Review Article

Grafting of Cellulose Based Materials: A Review

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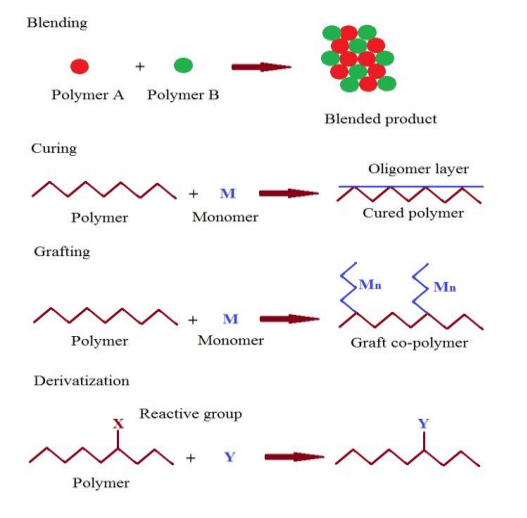
Abstract

Cellulose is the most abundant naturally occurring polymer which is biodegradable and, thus acceptable from the environmental point of view. The polymeric material with desired properties is a current need of the society. However to reach the required application properties, such as hydrophobicity, adhesivity, selectivity, drug delivery, wettability and thermo-sensitivity etc., graft co-polymerization of suitable monomer is an indispensable technique for cellulose modification. Graft co-polymerization of cellulose and cellulose derivatives has received much attention recently. In principle graft co-polymerization initiated by chemical treatment, photo-irradiation, high energy radiation technique etc. is documented in this chapter. Several prime controlling factors such as nature of backbone, effect of monomer, solvent, initiator etc. on grafting are also discussed.

Keywords: Cellulose, cellulose acetate, heterogeneous grafting, homogeneous grafting, ceric ammonium nitrate, benzoyl peroxide, tin-bis(2-ethyl hexanoate).



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Introduction

The chemical modification of cellulose and its derivatives by graft copolymerization has generated interest among researchers, because few comonomer molecules change significantly a number of characteristics of the original natural polymer. In the polymeric age, it is essential to modify the properties of a polymer according to tailor-made specifications designed for target applications. There are several means to modify the properties of a polymer, viz. blending, curing, grafting and derivatization. Blending is the physical mixture of two (or more) polymers to obtain the requisite properties. In curing, the polymerization of an oligomer mixture forms a coating which adheres to the substrate by physical forces, where as in grafting, the monomers are covalently bonded and polymerized onto the polymer chain. The process of grafting can take minutes, hours or even days for completion, whereas curing is a very rapid process and occurs in a fraction of second. In derivatization, simple molecules are substituted with the reactive groups of the polymer chain. The most common derivatization reactions of cellulose are esterification and etherification. The schematic presentation of the polymer modification is presented in **Figure** 1. In this review, different techniques of grafting of cellulose and cellulose derivatives have been discussed in the first part. The second part consists of the discussion about the primary factors which control the grafting.

Techniques of grafting

Considerable work has been carried out on the techniques of graft co-polymerization of different monomers on cellulose backbone. These techniques include chemical, radiation, photochemical and enzymatic grafting.

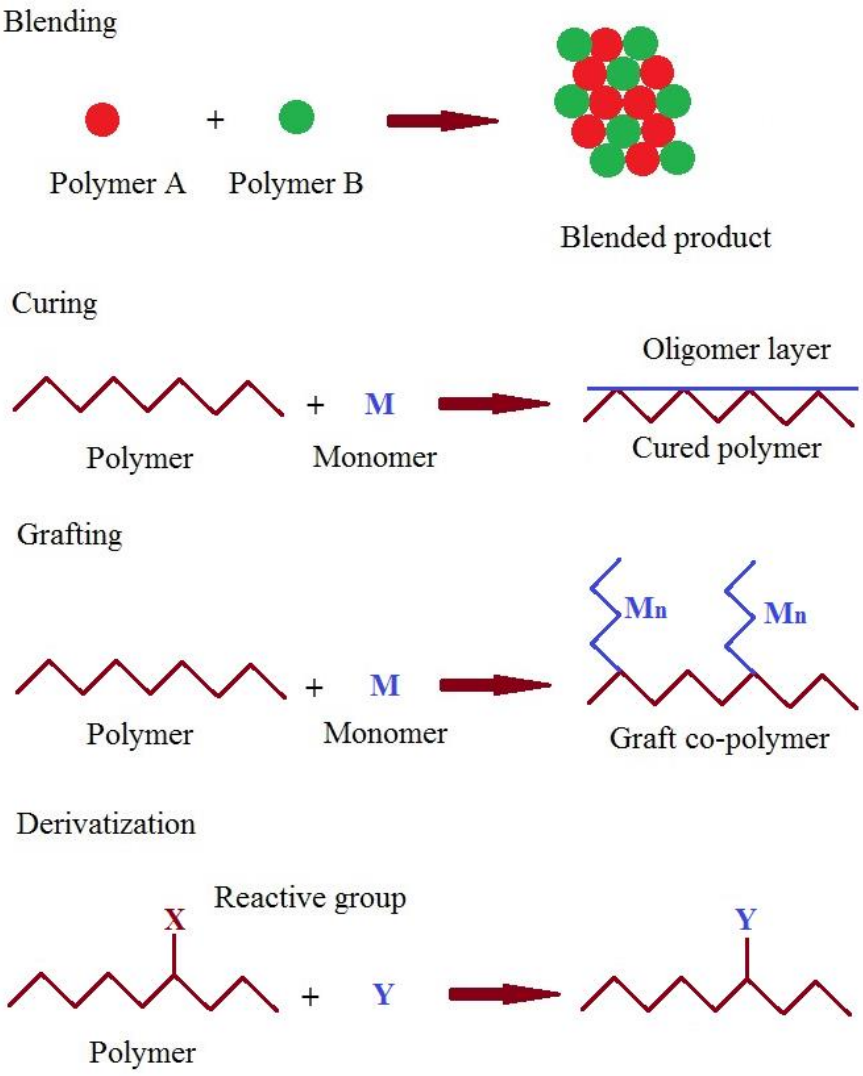


Figure 1 Methods for polymer modification

Grafting initiated by chemical means

This type of grafting can proceed along two major paths, viz. free-radical and ionic. In this process the role of initiator is very important as it determines the path of the grafting process. Apart from the general free-radical grafting, grafting by atom transfer radical polymerization (ATRP) is also interesting technique to carry out grafting.

Initiators used for grafting of cellulosic materials

It is known that the type of initiator has an important effect on the grafting, and it determines the grafting percentage depending on the monomer to be grafted. In the grafting of vinyl monomers onto cellulose or cellulose derivatives, the initiation can be performed by chemical initiators or by irradiation. The grafting of non-vinyl monomers is performed by reaction of monomer with the reactive functional groups of the cellulose. As chemical initiators, redox initiators such as ceric (IV) ion (ceric ammonium nitrate: $(NH_4)_2Ce(NO_3)_6$) (CAN) [1-7] or cerium (IV) sulphate [8], ceric ammonium sulfate (CAS) [9], iron(II)–hydrogen peroxide (Fe^{2+}-H_2O_2: Fenton reagent), cobalt (III) acetylacetonate complex salts [10], Co (II) – potassium monopersulfate [11], sodium sulfite –ammonium persulfate

[12], and free radical generators such as azobisisobutyronitrile ($C_8H_{12}N_4$: AIBN) [13], potassium persulfate ($K_2S_2O_8$: KPS) [14-17], ammonium persulfate ($(NH_4)_2S_2O_8$:APS) [14, 15], and benzoyl peroxide ($C_{14}H_{10}O_4$: BPO) [3-5, 14, 15] can be used.

Fe(II)-H_2O_2

Iron (II)–hydrogen peroxide system (Fenton reagent) is a cheap and easy available redox initiator, and the grafting with that initiator may be carried out in low temperatures [18]. The mechanism for the creation of $^{\bullet}OH$ radicals by one electron transfer by the reaction of Fe(II) ion with hydrogen peroxide is given below:

$$Fe^{2+} + H_2O_2 \longrightarrow {}^{\bullet}OH + OH^- + Fe^{3+}$$

$$^{\bullet}OH + Fe^{2+} \longrightarrow OH^- + Fe^{3+}$$

$$^{\bullet}OH + H_2O_2 \longrightarrow H_2O + {}^{\bullet}OOH$$

$$^{\bullet}OOH + H_2O_2 \longrightarrow {}^{\bullet}OH + O_2 + H_2O$$

The hydrogen peroxide molecules react with ferrous (Fe^{2+}) ions, and thus, ferric (Fe^{3+}) ions and primary hydroxyl radicals are created. Then, the primary hydroxyl radicals abstract a hydrogen atom from cellulose resulting in a secondary cellulose radical, and the grafting is initiated from these hydrogen-abstracted sites on the cellulose backbone. When the molar ratio of Fe^{2+}/H_2O_2 is higher than 1, some of the $^{\bullet}OH$ radicals that are created in the above equations are consumed by Fe^{2+} and Fe^{3+} ions affect the grafting adversely and lead to decrease in the grafting percentage. H_2O_2 alone does not lead to the formation of radicals, and it can only create the radicals together with metal impurities which are considered as reducing agent. In order to avoid the negative effect of Fe^{3+} ions on the grafting, the grafting has been carried out in the presence of some complexing agents with Fe^{3+} ions such as ascorbic acid, potassium fluoride (KF), and ethylenediaminetetraacetic acid (EDTA) [18]. In order to minimize the formation of homopolymer and the wastage of primary hydroxyl ($^{\bullet}OH$) radicals by Fe^{3+} ions, Fe^{2+} ions are adsorbed on the lignocellulose by contacting it with an Fe^{2+} salt solution in a given time period (15 min) and then the Fe^{2+} ion-adsorbed cellulose is separated from the solution containing excess Fe^{2+} ions by filtration. Then, methyl methacrylate (MMA) is grafted onto that Fe^{2+} salt pretreated-lignocellulose [19].

Ceric Ion

Among the various types of redox initiators, ceric ion offers many advantages because of its high grafting efficiency and lower amount of homopolymer formation. When Ce^{4+} salts such as cerium sulfate or ceric ammonium nitrate (CAN) is used as initiator in the grafting of vinyl monomers onto cellulose, at first a ceric ion–cellulose complex occurs, and then it decomposes to cerous (Ce^{3+}) ion, and cellulose radicals created by hydrogen abstraction from cellulose [2-7]. Thus, the initiation sites for grafting are created on the cellulose backbone. The radical formation on the cellulose backbone may occur on the oxygen atom of methylol ($–CH_2OH$) group as given below:

$$Ce^{4+} + Cell - OH \longrightarrow Complex \longrightarrow Cell - O^{\bullet} + Ce^{3+} + H^+$$

or the grafting may also be initiated on C_2 carbon by the ring opening of cellulose backbone as given in **figure** 2.
It is proposed that the grafting occurs mainly at the C_2–C_3 glycol unit, and to a lesser amount at the C_6-hydroxyl in the grafting of acrylonitrile onto *Cassia tora* gum which is a common herbaceous annual weed growing in India [20].

Although Ce^{4+} is an efficient initiator for the grafting of vinyl monomers onto cellulose, it requires the use of an acid together in order to create initiation sites (radicals) on graft substrate since the ceric ion undergoes hydrolysis in

neutral medium [21] through $Ce(OH)^{3+}$ finally to $[Ce–O–Ce]^{6+}$ ion which has no or low activity [20] for the creation of radicals via the reactions as shown below:

$$Ce^{4+} + H_2O \longrightarrow [Ce(OH)]^{3+} + H^+$$

$$2\,[Ce(OH)]^{3+} \longrightarrow [Ce - O - Ce]^{6+} + H_2O$$

In the absence of acid, no grafting on wool was determined most probably because $[Ce\text{-}O\text{-}Ce]^{6+}$, which is the hydrolysis product of Ce^{4+} ions, could not form a complex with wool [22]. Since the grafting efficiency of Ce^{4+} ion in neutral medium is low [23], it is used together with an acid, mostly nitric acid (HNO_3). In order to reduce the formation of homopolymer accompanying the grafting, the reaction has been carried out in the absence of the excess of ceric ions. For that reason, ceric ion solution has been contacted with cellulose in acidic medium for a pre-determined time duration, and ceric ions are adsorbed on the cellulose, and then the excess of ceric ions in the mixture (non-adsorbed ceric ions) are removed from the ceric ion-adsorbed cellulose by filtration [23-25]. The rate of disappearance of ceric ions during the grafting of binary monomers (acrylamide and ethyl acrylate) onto cellulose [26] was found to be very high in the initial 1-h period of grafting, and the disappearance of ceric ions was attributed to their consumption for the creation of active sites on cellulose. After that initial 1-h period, no significant change in the concentration of ceric ions has been observed. In homogeneous grafting conditions, where HNO_3 forms gel in cellulose solution, CAN can be used with dimethyl sulfoxide (DMSO) to initiate the graft copolymerization reaction [2-7].

Persulfates

When potassium persulfate/cobalt sulphate ($K_2S_2O_8/CoSO_4$) system was used as redox initiator [16], at first the primary radicals, $SO_4^{\bullet-}$ and $^{\bullet}OH$, are generated by the decomposition of $K_2S_2O_8$ in the presence of $CoSO_4$, and then these primary $SO4^{\bullet-}$ and $^{\bullet}OH$ radicals abstract a hydrogen atom from cellulose backbone and create the secondary C- or O-centred cellulose radicals. The growth of graft chains carries on these hydrogen-abstracted active sites. Potassium persulfate (KPS) is the best radical initiator for hydrogen abstraction, and it is cheap and soluble in water. In the investigation of the grafting site via oxidative hydrogen abstraction by potassium persulfate without monomer, the carbon atoms of C_3 and C_4 on saccharide ring are reported to be probable grafting sites [17]. Besides these, there are other initiators which will be discussed in the forthcoming sections.

Free-radical grafting

To promote grafting reaction and avoid homo-polymerization of the monomers, radical initiators should preferably react with cellulose instead directly reacting with monomers. Radical initiators can undergo two different paths, addition to vinyl monomers or hydrogen abstraction from weak C-H sites on cellulose. Alkoxide radicals prefer to abstract hydrogen atoms from weak C-H bonds rather than addition to vinyl monomers, different from other initiator radicals [27].

In the chemical process, free-radicals are produced from the initiators and transferred to the substrate to react with monomer to form the graft co-polymers. In general, one can consider the generation of free-radicals by indirect or direct methods.
An example of free-radicals produced by an indirect method is the production through redox reaction, viz. M^{n+}/H_2O_2, persulphates [18, 28-32].

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + {}^{\bullet}OH$$

$$Fe^{2+} + {}^{-}O_3S\text{-}OO\text{-}SO_3^- \longrightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet-}$$

It may be observed that, the active species in the decomposition of H_2O_2 and potassium persulphate induced by Fe^{2+} are $^{\bullet}OH$ and $SO_4^{\bullet-}$ respectively.

There are different views regarding the activity of $SO_4^{\bullet-}$. Some authors reported that initially formed $SO_4^{\bullet-}$ reacts with water to form $^{\bullet}OH$, subsequently producing free-radicals on the polymeric backbone. Grafting process of methyl methacrylate (MMA) onto wood fiber was also studied using sodium bisulfite/potassium persulfate (SB/KPS) pair as the initiator. The sulfate radical ($SO_4^{\bullet-}$) was formed according to the following reaction [33]:

$$H_2O + HSO_3^- + 2S_2O_8^{2-} \longrightarrow 3HSO_4^- + 2SO_4^{\bullet-}$$

The $SO_4^{\bullet-}$ formed reacts directly with the polymeric backbone (cellulose) to produce the requisite radicals.

$$SO_4^{\bullet-} + Cell - OH \longrightarrow HSO_4^- + Cell - O^{\bullet}$$

However it is established that [29] during grafting of vinyl monomers onto wool/cellulose, $^{\bullet}OH$ is more reactive than $SO_4^{\bullet-}$. It was also reported that the decrements in grafting were attributed to increments in the initiator concentration, but also deactivation of the free radicals due to side reactions when bisulfite is used as shown below:

$$SO_4^{\bullet-} + H_2O \longrightarrow HSO_4^- + HO^{\bullet}$$

$$2SO_4^{\bullet-} + 3HSO_3^- \longrightarrow 2HSO_4^- + 3SO_3^{2-} + H^+$$

$$2HO^{\bullet} + HSO_3^- \longrightarrow SO_4^{2-} + H_2O + H^+$$

At a temperature of 60 – 80 °C potassium persulfate can produce $KSO_4^{\bullet}$ radical which can induce the grafting reaction of ethyl acrylate to hydroxyl propyl methyl cellulose [34], itaconic acid to cellulose fibers [35] and acrylic acid to cellulose microfibers using an epoxide [36] according to the following reactions:

$$Cell - OH + KSO_4^{\bullet} \longrightarrow KSO_4^- + Cell - O^{\bullet} + H^+$$

Hydroperoxides and Fe^{2+} comprise another important redox system, with free radicals generated by the interaction between them via thermal decomposition [37]. By analog with Fenton's reagent (Fe^{2+} - H_2O_2), the activity of tertiary butyl hydroperoxides – Fe^{2+} system is attributed to the formation of t-butoxy radical arising from one electron transfer between t-butyl hydroperoxide (TBHP) and Fe^{2+}:

$$t\text{-}BuOOH + Fe^{2+} \longrightarrow t\text{-}BuO^{\bullet} + OH^- + Fe^{3+}$$

The resulting $t\text{-}BuO^{\bullet}$ radical may participate in hydrogen abstraction reaction to generate $HO^{\bullet}$ and the macro-radical on polymeric backbone.

$$\text{With monomer: } t\text{-}BuO^{\bullet} + M \longrightarrow t\text{-}BuO - M^{\bullet} \longrightarrow t\text{-}BuO - M_n - M^{\bullet}$$

$$\text{With polymer: } t\text{-}BuO^{\bullet} + PH \longrightarrow t\text{-}BuOH + P^{\bullet}$$

$$\text{With water: } t\text{-}BuO^{\bullet} + H_2O \longrightarrow t\text{-}BuOH + HO^{\bullet}$$

Ceric ammonium nitrate (CAN) in the presence of nitric acid can be used as an efficient initiator for graft copolymerization of acrylic monomers onto cellulose [38-44]. The ceric (IV) ion initiation offers great advantages of forming radicals at cellulose backbone through a single-electron-transfer process to promote grafting of monomer onto cellulose. However, the ceric (IV) ion-initiated grafting depends on pH of the medium and the type of acid used for graft copolymerization. The proposed mechanism for such a process has been ascribed to the intermediate

formation of a metal ion – polymer chelate complex, viz. ceric ion is known to form a complex with hydroxyl groups on a polymeric backbone, which can be dissociated via one-electron transfer to give free-radicals [45-48].

$$Ce^{4+} + Cell - OH \longrightarrow Complex \longrightarrow Cell - O^{\bullet} + Ce^{3+} + H^{+}$$

$$Cell - O^{\bullet} + M \longrightarrow Cell - OM^{\bullet} \longrightarrow Cell - OMM^{\bullet}$$

In place of CAN, ceric sulfate ($Ce(SO_4)_2.4H_2O$) can also be used [8].

Another reaction mechanism of graft copolymerization of cellulosic materials, initiated by Ce (IV) ion is proposed by various workers [2-7, 49-51], in which the complex is formed at C_2 and C_3 of the anhydroglucose unit of cellulose, as shown in **figure** 2.

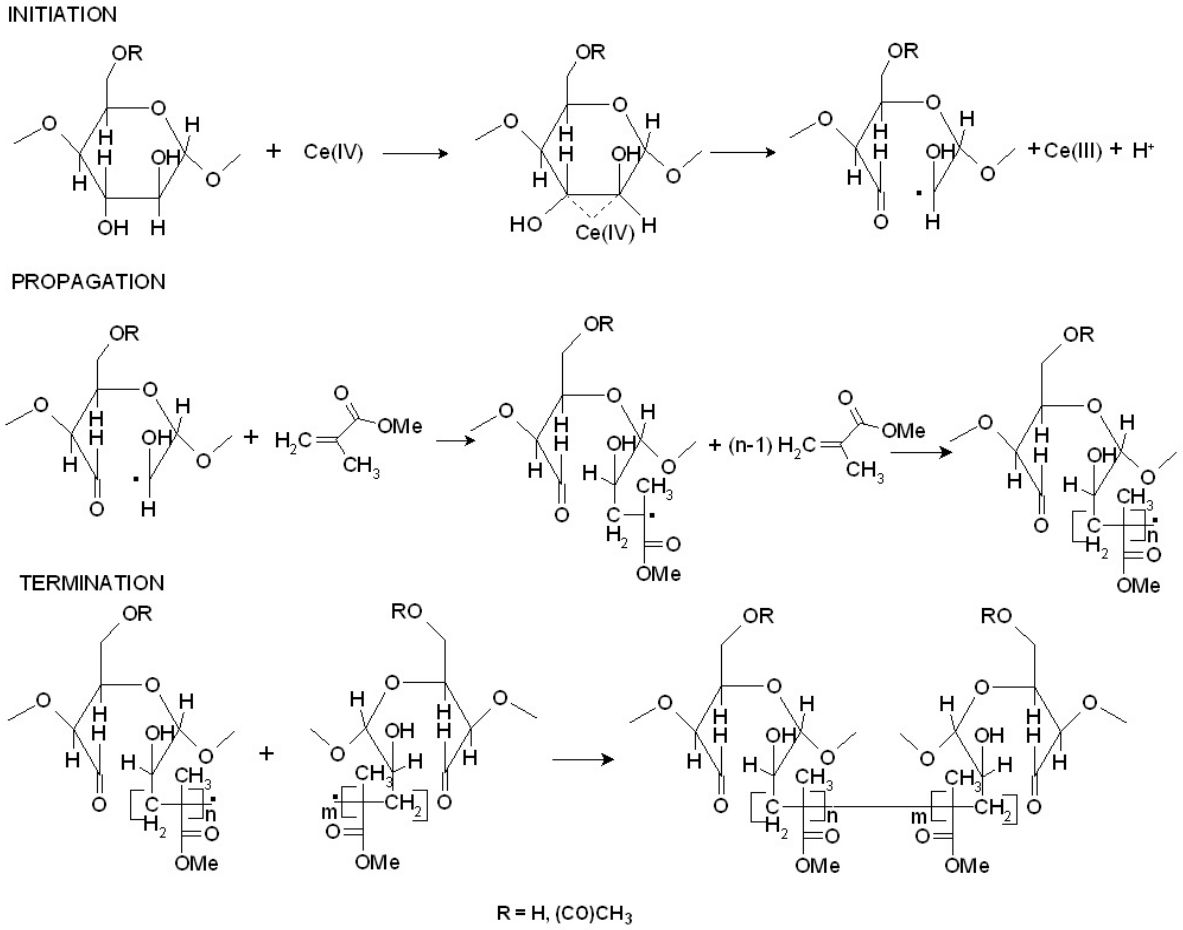


Figure 2 Mechanism of grafting of PMMA onto Cellulose/CA using CAN as the initiator

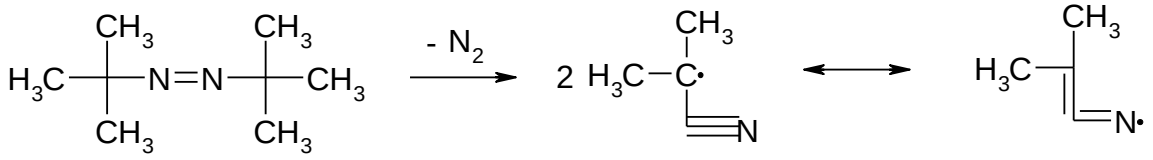
Accordingly, cerium salt (Ce^{4+}) functioned as a powerful oxidizing agent while cellulose itself acted as a reducing component in the redox system. The active centers are directly produced on the cellulose backbone and no charge transfer mechanism is necessary to initiate the cellulose graft copolymer formation. Cerium (IV) ions in acidic medium or in presence of dimethyl sulfoxide (DMSO) form chelates with the hydroxyl groups of carbons C_2 and C_3 of the anhydroglucose unit of cellulose. Transfer of electrons from cellulose the Ce (IV) gives Ce (III) which

dissociates from the chelate. The anhydroglucose ring scissions between C_2 and C_3 forming a short living radical. In the presence of the monomer, grafting reactions are initiated to produce the copolymer.
MnO^{4-} dissolves in the acid medium to give rise to Mn^{3+} ions via Mn^{4+}. These highly reactive Mn^{3+} ions are responsible for initiating graft copolymerization and homopolymerization [52].

$$PH + Mn(III) \longrightarrow PH\text{-}Mn(III)\ [Complex]$$
$$PH + Mn(III) \longrightarrow P^{\bullet} + Mn(II) + H+$$
$$P^{\bullet} + M \longrightarrow PM^{\bullet}$$
$$Mn(III) + M \longrightarrow M^{\bullet} + Mn(II) + H^{+}$$
$$PM^{\bullet} + nM \longrightarrow PM^{\bullet}_{n+1}$$
$$M^{\bullet} + nM \longrightarrow M^{\bullet}_{n+1}$$
$$PM_{n+1} + M(III) \longrightarrow PM_{n+1} + Mn(II) + H^{+}$$
$$P^{\bullet} + Mn(II) \longrightarrow Oxidised\ product + Mn(II)$$

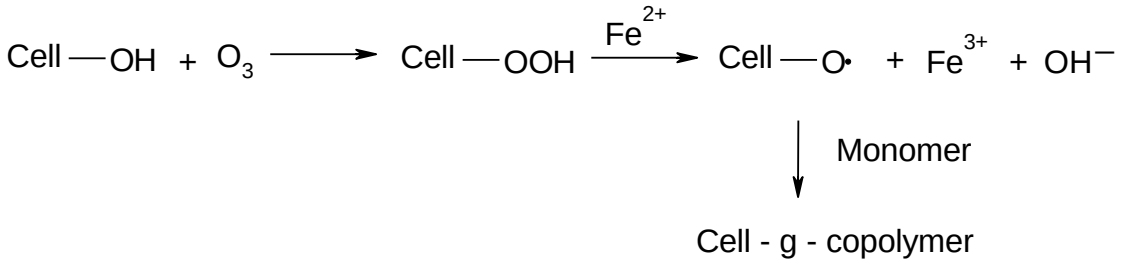
Where PH refers to polymer

Apart from the initiators discussed earlier, benzoyl peroxide (BPO) and azobisisobutyronitril (AIBN) are also effective in grafting reactions [3-5, 53-57]. This is important to note that the grafting efficiency is low with BPO and AIBN, compared with that obtained using one-electron-transfer agents. For example, not all of the radical species contribute towards grafting of poly (methyl methacrylate) on cellulose. Moreover, between the two, BPO is more reactive than AIBN, since the effects of resonance stabilization reduce the efficiency of the primary radical (I) from AIBN in generating active sites on the backbone.



(I)

Chemical pretreatment (e.g. ozonation) of the polymer backbone [58-60] may also generate free-radical sites upon reaction with Fe^{2+}, which can provide sites for grafting.



Ionic grafting

Grafting can also proceed through an ionic mode. Alkali metal suspensions in a Lewis base liquid, organometallic compounds and sodium naphthalenide are useful initiators in this purpose. Alkyl aluminum (R_3Al) and the backbone polymer in the halide form (ACl) interact to form carbonium ions along the polymer chain, which leads to copolymerization. The reaction proceeds through cationic mechanism.

$$ACl + R_3Al \longrightarrow A^{+}R_3AlCl^{-}$$

$$A^+ + M \longrightarrow AM^+ + M \longrightarrow \text{Graft copolymer}$$

BF_3 can also be used as a cationic catalyst.

In presence of tin-bis(2-ethyl hexanoate) [$Sn(Oct)_2$] as an initiator, ε-caprolactone and methyl methacrylate can be grafted onto cellulose and cellulose acetate [3-5, 61, 62]. The mechanism of polymerization when tin-bis(2-ethyl hexanoate) is used as the initiator is still in dubious. The most promising mechanism is a coordination-insertion mechanism where the hydroxyl group is thought to coordinate to $Sn(Oct)_2$, forming the tin alkoxide complex [63] and is given in **figure** 3 [3].

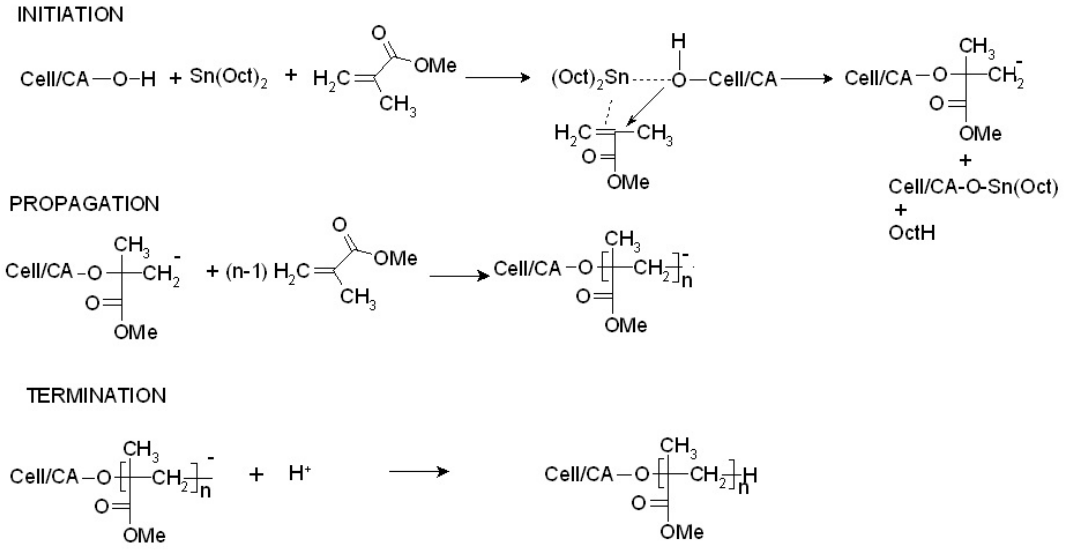


Figure 3 Mechanism of grafting of PMMA onto Cellulose/CA using $Sn(Oct)_2$ as the initiator

Grafting through living polymerization

In recent years, methods of 'living polymerization' have developed to provide a potential for grafting reactions. The definition of living polymer is 'that retains their ability to propagate for a long time and grow to a desired maximum size while their degree of termination or chain transfer is still negligible' [64]. Controlled free-radical polymerizations combine features of conventional free-radical and ionic polymerizations. Conventional free-radical polymerization requires continuous initiation, with termination of the growing chain radicals in coupling or disproportionation reactions, and as a result leads to unreactive ('dead') polymers and essentially time invariant degree of polymerization and broad molecular weight distribution. In case of living polymerization, it provides living polymers with regulated molecular weights and low polydispersities [65-72].

Controlled free-radical polymerization may be effective through atom transfer radical polymerization (ATRP). In recent years, a couple of papers have been appeared reporting on controlled grafting of cellulose using ATRP. First, the grafting can be performed in heterogeneous system, i.e. on the surface of cellulose fibers or particles, giving surface modified cellulose, which could be used, for instance, as a filler in appropriate polymer composites [73, 74]. Thus cellulose fibers (filter paper) were in the first step surface acylated with 2-bromoisoburyryl bromide, giving the fibers with chemically anchored initiating sites, which are subsequently used for ATRP grafting of methyl acrylate (MA) by immersing the modified filter paper into a reaction mixture containing MA, Cu(I)Br, tris-2-(dimethyl amino) ethylamine (Me_6-TREN), sacrificial initiator and ethyl acetate [75]. Further, these fibers with the anchored poly MA brush were used as macroinitiators of ATRP of 2-hydroxy ethyl methacrylate (HEMA), leading to poly (MA-b-HEMA) surface anchored polymer [76]. It is also reported that, cellulose powder can be surface-acylated with

chloroacetic acid chloride and the anchored chloroacetyl groups then used as initiating sites for ATRP grafting of styrene, MMA, methacrylamide or 4-acryloyl morpholine [77]. Cellulose diacetate was also acylated with 2-bromoisobutyryl bromide or dichloro acetyl chloride in presence of triethylamine (TEA) and 4-(dimethylamino) pyridine (DMAP) for ATRP grafting copolymerization of MMA, styrene and butyl acrylate under CuCl, $CuCl_2$, Cu powder/ hexamethyl triethylene tetraamine (HMTETA), pentamethyl diethylene triamine (PMDETA) catalyst [78] as shown in **figure** 4.

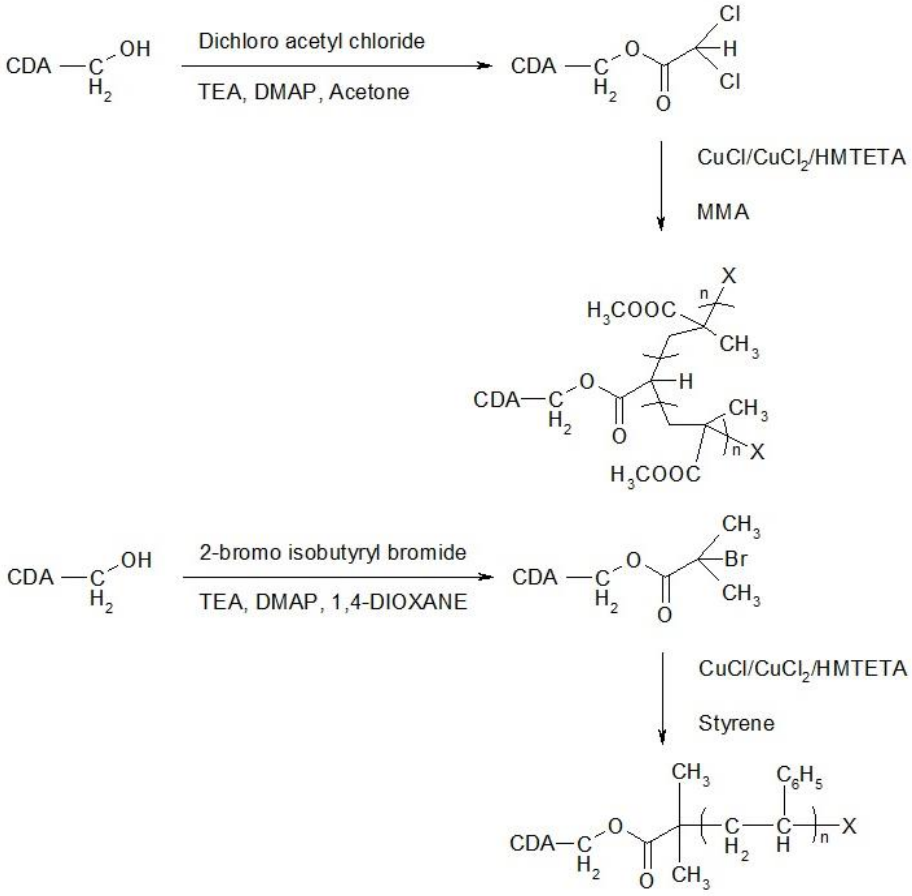


Figure 4 ATRP of MMA onto cellulose diacetate.

In another report, cellulose acetate was acylated with 2-bromoisobutyryl bromide in presence of TEA in tetrahydro furan to form the macroinitiator which was then grafted by methyl diethylene glycol methacrylate (MDEGMA) by ATRP mechanism [79] as shown in **figure** 5.

Hydroxyethyl cellulose-graft-polyacrylamide (HEC-g-PAM) was synthesized by using ATRP, in which the macroinitiator for ATRP was synthesized first by reacting HEC with 2-bromoisobutyryl bromide in presence of TEA and DMAP. Then acrylamide (AM) was grafted from this macroinitiator in presence of $CuBr/CuBr_2$ catalyst and 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra azomacro-cyclo tetradecane (Me_6[14]ane N_4) ligand [80].

Due to poor solubility of cellulose in common organic solvents, the graft copolymerization of cellulose by ATRP reported earlier only occurs on the surface of cellulose fiber due to heterogeneous process or otherwise cellulose derivatives are taken for grafting by ATRP. Homogeneous grafting of cellulose dissolved in DMAc/LiCl solvent system has also been carried out through ATRP [81] in which the macroinitiator was synthesized first by the reaction of cellulose with 2-bromoisobutyryl bromide in presence of pyridine. The macroinitiator was then reacted with N,N-dimethyl acrylamide in presence of CuBr and 2,2'-bipyridine in DMSO to get the graft copolymer as shown in **figure** 6.

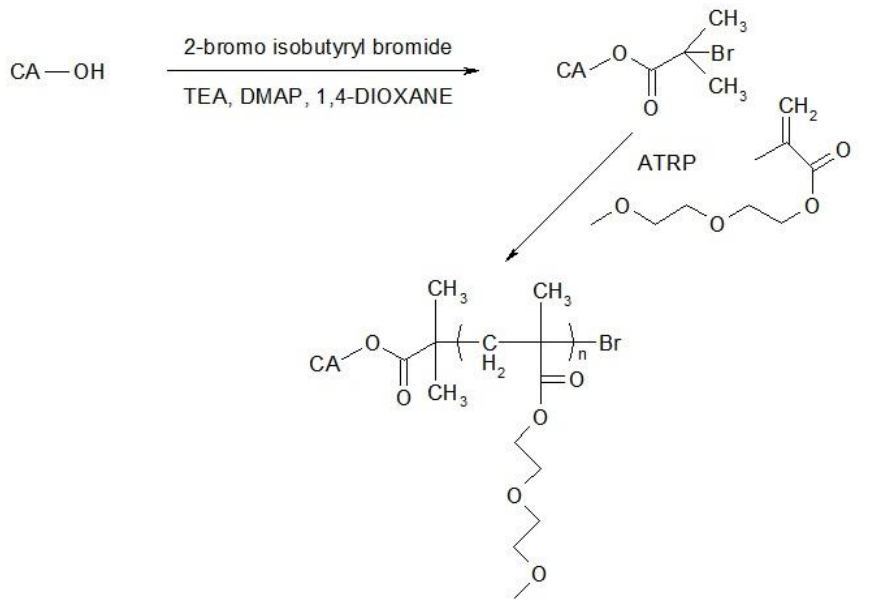


Figure 5 ATRP of MDEGMA onto cellulose acetate.

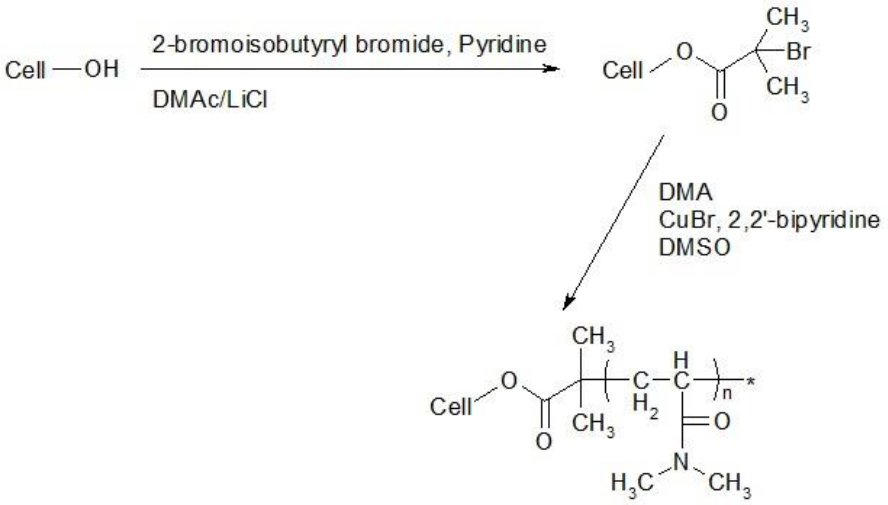


Figure 6 Homogeneous grafting of N,N-dimethylacrylamide onto cellulose through ATRP.

Reversible addition-fragmentation chain transfer (RAFT) polymerization, another 'living'/ controlled radical polymerization method, is of promising and particular interest, over other 'living'/controlled process, as a wider range of functional monomers can be used under the mild-demanding reaction conditions. Using the controlled RAFT technique a number of different functional monomers like MMA, MA and styrene were grafted onto the surface of cellulose [82-84].

Ring-opening polymerization

Ring-opening polymerization (ROP) is a well-established technique to polymerize cyclic monomers such as lactones and lactides. An alcohol (or hydroxyl group) is generally used as the initiator for ROP which makes it especially interesting to utilize ROP of cyclic monomers for the polymer modification of cellulose or cellulose derivatives [85]. ROP operates through different mechanism depending on the monomer, initiator and catalytic system that are utilized. Tin-bis-(2-ethyl hexanoate) [$Sn(Oct)_2$] is a commonly used catalyst for the polymerization of monomers such as ε-caprolactone, lacide and p-dioxanone. Several different mechanisms have been hypothesized for this system, but the most commonly accepted mechanism for the initiation is that, $Sn(Oct)_2$ is converted into tin alkoxide, the actual initiator, by reaction with alcohols i.e. the "coordination-insertion" mechanism [85-87].

$$Sn(Oct)_2 + R\text{-}OH \longrightarrow Oct\text{-}Sn\text{-}OR + OctH$$

$$Oct\text{-}Sn\text{-}OR + ROH \longrightarrow Sn(OR)_2 + OctH$$

Grafting initiated by radiation technique

The irradiation of macromolecules can cause homolytic cleavage and thus forms free-radicals on the polymer. In the radiation technique, the presence of an initiator is not essential. The medium is important in this case, e.g. if irradiation is carried out in air, peroxides may be formed on the polymer. The life time of the free-radical depends upon the nature of the polymer backbone. Grafting proceeds in three different ways: (a) pre-irradiation, (b) peroxidation and (c) mutual irradiation techniques. In pre-irradiation technique, the polymer backbone is first irradiated in vacuum or in the presence of an inert gas to form free-radicals. The irradiated polymer substrate is then treated with the monomer in liquid of vapor state or as a solution in a suitable solvent [88-92].

In the peroxidation grafting method, the trunk polymer is subjected to high-energy irradiation in presence of air or oxygen to form hydroperoxides or diperoxides, depending on the nature of the polymeric backbone and the irradiation conditions. The stable peroxy products are then treated with the monomer at high temperature, whence the peroxides undergo decomposition to radicals, which then initiate grafting. The advantage of this technique is that, the intermediate peroxy products can be stored for long periods before performing the grafting step. On the other hand, with the mutual irradiation technique, the polymer and the monomers are irradiated simultaneously, to form free-radicals and subsequent addition [93-100]. Since the monomers are not exposed in pre-irradiation technique, the obvious advantage is that, the method is relatively free from homopolymer formation, which occurs with the simultaneous technique. However the decided disadvantage of the pre-irradiation technique is scission of the base polymer due to its direct irradiation, which can result in the formation of block copolymer.

Photochemical grafting

When a chromophore on a macromolecule absorbs light, it goes to an excited state, which may dissociate into reactive free-radicals, whence the grafting process in initiated. If the absorption of light does not lead to the formation of free-radical sites through bund rupture, this process can be promoted by the addition of photosensitizers, e.g. benzoin ethyl ether, dyes such as Na-2,7-anthraquinone sulphonate or acrylate azo dye, aromatic ketones (such as benzophenone, xanthone) or metal ions UO_2^{2+}. That means the grafting process by photochemical technique can proceed in two ways: with or without a sensitizer [101-104]. The mechanism without sensitizer involves the generation of free-radicals on the backbone, which reacts with the monomer free-radical to form the grafted copolymer. On the other hand, in the mechanism 'with sensitizer' the sensitizer forms free-radicals, which can undergo diffusion so that they abstract hydrogen atoms from the base polymer, producing the radical sites required for grafting.

Enzymatic grafting

The enzymatic grafting of cellulose is quite new and only two reports in which enzymes are used to catalyze ring-opening polymerization from cellulose surface have been published [105, 106]. Lipase is used for the ROP of ε-caprolactone in close proximity to cellulose fibers in a filter paper. In the first step, the enzyme was immobilized on

the filter paper used as substrate, and in a second step the polymerization was performed. This did not create covalently bonded grafts, but the polycaprolactone formed is coated on the cellulose surface.

Controlling factors of grafting

The factors those control the grafting reactions onto cellulosic materials will be discussed in the following sections. These factors include nature of the backbone, monomer, solvent, initiator, additives, temperature etc.

Nature of the backbone

As grafting involves covalent attachment of a monomer to a pre-formed polymeric backbone, the nature of the backbone (physical nature and chemical composition) plays an important role in the process. It is reported that, crystallinity decreases with increasing degree of substitution of cellulose derivatives, affecting the grafting of acrylamide on acetylated wood pulp [107]. As the crystallinity decreases, it is less ordered and facilitating the grafting reaction.

There are various reports regarding the role of chemical composition on grafting. For example, the presence of lignin (phenolic –OH) in straw, affects the grafting of 2-methyl vinyl pyridine, since lignin is a good scavenger of radicals [108]. This phenomenon has also been observed in ethyl acrylate grafted to a sisal fiber system; sisal fiber contains 8% lignin. The grafting rate is higher when NaOH is used as a lignin remover, but the reverse has also been reported, i.e. the presence of lignin increases the graft yield if the backbone is ozonized and grafted using Fe^{2+}-H_2O_2 as initiator. In that case, lignin is oxidized with ozone, as a result of which the carboxylic group is formed in the lignin structure, favoring the free-radical formation influences grafting [109]. This phenomenon has also been observed is acrylonitrile grafted on pulp by xanthation method. In cases in which lignin is present in the cellulose structure, chain transfer may occur to lignin from the $^{\cdot}OH$ radical, giving rise to less reactive lignin radical [110].

The presence of functional groups in the backbone also influences grafting. Styrene is grafted relatively with high efficiency on cellulose acetate-p-nitro benzoate. This result indicates that the pendant aromatic nitro group is more effective in obtaining a graft copolymer [111]. Replacement of –OH by –SH groups in a cellulose substrate increases the level of grafting as initiation by Ce^{4+} ion occurs by H-abstraction from C-atom having –OH groups. But in case of MMA grafting on holocellulose (comprising a mixture of α-cellulose and hemicellulose) H-abstraction is not the mode of initiation, and –SH group is associated with a marked decrease in the level of grafting [112].

Effect of monomer

As with the nature of backbone, the reactivity of the monomer is also important in grafting. The reactivity of monomer depends upon the various factors, viz. polar and steric nature, swellability of backbone in the presence of the monomers and concentration of monomers. The difference in grafting of vinyl acetate (2.6%) and ethyl acrylate (60.8%) on wool can be explained on these monomers. Since vinyl acetate acts as electron donating monomer, it is extremely susceptible to monomer concentration, whereas ethyl acrylate is highly reactive to free radicals [113]. Thus, the percentage of grafting of ethyl acrylate is higher because the loss of ethyl acrylate in side reaction is minimal. On the other hand, being less reactive to radicals, vinyl acetate is reduced in side reactions.

In case of grafting of acrylonitrile, ethyl acrylate and methyl methacrylate onto starch, it is observed that, the reactivity is in order; AN>EA≈MMA. In this case, grafted polyethylacrylate forms gel over the starch granules, acting as a barrier to monomer diffusion to the vicinity of starch [114]. The order of the monomers on wool in terms of grafting is MA > EA > MMA > VAc > AAc. The reactivity of first three monomers is explained by steric considerations. Thus, MMA, being a highly crowded monomer, forms complex with Ce^{4+} less readily and affords minimum grafting. By contrast, VAc is susceptible to monomer transfer reaction and tends to terminate the growing grafted chain by that process, and resulting in poor grafting efficiency. Since AAc and its polymer are soluble in water, AAc tends to undergo homopolymerization preferentially, resulting in poor grafting efficiency.

The order of grafting of the substituted acrylamides onto cellulose acetate is acrylamide > methylacrylamide > N,N dimethylacrylamide [88]. The methyl group in methylacrylamide may reduce the mobility of the monomer,

thus suppressing grafting. The low grafting with methylacrylamide may also be due to the stability of the polymer radical, which is tertiary whereas polymer radical from acrylamide is secondary. The secondary radicals are more reactive than the tertiary. With N, N-dimethyl acrylamide, two methyl groups play a key role on the extent of grafting. Due to the steric effect of the two-methyl groups, the easy approach of the monomer to the backbone is maximally hindered, and thus the extent of grafting is the least. Earlier workers also observed this phenomenon in case of substituted acrylates. The grafting order on cellulose by means of a Ce^{4+} initiation is methyl acrylate > ethyl acrylate > butyl acrylate > methyl methacrylate. They offered an explanation of reactivity in terms of steric and polar effects. It was also proposed that grafting depends upon the stability of the radical. The polymer radical that is formed in case of methyl methacrylate is relatively stable, whereas in case of methyl methacrylate, which is the most reactive, the corresponding polymer radical is probably stable.

Effect of solvent

In grafting mechanisms, the solvent is the carrier by which monomers are transported to the vicinity of the backbone. The choice of the solvent depends upon several parameters, including the solubility of monomer in solvent, the solubility or swelling properties of the backbone, the miscibility of the solvents if more than one is used, the generation of free radical in the presence of the solvent, etc.

The solubility of the monomer depends on the nature of the solvent and the polymer, e.g. alcohols are useful solvents for grafting styrene onto cellulose or cellulose acetate [115-117]. This is because alcohols can swell the backbone effectively and can dissolve the styrene so that the monomer can easily diffuse in the cellulosic structure. The extent of grafting, however, decreases progressively when the alcohol is changed from methanol to ethanol to isopropanol and to t-butanol, this decrease in grafting is due to the gradually decreased swelling properties of the alcohol, known to be corroborated by the bulkiness of the alcohol molecules. The grafting of styrene is suppressed by the addition of water to alcohol in the grafting medium. Incidentally, although cellulose acetate has a greater affinity for water than MeOH, grafting from the alcohol-water mixture is affected by the decreased solubility of styrene in the solvent [115].

Homogeneous graft copolymerization of MMA onto cellulose and cellulose acetate is carried out in 1,4-dioxane, DMSO, DMSO/PF and DMAc/LiCl solvent systems [2-7]. The molecular weight and graft yield of the cellulose grafted product are higher in DMSO/PF solvent system concluding as a better solvent in comparison to DMAc/LiCl for graft copolymerization of MMA onto cellulose. Dissolution of cellulose in DMSO/PF solvent system forms methylol cellulose where as in DMAc/LiCl it forms a complex the structure of which hinders the reaction sites for the formation of free radicals for grafting and thereby decreases the graft yield [118-119].

Effect of initiator

As discussed earlier, apart from the radiation technique, all chemical grafting reactions require an initiator, and its nature, concentration, solubility as well as function need to be considered. Grafting percentage can be increased either by increasing the number of grafts (grafting frequency) per substrate chain or by increasing the molecular weight of grafted chains at constant number of graft. It is apparent that the initiator concentration affects both the number of grafts per cellulose chain and the molecular weights of graft chains. Radicalic sites may be created on cellulose by some transition metals such as Ce^{4+}, Co^{3+}, and Cr^{6+}. The number of active sites created on the cellulose backbone depends on the initiator concentration, namely, the ratio of initiator/cellulose. It is observed in the grafting of N-vinyl pyrrolidone (NVP) onto cellulose with $Co(acac)_3$–$HClO_4$ as the initiator, the amount of grafted NVP and the conversion of cellulose to graft copolymer first increased with the increase in the initiator concentration and then decreased with further increase in initiator concentration[10]. The similar finding, first the increase in grafting with the initiator and then the decrease with further increase of initiator has also been determined in the grafting reactions performed by the initiators CAN–HNO_3 [20, 21, 23, 26, 120, 121], ceric ammonium sulphate [9], persulfates [122, 123], and $KHSO_3$–$CoSO_4$ [11]. In the grafting of AAm–MA onto cellulose by CAN–HNO_3 initiator system, it is determined that the disappearance rate of Ce^{4+} ions did not change with the variation of monomer concentration from 0.1 to 0.5 M and concluded from this finding that the Ce^{4+} ions do not directly create active radicals on the monomers

[120]. The high efficiency of grafting with Ce^{4+} ions was attributed to the creation of active radicals by CAN initiator preferentially on the cellulose backbone than the monomers [26]. In addition, it is also observed that true grafting percentage (GT %) increased with the increase in Ce^{4+} concentration from 1.5 x 10^{-3} M to 7.5 x 10^{-3} M, but the higher concentrations of CAN than 7.5 x 10^{-3} M led to decrease in GT % due to hydrolysis of CAN and being the hydrolysis product inactive for the creation of active sites in the absence of sufficient amount of nitric acid (HNO_3). The increase in CAN concentration leads to decrease in grafting yield, but the increase in homopolymer formation [21]. CAN prefers to form complex with cellulose over the monomer. However, at higher concentrations of CAN, Ce^{4+} ions form complex with the monomer in addition to that with cellulose, and homopolymer formation can also occur. The termination of growing polymer radicals is also accelerated with Ce^{4+} concentration, and it leads to the decrease in grafting yield. When CAN was used as initiator, the acid, mostly HNO_3, has an important effect on the efficiency of initiator for grafting. As known, the reaction of CAN with aqueous HNO_3 occurs as written below:

$$Ce^{4+} + H_2O \rightleftharpoons Ce(OH)^{3+} + H^+$$

As known, ceric ion in CAN exists as the species of Ce^{4+}, $Ce(OH)^{3+}$, and $(Ce–O–Ce)^{6+}$ in its aqueous solution. It was reported that the efficiency of Ce^{4+} and $Ce(OH)^{3+}$ species to form radical sites on cellulose backbone is higher than that of $(Ce–O–Ce)^{6+}$ since the size of the former is smaller than that of the latter [121] and the former is more mobile than the latter. At high acid concentrations, Ce^{4+} and $Ce(OH)^{3+}$ species affects the grafting adversely, namely, the termination reaction dominates over the propagation. A possible explanation for this adverse effect of high acid concentration on the grafting may be the difficulty in hydrogen abstraction from graft substrate. The concentration of these species depends on the amount of acid present in the medium. At high nitric acid concentrations, the above equilibrium reaction shifts to the left and ceric ions in CAN occur in the form of Ce^{4+} which is responsible for the creation of active radicals preferably on the cellulose than monomer. In the case of low acid concentrations, the equilibrium shifts to the right, and the formation of high amount of $Ce(OH)^{3+}$ led to the formation of considerable amount of $(Ce–O–Ce)^{6+}$ which is not active for the creation of radical sites.

$$2\ Ce(OH)^{3+} \rightleftharpoons (Ce – O – Ce)^{6+} + H_2O$$

For that reason, CAN or another ceric salt should be used together with an acid (i.e. HNO_3). The increase in the concentration of HNO_3 from 0.3 M to 0.5 M led to 20 % increase in grafting percentage of NVP onto cellulose by CAN initiator, and further increase in HNO_3 concentration resulted in 10 % decrease in grafting percentage. The decrease in grafting with the increase in acid concentration beyond the optimum value was attributed to the effect of excess H^+ ions as free-radical terminator [21]. The effect of complexing agent such as KF, ascorbic acid, and EDTA on the grafting of ethyl acrylate (EA) onto cellulose by Fenton reagent (Fe^{2+}–H_2O_2) is investigated [18]. In order to avoid the negative effect of Fe^{3+} ions on the grafting, namely, the wastage of $^{\bullet}OH$ radicals by reaction with Fe^{3+} ions, the grafting was carried out in the presence of some complexing agents with Fe^{3+} ions such as ascorbic acid, potassium fluoride (KF), and ethylenediaminetetraacetic acid (EDTA) [18]. At low concentration (81 x 10^{-4} M), KF gave highest amount of grafting among the complexing agents, but its increase to 166 x 10^{-4}M reduced the grafting of EA significantly. The similar behaviour was observed for the grafting of VAc under the same conditions. KF makes complex with Fe^{3+} ions and favours the grafting. The decrease in grafting percentage with KF attributed to the oxidation of KF to elemental fluorine (F) which reacts with vinyl monomer giving as an addition product, and it leads to decrease in grafting. Both EDTA and ascorbic acid reduced the grafting of both EA and vinyl acetate (Vac) at all concentrations investigated. In the grafting of MMA onto stone ground wood by Fenton reagent, it is determined that graft yield increases with the molar ratio of Fe^{2+}–H_2O_2 up to 0.085, and after that concentration, the graft yield decreased slightly [19]. It is concluded that only a low molar ratio of Fe^{2+}–H_2O_2 is enough to succeed the grafting. The similar trend (first increase and then decrease) for the grafting with the concentration is also observed for of various persulfates such as KPS [16], and APS [122-124] is observed for AIBN [124] and BPO [122] too. The effects of various redox initiators, viz. APS, KPS, and BPO, in the grafting of AAm onto ethyl cellulose (EC) in dimethylsulfoxide (DMSO)/toluene solution has been studied [15]. It is determined that APS is a suitable initiator for grafting of AAm onto EC because it leads no degradation in EC chains. Again, the increase in APS concentration led

to decrease in grafting parameters such as grafting percentage or grafting yield due to termination of primary radicals, but the use of KPS in the same reaction increased the same grafting parameters. The opposite effects of the concentration of redox initiators APS and KPS on the grafting are attributed to the difference in the decomposition rates of initiators [125]. It is also determined that BPO (benzoyl peroxide) is not a suitable initiator since it leads to degradation of EC, and for that reason, BPO gave considerably lower grafting yield and efficiency in comparison to APS and KPS. Grafting of AN and MMA separately onto cellulose in DMSO/PF system (in homogeneous medium) using two types of initiators: APS and BPO has been investigated [124]. It is known that DMSO/PF system is a non-degrading solvent for cellulose. The nature of the initiator has an important effect on the grafting. AIBN is known to show resonance stabilization, but no such resonance exists in the peroxide initiators. For that reason, it is reported that higher grafting yield is obtained with APS, 87.3 % for AN and 52 % for MMA, in comparison to those with AIBN, i.e., 10 % for AN and 48 % for MMA. The number of grafts per cellulose chain by APS and AIBN initiator were found to be 3.9 and 0.5 for AN and 3.4 and 1.3 for MMA monomers. From the results it is suggested that, grafting occurred in higher parts of cellulose chain in homogeneous medium than heterogeneous medium in which the number of grafts per cellulose chain rarely exceed the unity. It is also found that the grafting onto cellulose hardly proceeded with AN–AIBN system, but appreciably in MMA–AIBN system.

Role of additives on grafting

Graft yield or the the extent of graft co-polymerization depends on the presence of additives such as metal ions, acids, and inorganic salts. Thus, the reaction between the monomer and the backbone must compete with any reactions between the monomer and additives. Although some additives may enhance the monomer/backbone reaction to augment the grafting efficiency, the reverse will be true if the reaction between the monomer and the additive is dominant.

The addition of acids and alkali can affect the nature of the backbone, solvent as well as the initiator, so that it can influence the grafting. For example, when ethyl acrylate and styrene are co-grafted on sisal fiber, the presence of sulfuric acid or alkali controls the grafting yield [126]. The increase in crystallinity due to the alkali treatment will result in reduction in the sorption capacity of the fiber. As a result, the amount of monomer solution sorbed in the fiber during the grafting process will be reduced. This accounts for the decrease in the grafting efficiency for sisal fibers subjected to alkali treatment. By contrast, when the fibers are subjected to the combined treatment, fibrillation due to the intracrystallite swelling by the acid facilitates the subsequent penetration of NaOH solution, resulting in better grafting onto cellulose. Moreover, the combined treatment may result in increase in ordering of the fibers in addition to an increase in the crystalline regions. These effects are reflected in the slight decrease in the grafting yield of fibers subjected to the combined treatment, compared to that of the fibers subjected to the alkali treatment alone.
In case of Ce^{4+}, taken as the initiator for grafting of methyl methacrylate onto cellulose, maximum grafting takes place in the presence of sulfuric acid [126-128]. In aqueous medium, initiator Ce^{4+} is believed to combine with water according to the reaction discussed in section 3.4. It is also clear that [Ce^{+4}] facilitates the formation of complex with the base polymer with increasing the concentration of H_2SO_4, as the equilibrium shifts towards formation of more and more of $Ce(OH)^{3+}$ and Ce^{4+} . Having smaller size, these species facilitate the formation of a complex between Ce^{4+} ion and cellulose, resulting in an increase in percentage of grafting.

The effect of amines upon ceric ion initiated grafting of poly (methyl acrylate) onto wool has been explained by assuming a complex formation between wool and the ceric ion [129] in the following manner:

$$Ce^{4+} + RNH_2 \rightleftharpoons \text{Complex} \longrightarrow Ce^{3+} + H^+ + RN^{\bullet}H$$

The ceric amine complex decomposes to give free-radical species, which at lower concentration generate more active sites on wool by H-abstraction. However, there exists as a critical concentration of amines that promotes grafting. With a further increase in concentration, the percentage of grafting decreases owing to termination of growing grafted chain-by-chain transfer with the amine.

The reactivity of amines followed the order diethylamine > dipropylamine > ammonia > triethylamine>triethanolamine > pyridine [130]. The grafting percentage increases linearly with an increase in basicity

of the amines. Though diethylamine is as nucleophilic as dipropylamine, only DEA enhances grafting rate tremendously, while in the presence of DPA no accelerating effect upon grafting efficiency is observed. This is explained by the steric factor, such that DEA, having a smaller steric requirement than DPA, easily forms a complex with Ce^{4+}. Ammonia, having a smaller steric requirement than TEA, forms a complex with Ce^{4+} more easily than does TEA. With triethanolamine and pyridine, all three factors i.e. basicity, nucleophilicity and steric size, are responsible for giving a low grafting efficiency.

The addition of $NaNO_3$ or NaCl in the grafting of vinyl acetate and methyl acrylate on cellulose acetate, affect the graft co-polymerization by enhancing the oxidation of cellulose by the transition metal ions (viz. Ce^{4+}), initiates the formation of free radicals for grafting, but it left the homopolymerization almost unaffected [131].

Effect of temperature

Temperature is one of the important factors that controls the kinetics of graft co-polymerization. In general, graft yield increases with increase in reaction temperature until a limit is attained, and then it decreases for persulfates [14, 15, 122, 124]. Similar results have also been reported in the literature for Ce^{4+} initiator [2-7, 15, 22, 24]. For example, Nishioka et al. [122, 123] found in the grafting in homogeneous medium by persulfate initiators that with the increase in temperature, the molecular weight of graft chains decreased, but the number of grafts increased up to a certain amount, and then leveled off. The optimum temperature for highest grafting depends on the initiator used. In the grafting of HEMA onto cellulose in DMSO/PF solvent system using various initiators [125], it is determined that the optimum temperatures are 40 °C for APS, 50 °C for KPS, and 60 °C for both AIBN and BPO. In the grafting of AA onto cellulose in heterogeneous medium by CAN–HNO_3 initiator [132], nearly the same grafting percentages were obtained at 30, 50, and 70 °C, but three to four times lower grafting percentages were obtained at 90 °C than those at former temperatures. The graft copolymer prepared at 30 °C had highest water absorption capacity probably due to difference in their grafting frequencies and graft lengths. Therefore, the optimum grafting temperature was determined as 30 °C for the grafting of AA onto cellulose by CAN–HNO_3 initiator[132]. It was also determined that the rate constants for the disappearance of AA during the grafting increased from 0.018 min^{-1} to 0.033 min^{-1} with the increase in temperature from 30 to 90 °C, and the increase in temperature favoured the formation of homopolymer poly(acrylic acid) (PAA).

Conclusions

The discussion above shows that, through grafting, a beautiful level of control on both structure and function of cellulosic materials can be implemented. In this report, we have sketched different mechanistic approaches for grafting by chemical method, radiation technique, photochemical and enzymatic techniques. Apart from the conventional grafting process, living radical polymerization and ring-opening polymerization are also focused. Different factors that control grafting, like the nature of the backbone, initiator, monomer etc. have also been discussed. Fortunately, the grafting process is now expanding rapidly through electron beam curing processes that can be achieved in a fraction of a second, and yield products in one step without further purification. Apart from the various advantages of the grafting, research takes step towards 'bio degradability'. It may solve some of the problems of environmental pollution caused by components that resist bio-degradation.

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