}{-}R_2 \longrightarrow R_1{-}\overset{R}{\underset{H}{C}}{-}\underset{\dot{O}}{N}{-}R_2$$

The trapped radicals were determined according to the characteristic values of the hyperfine splitting constants of nitrogen and β-hydrogen.

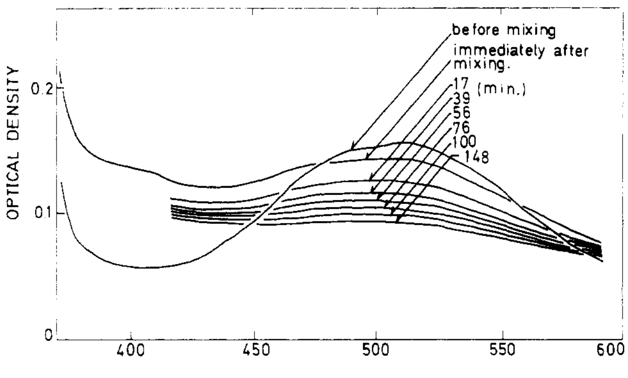


Figure 3. Change of the visible absorption spectra in the oxidation of cyclohexanediol with manganic pyrophosphate ion in sulfuric acid aqueous solution (pH 1.5).

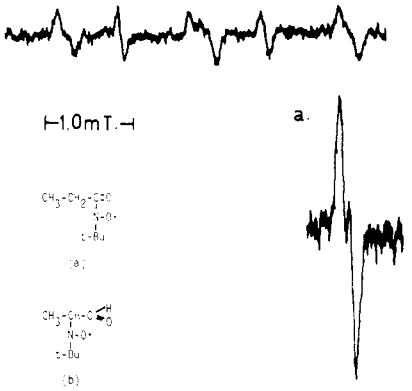


Figure 4. ESR spectra observed in the oxidation of propionaldehyde with manganic pyrophosphate ion. (a) Expanded signal in higher magnetic field.

(a) Oxidation of Aldehyde. Figure 4 shows the ESR spectrum observed in a neutral ethanol solution of propionaldehyde (10%) containing 2-methyl-2-nitrosopropane mixed with manganic pyrophosphate ion solution. This spectrum consists of two kinds of nitroxide radicals. One is a triplet with the hyperfine splitting of nitrogen (0.80 mT) and the other is a triplet of narrow doublets with the hyperfine splitting of nitrogen and hydrogen, 1.58 and 0.21 mT, respectively (1 mT = 10 G). According to previous reports,[23,24] the former triplet is assigned to an acyl radical spin adduct (a) and the latter to a secondary alkyl radical spin adduct (b).

For the purpose of comparison, the experiments have been carried out with other metal ion systems, e.g., cerium(IV), permanganic, chromic, vanadic, silver(I), and copper(II) ion systems. A very intense signal of the acyl radical spin adduct was observed in the cerium(IV) and permanganic ion systems. A weaker signal due to the same radical was observed in the chromic ion system, but not in the vanadic, silver(I), and copper(II) ion systems.

(b) Oxidation of Diols. In the oxidation of 2,3-butanediol, no radicals were observed when 2-methyl-2-nitrosopropane and α-phenyl-*N*-*tert*-butylnitrone were used as spin traps. In the oxidation of cyclohexanediol, the triplet signal with the coupling constant of nitrogen, 1.4 mT, was observed immediately after mixing of the manganic pyrophosphate ion solution, in addition to the signal of di-*tert*-butyl nitroxide radical generated from the decomposition of the spin trap itself as shown in Figure 5. Both signals decreased gradually and a new triplet signal of the characteristic acyl radical spin adduct appeared at about 30 min after mixing of solutions.

The same signal due to acyl radical spin adduct was observed in cerium ion oxidation of cyclohexanediol.

(c) Oxidation Mechanism of Aldehyde. In the measurement of oxidation rates in acidic aqueous solution,

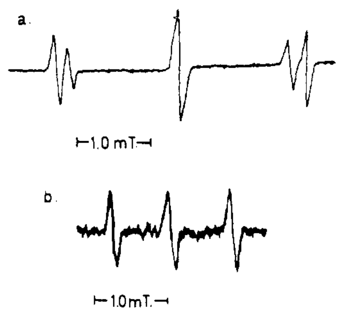


Figure 5. ESR spectra observed in the oxidation of cyclohexanediol with manganic pyrophosphate ion: (a) immediately after mixing of solutions of metal and cyclohexanediol; (b) about 30 min after mixing.

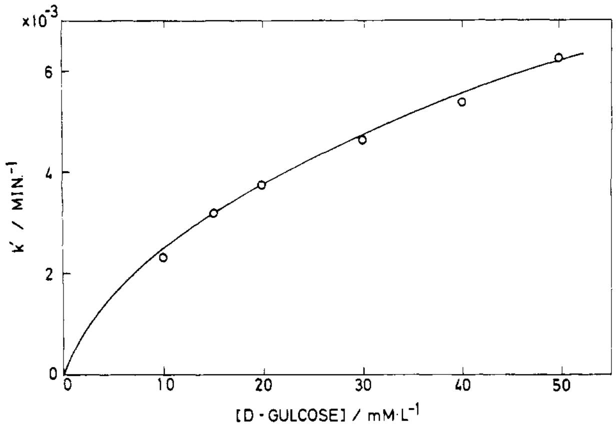
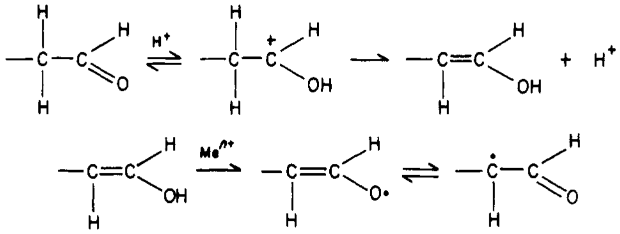


Figure 6. Effect of D-glucose concentration on the pseudo-first-order rate constant in the oxidation with manganic pyrophosphate ion at 25 °C in sulfuric acid aqueous solution (pH 1.5). Initial concentration of metal ion, 2 mmol/L.

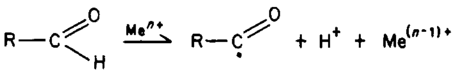
pH 1.5 and 0.5, zero-order kinetics was observed for propionaldehyde. This indicates an enolization mechanism for the oxidation with manganic pyrophosphate ion as shown below, in which enolization is the rate-determining step.[25]



Me^{n+} = manganic pyrophosphate ion

By means of the ESR spin trapping technique, the secondary alkyl radical was detected. The radical would be $-\dot{C}HCHO$ radical as an intermediate of the oxidation via enolization.

One of the radicals detected is the acyl radical which is generated by direct oxidation as shown as follows.



The observation of an intense signal due to acyl radical spin adduct in the cerium and permanganic ion systems indicates that these ions directly oxidize aldehyde groups very efficiently. Manganic pyrophosphate and chromic ions also oxidize aldehyde directly, but not so efficiently. No evidence of direct oxidation of aldehyde was obtained in the vanadic, silver, and copper ion systems. These ions prefer to oxidize aldehyde indirectly via enolization in strong acidic or alkaline media.[25]

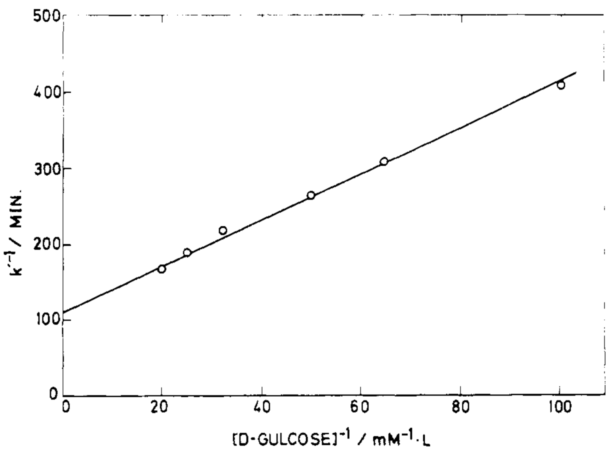
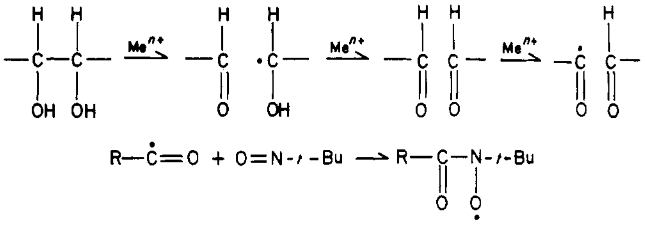


Figure 7. Reciprocal plot of kinetic data in the oxidation of D-glucose with manganic pyrophosphate ion at 25 °C in sulfuric acid aqueous solution (pH 1.5). Initial concentration of metal ion, 2 mmol/L.

(d) Oxidation Mechanism of Diols. High reactivity of 2,3-butanediol toward manganic pyrophosphate ion was observed in the measurement of oxidation rates by means of optical absorption spectra as mentioned in section 1A. However, no evidence of the presence of radicals has been observed by means of the ESR spin trapping technique. In addition, it has been reported in a previous study that acrylonitrile does not polymerize by the initiation of 2,3-butanediol oxidized with manganic pyrophosphate ion.[26] These results suggest that the oxidation of 2,3-butanediol is an ionic reaction and not a radical reaction.

Acyl radical spin adducts were detected in the oxidation of cyclohexanediol with spin trap present. This radical is generated by further oxidation of aldehyde as follows:



Hydroxyl radical might be generated in the first oxidation step. The failure to detect this radical may be due to the fact that the reaction of hydroxyl radical is much faster than the spin trapping reaction.

2. Model Compounds II. A. Character of Manganic Pyrophosphate Ion Oxidation. In order to know the character of manganic pyrophosphate ion oxidation of polysaccharides, the effects of substrate concentration and acidity on the oxidation rate were investigated by using D-glucose as a model compound.

Figures 6 and 7 show the effect of D-glucose concentration on the pseudo-first-order rate constants of oxidation. The plots of the rate constant vs. D-glucose concentration were definitely curved and the reciprocal plots were linear.

These results suggest that the oxidation proceeds via complex formation between D-glucose and manganic pyrophosphate ion. According to the theory of the coordination complex by Duke,[27] relationship 3 is derived. The conditions are that the complex is formed and disproportionated unimolecularly in the rate-determining step (eq 1), forming free radical R, which reacts further (eq 2). The complex formation equilibrium is rapidly established.

$$Me^{n+} + S \rightleftharpoons C \rightarrow R\cdot + Me^{(n-1)+} + H^+ \quad (1)$$

$$Me^{n+} + R\cdot \xrightarrow{\text{fast}} \text{product} + Me^{(n-1)+} + H^+ \quad (2)$$

$$1/k' = 1/k + 1/kK[S] \quad (3)$$

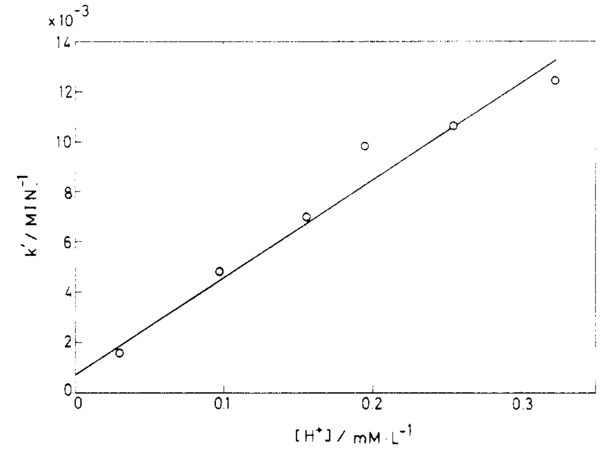


Figure 8. Dependence of the pseudo-first-order rate constants on acidity at 25 °C in manganic pyrophosphate ion oxidation of D-glucose. Initial concentration: metal ion, 2 mmol/L; substrate, 20 mmol/L.

k', k, K, and [S] are the pseudo-first-order rate constant, the rate constant of disproportionation, the equilibrium constant of complex formation, and the concentration of free substrate, respectively.

The linearity in Figure 7 shows that D-glucose and manganic pyrophosphate ion form the complex unimolecularly, as mentioned above. The equilibrium constant and the rate constant of disporportionation can be estimated as 36.5 M^{-1} and 9×10^{-3} s^{-1}, respectively, from the slope and the intercept in Figure 7 according to relationship 3. The equilibrium constant of complex formation obtained in this system is comparable with one obtained in the D-glucose–cerium ion system in 1 M perchloric acid at 20 °C (39.4 M^{-1}[9]) while the rate constant of disproportionation is considerably smaller than that in the cerium ion system (0.24 s^{-1}). Although the experimental conditions are not the same, it is suggested that the oxidation by manganic pyrophosphate ion proceeds via a stable complex, and the complex disproportionation is slow. The acidity affects mainly the rate of disproportionation of the complex.

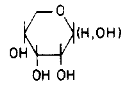
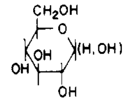
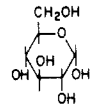
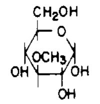
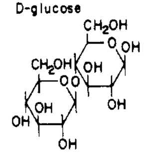
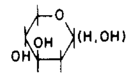
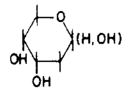
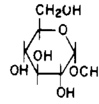
The variation of the pseudo-first-order reaction rates at various acidities is shown in Figure 8. The oxidation reaction proceeds considerably faster at higher acidity. It has been shown that both the structure and the oxidation potential of manganic pyrophosphate ion depend on the acidity.[28] The oxidation potential for reaction 4 has been estimated at 1.15 eV,[28] and this potential is reduced by a few tenths of a percent in the pH range 0–2. Generally,

$$Mn(H_2P_2O_7)_3^{3-} + 2H^+ + e^- \rightarrow Mn(H_2P_2O_7)_2^{2-} + H_4P_2O_7 \quad (4)$$

in the reciprocal description of relationship 3, $k' = kK[S]/(K[S] + 1)$, both k and K are dependent on acidity. The acidity dependence of pinacol oxidation with manganic pyrophosphate ion has been reported to be curved.[29] In the present system, the relationship of the pseudo-first-order rate of D-glucose oxidation to the acidity is almost linear. The disproportionation rate would be mainly affected by the change of acidity, as suggested from the comparison between the present system and the cerium ion system described above.

B. Oxidation Rates of Various Monosaccharides. Figure 9 shows the concentration changes of manganic pyrophosphate ion reacting with various monosaccharides and cellobiose. The reactions proceed in pseudo-first-order kinetics for most compounds except D-ribose. The reaction of D-ribose proceeds very rapidly in the initial period and then slows down. The order of decreasing reactivities was D-ribose, D-galactose, D-glucose, cellobiose, 2-deoxy-D-glucose, 2-deoxy-D-ribose, and α-methyl-D-glucoside as shown in Table II.

Table II
Pseudo-First-Order Rate Constants and Relative Reactivities of Various Monosaccharides and Cellobiose in Manganic Pyrophosphate Ion Oxidation at 25 °C in Aqueous Sulfuric Acid Solution (pH 1.5)[a]

	$k' \times 10^{-3}$, min^{-1}	rel react
 D-ribose	85	22.5
 D-galactose	4.9	1.35
 D-glucose	3.8	1.00
 3-O-methyl-D-glucose	2.3	0.61
 cellobiose	2.3	0.61
 2-deoxy-D-glucose	0.96	0.26
 2-deoxy-D-ribose	0.96	0.26
 α-methyl-D-glucoside	0.075	0.019

[a] Initial concentrations: manganic pyrophosphate ion, 2 mmol/L; substrates, 20 mmol/L.

Monosaccharides containing the C1–C2 glycol group showed apparently higher reactivities than others. D-Ribose showed an exceptionally high reactivity. This would be explained not only by the reactivity of the cis diols C1–C2 and C2–C3 but also by the existence of the large amount of the aldehyde form of D-ribose. About 10% D-ribose exists in aldehyde form in aqueous solution compared with 0.07% D-galactose and 0.012% D-glucose.[30]

The reactivity of monosaccharides in this system is reduced by the change of the glycol group conformation from cis to trans as shown in the comparison between D-galactose and D-glucose. The substitution of a methyl group on a hydroxyl also reduces the reactivity very effectively as shown in the comparison of data for D-glucose and α-methyl-D-glucoside.

No evidence has been observed that indicates any significant reactivity of hemiacetal groups as compared with glycol groups.

C. Comparison of the Cerium and Vanadic Ion Systems. For the purpose of comparison with the man-

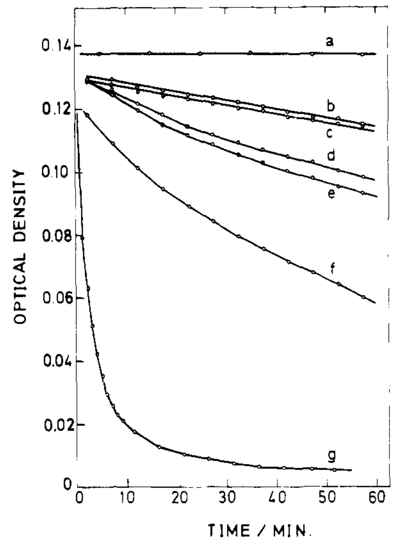


Figure 9. Concentration changes of manganic pyrophosphate ion reacting with various monosaccharides and cellobiose at 25 °C in sulfuric acid aqueous solution (pH 1.5): (a) α-methyl-D-glucoside; (b) 2-deoxy-D-ribose; (c) 2-deoxy-D-glucose; (d) cellobiose; (e) 3-*O*-methyl-D-glucose; (f) D-galactose; (g) D-ribose.

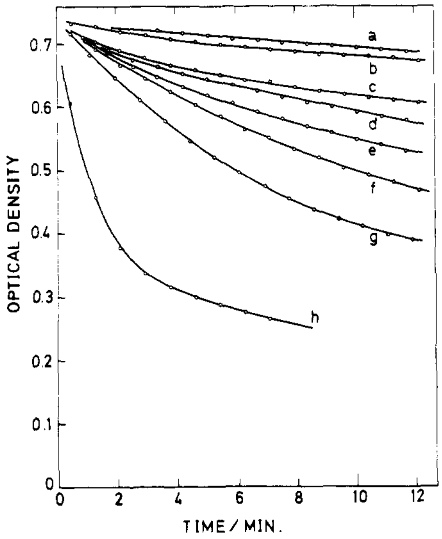


Figure 10. Concentration changes of cerium ion reacting with various monosaccharides and cellobiose at 25 °C in sulfuric acid aqueous solution (pH 1.5): (a) α-methyl-D-glucoside; (b) 2-deoxy-D-ribose; (c) 2-deoxy-D-glucose; (d) cellobiose; (e) D-glucose; (f) 3-*O*-methyl-D-glucose; (g) D-galactose; (h) D-ribose.

ganic pyrophosphate ion system, kinetic studies in cerium and vanadic ion systems were carried out as shown in Figures 10 and 11.

Cerium ion oxidation proceeds several times faster than manganic pyrophosphate ion oxidation. It is in first-order kinetics with respect to cerium ion concentration, except for D-ribose, which reacts very fast initially and then slows down as in the previous system. The oxidation potentials of cerium ion have been reported to be 1.44 eV in 1 N sulfuric acid and 1.6 eV in 1 N perchloric acid, respectively.[31] This means that the oxidation rate observed in our system with sulfuric acid is much slower than that in 1 M perchloric acid, reported previously.[9] The tendency of the relative reactivities of cerium ions toward various monosaccharides is similar to the manganic ion system as shown in Table III. However, the relative reactivities of 3-*O*-methyl-D-glucose and α-methyl-D-glucoside in the cerium ion system are much larger. This result suggests that the substitution of methyl group for hydroxyl hydrogen prevents the complex formation efficiently for the manganic pyrophosphate ion, itself a complex, but not so much for cerium ion. On the other hand, the instability of the ion/substrate complex induces a large disproportionation rate. Thus the pseudo-first-order rate of 3-*O*-methyl-D-glucose is larger than that of D-glucose in the cerium ion system.

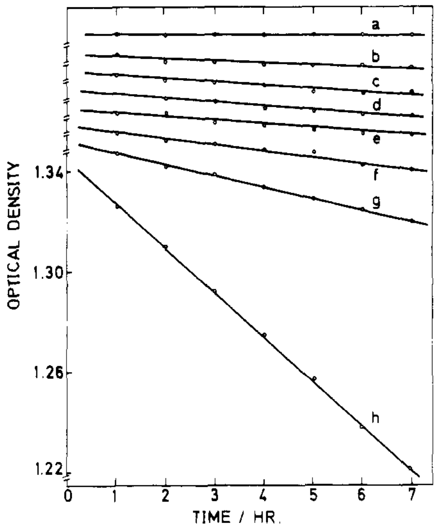


Figure 11. Concentration changes of vanadic ion reacting with various monosaccharides and cellobiose at 25 °C in sulfuric acid aqueous solution. Initial concentration: metal ion, 6 mmol/L; substrates, 60 mmol/L. (a) α-Methyl-D-glucoside; (b) 2-deoxy-D-ribose; (c) 2-deoxy-D-glucose; (d) cellobiose; (e) D-glucose; (f) 3-*O*-methyl-D-glucose; (g) D-galactose; (h) D-ribose.

Table III
Pseudo-First-Order Rate Constants and Relative Reactivities of Various Monosaccharides and Cellobiose at 25 °C in Aqueous Sulfuric Acid Solution (pH 1.5)

	$k'/[\mathrm{Ce(IV)}]$ $\times 10^{-2}$, min^{-1}	rel react			$k'/[\mathrm{V(V)}]$ $\times 10^{-5}$ min^{-1}
		Ce(IV)	Mn$^{\mathrm{III}}$(py)	V(V)	
D-ribose	14.7	14.1	22.5	6.8	9.9
D-galactose	2.4	2.3	1.3	1.6	2.4
D-glucose	1.04	1.0	1.0	1.0	1.46
3-*O*-methyl-D-glucose	1.6	1.5	0.61	0.59	0.86
cellobiose	0.79	0.76	0.61	0.61	0.88
2-deoxy-D-glucose	0.50	0.48	0.26	0.44	0.64
2-deoxy-D-ribose	0.32	0.30	0.26	0.30	0.44
α-methyl-D-glucoside	0.19	0.18	0.019	*b*	*b*

[a] Initial concentrations of the metal ions and substrates are 2 and 20 mmol/L in the manganic pyrophosphate and cerium ion systems and 6 and 60 mmol/L in the vanadic ion system, respectively. [b] Very small.

Vanadic ion oxidation was very slow since the oxidation strength of this ion is not large. The oxidation potential of this ion has been reported as 1.00 eV for the following reaction.[32]

$$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$$

The relative reactivities of monosaccharides with vanadic ion are very similar to those of the manganic pyrophosphate ion system, except for D-ribose and 2-deoxy-D-glucose.

D. Estimation of Relative Reactivities of Hydroxyl Groups. The differences in the rate constants between various monosaccharides provide a means for evaluating the relative reactivities of the C6 hydroxyl, cis-C1–C2 glycol, and cis-C3–C4 glycol groups in the manganic pyrophosphate ion system, assuming that differences in the physical and chemical properties of the monosaccharides,

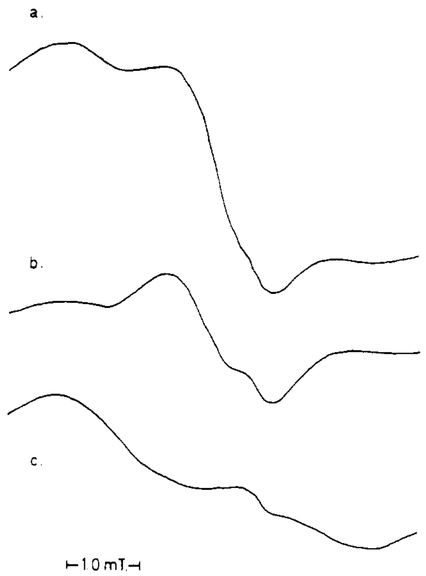


Figure 12. ESR spectra observed in the oxidation of dextrine (a) and cellulose (b) with manganic pyrophosphate ion at 77 K. (c) Signal due to $Mn^{II}(H_2O)_6$.

except D-ribose, do not affect the oxidation rate very much.

The same oxidation rates were observed for 2-deoxy-D-glucose and 2-deoxy-D-ribose. They show no effect of the presence of the C6 hydroxyl group in this system. This is in good agreement with the previous result described in section A that manganic pyrophosphate ion hardly reacts with ethanol at all. This is different from the cerium and vanadic ion systems.

The very low reactivity of the trans glycol group was shown in the result of α-methyl-D-glucoside.

The reactivity of cis-C3–C4 glycol group is estimated from the oxidation rate of 2-deoxy-D-glucose, in which only the C3–C4 glycol group is a reactive site. On the other hand, D-galactose contains cis-C1–C2 and cis-C3–C4 glycol groups and is oxidized 5 times faster than 2-deoxy-D-glucose. The reactivity of the cis-C1–C2 glycol group is roughly estimated to be 4 times larger than that of the cis-C3–C4 glycol group. The same ratio is also obtained from a comparison between D-glucose and 2-deoxy-D-glucose with the cis-C1–C2 and cis-C3–C4 glycol groups, respectively.

In summary it is shown that a cis-C1–C2 glycol group has a higher reactivity than other glycols. This implies the ease of oxidation of the reducing end group in polysaccharides based on measurement of oxidation rates of various monosaccharides.

E. ESR Spectra of Monosaccharide Radicals. By means of the spin trapping technique, acyl radical was detected as an intermediate in the oxidation of D-glucose and α-methyl-D-glucoside with manganic pyrophosphate and cerium ions as in the case of cyclohexanediol.

On the other hand, direct detection of intermediate radicals without spin traps was attempted in the oxidation of dextrine and cellulose, because the spin trapping technique is difficult to use in these systems due to the low solubility of dextrine and cellulose in alcohol and aqueous solution.

Figure 12 shows the ESR spectra obtained from dextrine and cellulose which were allowed to react with manganic pyrophosphate ion about 15 s at room temperature and then frozen by liquid nitrogen and measured at 77 K. Always a rather intense signal of $Mn^{2+}(H_2O)_6$ resulting from the reduction of manganic pyrophosphate ion was observed in the wide region of magnetic field. In the central region, a broad singlet signal was observed.

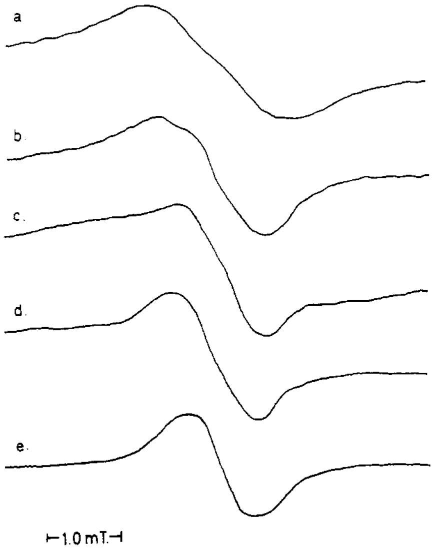


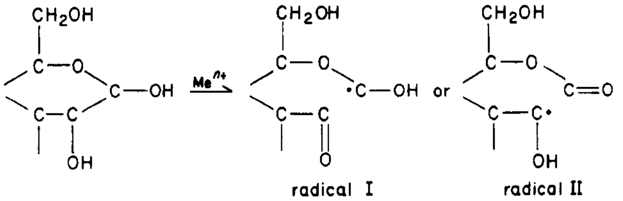
Figure 13. ESR spectra observed in the oxidation of dextrine (a), cellulose (b), 2-deoxy-D-ribose (c), 2-deoxy-D-glucose (d), and cyclohexanediol (e) at 77 K.

The same signals were observed more clearly in the cerium ion oxidation system as shown in Figure 13. The spectra obtained are similar to those reported previously.[7] The *g* values of these signals are determined as 2.004 based on the reference value 2.0036 for DPPH. In order to classify the character of these signals, ESR measurements under the same conditions have been carried out in the cerium ion oxidation of cyclohexanediol and various monosaccharides. All spectra were almost symmetrical singlet lines with a variation of the line width from 1.0 mT for cyclohexanediol to 2.0 mT for dextrine, and the *g* value was 2.004.

Introduction of air into the evacuated samples does not change the intensities and shapes of the ESR signals, which apparently agrees with the results described previously.[7] According to the *g* value, 2.004, and the observed stability in air, these signals seem to be due to peroxy radicals. The acyl radicals observed by the spin trapping technique have the *g* value 2.001[33,34] and should be unstable in air.

Higher reactivities were observed for monosaccharides containing the C1–C2 glycol group as mentioned before. However, no signals were observed in the oxidation of D-galactose, D-glucose, D-ribose, cellobiose, 3-*O*-methyl-D-glucose, and α-methyl-D-glucoside under the same experimental conditions both in air and under vacuum.

In the first step of oxidation of the reducing end group, there are two possibilities for the formation of radicals as follows.



If oxidation preferentially generates radical II, the same radical should be observed both from cyclohexanediol and from D-glucose, but if radical I is generated, the radical from D-glucose will be different from that of cyclohexanediol.

The observed radical may be radical II interacting with oxygen. From D-ribose, D-galactose, D-glucose, etc., radical I might be generated and immediately oxidized further before reaction with oxygen, because radical I is more electron-rich than radical II due to the neighboring oxygen on the radical site and prefers to be oxidized by metal ions. The same conclusion for the radical species generated in the oxidation of an end group in a polysaccharide was described by Taga et al.[10]

There are indications in earlier studies of grafting to cellulose using Ce(IV) ions that chain ends are the predominant reacting sites.[35,36] A mechanism for cellulose chain end grafting to form block copolymers has been proposed by Gaylord.[37]

Our previous studies[38] using Mn(III)-initiated grafting of cellulose fibers and cellulose ethers of low degree of substitution indicate, however, at least two grafted chains per cellulose molecule (viscosity averages are used).

Conclusion

Kinetic studies of oxidation with metal ions using D-glucose have shown that the oxidation proceeds via a stable complex and is almost first order with respect to proton concentration. Monosaccharides containing C1–C2 glycol groups were shown to have the highest reactivity in the oxidation of monosaccharides. Reactivity studies reveal that cis-C1–C2 glycol groups are oxidized 4 times faster than cis-C3–C4 glycol groups. Trans glycol groups and C6-hydroxyl groups have negligible reactivities. D-Glucose as a model compound for the reducing end group of polysaccharides was oxidized 50 times faster than α-methyl-D-glucoside as a model for the nonreducing end group. Considering the large amount of nonreducing diol groups along the polysaccharides chains, it is concluded that both C1–C2 and C2–C3 glycol groups are the predominant sites for initiation of graft copolymerization under the present experimental conditions. On the other hand, acyl radicals are detected in the metal ion oxidation of cyclohexanediol and monosaccharides by the ESR spin trapping technique. This radical is probably one of the predominant initiating sites of graft copolymerization.

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