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Cellulose-Monomer Interaction and a Revised Mechanism for Graft Copolymerization

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ABSTRACT

Graft copolymerization of electron acceptor acrylic monomers on cellulose involves cellulose-monomer complexation. Cellulose acts as a matrix promoting high localized concentrations of donor-acceptor complexes in which uncomplexed monomer, normally an electron acceptor, behaves as a donor relative to the complexed monomer which has been converted to a stronger acceptor. The cellulose-monomer complexation influences both homopolymerizability and grafting efficiency, e.g. acrylonitrile (AN) and methacrylonitrile (MAN) in the presence of a catalyst and methyl methacrylate (MMA) in the absence of a catalyst. The presence of water, cupric ion, aldehydes, and CCl_4 influence the course of the uncatalyzed reaction. When a donor monomer is present, equimolar alternating rather than random, grafted and ungrafted copolymers are produced, e.g., styrene or butadiene with MMA, MAN, or AN, as a result of the formation of an ordered array of donor-acceptor complexes on the cellulose. The revised mechanism of polymerization involves the homopolymerization of the donor-acceptor complexes, irrespective of the nature of the initiator, and grafting results from termination of the propagating chains by coupling with radicals on the cellulose.

INTRODUCTION

Graft copolymerization of vinyl monomers onto substrate polymers is generally considered to involve the generation of reactive sites on the polymer, followed by the addition of monomer which propagates in a conventional manner. The reactive sites, e.g., radicals, may be formed on the polymer as a result of attack by a species derived from a catalyst, radiation, catalyst-polymer complexation, or chain transfer from a propagating chain arising from the homopolymerization of the monomer. However, it has recently been proposed that polymer-monomer interaction, particularly in the case of cellulose, plays a major role in graft copolymerization [1].

The present paper will examine the evidence for cellulose-monomer interaction in the preparation of ungrafted and grafted homopolymers and binary copolymers, and present a revised mechanism for the polymerization of vinyl monomers in the presence of cellulose.

ACCEPTOR MONOMER HOMOPOLYMERIZATION AND GRAFT COPOLYMERIZATION

Graft copolymerization onto cellulose in the presence of hydrogen peroxide, persulfate, ceric ion, and redox systems such as persulfate-bisulfite and hydrogen peroxide-ferrous ion, as well as with UV irradiation, is generally presumed to proceed through a conventional radical mechanism, i.e., initiation from a radical site generated on the cellulose, with no interaction between the monomer and the cellulose. Monomers which have been effectively grafted onto cellulose in the presence of these radical precursors include acrylamide, acrylonitrile, acrylic esters, and their methacrylic analogs. However, while these electron-acceptor monomers readily undergo radical-initiated polymerization, electron-donor monomers including styrene, butadiene, and vinyl chloride, which equally readily undergo radical-catalyzed polymerization, do not generally graft onto cellulose in the presence of the catalysts and under the conditions which are effective with the acceptor monomers. This argues against a conventional radical-initiated graft copolymerization and suggests a specific cellulose-acceptor monomer interaction.

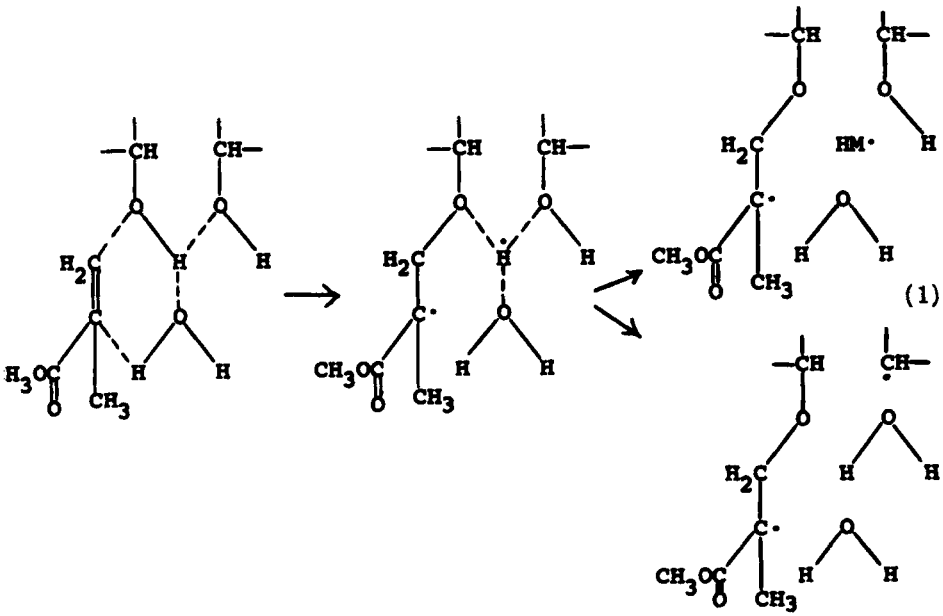
When methyl methacrylate is heated with cellulosic fibers such as cotton, rayon or hemp, or wood pulp at 90°C in an aqueous suspension in the absence of a radical initiator, graft copolymerization readily occurs. The graft copolymer is accompanied by high molecular weight poly(methyl methacrylate). The grafting and homopolymerization of methyl methacrylate occur in the presence of the fibers under conditions which yield negligible amounts of polymer in the

absence of the fibers [2, 3]. Styrene and acrylonitrile are not grafted to cellulose fibers under conditions which are effective for methyl methacrylate.

The graft polymerization of methyl methacrylate onto cellulose in the absence of initiator at 85°C can be carried out in water or a water-acetone mixture but does not occur in the absence of water, i.e., in pure methanol, acetone, benzene, dioxane, dimethylformamide, or tetrahydrofuran. The polymerization takes place in the dark as well as in the light [4].

The presence of hydroxyl groups and their location and steric arrangements all play an important role in the initiation mechanism. The polymers shown in Table 1 effectively initiate the homopolymerization and/or graft copolymerization of methyl methacrylate in the absence of an added initiator. Low molecular weight polyols and low or high molecular weight commercial poly(vinyl alcohol) and poly(vinyl acetate) are ineffective [5].

The mechanism proposed [3] for the initiation of the polymerization of methyl methacrylate in the presence of cellulose and water involves the formation of a complex between the polymeric –OH groups, water, and monomer:



(1)

The presence of oxygen promotes the polymerization of methyl methacrylate in the presence of cellulose-water [6-8]. Notwithstanding the care taken to exclude air or peroxides from the reaction

TABLE 1. Effective Substrates in Polymerization of Methyl Methacrylate

Cotton, rayon, hemp, paper, wood pulp
Starch, dialdehyde starch
Wool
Silk
Nylon
Partially formalized poly(vinyl alcohol)
Partially hydrolyzed poly(vinyl acetate)
Poly(methyl methacrylate-co-hydroxyethyl methacrylate)
Poly(methyl methacrylate-co-acrylic acid)
Poly(styrene-co-allyl alcohol)

mixture, the participation of oxygen, e.g., cellulose peroxide [8] or monomer peroxide [9], in the initiation step in the uncatalyzed reaction has been proposed.

Aldehyde groups generated by cleavage of the terminal hemiacetal groups of the cellulose chain have been suggested as sites for polymerization initiation and grafting [1]. The actual initiation has been attributed to peroxides or peracids generated by oxidation of the aldehydes or a specific donor-acceptor interaction between the aldehyde as donor and methyl methacrylate as acceptor [10].

The addition of glycolaldehyde or glyceraldehyde, model compounds for the terminal aldehyde groups in cellulose, to a cellulose-water-methyl methacrylate reaction mixture at 90°C results in increased polymerization. However, the grafting efficiency is decreased due to the competition of the added aldehydes with the aldehydes in the cellulose (Table 2) [10]. Acrylonitrile is not readily polymerized in the cellulose-water system at 90°C despite the addition of the aldehydes.

The presence of carbon tetrachloride promotes the rapid polymerization of methyl methacrylate in the presence of cellulose-water, although the extent of grafting is reduced [6, 11, 12]. The monomer conversion becomes quantitative in the presence of a small amount of CCl_4 at 85°C and then decreases as the CCl_4 content is increased further. No polymerization occurs in the presence of CCl_4 in the absence of water. Methyl acrylate also readily polymerizes at 85°C in the presence of cellulose, water, and CCl_4. However, the failure of acrylonitrile or styrene to polymerize in the presence of cellulose and water is not influenced by the presence of CCl_4.

TABLE 2. Graft Copolymerization of Methyl Methacrylate onto α-Cellulose in Presence of Aldehydes[a]

α-Cellulose (g)	Aldehyde[b] (mmoles)	Conversion[c] (%)	Grafting[d] (%)	Grafting efficiency[e] (%)
0	0	1.6		
0.25	0	15.0	32	22
0	A 2.5	29.8		
0.25	A 2.5	72.8	124	17
0	B 2.5	10.8		
0.25	B 2.5	60.0	48	8

[a] MMA, 25 mmoles; H_2O, 5.0 ml; 90°C; 2 hr.

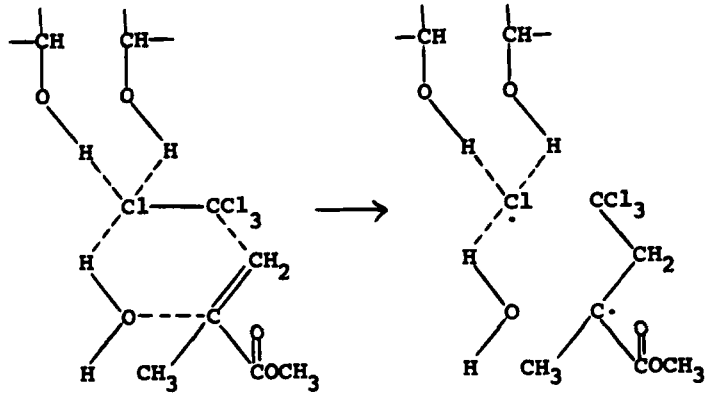
[b] A = CH_2CHO / OH B = CH_2CHCHO / $OH\ OH$

[c] $$\% \text{ Conversion} = \frac{\text{total product (g)} - \text{cellulose (g)}}{\text{monomer (g)}} \times 100.$$

[d] $$\% \text{ Grafting} = \frac{\text{graft copolymer (g)} - \text{cellulose (g)}}{\text{cellulose (g)}} \times 100.$$

[e] $$\% \text{ Grafting efficiency} = \frac{\text{graft copolymer (g)} - \text{cellulose (g)}}{\text{ungrafted PMMA (g)} + \text{grafted PMMA (g)}} \times 100.$$

Since the grafting efficiency in the cellulose-water-CCl_4 system is lower than in the absence of CCl_4, the reaction mechanism shown in Eq. (2) has been proposed:

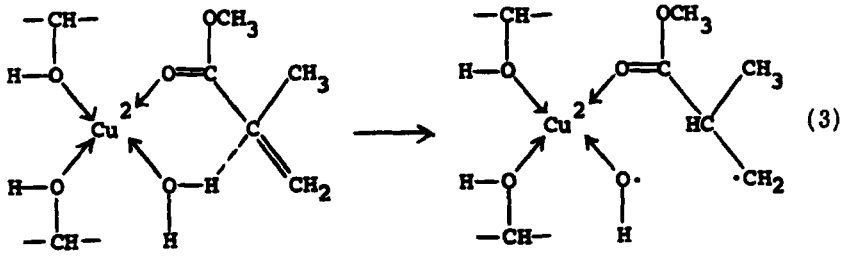


(2)

According to this mechanism, the formation of graft copolymer is due predominantly to chain transfer, although cellulose is a part of the complex initiator.

When the polymerization of methyl methacrylate in the cellulose-water-CCl_4 system at 90°C is carried out in the presence of glycolaldehyde and glyceraldehyde, the rate of polymerization is greatly increased and the grafting efficiency is dramatically reduced (Table 3) [10]. The increased rate is attributed to a radical-generating reaction between CCl_4 and the aldehydes, promoted by the presence of oxygen or peroxides.

The polymerization of methyl methacrylate in the presence of cellulose and water is promoted in the presence of cupric ion [7]. It has also been suggested that the uncatalyzed reaction in the absence of added cupric ion may be due to the presence of trace amounts of copper in the cellulose. The proposed complex initiator in the presence of cupric ion is shown by



(3)

TABLE 3. Graft Copolymerization of Methyl Methacrylate onto α-Cellulose in Presence of Aldehydes and CCl_4[a]

α-Cellulose (g)	Aldehyde[b] (mmoles)	Conversion (%)	Grafting (%)	Grafting efficiency (%)
0	0	3.6		
0.25	0	15.2	18	12
0	A 2.5	23.6		
0.25	A 2.5	95.5	8	1
0	B 2.5	38.6		
0.25	B 2.5	92.0	17	2

[a] MMA, 25 mmoles; H_2O, 4.9 ml; CCl_4, 0.1 ml; 90°C; 2 hr.

[b] A = CH_2CHO / OH B = CH_2CHCHO / OH OH

TABLE 4. Graft Copolymerization of Methyl Methacrylate onto Cellulose in Presence of Ferrocene-CCl_4[a]

Rayon, g	0	0	0.1
$CuCl_2 \cdot 2H_2O$, g	0	0.003	0.003
Ferrocene, g	0.103	0.103	0.103
CCl_4, ml	0.2	0.2	0.2
Conversion, %	10	28	100

[a]MMA, 5 ml; H_2O, 5 ml; 85°C; 5 hr.

The polymerization of methyl methacrylate is initiated by a ferrocene-CCl_4 complex. When this reaction is carried out in the presence of cupric ion, the conversion is increased. The addition of cellulose-water to the copper-containing system increases the conversion to an even greater extent (Table 4) [13].

The mechanisms discussed thus far have recognized the significant role of cellulose in promoting the polymerization of methyl methacrylate. However, the effect of additives in increasing the rate of polymerization in the presence of cellulose to a greater extent than is achieved in the absence of cellulose or additive suggests that the role of cellulose is not restricted to the initiation of polymerization.

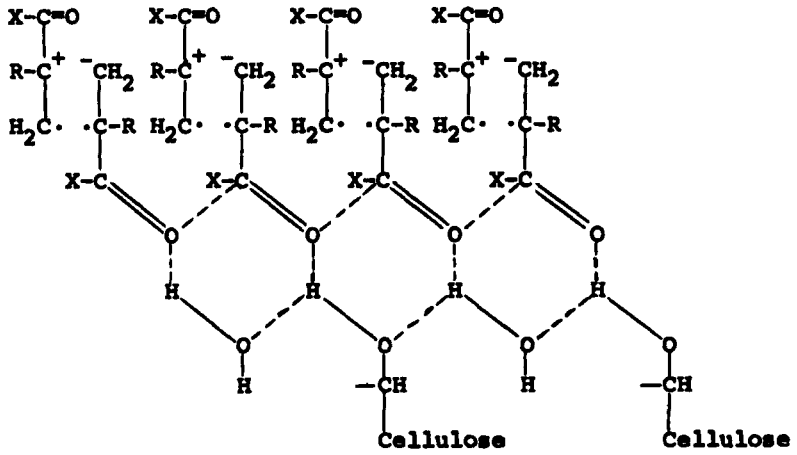
It has recently been proposed [1, 14] that cellulose-monomer interaction or complexation plays a major role in the grafting of acceptor monomers such as acrylic esters, amide, or nitrile on cellulose in the absence of catalysts, and that the behavior of the cellulose-monomer complex is analogous to that of donor-acceptor complexes generated from acceptor monomers or donor monomer-acceptor monomer pairs in the presence of metal halides or other Lewis acids [15].

The activation of polar monomers such as methyl methacrylate and acrylonitrile by complexation with metal halides such as zinc chloride results in an increased polymerization rate and the formation of a high molecular weight polymer under UV or gamma radiation or in the presence of oxygen or a free-radical initiator. It has been proposed [16] that the increased activity is the result of the formation of a donor-acceptor complex in which the uncomplexed monomer, normally an electron acceptor, behaves as a donor relative to the complexed monomer which has been converted to a stronger acceptor.

The enhanced reactivity results not only from complex formation but also from the association of complexes into a matrix or organized mobile array.

As applied to the homopolymerization of acceptor monomers in the presence of cellulose-water, this mechanism proposes that cellulose acts as a complexing agent for the activation of acceptor monomers

and as a matrix for the alignment of monomer-cellulose-water donor-acceptor complexes:



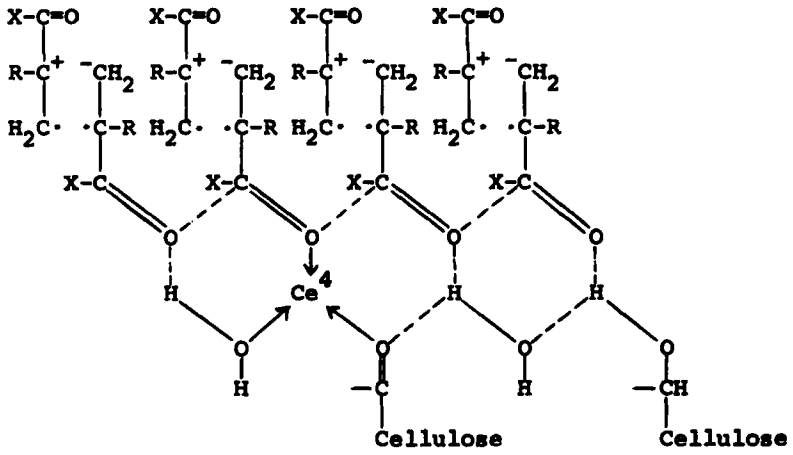
(4)

Ceric ion-cellulose interaction is an effective method for promoting the formation of graft copolymers on cellulose. It is presumed that as a result of ceric ion-cellulose complexation, a free radical is generated on the polymer backbone. It has been variously proposed that the radical and a carbonyl group are formed as a result of cleavage of the C_2-C_3 glycol group of the anhydroglucose unit or of the terminal hemiacetal group.

However, it has been suggested [1] that ceric ion promoted grafting on cellulose, which is generally effective only with acceptor monomers, involves the same donor-acceptor complexes as in the "uncatalyzed" reaction. When ceric ion is present, cellulose-monomer-water and ceric ion-monomer-water complexes are present. The complex containing ceric ion is anchored on the cellulose matrix by interaction of the ceric ion with the carbonyl groups present thereon initially or generated by the cellulose-ceric ion redox reaction as shown in Eq. (5).

The effect of cellulose-monomer interaction is clearly shown in the polymerization of methacrylonitrile using ceric ion or ammonium persulfate as initiator [14]. Although there is low or negligible monomer conversion in the absence of cellulose, as shown in Table 5, there is a dramatic increase in conversion, under the same conditions, in the presence of cellulose. Further, the product is predominantly graft copolymer.

Although acrylonitrile does undergo polymerization in the presence of ceric ion in the absence of cellulose, in contrast to the behavior of methacrylonitrile, the conversions are greatly increased at reduced



(5)

reaction times in the presence of cellulose and the grafting efficiency is extremely high (Table 6).

The polymerization of donor monomer-acceptor monomer complexes has numerous characteristics which are similar to those observed in the graft copolymerization of acceptor monomers on cellulose. Thus polymerization is initiated spontaneously or thermally when the concentration of complexes is sufficiently high, as

TABLE 5. Graft Copolymerization of Methacrylonitrile onto α-Cellulose[a]

α-Cellulose, g	0	5	0	5	5
Catalyst, mmoles	——CAN, 1——		——APS, 5——		
Temp., °C/time, hr	40/6	40/1.25	50/3	50/3	50/22
Conversion, %	< 1	35.4	< 1	6.1	82.2
Polymer					
Ungrafted, %	100	9	100	64	4
[η], dl/g[b]	0.15	2.7	0.28	3.0	4.3
Grafted, %		91		36	96
[η], dl/g[b]		3.2		5.3	6.0
Add-on, %		215		16	527

[a]MAN, 33.5 g (0.5 mole); H_2O, 38.5 g.
[b]DMF, 25°C.

TABLE 6. Graft Copolymerization of Acrylonitrile onto α-Cellulose

α-Cellulose, g	0	5	0	5
AN, g (moles)	13.25 (0.25)	26.5 (0.5)	13.25 (0.25)	26.5 (0.5)
H_2O, g	13.25	31.5	0	0
HNO_3 (1%), g	0	0	13.25	31.5
CAN, g (mmoles)	0.275 (0.5)	0.548 (1)	0.274 (0.5)	0.548 (1)
Temp., °C/time, hr	40/3	40/0.5	40/1	40/0.5
Conversion, %	11.0	61.5	47.5	85.9
Polymer				
Ungrafted, %	100	11.7	100	13.8
$[\eta]$, dl/g[a]	5.5	4.15	3.88	2.20
Grafted, %		88.3		86.2
$[\eta]$, dl/g[a]		3.75		3.18
Add-on, %		288		392

[a]DMF, 25°C.

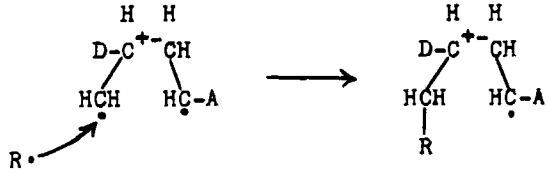
well as in the presence of oxygen, free-radical catalysts, and radiation. The polymers are of extremely high molecular weight and there is no chain transfer to conventional molecular weight modifiers containing halogen or active hydrogen.

Although the polymerization of donor-acceptor monomer complexes, initiated by free-radical catalysts, yields polymers which contain little or no catalyst residues, grafting occurs readily on substrate polymers which contain active hydrogen atoms. The question therefore arises as to the mechanism of the grafting reaction if radical sites generated on the substrate polymer do not become the initiating and bonding sites for the grafted polymer to any appreciable extent.

A previously proposed mechanism [1, 14] for the grafting of acceptor monomers onto cellulose involved grafting by termination, i.e., propagating chains from the polymerization of complexed monomers terminate on the cellulose by insertion of carbene end groups into aldehyde C–H bonds. A revised mechanism is herewith presented which does not require the generation or participation of carbene end groups in the grafting reaction.

As indicated in Eqs. (4) and (5), the monomer is considered to exist as donor-acceptor complexes aligned on the surface of the crystalline cellulose matrix. Polymerization is initiated by radical attack on the complexes. The initiating radicals may arise from aldehyde peroxides on the cellulose, monomer peroxides, aldehyde-CCl_4 reaction, cupric ion-cellulose-water-monomer complexation, and ceric ion-cellulose interaction, as well as from the attack of oxidizing agents such as persulfate or radicals therefrom on the cellulose.

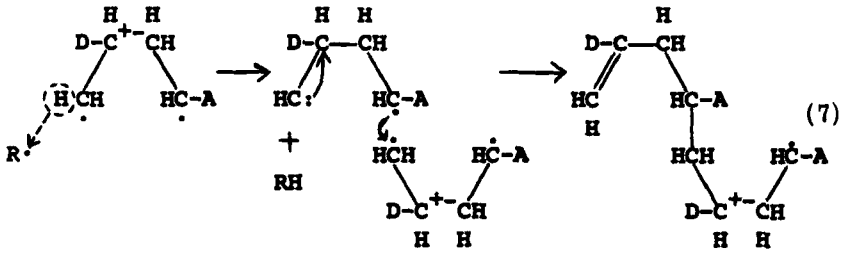
The radicals present on the cellulose as a result of these interactions may couple with the donor radical in the donor-acceptor complex:



(6)

This will initiate the growth of a grafted chain. However, since there are little or no catalyst residues in the polymers from donor-acceptor complex polymerization, this reaction must play a minor role in initiating grafting.

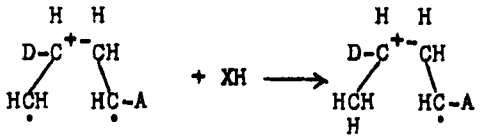
Radical-induced initiation without the incorporation of catalyst residues can occur through hydrogen abstraction. In this case, although chains are initiated, they are not grafted to the cellulose:



(7)

This should be the dominant reaction in the presence of radical species. Direct reaction between a radical from a catalyst, such as a persulfate or other peroxygen compound, and the donor-acceptor complex will similarly initiate an ungrafted chain.

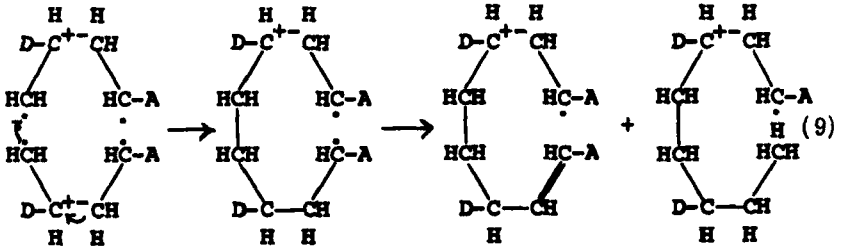
Spontaneous initiation is actually the result of thermal excitation of the donor-acceptor complexes. The latter can abstract a hydrogen from the monomer or the cellulose to initiate an ungrafted chain:



(8)

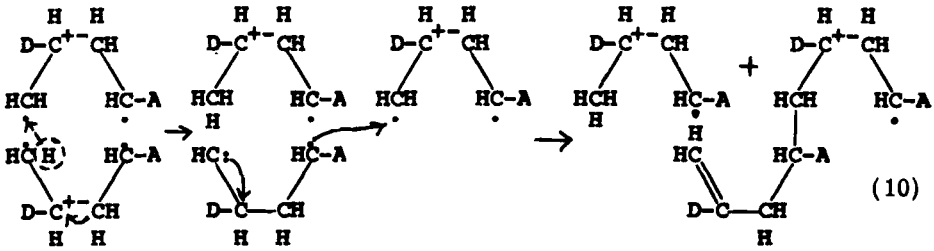
The resultant radical X· can also initiate polymerization as shown in Eqs. (6) and (7).

Spontaneous initiation may also occur through the coupling of complexes, as shown in Eq. (9), or hydrogen abstraction or transfer between complexes, as shown in Eq. (10).



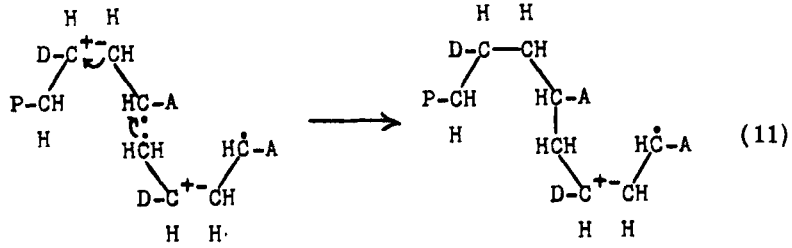
(9)

Irrespective of the mode of initiation, the donor-acceptor complex is converted to a species with a terminal donor cation which is tightly associated with an acceptor anion radical. Propagation involves the addition of a donor-acceptor complex to the terminal group on the chain, i.e., the donor cation radical of the approaching complex



(10)

enters the chain together with the acceptor anion radical of the terminal group:

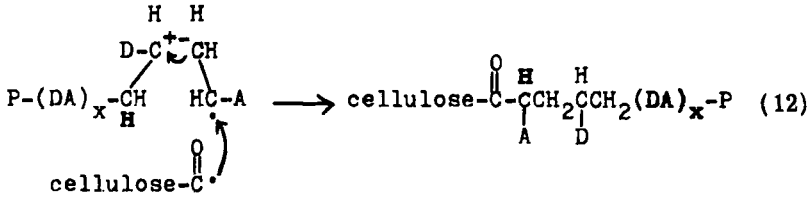


(11)

The grafting reaction may arise through several routes. Radical sites may be generated on the cellulose by any of the previously indicated methods. However, the aldehyde arising from the terminal hemiacetal unit on the cellulose would appear to be the preferred site of attack. Aside from the extreme susceptibility of the aldehyde group to oxidative or radical attack, due to the crystallinity of cellulose, the ends of the cellulose chains containing the aldehydes are in the more accessible, amorphous areas.

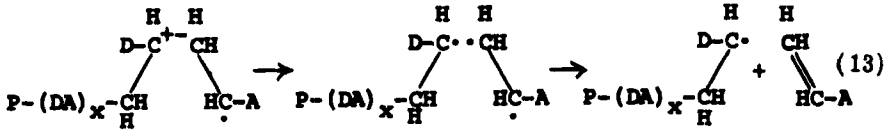
The finding that the ceric ion method [17], as well as others, yields graft copolymers containing a maximum of one branch per cellulose chain, supports the presence of a terminal branch, i.e., cellulose graft copolymers are actually block copolymers.

Grafting by initiation, i.e., the addition of donor-acceptor complexes to a radical site on the cellulose, as shown in Eq. (6), should be responsible for only a minor portion of the grafting. The major route to grafting is by termination, i.e., the coupling of radical sites on the cellulose with the propagating polymer chain:



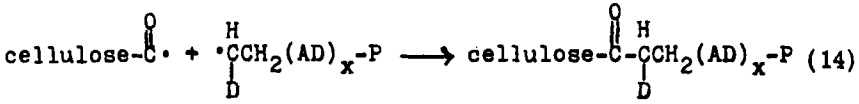
(12)

Under conditions of dilution, i.e., when the concentration of complexes is reduced, the terminal ion pair on a propagating polymer chain undergoes a reverse electron transfer to generate a terminal donor monomer radical and the acceptor monomer:



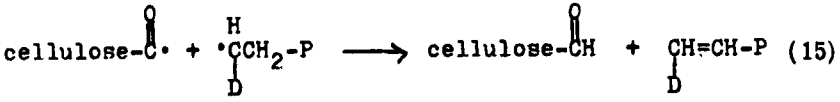
(13)

The resulting terminal radical may then couple with the radical site on the cellulose:



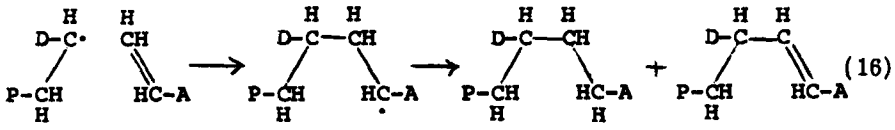
(14)

Grafting by termination, as shown in Eqs. (12) and (14), can occur with propagating chains, initiated either by hydrogen abstraction by radical species in the system or by spontaneous complex interactions, as shown in Eqs. (8)-(10). When the interaction of the terminal radical generated in Eq. (13) with the radical site on cellulose results in disproportionation rather than coupling, ungrafted polymer is formed:

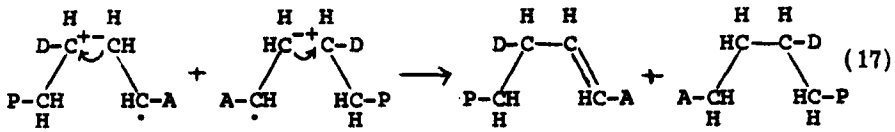


(15)

Termination of propagating chains may also occur unimolecularly as well as by reaction with other chains:



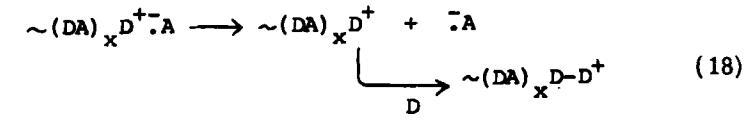
(16)



(17)

The terminal group in the propagating polymer chain has been represented as a tight ion pair in Eqs. (6)-(11). This is consistent

with the formation of cationic polymer in lieu of or accompanying the alternating copolymer in the copolymerization of donor monomers such as α-methylstyrene with complexed acceptor monomers, under conditions where the comonomer complex concentration is low [18]:



(18)

The ability of cations to propagate in an antagonistic environment when associated in a tight ion pair has recently been shown by the ease of polymerization of α-methylstyrene in the presence of $AlCl_3$ in polar solvents such as acetonitrile, propionitrile, ethyl acetate, ethyl propionate, and methyl isobutyrate as well as acrylic monomers such as acrylonitrile, methyl acrylate, and methyl methacrylate [19].

The multiplicity of hydroxyl groups on the surface of cellulose does not mitigate against the proposed cation-containing tight ion pair chain end. Paper has been treated with BF_3, followed by the application of isobutylene or α-methylstyrene, to produce a polymeric coating on the surface of the cellulose [20].

The presence of water in the cellulose systems presents no problem in the application of the proposed donor-acceptor complex polymerization mechanism. Thus acrylonitrile readily undergoes radical and photoinitiated polymerization in an aqueous system in the presence of $ZnCl_2$. The polymerizable species is presumably the $[AN^{+}\cdot\,{}^{-}AN\ldots ZnCl_2]$ complex.

N-Vinylcarbazole undergoes cationic polymerization, initiated by a vinylcarbazole-electron acceptor complex, in the presence of acceptors such as chloranil, tetranitromethane, and 2,4-dinitroresorcinol in an aqueous dispersion [21].

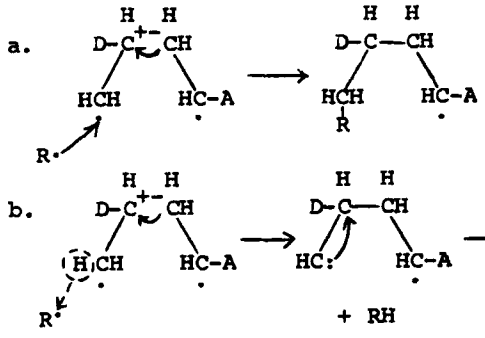
Styrene-acrylonitrile and other donor-acceptor comonomer pairs undergo radical-initiated polymerization in the presence of $ZnCl_2$ and other metal halides in an aqueous medium to yield alternating copolymers [22]. These copolymers are discussed in more detail in the next section.

Although this worker believes that the proposed mechanism is operative in the polymerization of acceptor monomers, as well as suitable binary comonomer compositions, in the presence of cellulose as well as other substrates, it is recognized that the conditions used in such reactions may present a special case. The following alternative mechanisms is therefore presented at this time, although this worker prefers the previously described mechanism.

In the alternative mechanism, the terminal group is the complexed acceptor monomer radical. The polymerizing species is still the donor-acceptor complex $[D^{+}\cdot\,{}^{-}A]$. The catalyzed and spontaneous initiation steps are shown in Eqs. (19)-(23).

Initiation

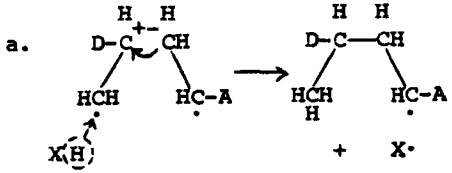
1. Catalyzed



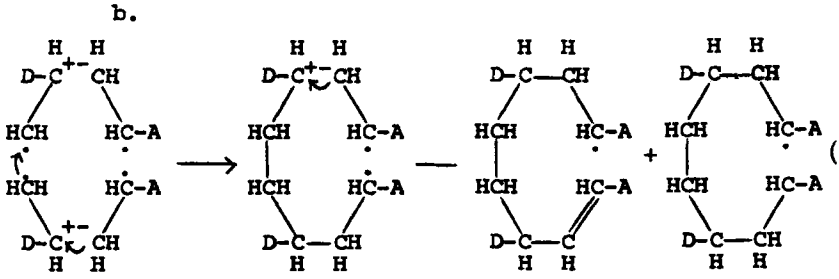
(19)

(20)

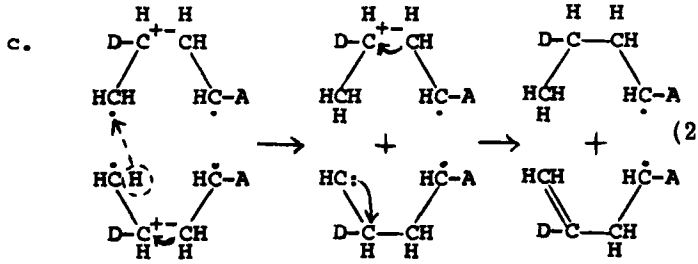
2. Spontaneous



(21)



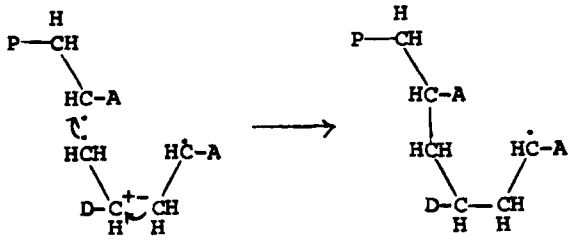
(22)



(23)

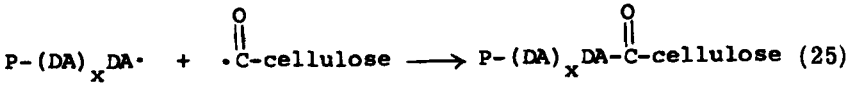
The propagation and grafting reactions are shown in Eqs. (24) and (25).

Propagation



(24)

Grafting



(25)

DONOR MONOMER-ACCEPTOR MONOMER COPOLYMERIZATION AND GRAFT COPOLYMERIZATION

When the copolymerization of styrene and acrylonitrile in the presence of zinc chloride is carried out in the presence of cellulose, under conditions which normally yield an alternating copolymer, i.e., in an aqueous system in the presence of a water-soluble radical precursor at a temperature below 60°C, the alternating copolymer is accompanied by cellulose graft copolymer in which the grafted chains have an equimolar, alternating structure. The monomer conversion is higher than when the reaction is carried out in the absence of cellulose, and both grafted copolymer (60 to 80% of the total copolymer) and ungrafted copolymer are of very high molecular weight [23].

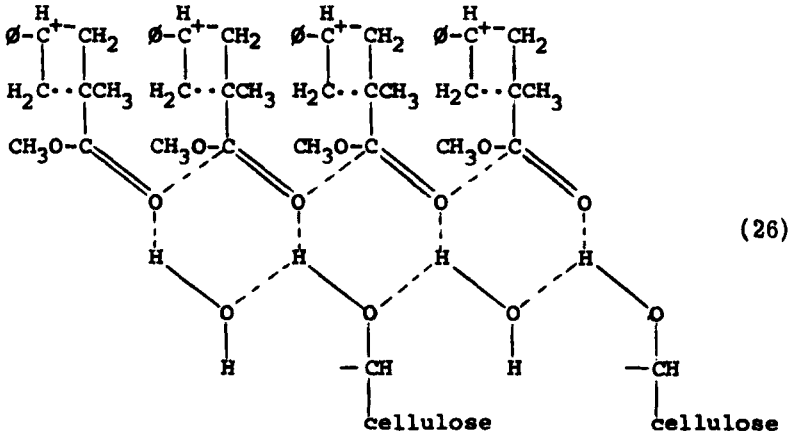
The comonomer complexes [S^{+} $^{-}$AN...$ZnCl_2$] are presumably anchored on the cellulose through the interaction of $ZnCl_2$ and the cellulosic hydroxyl groups, since aqueous solutions of the metal halide are known to break the hydrogen bonds in cellulose and reduce the crystallinity. The grafting reaction occurs through the same sequence of reactions described in the previous section. However, since styrene is a true donor monomer, the concentration of [D^{+} $^{-}$A] complexes is far higher than when the uncomplexed acceptor monomer acts as a donor relative to the metal halide or cellulose-complexed acceptor monomer.

The ability of cellulose to act as a complexing agent for the activation of aceptor monomer and as a matrix for the alignment of comonomer complexes [$D^{+\cdot}A^{-\cdot}$-cellulose-water] is demonstrated by the formation of equimolar, alternating copolymers from binary monomer mixtures in the absence as well as in the presence of catalysts.

When a mixture of butadiene and methyl methacrylate is heated at 90°C with an aqueous suspension of kraft wood pulp containing a small amount of nonionic surfactant, in the absence of a catalyst, essentially equimolar alternating butadiene-methyl methacrylate copolymer is grafted on the cellulose when the monomer charge contains 20 to 50 mole % methyl methacrylate [24].

The copolymerization of styrene and methyl methacrylate (90/10 molar ratio) in the presence of wood pulp at 90°C using $NaClO_2$ as catalysts results in the formation of equimolar grafted and ungrafted copolymers at a low conversion. However, while the grafted copolymer composition is still equimolar at a higher conversion, the ungrafted copolymer composition approaches that expected from the comonomer charge in accordance with a radical mechanism [25].

The proposed alignment of comonomer complexes on the cellulose matrix is shown by



(26)

The mutual γ-irradiation of viscose rayon immersed in a methanol solution containing butadiene and acrylonitrile at 30°C results in the formation of ungrafted copolymers having the compositions expected for a normal radical copolymerization over a wide range of monomer charge ratios. However, the grafted copolymers are essentially equimolar when the acrylonitrile content in the monomer charge ranges from 30 to 90 mole % [26].

Under similar conditions the graft polymerization of a mixture of

styrene and acrylonitrile on viscose rayon yields equimolar grafted copolymers and ungrafted copolymers with a radical composition when the monomer charge contains 25 to 75 mole % acrylonitrile.

Similar results are obtained in the radiation-induced graft copolymerization of butadiene-acrylonitrile and styrene-acrylonitrile onto poly(vinyl alcohol) fibers [26].

Alternating styrene-acrylonitrile and styrene-methacrylonitrile copolymers are produced both as ungrafted and cellulose graft copolymers when the compolymerizations are carried out at 40 to 50°C in the presence of cellulose using a persulfate, a persulfate-bisulfite redox system, or ceric ammonium nitrate as initiator [27].

When the copolymerization of styrene and acrylonitrile (S/AN mole ratio = 1) is carried out for 1 hr with a redox catalyst at 40°C in the presence of cellulose and 50 wt% water, based on total charge, the conversion increases with increasing cellulose content. The grafted and ungrafted S-AN copolymers have a radical composition when the cellulose content is below 1 wt% based on monomers and an alternating, equimolar composition at higher cellulose contents. The grafted S-AN copolymer represents 30 to 40% of the polymerized comonomers when prepared under these conditions (Fig. 1). Changes in reaction conditions, e.g., reaction time and/or catalyst concentration, result in essentially quantitative conversion to equimolar, alternating copolymer. The grafted S-AN copolymer may also be increased to up to 70% of the total copolymer [28].

Equimolar, alternating copolymers are also obtained as grafted and ungrafted copolymers when an equimolar mixture of styrene and acrylonitrile is subjected to UV irradiation in the presence of an aqueous suspension of cellulose [28].

SCOPE

The proposed mechanism for polymerizations carried out in the presence of cellulose and the grafting resulting therefrom under suitable conditions is generally applicable independent of the nature of the initiating species. However, since exposure of cellulose to ionizing radiation in the presence of a swelling agent causes extensive degradation, the resultant radicals are capable of initiating the graft copolymerization of both donor and acceptor monomers. Nevertheless, even under these conditions, cellulose-monomer interaction plays an important role, as indicated by the formation of equimolar grafted copolymers from binary donor-acceptor comonomer systems [26].

Cellulose-monomer interaction is probably also a factor when radicals are generated directly on the cellulose by modifications which convert the cellulose to a radical precursor, e.g., the cellulose thiocarbonate-hydrogen peroxide redox system [29]. However, the

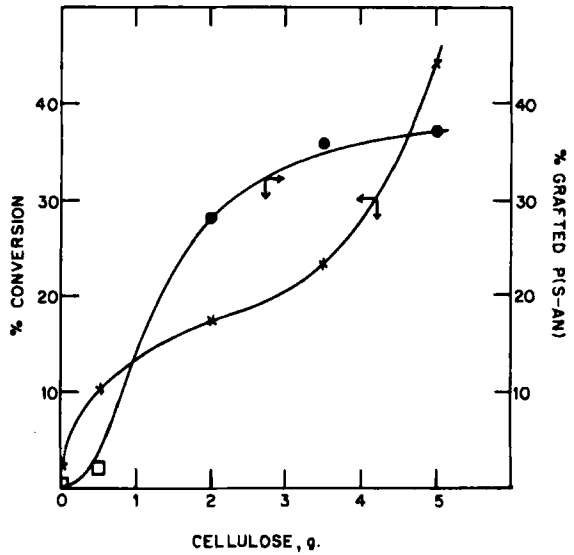


FIG. 1. Effect of cellulose concentration on conversion and grafting efficiency in styrene-acrylonitrile copolymerization. [S] = 52.0 g (0.5 mole); [AN] = 26.5 g (0.5 mole); [$K_2S_2O_8$] = 0.27 g (0.001 mole); [$Na_2S_2O_5$] = 0.19 g (0.001 mole); [α-cellulose] = variable (0 to 5.0 g), [H_2O] = variable (50 wt%); temperature, 40°C, time, 1 hr. (□) Radical copolymer; (●) alternating copolymer.

direct generation of radicals on the cellulose permits the initiated grafting of donor as well as acceptor monomers. Nevertheless, termination grafting of acceptor monomers is also probable.

The mechanism proposed herein is equally applicable to polymerizations carried out in the presence of, and the graft copolymerization onto, other natural and synthetic polymers including starch, silk, wool, casein, gelatin, and collagen. The radical site for termination grafting obviously varies with the substrate.

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