Role of ceric ion in the heterogeneous graft polymerization of olefins on cellulose

Ismael Casinos

Departamento de Ciencia y Tecnología de Polímeros, Facultad de Química,
Universidad del País Vasco, PO Box 1072, 20080 San Sebastián, Spain

The heterogeneous graft copolymerization of vinyl monomers on cellulose initiated by aqueous ceric ion is studied theoretically. Mechanistic aspects are considered. Some suggestions are made about: polymerization schemes; concerted disproportionation of cellulose–ceric ion complexes; oxidation sites in cellulose or cellulose sites of grafting (block and graft copolymer formation); reactivity of olefins towards cellulose radicals; reactivity of olefins in homopolymerization initiated by ceric ion; reactivity of radical chains in termination by ceric ion; estimation of reaction parameters (rate of graft copolymerization, rate of homopolymerization, rate of ceric ion consumption, grafting efficiency, molecular weight, number of polymer chains, grafting frequency and initiation efficiency) in terms of the reaction variables; and a polymerization scheme for electron-rich monomers. The effect of reaction variables on reaction parameters can be accounted for by equations developed in this paper. Consequently, some characteristics of the copolymers and copolymerization reactions can be understood. A way of demonstrating transitions between competitive reactions is developed.

(Keywords: graft polymerization; heterogeneous polymerization; ceric ion; cellulose; olefins; modelling)

INTRODUCTION

Ceric ion is a useful oxidant for a variety of organic substrates[1,2]. Grafting is a useful method for modifying some of the properties of natural polymers. During the last few decades much work has been carried out on the graft copolymerization of vinyl monomers on cellulosic substrates, and the work has been comprehensively reviewed[3–8]. Among the most interesting of the grafting methods is that of the formation of free radicals on the cellulose backbone by oxidation with ceric ion in an aqueous medium.

The precise kinetics and mechanism governing the grafting of vinyl monomers on cellulose are difficult to determine since the reaction is heterogeneous. Therefore, a great deal of work has been carried out using alcohols, diols and other soluble hydroxyl compounds as model compounds, with and without the presence of polymerizable monomers[9–15]. Consequently, a reaction scheme and an expression for the polymerization rate have been proposed for the radical polymerization of vinyl monomers initiated by ceric ion in the presence of a hydroxyl compound[10]. Complex formation between ceric ion and hydroxyl compound[12,15–18] and complex disproportionation as a rate-determining step[11,16,19] have been shown. It was proposed that mutual termination as well as termination by ceric ion occurred in the polymerization scheme. Ceric ion, with a coordination number of 6, forms complexes involving only one molecule of alcohol or diol, the rest of the ligands being hydroxide ion, nitrate ion and water[16]. Where the 1,2-diol structure is present, C–C bond cleavage occurs[9,11]. Reaction schemes similar to that for model compounds have been proposed for graft polymerization
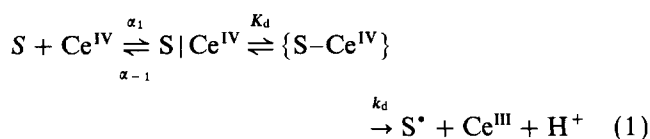
on cellulose[20–23]. It has been suggested, partly on the basis of studies on model compounds, that grafting on cellulose takes place predominantly at the reducing hemiacetal end-group and at the C2–C3 glycol in the anhydroglucose units as opposed to the C6 hydroxyl groups[11–15,20,24,25].
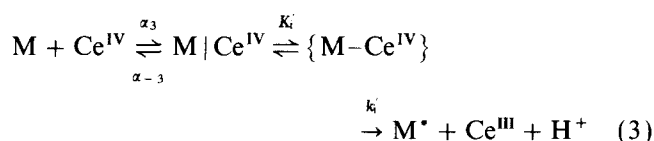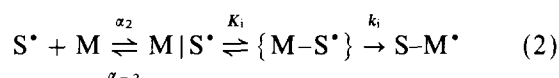
The graft polymerization of vinyl monomers on cellulose initiated by aqueous ceric ion is examined in this paper and its usual heterogeneous nature is taken into account.
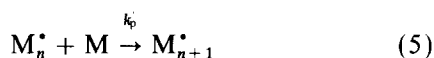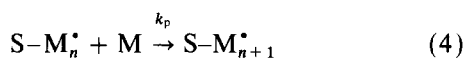
POLYMERIZATION SCHEME

The oxidizing behaviour of ceric ion on hydroxyl compounds has shown some mechanistic differences depending on the acid medium used[3]. The chemical system studied in this paper is made up of soluble ceric ammonium nitrate (CAN), insoluble cellulose and immiscible vinyl monomer in aqueous nitric acid. It is also assumed that the polymer formed is soluble in its monomer. This is a complex system and other cases would be simpler. The derivations shown later on can be adapted to simpler systems by means of facile simplifications. On the basis of previous suggestions[14,20,23], a more comprehensive polymerization scheme is proposed.

Initiation

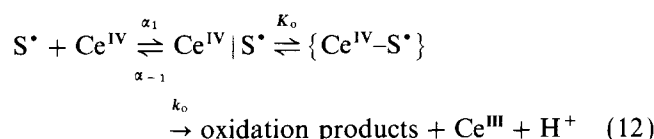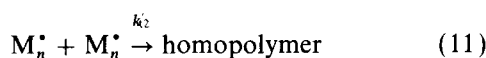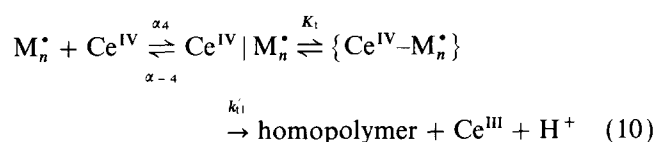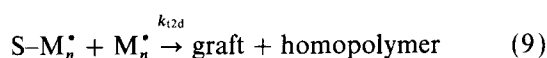$$S + Ce^{IV} \underset{\alpha_{-1}}{\overset{\alpha_1}{\rightleftharpoons}} S \,|\, Ce^{IV} \overset{K_d}{\rightleftharpoons} \{S\text{–}Ce^{IV}\}$$

$$\overset{k_d}{\rightarrow} S^{\bullet} + Ce^{III} + H^{+} \quad (1)$$

$$S^{\bullet} + M \underset{\alpha_{-2}}{\overset{\alpha_2}{\rightleftharpoons}} M \,|\, S^{\bullet} \overset{K_i}{\rightleftharpoons} \{M\text{-}S^{\bullet}\} \overset{k_i}{\rightarrow} S\text{-}M^{\bullet} \qquad (2)$$

$$M + Ce^{IV} \underset{\alpha_{-3}}{\overset{\alpha_3}{\rightleftharpoons}} M \,|\, Ce^{IV} \overset{K_i}{\rightleftharpoons} \{M\text{-}Ce^{IV}\}$$

$$\rightarrow M^{\bullet} + Ce^{III} + H^+ \qquad (3)$$

Propagation

$$S\text{-}M_n^{\bullet} + M \overset{k_p}{\rightarrow} S\text{-}M_{n+1}^{\bullet} \qquad (4)$$

$$M_n^{\bullet} + M \overset{k_p'}{\rightarrow} M_{n+1}^{\bullet} \qquad (5)$$

Termination

$$S\text{-}M_n^{\bullet} + Ce^{IV} \underset{\alpha_{-4}}{\overset{\alpha_4}{\rightleftharpoons}} Ce^{IV} \,|\, S\text{-}M_n^{\bullet} \overset{K_t}{\rightleftharpoons} \{Ce^{IV}\text{-}S\text{-}M_n^{\bullet}\}$$

$$\rightarrow graft + Ce^{III} + H^+ \qquad (6)$$

$$S\text{-}M_n^{\bullet} + S\text{-}M_n^{\bullet} \overset{k_{t2}}{\rightarrow} graft \qquad (7)$$

$$S\text{-}M_n^{\bullet} + M_n^{\bullet} \overset{k_{t2c}}{\rightarrow} graft \qquad (8)$$

$$S\text{-}M_n^{\bullet} + M_n^{\bullet} \overset{k_{t2d}}{\rightarrow} graft + homopolymer \qquad (9)$$

$$M_n^{\bullet} + Ce^{IV} \underset{\alpha_{-4}}{\overset{\alpha_4}{\rightleftharpoons}} Ce^{IV} \,|\, M_n^{\bullet} \overset{K_t}{\rightleftharpoons} \{Ce^{IV}\text{-}M_n^{\bullet}\}$$

$$\rightarrow homopolymer + Ce^{III} + H^+ \qquad (10)$$

$$M_n^{\bullet} + M_n^{\bullet} \overset{k_{t2}'}{\rightarrow} homopolymer \qquad (11)$$

$$S^{\bullet} + Ce^{IV} \underset{\alpha_{-1}}{\overset{\alpha_1}{\rightleftharpoons}} Ce^{IV} \,|\, S^{\bullet} \overset{K_o}{\rightleftharpoons} \{Ce^{IV}\text{-}S^{\bullet}\}$$
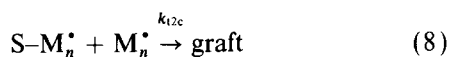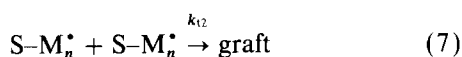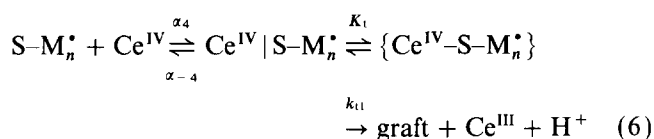
$$\rightarrow oxidation\ products + Ce^{III} + H^+ \qquad (12)$$

Here S is the cellulosic substrate, M is the monomer, α are diffusion constants of species between their own medium and a state of encounter suitable for species interaction, K represent the formation constants of two species to constitute a complex, k represent the rate constants of a reaction step, k_{t2} and k_{t2}' are rate constants of mutual termination of radical chains and k_{t2c} and k_{t2d} are termination rate constants by combination and disproportionation of radical chains, respectively.

Cellulosic radicals $S^{\bullet}$ formed according to equation (1) are trapped by M leading to grafting initiation (equation (2)) or they are oxidized by Ce^{IV} (equation (12)). The radicals $S^{\bullet}$ trapped by M lead to radical chains $S\text{-}M_n^{\bullet}$ by adding M through the propagation reaction (equation (4)) and then they undergo mutual termination (equation (7)), linear termination by Ce^{IV} (equation (6)) or mutual termination with radical chains $M_n^{\bullet}$ (equations (8) and (9)). If the latter termination is by combination (equation (8)) then the resulting polymer is graft copolymer, and if termination is by disproportionation (equation (9)) then $S\text{-}M_n^{\bullet}$ leads to graft copolymer and $M_n^{\bullet}$ leads to homopolymer. The monomer radicals $M^{\bullet}$ formed in equation (3) add monomer according to the propagation reaction (equation (5)) giving rise to radical chains $M_n^{\bullet}$, which undergo mutual termination (equation (11)), linear termination by ceric ion (equation (10)) or

mutual termination with $S\text{-}M_n^{\bullet}$ as stated above (equations (8) and (9)).

In order to take into account the heterogeneity of the graft polymerization, some diffusion parameters are considered in the chemical processes where the reactant species are located in different phases and should move to an appropriate state of encounter to allow the reaction between them to proceed. Cellulose fibres and films behave as semipermeable membranes and are swollen to different extents by aqueous media, depending on their morphology and degree of internal molecular order. While swelling in water is rapid, diffusion of solutes, other than simple ones of low molecular weight (cf. the size of a complexed Ce^{IV} ion), into the fibre is slower. The diffusion constant α and diffusion ratio of direct and reverse diffusion constants, X, are measures of the accessibility of the reactants to the state of encounter; α applies where reaction rate is diffusion-controlled and X applies in case of reactivity-controlled reaction rate. Agitation and temperature affect the processes in the polymerization scheme whose reactant species must diffuse to a state of encounter before the reaction proceeds. Only in particular cases where the reactants stay selectively in the state of encounter can the diffusion ratio be higher than unity.

It is assumed that the diffusion constants for ceric ion to cellulose or cellulose radical (equations (1) and (12)) are the same, as well as those of ceric ion to the $S\text{-}M_n^{\bullet}$ and $M_n^{\bullet}$ radical chains (equations (6) and (10)). It is also assumed that polymer radicals grafted from cellulose are less reactive than homopolymer radicals, i.e. $k_p < k_p'$, $k_{t2} < k_{t2}'$ and $k_{t1} < k_{t1}'$. This is because the former radicals are linked to insoluble cellulose, causing a restricted mobility in the radical chain[26].

Complex formation by cellulose[15,16] as well as monomer[23,27,28] and ceric ion has been reported (equations (1) and (3)). Other adducts[22] can also be formed (equations (2), (6), (10) and (12)) in systems where the donor–acceptor interaction is strong and the reactivity of the subsequent disproportionation step is slow. The formation constants in equations (6) and (10) are assumed to be the same.

Ceric ion in aqueous nitric acid solution forms complexes with water, hydroxide and nitrate ion as ligands[16]. When CAN is added to aqueous nitric acid it is partially hydrolysed, substituting some of its nitrate ligands for water and hydroxide ligands (because of the acid nature of ceric ion) in a proportion dependent on the HNO_3 concentration. In the presence of cellulose, a 1:1 cellulose–ceric ion complex is formed[16], exchanging two of the ligands for a glycol group of cellulose. The occurrence of acid–base equilibria between the hydroxyl groups of cellulose and the reaction medium suggests that neither or one or both glycol hydroxyls forming chelate are deprotonated and, consequently, they form different chelates with their own rates of disproportionation.

In the polymerization scheme where ceric ion intervenes, as usual[3], we have considered that one proton is formed as a consequence of the oxidation of an organic species. This suggests a decrease of pH with increasing reaction conversion. In the case of a slightly acid medium, the ceric ion complexes hold more than one hydroxyl ligand as a consequence of ceric ion hydrolysis. As the cerous ion resulting from disproportionation of the cellulose–ceric ion chelate is not acidic and more than one hydroxyl ligand is released, the overall result is an increase in the

pH of the medium. This effect was noticed when grafting a vinyl acetate–methyl acrylate mixture on cotton, where pH increased from 2.0 at the beginning of polymerization to 2.1 after 6 h.

REACTIONS WITH CERIC ION

Grafting site in cellulose

It has been proposed[9,11,14,16,29] that the 1:1 chelate formed by ceric ion and the C2–C3 glycol of the cellulose repeat unit disproportionates through a one-electron process with C2–C3 bond cleavage leading to the cellulosic radicals 1 or 2. As far as this author knows, there is no evidence for or against the formation of alkoxyl radicals in these studies on cellulose and its models. If they are formed, they must rearrange very rapidly before being trapped by monomer[9]. But it should be taken into account that the presence of alkoxyl radicals could not be demonstrated if the monomer is not reactive enough towards those radicals and if the carbon radicals

(chemical structures 1 and 2)
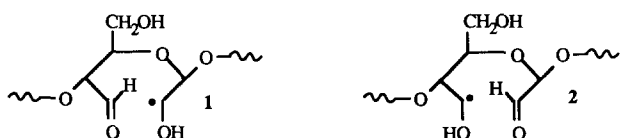
resulting from the rearrangement are stabilized, and consequently are favoured, as in this polyhydroxylic substrate. The absence of evidence for or against alkoxyl radical formation induces us to propose concerted Ce^{IV}–O bond and C–C bond cleavages in disproportionation of chelate to yield hydroxyalkyl radicals.

From molecular models of chelate at C2–C3 (octahedral complex and Ce^{IV}–O bond length of 2.5 Å), the alternative concerted cleavages of the C1–C2 and C3–C4 bonds leading to the cellulosic radicals 3 and 4, respectively, are also proposed. This is done on the following basis: (1)

(chemical structures 3 and 4)
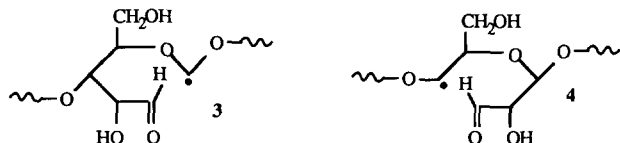
cellulose radicals 3 and 4 are probably no less stable than radicals 1 and 2, and (2) both C1–C2 and Ce^{IV}–O bonds, when they are homolytically cleaved through a one-electron transfer to the ceric ion in a concerted step, appear to display a greater coplanarity in the transition state than is the case for C2–C3 bond cleavage, which allows a greater sideways overlap of the forming orbitals in the transition state. Consequently, a higher rate of formation of the cellulosic radical 3 than of radicals 1 or 2 can be expected. The same consideration can be made about the C3–C4 bond and the resulting radical 4.

The hemiacetal group at the end of a cellulosic chain has been shown to be more reactive towards ceric ion than the glycol groups at every repeat unit[12,13,18,26,30,31]. Formation of the radical 5 after C1–OC5 bond cleavage[24]

(chemical structure 5)
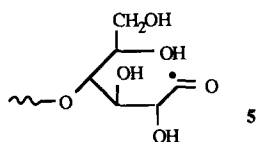
and of the radicals 6 and 7 after C1–C2 bond breaking through disproportionation of the complex of ceric ion and the C1–C2 glycol unit[13,31] have been proposed.

(chemical structures 6 and 7)
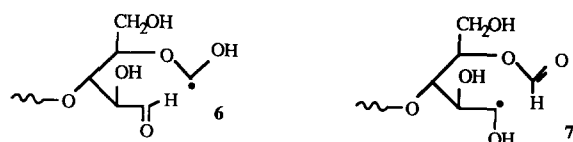
By analogy with the above alternatives to C2–C3 bond cleavage through the C2–C3 glycol complex, alternatives to C1–C2 bond cleavage through the C1–C2 glycol complex are proposed as follows. Two complexes can be formed depending on the axial or equatorial orientation of the hydroxyl group at C1. If the hydroxyl group at C1 is equatorial, both the C2–C3 and the C1–OC5 bond cleavages, leading to C3 and O cellulosic radicals 8 and 9, respectively, show higher coplanarity with their respective Ce^{IV}–O bond to be cleaved than the C1–C2 bond does. The alkoxyl radical 9 can subsequently give 5

(chemical structure 8)
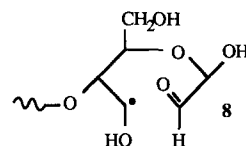
by transfer to C1. On the other hand, when the hydroxyl group at C1 is axial, C1–C2 and C2–C3 bond cleavages are not favoured owing to absence of coplanarity. But the C1–OC5 bond cleavage is allowed through a stabilized transition state, leading to radical 5 after transfer from radical 9 as before.

*(chemical structure 9, with $\rightleftharpoons$ 5)*
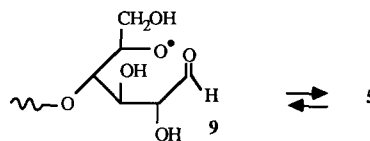
In general, cleavage of the C–C bond that forms part of a cellulose–ceric ion chelate is probably less favoured than the other α-cleavages, because one of the two carbons stays apart from the plane that the other four elements of the ring tend to form. This prevents the C–C bond from staying on the same plane as the Ce–O bond to be cleaved and, consequently, avoids the highest sideways overlap of the forming orbitals in the transition state of the concerted disproportionation of the complex.

Hintz and Johnson[11] studied the oxidation of *trans*-1,2-cyclohexanediol and *trans*-2-methoxycyclohexanol by ceric ion and found very similar values for the product of the complex formation constant and the rate constant of complex disproportionation in both alcohols (6.48 and 6.93, respectively). This result indicates a similar reactivity for both chemical groups. By analogy, it is now suggested that reaction at C3–C4 in the repeat unit of cellulose can also contribute to radical formation, if steric hindrance does not preclude interaction with complexed aqueous ceric ion. Considerations such as those mentioned above allow us to suggest the formation of radicals 1 and 4, after cleavages at C2–C3 and C3–C4, respectively, where 4 will probably be less favoured in its transition state. The formation of the radicals 10 (after cleavage C3–C4) and

(chemical structures 10 and 11)
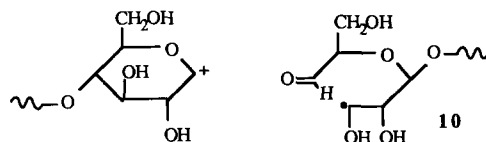
11 (after cleavage C4–C5), where the former is less favoured in its transition state, is accompanied by cellulose chain cleavage. This additional C–O bond breaking also
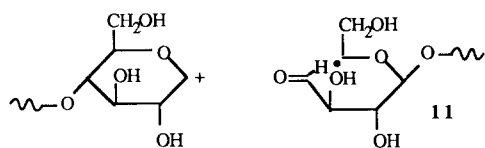
yields a carbenium ion (a relatively unstable species), which should probably put the formation of **10** and **11** at a disadvantage. So, formation of radicals **10** and **11** would be less important than the formation of radicals **1** and **4**. Moreover, the same considerations can be applied to the C1–C2 monosubstituted glycol of the repeat units of cellulose. This allows us to suggest the formation of radicals **2** and **3**. The formation of radicals **5** (cleavage C1–OC5) and **7** (cleavage C1–C2) is accompanied by
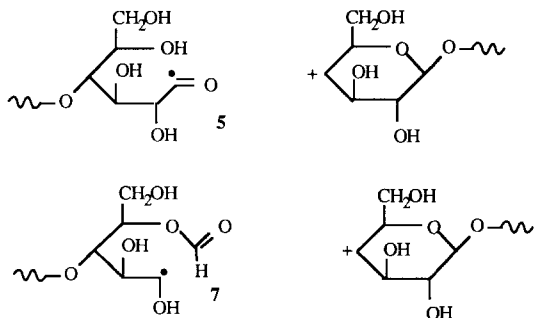
cellulose chain cleavage, leading to non-stabilized species that will be little favoured. Acetal bond breaking by formation of radicals **10, 11, 5** and **7** and the corresponding transient cations may account for the lowering in the molecular weight of cellulose during the grafting copolymerization. This effect would be simultaneous with the acid hydrolysis of acetal groups[32].

In short, if concerted disproportionation of the cellulose–ceric ion complexes and absence of steric hindrance for the cellulose–ceric ion interaction are assumed, the intermediate radicals **1** to **4**, with apparently slight differences in their capacity of formation, are favoured for the anhydroglucose repeat unit and the radicals **5** to **8** (and probably much less so **10** and **11**) for the hemiacetal terminal group of the cellulose chain.

In the presence of a suitable monomer, radicals **1** to **4** lead to a graft copolymer and radicals **5** to **11** lead to a block copolymer. Block and graft copolymers are formed from cellulose depending on the reaction conditions[3,30]. The radical **6** probably leads to homopolymer because of the expected rapid hydrolysis of the hemiacetal group in acid medium. If, in fact, this hydrolysis occurs, radical **6** is not a reactive site, which accounts for the above-mentioned results where a cellulose radical in the hemiacetal unit is trapped more rapidly by a monomer than a radical in the repeat unit.

The reactivity of different cellulose sites towards ceric ions to form the corresponding radicals, as above discussed, can be notably affected by their accessibility to ceric ions, depending on their location in the differently ordered regions of the semicrystalline cellulose.

Grafting initiation

An approach to the understanding of grafting initiation can be made through frontier orbital theory[33,34], considering the interactions of the frontier orbitals of cellulose radical and olefin monomer.

All the cellulose radicals proposed above have a high-energy singly occupied molecular orbital (SOMO). This is because of the electron-donating character of the

oxygen substituent, which raises the energy of the unpaired electron at carbon and increases the radical nucleophilicity. A radical of this nature should add more rapidly to olefins with a low-energy lowest unoccupied molecular orbital (LUMO), because in this case both SOMO and LUMO are similar in energy, leading to the largest energy lowering in the transition state energy. Olefins with a low-energy LUMO are those with electron-withdrawing substituents. On the other hand, olefins with a high-energy highest occupied molecular orbital (HOMO), i.e. those with electron-donating substituents, should add to a radical with high-energy SOMO at a very low rate. These ideas agree with results on olefins of both types[35,36].
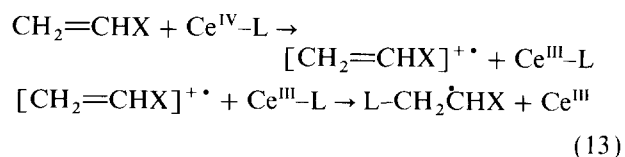
However, the initiation efficiency in the process of grafting a monomer from cellulose can also be influenced by another factor: monomer solubility affects diffusion to the cellulose radicals and is able to control the access of the monomer to the reactive sites in cellulose and thus the capacity of the monomer to be grafted.

Consequently, where monomer diffusion to cellulose is not rate-controlling, olefins substituted with electron-withdrawing groups are the monomers with the highest initiation efficiency. Moreover, an electron-poor monomer, which copolymerizes properly with an electron-rich monomer (i.e. they have suitable monomer reactivity ratios), can assist grafting of the latter from cellulose because of its higher reactivity with cellulose radicals[35].
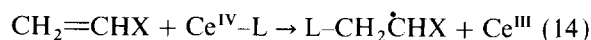
Homopolymerization initiation

Homopolymerization is initiated by the action of ceric ion on the olefin monomer as indicated in equation (3). Ceric ion is a hard cation as are its ligands, water, hydroxide and nitrate ions. So, these ligands are not oxidizable[37,38] by ceric ion under the usual polymerization conditions, and consequently the corresponding free radicals cannot in fact be considered as the initiating radicals of homopolymerization. Other initiating radicals should be formed.

Two different classes of olefins are considered: those with electron-withdrawing substituents and those with electron-donating substituents. Notable characteristics are a low-energy LUMO of the former and a high-energy HOMO of the latter. Depending on the donor nature of the substituent, the olefin will or will not act as a ligand in the ceric ion complexes. Taking as a base the work of Baciocchi *et al.*[39] on the oxidation of alkenylbenzenes with CAN in acetonitrile, it is suggested that olefins with high-energy HOMO are oxidized much more rapidly in an electron transfer process (equation (13)) than olefins with low-energy LUMO, which are oxidized in a ligand transfer process (equation (14)). The behaviour of methyl acrylate and vinyl acetate is explained[35] in this way. Only one ligand, L, of the ceric ion complex is indicated in equations (13) and (14):

$$CH_2{=}CHX + Ce^{IV}{-}L \rightarrow$$
$$[CH_2{=}CHX]^{+\bullet} + Ce^{III}{-}L$$
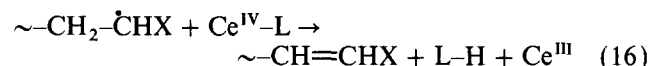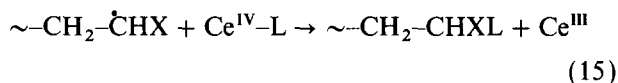$$[CH_2{=}CHX]^{+\bullet} + Ce^{III}{-}L \rightarrow L{-}CH_2\overset{\bullet}{C}HX + Ce^{III}$$

$$(13)$$

Any nucleophile present in the reaction medium is also likely to interact with the radical cation in equation (13):

$$CH_2{=}CHX + Ce^{IV}{-}L \rightarrow L{-}CH_2\overset{\bullet}{C}HX + Ce^{III} \quad (14)$$

The monomeric radical formed in any one of these ways is then responsible for homopolymerization initiation.

Radical chain termination

Radical chains can undergo linear termination by ceric ion as indicated in equations (6) and (10). The reactions (15) and (16) show two ways of termination of the radical chains:

$$\sim\text{-CH}_2\text{-}\overset{\bullet}{\text{C}}\text{HX} + \text{Ce}^{\text{IV}}\text{-L} \rightarrow \sim\text{-CH}_2\text{-CHXL} + \text{Ce}^{\text{III}}$$

$$(15)$$

$$\sim\text{-CH}_2\text{-}\overset{\bullet}{\text{C}}\text{HX} + \text{Ce}^{\text{IV}}\text{-L} \rightarrow$$
$$\sim\text{-CH}=\text{CHX} + \text{L-H} + \text{Ce}^{\text{III}} \quad (16)$$

As ligands of the Ce^{IV} complex are hard, an electron transfer mechanism for the reactions (15) and (16) is expected when the substituent X in the olefin is a good electron donor, e.g. alkoxyl, giving rise to a high rate of termination[35] through the stabilized species $\sim\text{-CH}_2\text{-}^+\text{C}\overset{\bullet}{\text{H}}\text{X} \leftrightarrow \sim\text{-CH}_2\text{-CH}=\text{X}^+$. In the case of an electron-poor olefin, a low rate of termination by a ligand transfer mechanism for the reactions (15) and (16) is suggested.

REACTION PARAMETERS AND REACTION VARIABLES

Estimation of reaction parameters

In the following, expressions showing the relationship between reaction parameters and reaction variables are developed.

Applying steady-state conditions to each concentration $[\text{S}^\bullet]$, $[\text{S-M}_n^\bullet]$ and $[\text{M}_n^\bullet]$, expressions for the following reaction parameters are derived in this section: R_g is the grafting reaction rate; R_h is the rate of homopolymer formation; R_p is the rate of total polymer formation; R_{Ce} is the rate of consumption of ceric ion; GE (grafting efficiency) is the fraction of the total polymer formed that is grafted on cellulose; v_g is the chain length of the grafted polymer; v_h is the chain length of the homopolymer; N_g is the (mole) number of grafted polymer chains; N_h is the (mole) number of homopolymer chains; GF (grafting frequency) is the number of grafts per cellulose chain; and IE (initiation efficiency) is the fraction of cellulose radicals that are trapped by monomer.

The expressions for the reaction parameters are developed assuming that the slow step that controls the rate of each reaction of the polymerization scheme is that indicated in the scheme by the rate constant k. When any reaction of the polymerization scheme is diffusion-controlled, new expressions for the polymerization parameters can be easily derived (but they are not written out here) by substituting the product kKX in the following expressions by the corresponding diffusion constant α of the same reaction. This will happen in cases where the reactivity of the interacting species is very high and/or their mutual accessibility is very low. This might occur in the fast reaction of oxidation of cellulose radicals by ceric ion (equation (12)). Furthermore, the reactions of the polymerization scheme and the corresponding expressions for the reaction parameters are easily adapted to cases where the hydroxyl or polyhydroxyl substrate and/or the monomer are soluble in the reaction medium, either because of their water solubility or because of the effect of the addition of a miscibilizing solvent. This

adaptation is carried out by eliminating the diffusion ratios or diffusion constants from the proper reactions of the polymerization scheme and, correspondingly, from the expressions of the reaction parameters. Analogously, particular cases where a reaction of the polymerization scheme does not include a complex are adapted by eliminating the corresponding step with its K.

When the linear termination of radical chains by ceric ion is negligible, that is, mutual termination is predominant, the total grafted polymer is the polymer formed by the growth of the radical chains $\text{S-M}_n^\bullet$ (equation (4)) plus the polymer formed by the growth of a fraction β of the radical chains $\text{M}_n^\bullet$ (equation (5)) that terminates precisely by combination with $\text{S-M}_n^\bullet$ (equation (8)). The homopolymer formed comes from the total radical chains $\text{M}_n^\bullet$ minus the polymer formed from the fraction of $\text{M}_n^\bullet$ that terminates by combination with $\text{S-M}_n^\bullet$.

Two pairs of competitive reactions are present in the polymerization scheme: mutual termination (equations (7) and (11)) and linear termination by ceric ion (equations (6) and (10)), and initiation of grafting (equation (2)) and oxidation of cellulose radicals (equation (12)). Four cases, (Aa), (Ab), (Ba) and (Bb), appear as a consequence of applying the following approximations: (A) implies that mutual termination is much faster than linear termination by ceric ion ((B) means the opposite to (A)); and (a) implies that the initiation rate of grafting is much faster than the oxidation rate of cellulose radicals ((b) means the opposite to (a)). These cases comprise the cases (A) and (B) for the homopolymerization reaction.

Case (Aa)

$$R_g = \frac{(k_p k_d K_d X_1 [\text{S}] + \beta k_p' k_i' K_i' X_3 [\text{M}])[\text{M}][\text{Ce}^{\text{IV}}]^{0.5}}{(2k_{t2})^{0.5}(k_d K_d X_1 [\text{S}] + k_i' K_i' X_3 [\text{M}])^{0.5}}$$

$$(17)$$

$$R_h = \frac{(1 - \beta)k_p' K_i' X_3 [\text{M}]^2 [\text{Ce}^{\text{IV}}]^{0.5}}{(2k_{t2}')^{0.5}(k_i' K_i' X_3 [\text{M}] + k_d K_d X_1 [\text{S}])^{0.5}}$$

$$(18)$$

$$R_p = R_g + R_h \quad (19)$$

$$R_{\text{Ce}} = [\text{Ce}^{\text{IV}}](k_d K_d X_1 [\text{S}] + k_i' K_i' X_3 [\text{M}]) \quad (20)$$

$$GE =$$

$$\frac{(2k_{t2}')^{0.5}(k_p k_d K_d X_1 [\text{S}] + \beta k_p' k_i' K_i' X_3 [\text{M}])}{(2k_{t2}')^{0.5}(k_p k_d K_d X_1 [\text{S}] + \beta k_p' k_i' K_i' X_3 [\text{M}]) + (1 - \beta)(2k_{t2})^{0.5} k_p' k_i' K_i' X_3 [\text{M}]}$$

$$(21)$$

$$v_g =$$

$$\frac{(k_p k_d K_d X_1 [\text{S}] + \beta k_p' k_i' K_i' X_3 [\text{M}])[\text{M}]}{(2k_{t2})^{0.5}(k_d K_d X_1 [\text{S}] + k_i' K_i' X_3 [\text{M}])^{0.5} k_d K_d X_1 [\text{S}][\text{Ce}^{\text{IV}}]^{0.5}}$$

$$(22)$$

$$v_h = \frac{(1 - \beta)k_p' [\text{M}]}{(2k_{t2}')(k_i' K_i' X_3 [\text{M}] + k_d K_d X_1 [\text{S}])^{0.5}[\text{Ce}^{\text{IV}}]^{0.5}}$$

$$(23)$$

$$N_g \propto R_i = k_d K_d X_1 [\text{S}][\text{Ce}^{\text{IV}}] \quad (24)$$

$$N_h \propto R_i' = k_i' K_i' X_3 [\text{M}][\text{Ce}^{\text{IV}}] \quad (25)$$

$$GF \propto N_{g} \tag{26}$$

$$IE = 1 \tag{27}$$

where R_i is the initiation rate of grafting and R_i' is the initiation rate of homopolymerization.

In the cases where the mutual accessibility of the growing chains $S-M_n^{\bullet}$ and $M_n^{\bullet}$ is inhibited because the graft polymerization site and the homopolymerization site are not the same, the equations (8) and (9) are negligible and the above expressions (17) to (27) are simplified to the following ones:

$$R_{g} = k_{p}[M](k_{d}K_{d}X_{1}[S][Ce^{IV}]/2k_{t2})^{0.5} \tag{17'}$$

$$R_{h} = k_{p}'[M]^{1.5}(k_{i}'K_{i}'X_{3}[Ce^{IV}]/2k_{t2}')^{0.5} \tag{18'}$$

$$R_{p} = R_{g} + R_{h} \tag{19'}$$

$$R_{Ce} = [Ce^{IV}](k_{d}K_{d}X_{1}[S] + k_{i}'K_{i}'X_{3}[M]) \tag{20}$$

$$GE = \frac{k_{p}(2k_{t2}'k_{d}K_{d}X_{1}[S])^{0.5}}{k_{p}(2k_{t2}'k_{d}K_{d}X_{1}[S])^{0.5} + k_{p}'(2k_{t2}k_{i}'K_{i}'X_{3}[M])^{0.5}} \tag{21'}$$

$$v_{g} = k_{p}[M]/(2k_{t2}k_{d}K_{d}X_{1}[S][Ce^{IV}])^{0.5} \tag{22'}$$

$$v_{h} = k_{p}'[M]^{0.5}/(2k_{t2}'k_{i}'K_{i}'X_{3}[Ce^{IV}])^{0.5} \tag{23'}$$

$$N_{g} = nk_{d}K_{d}X_{1}[S][Ce^{IV}] \tag{24'}$$

$$N_{h} = nk_{i}'K_{i}'X_{3}[M][Ce^{IV}] \tag{25'}$$

$$GE \propto N_{g} \tag{26}$$

$$IE = 1 \tag{27}$$

Case (Ab)

$$R_{g} =$$
$$\frac{(k_{p}k_{d}K_{d}k_{i}K_{i}X_{2}[S] + \beta k_{p}'k_{o}K_{o}k_{i}'K_{i}'X_{3}[Ce^{IV}])[M]^{1.5}}{(2k_{t2}k_{o}K_{o})^{0.5}(k_{d}K_{d}k_{i}K_{i}X_{2}[S] + k_{o}K_{o}k_{i}'K_{i}'X_{3}[Ce^{IV}])^{0.5}} \tag{28}$$

$$R_{h} = \frac{(1 - \beta)k_{p}'k_{o}^{0.5}K_{o}^{0.5}k_{i}'K_{i}'X_{3}[M]^{1.5}[Ce^{IV}]}{(2k_{t2}')^{0.5}(k_{o}K_{o}k_{i}'K_{i}'X_{3}[Ce^{IV}]+k_{d}K_{d}k_{i}K_{i}X_{2}[S])^{0.5}} \tag{29}$$

$$R_{p} = R_{g} + R_{h} \tag{30}$$

$$R_{Ce} = [Ce^{IV}](2k_{d}K_{d}X_{1}[S] + k_{i}'K_{i}'X_{3}[M]) \tag{31}$$

$$GE =$$
$$\frac{(2k_{t2}')^{0.5}(k_{p}k_{d}K_{d}k_{i}K_{i}X_{2}[S] + \beta k_{o}K_{o}k_{p}'k_{i}'K_{i}'X_{3}[Ce^{IV}])}{(2k_{t2}')^{0.5}(k_{p}k_{d}K_{d}k_{i}K_{i}X_{2}[S] + \beta k_{o}K_{o}k_{p}'k_{i}'K_{i}'X_{3}[Ce^{IV}]) + (1 - \beta)(2k_{t2})^{0.5}k_{o}K_{o}k_{p}'k_{i}'K_{i}'X_{3}[Ce^{IV}]} \tag{32}$$

$$v_{g} =$$
$$\frac{(k_{p}k_{d}K_{d}k_{i}K_{i}X_{2}[S]+\beta k_{o}K_{o}k_{p}'k_{i}'K_{i}'X_{3}[Ce^{IV}])(k_{o}K_{o}[M])^{0.5}}{(2k_{t2})^{0.5}(k_{o}K_{o}k_{i}'K_{i}'X_{3}[Ce^{IV}] + k_{d}K_{d}k_{i}K_{i}X_{2}[S])^{0.5}k_{d}K_{d}k_{i}K_{i}X_{2}[S]} \tag{33}$$

$$v_{h} = \frac{(1 - \beta)(k_{o}K_{o}k_{p}'[M])^{0.5}}{(2k_{t2}')^{0.5}(k_{o}K_{o}k_{i}'K_{i}'X_{3}[Ce^{IV}]+k_{d}K_{d}k_{i}K_{i}X_{2}[S])^{0.5}} \tag{34}$$

$$N_{g} \propto R_{i} = k_{d}K_{d}k_{i}K_{i}X_{2}[S][M]/k_{o}K_{o} \tag{35}$$

$$N_{h} \propto R_{i}' = k_{i}'K_{i}'X_{3}[M][Ce^{IV}] \tag{25}$$

$$GF \propto N_{g} \tag{36}$$

$$IE = k_{i}K_{i}X_{2}[M]/k_{o}K_{o}X_{1}[Ce^{IV}] \tag{37}$$

Assuming that equations (8) and (9) are negligible, as in case (Aa), the above expressions (28) to (37) are simplified to the following ones:

$$R_{g} = k_{p}[M]^{1.5}(k_{d}K_{d}k_{i}K_{i}X_{2}[S]/2k_{t2}k_{o}K_{o})^{0.5} \tag{28'}$$

$$R_{h} = k_{p}'[M]^{1.5}(k_{i}'K_{i}'X_{3}[Ce^{IV}]/2k_{t2}')^{0.5} \tag{18'}$$

$$R_{p} = R_{g} + R_{h} \tag{30'}$$

$$R_{Ce} = [Ce^{IV}](2k_{d}K_{d}X_{1}[S] + k_{i}'K_{i}'X_{3}[M]) \tag{31}$$

$$GE =$$
$$\frac{k_{p}(2k_{t2}'k_{d}K_{d}k_{i}K_{i}X_{2}[S])^{0.5}}{k_{p}(2k_{t2}'k_{d}K_{d}k_{i}K_{i}X_{2}[S])^{0.5} + k_{p}'(2k_{t2}k_{o}K_{o}k_{i}'K_{i}'X_{3}[Ce^{IV}])^{0.5}} \tag{32'}$$

$$v_{g} = k_{p}(k_{o}K_{o}[M])^{0.5}/(2k_{t2}k_{d}K_{d}k_{i}K_{i}X_{2}[S])^{0.5} \tag{33'}$$

$$v_{h} = k_{p}'[M]^{0.5}/(2k_{t2}'k_{i}'K_{i}'X_{3}[Ce^{IV}])^{0.5} \tag{23'}$$

$$N_{g} = nk_{d}K_{d}k_{i}K_{i}X_{2}[S][M]/k_{o}K_{o} \tag{35'}$$

$$N_{h} = nk_{i}'K_{i}'X_{3}[M][Ce^{IV}] \tag{25'}$$

$$GF \propto N_{g} \tag{36}$$

$$IE = k_{i}K_{i}X_{2}[M]/k_{o}K_{o}X_{1}[Ce^{IV}] \tag{37}$$

Case (Ba)

$$R_{g} = k_{p}k_{d}K_{d}X_{1}[M][S]/k_{t1}K_{t}X_{4} \tag{38}$$

$$R_{h} = k_{p}'k_{i}'K_{i}'X_{3}[M]^{2}/k_{t1}'K_{t}X_{4} \tag{39}$$

$$R_{p} = R_{g} + R_{h} \tag{40}$$

$$R_{Ce} = 2[Ce^{IV}](k_{d}K_{d}X_{1}[S] + k_{i}'K_{i}'X_{3}[M]) \tag{41}$$

$$GE = k_{t1}'k_{p}k_{d}K_{d}X_{1}[S]/(k_{t1}'k_{p}k_{d}K_{d}X_{1}[S] + k_{t1}k_{p}'k_{i}'K_{i}'X_{3}[M]) \tag{42}$$

$$v_{g} = k_{p}[M]/k_{t1}K_{t}X_{4}[Ce^{IV}] \tag{43}$$

$$v_{h} = k_{p}'[M]/k_{t1}'K_{t}X_{4}[Ce^{IV}] \tag{44}$$

$$N_{g} = k_{d}K_{d}X_{1}[S][Ce^{IV}] \tag{45}$$

$$N_{h} = k_{i}'K_{i}'X_{3}[M][Ce^{IV}] \tag{46}$$

$$GF \propto N_{g} \tag{26}$$

$$IE = 1 \tag{27}$$

Case (Bb)

$$R_{g} = k_{p}k_{d}K_{d}k_{i}K_{i}X_{2}[M]^{2}[S]/k_{o}K_{o}k_{t1}K_{t}X_{4}[Ce^{IV}] \tag{47}$$

$$R_{h} = k_{p}'k_{i}'K_{i}'X_{3}[M]^{2}/k_{t1}'K_{t}X_{4} \tag{39}$$

$$R_{p} = R_{g} + R_{h} \tag{48}$$

$$R_{Ce} = 2[Ce^{IV}](k_{d}K_{d}X_{1}[S] + k_{i}'K_{i}'X_{3}[M]) \tag{41}$$

$$GE = \frac{k_{t1}'k_{p}k_{d}K_{d}k_{i}K_{i}X_{2}[S]}{k_{t1}'k_{p}k_{d}K_{d}k_{i}K_{i}X_{2}[S] + k_{t1}k_{p}'k_{o}K_{o}k_{i}'K_{i}'X_{3}[Ce^{IV}]} \tag{49}$$

$$v_{g} = k_{p}[M]/k_{t1}K_{t}X_{4}[Ce^{IV}] \tag{43}$$

$$v_{h} = k_{p}'[M]/k_{t1}'K_{t}X_{4}[Ce^{IV}] \tag{44}$$

$$N_{g} = k_{d}K_{d}k_{i}K_{i}X_{2}[S][M]/k_{o}K_{o} \tag{50}$$

$$N_h = k_i' K_i' X_3 [M][Ce^{IV}] \tag{46}$$

$$GF \propto N_g \tag{36}$$

$$IE = k_i K_i X_2 [M] / k_o K_o X_1 [Ce^{IV}] \tag{37}$$

The proportionality coefficient n, present in equations (24'), (35') and (25') (cases (Aa) and (Ab)), takes values in the range 0.5–1. The value 0.5 corresponds to termination of polymer chains by pure combination and the value 1 corresponds to pure disproportionation.

Other important reaction variables (nitric acid concentration, inorganic salt concentration, agitation, temperature) are not explicit in either the polymerization scheme or derived equations because they affect k, K and X. Nitric acid concentration, for example, affects the nature of the ceric ion complexes (determining the proportion of hydroxide, water and nitrate ion ligands) and consequently their oxidation reactivity. However, the role of nitric acid in the copolymerization reaction can be tentatively visualized in equations (17) to (50) by enclosing $[H^+]$ into $[Ce^{IV}]$. This can be rationalized by considering that nitric acid catalyses the disproportionation of an oxidizable ligand–ceric ion complex by protonating another ligand (probably hydroxide), which enhances the capacity of ceric ion to take one electron from the oxidizable ligand (e.g. cellulose). So, it has been considered that the greatest effect of nitric acid is a consequence of its acid nature, and the effect of its contribution with nitrate ligands to the ceric ion complexes has not been taken into consideration. In this way, both ceric ion and nitric acid would occur in parallel in the same reactions of the polymerization scheme and, because of that, in the corresponding expressions for the polymerization parameters. Actually, similar behaviour of the reaction parameters by changing either ceric ion or nitric acid concentration has been found experimentally[3,40]. Other additives, such as nitrate salts, affect the ionic strength of the medium and the nature of the ceric ion complexes by acting as ligands, producing an increase in the oxidation potential of ceric ion[41]. The effect of agitation has been studied in some polymerizing systems[41,42]. Some considerations about agitation and temperature will be made in the following section.

In the cases (Aa) and (Ab), where mutual termination of radical chains is predominant over linear termination by ceric ion, a set of simplified equations has been derived by neglecting the mutual termination between the homopolymer and grafted radicals (equations (8) and (9) in the polymerization scheme). This approximation is useful in heterogeneous systems where the graft polymerization site and the homopolymerization site are not the same. It would occur, for instance, in systems where the homopolymer radicals cannot reach channels and pores in cellulose fibres where a portion of the grafted chains would be linked.

Table 1 Applicability of equations (17) to (50) and their comprising cases when reactivity-controlled rates are assumed

Case	Kinetic terms with a 'high' value	Kinetic terms with a 'low' value
(Aa)	$k_{12} k_d K_d k_i K_i X_2 [S][M]$	$k_o K_o X_1 k_{11} K_i X_4 [Ce^{IV}]([H^+])$
(Ab)	$k_{12} k_d K_d k_o K_o X_1 [S]$	$k_i K_i X_2 k_{11} K_i X_4 [M]$
(Ba)	$k_i K_i X_2 k_{11} K_i X_4 [M]$	$k_{12} k_d K_d k_o K_o X_1 [S]$
(Bb)	$k_o K_o X_1 k_{11} K_i X_4 [Ce^{IV}]([H^+])$	$k_{12} k_d K_d k_i K_i X_2 [S][M]$
(A)	$k_{12}' k_i' K_i' X_3 [M]$	$k_{11}' K_i X_4 [Ce^{IV}]([H^+])$
(B)	$k_{11}' K_i X_4 [Ce^{IV}]([H^+])$	$k_{12}' k_i' K_i' X_3 [M]$

Table 2 Applicability of equations (17) to (50) and their comprising cases when diffusion-controlled reaction rates are assumed

Case	Kinetic terms with a 'high' value	Kinetic terms with a 'low' value
(Aa)	$k_{12} \alpha_2 [S][M]$	$\alpha_1 \alpha_4 [Ce^{IV}]([H^+])$
(Ab)	$k_{12} \alpha_1 [S]$	$\alpha_2 \alpha_4 [M]$
(Ba)	$\alpha_2 \alpha_4 [M]$	$k_{12} \alpha_1 [S]$
(Bb)	$\alpha_1 \alpha_4 [Ce^{IV}]([H^+])$	$k_{12} \alpha_2 [S][M]$
(A)	$k_{12}' \alpha_3 [M]$	$\alpha_4 [Ce^{IV}]([H^+])$
(B)	$\alpha_4 [Ce^{IV}]([H^+])$	$k_{12}' \alpha_3 [M]$

Competitive reactions and derived cases

As indicated above, four cases ((Aa), (Ab), (Ba) and (Bb)) have appeared as a consequence of the predominance of two of the following four competitive reactions in the polymerization scheme: mutual termination and linear termination by ceric ion, and initiation of grafting and oxidation of cellulose radicals. Consideration of these competitive reactions allows us to establish the reaction terms under which each of the four cases applies. Any reaction term favours one case or another depending on whether its value in the polymerization system is 'high' or 'low'. Each of the four cases is applicable when a group of particular terms applies, as can be seen in *Tables 1* and *2*. Although the influence of nitric acid on polymerization should be considered in K, k and X for the reactions where ceric ion is involved, it is interesting to make its role in favouring any one of the cases explicit and it is indicated in parentheses in *Tables 1* and *2*. As can be seen in *Tables 1* and *2*, low values of $[Ce^{IV}]$ or $[H^+]$ favour the applicability of the case (Aa) and, on the other hand, high values favour the case (Bb). Intermediate values of $[Ce^{IV}]$ or $[H^+]$ favour the case (Ab) if $[S]$ is high and $[M]$ is low, or (Ba) if $[S]$ is low and $[M]$ is high. Low values of $[S]$ and $[M]$ favour the case (Bb) and high values favour the case (Aa). Low value of $[M]$ and high value of $[S]$ favour the case (Ab), and the opposite values favour the case (Ba). Parallel to the graft polymerization, in homopolymerization, low values of $[Ce^{IV}]$ or $[H^+]$ favour the case (A) and high values favour the case (B). A low value of $[M]$ favours the case (B) and a high value favours the case (A).

If any reaction in the polymerization scheme is diffusion-controlled, the product kKX is substituted by the corresponding α. In *Table 2* the same cases as in *Table 1* are shown, but assuming diffusion-controlled reaction rates. Low values of α_1 favour both (Aa) and (Ba) and high values favour (Ab) as well as (Bb); α_2 works in an opposite manner to α_1. Low values of α_4 favour both (Aa) and (Ab) (and case (A) of homopolymerization) and high values favour (Ba) as well as (Bb) (and case (B) of homopolymerization). Low values of α_3 favour (B) and high values favour (A). As diffusion constants are dependent on agitation and temperature for a given morphology of cellulose, these reaction variables can be tentatively introduced by substituting α wherever it appears.

By increasing agitation or temperature, α is increased, and this situation of diffusion-controlled reaction rate can be left and a new situation of reactivity-controlled reaction rate, governed by the product kKX, be reached. This product is affected by increasing temperature but is not affected by agitation.

On the basis of the conditions established for the applicability of the above cases and their corresponding equations, the behaviour of each reaction parameter for each reaction variable can be ascertained from the corresponding expressions of the preceding section. We can consider, as an example of handling *Tables 1* and *2*, the behaviour of the reaction parameter R_g when the reaction variable $[Ce^{IV}]$ is varied in a polymerizing system. At low enough values of $[Ce^{IV}]$, the case (Aa) applies and the corresponding R_g expression (17') shows that R_g increases with increasing $[Ce^{IV}]$. At high enough values of $[Ce^{IV}]$, the case (Ab) (if $[S]$ is high and $[M]$ is low) or the case (Ba) (if $[S]$ is low and $[M]$ is high) applies and consequently any R_g expression (28') or (38), respectively, shows that R_g is independent of $[Ce^{IV}]$. After a higher increase of $[Ce^{IV}]$ the case (Bb) applies and equation (47) shows that R_g decreases on increasing $[Ce^{IV}]$. The general results reviewed by McDowall *et al.*[3] fit into this explanation.

Some structural characteristics of the copolymer can be derived from this explanation and the applicable cases. In the first step of varying $[Ce^{IV}]$, at the lowest $[Ce^{IV}]$, most of the cellulose radicals formed are trapped by the monomer and the radical chains are predominantly terminated by combination and disproportionation. In the former case, the synthetic polymer forms some loops and crosslinks with cellulose; in the other case, both saturated and unsaturated end-groups are formed. At higher $[Ce^{IV}]$, in the second step, if the case (Ab) is applicable, a minor amount of the cellulose radicals are trapped by the monomer (there is an extensive oxidation of cellulose) and the radical chains yield mutual termination as before; but if the case (Ba) is applicable, most of the cellulose radicals are trapped by the monomer and the end-groups of the polymer chains are introduced by the oxidation of the radical chains by the ceric ions. In the third step, at the highest $[Ce^{IV}]$, a minor amount of the cellulose radicals formed are trapped by the monomer and the radical chains are terminated by the ceric ions.

Transitions between competitive reactions

In addition to the four cases previously described, another consequence of the predominance of some of the aforementioned competitive reactions is the presence of three reaction transitions, R_i-R_o, $R_{t2}-R_{t1}$ and $R'_{t2}-R'_{t1}$, between the competitive reactions as the reaction variables change, connecting the applicability of the four cases. (R_i is the initiation rate of grafting, R_o is the oxidation rate of cellulose radicals by ceric ion, R_{t2} is the mutual termination of grafted chains, R_{t1} is the linear termination of grafted chains by ceric ions, R'_{t2} is the mutual termination of homopolymer chains and R'_{t1} is the linear termination of homopolymer chains by ceric ions.) The reaction transitions occur on changing the reaction variables sufficiently (see *Tables 1* and *2*), in such a way that $[S]$ can cause the transition $R_{t2}-R_{t1}$, $[M]$ can cause the transitions R_i-R_o and $R'_{t2}-R'_{t1}$ and $[Ce^{IV}]$ (and $[H^+]$) can cause the transitions R_i-R_o, $R_{t2}-R_{t1}$ and $R'_{t2}-R'_{t1}$.

When the case (Aa) or (Ba) applies, the initiation rate of grafting, R_i, is higher than the oxidation rate of cellulose radicals, R_o, and increasing $[Ce^{IV}]$, for example, causes R_o to increase, until R_i is reached and then surpassed, leading to case (Ab) or (Bb), respectively. In this R_i-R_o transition, the following expression (51)

applies:

$$[Ce^{IV}]_i = k_i K_i X_2 [M]/k_o K_o X_1 \qquad (51)$$

Using this expression to compare the behaviour of different monomers, it can be observed that the higher the capacity of a monomer to react with cellulose radicals, the higher $[Ce^{IV}]_i$ at which the transition occurs. That is, a sequence in the reactivity of monomers towards cellulose radicals can be established by using equation (51). An analogous consideration can be made for $[M]$ by using the same equation (51).

Also, when the case (Aa) or (Ab) applies, increasing $[Ce^{IV}]$, for example, causes the linear termination by ceric ion, R_{t1}, to increase until mutual termination, R_{t2}, is reached and then surpassed, leading to the case (Ba) or (Bb), respectively. In this $R_{t2}-R_{t1}$ transition, expression (52) applies when R_i is much higher than R_o and expression (53) in the opposite case:

$$[Ce^{IV}]_i = k_{t2} k_d K_d X_1 [S]/(k_{t1} K_t X_4)^2 \qquad (52)$$

$$[Ce^{IV}]_i = \{k_{t2} k_d K_d k_i K_i X_2 [S][M]/(k_{t1} K_t X_4)^2 k_o K_o\}^{0.5} \qquad (53)$$

These expressions can be used to compare the behaviour of different monomers. It can be seen that the greater the capacity of a monomer for adding onto cellulosic radicals and for yielding mutual termination and the lower its capacity for linear termination, the higher is $[Ce^{IV}]_i$ at which the transition occurs. Analogous considerations can be made for $[M]$ and $[S]$ by using the same equations (52) and (53).

Analogously, the transition $R'_{t2}-R'_{t1}$ between the cases (A) and (B) for the homopolymerization reaction occurs by changing $[Ce^{IV}]$ (or $[M]$) to a sufficient degree and it gives rise to the expression (54):

$$[Ce^{IV}]_i = k'_{t2} k'_i K'_i X_3 [M]/(k'_{t1} K_t X_4)^2 \qquad (54)$$

The nature of the monomer affects the $[Ce^{IV}]$ (or $[M]$) value for this transition in an analogous manner as has been shown with the transition $R_{t2}-R_{t1}$.

The products kKX in equations (51) to (54) should be substituted by the corresponding α when the corresponding reactions in the polymerization scheme are diffusion-controlled.

Estimation of the reaction transitions

Each transition R_i-R_o, $R_{t2}-R_{t1}$ and $R'_{t2}-R'_{t1}$ can be estimated by plotting appropriate equations in a suitable manner in order to obtain straight lines whose intersection, *IV*, and the difference of the values of the respective ordinates at the origin, *DOO*, show the value of the reaction variable involved in the transition. An estimation of transitions is shown in *Table 3*.

The most appropriate equations are those corresponding to reaction parameters that show only one transition when a reaction variable is varied. For instance, the transition R_i-R_o can be estimated by plotting lg N_g *versus* lg$[Ce^{IV}]$. Depending on the values fixed for the other reaction variables (*Table 1*), this plot agrees with the consecutive application (see *Table 3*) of equations (24') and (35') (cases (Aa) and (Ab)) or equations (45) and (50) (cases (Ba) and (Bb)). In any case, two straight lines with slopes 1 and 0 are yielded. The intersection of those straight lines and the difference of the values of the respective ordinates at the origin yield the value of the ceric ion concentration at which

Table 3 Estimation of the reaction transitions in the case of reactivity-controlled reaction rates

Equation plotted	Equations[a]	Slopes[a]	IV[b]	DOO[b]	Transition[a]
$\lg N_g$ vs. $\lg[Ce^{IV}]$	(24') and (35')	1 and 0	$\lg[Ce^{IV}]_i$	$\lg[Ce]_i$	(Aa)-(Ab), R_i-R_o
	(45) and (50)	1 and 0	$\lg[Ce^{IV}]_i$	$\lg[Ce]_i$	(Ba)-(Bb), R_i-R_o
$\lg N_g$ vs. $\lg[M]$	(50) and (45)	1 and 0	$\lg[M]_i$	$\lg[M]_i$	(Ab)-(Aa), R_i-R_o
	(35') and (24')	1 and 0	$\lg[M]_i$	$\lg[M]_i$	(Bb)-(Ba), R_i-R_o
$\lg v_g$ vs. $\lg[M]$	(33') and (22')	0.5 and 1	$\lg[M]_i$	$0.5\,\lg[M]_i$	(Ab)-(Aa), R_i-R_o
$\lg(1/v_g)$ vs. $\lg[Ce^{IV}]$	(22') and (33')	0.5 and 0	$\lg[Ce^{IV}]_i$	$0.5\,\lg[Ce^{IV}]_i$	(Aa)-(Ab), R_i-R_o
	(22') and (43)	0.5 and 1	$\lg[Ce^{IV}]_i$	$0.15 + 0.5\,\lg[Ce^{IV}]_i$	(Aa)-(Ba), $R_{t2}-R_{t1}$
	(33') and (43)	0 and 1	$\lg[Ce^{IV}]_i$	$0.15 + \lg[Ce^{IV}]_i$	(Ab)-(Bb), $R_{t2}-R_{t1}$
$\lg(1/v_g)$ vs. $\lg[S]$	(43) and (22')	0 and 0.5	$\lg[S]_i$	$-0.15 + 0.5\,\lg[S]_i$	(Ba)-(Aa), $R_{t2}-R_{t1}$
	(43) and (33')	0 and 0.5	$\lg[S]_i$	$-0.15 + 0.5\,\lg[S]_i$	(Bb)-(Ab), $R_{t2}-R_{t1}$
$\lg R_g$ vs. $\lg[Ce^{IV}]$	(17') and (28')	0.5 and 0	$\lg[Ce^{IV}]_i$	$0.5\,\lg[Ce^{IV}]_i$	(Aa)-(Ab), R_i-R_o
	(17') and (38)	0.5 and 0	$\lg[Ce^{IV}]_i$	$0.15 + 0.5\,\lg[Ce^{IV}]_i$	(Aa)-(Ba), $R_{t2}-R_{t1}$
	(28') and (47)	0 and -1	$\lg[Ce^{IV}]_i$	$0.15 + \lg[Ce^{IV}]_i$	(Ab)-(Bb), $R_{t2}-R_{t1}$
	(38) and (47)	0 and -1	$\lg[Ce^{IV}]_i$	$\lg[Ce^{IV}]_i$	(Ba)-(Bb), R_i-R_o
$\lg R_g$ vs. $\lg[M]$	(28') and (17')	1.5 and 1	$\lg[M]_i$	$0.5\,\lg[M]_i$	(Ab)-(Aa), R_i-R_o
	(47) and (38)	2 and 1	$\lg[M]_i$	$\lg[M]_i$	(Bb)-(Ba), R_i-R_o
$\lg R_g$ vs. $\lg[S]$	(38) and (17')	1 and 0.5	$\lg[S]_i$	$-0.15 + 0.5\,\lg[S]_i$	(Ba)-(Aa), $R_{t2}-R_{t1}$
	(47) and (28')	1 and 0.5	$\lg[S]_i$	$-0.15 + 0.5\,\lg[S]_i$	(Bb)-(Ab), $R_{t2}-R_{t1}$
$\lg R_h$ vs. $\lg[Ce^{IV}]$	(18') and (39)	0.5 and 0	$\lg[Ce^{IV}]_i$	$0.15 + 0.5\,\lg[Ce^{IV}]_i$	(A)-(B), $R'_{t2}-R'_{t1}$
$\lg R_h$ vs. $\lg[M]$	(39) and (18')	2 and 1.5	$\lg[M]_i$	$-0.15 + 0.5\,\lg[M]_i$	(B)-(A), $R'_{t2}-R'_{t1}$
$\lg(1/v_h)$ vs. $\lg[Ce^{IV}]$	(23') and (44)	0.5 and 1	$\lg[Ce^{IV}]_i$	$0.15 + 0.5\,\lg[Ce^{IV}]_i$	(A)-(B), $R'_{t2}-R'_{t1}$
$\lg v_h$ vs. $\lg[M]$	(44) and (23')	1 and 0.5	$\lg[M]_i$	$-0.15 + 0.5\,\lg[M]_i$	(B)-(A), $R'_{t2}-R'_{t1}$

[a] The equation numbers, the corresponding slope values and the applicable cases are written, for each transition, in the order of their application according to the increasing values of the reaction variable involved

[b] IV is the value of the reaction variable at the intersection of the two straight lines. DOO is the difference of the values of the ordinates at the origin

the transition occurs. So, the transition R_i-R_o appears because the applicability of the case (Aa) changes to the case (Ab) or the applicability of the case (Ba) changes to the case (Bb) when $[Ce^{IV}]$ is increased.

Some of the other reaction parameters can show more than one reaction transition (*Table 3*). For instance, by plotting $\lg(1/v_g)$ versus $\lg[Ce^{IV}]$, both transitions R_i-R_o and $R_{t2}-R_{t1}$ appear when $[Ce^{IV}]$ is sufficiently increased, if the values fixed for the other reaction variables are those appropriate (*Table 1*) for successively applying the cases (Aa), (Ab) and (Bb) (equations (22'), (33') and (43), respectively). However, only the transition $R_{t2}-R_{t1}$ appears if the values fixed for the other reaction variables are those appropriate (*Table 1*) for successively applying the cases (Aa) and (Ba) (equations (22') and (43), respectively). The corresponding geometrical characteristics (slopes, IV and DOO) of these plots are indicated in *Table 3*.

An estimation of the reaction transitions in the case of diffusion-controlled reaction rates is now considered. Diffusion constants are dependent on agitation and temperature, for a given morphology of cellulose. Temperature also affects the rate constants of the chemical processes in the polymerization scheme. In the following, it is assumed that the predominant effect of temperature is that it acts on α. In this way, a temperature effect on the reaction parameters similar to that of agitation is expected. In *Table 4*, the estimations of reaction transitions when agitation or temperature is varied in order to modify diffusion constants are shown. Some appropriate equations are chosen as above, and the geometrical methodology is also analogous to the

one described for *Table 3*. The reaction transitions occur by changing α sufficiently as indicated in *Table 4*, but a new situation can also arise by increasing α in which the reaction rate is not diffusion-controlled but reactivity-controlled by the product kKX. In this new situation an agitation change does not affect any reaction parameter.

Also, an estimation of transitions on the basis of varying the reaction variables considered in *Table 3* can also be made when the reaction rates are diffusion-controlled by using *Table 4*.

Experimental data obtained by testing the reaction variables indicated in *Tables 3* and *4* will allow us to show the reaction transitions and also to ascertain values of the reaction variables at which the transitions occur for certain fixed reaction conditions. These values and equations (51) to (54) will allow us to calculate new values of reaction variables at which the transitions should occur for any other reaction conditions.

POLYMERIZATION SCHEME FOR ELECTRON-RICH OLEFINS

As discussed in a previous section, olefins with electron-withdrawing substituents add faster to the nucleophilic cellulose radicals than do olefins with electron-donating substituents. Consequently, electron-rich olefins show a low initiation efficiency (see equation (37)) in the graft polymerization. On the other hand, olefins with electron-donating substituents are more easily oxidizable by ceric ion than olefins with electron-withdrawing substituents (also discussed in a previous section). So, electron-rich olefins undergo a more rapid initiation of homopoly-

Table 4 Estimation of the reaction transitions in the case of diffusion-controlled reaction rates. α is varied by changing agitation or temperature

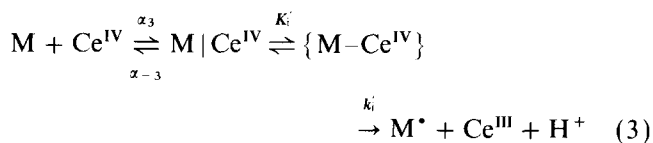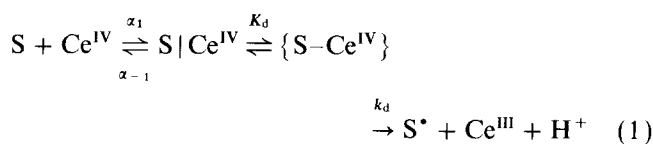| Equation plotted	Equations[a]	Slopes[a]	IV^b	DOO^b	Transition[a]
$\lg N_g$ vs. $\lg \alpha_2$	(35') and (24')	1 and 0	$\lg(\alpha_2)_i$	$\lg(\alpha_2)_i$	$(Ab)-(Aa), R_i-R_o$
	(50) and (45)	1 and 0	$\lg(\alpha_2)_i$	$\lg(\alpha_2)_i$	$(Bb)-(Ba), R_i-R_o$
$\lg N_g$ vs. $\lg \alpha_1$	(24') and (35')	1 and 0	$\lg(\alpha_1)_i$	$\lg(\alpha_1)_i$	$(Aa)-(Ab), R_i-R_o$
	(45) and (50)	1 and 0	$\lg(\alpha_1)_i$	$\lg(\alpha_1)_i$	$(Ba)-(Bb), R_i-R_o$
$\lg(1/v_g)$ vs. $\lg \alpha_1$	(22') and (33')	0.5 and 0	$\lg(\alpha_1)_i$	$0.5\,\lg(\alpha_1)_i$	$(Aa)-(Ab), R_i-R_o$
$\lg 1/v_g$ vs. $\lg \alpha_2$	(33') and (22')	0.5 and 0	$\lg(\alpha_2)_i$	$0.5\,\lg(\alpha_2)_i$	$(Ab)-(Aa), R_i-R_o$
$\lg(1/v_g)$ vs. $\lg \alpha_4$	(22') and (43)	0 and 1	$\lg(\alpha_4)_i$	$0.15 + \lg(\alpha_4)_i$	$(Aa)-(Ba), R_{12}-R_{11}$
	(33') and (43)	0 and 1	$\lg(\alpha_4)_i$	$0.15 + \lg(\alpha_4)_i$	$(Ab)-(Bb), R_{12}-R_{11}$
$\lg R_g$ vs. $\lg \alpha_1$	(17') and (28')	0.5 and 0	$\lg(\alpha_1)_i$	$0.5\,\lg(\alpha_1)_i$	$(Aa)-(Ab), R_i-R_o$
	(38) and (47)	1 and 0	$\lg(\alpha_1)_i$	$\lg(\alpha_1)_i$	$(Ba)-(Bb), R_i-R_o$
$\lg R_g$ vs. $\lg \alpha_2$	(28') and (17')	0.5 and 0	$\lg(\alpha_2)_i$	$0.5\,\lg(\alpha_2)_i$	$(Ab)-(Aa), R_i-R_o$
	(47) and (38)	1 and 0	$\lg(\alpha_2)_i$	$\lg(\alpha_2)_i$	$(Bb)-(Ba), R_i-R_o$
$\lg(1/R_g)$ vs. $\lg \alpha_4$	(17') and (38)	0 and 1	$\lg(\alpha_4)_i$	$0.15 + \lg(\alpha_4)_i$	$(Aa)-(Ba), R_{12}-R_{11}$
	(28') and (47)	0 and 1	$\lg(\alpha_4)_i$	$0.15 + \lg(\alpha_4)_i$	$(Ab)-(Bb), R_{12}-R_{11}$
$\lg(1/v_h)$ vs. $\lg \alpha_3$	(44) and (23')	0 and 0.5	$\lg(\alpha_3)_i$	$-0.15 + 0.5\,\lg(\alpha_3)_i$	$(B)-(A), \quad R'_{12}-R'_{11}$
$\lg(1/v_h)$ vs. $\lg \alpha_4$	(23') and (44)	0 and 1	$\lg(\alpha_4)_i$	$0.15 + \lg(\alpha_4)_i$	$(A)-(B), \quad R'_{12}-R'_{11}$
$\lg(1/R_h)$ vs. $\lg \alpha_4$	(18') and (39)	0 and 1	$\lg(\alpha_4)_i$	$0.15 + \lg(\alpha_4)_i$	$(A)-(B), \quad R'_{12}-R'_{11}$
$\lg R_h$ vs. $\lg \alpha_3$	(39) and (18')	1 and 0.5	$\lg(\alpha_3)_i$	$-0.15 + 0.5\,\lg(\alpha_3)_i$	$(B)-(A), \quad R'_{12}-R'_{11}$
$\lg N_h$ vs. $\lg \alpha_3$	(46) and (25')	1 and 1	$\lg(\alpha_3)_i$	$\lg(1/n)^c$	$(B)-(A), \quad R'_{12}-R'_{11}$

[a] The equation numbers, the corresponding slope values and the applicable cases are written, for each transition, in the order of their application according to increasing α (i.e. agitation or temperature)
[b] IV is the value of the reaction variable at the intersection of the two straight lines. DOO is the difference of the values of the ordinates at the origin
[c] n can take values in the range 0.5–1, where 0.5 corresponds to termination by pure combination and 1 to pure disproportionation

merization. This behaviour of electron-rich monomers towards cellulose radicals and ceric ions allows us to suggest the following polymerization scheme, which should be of prime importance for this type of monomer but of much less significance for the electron-poor olefin monomers. In this proposal, grafting is predominantly due to the combination of homopolymer radicals and cellulose radicals.
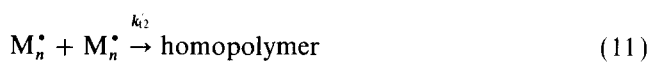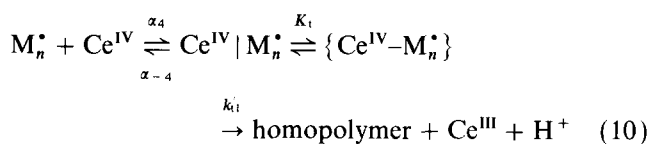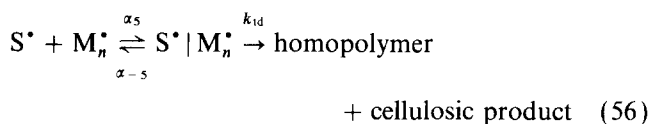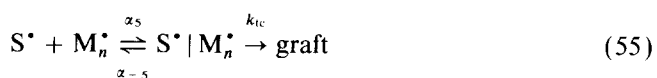
Initiation

$$S + Ce^{IV} \underset{\alpha-1}{\overset{\alpha_1}{\rightleftharpoons}} S\,|\,Ce^{IV} \overset{K_d}{\rightleftharpoons} \{S-Ce^{IV}\}$$

$$\overset{k_d}{\rightarrow} S^\bullet + Ce^{III} + H^+ \quad (1)$$

$$M + Ce^{IV} \underset{\alpha-3}{\overset{\alpha_3}{\rightleftharpoons}} M\,|\,Ce^{IV} \overset{K_i}{\rightleftharpoons} \{M-Ce^{IV}\}$$

$$\overset{k_i}{\rightarrow} M^\bullet + Ce^{III} + H^+ \quad (3)$$

Propagation

$$M_n^\bullet + M \overset{k_p}{\rightarrow} M_{n+1}^\bullet \quad (5)$$

Termination

$$S^\bullet + Ce^{IV} \underset{\alpha-1}{\overset{\alpha_1}{\rightleftharpoons}} Ce^{IV}\,|\,S^\bullet \overset{K_o}{\rightleftharpoons} \{Ce^{IV} - S^\bullet\}$$

$$\overset{k_o}{\rightarrow} \text{oxidation products} + Ce^{III} + H^+ \quad (12)$$

$$S^\bullet + M_n^\bullet \underset{\alpha-5}{\overset{\alpha_5}{\rightleftharpoons}} S^\bullet\,|\,M_n^\bullet \overset{k_{tc}}{\rightarrow} \text{graft} \quad (55)$$

$$S^\bullet + M_n^\bullet \underset{\alpha-5}{\overset{\alpha_5}{\rightleftharpoons}} S^\bullet\,|\,M_n^\bullet \overset{k_{td}}{\rightarrow} \text{homopolymer}$$

$$+ \text{cellulosic product} \quad (56)$$

$$M_n^\bullet + Ce^{IV} \underset{\alpha-4}{\overset{\alpha_4}{\rightleftharpoons}} Ce^{IV}\,|\,M_n^\bullet \overset{K_t}{\rightleftharpoons} \{Ce^{IV} - M_n^\bullet\}$$

$$\overset{k_{t1}}{\rightarrow} \text{homopolymer} + Ce^{III} + H^+ \quad (10)$$

$$M_n^\bullet + M_n^\bullet \overset{k_{t2}}{\rightarrow} \text{homopolymer} \quad (11)$$
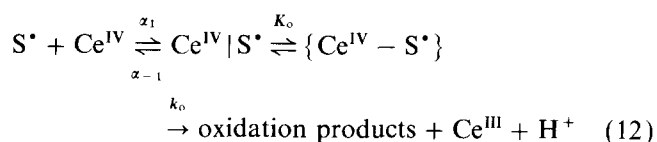
where k_{tc} and k_{td} are termination rate constants by combination and disproportionation, respectively.

The monomer radicals $M^\bullet$ formed in equation (3) add monomer according to the propagation reaction (equation (5)), giving rise to the radical chains $M_n^\bullet$. These polymer radicals terminate linearly by ceric ion (equation (10)) or mutually (equation (11)) to yield homopolymer. They can also terminate by reacting with cellulose radicals by combination (equation (52)) to yield graft copolymer or by disproportionation (equation (53)) to yield homopolymer and a cellulosic product.

This mechanism of polymerization leads to a notable characteristic on grafting onto insoluble cellulose: formation of superficial grafting. It is attributable to the difficulty of the homopolymer radical chains to reach the cellulose radicals removed from the surface of the cellulosic fibres through channels and pores, because of the relatively large size of the growing chains. This mechanism has been proposed when grafting vinyl acetate onto cellulose[35].

Applying steady-state conditions to the concentrations $[S^\bullet]$ and $[M_n^\bullet]$, some reaction parameters, defined as above, are derived as follows. Now, the initiation

efficiency, IE, is more conveniently defined as the fraction of radical chains that terminate by combination with cellulose radicals. The total grafted polymer formed occurs by growing a fraction γ of the radical chains $M_n^{\bullet}$ (equation (5)) that terminate precisely by combination with cellulosic radicals (equation (52)). The homopolymer formed comes from the total radical chains $M_n^{\bullet}$ minus the polymer formed from the fraction of $M_n^{\bullet}$ that terminate by combination with cellulosic radicals:

$$R_g = \gamma k_p'[M][M_n^{\bullet}] = \gamma A \tag{57}$$

where

$$A = \frac{\gamma k_p' k_o K_o X_1 k_i' K_i' X_3 [M][Ce^{IV}]}{2k_{tc} X_5 k_d K_d X_1 [S] - 2\gamma k_t X_5 k_i' K_i' X_3 [M]} \tag{58}$$

and

$$k_t = k_{tc} + k_{td} \tag{59}$$

$$R_h = (1 - \gamma)k_p'[M][M_n^{\bullet}] = (1 - \gamma)A \tag{60}$$

$$R_p = R_g + R_h = A \tag{61}$$

$$GE = R_g/R_p = \gamma \tag{62}$$

$$v_g = R_g/\gamma R_i' = \gamma k_p' k_o K_o X_1/(2k_{tc} X_5 k_d K_d X_1 [S]$$
$$- 2\gamma k_t X_5 k_i' K_i' X_3 [M]) \tag{63}$$

$$v_h = R_h/(1 - \gamma)R_i' = \gamma k_p' k_o K_o X_1/(2k_{tc} X_5 k_d K_d X_1 [S]$$
$$- 2\gamma k_t X_5 k_i' K_i' X_3 [M]) \tag{64}$$

$$N_g = \gamma R_i' = \gamma k_i' K_i' X_3 [M][Ce^{IV}] \tag{65}$$

$$N_h = (1 - \gamma)R_i' = (1 - \gamma)k_i' K_i' X_3 [M][Ce^{IV}] \tag{66}$$

$$GF \propto N_g \tag{67}$$

$$IE = \gamma \tag{68}$$

The fraction of radical chains $M_n^{\bullet}$ that give rise to graft polymer by combination with cellulose radicals can be estimated by measuring the grafting efficiency, as indicated in equation (62). Grafting efficiency and initiation efficiency take the same value in this type of polymerization.

CONCLUSIONS

The heterogeneous graft polymerization of vinyl monomers on cellulose initiated by ceric ion has been extensively studied, but only partially understood. In this report, an effort has been made to gain some insight into this complex polymerization reaction.

An approach has been made to the heterogeneous nature of the polymerization reaction, grafting site at cellulose, grafting initiation, homopolymerization initiation and termination of the radical chains.

Two polymerization mechanisms have been proposed for the heterogeneous graft polymerization on cellulose: one is based on the addition of the monomer to the cellulose radicals formed by the ceric ions, and the other is based on the combination reaction of synthetic polymer radicals and cellulose radicals. The former mechanism is proposed for electron-poor olefins and the latter for electron-rich olefins. The mechanisms given for grafting on cellulose are easily extended to other (poly)hydroxylic substrates and homogeneous systems.

Appropriate expressions relate some reaction parameters, which characterize the reaction polymerization and the polymer obtained, with the reaction variables.

Knowledge of the polymerization reaction will allow one to design the cellulose copolymer: block or graft copolymer, molecular weight, nature of the end-group of the synthetic polymer chains and crosslinking of cellulose by the synthetic polymer.

REFERENCES

1 Ho, T.-L. *Synthesis* 1973, 347
2 Richardson, W. H. in 'Oxidation in Organic Chemistry' (Ed. K. B. Wiberg), Academic Press, New York, 1965, Ch. IV
3 McDowall, D. J., Gupta, B. S. and Stannett, V. T. *Prog. Polym. Sci.* 1984, **10**, 1
4 Morin, B. P., Breusova, I. P. and Rogovin, Z. A. *Adv. Polym. Sci.* 1982, **42**, 139
5 Hebeish, A. and Guthrie, J. T. 'The Chemistry and Technology of Cellulosic Copolymers', Springer-Verlag, Berlin, 1981
6 'Graft Copolymerization of Lignocellulosic Fibers' (Ed. D. N.-S. Hon), ACS Symp. Ser. 187, American Chemical Society, Washington, DC, 1982
7 Bhattacharyya, S. N. and Maldas, D. *Prog. Polym. Sci.* 1984, **10**, 171
8 Samal, R. K., Sahoo, P. K. and Samantaray, H. S. *J. Macromol. Sci.-Rev. Macromol. Chem.* (*C*) 1986, **26**, 81
9 Mino, G., Kaizerman, S. and Rasmussen, E. *J. Am. Chem. Soc.* 1959, **81**, 1494
10 Katai, A. A., Kulshrestha, V. K. and Marchessault, R. H. *J. Polym. Sci.* (*C*) 1963, **2**, 403
11 Hintz, H. L. and Johnson, D. C. *J. Org. Chem.* 1967, **32**, 556
12 Kulkarni, A. J. and Mehta, P. C. *J. Appl. Polym. Sci.* 1968, **12**, 1321
13 Pottenger, C. R. and Johnson, D. C. *J. Polym. Sci.* (*A-1*) 1970, **8**, 301
14 Arthur, J. C. Jr, Baugh, P. J. and Hinojosa, O. *J. Appl. Polym. Sci.* 1966, **10**, 1591
15 Kurlyankina, V. I., Molotkov, V. A., Koz'mina, O. P., Khripunov, A. K. and Shtennikova, I. N. *Eur. Polym. J., Suppl.* 1969, 441
16 Duke, F. R. and Forist, A. A. *J. Am. Chem. Soc.* 1949, **71**, 2790
17 Duke, F. R. and Bremer, R. F. *J. Am. Chem. Soc.* 1951, **73**, 5179
18 Ogiwara, Y., Ogiwara, Y. and Kubota, H. *J. Polym. Sci.* (*A-1*) 1968, **6**, 1489
19 Mino, G., Kaizerman, J. and Rasmussen, E. *J. Polym. Sci.* 1959, **39**, 523
20 Ogiwara, Y., Ogiwara, Y. and Kubota, H. *J. Polym. Sci.* (*A-1*) 1967, **5**, 2791
21 Warma, D. S. and Narasimhan, V. *J. Appl. Polym. Sci.* 1972, **16**, 3325
22 Gaylord, N. G. and Anand, L. C. *J. Polym. Sci., Polym. Lett. Edn.* 1972, **10**, 285
23 Graczyk, T. and Hornof, V. *J. Macromol. Sci.-Chem.* (*A*) 1988, **25**, 1633
24 Imai, Y., Masuhara, E. and Iwakura, Y. *J. Polym. Sci.* (*B*) 1970, **8**, 75
25 Hebeish, A. and Mehta, P. C. *J. Appl. Polym. Sci.* 1968, **12**, 1625
26 Fernández, M. J., Casinos, I. and Guzmán, G. M. *Makromol. Chem.* 1990, **191**, 1287
27 Narita, H., Okimoto, T. and Machida, S. *Makromol. Chem.* 1974, **175**, 111
28 Takahasi, T., Nagata, M., Hori, Y. and Sato, I. *J. Polym. Sci., Polym. Lett.* 1967, **5**, 509
29 Trahanovsky, W. S., Young, L. H. and Bierman, M. H. *J. Am. Chem. Soc.* 1969, **34**, 869

30   Fernández, M. J., Casinos, I. and Guzmán, G. M. *J. Polym. Sci., Polym. Chem. Edn.* 1990, **28**, 2275

31   Doba, T., Rodehed, C. and Rånby, B. *Macromolecules* 1984, **17**, 2512

32   Fernández, M. J., Casinos, I. and Guzmán, G. M. *J. Polym. Sci., Polym. Chem. Edn.* 1990, **28**, 2303

33   Fleming, I. 'Frontier Orbitals and Organic Chemical Reactions', Wiley-Interscience, New York, 1976

34   Giese, B. *Angew. Chem. Int. Edn. Engl.* 1983, **22**, 753

35   Fernández, M. J., Casinos, I. and Guzmán, G. M. *J. Macromol. Sci.-Chem. (A)* 1990, **27**, 969

36   Gaylord, N. G. *J. Macromol. Sci.-Chem. (A)* 1976, **10**, 737

37   Sheldon, R. A. and Kochi, J. K. 'Metal-Catalyzed Oxidations of Organic Compounds', Academic Press, New York, 1981, p. 34

38   Fernández, M. J., Casinos, I. and Guzmán, G. M. *J. Appl. Polym. Sci.* 1991, **42**, 767

39   Baciocchi, E., Rol, C., Sebastiani, G. V. and Zampini, A. *J. Chem. Soc., Chem. Commun.* 1982, 1045

40   Fernández, M. J., Casinos, I. and Guzmán, G. M. *J. Appl. Polym. Sci.* 1990, **41**, 2221

41   Leza, M. L., Casinos, I. and Guzmán, G. M. *Br. Polym. J.* 1990, **23**, 341

42   Fernández, M. J., Casinos, I. and Guzmán, G. M. *J. Macromol. Sci.-Chem. (A)* 1990, **27**, 947