

CHEMICAL MECHANISMS IN THE GRAFTING OF CELLULOSE

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INTRODUCTION

The detailed mechanism of the various processes used in grafting synthetic polymers onto cellulose is not always known. The suggestions that have been made are based on a comparison with what is known of similar reactions with low molecular weight model compounds, and are of necessity highly speculative. The discussion will be restricted to polymerization and grafting initiated by radicals.

Before discussing mechanisms of grafting, some general remarks are in order.

Physical conditions affecting grafting

Until comparatively recently, most attempts to achieve grafting onto cellulose gave poor results. The reason for the greater success of later work is frequently related to the physical rather than the chemical conditions. Most of the work has been done with fibres and films, and it is now realized that swelling is an important pre-requisite to render the system accessible to monomer. Although cellulose does not swell spontaneously in most organic liquids, it can be made to hold large amounts of these liquids if water is stepwise removed, first by alcohol-water mixtures of gradually increasing alcohol content and, subsequently, by the organic liquid in question (*solvent-exchange*).

However, essential though this swelling may be for the penetration of the monomer, this is not the only factor of importance. Swollen films or fibres are systems in which the cellulose concentration is very high. As a result, the cellulose can compete successfully with monomer or with other compounds to give reactions that lead to grafting. It is believed, for example, that the reaction between cellulose and hydroxyl radicals falls in this category (see below).

The problem of swelling and accessibility brings up another question which sometimes may be a determinative factor in grafting experiments: the rôle of diffusion. This has not been studied systematically, but there are indications that under certain conditions diffusion can be rate controlling¹.

The possible rôle of swelling and diffusion will often render the quantitative interpretation a very difficult task. Even if none of the reactions is diffusion controlled, the composition of the fibre or film changes gradually as grafting proceeds, and the solubility of the compounds participating in the process

will likewise change. From this point of view, studies in homogeneous solutions are preferable, but in practice this is not always possible.

Another conclusion which may be drawn is that the process of grafting onto paper is not necessarily wholly comparable to that of grafting onto swollen cellophane or rayon. The grafting onto paper fibres may be much more in the nature of a surface phenomenon.

Proof of grafting

When the reaction has taken place in a homogeneous solution, proof of chemical grafting must often be based on time-consuming fractionations to separate the graft copolymer from the homopolymer. In this respect, the use of fibres or films has an advantage. One extracts with a liquid which is a solvent for the homopolymer, then dries, and considers the weight increase as a measure of grafting. It is clear, however, that this is permissible only when all the homopolymer can be removed by extraction. This is seldom true, and it is probably less true when the weight increase is larger than when it is slight.

A number of qualitative tests can be applied, however, to show that the product contains graft copolymer, although they do not give us quantitative information about the ratio of graft to homopolymer. In these tests it is recommendable, and sometimes essential, to compare the properties of the product believed to be a graft, with those of a physical mixture of the two types of macromolecules. This mixture should have the same over-all composition as the graft and, if at all possible, the average molecular weight of the polymer grafted on to the cellulosic material should be the same as that of the homopolymer in the physical mixture. One attempt to meet this last requirement is to extract the homopolymer from the fibre or film onto which grafting took place; however, even this may not always be sufficient guarantee that the desired goal has been reached, because if the extraction of the homopolymer is incomplete it is likely that the molecules with relatively low molecular weight were extracted in preference to those of high molecular weight.

Easily accessible properties of the graft copolymer which may be compared with those of a physical mixture are the intrinsic viscosity and the concentration dependence of the viscosity². Any difference between the two products is indicative of grafting. Another property is the solubility. By way of example, mention is made of the following experiments³.

Acrylamide was grafted onto cellophane. The product was dissolved in cuprammonium, and the solution acidified. The amount of precipitate formed was always larger than the amount of cellulose present, and infra-red absorption showed the presence of polyacrylamide. When the same experiment was performed with a physical mixture of cellulose and polyacrylamide of the same composition, only the cellulose was precipitated. The experimental data are shown in *Figure 1*.

Sometimes the grafting process itself shows features which are incompatible with the assumption that only homopolymer is formed. For example, if the rate at which the weight of the film increases becomes gradually lower with increasing time while the homopolymerization outside the film shows no such tendency, this does not constitute a proof, but it can sometimes be

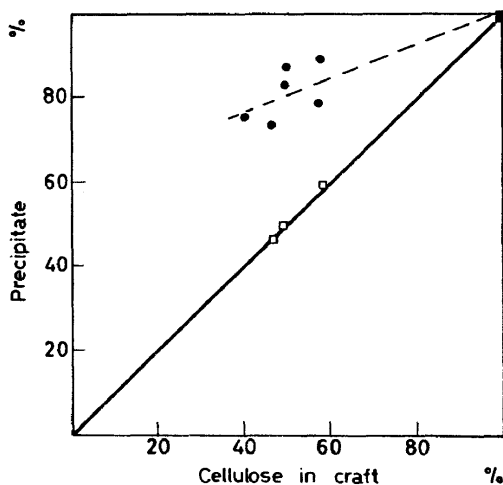


Figure 1. Weight of precipitate after acidifying a cuprammonium solution of cellulose-polyacrylamide, as a function of the amount of cellulose in the system; ●: graft copolymer; □: physical mixture

considered an indication of grafting. In one case² the failure to observe a weight increase in the presence of acetone could be considered as evidence for grafting in the absence of acetone, because the homopolymerization takes place in either case.

Molecular weight of grafted polymer

Data concerning the chain length of the polymers grafted onto cellulose are very scarce. The polystyrene grafted onto mercapto-ethylated cellulose acetate films through chain transfer was shown to have a molecular weight of more than 1 million⁴, which means that even when the weight increase is 100 per cent and is entirely due to grafting, only 1 out of more than 5,000 glucose units carries a polystyrene side chain. Similar conclusions can be drawn from the results obtained by Rapson⁵ and by Kobayashi⁶ in their experiments on γ -ray-induced grafting. This discouraging result raises the question of whether the product was a graft copolymer in the usual sense. It could mean that grafting occurred only at the ends of cellulose chains, in which case the product should, more properly, be called a block copolymer.

A possible explanation of this high molecular weight is a reduction in the rate of termination due to the low mobility of the polystyrene chain radicals inside the film or fibre.

HIGH ENERGY IRRADIATION

Gamma irradiation has been applied to a very large number of polymer-monomer systems. Applications to cellulose were not very successful at first, owing to the degradation inflicted on the cellulose. Recent work has shown, however, that this degradation can be suppressed to a considerable degree if care is taken that the cellulose is accessible to the monomer⁵⁻¹⁰.

This is a typical example of the rôle of swelling and solvent-exchange mentioned in the introduction.

Judging from what is known of the effect of high energy irradiation on other polymers, it may be assumed that hydrogen atoms are abstracted from the cellulose. If this takes place in the presence of a monomer, grafting can occur immediately. It is also possible, however, to use the pre-irradiation technique: irradiation in the absence of monomer, followed by immersion in a solution of the monomer⁶. This shows that some of the radicals formed on the cellulosic backbone are long-lived; the pre-irradiation method, however, is more likely to cause degradation.

It should also be mentioned that to the author's knowledge no proof has so far been given that the products obtained by γ -irradiation of cellulose are true grafts, although this may be considered as very likely.

Although direct hydrogen abstraction is a likely process, it must still be considered an hypothesis, and it is almost certain that, in the presence of water, hydroxyl radicals play a prominent part. Leavitt¹¹ has observed crosslinking of cellulose derivatives in aqueous solutions when exposed to γ -irradiation, and has formulated the hypothesis that the first step in this process is the production of OH radicals from water. It is believed that these OH radicals subsequently abstract hydrogen from the cellulosic macromolecules. The same mechanism has been postulated to explain the effect of γ -irradiation on gelatine¹², which produces crosslinks in the presence, but not in the absence, of water.

This raises a question in connection with the effect of OH radicals produced by the reaction between ferrous ions and hydrogen peroxide (see below). It may be expected that these, too, give rise to some crosslinking, although evidence for this has not been found.

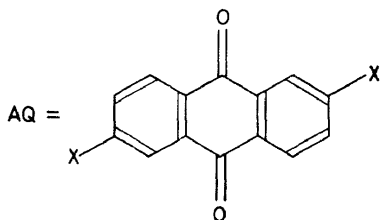
PHOTOSENSITIZERS

Polymerization may be initiated by low energy photons if the irradiation takes place in the presence of a photosensitizer. Photosensitizing action has been found in well-known radical producing catalysts such as 2-azo-bis-isobutyronitrile¹³ and benzoylperoxide¹⁴. Most studies have been done, however, with dyes, in particular with dyes that have phototendering activity, *i.e.* they cause degradation of cellulose fibres when these fibres are exposed to light. It is now fairly generally accepted that this phototendering action is due to radical reactions. A wealth of interesting data can be found in the proceedings of a symposium¹⁵. A recent discussion was given by Bridge¹⁶.

The mechanism of phototendering has been elucidated to a large extent by work with low molecular weight model compounds¹⁷. The reaction between the photo-excited dye molecule and an alcohol produces radicals, which may then initiate the polymerization of a monomer. If the alcohol is itself a polymer, this polymerization may produce a graft.

Application of photosensitizers to polymerization and grafting

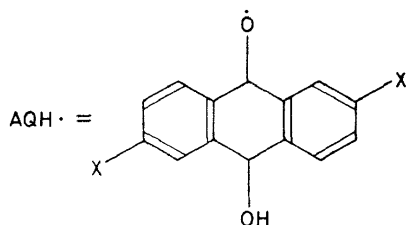
Detailed studies of this type of polymerization and grafting have been carried out by Geacintov^{3, 18}, using anthraquinoid dyes of the type



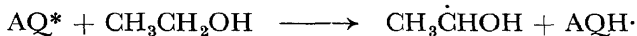
where X was SO_3Na when a water-soluble dye was desired, but CH_3 in the case of organic solvents. This latter compound will be abbreviated MeAQ. The reaction between the excited dye molecule and an alcohol is¹⁷



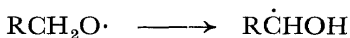
where



It is usually assumed that the hydrogen abstraction takes place from the carbon atom carrying the OH group. For example, with ethanol,



It is of some interest to note, however, that the rate of photopolymerization of styrene in benzene, in the presence of MeAQ, was increased to an even greater extent by t-butanol than by s-butanol, n-butanol or ethanol³. Since no α -hydrogen is present in the t-butanol, this suggests that the $(\text{CH}_3)_3\text{CO}\cdot$ radical is formed, which perhaps decomposes subsequently to acetone and the methyl radical¹⁹. This hydrogen abstraction from the oxygen atom may be the normal process if the anthraquinone, *via* its carbonyl groups, complexes with the hydroxyl group of the alcohol. If α -hydrogen is present, the radical formed may be expected to rearrange readily:



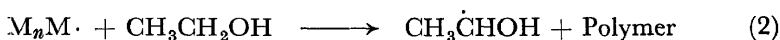
Some studies were made with carbon-14 labelled ethanol to measure the amount of alcohol in the polymer produced. The monomer was methylmethacrylate (MMA) or styrene (Sty) in benzene, to which varying amounts of radioactive alcohol were added. The photosensitizer was the dye MeAQ, and the light-source a GE-H-400 E-1 400 Watt mercury lamp, of which only the light of wavelengths larger than $320\text{ m}\mu$ was allowed to reach the reaction vessel. By way of comparison, the photosensitizer, in some experiments, was replaced by azo-*bis*-isobutyronitrile (ABN).

Table 1. Photo-initiated polymerization of methylmethacrylate (MMA) and of styrene (Sty) in the presence of 20 vol per cent ethanol; N is the number of polymer chains per ethanol molecule in the polymer

Monomer	Initiator	t (h)	Conversion (%)	D.P.	N
MMA	MeAQ	3	24	80	5
MMA	ABN	3	26	120	220
Sty	MeAQ	20	15	70	6
Sty	ABN	20	18	70	53

It was found that the photosensitized polymerization of MMA was four to five times faster in the presence of 20 vol. per cent ethanol than in the absence of ethanol. No accelerating effect of the alcohol was observed when ABN was used as initiator.

The degree of polymerization of the polymer was measured, and the number of polymer chains per alcohol molecule found in the polymer was calculated from the radioactivity, with the results shown in Table 1. The small amount of ethanol found in the polymer when initiating with ABN is probably due to chain transfer from polymer radicals to ethanol, with subsequent initiation by the alcohol radical.



The poly-MMA formed by MeAQ-sensitized photo-initiation contains only one molecule of alcohol for every 5 chains. Taking into account that for this polymer 75 per cent of the termination is by disproportionation and 25 per cent by combination, it follows from a simple calculation that one out of about 6 chains is initiated by addition of an alcohol radical. This neglects the possible termination by alcohol radicals. In the polymerization of styrene, termination is mainly by combination and one must conclude that one out of about 12 chains is initiated by addition of alcohol. Although these figures are considerably lower than expected, the results show convincingly that alcohol radicals are formed and play a rôle in the initiation.

It has not been possible to describe the kinetics of the process in a satisfactory manner. If the rate of polymerization is represented by an equation of the form:

$$-dM/dt = kI^m D^n A^p M^q, \quad (4)$$

where I is the light-intensity, D the dye concentration, A the alcohol concentration and M the monomer content, it is found that the exponent n is about 0.3 at low alcohol content but decreases to half this value when A becomes large. The value of m is only 0.25, p is about 0.55 and q about 1.3. This behaviour suggests that the kinetics are complex. Kinetic schemes can be developed that predict $m = 0.5$, $n = 0.5$, p between zero and 0.5, and

$q = 1$. Other schemes lead to $m = 0$, $n = 0$, $p = 1$ and $q = 2$. The actual behaviour may be due to a mixture of mechanisms, but the details are as yet so speculative that it is considered premature to enter into this matter any further.

If the behaviour of ethanol is indicative of that of cellulose, reaction (3) may lead to a graft copolymer. The kinetics of this grafting were found to be as complicated as that of the homopolymerization. They were further complicated by the fact that grafting took place in a film of cellophane or cellulose acetate immersed in the reaction mixture. Evidence of grafting was obtained by the techniques described in the introduction.

REDOX SYSTEMS

The reaction (1) between the dye and the alcohol is an example of an oxidation-reduction reaction that involves radical species. Many oxidation-reduction reactions are of this type, and some of them have been used to initiate grafting.

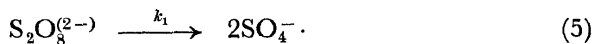
Persulphate initiation

Grafting on to cellophane has been achieved through initiation by persulphate ions. Some experiments were done with cotton in acrylonitrile vapour by Haydel *et al.*²⁰, but these authors did not investigate whether real grafting occurred and referred to the process as deposition in and coating of the cotton. There is little doubt that the product obtained by Chaudhuri²¹ who used cellophane instead of cotton was a graft copolymer; this was proved by some of the methods described in the introduction.

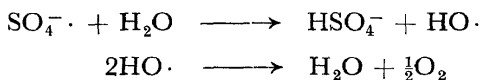
It is believed that the conditions for grafting in Chaudhuri's experiments were particularly favourable. The cellophane was soaked in an aqueous solution of persulphate, and the wet film immersed in hot acrylonitrile. The monomer diffuses into the film, but very little of the catalyst diffuses into the monomer because the solubility in the monomer is low. Consequently, little if any homopolymer is formed outside the film. Inside the film the concentration of cellulose is high, which is likely to favour reaction of cellulose with persulphate radicals (or with hydroxyl radicals if these are formed).

Mechanism of the initiation by persulphate

Kolthoff and Miller²² have shown that persulphate ions in aqueous solution, when heated, decompose according to two mechanisms, only one of which is believed to produce radicals:



This is a first-order reaction. The sulphate radicals formed may react with water to produce hydroxyl radicals and, finally, oxygen,



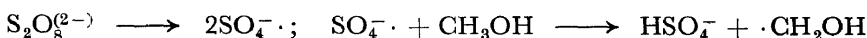
Polymerization may thus be initiated either by $\text{SO}_4^{\cdot-}$ or by $\text{OH}\cdot$. That $\text{SO}_4^{\cdot-}$ radicals do take part in the initiation is shown by the fact that sulphur occurs in the polymer^{23, 24}.

Simultaneous with process (5) there takes place a decomposition of the persulphate which does not produce radicals. The rate of this second decomposition is proportional to the concentration of hydrogen ions and is markedly affected by ionic strength. The total rate constant for the decomposition is, therefore,

$$k = k_1 + k_2(\text{H}^+)$$

When studying the mechanism of oxidation or initiation by persulphate, it is convenient to keep the hydrogen ion concentration below 10^{-4}M , because under these conditions $k_2(\text{H}^+)$ is negligible compared with k_1 .

The decomposition of persulphate has been studied also in the presence of alcohols. As early as 1903 Marie and Bunel²⁵ published data to show that methanol accelerates the persulphate decomposition considerably. This has been confirmed by Kolthoff, Meehan and Carr²⁶, who proved that the reaction is not between the persulphate ion and methanol, but between the sulphate ion radical and methanol,



This is proved by the fact that the rate of decomposition of persulphate is reduced to the same low value as when allyl acetate is added in the absence of alcohol. The accelerating effect of the alcohol is, therefore, attributed to a reaction with the CH_2OH radicals,



On addition of allyl acetate, the $\text{SO}_4^{\cdot-}$ radical reacts with the monomer rather than with the alcohol, so that no CH_2OH radicals are formed and reaction (6) can no longer take place. This scheme is confirmed by the fact that formaldehyde is formed in the absence, but not in the presence of, allyl acetate.

Likewise, there is no direct reaction between the persulphate and the monomer. It should be noted, however, that in this respect Kolthoff's results are not in agreement with those of Bartlett and Nozaki²⁴, who found that the decomposition of persulphate is accelerated by allyl acetate.

It is clear that if cellulose reacts in the same manner as methanol, no grafting would take place, because the $\text{SO}_4^{\cdot-}$ radicals would react with monomer rather than with cellulose. Chaudhuri's experiments²¹, which indicate that grafting did occur, would thus appear to constitute a discrepancy. However, several factors must be borne in mind.

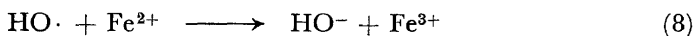
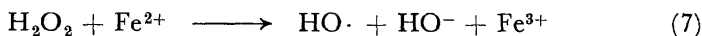
(i) The results obtained by Kolthoff *et al.* suggest that the result of the competition between monomer and cellulose will decide whether grafting takes place. If cellulose is present in excess—which may be the case in a swollen film or fibre—a substantial amount of $\text{SO}_4^{\cdot-}$ (or $\text{OH}\cdot$ if $\text{SO}_4^{\cdot-}$ reacts with water) may attack the cellulose.

(ii) For the same reason the result of the experiment will depend on the nature of the monomer.

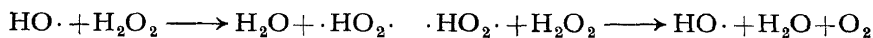
(iii) We have no guarantee that all alcohols react the same way. Preliminary results recently obtained at Syracuse in a study of persulphate decomposition in the presence of pinacol appear to indicate that the rate of this decomposition is independent of the pinacol concentration, although oxidation of the pinacol does take place. It is obvious, therefore, that further experiments are needed.

Initiation by hydroxyl radicals

A well-known example of an oxidation-reduction reaction in which radicals are produced is the decomposition of hydrogen peroxide by ferrous ions, for which Haber and Weiss²⁷ developed the following scheme:



This is accompanied by a chain reaction in which HO radicals decompose H_2O_2



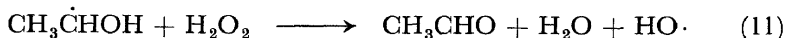
but, according to Kolthoff and Parry²⁸, this takes place to any appreciable extent only if H_2O_2 is present in large excess over ferrous ion.

Baxendale, Evans and Park²⁹ in a classical study showed that the HO radicals produced in reaction (7) can initiate polymerization. As the monomer concentration is increased, reaction (8) is suppressed to an ever-increasing extent until, finally, at high monomer content, all the OH radicals react with the monomer to produce polymer.

It is been claimed³⁰ that the reaction between H_2O_2 and Fe^{2+} in the presence of cellulose and a monomer produces a graft copolymer, and the reaction which is believed to be responsible for this is abstraction of hydrogen:



This is based on known reactions with low molecular weight alcohols. According to Kolthoff and Medalia³¹, for example, OH radicals in the presence of hydrogen peroxide are capable of oxidizing ethanol in a chain reaction, as follows:

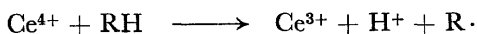


Here again it was shown that acrylonitrile can capture all the OH radicals, so that in the presence of this monomer not only reaction (8) but also (10) is suppressed. Hence, if cellulose gives essentially the same reaction as ethanol, *i.e.* reaction (10), it will have to compete with the monomer while, at the same time, for grafting to occur, the cellulosic radical formed must be able to react with monomer. It is clear that under these circumstances

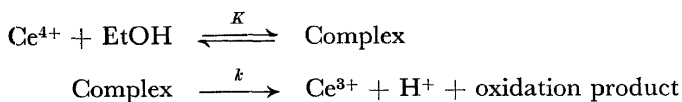
the yield of graft copolymer must depend to a large extent on the conditions of the experiment. The best technique appears to be to first expose the cellulose to a solution of a ferrous salt. The ferrous ions are adsorbed by the cellulose, and the subsequent reaction with hydrogen peroxide in the presence of a monomer will, therefore, take place in close proximity to cellulose molecules at a large concentration of these molecules. It is to be expected that factors favouring the adsorption of the ferrous ions (for example the presence of carboxyl groups in the cellulose) will affect the grafting. For the same reason, one may expect that more polymer will be deposited in (and/or grafted on to) the cellulose in neutral media than in acid media.

Salts of cerium (IV)

An oxidizing agent that has received much attention in recent years is the ceric ion. The reaction by which this ion produces radicals when reacting with certain organic compounds is believed to be



Quantitative studies appear to have been made mainly with alcohols, although many other organic compounds are likewise susceptible to this oxidation. There is much evidence³² that the oxidation of alcohols proceeds through the disproportionation of a co-ordination complex. The evidence for this is partly from absorption spectra and partly from the kinetics of the oxidation itself. Either method has been used, also, to obtain the instability constants of the complexes involved. Ardon³³, for example, described the oxidation of ethanol in aqueous solutions of ceric perchlorate by the reactions



The alcohol was present in excess. If the complexing equilibrium is established rapidly, one should expect that the concentration c of the complex obeys the equation

$$c = KA([\text{Ce}] - c), \text{ or } c = (1 + KA)^{-1}KA[\text{Ce}]$$

where A represents the alcohol concentration and $[\text{Ce}]$ the total ceric content. The rate at which ceric is reduced will be kc or $k^1[\text{Ce}]$, where

$$k^1 = kKA(1 + KA)^{-1}$$

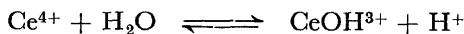
This means that k and kK can be derived from a plot of $1/k^1$ v. $1/A$. The linearity of this plot was confirmed by experiment, and the composition of the complex was confirmed independently by spectrophotometric measurements.

Similar studies with other systems, in which the ethanol was replaced by other compounds^{32, 34} or the cerium (IV) by other metals³⁵ have led to similar results.

However, the analysis of the data is not always simple. This is due to the fact that the aqueous solutions of ceric salts, even in the absence of alcohol, are quite complex, owing to the strong tendency of ceric ions to form complexes with anions. In aqueous solutions of ceric sulphates the following species have been postulated³⁶⁻³⁸: CeSO_4^{2+} , $\text{Ce}(\text{SO}_4)_2$ and $\text{Ce}(\text{SO}_4)_3^{2-}$, and the stability constants of these complexes have been estimated. Ceric nitrate solutions show less complexing, and the perchlorate anion does not complex with Ce(IV) to any appreciable extent. This does not mean, however, that aqueous solutions of ceric perchlorate contain free cerium (IV) ions. According to Hardwick and Robertson³⁶, Sherrill³⁹ and Offner⁴⁰, the ceric ions in these solutions, even at quite low pH, are complexed with hydroxyl ions to CeOH^{3+} and $\text{Ce}(\text{OH})_2^{2+}$.

A further complication arises from the fact that dimers occur and—depending on pH and on concentration—trimeric, tetrameric and other polymeric ions.

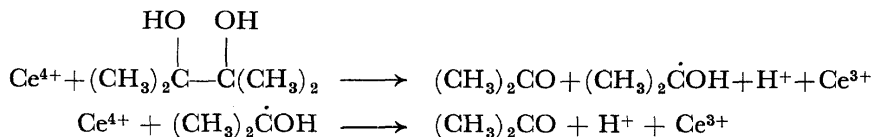
A few examples may illustrate the situation. The stability constant of the ceric-ethanol complex³³ depends on pH. This dependence was explained by Ardon³³ on the basis of the equilibrium



This same equilibrium was used by Hargreaves and Sutcliffe³⁴ to explain the effect of HClO_4 content on the rate of oxidation of formaldehyde by ceric perchlorate. It leads to the prediction that the reciprocal of the rate constant for this oxidation is a linear function of the reciprocal of the acid concentration, in accordance with the experimental results. Addition of sodium perchlorate to ceric perchlorate solutions has only a small effect on the rate of oxidation, indicating that perchlorate ions do not complex with Ce(IV). Addition of neutral sulphate to ceric sulphate solutions, however, reduces the rate of oxidation. On the other hand, addition of sulphuric acid to ceric sulphate may lead to *increased* oxidation rates. Hargreaves and Sutcliffe³⁴ explained this by postulating a special complexing scheme involving both sulphate ions and hydrogen ions. It will be clear from these data that the quantitative results in any one series of experiments may depend strongly on the concentrations of the various species present.

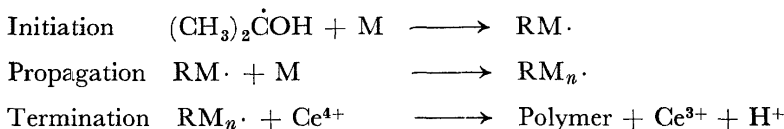
Initiation by cerium (IV) ions

A study which is of great interest in the understanding of grafting is the oxidation of pinacol by ceric sulphate, which was published by Mino, Kaizerman and Rasmussen⁴¹. The ceric salt concentration varied from about 2×10^{-3} to 10×10^{-3} M, the pinacol concentration from 0.03 to 0.16M. The rate at which Ce(IV) was reduced was proportional to both the ceric and the pinacol content, and 2 moles of acetone were produced for every 2 moles of Ce(IV) reduced. The reactions describing this are:



in which the first of the two reactions is rate determining.

In the presence of (excess) acrylamide, only one mole of acetone was produced per mole of Ce(IV) reduced. Since it is known from kinetic studies of the polymerization, that the termination step involves reaction with a ceric ion, the following reactions are believed to take place ($M = \text{monomer}$):

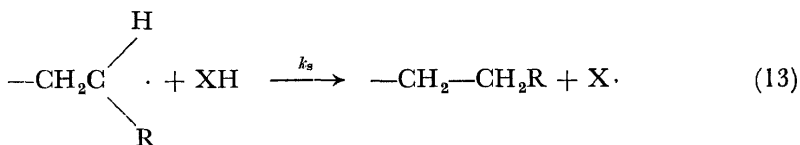
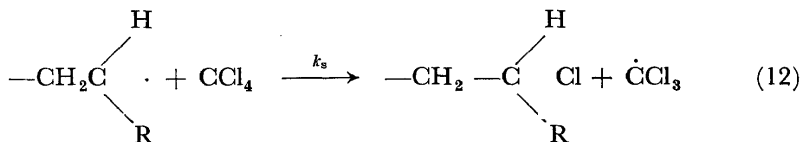


This termination could conceivably consist of oxidation to an hydroxyl end group in the polymer chain.

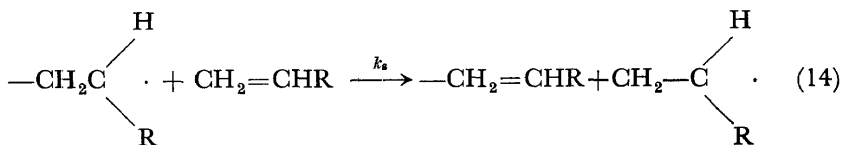
It is clear that if the initiation step involves addition of the alcohol radical, and assuming that cellulose reacts similarly, one may expect grafting⁴². The method has been used to graft a number of monomers onto paper, and both the tensile strength and the burst strength of the paper were shown to be improved considerably⁴³. At the same time the rate of water absorption was decreased, although the equilibrium water absorption per unit weight of cellulose did not change.

CHAIN TRANSFER

Growing polymer radicals are capable of transferring the radical character to certain compounds called chain transfer agents. The process is called chain transfer; it terminates the polymer chain and leaves the chain transfer agent in the form of a radical that may subsequently initiate another polymerization reaction. In many cases chain transfer takes place by abstraction of a hydrogen or halogen atom, *e.g.*:



but in chain transfer to monomer, hydrogen donation is more likely than hydrogen abstraction:

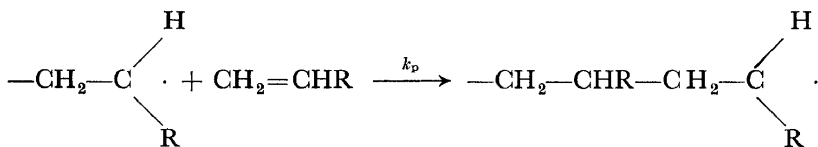


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Since in a polymerization process the chain transfer agent has to compete with the monomer, the quantity that determines the relative frequency of chain transfer is the "chain transfer constant"

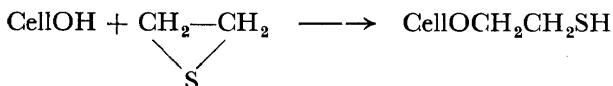
$$C_s = k_s/k_p \quad (15)$$

where k_s is the rate constant for the bimolecular reaction of type (12), (13) or (14) and k_p the propagation rate constant for the bimolecular addition reaction between growing polymer radicals and monomer molecules:



Clearly, if the chain transfer agent is itself a polymer, the polymerization, initiated by the radical formed in the chain transfer process, may lead to a graft copolymer. In the earliest attempts to apply this to cellulosic compounds, halogen-substituted cellulose⁴⁴ were used, but the yields were very low. As will be discussed below, chain transfer with subsequent grafting takes place to some extent even in the absence of halogen. The failure to produce graft from the halogen-substituted cellulose must therefore be attributed to the conditions used in the experiments.

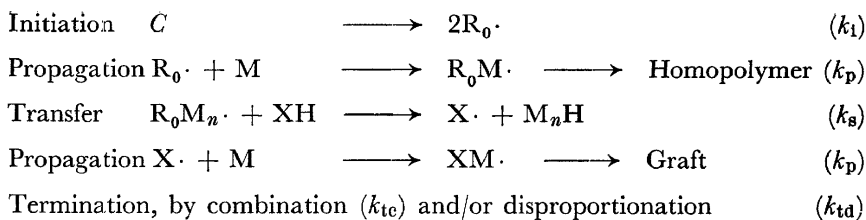
Mercaptans are known to show particularly high chain transfer constants, and this has led to several attempts to introduce SH groups in polymers. The methods proposed⁴⁵ were complicated, but recently Chaudhuri² succeeded in preparing mercapto-ethylated films of cellophane and cellulose acetate by an addition reaction with ethylene sulphide:



This reaction takes place readily when the cellulose acetate is swollen in benzene. To achieve the same result with cellophane, it is necessary to first solvent-exchange the water, *via* alcohol, by benzene. After washing the mercapto-ethylated film with benzene, styrene was added and its polymerization initiated by azo-*bis*-isobutyronitrile at 65°. The rate of grafting was of the order of 10 weight per cent per hour.

Kinetics of grafting through chain transfer

A quantitative treatment of the kinetics of grafting by chain transfer in a homogeneous system was given by Voeks⁴⁶ and by Fox *et al.*⁴⁷. Assuming that the polymerization is initiated by the decomposition of some radical-producing catalyst, C , the main processes to be considered are (M = monomer):



In the case under consideration, XH is the cellulosic macromolecule. The usual approximation, *i.e.* that the rate at which the various radicals react with monomer, chain transfer agent and each other is independent of the nature of the radical, is made. Under these conditions the total steady state concentration of radicals is found to be the same as in the absence of chain transfer agent:

$$[R_{tot} \cdot] = a = (k_i f c / k_t)^{\frac{1}{2}} \quad (16)$$

where c is the catalyst concentration and f the efficiency of initiation; $k_t = k_{tc} + k_{td}$. The rate of monomer consumption is therefore likewise independent of the presence of chain transfer agent:

$$-dM/dt = k_p a M \quad (17)$$

while the chain transfer agent is consumed at a rate:

$$-d[XH]/dt = C_s k_p a [XH] \quad (18)$$

It follows from these equations that both M and $[XH]$ decrease exponentially with increasing time. The weight at which the weight G of graft copolymer increases is found to be:

$$\frac{dG}{dt} = m M_0 k_p a \exp(-k_p a t) \frac{x}{1+x} \left[1 - \frac{k_{tc}/k_t}{(1+x)^2} \right] \quad (19)$$

where

$$x = \frac{k_s [XH]_0}{2k_{ta}} \exp(-k_s a t) \quad (20)$$

m is the molecular weight of the monomer and the subscript zero indicates zero time.

In Chaudhuri's grafting experiments, the constant $k_s [XH]_0 / 2k_{ta}$ in equation (20) was very large compared to unity, so that the initial rate of grafting becomes

$$(dG/dt)_0 = m M_0 k_p a = B M_0 f^{\frac{1}{2}} c^{\frac{1}{2}} \quad (21)$$

B being a constant which is independent of M_0 and c . To compare equation (21) with the experimental data, it must be taken into account that the efficiency of the initiation, f , changes somewhat with the monomer concentration M_0 . It is assumed that this change was (relatively) the same as that outside the cellulose film. The result of the calculation is given in

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Figures 2 and 3. It could further be shown⁴ that the way in which grafting proceeds at later times is also in surprisingly good agreement with the theory. In fact, the agreement is better than could have been expected, and it is believed that this is partly fortuitous and due to a number of factors that partially compensate each other:

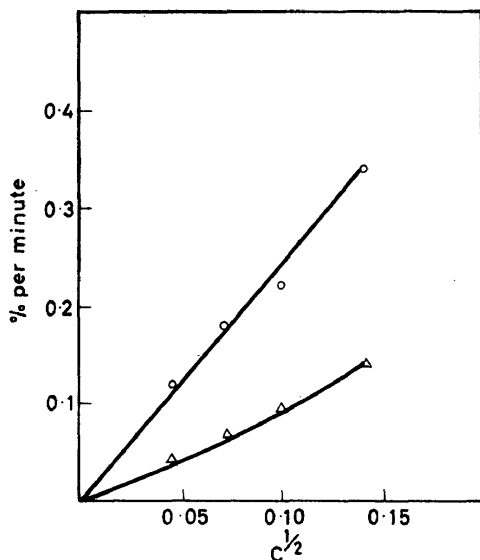


Figure 2. Initial rate of grafting due to chain transfer as a function of the square root of initiator concentration; ○: grafting; △: homopolymerization

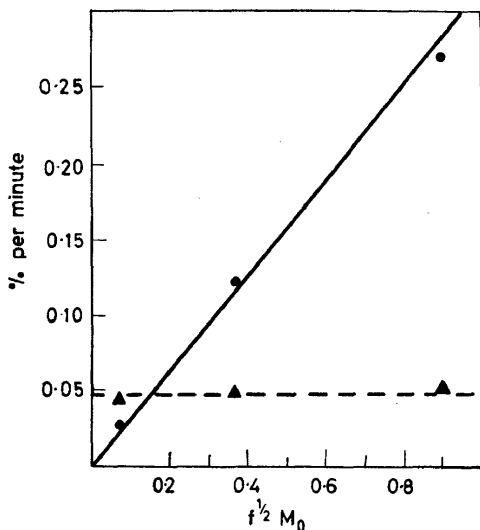


Figure 3. Initial rate of grafting due to chain transfer as a function of $M_0 f^{1/2}$ where M_0 is the monomer concentration and f the efficiency of the initiation; ●: grafting; ▲: homopolymerization

(i) The theory assumes that M_0 , $[XH]_0$ and all the rate constants can be treated as independent of time. In reality, as grafting proceeds, the composition of the film changes and the film material will become more and more compatible with both styrene and benzene.

(ii) The amount of grafting was identified with the weight increase after thorough extraction with benzene. Although the evidence for grafting was quite convincing, it is always accompanied by some homopolymerization, and it is doubtful whether all the homopolymer can be removed by extraction in those cases where the weight increase is large.

(iii) Perhaps most important of all is the observation which was made in later experiments. A substantial amount of grafting onto cellulose acetate film took place also in the absence of SH groups. Under the conditions of the experiments this amounted to about 20 per cent of the total grafting, and one must conclude that the chain transfer constant to be used in the equations is an average over different atoms.

On the basis of this result it is believed that the failure to observe grafting by chain transfer to halogen-substituted celluloses⁴⁴ was due to unfavourable experimental conditions.

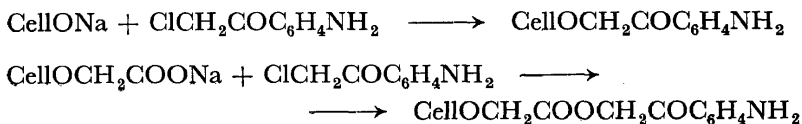
RADICAL PRODUCING SUBSTITUENTS IN THE CELLULOSIC MOLECULE

Other methods of producing radicals attached to cellulosic macromolecules have been suggested, and although they are less likely to become of practical interest than are the previously discussed procedures, they possess some very interesting features.

Ceresa⁴⁸ applied the process of mastication to cellulose derivatives. The cellulosic material is mixed with a monomer and then masticated under high shearing forces. In this process the cellulosic molecules are torn apart, and the newly formed chain ends have radical character. These ends may initiate polymerization, thus forming a block copolymer.

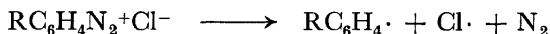
Whereas Ceresa's method produces radicals by mechanical forces, it is possible to achieve this also by chemical decomposition of radical-producing substituents. This has been done with peroxides and hydroperoxides of cellulose ethers⁴⁹, but it was found that these led to excessive homopolymerization and very little grafting. Kargin, Usmanov and Aikhodzhaev⁵⁰ reported on peroxidation of rayon by ozone, followed by grafting of styrene or acrylonitrile.

Richards⁵¹ used a method in which the number of radical-producing groups can be chemically controlled and easily determined. This consists of introducing amino groups through reaction of a halogenated amine with either a cellulose or the sodium salt of carboxymethylcellulose.

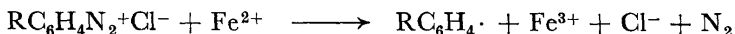


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The second product is an ester, the first an ether. By diazotizing, a diazonium salt is obtained which, on heating, produces radicals. A possible scheme for this is:



If this takes place in the presence of a monomer, one may obtain both homopolymer (initiation by $\text{Cl}\cdot$) and graft copolymer (initiation by $\text{RC}_6\text{H}_4\cdot$). This is interesting as it opens a possibility of suppressing the homopolymerization by the addition of ferrous ions which will react as follows:



Another interesting aspect of the method is the ease with which the grafted polymer chains can be removed by hydrolysis, if the grafting has been done through ester linkages. This has advantages for fundamental studies concerning the molecular weight of the grafted chains and the effect of the grafting on the molecular weight of the cellulose.

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