Grafting and Initiation Reactions

Bengt Rånby

Department of Polymer Technology, Royal Institute of Technology,
SE-100 44 Stockholm, Sweden

SUMMARY: Grafting of acrylic monomers onto cellulose substrates in acid aqueous medium using complex of Mn^{3+} ions as a redox initiator is described. Assuming that the /Mn^{3+}/ ions react with aldehydes and vicinal diols, the rate of these reactions has been measured spectroscopically. (ESR and visible light) using model compounds. It is concluded that the /Mn^{3+}/ grafting onto cellulose is a radical reaction initiated mainly by oxidation of aldehydes at reducing end groups and C-C bond scission of vicinal diols at the end groups and along the cellulose chains. The initiation rates of the Ce^{4+}, /Mn^{3+}/ and VO_2^{2+} redox ions are related to their oxidation potential.

Introduction

Grafting of vinyl monomers onto substrates of polysaccharides has been extensively studied, mainly as basis for methods to modify the properties of cellulose (1,2) and starch (3,4). Our research work has largely dealt with grafting reactions using metal ion complexes in redox systems, especially initiation with Mn^{3+} pyrophosphate ions in acid aqueous solution. These Mn^{3+} complexes are stable in aqueous solutions of pH ≤ 2. They react with aliphatic 1,2 - diols, aliphatic aldehydes, and mono - and polysaccharides at room temperature. This paper describes

i. the application of the Mn^{3+} initiator to the grafting of cellulose substrates with acrylic monomers;
ii. a study of Mn^{3+} reactions with model compounds; and
iii. discusses the mechanism of the initiation reaction of grafting onto cellulose substrates.

A series of papers by Fanta et al. (5) of the grafting of vinyl monomers onto polysaccharides formed the background to our work. The most efficient grafting systems involve redox reactions with selective oxidation of the substrate. The pioneering invention of Ce^{4+} ions as initiator for grafting onto polysaccharides was made by Mino and Kaizerman (6). We have preferred redox systems with lower oxidation potential than Ce^{4+} and used Mn^{3+} and VO_2^+ to decrease side reactions. At room temperature the Mn^{3+} complex ions react at convenient rates for laboratory experiments.

Grafting onto cellulose and starch

Our research on grafting with Mn^{3+} complex ions started with starch as substrate (3). In a series of papers we established an efficient laboratory process to prepare the Mn^{3+} pyrophosphate ions in situ as potassium salt in acid aqueous solution. Stoichiometric amounts of mangano sulfate ($Mn SO_4$) and potassium permanganate ($K_2Mn_2O_7$) in aqueous solutions at pH 1,5 - 2.0 with potassium pyrophosphate ($K_4P_2O_7$) added are mixed at room temperature. The resulting reaction gives the stable mangani salt complex (Equ.1):

$$4\ Mn^{2+} + Mn^{7+\ \text{pyrophosphate}}\ 5\ /\ Mn^{3+}\ / \qquad \text{(Equ.1)}$$

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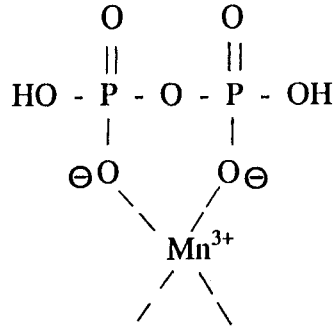
Without complexation, the mangani ions disproportionate to mangano Mn^{2+} and Mn^{4+} ions of which the latter precipitate as manganese dioxide (MnO_2). The pyrophosphate ions in acid solution form a stable complex $(Mn^{3+})_2$ $(H_2P_2O_7^{2-})_3$ with the schematic bonding (Equ. 2):

STABLE COMPLEX

$(Mn^{3+})_2 (H_2P_2O_7^{2-})_3$



(Equ.2)

The grafting of acrylonitrile (H_2C = CH - CN) onto starch was further studied (7). Hydrolysis of the nitrile groups with dilute alkali (aq. NaOH) produced amide and carboxyl groups on the grafted acrylic chains. The resulting grafted starch absorbed large amounts of water as a "super slurper". Other superabsorbent polymers were prepared by grafting cellulose fibers (8) and water-soluble methyl cellulose (9) with acrylonitrile and hydrolysis of the grafted cellulose with alkali.

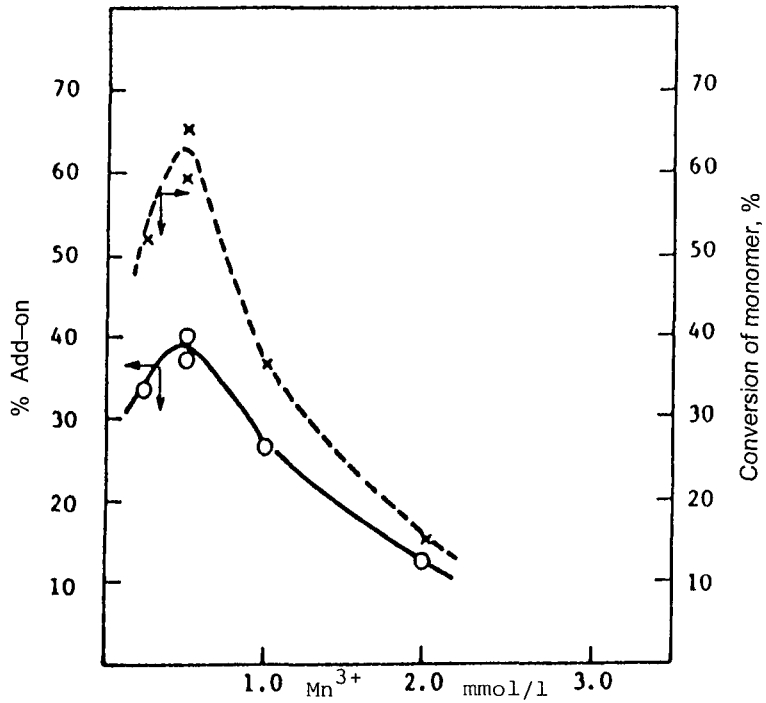


Figure 1. Add-on (—O—) and total conversion of monomer to polymer (---X---) in grafting of acrylonitrile onto chemical cotton. Reaction conditions: concentration of cotton, 20.0 gl^{-1}; acrylonitrile, 20.0 gl^{-1}. [$Na_4P_2O_7$], 2.0 mM/mM Mn^{3+}; [H_2SO_4], 80 mMl^{-1}. Reaction time, 3 h; temp, 30°C. Monomer was added to slurry of cotton in acidified water and initiator.

Relevant for the understanding of the mechanism of initiation are grafting experiments with chemical cotton, a pure form of native cellulose (10). The initiator is an aqueous H_2SO_4 solution of pH 1.5 - 2.0, with Mn^{3+} concentration 1 - 3 mMol/l, pyrophosphate/M^{3+} ratio 2 - 3, acrylic monomer 10 - 15 g/l and cellulose substrate 10 - 30 g/l. The fibers are reacted at 30°C for 1 to 3 hours. The experiments show an optimal grafting of acrylonitrile at about 0.5 mMol Mn^{3+} (Fig. 1) measured as conversion of monomer to polymer (%) and "add-on" (%) which is the amount of grafted polymer divided by the total weight of grafted copolymer. The grafting has an optimum at a ratio of acrylonitrile/substrate of about 2 (Fig. 2). The grafting ratio (= the ratio of grafted polymer/cellulose) for acrylonitrile (AN), methyl (methacrylate) (MMA) and acrylamide (AAm) has also a maximum at a ratio of monomer/cellulose of about 2 (Fig. 3). The grafting efficiency, defined as the ratio of grafted polymer/total polymer formed is approaching 100% for AN and shows lower values for MMA and AAm (Fig. 4). The low values for MMA are due to chain transfer and for AAm due to side reaction of Mn^{3+} with the amide groups.

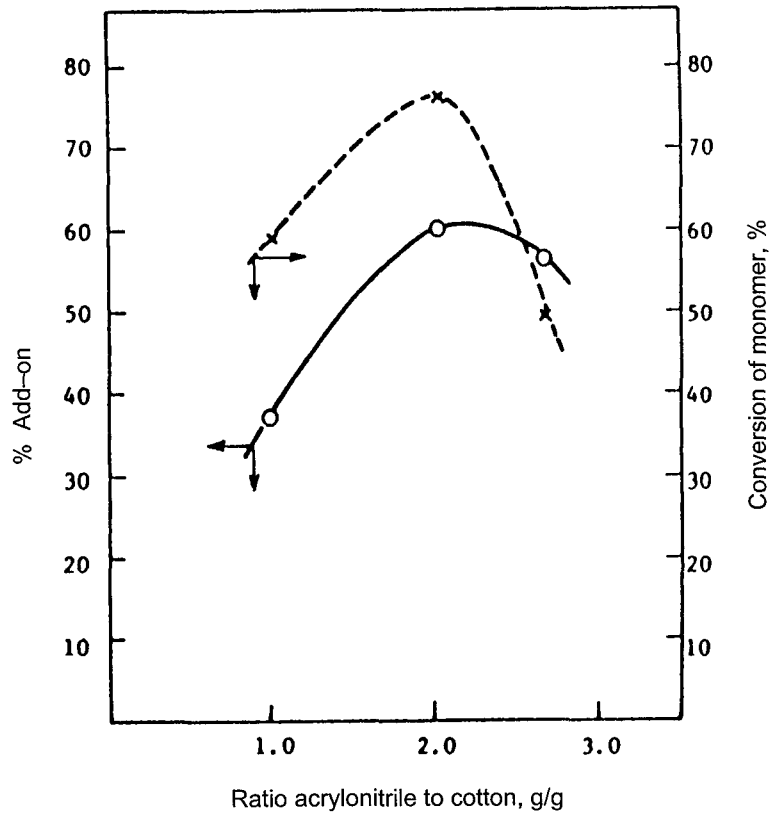


Figure 2. Add-on (—O—) and total conversion of monomer to polymer (---X---) in grafting of acrylonitrile onto cotton. Reaction conditions; concentration of cotton in reaction solution, 20.0 gl^{-1}; [Mn^{3+}], 0.5 mMl^{-1}; $Na_4P_2O_7$, 1.3 Ml^{-1}; H_2SO_4], 80 mMl^{-1}. Reaction time, 3 h; temp, 30°C.

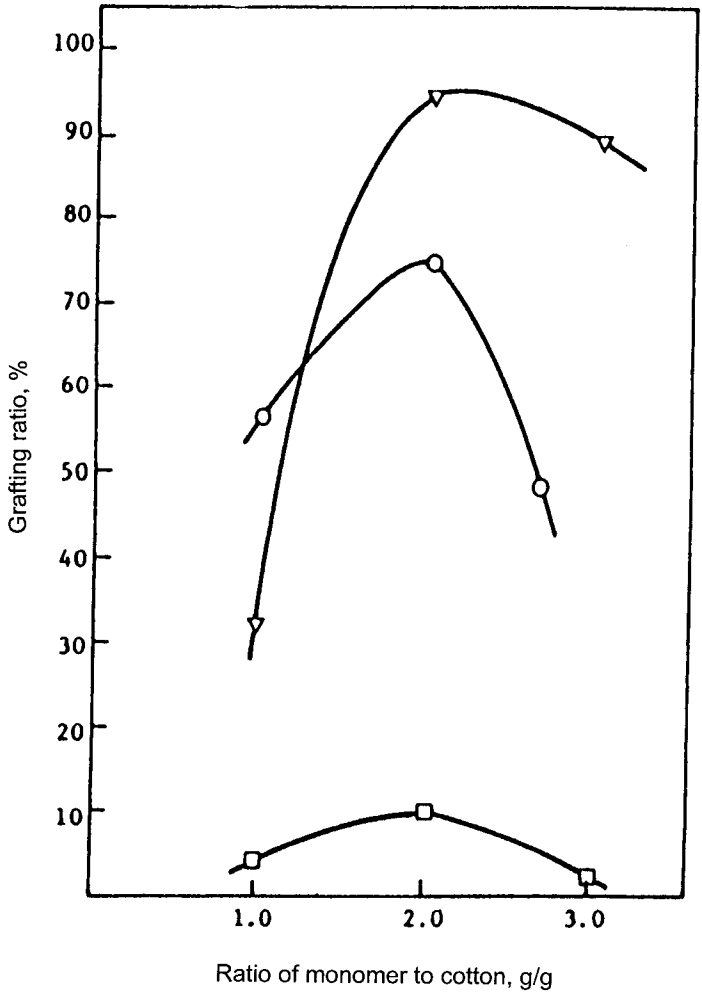


Figure 3. Grafting ratio in cotton-polyacrylonitrile (O),cotton-poly(methyl methacrylate) (▽), and cotton-polyacrylamide (□) graft copolymers.

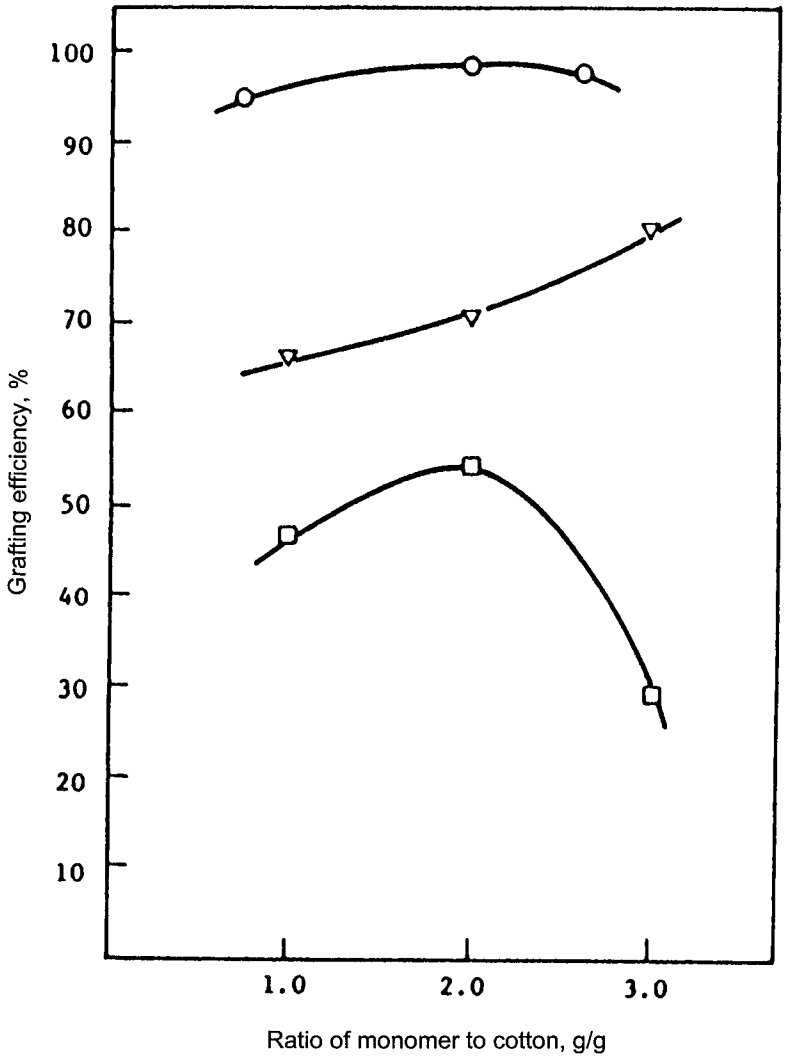
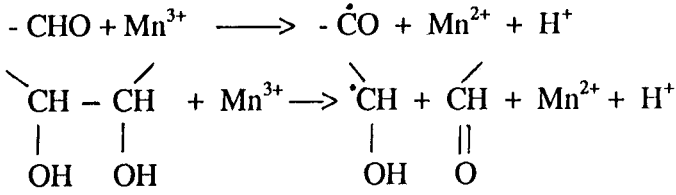


Figure 4. Grafting efficiency in graft copolymerization of cotton with acrylonitrile (O), methyl methacrylate (∇), and acrylamide (□).

The Mn^{3+} initiator is the most efficient initiator known for grafting of acrylonitrile to cellulose. The mechanism of initiation is, therefore, of great interest. Experiments with different polysaccharides indicate that initiation occurs both at endgroups (which gives block copolymers) and along the polysaccharide chains (Table 1). The amylopectin fraction of the starch is branched and water soluble. With a molecular mass of about 10^6 Dalton, 7 endgroups per molecule, and 15 grafted chains of polyacrylonitrile (of molecular mass 70.000 Dalton) per starch molecule, it is concluded that the number of grafted PAN chains per starch molecule is twice the number of endgroups. For cotton and wood cellulose, the data are less conclusive. These substrates consist of partly crystalline microfibrils which are accessible to initiation reactions only at the surface. Assuming that only the reducing endgroup is reacting, grafted wood and cotton cellulose have 2 and 4 times as many grafted chains as endgroups. The hydrocellulose, which is a bleached wood cellulose hydrolyzed in boiling dilute sulfuric acid (0.1 N) to remove amorphous cellulose, the accessibility to grafting is very low with only one grafted chain for 10 cellulose molecules. Apparently the high degree of crystallinity of the hydrocellulose substrate makes also many endgroups inaccessible to initiation of grafting. The available data for grafting of polysaccharides with Mn^{3+} as initiator indicate that the grafting reaction is initiated by oxidation of aldehyde endgroups to acyl radicals and of 1.2 - diol groups to alkoxy radicals, i.e. breaking the C-C bonds (Equ. 3):



(Equ.3)

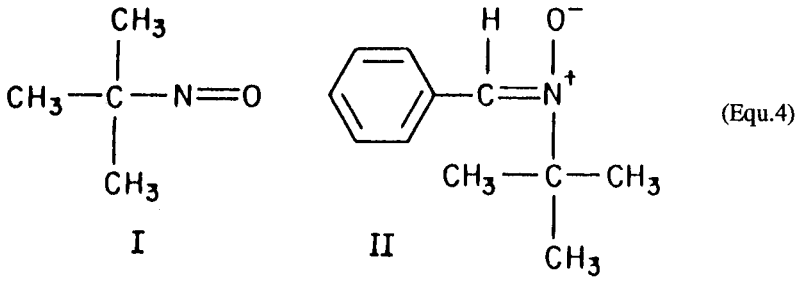
Tab.1. Number of endgroups and number of grafted polyacrylonitrile (PAN) chains per polysaccharide molecule for starch and cellulose of given molecular mass and chain length (DP). The grafted PAN chains have average molecular mass of 70.000 to 100.000.

Substrate	Mol.Mass (DP)	No of Endgroups per Molecule	No of Grafted Chains per Molecule
Starch	10^6 (∿ 6000)	5-9 7	15
Cotton cellulose	240.000 (∿1500)	1+(1)	3.5
Wood cellulose	120.000 (∿750)	1+ (1)	1.7
Hydro-cellulose	32.000 (∿ 200)	1+ (1)	0.1

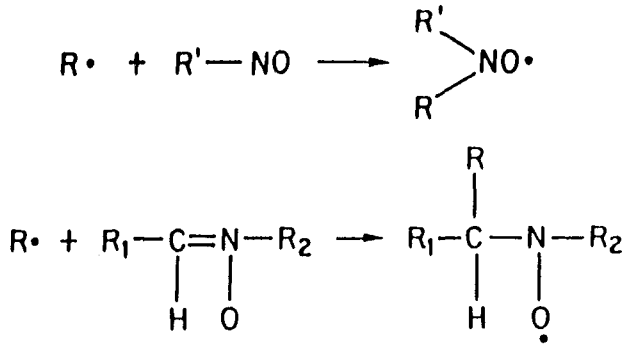
The initiation of grafting with Mn^{3+} ions studied with model compounds

The mechanism of graft copolymerization is assumed to involve aldehyde groups from ringo-pened reducing endgroups and vicinal diols along the polysaccharide chains. Three types of model compounds were studied: propionaldehyde, 2,3-butanediol and vicinal cyclohexanediol, and several monosaccharides. The model compounds were reacted with Mn^{3+} pyrophosphate ions prepared as previously described (11).

The radicals formed were trapped with 2-nitrosopropane (I) and α-phenyl - N - tertbutylnitrone (II), (Equ.4) and analyzed by ESR spectroscopy in an X-band Bruker ER-420 spectrometer. The trapped radicals are shown in Equ.5.



I II (Equ.4)



(Equ.5)

When propionaldehyde was mixed with the manganic ion solution containing spin trap I the ESR spectrum of Fig. 5 was obtained. It contains two radicals: one acyl radical generated by direct oxidation of the aldehyde group as shown in Equ.6, and one secondary alkyl radical formed as an intermediate of the oxidation via enolization (Equ.7).

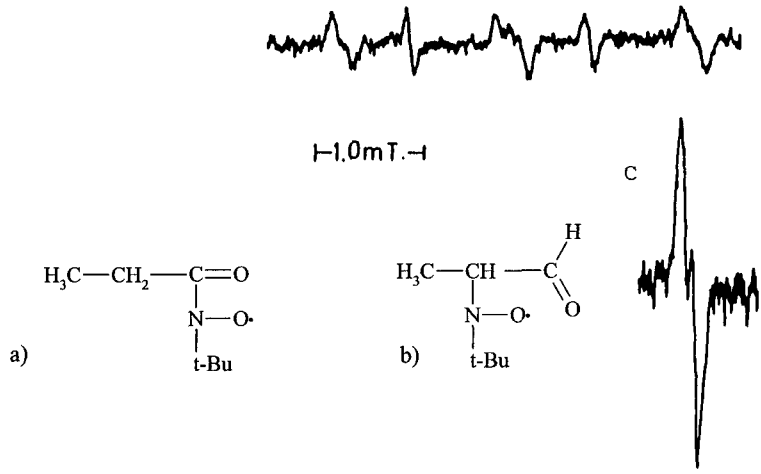
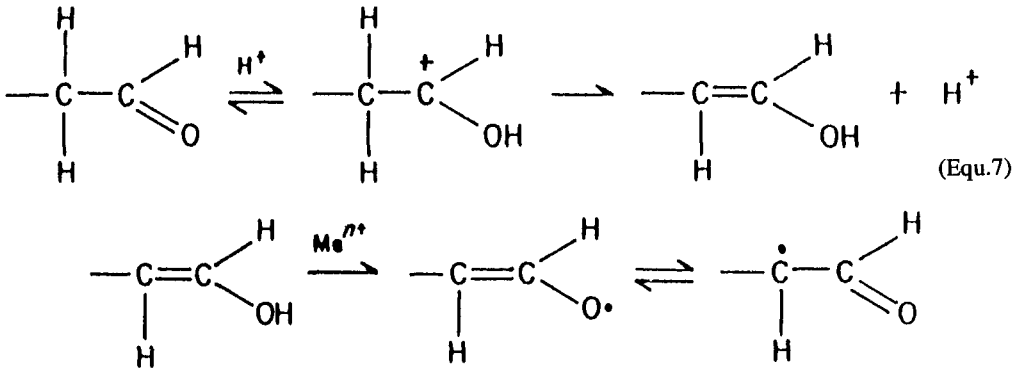


Figure 5. ESR spectra of two radicals (a) and (b) observed in the oxidation of propionaldehyde with manganic pyrophosphate ion. C. Expanded signal in higher magnetic field showing the doublet.

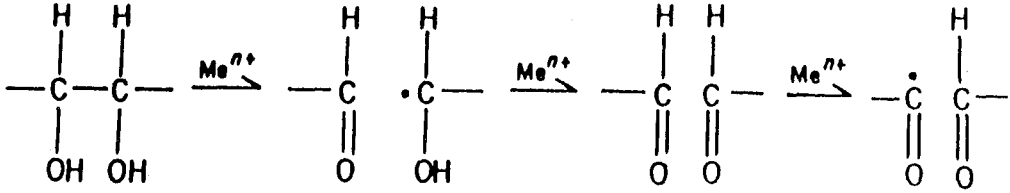
(Equ.6)

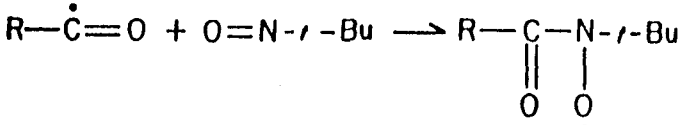


(Equ.7)

Me^{n+} = manganic pyrophosphate ion

The 2,3-butanediol reacts with manganic ions but gives no trapped radical. The reaction is probably ionic. The vicinal cyclohexanediol reacts rapidly with the manganic ions. Immediately after mixing, the ESR spectrum (a) in Fig. 6 was recorded. It contains two components: a triplet with the coupling constant 1.4 mT (due to the alkoxy radical) and another weaker triplet due to the di-*tert*-butyl nitroxide radical generated from the decomposition of the spintrap itself. Both signals decreased gradually and a new triplet (b) appeared after 30 min which is characteristic of the acyl radical spin adduct. The reactions are shown in Equ.8.





(Equ.8)

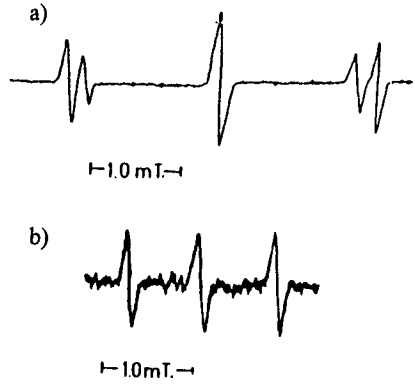


Figure 6. ESR spectra observed in the oxidation of cyclohexanediol with manganic pyrophosphate ion: (a) immediately after mixing of solutions of metal ion and cyclohexanediol solutions; (b) about 30 min after mixing.

The reaction rate of manganic ions with cyclohexanediol was studied in the visible spectrum of the manganic ion complex (Fig. 7). Immediately after mixing the spectrum shows a broad maximum at about 400 nm which is interpreted as due to a complex formation of Mn^{3+} ions and diol groups as indicated in Equ 9. The broad maximum for manganic ion complex at about 500 nm gradually decreases and is used to measure the rate of oxidation of the diol.

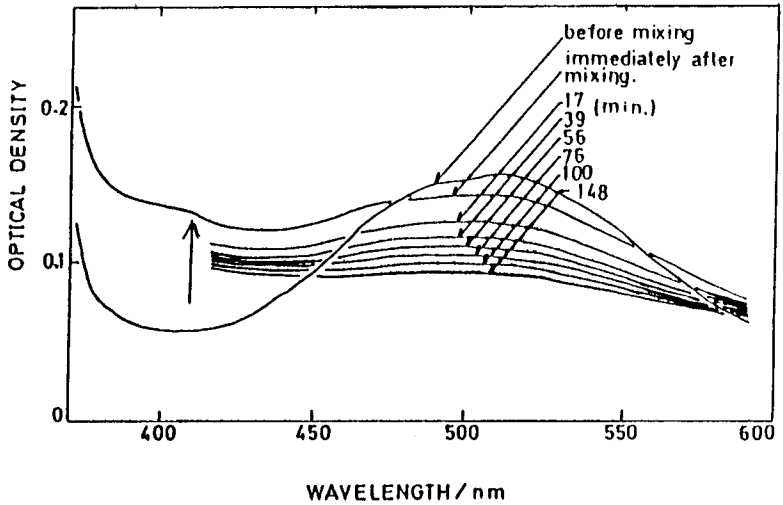
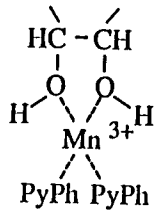


Figure 7. Change of the visible absorption spectra in the oxidation of cyclohexanediol with manganic pyrophosphate ion in sulfuric acid aqueous solution of pH 1.5.

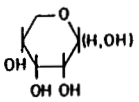
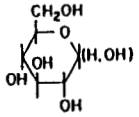
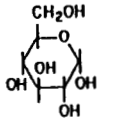
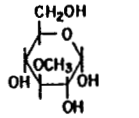
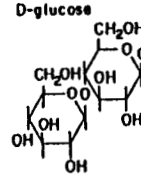
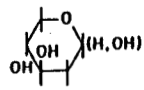
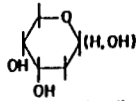
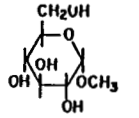


(Equ. 9)

The character of the manganic pyrophosphate ion oxidation of polysaccharides was studied by using D-glucose as model compound. The reaction rate (k) of the oxidation vs D-glucose concentration (c) is a curved line. The reciprocal plot (1/k) vs 1/c is a straight line. It is suggested that the oxidation reaction proceeds via complex formation between D-glucose and manganic pyrophosphate ion, analogous with equ. 9 for vicinal cyclohexane diol. The reaction rate increases linearly with the acidity. At the pH and temperature chosen, 1.5 and 25°C respectively, the oxidation rate is pseudo-first-order as measured spectroscopically for manganic pyrophosphate ion concentration according to Duke´s theory (12). The broad absorption maximum at 400 nm observed for cyclohexane - 1,2-diol/manganic ion could not be recorded for the monosaccharides, probably because more than one complex is formed.

Rate constants for the pseudo-first-order oxidation of various monosaccharides and cellobiose with manganic pyrophosphate ions at 25°C in aqueous sulfuric acid solution (pH 1.5) are given in Table 2, which also lists relative reactivities, referred to D-glucose as 1.00. The measured reaction rates are reasonably constant except for D-ribose which has the highest initiated rate. The reaction rate slows down later (Fig. 8). This is interpreted as due to reactions of C1-C2 and C2-C3 glycol and also oxidation of the aldehyde form of D-ribose which exists in large amounts in D-ribose (about 10%) compared with very small amounts in other monosaccharides, e.g. 0.07% for D-galaetose and 0.12% for D-glucose (13). Monosaccharides and cellobiose with C1-C2 glycol groups react faster than those without this glycol group. The reduction of the C2-hydroxyl and the substitution of this hydroxyl with a methyl group decreases the rate of oxidation very effectively, e.g. shown by data for D-glucose and α-methyl-D-glucoside. Hemiactal groups show no significant reactivity.

Tab.2. 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]

substrate	k' x 10^{-3}, min^{-1}	rel.reactivity
 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.

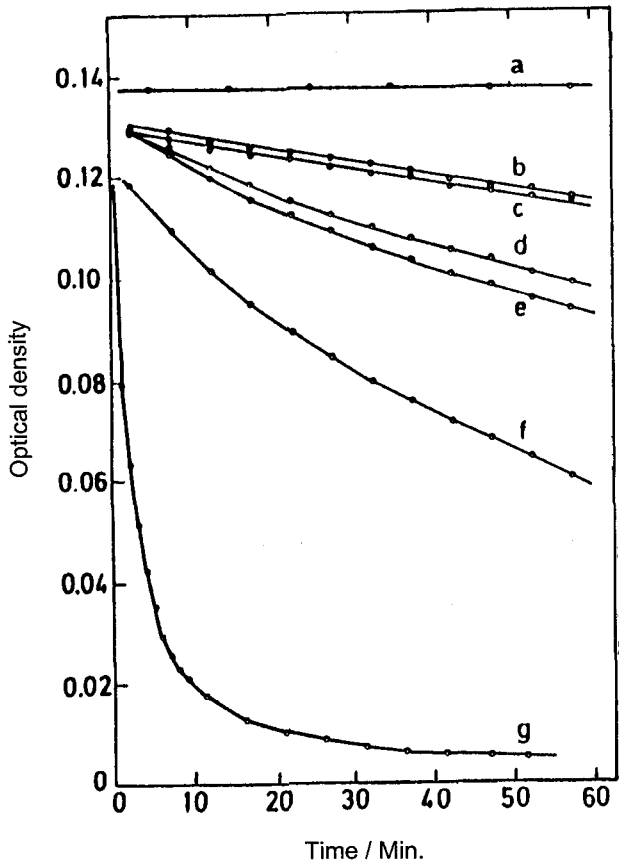
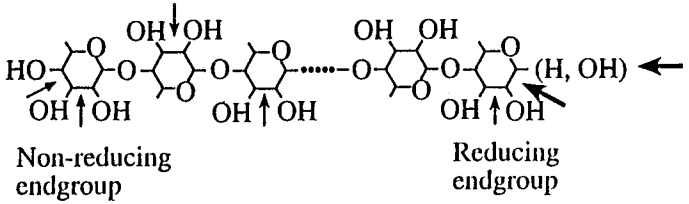


Figure 8. Concentration changes of manganic pyrophosphate ion reacting with various monosaccharides and cellobiose at 25°C in sulfuric acid aqueous solution (pH 1.5): (a) α-methyl-D-glucoside, (b) 2-deoxy-D-ribose, (c) 2-deoxy-D-glucose, (d) cellobiose, (e) 2-0-methyl-D-glucose, (f) D-galactose, and (g) D-ribose.

C6 hydroxyl groups do not react significantly with the manganic pyrophosphate ions: the same oxidation rate was observed for 2-deoxy-D-glucose with and 2-deoxy-D-ribose without C6 group. This agrees with our earlier finding that ethanol hardly reacts with the manganic pyrophosphate ion. The very low reactivity of the trans glycol group is shown in the result for α-methyl-D-glucoside where all diols are trans. The reactivity of the cis-C1-C2 glycol groups is estimated to be 4 times larger than the cis-C3-C4 glucol group. The reactivity of cis-C3-C4 glycol groups is estimated from the oxidation rate of 2-deoxy-D-glucose in which only the C3-C4 glycol group is a reactive site. D-galactose contains cis-C1-C2 and trans C3-C4 glycol groups and is oxidized 5 times faster than 2-deoxy-D-glucose. It is concluded that a cis-C1-C2 glycol group has higher reactivity than other glycols by a factor of approximatively 5. This implies that the reducing

endgroup in a polysaccharide like cellulose is the most reactive site for oxidation with manganic pyrophosphate ions. Using α-methyl-D-glucose as model for non-reducing endgroups of cellulose, it is concluded that reducing endgroups (with D-glucose as model) are 50 times more reactive than the non-reducing endgroups.

There are indications in earlier studies of grafting with Ce^{4+} ions as initiator that chain ends are the predominant reacting sites (14). A mechanism for chain and grafting to form block copolymers has also been proposed by Gaylord (15). In our previous studies using manganic pyrophosphate ions as initiator for grafting onto cellulose and cellulose ethers of low degree of substitution indicate, however, at least two grafted chains per cellulose molecule (viscosity averages are used, cf Table 1). (9). The initiation reactions for grafting onto a cellulose chains are indicated in Equ. 10.



(Equ. 10)

Comparison of redox ion oxidation of model compounds

In a series of experiments the rate of oxidation of two model compounds, D-glucose and α-deoxy-D-ribose, with three different redox ions were compared (11). The schematic reactions are analogous for Ce^{4+}, Mn^{3+} and VO_2^{2+} ions (Equ. 11). The Ce^{4+} ions give the highest oxidation rate and VO_2^{2+} ions the lowest of the three (Table 3). The decreasing oxidation rates for Ce^{4+}, Mn^{3+} and VO_2^{2+} are directly related to the decreasing oxidation potential in aqueous acid solution for the three ions as reported in the literature (16). The VO_2^{2+} ions do not oxidize aldehyde groups directly to acyl radicals. Only the enol form is oxidized.

Oxidation Reactions of Redox Ions (Equ. 11)

CERIC $Ce^{4+} + RH$ ------ $Ce^{3+} + R^{\cdot} + H^{+}$

MANGANIC $Mn^{3+} + RH$ ------ $Mn^{3+} + R^{\cdot} + H^{+}$

VANADIC $VO_2^{2+} + RH$ ------- $VO_2^{+} + R^{\cdot} + H^{+}$

Tab.3. Oxidation rates of three redox ions for D-glucose and 2-deoxy - D-ribose in acid aqueous solution.

Ion	Oxidation Potential eV	Oxidation Rates D-Glucose	k/Me^{n+} min^{-1} 2-Deoxy - D-ribose
Ce^{4+}	1.44-1.60	$1\text{-}04 \times 10^{-2}$	0.32×10^{-2}
$(Mn^{3+})_{compl.}$	1.3	3.8×10^{-3}	0.96×10^{-3}
VO_2^{2+}	1.0	1.46×10^{-5}	0.44×10^{-5}

Conclusions

1. Manganic pyrophosphate complex ions /Mn^{3+}/ are stable in aqueous acid solution of pH 1.5-2.0 and oxidize alifatic aldehyde groups and 1.2 diol or glycol groups to organic radicals. Applied to polysaccharides, the Mn^{3+} ion complex is an efficient initiator for grafting acrylic monomers onto starch and cellulose, e.g. giving high conversion of monomer to polymer (80-85%) and high grafting efficiency (90-95% of the polymer formed is grafted).

2. The mechanism of initiation of the grafting reaction has been studied using model compounds: propioaldehyde, 2,3-butanediol, cyclohexane-1.2-diol and various monosaccharides and cellobiose, spin-trapping of the radicals formed and ESR spectroscopy for analysis of the trapped radicals.

3. D-Ribose with 3 OH groups (on C_2, C_3 and C_4) all in cis-glycol structure and 10% of the pyranose in aldehyde form shows the fastest reaction rate with Mn^{3+} ions. D-glucose is about 50 times more reactive than α-methyl-D-glucose and 4 times more reactive to Mn^{3+} ions than 2-deoxy-D-glucose. The C1 aldehydes and the C1-C2 glycol groups are the most reactive sites for oxidation with Mn^{3+} ions.

4. From the model experiments it is concluded that the reducing endgroups of a cellulose chain react about 50 times faster with Mn^{3+} ions than the C_2-C_3 glycol groups along the chains and at the non-reducing endgroups. This indicates that both block and graft copolymers are formed when the Mn^{3+} complex ion is used as initiator for grafting onto long cellulose chains.

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