

Chapter 2

Cellulose Graft Copolymers: Synthesis, Properties, and Applications

Gülten Gürdağ and Shokat Sarmad

Abstract Grafting of vinyl monomers onto cellulose is an important tool for the modification of cellulose. Depending on the monomer grafted onto cellulose, it gains new properties. The grafting can be performed in heterogeneous or homogeneous medium. In the grafting performed in heterogeneous medium, the reaction is carried out in aqueous medium using a suitable initiator. As initiator, the radiation or chemical initiators such as ceric ammonium nitrate (CAN), various persulfates, azobisisobutyronitrile (AIBN), and Fenton reagent (Fe(II)–H₂O₂) are mostly used. In case of CAN initiator, the grafting should be performed in acidic medium in order to prevent its hydrolysis. In the homogeneous grafting reactions, either a water-soluble cellulose derivative is used in the grafting or cellulose is dissolved in a suitable solvent, and then the grafting is performed. Higher number of grafts per cellulose chain is obtained in homogeneous grafting than those in heterogeneous medium.

Keywords Cellulose • Grafting • Homogeneous medium • Heterogeneous medium • Grafting percentage • Grafting efficiency • Number of grafts per cellulose chain • Ceric ammonium nitrate • Fenton reagent • Persulfates

2.1 Introduction

Cellulose is a naturally occurring polymer, and it is the most abundant and renewable polymer in the world. In addition, it is one of the most promising raw materials due to its abundance, easy availability, and low cost. It is a linear polysaccharide with long chains which consists of β -D-glucopyranose units joined by β -1,4

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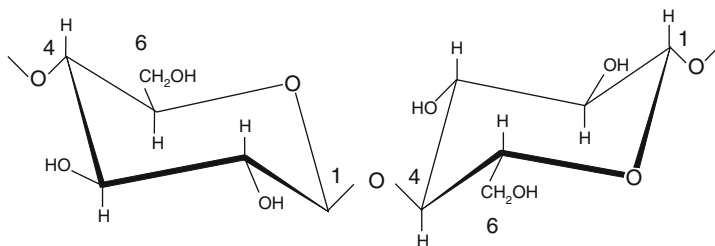


Fig. 2.1 Cellulose formula [4]

glycosidic linkages [1–3]. In one repeating unit of cellulose molecule, there are one methylol and two hydroxyl groups as functional groups [4].

Due to absence of side chains or branching, cellulose chains can exist in an ordered structure. Therefore, cellulose is a semicrystalline polymer, and it contains both crystalline and amorphous phases. Although it is a linear polymer and contains two types of hydroxyl groups, primary hydroxyl in methylol group ($-\text{CH}_2\text{OH}$) at C-6 and secondary hydroxyl groups ($-\text{OH}$) at C-3 and C-4, both of which are hydrophilic, it does not dissolve in water and in common solvents due to strong hydrogen bondings between the cellulose chains. The hydrogen bondings between the cellulose chains and van der Waals forces between the glucose units lead to the formation of crystalline regions in cellulose [5]. In cellulose, there are two types of hydrogen bondings: intramolecular and intermolecular [6]. Intramolecular hydrogen bondings are of two types, i.e., $\text{O}-2-\text{H} \cdots \text{O}-6$ and $-3-\text{H} \cdots \text{O}-5$ links [6]. It can be dissolved in DMSO–PF (dimethyl sulfoxide–paraformaldehyde), LiCl–DMAc (lithium chloride–dimethylacetamide) [7], *N*-methylpyrrolidone–lithium chloride (NMP–LiCl) [7], etc. Cellulose also dissolves in strong concentrated acids such as H_2SO_4 and H_3PO_4 and certain metal complexes such as cuprammonium (cuam) or cupriethylenediamine (cuen) that they break the hydrogen bonds between the cellulose chains.

Cellulose has two crystal forms: cellulose I and cellulose II [4]. In the former, cellulose chains are oriented in parallel conformation, and in the latter, antiparallel one [4] (Fig. 2.1). Cellulose has other polymorphic forms of cellulose III and cellulose IV. According to XRD data [8], the crystallinity of cotton cellulose is 60 % which is in cellulose I form, and the rest is amorphous cellulose. The degree of crystallinity (CrI) of cellulose, namely, the fraction of crystalline content in the cellulose sample, is calculated from XRD patterns by using the peak intensities at $2\theta = 18^\circ$ (I_{am} : intensity due to amorphous portion) and at $2\theta = 22.5^\circ$ (I_{200} : intensity attributed to both amorphous and crystalline phases) [6, 9].

$$\text{CrI} = [(I_{200} - I_{\text{am}})/I_{200}] \times 100 \quad (2.1)$$

Hermans et al. [10] calculated the crystallinity of cellulose (X_c) by another equation given below:

$$X_c = I_c / (I_c + K + I_{\text{am}}) \quad (2.2)$$

where I_c is the intensity of crystalline portions, I_{am} is the intensity of amorphous portions, and K is an empirical constant.

Although the properties of cellulose cannot be modified by conventional copolymerization methods, they can be changed by physical or chemical techniques. The change in the physical structure of cellulose can be performed by swelling it in concentrated (~20 %) NaOH solution and then by regeneration (mercerization) [11]. By this way, cellulose I is irreversibly converted to cellulose II, and the physical properties of cellulose are changed. Mercerization increases the amorphous content, tensile strength, and modulus of cellulose [2, 8], and it makes cellulose more reactive since amorphous regions are more accessible and more reactive than crystalline regions [6]. Chemical properties of cellulose can be changed in three ways:

1. By preparing an ester or ether derivative of cellulose
2. By preparing a cross-linked derivative of cellulose
3. By preparing a graft copolymer of cellulose, namely, a branched derivative of cellulose

2.2 Synthesis of Cellulose Graft Copolymers

Graft copolymerization is a commonly used method for the modification of surfaces of polymers [12, 13], and it is an important tool in order to modify the physical or chemical properties of polymers. During grafting, the side chains are covalently bonded to the main polymer backbone or substrate to form a copolymer with branched structure. Graft copolymers have many different and useful properties different from those which each has alone. Grafting methods can be classified mainly according to grafting medium and the type of initiation mechanisms. Grafting can be performed in a homogeneous or in a heterogeneous medium. Initiation mechanisms can be investigated in three groups:

1. The polymerization of a vinyl monomer in the presence of a polymer in which the propagation reaction is initiated on the polymer backbone by a chain transfer, and the growth of graft chains begin from the active sites on the polymer backbone. This method is called as “grafting from” approach. In that approach [14], the grafting is performed either with a single monomer or with a binary monomer mixture. With single monomer, the grafting usually occurs in a single step, but in the grafting with binary monomer mixture, the reaction is carried out with either the simultaneous or sequential use of the two monomers. In the mosaic grafting, two kinds of monomer are grafted side by side to obtain the required property. This is the origin of bipolar membranes [14].
2. The polymerization of a vinyl monomer in the presence of a polymer with reactive functional end groups. These functional end groups can be activated by means of heat, light, or other ways. This method can be performed by two ways: In “grafting to” approach, a polymer with reactive end groups is reacted

with the functional groups of substrate polymer backbone. In the “grafting through” approach, a macro monomer or a macromer, i.e., a vinyl derivative of cellulose is polymerized with the same or another vinyl monomer [15].

3. The grafting of a monomer onto a polymer backbone by high-energy irradiation. The radiation grafting can be performed by direct/mutual method in which the monomer and the polymer (graft substrate) is irradiated together simultaneously to create the radicals which are starting the polymerization or by preirradiation/indirect grafting in which the monomer is contacted with the polymer backbone irradiated alone before.

Depending on the chemical structure of the monomer grafted onto cellulose, graft copolymers gain new properties such as water absorption [16], improved elasticity, hydrophilic or hydrophobic character, ion-exchange [17–23] and dye-adsorption capabilities [19, 24], heat resistance [16, 25–28], thermosensitivity [29, 30], pH sensitivity [31], antibacterial effect [32], resistance to microbiological attack, etc. [33, 34]. While the internal grafting changes the dyeing behavior of cellulose fibers, surface grafting improves the abrasion resistance [7]. In order to obtain a cellulose graft copolymer with high water or moisture absorbency, hydrophilic monomers such as acrylic acid (AA), acrylamide (AAM), 2-acrylamido-methylpropane sulfonic acid (AASO₃H), etc. should be grafted onto cellulose. In order to improve the compatibility and adhesion of hydrophilic cellulose fibers to the components of hydrophobic composites, hydrophobic monomers such as methyl methacrylate, styrene, acrylonitrile, butadiene, isobutyl vinyl ether, and vinyl acetate should be grafted onto the surface of cellulose [35–38].

The synthesis of cellulose graft copolymers are different from that of the completely synthetic graft copolymers since cellulose does not dissolve in common solvents, and the grafting takes place in a heterogeneous medium. Therefore, the physical structure and the state of aggregation play an important role in the grafting reaction if it is performed in heterogeneous medium. In the grafting in a heterogeneous medium, cellulose exists in dispersed form in an aqueous medium. It is known that in the grafting onto cellulose under heterogeneous conditions, the reaction proceeds only in the amorphous regions of cellulose [39–42]. For that reason, unpurified graft product is not homogeneous, and it consists of cellulose graft copolymer, ungrafted cellulose, and homopolymer [35, 43]. In addition, chain degradation of cellulose backbone takes place during the creation of free radicals in heterogeneous grafting. Another drawback of the heterogeneous grafting is nonuniformity of graft chain lengths, namely, the formation of short and very long graft chains or high molecular weight distribution of graft chains. Strong hydrogen bonds between the cellulose chains hinder grafting when vinyl monomers are used without an appropriate swelling agent, such as water [44]. In heterogeneous grafting reactions [45], grafting percentage decreases with the increase in crystallinity and intermolecular hydrogen bondings in cellulose. As the swelling power of the solvent or the amount of the swelling agent increases, the rate of diffusion of monomer and, in turn, the rate of grafting increases [44, 45]. However, the swelling agent also affects the rate of termination of the graft copolymerization [44]. In the

case of the grafting in a homogeneous medium in which the cellulose dissolves molecularly, it is known that all the cellulose chains participate in grafting reaction [41, 46]. By performing the grafting reaction using soluble cellulose derivatives in a homogeneous medium, the extent and frequency of grafting and the molecular weight of graft chains and homopolymer can be controlled better, the formation of by product homopolymer is minimized, the homogeneity of graft product or uniform distribution of graft chains can be ensured, etc. [35, 47]. In addition, in homogeneous grafting, the molecular weight of graft chains is similar to that of homopolymer occurring simultaneously with the graft copolymer [48]. The grafting reactions in homogeneous medium can be performed by using a soluble cellulose derivative (mostly water-soluble cellulose derivative) such as hydroxyethyl cellulose (HEC), carboxymethyl cellulose sodium salt (CMCNa) [49, 50], carboxymethyl cellulose (CMC) [51], methyl cellulose (MC) [52, 53], cellulose acetate [54], and ethyl cellulose [42, 46] or dissolving the cellulose in a suitable solvent pair such as *N,N*-dimethylacetamide/LiCl system [43], dimethyl sulfoxide–paraformaldehyde (DMSO–PF) system [39–41, 55] and using carboxymethyl cellulose by xanthate method [56]. In another group of homogeneous grafting works, the reaction is performed in two steps. In the first step, a derivative of cellulose is prepared, and then the product of the first step is reacted with the monomer in the second step. For example, Bianchi et al. [7, 43] prepared a cellulose derivative, such as cellulose acrylate or cellulose methacrylate, by reacting cellulose dissolved in DMAc–LiCl with acryloyl chloride and methacryloyl chloride (MACl), respectively, and then they grafted the acrylonitrile (AN) or methyl methacrylate (MMA) onto acrylate or methacrylate derivative of cellulose in homogeneous medium, respectively. In another work, Wang et al. [57] grafted poly(caprolactone monoacrylate) (PCLA) with isocyanate end groups (NCO) (NCO-PCLA) onto cellulose diacetate (CDA) in homogeneous medium of acetone. Lin et al. [58] grafted acrylic acid (AA) onto cellulose dissolved in an ionic liquid (IL) of 1-*N*-butyl-3-methylimidazolium chloride (BMIMCl) by microwave irradiation in a short irradiation duration such as 3 min. ILs which are organic salts are good solvents [59] and good reaction media for cellulose. They are environmental friendly alternatives to volatile organic compounds (VOC) due to their nonvolatility, nonflammability, thermal stability, chemically inertness, and recyclability [60]. Due to their high ionic conductivities and polarizability properties, they absorb microwave irradiation, and as a consequence they provide high heating rates and shorten the reaction duration [58]. Zhu et al. [61] grafted poly(*p*-dioxanone) (PDO) onto ethyl cellulose (EC) by ring-opening polymerization with a tin-2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) as catalyst in bulk at 120 °C. In the grafting of PDO onto EC in homogeneous medium by $\text{Sn}(\text{Oct})_2$ catalyst, it was not necessary to add any solvent in reaction mixture [61] due to well solubility of EC in PDO. In the grafting methods summarized above, the grafting is performed mostly by creation of free-radical sites on the cellulose backbone either by chemical means or by irradiation. The growth of side chains from vinyl monomers is initiated from these radical sites on the cellulose backbone. However, these techniques have some drawbacks as stated above. More advanced, controlled/living polymerization

methods such as atom-transfer radical polymerization (ATRP) (or metal-catalyzed living-radical polymerization) [30, 31, 60, 62–67], nitroxide-mediated polymerization (NMP) [68], and reversible addition-fragmentation chain transfer (RAFT) [69–72] polymerization are promising methods for the synthesis of well-defined graft polymers with sophisticated architectures such as comb and star polymers, copolymers with the same length of graft chains (low polydispersity/or narrow molecular weight distribution for graft chains), homogeneous grafting frequency, and no homopolymer formation. The main advantage of ATRP is resulting from the relatively low radical concentration in grafting medium which suppresses the termination in comparison to propagation reaction [73–75]. Hiltunen et al. [76] prepared cellulose-graft-polyacrylamide and cellulose-graft-poly(*N,N*-dimethylacrylamide) copolymers by single-electron transfer living radical polymerization (SET-LRP) in DMSO solution. In the first step of grafting, they [76] synthesized cellulose macroinitiators by direct acylation of cellulose with 2-bromoisobutyryl bromide (BiB) in LiCl/DMAc (dimethylacetamide). Then, the grafting of acrylamide (AAm) or *N,N*-dimethylacrylamide (DMAAm) onto cellulose macroinitiator was performed in LiCl/DMAc solvent pair under nitrogen atmosphere using CuCl/PMDETA (*N,N,N',N',N'*-pentamethyldiethylenetriamine) as catalyst.

A detailed list about the grafting reactions performed in homogeneous or heterogeneous media was given in Table 2.1.

2.2.1 *Initiators Used in the Preparation of Cellulose Graft Copolymers*

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 (ir)radiation. 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: $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$) (CAN) [77] or cerium (IV) sulfate [21], ceric ammonium sulfate (CAS) [49, 50], iron(II)–hydrogen peroxide (Fe^{2+} – H_2O_2 : Fenton reagent), cobalt (III) acetylacetonate complex salts [45], Co(II)–potassium monopersulfate [78], and sodium sulfite–ammonium persulfate [51], and free radical generators such as azobisisobutyronitrile ($\text{C}_8\text{H}_{12}\text{N}_4$: AIBN) [79], potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$: KPS) [42, 46, 52, 80–82], ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$: APS) [42, 46, 53], and benzoyl peroxide ($\text{C}_{14}\text{H}_{10}\text{O}_4$: BPO) [42, 46] can be used. The grafting is also performed by radiation [54, 83] or microwave irradiation [54, 58, 84]. Redox initiator systems can be used at low temperatures, and they react only with the amorphous region of cellulose because the latter are more reactive than the crystalline phase.

Table 2.1 Grafting onto cellulose and its derivatives performed in homogeneous or heterogeneous media

Graft substrate	Monomer	Initiator	Reaction medium	References
Grafting in homogeneous medium				
Cellulose	Methyl methacrylate	Cellulose chloroacetate (macroinitiator)	1-Butyl-3-methylimidazolium chloride	[60]
Cellulose	<i>N</i> -isopropylacrylamide	6-O-bromoisobutyryl-2,3-di-O-methyl cellulose (macroinitiator)	Dimethylacetamide/lithium chloride	[30]
Ethyl cellulose	2-Hydroxyethyl methacrylate	EC, 2-Bromoisobutyryl bromide (macroinitiator)	Methanol	[67]
Carboxymethyl cellulose	Styrene	Bulk polymerization	Tetrahydrofuran	[68]
Cellulose	Styrene, methyl methacrylate, methacrylamide, and acryloylmorpholine	Cellulose chloroacetate (macroinitiator)	Dimethyl formamide	[66]
Cellulose	<i>p</i> -dioxanone	Tin 2-ethyl-hexanoate (catalyst)	1-Butyl-3-methylimidazolium chloride	[110]
Cellulose	Styrene	Azobisisobutyronitrile	Toluene	[35]
Cellulose	Methyl methacrylate and styrene	Cellulose 2-bromoisobutyrylate (macroinitiator)	1-Allyl-3-methylimidazolium chloride	[112]
Cellulose filter paper	Acrylonitrile	Gamma rays of ⁶⁰ Co	Dimethyl formamide	[141]
Carboxymethyl/cellulose	Acrylamide	Sodium bisulfate/ammonium persulfate	Sulfate acid–potassium dichromate	[56]
Ethyl cellulose	2-(diethylamino) ethyl methacrylate	Cellulose 2-bromoisobutyrylate (macroinitiator)	Dimethyl formamide	[31]
Ethyl cellulose	Methyl methacrylate	Ammonium persulfate, potassium persulfate, and benzoyl peroxide	Benzene/DMSO	[42]
Methacrylate-modified cellulose	Methyl methacrylate	Azobisisobutyronitrile	Dimethylacetamide/lithium chloride	[7]
Ethyl cellulose	Azobenzene-containing polymethacrylates	Ethyl cellulose based macroinitiator	Anisole	[113]

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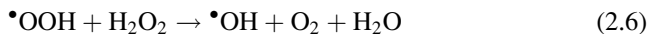
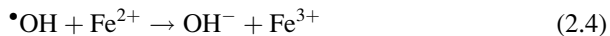
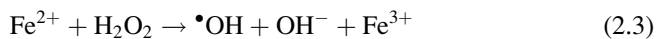
Table 2.1 (continued)

Graft substrate	Monomer	Initiator	Reaction medium	References
Ethyl cellulose	Acrylamide	Ammonium persulfate, potassium persulfate, and benzoyl peroxide	Dimethyl sulfoxide/toluene	[46]
Cellulose	Acrylamide and poly(<i>N,N</i> -dimethylacrylamide)	2-Bromoisobutyl bromide (macroinitiator)	LiCl/dimethylacetamide	[76]
Cellulose	Acrylic acid	Ammonium persulfate	1-Butyl-3-methylimidazolium chloride	[58]
Cellulose	Acrylonitrile and methyl methacrylate	Ammonium persulfate,	Dimethylsulfoxide–paraformaldehyde	[40]
Cellulose	Acrylonitrile and methyl methacrylate	Azobisisobutyronitrile	Dimethylsulfoxide–paraformaldehyde	[41]
Cellulose	Acrylonitrile	Ammonium persulfate, azobisisobutyronitrile	<i>N,N</i> -dimethylacetamide/LiCl	[43]
Cellulose diacetate	Caprolactone monoacrylate	Dibutyltin dilaurate (catalyst)	Acetone	[57]
Cellulose	Methyl acrylate	Ammonium persulfate, Azobisisobutyronitrile, benzoyl peroxide	Dimethylsulfoxide–paraformaldehyde	[39]
Cellulose acetate	Styrene and acrylamide	Gamma rays of ⁶⁰ Co	Water, methanol, ethanol, isopropanol, and <i>t</i> -butanol	[54]
Mixture of carboxymethylcellulose and its sodium salt with hydroxyethylcellulose	<i>N</i> -vinyl-2-pyrrolidone	Ceric ammonium sulfate	Aqueous	[49, 50]
Carboxymethyl cellulose	Acrylamide	Ammonium persulfate and sodium sulfite	Aqueous	[51]
Methyl cellulose	Acrylamide	Potassium persulfate	Water	[52]
Cellulose	2-Hydroxyethyl methacrylate	Ammonium persulfate, potassium persulfate, azobisisobutyronitrile	Dimethylsulfoxide–paraformaldehyde	[55]
Grafting in heterogeneous medium				
Cellulose	Acrylamide and ethyl acrylate	Ceric ammonium nitrate	Aqueous	[100]
Wood pulp	Acrylamide	Ceric ammonium nitrate	Acidic	[98]

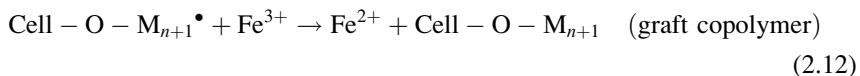
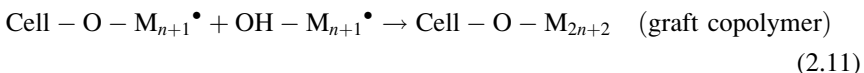
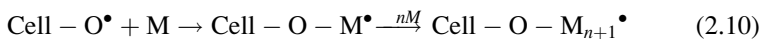
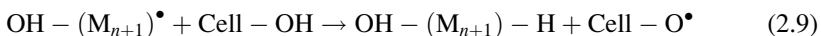
Cassia tora gum	Acrylonitrile	Ceric ammonium nitrate–nitric acid	Aqueous	[95]
Tamarind kernel powder	Acrylamide	Ceric ammonium nitrate–nitric acid	Aqueous	[124]
Stone ground wood	Methyl methacrylate	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$	Distilled water	[90]
Carboxymethyl cellulose	Methyl acrylate	Ammonium persulfate	Aqueous	[53]
Cotton fibers	Acrylic acid, methacrylic acid and acrylamide	Potassium persulfate	Aqueous	[80]
Cotton cellulose	Allyl–dimethylhydantion	Potassium persulfate	Aqueous	[81]
Henequen cellulose microfibrils	Acrylic acid	Potassium persulfate	Water	[105]
Cotton cellulose	Acrylamide	Potassium monopersulfate	Acetic acid, formic acid, and methanol	[78]
Cellulose	Acrylic acid	Ceric ammonium nitrate	Aqueous	[44]
Cellulose	Acrylic acid	Xanthone, 2-chloroanthraquinone and hydrogen peroxide (photoinitiator)	Aqueous	[106]
Cellulose	<i>N</i> -isopropylacrylamide	Ammonium cerium(IV) nitrate	Aqueous	[29]
Cellulose fibers	Acrylonitrile	Azobisisobutyronitrile	Bulk polymerization	[79]
Cellulose	4-Vinyl pyridine	Gamma rays of ^{60}Co	Water	[114]
Cellulose	Ethyl acrylate	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$	Aqueous	[89]
Cellulose fluff pulp	Acrylic acid, acrylonitrile	Ceric ammonium nitrate	Aqueous	[109]
Cellulose	Acrylamide–methyl acrylate	Ceric ammonium nitrate	Aqueous	[103]
Ethyl cellulose	<i>p</i> -dioxanone	Tin 2-ethyl-hexanoate (catalyst)	Bulk polymerization	[61]
Cellulose	<i>N</i> -vinyl pyrrolidone	Cobalt acetylacetonate	Aqueous	[45]
Cellulose	4-Vinyl pyridine	Ceric ammonium nitrate	Aqueous	[96]
Hollocellulose	Acrylic acid	Ceric ion	Aqueous	[77]
Cellulose fiber	Acrylic and methacrylic acid	Gamma rays of ^{60}Co	Water	[83]
Cellulose	Vinyl acetate	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$	Aqueous	[85]
Cellulose	Acrylamide	Cerium sulfate	Water	[21]
Cellulose	<i>N</i> -isopropylacrylamide and methyl acrylate	Potassium persulfate and ceric ammonium nitrate	Aqueous	[84]

2.2.1.1 Fe(II)–H₂O₂

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 [85]. The mechanism for the creation of $\bullet\text{OH}$ radicals by one electron transfer by the reaction of Fe(II) ion with hydrogen peroxide was proposed for the first time by Haber and Weiss [86, 87], and it was given in Eqs. (2.3)–(2.6) below:

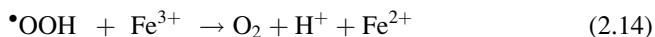
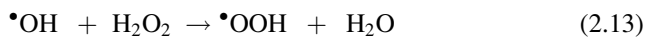


The hydrogen peroxide molecules react with ferrous (Fe^{2+}) ions, and thus, ferric (Fe^{3+}) ions and primary hydroxyl radicals are created. Then, the primary hydroxyl radicals abstract a hydrogen atom from cellulose resulting in a secondary cellulose radical, and the grafting is initiated from these hydrogen-abstracted sites on the cellulose backbone, or the hydroxyl radicals react with monomer to produce homopolymer. Merz and Waters [88] suggested for the first time that the hydroxyl radicals ($\bullet\text{OH}$) created in reaction (2.3) can be used for the grafting of vinyl monomers onto cellulose. The grafting of vinyl acetate onto cellulose by Fenton reagent was proposed to occur by the following mechanism given in Eqs. (2.7)–(2.12) [85];



The grafting yield or the grafting percentage is dependent on the molar ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$. As seen in Eq. (2.12), Fe^{3+} ion, which is created in Eq. (2.3), leads to the

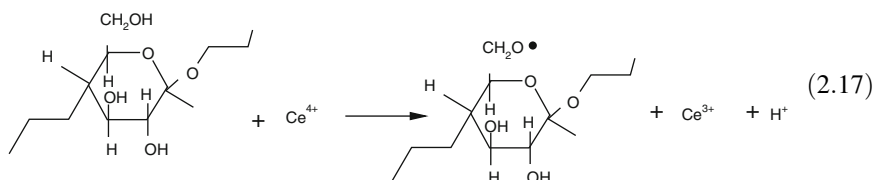
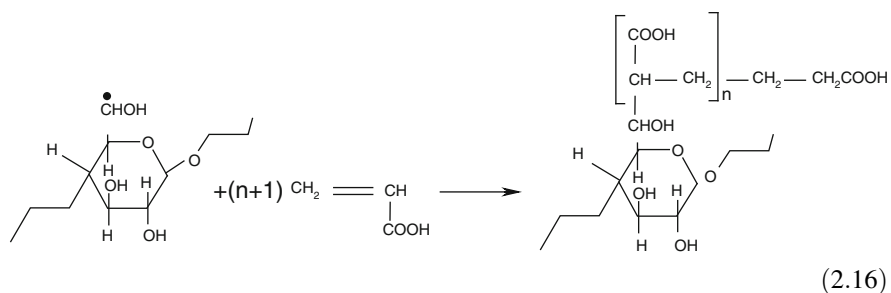
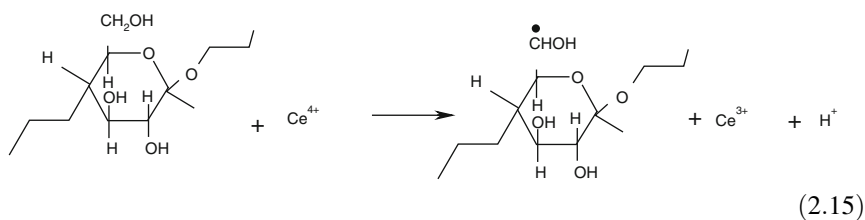
termination of growing side chain on cellulose, and it negatively affects the grafting. When the molar ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ is higher than 1, some of the $\cdot\text{OH}$ radicals that are created in Eq. (2.3) are consumed by Fe^{2+} ions [Eq. (2.4)], and Fe^{3+} ions affecting the grafting adversely are introduced to the reaction system. Both lead to decrease in the grafting percentage. When the molar ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ is lower than 1, namely, the concentration of H_2O_2 is higher than optimum value, $\cdot\text{OH}$ radicals are also consumed in the reactions given below [89]:



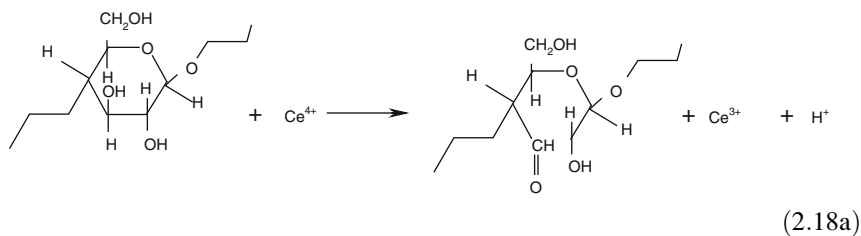
H_2O_2 alone does not lead to the formation of radicals, and it can only create the radicals together with metal impurities which are considered as reducing agent. In the grafting of ethyl acrylate onto the cellulose by Fenton reagent at 30 °C, the optimum value for the molar ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ was found to be 1.04:1, and the maximum amount of vinyl acetate (12 % grafting) was grafted at that ratio [85]. 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) [85, 89]. In order to minimize the formation of homopolymer and the wastage of primary hydroxyl ($\cdot\text{OH}$) radicals by Fe^{3+} ions, Huang et al. [90] adsorbed Fe^{2+} ions on the lignocellulose by contacting it with an Fe^{2+} salt solution in a given time period (15 min) and separated the Fe^{2+} ion-adsorbed cellulose from the solution containing excess Fe^{2+} ions by filtration. Then, they grafted methyl methacrylate (MMA) onto that Fe^{2+} salt pretreated-lignocellulose.

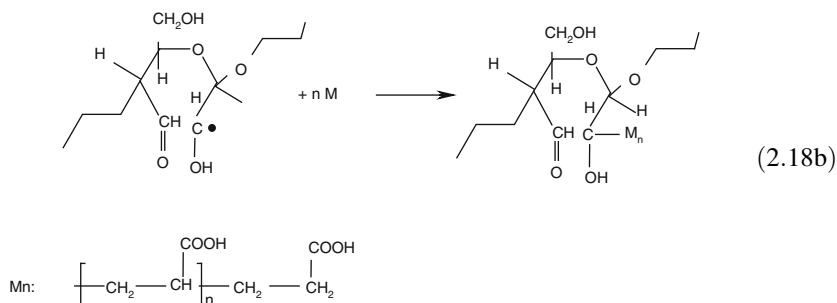
2.2.1.2 Ceric Ion

Among the various types of redox initiators, ceric ion offers many advantages because of its high grafting efficiency and lower amount of homopolymer formation [91]. When Ce^{4+} salts such as cerium sulfate or cerium 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 [85, 92]. Thus, the initiation sites for grafting are created on the cellulose backbone. The presence of radicals on the cellulose backbone has been confirmed by electron spin resonance (ESR) measurements [93]. The probable positions for grafting to occur are given in equations below [92, 94]. The radical formation on the cellulose backbone may occur either on the carbon (C-6) or oxygen atom of methylol ($-\text{CH}_2\text{OH}$) group [Eqs. (2.15)–(2.17)] [92].

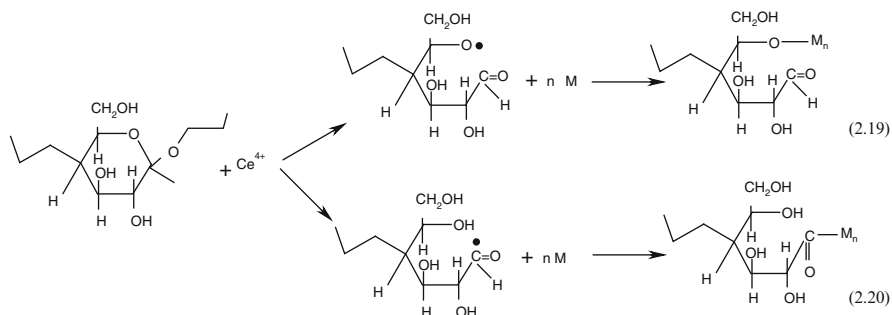


According to Gaylord [94], the grafting may also initiate on C-2 carbon by the ring opening of cellulose backbone [Eqs. (2.18a) and (2.18b)].

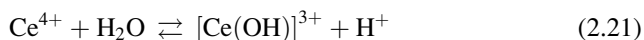




Consistent with the finding of Gaylord [94], Sharma et al. [95] proposed that the grafting occurs mainly at the C2–C3 glycol unit, and to a lesser amount at the C6-hydroxyl in the grafting of acrylonitrile onto cassia tora gum which is a common herbaceous annual weed growing in India. The following mechanism was also reported to be a probable mechanism for the grafting by Ce^{4+} ion [94]:



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 [96] through $\text{Ce}(\text{OH})^{3+}$ finally to $[\text{Ce}-\text{O}-\text{Ce}]^{6+}$ ion which has no or low activity [95] for the creation of radicals via the reactions as shown below:



In the absence of acid, no grafting on wool was determined most probably because $[\text{Ce}-\text{O}-\text{Ce}]^{6+}$, which is the hydrolysis product of Ce^{4+} ions, could not form a complex with wool [97]. Since the grafting efficiency of Ce^{4+} ion in neutral medium is low [98], 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 predetermined 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 [98–100]. The rate of disappearance of ceric ions during the grafting of binary monomers (acrylamide and ethyl acrylate) onto cellulose [101] 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 [101].

2.2.1.3 Persulfates

When $K_2S_2O_8/CoSO_4$ system was used as redox initiator [80], 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 $SO_4^{\bullet-}$ and $\bullet OH$ radicals abstract a hydrogen atom from cellulose backbone and create the secondary C- or O-centered cellulose radicals. The growth of graft chains carries on these hydrogen-abstracted active sites [53]. The possible reaction mechanism by a persulfate initiator in the presence of a metal ion (Co(II)) was given in Fig. 2.2 [80].

Potassium persulfate (KPS) is the best radical initiator for hydrogen abstraction [81], 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 C3 and C4 on saccharide ring are reported to be probable grafting sites [81]. The radical formation of cellulose backbone by KPS was confirmed by both scanning electron microprobe and elemental analyses [81].

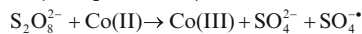
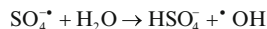
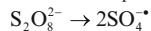
2.3 Characterization of Cellulose Graft Copolymers

After grafting of various vinyl monomers onto linear-chained cellulose backbone, a branched cellulose copolymer is obtained. The physical and chemical properties of a cellulose graft copolymer depend on the kind and amount of monomer grafted onto cellulose, the length of graft chains, the frequency of grafting or the number of grafts per one cellulose chain, etc. After grafting reaction in a heterogeneous medium, the cellulose graft copolymer is purified by completely removing the homopolymer from grafting mixture generally by extraction with a suitable solvent. In case of homogeneous grafting performed with soluble cellulose derivatives or dissolving the cellulose in a suitable solvent pair, the graft copolymer is purified by precipitation. Then, it is mainly characterized by the parameters such as grafting percentage (GP %), grafting efficiency (GE %), and the number of grafts per cellulose chain (N_g). The grafting percentage can be determined simply by gravimetry or volumetry [44] if the monomer has suitable functional group such as carboxyl groups. In the volumetric method, the functional groups (carboxyl groups)

Fig. 2.2 The mechanism for graft polymerization of vinyl monomers onto cotton fibers by $K_2S_2O_8/CoSO_4$ redox system [80]

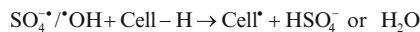
Initiation

1. Creation of primary radicals



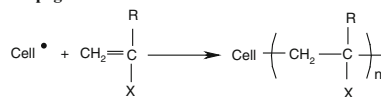
$SO_4^{\bullet -}$ and $\bullet OH$ are primary radicals.

2. Creation of secondary radicalic sites on the cellulose (Cell) backbone



$Cell^{\bullet}$ is secondary radical.

Propagation and termination



$R = H, X = COOH, COOCH_3, CONH_2, OCOCH_3$

of graft copolymer are titrated with a base solution [44]. The grafting percentage can also be determined by elemental analysis. Thus, the grafting percentage in cellulose-graft-polyacrylamide copolymer can be determined by nitrogen (N) content since only polyacrylamide contains nitrogen, but cellulose does not. Besides these main grafting parameters, other parameters such as monomer conversion % and cellulose conversion % have also been determined.

2.3.1 Grafting Percentage and Grafting Efficiency

The grafting percentage (GP) indicates the increase in weight of original cellulose subjected to grafting with a monomer and is calculated generally by the following equation:

$$\begin{aligned} \text{Grafting percentage (GP) (\%)} &= \frac{\text{Weight of polymer grafted}}{\text{Initial weight of backbone}} \times 100 \\ &= \frac{W_1 - W_0}{W_0} \times 100 \end{aligned} \quad (2.23)$$

where W_1 and W_0 are the weights of the cellulose graft copolymer and the original cellulose, respectively. GP (%) defined above has also been defined as apparent graft yield (GY %) which is a weight ratio of grafted polymer to original cellulose [100].

Grafting efficiency (GE) shows the fraction of monomer grafted onto cellulose among the amount of monomer converted to graft polymer plus the homopolymer, in other words, the fraction of polymer which is grafted to cellulose in total polymer, and it is calculated by the equation given below:

Grafting Efficiency (GE) (%)

$$\begin{aligned}
 &= \frac{\text{Weight of polymer grafted}}{\text{Weight of polymer grafted} + \text{Weight of homopolymer}} \times 100 \\
 &= [W_1 - W_0] / [W_1 - W_0 + W_2] \times 100
 \end{aligned}
 \tag{2.24}$$

where W_1 , W_0 , and W_2 are the weights of the cellulose graft copolymer, the original cellulose, and the homopolymer, respectively. The weight of homopolymer (W_2) can be calculated by subtracting the amount of grafted polymer plus the amount of unreacted monomer from the initial amount of monomer. The amount of monomer remaining without reacting after grafting can be determined by volumetric method (bromide–bromate method) [102] or by spectrophotometric methods.

Naturally, the GP (%) and GE (%) values given above are apparent or crude values, and they do not indicate the true values since they are calculated for the mixture consisting of true graft copolymer and the non-grafted cellulose. In some papers [100], the true values, for example, true grafting percentage (GP_T %) which is the weight ratio of grafted polymer to true-grafted polymer, have also been determined after separating the non-grafted cellulose from the apparent cellulose graft copolymer.

2.3.2 Molecular Weight of Grafted Polymer Chains and the Frequency of Grafting

The molecular weight of graft chains is determined generally by viscometric method [39–41, 76, 101], by gel permeation chromatography (GPC) [30], and by $^1\text{H-NMR}$ spectroscopy after separating the graft chains from the graft copolymer, i.e., by hydrolyzing the cellulose backbone of graft copolymer using 72 % H_2SO_4 [100]. Grafting frequency (G_F) is defined as the number of grafted polymer chains (N_g) per chain of cellulose [39, 101, 103].

Number of grafts per cellulose chain ($\bar{N}_g$) :

$$\frac{\text{Molecular weight of cellulose}}{\text{Molecular weight of graft copolymer}} \times \frac{\text{Grafting percentage}}{100} \tag{2.25}$$

When the grafting process occurs mainly on the surface of the cellulose backbone, in other words the grafting is performed in heterogeneous medium, the number of grafted polymer chains per cellulose chain is in the range of unity, and it rarely exceeds the unity [104]. In addition, the molecular weight of graft chains may be in the order of 10^5 [7]. Nishioka and Kosai [41] reported that in homogeneous grafting carried out in dimethyl sulfoxide–paraformaldehyde (DMSO–PF)

binary solvent system with AIBN initiator, the number of grafts per cellulose chain was 1.3. In the grafting of methyl methacrylate (MMA) onto methacrylate-modified cellulose in homogeneous medium (DMAc-LiCl) [7], the number of grafts per cellulose chain was found to be about 6 at both 60 and 70 °C.

2.3.3 Water Absorption Capacity

When hydrophilic or ionic monomers such as acrylamide (AAm), acrylic acid (AA), or 2-acrylamido-methyl propane sulfonic acid (AASO₃H) or their binary mixture are grafted onto cellulose, the cellulose gains hydrophilic character, and the copolymer will absorb high amount of water depending on ionization degree of graft chains, grafting percentage, length of graft chains, and ionic strength of swelling medium. For example, the water absorption capacity of poly(acrylic acid) (PAA)-grafted cellulose microfibrils was found to be three times higher than that of original cellulose microfibrils [105]. The water absorption capacity of cellulose graft copolymers is determined by the following equation [44, 99, 106]:

$$\begin{aligned} & \text{Water absorption capacity (gH}_2\text{O/g copolymer)} \\ &= \frac{\text{Weight of swollen copolymer (W}_s\text{)} - \text{Weight of dry copolymer (W}_d\text{)}}{\text{Weight of dry copolymer (W}_d\text{)}} \end{aligned} \quad (2.26)$$

2.3.4 Mechanical Properties

Grafting changes the mechanical properties of substrate polymer. The mechanical properties of acrylonitrile-grafted hemp varied with the amount of grafting [79], and the grafting led little degradation effect on the mechanical properties. It has been reported that grafting of isocyanate-terminated poly(caprolactone monoacrylate) (NCO-PCLA) onto cellulose diacetate (CDA) backbone broke intermolecular hydrogen bonds and increased the elongation of the graft copolymers (PCLA-g-CDA) [57]. The amount of elongation increased with the increase in grafting percentage. The introduction of flexible PCLA segments to CDA by grafting improved the tenacity of the graft copolymers too [57]. The grafting of vinyl monomers onto amine-treated cotton fibers has been found to improve the moisture sorption ability, and it had little impact on the mechanical properties [80].

2.3.5 Biodegradability

Depending on the monomer grafted onto cellulose, the copolymer gains biodegradability. Wang et al. [57] grafted isocyanate-terminated poly(caprolactone

monoacrylate) (NCO-PCLA) onto cellulose diacetate (CDA) and determined from the soil burial tests and active sludge tests that graft copolymers have good biodegradability in natural conditions.

2.3.6 Confirmation of Grafting

The proof of grafting can be checked by various methods such as swelling, thermal (by DTA/TGA) and mechanical property measurements, FTIR, DSC, XRD, NMR, SEM, and XPS.

Grafting has been confirmed mostly by FTIR analysis which is performed by ATR or KBr technique. While ATR technique gives information about the changes due to grafting in the surface of graft copolymer [107], KBr technique indicates the changes occurred both inside and in the surface of graft product [4]. The band in the FTIR spectrum of graft product, which is not present in the spectrum of graft substrate, is the proof of grafting if substrate has no FTIR band at the same wave number. In the case of a graft copolymer consisting of a vinyl monomer such as acrylamide or acrylic acid and cellulose, FTIR band assigned to the stretching vibration of carbonyl ($\nu_{C=O}$) is generally used for the confirmation of grafting. An example for the characteristic band positions and assignments used in the characterization of various graft products by FTIR was listed in Table 2.2 with their references.

The grafting also leads to changes in the thermal properties. As known, the original cellulose has no glass transition temperature (T_g) and melting temperature (T_m) due to strong inter- and intramolecular hydrogen bondings [108]. For that reason, depending on structure the polymer grafted and the lengths of graft chains, a slight deviation in baseline in the DSC curve of graft copolymer will be a good indicator for both the presence of a T_g due to the graft side chains on the cellulose backbone and for the proof of grafting. For example, Zhe et al. [53] determined in the grafting of methyl acrylate onto carboxymethyl cellulose (CMC) that while CMC does not display any transition between -40 and 60 °C, poly(methyl acrylate)-grafted CMC and poly(methyl acrylate) have T_g 's at 19.2 and 13.75 °C, respectively. Wang et al. [57] reported that the grafting of poly(caprolactone monoacrylate) (PCLA) onto isocyanate-terminated cellulose diacetate (CDA) decreased the flow temperatures of graft copolymers in comparison to that of CDA, and the processibility of CDA-g-PCLA copolymers was easier than that of original CDA. The introduction of PNIPAM onto cellulose backbone by grafting increased the T_g of graft copolymer [30]. Thermal degradation or stability of cellulose can also change with grafting. Dahou et al. [109] reported that the thermal stability of cellulose-g-PAN or cellulose-g-PAA is higher than that of ungrafted cellulose. A similar improvement in the thermal stability observed by grafting was determined for polyacrylamide-grafted carboxymethyl cellulose [51] and *N*-isopropylacrylamide- and methyl acrylate-grafted cellulose [84], poly(acrylic acid)-grafted cellulose microfiber [105], cellulose-graft-poly(*N,N*-

Table 2.2 The characteristic band positions and assignments used in the characterization of various graft products by FTIR

Wave number, cm ⁻¹	Peak assignment	References
Original cellulose		
3,570–3,460	Intramolecular OH bending	[130]
3,460	Intramolecular OH bending	[131]
3,418–3,250	Intermolecular OH bending	[130]
3,346	Intermolecular OH bending	[131]
3,400–2,750	–OH stretching	[56]
3,100–3,500	–OH vibration	[105]
3,400	–OH	[8, 50, 57]
3,471	–OH stretching	[114]
3,413	–OH stretching	[132]
1,640	H–O–H intermolecular stretching	[105]
1,645	OH bending	[114]
1,648–1,620	OH bending (absorbed water)	[130]
1,640	OH bending (absorbed water)	[131]
2,920–2,848	Symmetrical CH ₂ stretching	[130]
2,908	Symmetrical CH ₂ stretching	[131]
2,902	C–H stretching	[96]
2,854	–CH ₂ –symmetric stretching	[53]
2,927	C–H stretching	[114]
2,901	C–H stretching	[132]
2,904–2,891	Stretching of the C–H bond in –CH ₂ group	[105]
2,983	C–H stretching	[50]
2,903	C–H stretching	[96]
1,430–1,376	C–H deformation	[96]
1,384–1,360	C–H deformation	[130]
1,370	C–H deformation	[131]
1,740	C=O stretching vibration	[130]
1,745	C=O stretching vibration	[131]
1,750	C=O stretching vibration	[60]
1,655	C=O stretching vibration	[56]
1,745	C=O stretching vibration	[31]
1,747	C=O stretching vibration	[35]
1,750	C=O stretching vibration	[66]
1,175–1,160	Assym. C–O–C bridge stretching	[130]
1,175	Assym. C–O–C bridge stretching	[131]
1,150	Assym. C–O–C stretching	[109]
1,165	C–O–C stretching	[114]
1,138–1,124	Assym. C–O–C bridge	[130]
1,130	Assym. C–O–C bridge	[131]
1,300–1,000	C–O stretching	[132]
1,221	C–O stretching	[56]
1,280 and 1,185	C–O stretching	[35]
1,375–1,030	C–O stretching	[96]
667–706	C=C out-of-plane ring bending	[132]
1,653	Double bond stretching in alkenes	[132]
905–880	Assym. out-of-phase ring	[130]

(continued)

Table 2.2 (continued)

Wave number, cm ⁻¹	Peak assignment	References
896	Stretch C ₁ –O–C ₄	[131]
694	Out-of-plane C–H bending	[35]
Cellulose graft copolymer		
1,660	C=O stretching, <i>N</i> -vinylpyrrolidone	[133]
1,735	C=O stretching, glycidyl methacrylate	[134]
1,670	C=O stretching, acrylamide	[134]
1,617	C=O stretching, acrylic acid	[134]
1,718	C=O stretching, acrylic acid	[135]
1,738	C=O stretching, O-butyryl chitosan	[107]
1,700	C=O stretching, acrylonitrile/methacrylic acid	[132]
1,750	C=O stretching, poly(methyl methacrylate)	[60]
1,676	Carbamide group of acrylamide, acrylamide–methyl acrylate	[103]
1,783	Ester carbonyl of methacrylate, acrylamide–methyl acrylate	[103]
790	C–Cl stretching, poly(methyl methacrylate)	[60]
3,400–2,750	O–H stretching, acrylamide	[56]
3,164 and 3,047	N–H stretching, acrylamide	[56]
1,665	C=O, Acrylamide	[56]
1,406	C–N, Acrylamide	[56]
1,221	C–O, Acrylamide	[56]
1,731	C=O, 2-(diethylamino) ethyl methacrylate	[31]
3,476	–OH, 2-(diethylamino) ethyl methacrylate	[31]
3,043	=C–H heteroaromatic group, poly(4-vinyl pyridine)	[96]
1,352	C=C, poly(4-vinyl pyridine)	[96]
1,521	C=C, poly(4-vinyl pyridine)	[96]
1,644	C=C, poly(4-vinyl pyridine)	[96]
1,352	C=N, poly(4-vinyl pyridine)	[96]
1,521	C=N, poly(4-vinyl pyridine)	[96]
1,644	C=N, poly(4-vinyl pyridine)	[96]
1,176–1,031	C–O, poly(4-vinyl pyridine)	[96]
1,660	Amide I (C=O), acrylamide	[98]
1,600	Amide II (N–H), acrylamide	[98]
1,700	Assym. stretching of carboxylate anion, acrylamide	[98]
1,560	Symm. stretching of carboxylate anion, acrylamide	[98]
3,430	–OH, methyl acrylate	[53]
1,120	C–O stretching, methyl acrylate	[53]
1,639	–COO– bending, methyl acrylate	[53]
2,854	–CH ₂ symm. stretching, methyl acrylate	[53]
1,740	C=O, methyl methacrylate	[42]
1,727	C–O, poly(acrylic acid)	[105, 136]
1,725	C=O, acrylic acid	[58]
1,262	C–O, acrylic acid	[58]
890–1,160	Polysaccharide	[135]
2,243	C–N stretching, acrylonitrile	[43]
1,259	COOH, acrylic acid	[135]
1,270	C=O stretching of saturated ester, glycidyl methacrylate	[138]
1,270	C(=O)–O stretching of unsaturated ester, glycidyl methacrylate	[138]

(continued)

Table 2.2 (continued)

Wave number, cm ⁻¹	Peak assignment	References
800	C–O–C assym. stretching of unsaturated ester, glycidyl methacrylate	[138]
1,655	C=N stretching overlapped with C=O, acrylonitrile/methacrylic acid	[132]
2,238	C≡N, acrylonitrile	[137, 139]
2,241	C≡N, acrylonitrile	[134]
2,243	C≡N, acrylonitrile	[132]
2,273	NCO, poly(caprolactone monocrylate)	[57]
1,583	Amide N–H, poly(caprolactone monocrylate)	[57]
~1,735	C=O stretching vibration of ester group, acrylic acid and acrylonitrile	[109]
2,240	–CN vibration of nitrile group, acrylonitrile	[109]
1,710	C=O stretching, acrylic acid	[109]
1,758–1,704	Carbonyl groups, allyl-dimethylhydantion	[81]
3,444	O–H group, polyacrylamide	[51]
1,625	Carboxyl group, polyacrylamide	[51]
1,068	CH–O–CH ₂ , polyacrylamide	[51]
695	Deformation vibration of –CH–, polystyrene	[35]
700	Cellulose-g-polystyrene, polystyrene	[140]
1,665	C=O in the amide group, methacrylamide	[66]
3,200	N–H in NH ₂ group, methacrylamide	[66]
1,640	C=O in the amide group, acryloylmorpholine	[66]
1,735	C=O in the ester group, methyl methacrylate	[66]
3,190	N–H stretching vibration, polyacrylamide and poly(<i>N,N</i> -dimethylacrylamide)	[76]
1,650	Amide I, polyacrylamide and poly(<i>N,N</i> -dimethylacrylamide)	[76]
1,610	Amide II, polyacrylamide and poly(<i>N,N</i> -dimethylacrylamide)	[76]
1,623–1,597	C=N stretching, poly(4-vinyl pyridine)	[114]
1,416 and 1,552	C=C stretching, poly(4-vinyl pyridine)	[114]
3,185	OH stretching, poly(4-vinyl pyridine)	[114]
1,638–1,641	C=N, poly(4-vinyl pyridine)	[114]
1,513 and 1,455	Phenyl ring, poly(4-vinyl pyridine)	[114]
1,719 and 1,751	C=O stretching of the five-member anhydride ring, poly(4-vinyl pyridine)	[114]

dimethylacrylamide) [76], NIPAM-grafted-cellulose derivatives [30], and polyacrylamide-grafted cellulose [103]. Wojnárovits et al. [4] claim that although the grafting does not change basically the XRD pattern of cellulose, it dilutes the cellulose fraction and crystalline fraction of cellulose in graft copolymer. Therefore, the intensity of the characteristic peak due to crystalline structure of cellulose decreases, and the intensity of the peak attributed to the amorphous phase becomes more apparent. Although the claim of Wojnárovits et al. [4] is reasonable, chain scission in cellulose occurs during the grafting due to the oxidative effect of initiator. Similar to the finding of Wojnárovits et al. [4], we [110] have observed

on the grafting of acrylic acid on the cellulose that cellulose chains shorten during grafting as can be seen in the SEM pictures in Fig. 2.3. In addition, the change in molecular weight can also occur due to dissolution of cellulose in a suitable solvent or solvent pair when the grafting is performed in homogeneous medium. For that reason, a different XRD pattern can be expected after grafting.

Zhu et al. [111] reported that native cellulose shows two characteristic diffraction peaks at $2\theta = 15.7$ and 22.5° assigned to the diffraction patterns of cellulose I. They also investigated the XRD pattern of regenerated cellulose after dissolving the cellulose in an ionic liquid and then coagulating it with water. They observed that regenerated cellulose exhibits diffraction patterns for cellulose II at $2\theta = 20.3^\circ$ and 21.2° [111]. So, they concluded that the crystallization of cellulose was affected not only by grafting but also by its dissolution and precipitation. The confirmation of grafting can also be performed by the analyses of ^{13}C NMR and ^1H NMR spectra of graft copolymers and ungrafted substrate [31, 42, 43, 57, 60, 61, 76, 111–113]. SEM pictures of both graft copolymers and ungrafted cellulose may confirm the grafting of monomer [58, 109, 111, 114] too.

2.4 Effect of Reaction Conditions on the Grafting Parameters and Properties of Cellulose Graft Copolymers

The factors affecting the grafting can be listed as the nature of the backbone, the pretreatment of cellulose substrate with initiator or a swelling agent, the type of monomer (hydrophilic or hydrophobic) and the presence of comonomer, the type of solvent or grafting medium (homogeneous/heterogeneous), the type and the concentration of the initiator, the presence of additives, temperature, the grafting duration, the presence or absence of oxygen during grafting, etc. [16, 44, 98–100]. A detailed list of optimum grafting conditions was given in Table 2.3.

2.4.1 Pretreatment of Cellulose Before Grafting

When the grafting onto cellulose is carried out in a heterogeneous medium, the accessibility of cellulose by the initiator and the vinyl monomer is an important parameter determining the grafting yield or the grafting percentage. Although cellulose is a linear polymer, the presence of crystalline regions and the strong intermolecular hydrogen bondings decrease its accessibility or reactivity for the grafting reaction. However, in water, the intercrystalline swelling of cellulose occurs mainly on its accessible or amorphous regions, and it enhances the grafting efficiency. It is known that the grafting occurs preferably on the amorphous regions of cellulose due to high reactivity and accessibility of these regions. The grafting efficiency can be increased by increasing the ratio of cellulose/monomer either by

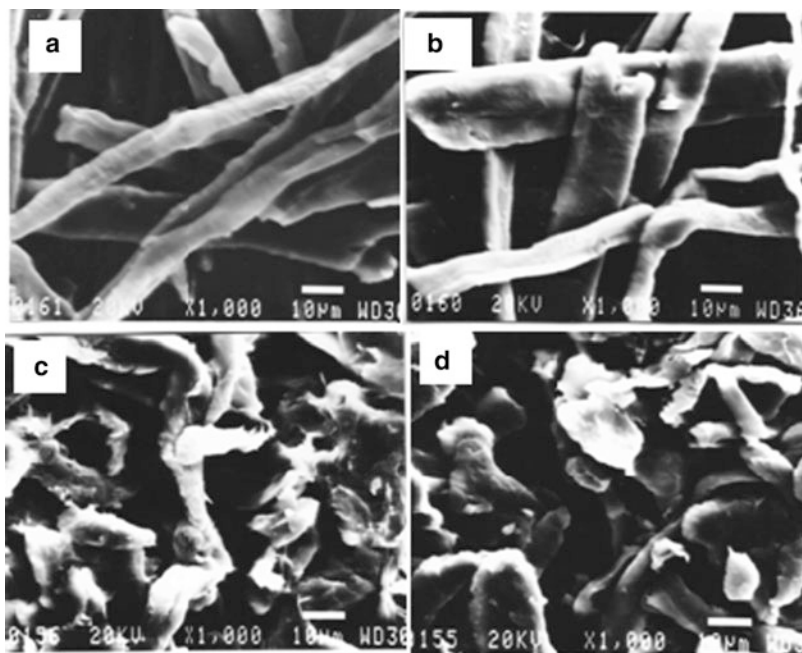


Fig. 2.3 SEM pictures of (a) original cellulose, (b) cellulose-graft-PAA with low grafting %, (c) Na salt of cellulose-graft-PAA with high grafting %, and (d) cellulose-graft-PAA with high grafting % [110]

swelling the cellulose before the reaction or by performing the grafting reaction in a medium in which cellulose swells [99]. Namely, the accessibility or reactivity of cellulose for grafting can be enhanced by decreasing its crystallinity or by increasing the content of amorphous phase since the grafting occurs mainly on the amorphous regions [16, 24]. Therefore, Okieimen [22] and Stannet et al. [115–117] decrystallized the poly(acrylic acid)-grafted cellophane and rayon by treating them with 70 wt% ZnCl_2 solution in order to enhance the water absorption capacity of graft products. They determined that the decrystallization of graft copolymer with ZnCl_2 solution alone was not enough to increase its water absorbency, and it should be performed by the solutions of both ZnCl_2 and NaOH . Fernandez et al. [100] grafted vinyl acetate and methyl acrylate onto the cotton mercerized with 20 % NaOH solution. They carried out the grafting reaction by using two types of cellulose: In the first one, they contacted mercerized or non-pretreated cellulose with ceric ion solution, and then they removed the excess of ceric ions by filtration. In the second, they grafted vinyl monomers onto mercerized or non-pretreated cellulose without any treatment by ceric ions. They [100] determined that the grafting frequency and molecular weight of graft chains are higher in the case of the removal of excess ceric ions. In addition, they found that the ceric ion consumption with mercerized cotton is slightly higher [100]. Gürdağ et al. [99] investigated the effect of pretreatment of cellulose on the grafting of acrylic acid by

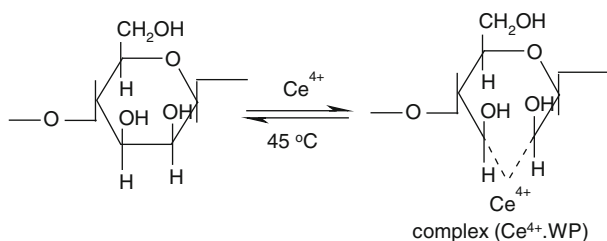
Table 2.3 The optimum reaction conditions at which the maximum grafting was obtained in some works

Monomer and its optimum concentration (M)	Max. grafting percentage (%)	Initiator and its concentration	Reaction conditions (temp. and medium)	References
N-vinyl pyrrolidone/ $30.0 \times 10^{-3} \text{ mol dm}^{-3}$	~200	Cobalt acetylacetonate/ $10 \times 10^{-5} \text{ mol dm}^{-3}$	Aqueous/50 °C	[45]
Acrylamide/ $2.5 \text{ g} \cdot 100 \text{ cm}^{-3}$	~300	Ammonium persulfate/ $0.4 \text{ g} \cdot 100 \text{ cm}^{-3}$	Dimethylsulfoxide-toluene/50 °C	[46]
Acrylamide/ $1 \text{ g} \cdot 100 \text{ cm}^{-3}$	400	Potassium persulfate/ $0.4 \text{ g} \cdot 100 \text{ cm}^{-3}$	Dimethylsulfoxide-toluene/50 °C	[46]
Acrylamide	BPO is an unsuitable initiator	Benzoyl peroxide	Dimethylsulfoxide-toluene/50 °C	[46]
4-vinyl pyridine/ 0.927 mol/L	585	Ceric ammonium nitrate/ 0.018 mol L^{-1}	Aqueous/45 °C	[96]
Acrylonitrile/ 0.42 mol	211.57	Ceric ammonium nitrate/ 0.02 mol	Aqueous/30 °C	[95]
2-hydroxyethyl methacrylate/ 10 g in 100 g DMSO	~120	Ammonium persulfate/ 0.4 g	Dimethylsulfoxide-paraformaldehyde/ 40 °C	[55]
2-hydroxyethyl methacrylate/ 10 g in 100 g DMSO	KPS is an unsuitable initiator	Potassium persulfate/ 0.4 g	Dimethylsulfoxide-paraformaldehyde/ 50 °C	[55]
2-hydroxyethyl methacrylate/ 10 g in 100 g DMSO	n.a. (not available)	Azobisisobutyronitrile/ 0.4 g	Dimethylsulfoxide-paraformaldehyde/ 60 °C	[55]
Acrylamide/ 0.099 mol	229.68	Ceric ammonium nitrate/ 0.035 mol	Aqueous/30 °C	[124]
Methyl acrylate/ 40 ml	700	Ammonium persulfate/ 150 mg	Aqueous/70 °C	[53]
Methyl methacrylate/ 8 g in 100 cm^{-3}	~140	Ammonium persulfate/ $0.2 \text{ g}/100 \text{ cm}^{-3}$	Benzene/DMSO/50 °C	[42]
Methyl methacrylate/ 16 g in 100 cm^{-3}	~140	Potassium persulfate/ $0.2 \text{ g}/100 \text{ cm}^{-3}$	Benzene/DMSO/50 °C	[42]
Methyl methacrylate	BPO is an unsuitable initiator	Benzoyl peroxide	Benzene/DMSO/50 °C	[42]
Acrylic acid/ 2 (g/g CE)	~98	Ammonium persulfate/ 0.05 (g/g CE)	1-Butyl-3-methylimidazolium chloride/60 °C	[58]
Acrylonitrile/ 4 g in 100 g DMSO solution	~90	Ammonium persulfate/ 0.8 g in 100 g DMSO solution	Dimethylsulfoxide-paraformaldehyde/ 40 °C	[40]
Methyl methacrylate/ 4 g in 100 g DMSO solution	50	Ammonium persulfate/ 0.2 g in 100 g DMSO solution	Dimethylsulfoxide-paraformaldehyde/ 40 °C	[40]
Acrylonitrile	AIBN is an unsuitable initiator	Azobisisobutyronitrile	Dimethylsulfoxide-paraformaldehyde/ 60 °C	[40]

Methyl methacrylate/4 g in 100 g DMSO solution	50	Azobisisobutyronitrile/0.08 g in 100 g DMSO solution	Dimethylsulfoxide-paraformaldehyde/ 60 °C	[40]
Acrylonitrile/4 g in 100 g DMSO solution	90	Ammonium persulfate/0.8 g in 100 g DMSO solution	Dimethylsulfoxide-paraformaldehyde/ 40 °C	[41]
Methyl methacrylate/4 g in 100 g DMSO solution	50	Ammonium persulfate/0.2 g in 100 g DMSO solution	Dimethylsulfoxide-paraformaldehyde/ 40 °C	[41]
Acrylonitrile	AIBN is an unsuitable initiator	Azobisisobutyronitrile	Dimethylsulfoxide-paraformaldehyde	[41]
Methyl methacrylate/4 g in 100 g DMSO solution	50	Azobisisobutyronitrile/0.08 g in 100 g DMSO solution	Dimethylsulfoxide-paraformaldehyde/ 60 °C	[41]
Methyl acrylate/4 g in 100 g DMSO solution	40	Ammonium persulfate/0.4 g in 100 g DMSO solution	Dimethylsulfoxide-paraformaldehyde/ 40 °C	[39]
Methyl acrylate/4 g in 100 g DMSO solution	n.a. (not available)	Azobisisobutyronitrile/0.08 g in 100 g DMSO solution	Dimethylsulfoxide-paraformaldehyde/ 60 °C	[39]
Methyl acrylate / 4 g in 100 g DMSO solution	BPO is an unsuitable initiator	Benzoyl peroxide	Dimethylsulfoxide-paraformaldehyde/ 40 °C	[39]

ceric ammonium nitrate–nitric acid (CAN–HNO₃) initiator system onto cellulose. For that aim, they [99] pretreated the cellulose before grafting reactions with either 2 or 20 wt% NaOH solutions for 24 or 2 h, respectively. As another pretreatment for cellulose, they heated it in distilled water or in aqueous nitric acid (2.5×10^{-3} M) solution at 55 °C in order to enhance the accessibility of cellulose by the initiator and the monomer. In addition, they also carried out the grafting reaction by ceric ion-pretreated and non-pretreated cellulose in order to determine how the excess of initiator affects the grafting percentage and homopolymer formation and determined that in the presence of excess ceric ions, higher grafting percentages were obtained. In the presence of excess ceric ions, higher grafting percentages were obtained with the cellulose which is swelled in aqueous nitric acid than that swelled in water. When the excess of ceric ions were removed by filtration and the grafting was carried out with ceric ion-pretreated cellulose, swelling of cellulose in water resulted in higher amount of grafting than that in acid solution. The same authors [99] also determined that the pretreatment of cellulose with dilute or concentrated NaOH solutions made no improvement on the grafting percentages of copolymers; on the contrary grafting values decreased due to treatment with NaOH. Kim and Mun [98] treated wood pulp (WP) with CAN in 0.24 M nitric acid solution and removed the excess of Ce⁴⁺ ions by filtration from the WP. Then, they grafted acrylamide onto Ce⁴⁺-pretreated WP. They [98] determined that the rate of grafting of acrylamide onto Ce⁴⁺-pretreated WP is higher than that onto non-pretreated WP, and the grafting yield increased with the concentration of Ce⁴⁺ in the pretreatment solution from 1×10^{-3} M to 2×10^{-3} M, but its further increase to 5×10^{-3} and 10×10^{-3} M decreased the amount of grafting. In addition, the graft copolymers prepared by Ce⁴⁺-pretreated WP displayed higher water and saline absorbency than those with non-pretreated WP due to uniformity of grafting with former cellulose substrate [98] (Fig. 2.4).

Ouajai et al. [79] grafted acrylonitrile onto modified natural cellulose fibers (hemp: *Cannabis sativa*) by using AIBN as initiator. With this aim, they modified natural cellulose fibers (hemp: *Cannabis sativa*) by first acetone extraction in order to remove wax and lignin and then by pretreatment with the solutions of NaOH at various concentrations (3, 5, 8, 10, 12, 15, and 20 wt/vol%). They [79] determined from the WA-XRD data that the treatment with NaOH at high concentrations (10–20 wt/vol%) led to transformation of cellulose fibers from cellulose I to cellulose II structure. The formation of amorphous cellulose and cellulose II by mercerization (namely, by NaOH treatment) in the structure of fibers was also confirmed by crystallinity index calculated by the FTIR analyses. In addition, no crystalline transformation in AN-grafted cellulose fibers was determined due to grafting [79]. Various methods such as ozonation/oxidation and pretreatment with alkali, amine, or water have been tried to enhance the reactivity of cellulose for modification reactions [24, 117]. In these methods, the enhancement in accessibility is based on the depolymerization as well as decrystallization of cellulose. The treatment of cellulose with amines leads to swelling and decrystallization of cellulose; thus, the reactivity and properties of amine-treated cellulose changes [118–120]. Mondal et al. [80] investigated the grafting of water-soluble monomers

(I) Pretreatment with Ce^{4+} ion:

(II) grafting of acrylamide (AAM)

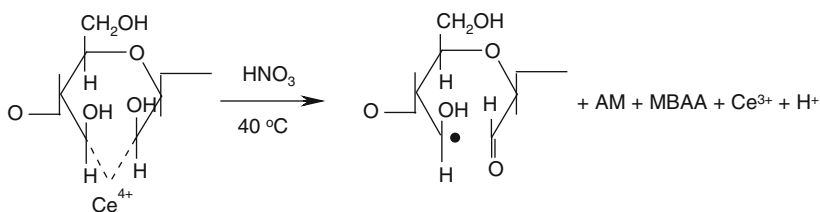


Fig. 2.4 The formation of complex ($\text{Ce}^{4+}\cdot\text{WP}$) between Ce^{4+} ions and wood pulp (WP) (I) and the grafting of acrylamide (AM) onto $\text{Ce}^{4+}\cdot\text{WP}$ (ceric ion-adsorbed WP) (II) [98]

such as acrylic acid (AA), methacrylic acid (MAA), and acrylamide (AM) and water-insoluble monomers such as methacrylate (MA), methyl methacrylate (MMA), and vinyl acetate (VAc) on the amine-treated cotton fiber using potassium persulfate (KPS) and CoSO_4 as initiator system. Ethylenediamine (EDA), 1,2-propanediamine (PDA), and diethylenetriamine (DTA) have been used as the pretreatment agent by Mondal et al. [80]. Treatment of cotton fibers with amines, ethylenediamine (EDA) in particular, decreased the crystallinity and tensile strength of the cotton fibers and improved the moisture sorption. Depending on the amine used for treatment, the following decreases (given in parenthesis) in the crystallinity was determined: EDA (51.4 %), DTA (67.7 %), PDA (68.7), EA (82.9 %), and water (84 %). While in the grafting of water-soluble monomers, amine treatment of cellulose fibers gave higher grafting yields than water treatment; lower amount of grafting was obtained with water-insoluble monomers. The grafting of vinyl monomers onto amine-treated cotton fibers has improved the moisture sorption ability [80]. Toledano-Thompson et al. [105] modified henequen cellulosic microfibrils (CM) by the reaction with an epoxide containing a terminal double bond [105], and then, they grafted the poly(acrylic acid) (PAA) onto the cellulosic fibers with terminal double bond. They determined that the water sorption capacity of cellulosic fibers with 21 wt% PAA grafting increased up to three times [105].

2.4.2 Effect of the Kind and Concentration of the Monomer

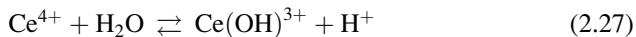
The kind and the concentration of monomer are also important parameters as well as graft substrate and the grafting medium. The graft yield or grafting percentage depend on various properties of monomers such as polarity and steric nature, the power of swelling for graft substrate [14], and reactivity ratios and the presence or absence of synergistic effects between the comonomers in case of the grafting of binary monomer mixture as well as the concentration of monomer. Bhattacharya et al. [121] reported that the grafting of substituted acrylamides such as acrylamide (AAm), methylacrylamide (MAAm), and *N,N*-dimethylacrylamide (DMAAm) onto cellulose acetate occurs in the order $\text{AAm} > \text{MAAm} > \text{DMAAm}$. The low grafting efficiency of MAAm was attributed to the decrease in the mobility of monomer due to the presence of methyl group and also to the stability of polymer radical. The polymeric radicals that occur from AAm and MAAm are secondary and tertiary in structure, respectively, and secondary radicals are more reactive than the tertiary ones. The extent of grafting with DMAAm was found to be the least among the monomers investigated due to steric inhibition of methyl groups [121]. Similar findings were also determined for the grafting of acrylates such as methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), and methyl methacrylate (MMA) onto cellulose with Ce^{4+} initiator [122, 123]. The grafting order was found to be $\text{MA} > \text{EA} > \text{BA} > \text{MMA}$ due to steric and polar effects as well as stability of polymer radical. Mondal et al. [80] investigated the grafting of the water-soluble and water-insoluble monomers onto cellulose pretreated by heating in water using $\text{K}_2\text{S}_2\text{O}_8$ (KPS)/ CoSO_4 redox initiator at 60 °C and reported that the graft yields or grafting percentages of water-insoluble monomers are higher than those of water-soluble ones. They explained this finding by the difference in the affinity of monomers towards the cellulose and the grafting. Dahou et al. [109] grafted acrylic acid (AA) and acrylonitrile (AN) monomers onto cellulose by CAN-HNO_3 initiator separately, and they have found that the grafting percentage of AN was 12–20 % higher than that of AA. Gupta and Khandekar [103] investigated the grafting of binary monomer mixture of acrylamide (AAm) and methacrylate (MA) onto cellulose using CAN-HNO_3 ($7.5 \times 10^{-3} \text{ M} - 6 \times 10^{-3} \text{ M}$) initiator system at 25 °C. They determined that the grafting of binary mixture onto cellulose takes place by a second-order reaction according to the monomer concentration, and the presence of acrylamide in the binary monomer mixture increased the graft yields because of its synergistic effect. The same synergistic effect of acrylamide was also observed by the same authors in the grafting of the binary mixture of acrylamide (AAm) and ethyl acrylate (EA) onto cellulose by CAN-HNO_3 initiator system ($6 \times 10^{-3} \text{ M} - 6 \times 10^{-2} \text{ M}$) at 25 °C [101]. The activation energies (E_a) in the grafting of AAm-MA and AAm-EA onto cellulose by CAN-HNO_3 initiator by a second-order reaction were found to be 6.96 kJ mol^{-1} [103] and 5.57 kJ mol^{-1} [101], respectively. However, in the graft copolymerization of acrylic acid (AA) onto cellulose by using the same initiator (CAN-HNO_3) system, the overall activation energy (E_a) for the first-order reaction between 30 and 90 °C was found to be

2.3 kcal mol⁻¹ [44]. Gupta and Sahoo [45] investigated the grafting of *N*-vinyl pyrrolidone (NVP) onto cellulose with the initiator of Co(III) acetylacetonate (Co(acac)₃)–HClO₄ complex between 40 and 60 °C and found that the activation energy of (*E*_a) for grafting of NVP onto cellulose was 22.7 kJ mol⁻¹. The synergistic effect of comonomer was observed by Gürdağ et al. [99] in the grafting of AASO₃H and AA onto cellulose using CAN–HNO₃ (4×10^{-3} M – 7.5×10^{-3} M) as initiator system at 30 °C. The presence of 10 mol% AASO₃H in the binary monomer mixture led to twice increase in grafting percentage in comparison to the grafting of AA alone. In the grafting reactions, normally, the increase in the monomer concentration increases the grafting percentage and grafting efficiency up a certain value independent from the kind of initiator, monomer, and the medium of grafting (homogeneous/heterogeneous) [41, 46, 55, 89, 95, 96, 98, 101, 103, 124]. Further increases in monomer concentration beyond the optimum value decrease the grafting percentage and grafting values since the homopolymer formation dominates over the grafting, although the optimum monomer concentration differs for each grafting reaction depending on the kind of monomer and substrate, and the reaction conditions.

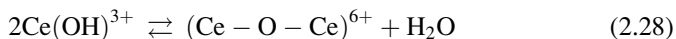
2.4.3 Effect of the Kind and Concentration of Initiator

Except the radiation technique, all chemical grafting reactions require an initiator, and its nature, concentration, solubility, as well as radical creation mechanism affect the grafting [14]. Various kinds of initiators have been used for grafting reactions: (Fe²⁺–H₂O₂), azobisisobutyronitrile (AIBN), K₂S₂O₈, Ce⁴⁺, etc. 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 also be created on cellulose by some transition metals such as Ce⁴⁺, Co³⁺, V⁵⁺, and Cr⁶⁺ [14]. The redox potential of the metal ion determines its grafting ability. In general, metal ions with low oxidation potential provides higher grafting efficiency [14]. The number of active sites created on the cellulose backbone depends on the initiator concentration, namely, the ratio of initiator/cellulose. Gupta and Sahoo [45] observed in the grafting of NVP onto cellulose with Co(acac)₃–HClO₄ initiator at the concentrations of (2×10^{-5} – 20×10^{-5}) – 2.5×10^{-3} M, respectively, that the amount of grafted NVP and the conversion of cellulose to graft copolymer increased up to 15×10^{-5} M Co (acac)₃, but beyond this concentration they decreased. While the number of grafts per cellulose chains increased from 1.23×10^{-6} to 5.5×10^{-6} with the increase of Co(acac)₃ concentration from 2 to 20×10^{-5} M, number average molecular weights (*M*_n) of graft chains decreased from 105×10^3 to 56×10^3 . The similar finding, first the increase in grafting with the initiator and then the decrease with further increase of initiator, observed for Co(acac)₃–HClO₄ initiator was also

determined in the grafting reactions performed by the initiators CAN–HNO₃ [95, 96, 101, 103, 124], ceric ammonium sulfate [49], persulfates [39, 40, 52], and KHSO₃–CoSO₄ [78]. In the grafting of AAm–MA onto cellulose by CAN–HNO₃ initiator system, Gupta and Khandekar [103] determined that the disappearance rate of Ce⁴⁺ ions did not change with the variation of monomer concentration from 0.1 to 0.5 M and concluded from this finding that the Ce⁴⁺ ions do not directly create active radicals on the monomers. The high efficiency of grafting with Ce⁴⁺ ions was attributed to the creation of active radicals by CAN initiator preferentially on the cellulose backbone than the monomers [92, 101, 125]. In addition, they [101] observed that true grafting percentage (G_T %) increased with the increase in Ce⁴⁺ concentration from 1.5×10^{-3} M to 7.5×10^{-3} M, but the higher concentrations of CAN than 7.5×10^{-3} M led to decrease in G_T % 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 (HNO₃). They [101] have also determined that the rate of grafting of these comonomers onto cellulose is dependent on the square root of CAN concentration [103]. The similar findings were observed for the grafting of EA and AAm onto cellulose by CAN–HNO₃. Kim and Mun [98] investigated the effect of the concentration of CAN in the solution pretreated with wood pulp (WP) on the grafting of AAm in the presence of BAAM as cross-linker. They [98] determined that grafting percentage increases with the increase in CAN concentration of the solution pretreated with WP from 1×10^{-3} to 2×10^{-3} M because the number of grafting sites on the cellulose backbone increases. The further increase in the concentration of CAN solution to 5×10^{-3} and 10×10^{-3} M decreased the grafting percentage. The similar relationship was also determined between the water absorbency of AAm-grafted Ce⁴⁺·WP and the concentration of CAN in the pretreatment solution [98]. The maximum amount of water absorption (2,700 g/g) was observed for the copolymer with grafting percentage of ca. 240 % which was prepared from Ce⁴⁺·WP treated with 5×10^{-3} M CAN solution before the grafting. The water absorbency of AAm-grafted Ce⁴⁺·WP is very high, but it should be taken into consideration that the grafting was performed in the presence of cross-linker (the opinion of Gürdağ). Although the authors [98] have reported that they extracted the ungrafted homopolymer PAAm by successive washings of graft product with the mixture 70 % isopropanol–water, it cannot be completely removed from the reaction mixture since the grafting was performed in the presence of cross-linker MBAAM, and the cross-linked homopolymer will not be extracted by any solvent (the opinion of Gürdağ). The increase in CAN concentration leads to decrease in grafting yield, but the increase in homopolymer formation [96]. CAN prefers to form complex with cellulose over the monomer [96]. However, at higher concentrations of CAN, Ce⁴⁺ 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 Ce⁴⁺ concentration, and it leads to the decrease in grafting yield. When CAN was used as initiator, the acid, mostly HNO₃, has an important effect on the efficiency of initiator for grafting. As known, the reaction of CAN with aqueous HNO₃ occurs as written below:



As known, ceric ion in CAN exists as the species of Ce^{4+} , $\text{Ce}(\text{OH})^{3+}$, and $(\text{Ce}-\text{O}-\text{Ce})^{6+}$ in its aqueous solution. It was reported that the efficiency of Ce^{4+} and $\text{Ce}(\text{OH})^{3+}$ species to form radicalic sites on cellulose backbone is higher than that of $(\text{Ce}-\text{O}-\text{Ce})^{6+}$ since the size of the former is smaller than that of the latter [124] and the former is more mobile than the latter. Goya et al. [124] also reported that at high acid concentrations, Ce^{4+} and $\text{Ce}(\text{OH})^{3+}$ 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 (opinion of Gürdağ). The concentration of these species depends on the amount of acid present in the medium. At high nitric acid concentrations, the equilibrium reaction (2.27) shifts to the left and ceric ions in CAN occur in the form of Ce^{4+} which are 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 $\text{Ce}(\text{OH})^{3+}$ led to the formation of considerable amount of $(\text{Ce}-\text{O}-\text{Ce})^{6+}$ which is not active for the creation of radicalic sites.



For that reason, CAN or another ceric salt should be used together with an acid. Dhiman et al. [96] found that the increase in the concentration of HNO_3 from 0.3 M to 0.5 M led to ca. 20 % increase in grafting percentage of 4-VP onto cellulose by CAN initiator, and further increase in HNO_3 concentration resulted in ca. 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 [96]. Ibrahim et al. [49, 50] investigated the effects of reaction parameters on the water absorbency of graft products in the grafting of NVP onto CMCNa/HEC in homogeneous medium using ceric ammonium sulfate (CAS) as initiator. They determined that the increase in Ce^{4+} concentration from 0.02 % to 0.2 % reduced the water absorption capacity of graft product from 209 g/g to 131 g/g. They explained this finding so that higher initiator concentrations lead to the increase in grafting frequency, namely, a graft product with high amount of short graft chains occurs. As known, the increase in polymer chain ends does not contribute to the water absorption capacity [49, 50]. Therefore, the water absorption capacity of NVP-grafted CMCNa/HEC decreased with the initiator CAS. Misra et al. [89] investigated the effect of complexing agent such as KF, ascorbic acid, and EDTA on the grafting of ethyl acrylate (EA) onto cellulose by Fenton reagent ($\text{Fe}^{2+}-\text{H}_2\text{O}_2$). In order to avoid the negative effect of Fe^{3+} ions on the grafting, namely, the wastage of $\cdot\text{OH}$ 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) [85, 89]. At low concentration (81×10^{-4} M), KF gave highest amount

of grafting among the complexing agents, but its increase to 166×10^{-4} M reduced the grafting of EA significantly [89]. The similar behavior was observed for the grafting of VAc under the same conditions. KF makes complex with Fe^{3+} ions and favors 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 [89] and vinyl acetate (VAc) [85] at all concentrations investigated. Huang et al. [90] grafted MMA onto stone ground-wood by Fenton reagent and determined that graft yield increased with the molar ratio of Fe^{2+} – H_2O_2 up to 0.085, and after that concentration, the graft yield decreased slightly. They concluded that only a low molar ratio of Fe^{2+} – H_2O_2 is enough to succeed the grafting [90]. The similar trend (first increase and then decrease) for the grafting with the concentration of various persulfates such as KPS [52, 80], and APS [39–41, 53] was observed for AIBN [41] and BPO [39] too. The radicals created by the redox initiators on cellulose backbone are short-lived and temperature sensitive [126]. Abdel-Razik [46] investigated the effects of various redox initiators, APS, KPS, and BPO, in the grafting of AAm onto ethyl cellulose (EC) in dimethylsulfoxide (DMSO)/toluene solution. He [46] determined that APS is a suitable initiator for grafting of AAm onto EC because it leads no degradation in EC chains [46]. He also determined that 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 were attributed to the difference in the decomposition rates of initiators [55]. In the same paper, it was 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. Bardhan et al. [52] reported that maximum grafting efficiency was obtained at KPS concentration of 3.7×10^{-4} M in the grafting of acrylamide onto methyl cellulose in aqueous solution, and both the grafting percentage and the grafting efficiency decreased with the initiator concentration at all monomer/substrate ratios (1:1–2.5:1). The similar effect of APS, KPS, and BPO with that observed in the grafting of AAm onto EC in previous work [46] was also observed in the grafting of methyl methacrylate (MMA) onto EC in benzene/DMSO (1:1) solution [42]. He performed the grafting in the 1:1 mixture of DMSO and a solvent such as chloroform, toluene, and benzene, using two different initiators, APS and KPS, and determined that grafting yield was dependent on dielectric constant of the solvent, namely, the highest yield was observed for the solvent with highest dielectric constant. The order of solvents was found to be chloroform > toluene > benzene with respect to their contribution to increase in grafting yield. The increase in grafting with increasing initiator concentration up to an optimum value takes place due to increase in radical sites created on the graft substrate. The further increase in KPS concentration beyond the optimum value results in the decrease in grafting % due to terminations of both the growing graft polymer chains and primary

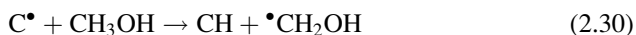
radicals by the excess amount of radicals present [53]. Nishioka and Kosai [41] investigated the grafting of two monomers AN and MMA separately onto cellulose in DMSO/PF system (in homogeneous medium) using two types of initiators: APS and BPO. It is known that DMSO/PF system is a non-degrading solvent for cellulose [41]. 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 [41]. For that reason, they 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. They [41] suggested from the results 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. They also found that the grafting onto cellulose hardly proceeded with AN–AIBN system, but appreciably in MMA–AIBN system. The solution of cellulose in DMSO/PF had a high viscosity, and the maximum amount of cellulose which could be dissolved in DMSO/PF solution was 4 wt% [41]. At 2 wt% cellulose concentrations in DMSO/PF solvent, the optimum molar ratios of monomer/initiator ($[M]/[I]$) were found to be 22 and 46 for AN and MMA, respectively. Nishioka et al. [39] investigated the grafting of methyl acrylate (MA) onto cellulose in homogeneous (DMSO/PF) medium and determined that grafting proceeded with APS (the highest number of grafts per cellulose chain was 1.5), but hardly at all with BPO and AIBN initiators. In addition, BPO was found to be unsuitable as initiator for the grafting of MA onto cellulose in homogeneous medium because it led to degradation of cellulose chains [39]. It is known that while redox initiators and radiation lead to the oxidative degradation of cellulose in the absence of monomer [127–129], the degradation of cellulose is minimized in the presence of monomer [24]. Nishioka et al. [55] investigated the grafting of 2-hydroxyethyl methacrylate (HEMA) onto cellulose in DMSO/PF system using various initiators, APS, KPS, and AIBN. They [55] determined that the grafting hardly proceeded with AIBN initiator similar to their previous works [39–41], and KPS is not a suitable initiator for the grafting of HEMA in this system since it led to degradation of cellulose. The maximum rate of propagation in the grafting of MMA onto EC in benzene/DMSO solvent system was determined depending on the kind of initiator [42] and found to be $0.2 \times 10^{-2} \text{ min}^{-1}$ and $0.08 \times 10^{-2} \text{ min}^{-1}$ for APS and KPS, respectively. For that reason, higher grafting yield was obtained with APS than KPS [42].

2.4.4 Effect of Solvent

The reaction medium or solvent has also an effect on the grafting yield or percentage in the grafting reactions. Jun et al. [142] investigated the effect of solvent such as alcohols and acetone in the grafting of *N*-isopropylacrylamide (NIPAM) onto

cotton cellulose preirradiated in air by ^{60}Co - γ -rays using mixture of water and alcohols such as methanol, ethanol, propanol, or acetone. They reported that in the grafting in solvent mixture of water and ethanol, propanol, isopropanol, and acetone, the grafting decreased continuously from pure water to pure organic solvents, where the grafting yields were almost zero. They concluded that the alcohols had different degrees of inhibiting effects on the grafting of NIPAM, but acetone was inert. The alcohols are good swelling agents for cellulose [42]. However, they also play role as chain transfer agent during polymerization reaction. In the case of methanol as cosolvent, the size of methanol is small, and its effect as chain transfer agent is lower than that of its swelling power for cellulose at low concentrations. At high methanol concentrations, its chain transfer role becomes higher than that of swelling power, and it affects the swelling adversely. Since the molecular sizes of ethanol, propanol, and isopropanol are high, their swelling power for cellulose were lower in comparison to their chain transfer properties, and they led to decrease in grafting. Abdel-Razik [42] investigated the effect of solvent (benzene, toluene, and chloroform) in homogeneous grafting of MMA onto ethyl cellulose in solvent/DMSO (1:1 v/v) solvent system with two persulfate initiator, APS and KPS. In the grafting with APS and KPS initiators, the highest grafting yields 84.5 % and 44 %, respectively, were observed in chloroform. It was concluded that grafting was correlated with the dielectric constant of solvent used, and their increasing effect on grafting yield was found in the order chloroform > toluene > benzene [42].

The efficiency of grafting in a solution will depend upon the competition between the relative reactivity of monomer and solvent for the radicals created on the graft substrate as shown in the equations below [54]:



where $\text{C}^{\bullet}$ represents the radicalic site created on the graft substrate and X the monomer styrene or acrylamide. The rate constant for hydrogen abstraction is known to be in the order isopropanol > ethanol > methanol > *t*-butanol [54]. When reaction (2.29) is dominant over reaction (2.30), a graft copolymer will be obtained, but in case of the domination of reaction (2.30) over the reaction (2.29), the radical on the graft substrate abstracts one hydrogen atom from alcohol, and produces $\bullet\text{CH}_2\text{OH}$ radicals, leading to the formation of a homopolymer rather than a graft product. It was determined that in grafting of styrene onto cellulose acetate, reaction (2.29) is faster; but reaction (2.30) is faster in the grafting of the acrylamide [54]. Therefore, alcohols are suitable solvents for the grafting of styrene onto cellulose acetate, but not for the acrylamide. The addition of water in alcohol system increased the extent of grafting of acrylamide, but it suppressed the grafting of styrene due to decrease in the solubility of styrene in aqueous alcohol [123].

2.4.5 *Effect of Temperature*

The temperature is one of the important reaction parameters determining the grafting kinetics. Generally, the grafting yield or percentage first increase with temperature up to a certain value, and then it decreases for persulfates [39, 41, 42, 46, 53]. Similar results have also been reported in the literature for Ce^{4+} initiator [41, 97, 99, 104, 125]. For example, Nishioka et al. [39, 40] 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, Nishioka et al. [55] 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 [44], 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 [44]. 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 [44], and the increase in temperature favored the formation of homopolymer poly(acrylic acid) (PAA). The decreasing effect of increasing temperature from 30 to 90 °C on the water absorbency of graft copolymer was also observed in the Ce^{4+} -initiated grafting of NVP onto CMCNa/HEC [49, 50], and the maximum water absorption was displayed by the graft copolymer which was prepared at 30 °C. With the increase in temperature, a graft copolymer with shorter graft chains will be obtained, and the number of polymer chain end will increase. Since the polymer ends with short length in the graft copolymer do not positively contribute to the swelling, the increase in grafting temperature affects negatively the water absorption capacity of graft copolymer.

2.5 Applications of Cellulose Graft Copolymers

The applications of cellulose graft copolymers change with the structure of polymer grafted on cellulose. For example, cellulose graft copolymers with poly(acrylic acid), *N*-vinyl-2-pyrrolidone or polyacrylamide grafts which are hydrophilic in structure, have high water absorption capacity [44, 49]. For that reason, they could be used as body fluid absorbent in medical applications [105]. For example, the water and saline absorbencies of polyacrylamide-grafted Ce^{4+} -treated wood

pulp were found to be 2,500–2,700 g/g and 40–60 g/g, respectively [98]. The grafting of water-soluble vinyl monomers onto amine-treated cotton fiber gave a graft copolymer with enhanced moisture sorption ability that can be used in fabrics, such as underwear and athletic wear [80]. Cellulose graft copolymers synthesized in DMSO–PF solvent system has been used as permselective membranes [143, 144]. Cellulose-thiocarbamate-g-PAN had high antimicrobial activity. Matahwa et al. [84] reported that *N*-isopropyl acrylamide and methyl acrylate-grafted cellulose as template in the crystallization of CaCO_3 has better nucleating property than cellulose. In addition, the cellulose graft copolymers obtained by grafting of vinyl monomers with functional groups such as acrylamide [21], acrylic acid [58, 145–147], acrylonitrile, and 2-acrylamidomethylpropane sulfonic acid [145] have been used in the adsorption of hazardous contaminants such as heavy metal ions or dyes [66] from aqueous solutions [148, 149]. The product of poly(4-vinyl pyridine)-grafted cellulose with sodium borohydride has been used as reducing agents for various carbonyl compound such as benzaldehyde, cyclohexanone, crotonaldehyde, acetone, and furfural [96]. Wang et al. [31] reported that pH-responsive poly(2-diethylamino) ethyl methacrylate grafted-ethyl cellulose (EC-g-PDEAEMA) synthesized by ATRP can be used in the pH-responsive release of rifampicin (RIF). In addition, another graft product obtained by ATRP, which is graft copolymer of ethyl cellulose with azobenzene-containing polymethacrylates [113], was reported to be used in the some applications such as sensors and optical materials. In recent years, cellulose graft copolymers with thermosensitive graft chains such as poly(*N*-isopropylacrylamide or poly(*N,N*-diethylacrylamide) have been used in the removal of heavy metal ions from aqueous solutions by temperature swing adsorption (TSA) which is different from the removal of metal ions by complexation or ion exchange [29, 30, 150–154].

2.6 Conclusion

Cellulose graft copolymers can be prepared in homogeneous or in heterogeneous medium. Grafting can be confirmed by gravimetry, volumetric method (a simple acid–base titration), or spectroscopic methods such as FTIR, NMR, and SEM. Cellulose gains hydrophilic or hydrophobic character depending on the monomer grafted. Therefore, cellulose graft copolymers have many applications. Among them, heavy metal and dye removal from aqueous solutions are the most prominent ones. In the grafting reactions performed in homogeneous medium, the grafting can be controlled better, and higher number of grafts per cellulose chain is obtained. By these methods such as RAFT and ATRP methods, tailor-made copolymers such as comb- or brush-type cellulose graft copolymers can be synthesized. The applications of these special polymers will be studied more in the near future.

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