Chapter 3

Cellulose Grafting by Atom Transfer Radical Polymerization Method

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Additional information is available at the end of the chapter

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Abstract

Increased public awareness on environmental issues, fluctuations in raw material prices, and global difficulties in raw material supplies have made it necessary to find new, sustainable, environment-friendly, and inexpensive natural polymer sources. Cellulose and its derivatives, at this point, have become an important research matter once again, because of its easy accessibility, abundance, price, minimal effect on the environment, and new properties discovered with the help of technology.

This study explains cellulose and its modification, and gives information about ATRP, which is a controlled radical polymerization. Later, detailed information on grafting of cellulose by ATRP in both, the author's studies and other existing researches is provided.

Keywords: Cellulose, Grafting, Graft Copolymer, Atom Transfer Radical Polymerization (ATRP), Controlled Radical Polymerization (CRP)

1. Introduction

Cellulose is the most abundant natural polymer, which is used raw or substituted in a number of applications, for instance in paper, packaging, or lacquer technologies. Moreover, cellulose is biodegradable and renewable, which makes it preferable from an environment point of view. On the other hand, since its utilization would be limited in its natural form, cellulose has to be modified. This modification is mostly achieved by reaction of hydroxyl groups, yielding to cellulose esters or ethers. Besides, cellulose backbone can be grafted with synthetic polymers by either "grafting from" or "grafting onto" it, using various polymerization methods [1].

Thus, different materials with many different properties, such as elasticity, ion exchange ability, thermal stability, and mechanical properties can be obtained by grafting. Grafting is mostly realized via free-radical polymerization initiated with redox systems, mostly based on ceric or ferrous salts or sodium hydrogen sulfite systems together with peroxides. Using these methods, many new cellulose–backbone graft copolymers have been synthesized but key properties like number, density, length, and molecular mass distribution were out of control. In addition to the vinyl monomers, heterocyclic lactones can be grafted from cellulose or its derivatives by ring-opening polymerization (ROP), giving, in principle, biodegradable polymeric materials [2]. Also, nitroxide-mediated polymerization (NMP) [3] or reversible addition–fragmentation chain transfer process (RAFT) [4] have recently been applied into controlled grafting of cellulose with synthetic polymers. In recent years, a couple of papers reporting controlled cellulose grafting using ATRP have been published [5-6].

This chapter provides information about cellulose, ATRP and cellulose grafting by ATRP method. Later, some research conducted on cellulose grafting by ATRP are discussed.

2. Cellulose

Natural polymers are polymers that are biologically produced and have unique functional attributes. Polysaccharides (cellulose, starch, chitin, chitosan, dextran, inulin, levan etc.), proteins (collagen, gelatin, elastin, actin, etc.), and polynucleotides (DNA and RNA) are natural polymers. Increasing attention is being given to more complex carbohydrate polymers produced by bacteria and fungi, especially to polysaccharides such as xanthan, curdlan, pullulan, and hyaluronic acid.

Cellulose is regarded as the most abundant and renewable biopolymer in nature and the most common organic natural polymer, representing about 1.5×10^{12} tons of the annual biomass [7]. Together with its abundancy, cellulose has several other factors that make it a superior material, such as its renewability; high chemical stability; low price; high tenacity in the wet state; ability to yield to thin membranes; ease of the control of pore size, ranging from 1 to 100 nm in diameter; and controllable porosity [8].

2.1. Structure of cellulose

Natural and unprocessed cellulose in crystal form is called cellulose I (natural-raw cellulose). Crystal form of cellulose changes with external effects like chemical processes and temperature, which yields to various crystalline modifications depending on these processes. Cellulose II is obtained by mercerization of cellulose with concentrated alkaline solution, while cellulose III is obtained by inflating and decomposing of cellulose I or II with liquid ammonia (under -30°C). Cellulose IV is a high-temperature form and is prepared by heating cellulose I, II, or III in glycerol. When various crystalline forms of cellulose are heated up to 250°C, intramolecular hydrogen bonds loosen, which results in a different crystal structure. Cellulose V is obtained by processing cotton or paper with strong phosphoric acid or hydrochloric acid [9]. It is also one of the most promising raw materials for the modern industry, because of its low

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cost and convertibility to various functional materials. Cellulose is a carbohydrate homopolymer consisting of β-D-glucopyranose units joined together by β-1,4-glycosidic linkages (Fig. 1). Unlike starch, glucose units in cellulose have long and unbranched chains caused by $-CH_2OH$ groups alternating above and below the plane of rings. Lack of side chains lets cellulose molecules form organized structures. Cellulose has both crystallized (higher packing density) and amorphous (lower packing density) regions. Hydrogen bonds connect cellulose chains in the crystallized region, as well as van der Waals forces, which is also important in the lattice energy. Cellulose chains can either have parallel or antiparallel orientation, which is the source of the names of cellulose I and II, respectively. These two forms of cellulose have different structures. Other polymorphic forms are called cellulose III and IV. X-ray diffraction measurements prove that cotton cellulose contains about 60% crystalline cellulose I and 40% amorphous cellulose [10]. By delignification, removal of noncellulosic polysaccharides and low molecular mass cellulose components (called β- and γ-cellulose) the raw materials containing cellulose can be transformed to pure long-chain cellulose called α-cellulose. Pulp analysis of cellulose shows that it contains 44% carbon, 6.2% hydrogen, and 49% oxygen. Pure cellulose yields to approximately 95% D-glucose ($C_6H_{12}O_6$) when hydrolyzed [11].

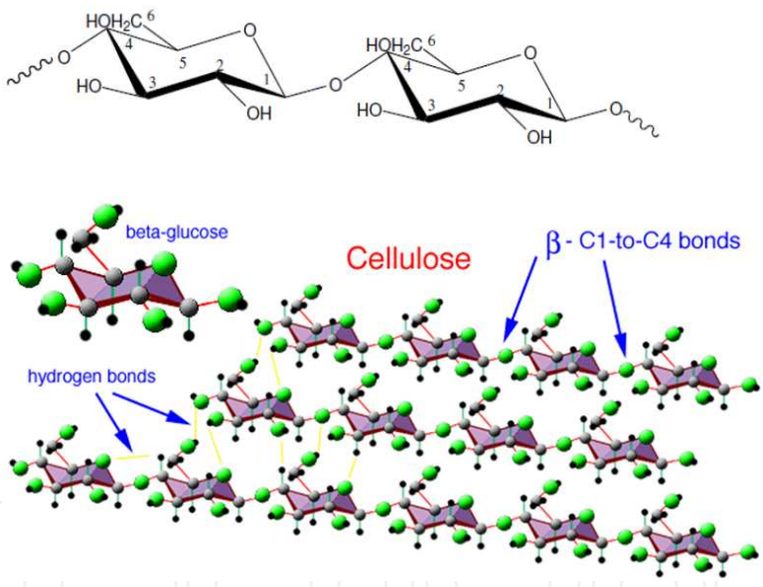

Figure 1. Cellobiose unit: two β-D-glucopyranose units joined together by β-1,4-glycosidic linkage [12]

Polymerization degree of natural cellulose is strongly related with cellulose source and separation/purification methods that are used. Cotton cellulose has the highest molecular mass which is around 800 000, while wood and other sources of cellulose have molecular masses around 160 000. Hydroxyl groups cause intense intra- and intermolecular hydrogen bonds in cellulose in solid form. These hydrogen bonds and high molecular mass make cellulose insoluble in classic solvents. Dissolving becomes possible when appropriate solvents (like Schweitzer solution –copper-II-hydroxide with concentrated ammonium hydroxide mixture) are used, or by modification of cellulose into derivatives like cellulose triacetate and cellulose nitrate [13-15].

When the distance between oxygen and hydrogen atoms in a cellulose molecule is less than 3 Å, these molecules interact with each other and form intra- or intermolecular hydrogen bonds (Fig. 2) [16].

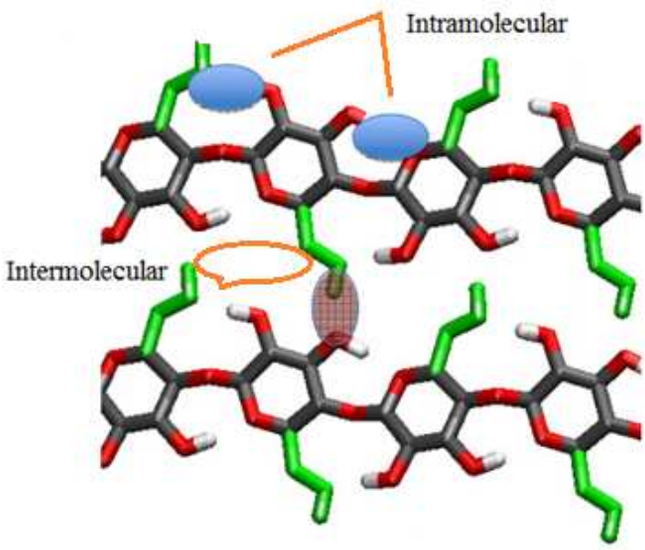

Figure 2. Intra and intermolecular hydrogen binding of cellulose

Equatorial orientation of the hydroxyl group together with the linear structure of cellulose results in both intermolecular and intramolecular hydrogen bonds. Sheet-like structure and crystalline form of the polymer are a result of intermolecular hydrogen bonds. Microfibrils formed by the cellulose molecules (Fig. 3) stack together and make up the fibrils, which gives the cellulose fibers. Hydrophilic property of the polymer is a result of hydroxyl groups. This makes it readily adsorb water [17].

2.2. Modification of cellulose and its derivatives

Its specific structure makes cellulose attractive. Cellulose consists of repetitive glucose units, which makes it more specific, architecturally diverse, reactive, and multifunctional. Some parameters that make cellulose a unique material to study are: isolation process itself, amount of hydrogen bonds, chain length and distribution, crystallinity, and functional group distribution in a repeating unit. They are also the factors that determine the reactions and properties of cellulose [7].

The first question that comes to mind: why should cellulose derivatives be established?

Compounds obtained by chemical changes of cellulose are called **cellulose derivatives**. While cellulose transforms into its derivatives, hydroxyl groups react and yield esters with organic and inorganic acids, ethers with some alcohols, alcoholates with bases and oxidation products with acids. They also react with halides, amines, and some complexes. Most important industrial derivatives of cellulose are cellulose esters and ethers. Producing alkali cellulose is a starting process to obtain these two products [18].

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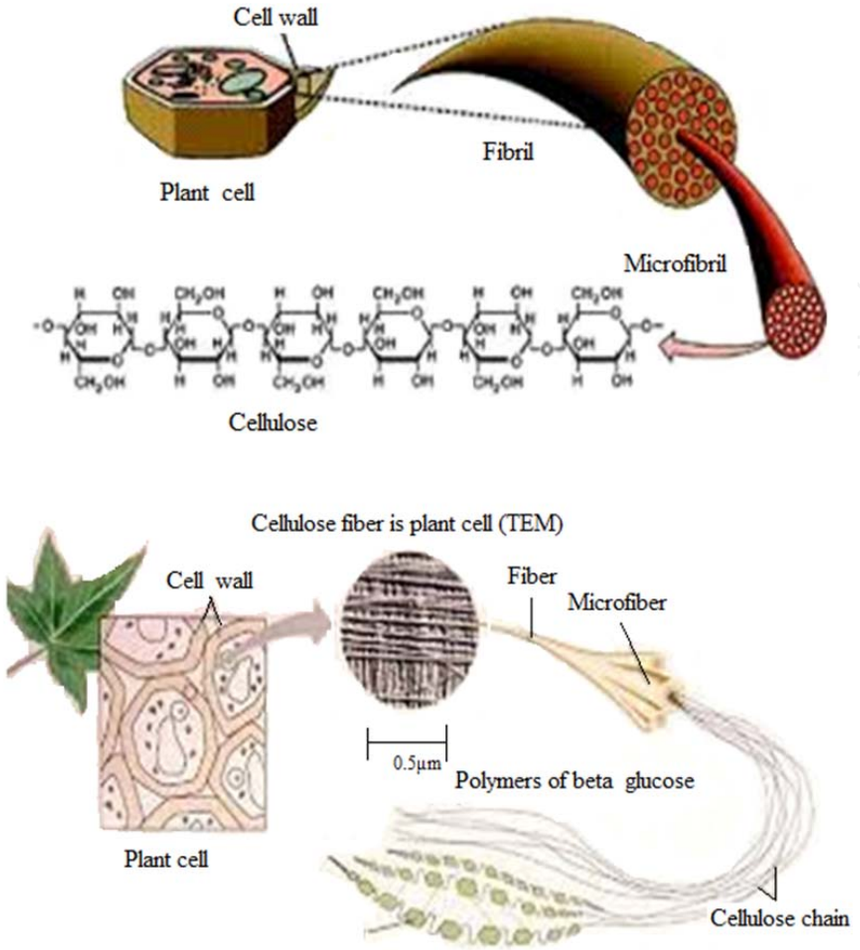

Figure 3. Structure of cellulose fibers and fibrils

Substitute groups in cellulose molecules are revealed when preparing cellulose derivatives. This process results in changes in physical properties, which makes cellulose derivatives industrially practical. This effect is revealed by both natural substitute groups and degree of substitution. Mechanical and physical properties of cellulose and cellulose derivatives differ with respect to average molecular mass. Increase in molecular mass also increases resistivity values; however, this effect becomes less significant after a certain degree [18, 19].

Although it has many useful properties, it is short of some properties that synthetic polymers have. Graft copolymerization is a significant way to alter the physical and chemical properties of cellulose like heat resistance, elasticity, resistance to abrasion and wear, ion-exchange capabilities, oil and water repellency, and antibacterial activity [20]. In the preparation of cellulose derivatives, making them soluble is often the decisive quality criterion, because cellulose is insoluble in organic solvents such as water, alcohol, acetone, benzene, chloroform etc. The usefulness of cellulose as a starting material for edible and biodegradable polymer is extended by chemical modification. Additionally, high solution viscosity is a desired property.

There are three ways to change the chemical properties of cellulose, as given in other sources [21]:

1. By preparing an ester or ether derivative of cellulose, **ethers** , e.g., ethyl cellulose (EC), methyl cellulose (MC), propyl cellulose (PC), hydroxypropyl cellulose (HPC), hydroxypropyl methyl cellulose (HPMC), hydroxylethyl cellulose (HEC), hydroxylethyl methyl cellulose (HEMC), methyl hydroxypropyl cellulose (MHPC), ethyl hydroxylethyl cellulose (EHEC), carboxymethyl cellulose (CMC), benzyl cellulose (BC); **esters** like cellulose acetate (CA) and cellulose xanthate, which are used to process cellulose into either fiber or film forms, during which the cellulose is regenerated by controlled hydrolysis; **acetals,** especially the cyclic acetal formed between secondary hydroxyl groups and butyraldehyde cellulose acetate, cellulose propionate, and cellulose acetate-butyrate [22].
2. By preparing a cross-linked derivative of cellulose.
3. By preparing a graft copolymer of cellulose, namely, a branched derivative of cellulose (This study reports about cellulose grafting by ATRP).

The most significant cellulosic applications are in the paper, wood products, textiles, film, and fiber industries. However, recently it has also attracted significant interest as a source of biofuel production [23]. Some usages of soluble cellulose are given in Table 1 [24].

Cellulose derivatives	Areas of utilization
Ethers	
MC-EC (methylcellulose- ethylcellulose)	Foods, dyes, drugs, detergents, cosmetics, textiles, lacquers, finishing, inks, glues, electrical insulators, fire extinguishers, electrical appliances, water retainers, stabilizers, borehole liquids, etc.
CMC-NaCMC (carboxymethylcellulose-sodiumcarboxymethylcellulose) (E-466)	Foods, cosmetics, textiles, drugs, paper, detergents, glues, etc.
HEC (hydroxyethlycellulose)	Dyes, chemicals, liquid detergents, rubber, oil wells, polymerization emulsions, etc.
HPC-HPMC (hydroxypropylcellulose-hydroxypropylmethylcellulose)	Foods, drugs, papers, plastics, ceramics, gels (as water retainers), eye lenses, stabilizers, etc.
Esters	
Acetates (organic esters: cellulose acetate, cellulose triacetate, cellulose propionate, cellulose acetate propionate, propionate, cellulose acetate butyrate, etc.	Textiles, films, plates, sheaths, coils, isolation, and nonconductive parts
Filaments	Garments, threads, furniture, packaging, etc.
Plastics	Various
Tows (linen and cannabis fibers)	Textiles, yarns, cigarette filters, etc.
Nitrates (Nitrocellulose) (inorganic ester)	Automotive, textiles, dyes, lacquers, polishes, films, explosives, cement, plates, etc.
Nitriles	Food and other packaging

Table 1. Usage of soluble cellulose

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2.3. Nanocellulose

Mechanical properties of natural materials like elasticity or endurance could differ from nanoscale to macroscale. First-generation cellulosic engineering products like cotton and wood have been used in various fields depending on their structural sizes. However, some vital properties like functionality, durability, and homogeneity could not have been obtained in following generation cellulose-based products by using conventional cellulosic materials. Although conventional forestry products are still being widely used, these products have failed to meet the requirements of high-performance materials. Deep research interest in forestry products and by-products triggered by the necessity of sustainability has gone into a further phase after the invention of cellulose nanoparticles. Since cellulose extracted at nanoscale did not have compositional errors at hierarchical dimension like first-generation cellulose, this new method has paved the way to the development of next-generation cellulose based on composite materials. Although wood pulp is commonly used, nanocellulose can be produced from any cellulose material. Fibrils are isolated from wood-based fibers by using high-pressure homogenizer. Amorphous part in natural cellulose is hydrolyzed by acid hydrolyzation and crystal part at nanoscale is expelled by centrifuge (Fig. 4) [14, 25].

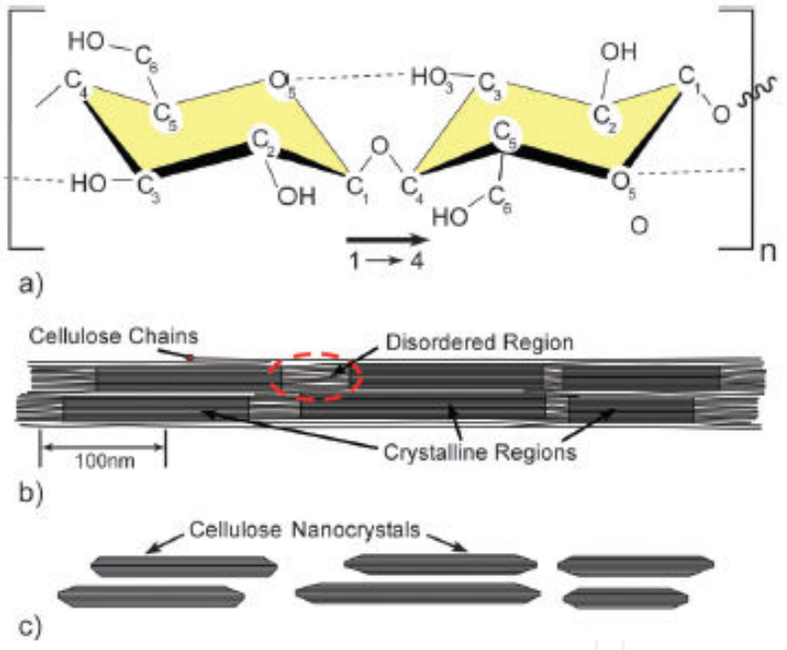

Figure 4. Schematics of (a) repeating single cellulose chain unit with the directionality of the -4 linkage and intra chain hydrogen bonding (dotted line), (b) idealized cellulose microfibril illustrating a suggested configuration of the crystalline and amorphous regions, and (c) cellulose nanocrystals with disordered regions dissolved in acid

3. Atom Transfer Radical Polymerization (ATRP)

Ostu, et al. (1982) invented of the term "Living/controlled radical polymerization" in their work on the iniferter mechanism [26]. Various studies have proven that Controlled Radical

Polymerization (CRP) is the most versatile method for surface-initiated polymerization (SIP) on model surfaces, and it includes methods such as Atom Transfer Radical Polymerization (ATRP), nitroxide-mediated and iniferter-based (INItiators-transFER-terminaTER agent) polymerizations (NMP) and Reversible Addition–Fragmentation chain Transfer (Radical Addition Fragmentation Transfer) (RAFT) polymerization [27]. The polymerization is obtained by implication of techniques generally based on the reversible homolytic cleavage of (a) a dormant chain end group into the corresponding polymeric radical (which induces chain propagation) and (b) a stable, persistent radical that cannot undergo addition to monomer [27, 28]. The radical-dormant adduct equilibrium can be reached by the application of thermal energy, light, or the addition of a catalyst as a function of the particular method considered [27].

ATRP, which is quite versatile in yielding to polymers with low polydispersity and controlled molecular weight, is probably the most widely studied CRP [29]. Moreover, ATRP has proven to be useful in synthesizing graft copolymers with well-defined structures utilizing a variety of monomers. The application of ATRP to cellulose could prove to be attractive when preparing novel cellulose derivatives with well-defined side-chain structures. Besides, reports on ATRP and the synthesis of cellulosic graft copolymers show that the method is promising [30-32].

3.1. Mechanism of ATRP

In 1995, two different research groups separately reported very similar controlled radical polymerization techniques, the ATRP, both based on catalytic systems used for the atom transfer radical addition reaction (ATRA), or in other words, Kharasch reaction, a method of forming carbon-carbon bonds between organic halides and alkenes known to be productive. The other system, reported by Matyjaszewski, *et al.*, is the polymerization of styrene under catalyzation of CuCl/ 2, 2'-bipyridyl (bpy) with 1-phenylethyl chloride as an initiator. Since the outset of reports, many reports have been published on ATRP of styrene, acrylates, methacrylates, and acrylonitrile by different transition metal complexes. ATRP proves to be versatile when compared to other controlled radical polymerization methods, providing control in the polymerization of various monomers under different reaction conditions and enabling to prepare polymers with a wide range of architectures. Some examples are blocks, grafts, gradient copolymers, stars, combs, branched, and hyper-branched. ATRP is one of the fastest growing subjects in chemistry, with the number of publications approximately doubling each year [26].

The mechanism of ATRP can be seen in Scheme 1. In or der to generate a growing radical or an active species ($P_n^{\cdot}$), a transition metal complex (M^n-Y/L) undergoes one-electron oxidation together with abstraction of a halogen (X) from an initiator or a dormant species (P_n-X). The active species initiate monomers ($CH_2{=}CH_2R_1$) to yield new growing radicals. This reaction may continue until the release of halogen atoms from the oxidized metal back to form dormant species. This turns the polymer chain ends from a dormant to a propagating and active state. In this process, the oxidized metal complexes (X-M^{n+1}-Y/L) are utilized as persistent radicals and reduce the rippling concentration of growing radicals in order to terminate by generation of a steady low concentration of active radical chain ends with short life span. This mechanism has the advantage of keeping concentration of radical intermediates in the reaction medium

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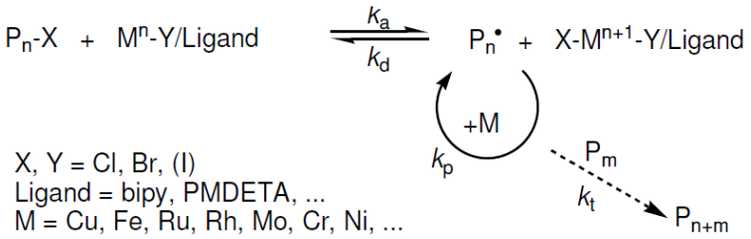
low before adding new monomers, because of fast but reversible transformation into nonactive species. Speedy initiation and the fast reversible deactivation provide uniform growth in all chains, which in turn allows achieving narrow polydispersities. Besides, it leads to suppression of termination reactions. An ATRP reaction is considered to be successful if it has a small contribution of terminated chains, and a uniform growth of all the chains, managed by fast initiation and rapid reversible deactivation. This process, shown in Scheme 1, takes place with a rate constant of activation ($k_{a)}$ and deactivation ($k_{d)}$. The growth of polymer chains comes by the addition of the intermediate radicals to monomers in a similar manner to a constant of propagation ($k_{p)}$. Termination reactions (k_t) would also occur through radical coupling and disproportionation in ATRP in a great amount [5, 24, 29, 31, 32-39].



Sheme 1. Mechanism of metal-catalyzed ATRP

3.2. Ligands and initiators commonly used in ATRP

Various transition metals, usually in the form of salts, have been used in ATRP together with various complexing ligands. Copper is the most common of them, due to its low cost and versatility. Ligand's duty is to solubilize the metal ion, and this affects the reduction potential of the transition metal ion too. Although alkyl iodides have been used too, alkyl bromides and chlorides are more common initiators [40]. Some common ligands and alkyl halides are 2,2'-bipyridine and ligands bound nitrogen. For example: N,N,N/,N//,N///–pentamethyl diethylene triamine (PMDETA), tetramethyl ethylene diamine (TMEDA), 1,14,7,10,10- hexamethyl triethylene tetramine (HMTETA), hexahexyl triethylenetetramine (HHTETA) [41], tris [2-diamethylamino ethylamine (Me_6-TREN)], alkyl pyridyl methanimine [34]. Some general copper containing ligands are given in Fig. 5 [39].

3.3. Catalysts commonly used in ATRP

The catalyst is arguably the most important component in ATRP, since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. A transition metal catalyst needs to fulfill some requirements in order to be considered as efficient. These are: the metal having at least two oxidation states separated by one electron; the metal center having reasonable affinity toward a halogen; and the coordination sphere around the metal being expandable upon oxidation to accommodate a (pseudo)-halogen; and the ligand being relatively strongly. Moreover, the dynamics and position of the ATRP equilibrium is expected to be appropriate for the particular system [31].

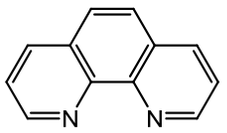
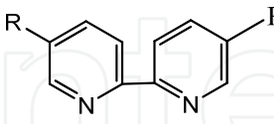
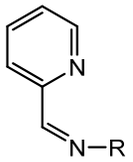
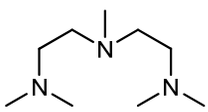
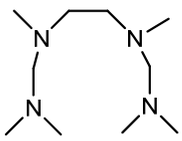
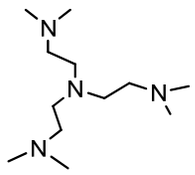
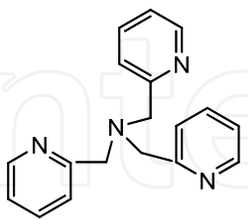
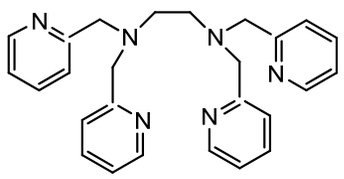
Structure	Name	Reference
	1,10-Phenonthroline (*o*-phen)	42
 R=H	2-2'-bipyridine (bpy)	43
R=C_7H_{15}	4,4'-di-n-heptyl-2,2'-bipyridine(dHbpy)	43
R=$CH(CH_2CH_2CH_2CH_3)_2$	4,4'-d-(5-nonyl)-2,2'-bipyridine (dNbpy)	43
 R=C_3H_7	N-(n-propyl)pyridyl methanimine (NPPMI)	44
R=C_8H_{17}	N-(n-octyl)pyridyl methanimine (NOPMI)	44
	N,N,N',N'',N'''-pentamethyl diethylenetriamine (PMDETA)	45
	1,1,4,7,10,10-hexamethyl triethylenetetramine (HMTETA)	45
	tris[(2-dimethylamino)ethyl] amine (Me_6TREN)	46
	tris[(2-pyridyl)methyl] amine (TPMA)	47
	N,N,N',N'-tetrakis (2-pyridylmethyl) ethylenediamine (TPEN)	48

Figure 5. Examples of some ligands used in copper mediated ATRP

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3.4. Halide exchange effect in ATRP

Replacing a chloride catalyst with a bromide catalyst is an effective way to achieve initiation rates higher than propagation. This results in halide exchange giving predominantly Cl-ended polymer and bromide catalyst by a mechanism (shown in Fig. 6). Utilizing a bromide catalyst with a soluble chloride salt would yield the same effect too. The ongoing radical effect brings two activation- deactivation equilibria involving P· with equilibrium constants K_1 and K_2, K_2 being greater than K_1 since $K_{ex} >> 1$. The halide exchange is not great with the initiator when compared with the polymer as a result of the lower concentration of R· than that would have been established by the regular persistent radical effect because of the capture by the monomer, so the initiator remains a bromide, while the polymer becomes a chloride predominantly. Initiation becomes faster than propagation as a result of the weaker C–Br bond in the initiator compared to the stronger C–Cl bond in the polymer. On the other hand, although majority of the polymers are Cl- ended, most of the deactivation events occur by the faster process of Br atom transfer, inasmuch as $k_{da2} > k_{da1}$, resulting in narrow molecular weight distribution polymers. Nevertheless, its slower frequency of activation results in P–Cl build up. Since P–Cl being more stable than P–Br, the end group loss due to side reactions at higher conversions becomes much less [39].

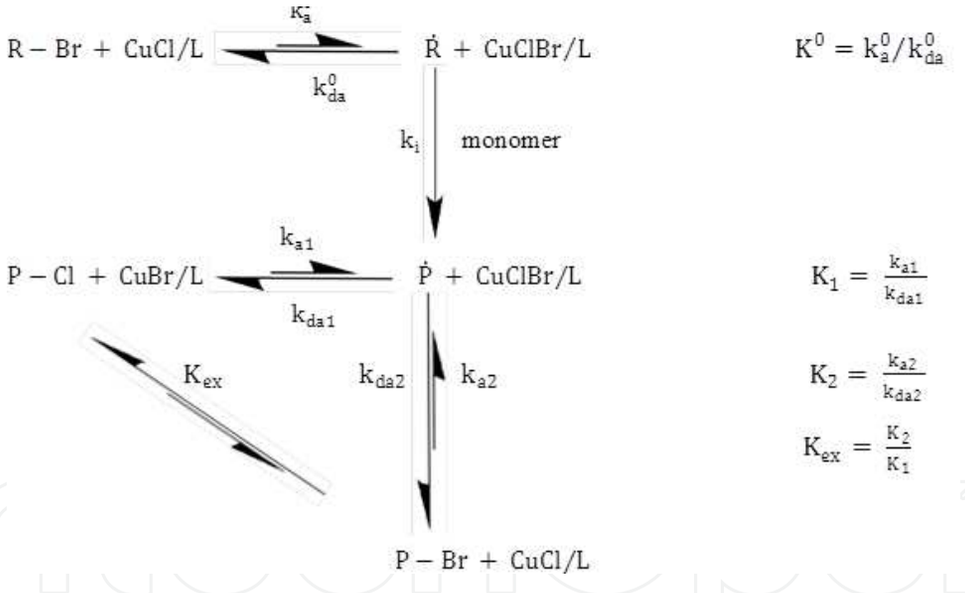

Figure 6. Halide exchange using bromide initiator and chloride catalyst

4. Some studies about cellulose grafting by atom transfer radical polymerization method

Graft copolymers of cellulose are obtained by binding synthetic polymers to cellulose – a natural polymer – with covalent bonds. This process – called grafting – changes behaviors and properties of cellulose. Numerous researchers have studied this subject. Below are some

researches on grafting by ATRP method. Other than grafting studies on cellulose, there are other natural polymers grafting studies.

Coşkun M. et al grafted styrene, methyl methacrylate, methacrylamide and acrylomorpholine on pulverized-raw cellulose by using ATRP method. They prepared cellulose chloroacetate as macroinitiator by reacting chloroacetyl chloride with OH group of primary alcohol in pulverized cellulose. CuBr and 1,2-dipiperidinoethane was used as catalyst and transient metal compound. The reactions were followed by FT-IR and mass increase in cellulose chloroacetate. Dye affinity and dye absorption values of cellulose, macroinitiator, and graft polymers were determined by acidic alizarin yellow and alkaline bromocresole green, while humidity, water, and dye absorption capacities were measured by thermal stability [35].

Our research group grafted cellulose by using two different methods, through free-radical graft copolymerization and atom transfer radical polymerization (ATRP). N-(4-nitrophenyl) acrylamide (4NPA), and N-cyclohexylacrylamide (NCA) monomers were synthesized by the researchers, while some commercial monomers were used for this grafting. In the first method, primary OH groups in powder cellulose were first transformed to ester groups with methacryloyl chloride and cellulose methacrylate was obtained. This cellulose methacrylate was grafted with the synthesized monomers of N-(4-nitrophenyl) acrylamide (4NPA) and N-cyclohexylacrylamide (NCA); 4-vinylpyridine (4VP), acrylamide (AM), methacrylamide (MAM), diacetone acrylamide (DAAM), and methylmethacrylate (MMA) monomers, in the presence of 2,2'-azobis (isobutyronitrile) in acetonitrile as solvent. In the second method, with the ATRP, primary OH groups of powder-raw cellulose were firstly reacted with chloroacetyl chloride and cellulose chloroacetate was obtained, where cellulose chloroacetate was used as macroinitiator. 4NPA, NCA, 4VP, AM, and DAAM monomers reacted in the presence of copper (I) chloride and 2,2'-bipyridine as ligands at 130°C in the N,N-Dimethylformamide (DMF), where cellulose chloroacetate was used as macroinitiator. In the third method, Poly [Cell-g-(N-(4-nitrophenyl) acrylamide-co-methyl methacrylate)] {Poly [Cell-g-(4NPA-co-MMA)]} was prepared in the presence of CuCI/2,2'-bipyridine. In the fourth method, Poly [Cell-g-(N-cyclohexylacrylamide)-co-methyl methacrylate)] {Poly [Cell-g-(NCA-co-MMA)]} was prepared similarly. The monomer reactivity ratios of both graft copolymerization reactions were calculated by using Fineman-Ross (F–R), Inverted Fineman-Ross (I–F–R), Yezrielev-Brokhina-Roskin (Y–B–R), Kelen-Tüdos (K–T), and Extended Kelen-Tüdos (E–K–T) methods. All of the graft copolymers were characterized by elemental analysis, IR, TGA techniques. Water and metal ion (by Atomic Absorption Spectrum) uptake properties of the graft copolymers obtained with the first method were determined. Electrical conductivity of the graft copolymers by ATRP obtained with the second method was determined. The results are discussed below [24].

Cankaya et al. synthesized the graft copolymers of cellulose methacrylate by free- radical polymerization. Cellulose methacrylate was prepared by esterification of primary -OH group on raw-powder cellulose with methacryloyl chloride with a 21.3% yield by mole. The vinyl monomers such as 4NPA, NCA, 4VP, AM, MAM, DAAM, and MMA were grafted into the cellulose methacrylate via free-radical polymerization using 2,2'-azobis (isobutyronitrile) as an initiator in acetonitrile. The graft copolymers were characterized by FT-IR spectra, elemental

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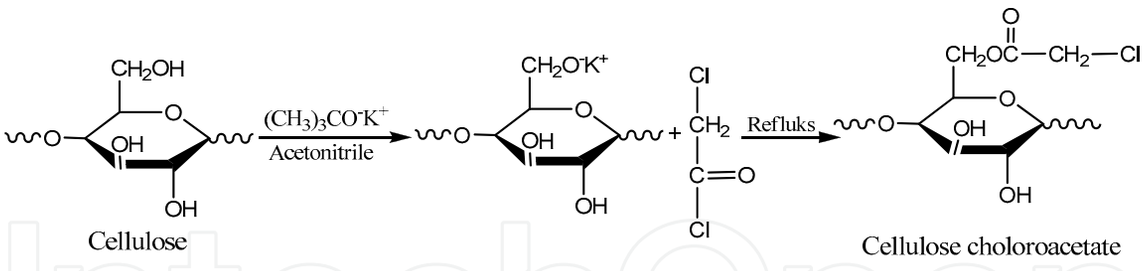
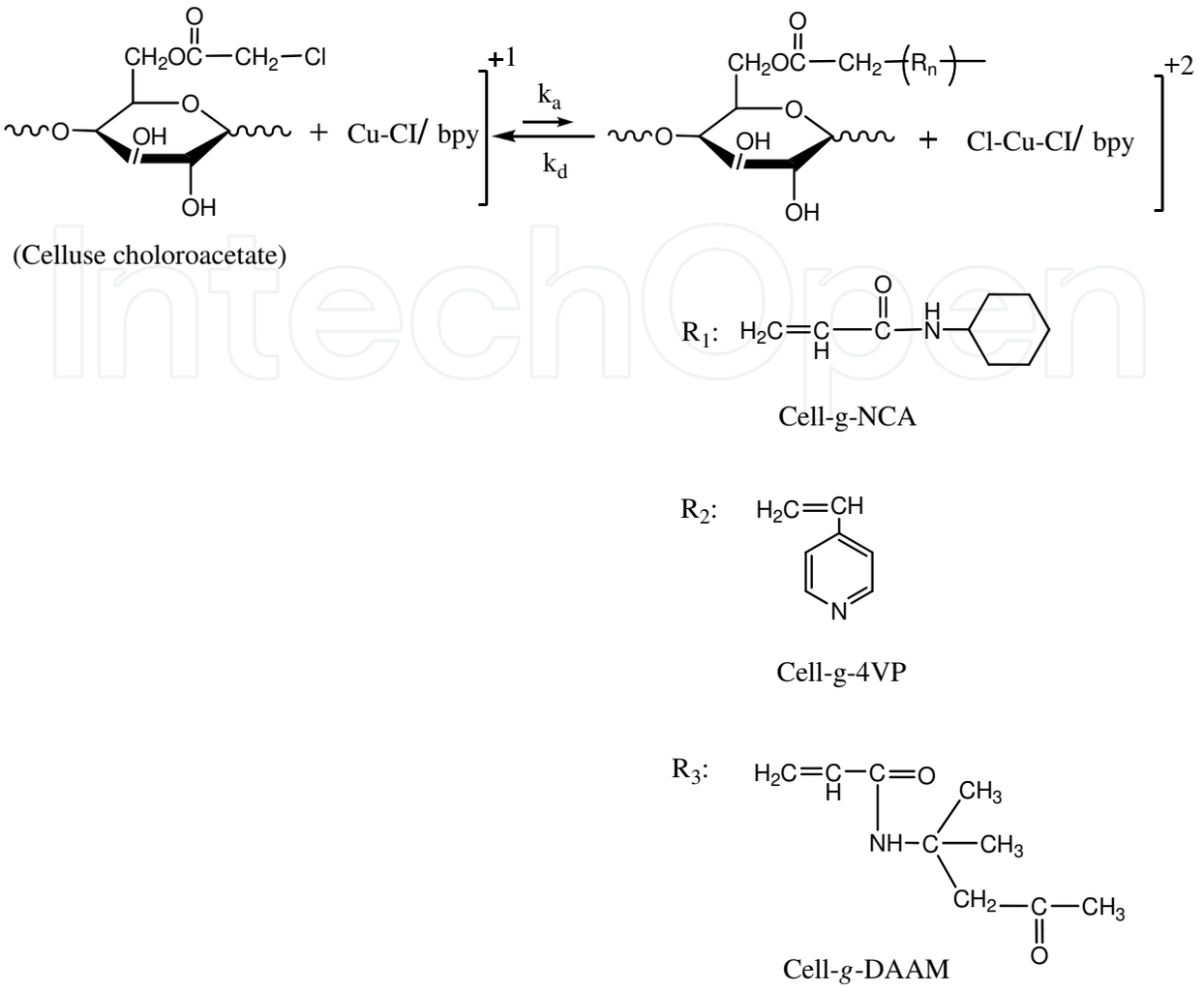
analysis, and thermal analysis. Thermal stabilities of the graft copolymers were determined by TGA method and thermal stability of the copolymers decreased with grafting. Water-uptake capacities increased the grafting and its metal ion sorption tendency (Ni^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Fe^{3+} and Cr^{3+}) improved with the grafting. –The study was conducted by using 8 graft copolymers and 7 metals and no comparison between graft copolymers and metals was possible, which is an expected result. It could be concluded that +3 valence metals were held by graft copolymers more than +2 valence metals, and cellulose methacrylate holds metals more than cellulose [49].

Cankaya et al. synthesized graft copolymers of cellulose chloroacetate by ATRP. Cellulose chloroacetate was prepared by esterification of primary alcoholic OH groups on raw-powdered cellulose. Cellulose was first esterified with chloroacetyl chloride, yielding cellulose chloroacetate which behaves as a macroinitiator because of chloroacetyl groups on it (Scheme 2). The graft copolymers of cellulose with some monomers such as NCA, 4VP, and DAAM were prepared by means of these groups using the Cu(I)/2,2′-bipyridine complex as a catalyst in DMF at 130°C by ATRP. Reactions of grafting on cellulose are indicated in Scheme 3. Formed homopolymers were removed from graft copolymers. The electrical conductivity of the graft copolymers was measured as a function of temperature. The electrical conductivity of the copolymers increased with increase in temperature, and this indicates that the studied copolymers exhibit semiconducting behavior. The electrical and optical properties of all the copolymers changed with grafted monomers. The cellulose exhibits the highest conductivity and lowest optical absorption edge with 4VP monomer [32].



Sheme 2. Synthesis of cellulose chloroacetate macroinitiator

Cankaya et al. prepared graft copolymers with 4NPA and MMA of cellulose chloroacetate, using cellulose chloroacetate/Cu(I)/2,2′-bipyridine complex as a catalyst in DMF at 130°C, by ATRP. Cellulose chloroacetate behaved as a macroinitiator because of chloroacetyl groups on it (Scheme 4). Poly [Cell-g-(N-(4-nitrophenyl) acrylamide-co-methyl methacrylate)] {Poly [Cell-g-(4NPA-co-MMA)]} graft copolymers were characterized by elemental analysis, FT-IR spectra, and thermal analysis. FT-IR spectra of Cell-*g*-(4NPA-*co*-MMA) graft copolymer showed that as 4NPA content decreased, 1670 cm^{-1} amide carbonyl peak sharpness decreased and as MMA content increased, 1745 cm^{-1} ester sharpness increased. Also, 1745 cm^{-1} ester band in the cellulose chloroacetate macroinitiator was observed for each graft copolymer (Fig.7). Thermal stabilities of the graft copolymers were determined by TGA method and thermal



Sheme 3. The grafting of cellulose chloroacetate with some monomers by ATRP

stability of the copolymers increased with the increase in amount of MMA, while it decreased with the increase in amount of 4NPA (Fig.8). In order to investigate the effect of 4NPA with MMA monomers interactions on grafting, the graft copolymerization was also studied using different feed compositions ranging from 0.15 to 0.85. This study was undertaken in order to determine of the monomer reactivity ratios in the grafting of cellulose with 4NPA and MMA by ATRP, with linear methods such as the F–R, Inverted F–R, Y–B–R, K–T, and Extended K–T methods. The reactivity ratios of 4NPA and MMA in the graft copolymerization found was r_1=0.017–0.116 and r_2=1.209–1.472, with various methods (Table 2). According to these methods, the r_1 and r_2 values were 0.011 and 1.263; $r_1.r_2$= 0.014, respectively. The values calculated by all methods were found to be equal to each other. Two monomer mixtures on cellulose had a tendency to form alternative copolymers because the $r_1.r_2$ was close to zero. It could be concluded that 4NPA monomer with amide group and larger molecule size was less reactive on grafting onto cellulose with respect to MMA monomer with ester group and smaller molecule size [30].

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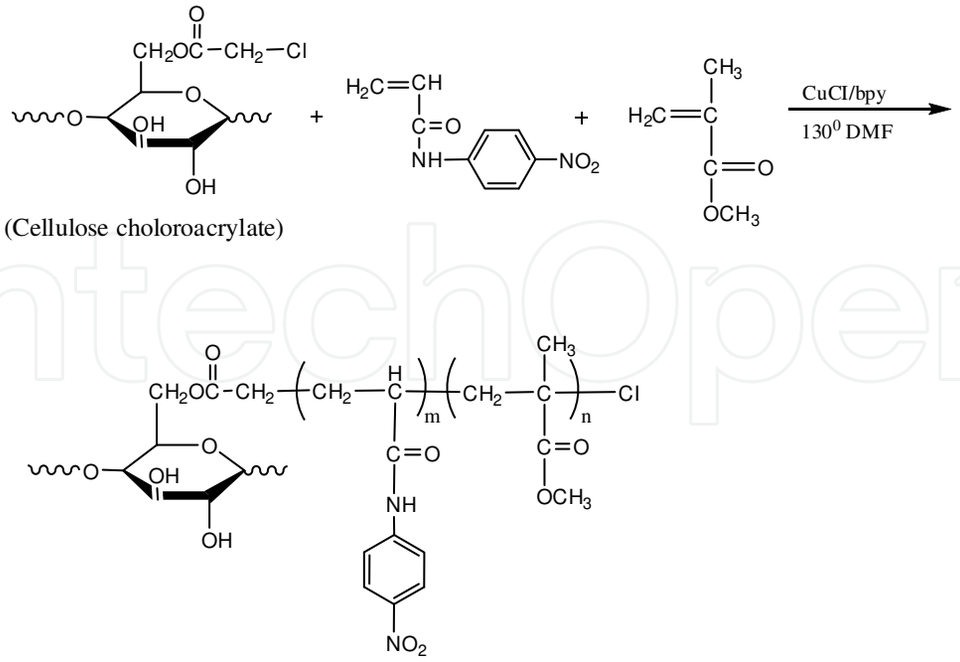

Sheme 4. Synthesis of the serials Cell-*g*-(4NPA-*co*-MMA)

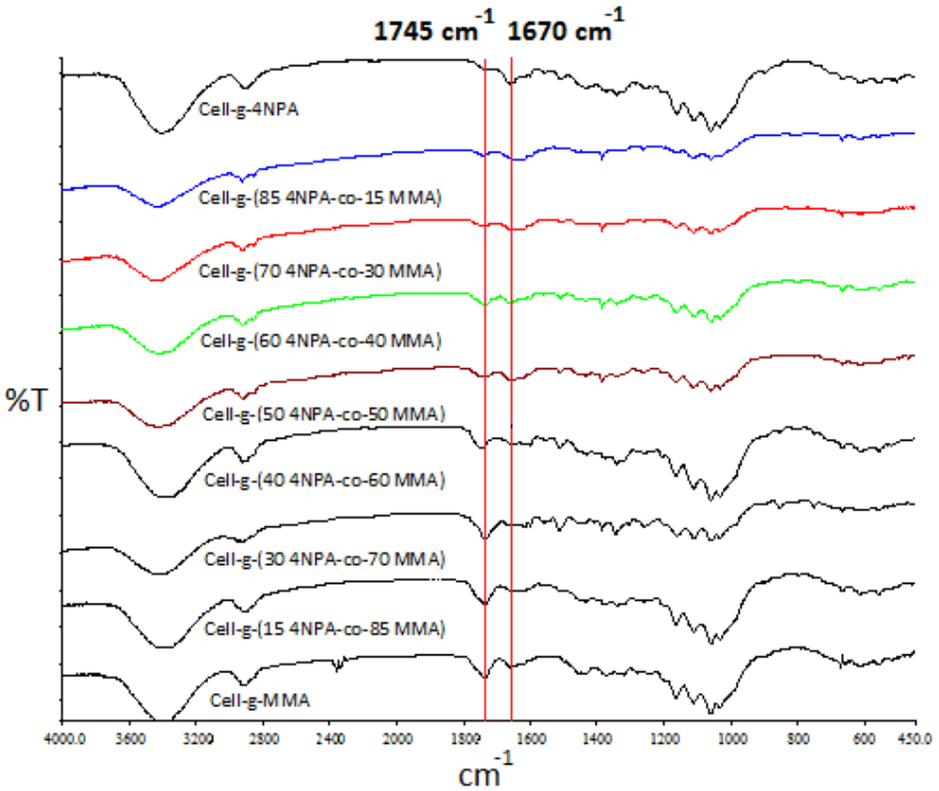

Figure 7. FT-IR spectra of the serials Poly [Cell-g-(4NPA-co-MMA)] graft copolymers

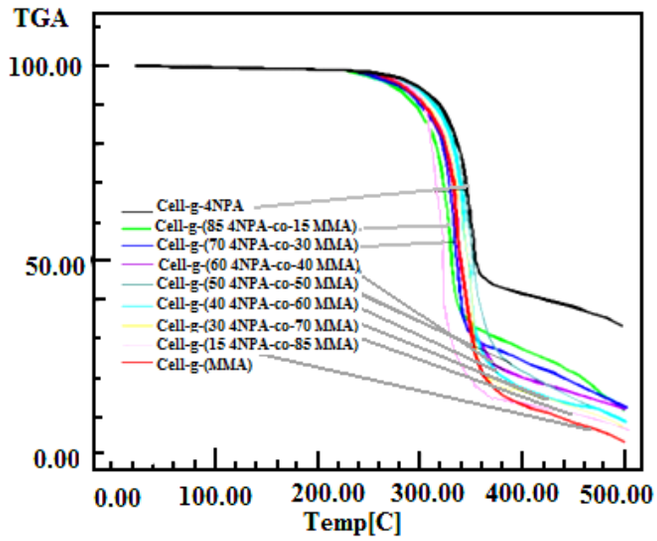

Figure 8. Thermal Gravimetric Analysis curves of the serials Poly [Cell-g-(4NPA-co-MMA)] graft copolymers

Methods	r_{4NPA}	r_{MMA}	$r_1.r_2$
FR	0.096	1.365	0.130
IFR	0.011	1.263	0.014
YBR	0.017	1.209	0.021
KT	0.116	1.455	0.169
EKT	0.109	1.472	0.160

Table 2. Comparison of monomer reactivity ratios for Poly [Cell-g-(4NPA-co-MMA)] graft copolymers with five methods

The same method was utilized to graft NCA and MMA monomers on cellulose. For this purpose, poly [Cell-g-(N-cyclohexylacrylamide-co-methyl methacrylate)] {Poly [Cell-g-(NCA-co-MMA)]} graft copolymers were synthesized (Scheme 5). Cellulose graft copolymers were characterized by elemental analysis, FT-IR spectra, and thermogravimetric analysis. The FT-IR spectra of the graft copolymers are presented in Fig. 9. In the FT-IR spectra, the ester band of cellulose chloroacetate macro initiator at 1745 cm^{-1} was observed for each graft copolymer. Also, the FT-IR spectra of Cell-*g*-(NCA-*co*-MMA) showed that as the NCA content decreased in the graft copolymer, the amide carbonyl peak sharpness (band at 1670 cm^{-1}) decreased too, and the 1745 cm^{-1} ester sharpness increased with MMA content. (Fig.9). Thermal stabilities were compared considering the thermogravimetric curves. Residual percentage in the graft copolymers decreased at 500 °C, while the MMA amount decreased (Fig.10). Also, the monomer reactivity ratios in the grafting of cellulose with NCA and MMA were calculated by using 7 different feed compositions ranging from 0.15 to 0.85 by ATRP. Reactivity ratios were determined by linear methods, such as the F–R, Inverted F–R, Y–B–R, K–T, and Extended

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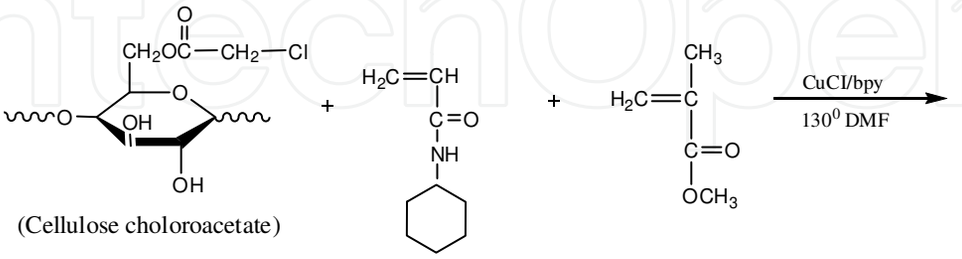
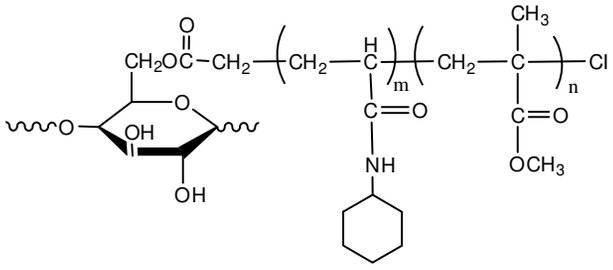
K–T methods, which were r_1 = 0.004-0.128 for NCA cellulose graft copolymer and r_2 = 0.657-0.907 for MMA cellulose graft copolymer (Table 3). Two monomer mixtures on cellulose had a tendency to form an alternating copolymer, because the value of r_1, r_2, and $r_1.r_2$ approached zero. It was concluded that MMA monomer with ester group and smaller molecular size was more reactive on grafting onto cellulose with respect to NCA molecule with amide group and larger molecular size [1].



(Cellulose choloroacetate)



Cell-*g*-(NCA-co-MMA)

Sheme 5. Synthesis of the serials Cell-g-(NCA-co-MMA)

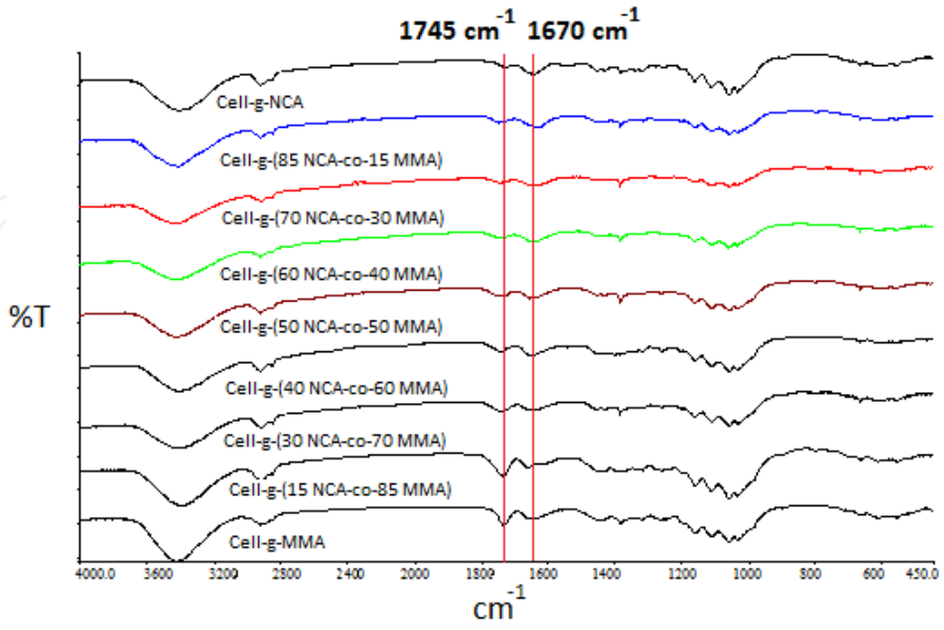


Figure 9. FT-IR spectral area of the serials Poly [Cell-g-(NCA-co-MMA)] graft copolymers

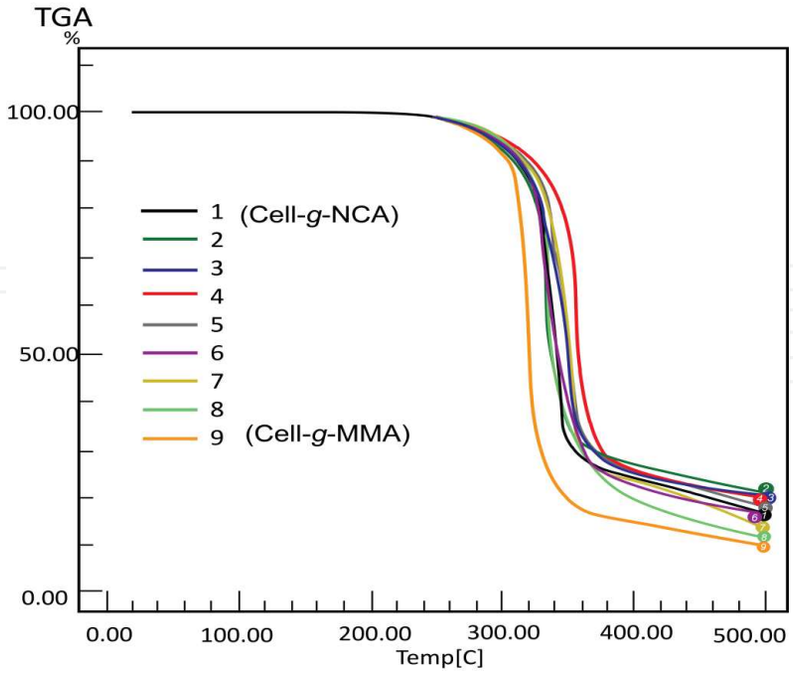


Figure 10. TGA curves of the serials Poly [Cell-g-(NCA-co-MMA)] graft copolymers

Methods	r_{NCA}	r_{MMA}	$r_1.r_2$
FR	0.022	0.696	0.015
IFR	0.128	0.907	0.116
YBR	0.004	0.657	0.003
KT	0.066	0.832	0.055
EKT	0.065	0.837	0.054
Average	0.057	0.786	0.049

Table 3. Comparison of monomer reactivity ratios for Poly [Cell-g-(4NPA-co-MMA)] graft copolymers by different methods

Billy M. et al. obtained more flexible and hydrophilic graft copolymers with various hydrophilic/hydrophobic balances by implanting methyldiethylene glycolmethacrylate (MDEGMA) on cellulose acetate with 2-bromoisobutyrilbromine initiator in cyclopentanone solvent with ATRP method. It was observed that MDEGMA copolymerization is in line with Hanns Fischer's kinetic modeling with radical persistency. Then ATRP grafting of two different cellulose acetate with different ATRP initiator group numbers were studied with respect to macroinitiator, which yielded two graft copolymers with different nanostructures, one being a short graft copolymer, and the other, a longer graft copolymer with the same mass ratio. Their morphologies were analyzed by X-ray diffraction method and it was found that phase separation depended on the number and length of poly (MDEGMA) grafts. As a result,

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cellulose acetate copolymers yielded to powerful films that could be utilized in membrane applications [50].

Chun-xiang L. et al. obtained cellulose graft poly (methylmethacrylate) copolymers in 1-allyl-3-methylimidazolium chloride (BMIMCl) which is an ionic liquid, using 2,2/-bipyridine and CuBr as catalysts. Cellulose chloroacetate as macroinitiator was synthesized by direct acetylation of cellulose with chloroacetyl chloride in BMIMCl in the absence of catalyst. Copolymerization was done in ionic liquid BMIMCl in the absence of homopolymer by-product. When an ionic liquid was used, polymers separated from the catalysts easily. Grafted polymers were characterized by ^{1}H-NMR, GPC (gel permeation chromatography), and AFM (atomic force microscope) methods. According to the findings from AFM, cellulose-grafted copolymers in the solution merged into a sphere-like shape [51].

Glaied O. et al. grafted cationic poly [2-(methacryloyloxy)ethyl]-trimethylammonium chloride (PMeDMA) on cellulose fibers in aqueous solution by using ATRP. Binding 2-bromoisobutyryl bromide – which is an efficient initiator – on hydroxyl groups on cellulose surface, cellulose macroinitiator, was synthesized. Obtained fiber/ PMeDMA complex was characterized by infrared, SEM, and XPS (X-ray photoelectron spectroscopy), which yielded some evidences that showed the polymerization was on the surface of the cellulose. Different initiators were added and withdrawn in order to better define the polymers and it was proven that polymerization was under control in this heterogeneous media by SEC (size exclusion chromatography). It was concluded that cellulose modified by cationic PMeDMA grafting had better mechanical properties [52].

Meng T. et al. synthesized methylmethacrylate and styrene graft copolymers by direct acetylation of cellulose with ATRP method in 1-alyl-3-methylimidazoliumchloride (AMIMCl) – which is an ionic liquid at room temperature – in the absence of catalysts and chemical preservative by using 2-bromoisobutyrylate as macroinitiator. Synthesized cellulose graft copolymers were characterized by using FT-IR, ^{1}H-NMR, ^{13}C-NMR, and GPC methods. It was concluded by TEM (transmission electron microscopy) and static and dynamic laser scattering measurements that cellulose graft copolymers in the solution could aggregate into a sphere-like polymer structure [53].

Yan Q. et al. grafted cellulose-g-poly (N,Ndimethlyamino ethylmetacrylate)-g-poly (ε-caprolactone) (EC-g-PDMAEMA-g-PCL) by using ring opening and ATRP methods. Unlike others, (EC-g-PDMAEMA-g-PCL) brush copolymers show unique physicochemical properties and have multifunctional structure. These bio adaptive copolymers formed mycelia in water and these mycelia merged more with altered pH value. Therefore, it was concluded that these mycelia could be used as perfect nanocarriers for controlled drug release. It was also concluded that crystal structure and crystal morphology of the copolymers could be controlled by altering the length of side chains [54].

Yi J. et al. synthesized temperature-dependent cellulose nanocrystals-g-(N,N-dimethylamino ethylmethacrylate) (CNC-g-PDMAEMA) with ATRP method. Graft copolymers were characterized by FT-IR, TGA, GPC methods. AFM characterization showed that the width of the nanocrystals was 10–40 nm, while their length was 100–400 nm. The liquid-crystal ratio of the

graft copolymers was studied by polarized optical microscopy. It was observed that graft copolymers showed lyotropic property and change of copolymer chains with respect to temperature studied [55].

Xu Q et al. synthesized a new amphoteric polymer by grafting azo polymers to cellulose nanocrystals that showed liquid crystal behavior both in solvent and during heating process. This new crystal prepared by hydrolyzing filter paper with acid was defined by AFM. Liquid crystal polymers poly {6-[4-(4-methoxyphenylazo) phenoxy] hexyl methacrylate} (PMMAZO) were successfully grafted to cellulose nanocrystals by ATRP. The structure and thermal properties of PMMAZO-grafted nanocrystals were investigated by FT-IR and TGA methods; phase structure and transition were studied by DSC and polarized optical microscopy (POM) methods. Experiment results showed that PMMAZO-grafted cellulose nanocrystals showed both thermotropic and lyotropic properties of liquid crystal formation [56].

Bhut B.V. et al. grafted poly (2-dimethylaminoethylmetacrylate) on cellulose successfully by ATRP method. Surface topography, porous membrane morphology as a result of modification, and changes in chemical functions was characterized by ATR-FTIR AFM and SEM. In order to evaluate protein binding capacity of the graft copolymer Bovine serum albumin was utilized and it was concluded that graft has increased in time [57].

Yan L. and Tao W. synthesized graft copolymer of cellulose with N,N-dimethyl acrylamide (DMA) in homogeneous media by ATRP method. First, cellulose was dissolved in N,N-dimethylacetoamide (DMAc)/LiCl system and 2-bromoisobutyloylbromide (B*i*BBr)-Cell-B*i*B macroinitiator was formed. Then DMA was polymerized with cellulose chain under existence of Cell-B*i*B at dimethyl sulfoxide. FT-IR, NMR, and GPC measurements showed that Cell-PDMA graft copolymer was formed. Protein adsorption studies proved that modified cellulose membranes prepared as Cell-PDMA had good protein adsorption resistivity [58].

Sui X. et al. synthesized cellulose-*g*-poly (*N*,*N*-dimethylamino-2-ethylmetacrylate) (cellulose-*g*-PDMAEMA) graft copolymer with ATRP method. Macroinitiator was obtained by direct acetylation of cellulose with 2-bromopropionyl bromide in 1-alyl-3-methylimidazoliumchloride, which is an ionic liquid at room conditions. Copolymers were obtained by undertaking DMAEMA into ATRP process in the presence of CuBr/PMDETA (pentamethyldiethylenetriamine) –as catalyst in DMF solvent without homopolymer by-product. Grafted copolymers were characterized by ^{1}H-NMR, FT-IR, and TGA, and the results proved that PDMAEMA bonded to cellulose with covalent bond. Moreover, cellulose grafted PDMAEMA in aqua was studied under various concentration, temperature, and pH values with UV, TEM, AFM, and DLS (Dynamic light scattering) methods, and was observed that copolymers showed properties expected from PDMAEMA to temperature and pH. It is thought that the method used in this study could be used in preparation of polysaccharides in various biomaterials [59].

Kang H. et al. synthesized ethyl cellulose-g-poly (2-hydroxyethylmetacrylate) (EC-g-PHEMA) in methanol by ATRP method and characterized with GPC and ^{1}H-NMR. Kinetic study showed that polymerization was controllable and (EC-g-PHEMA) aggregated in aqua as mycelia. Morphology of mycelia was determined by DLS and TEM and its formation was discussed [60].

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Kang H. et al. synthesized ethyl cellulose-g-poly (acrylic acid) (EC-g-PAA) and ethyl cellulose-g-*tert*-butylacrylate (EC-g-P*t*BA) copolymers by ATRP method. Using 2-bromoisobutyrilbromide as initiator, hydroxyl groups in ethyl cellulose were esterified and in existence of ethyl cellulose as macroinitiator EC-g-PAA and EC-g-P*t*BA graft copolymers were synthesized and were characterized by FT-IR, ^{1}H-NMR, and GPC methods. Molecular mass of the copolymers increased with polymerization while polydispersity decreased. This study showed that polymerization had kinetics of first degree [61].

Vlcek P. et al. acetylated cellulose diacetate (CDA) with 2-bromoisobutyryl bromide or dichloroacetyl chloride and obtained a new macroinitiator with functionality for ATRP method for different reaction conditions and synthesized new graft copolymers of styrene (St), MMA and butyl acrylate (BuA) with it. Poly (CDA-g-St) and poly (CDA-g-MMA) were used as macroinitiator of BuA polymer and consequently poly [CDA-g-(St-b-BuA)] and poly [CDA-g-(MMA-b-BuA)] diblock graft polymers were obtained, showing that different graft copolymer macroinitiators and different monomers could change graft polymers' length and density [62].

Shen D. et al. grafted polystyrene copolymer on ethyl cellulose (EC) by ATRP method and characterized mycelium properties of the graft copolymer by using DLS, AFM and TEM. Increased concentration resulted in increased mycelia. TEM and AFM images revealed that mycelia had spherical shapes and nucleus-crust structure. All of the macroinitiator was used; molecular mass of the graft copolymers increased and polydispersity decreased. Kinetic study showed that polymerization was of first degree [63].

Shen D. et al. synthesized graft copolymers of ethyl cellulose with polystyrene and polymethylmethacrylate by ATRP method. OH groups in ethyl cellulose reacted with 2-bromoisobutyrilbromide, which is known as an effective ATRP initiator. Functionalized ethyl cellulose has been synthesized as ATRP initiator in toluene, where CuBr/N,N,N′,N′′,N′′- pentamethyldiethylenetriamine was used as catalyst. Molecular mass of the macroinitiators copolymer increased, and polydispersity decreased. Kinetic studies showed that polymerization took place in the first minutes. Graft copolymers were characterized by LLS (laser light scattering) and approved by AFM [64].

Shen D. et al. grafted polymethylmethacrylate (PMMA) on cellulose diacetate by using ATRP method and characterized by ^{1}H-NMR and GPC. OH groups in CDA reacted with 2-bromoisobutyryl bromide, which is known to be an effective initiator for ATRP and was used as functional CDA macroinitiator in MMA graft copolymer. Polymerization was performed under 70°C and in N,N,N′,N′′,N′′- pentamethyldiethylenetriamine/CuBr/1,4-dioxane system. All of the macroinitiator was used, molecular mass increased, and polydispersity decreased. Kinetic studies showed that polymerization was of first degree [65].

Wang et al. [66] reported that pH responsive poly [ethyl cellulose-grafted-(2-diethylamino) ethyl methacrylate] (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 [67], has been reported to be used in some applications such as sensors and optical materials.

5. Conclusion

Cellulose graft copolymers can be obtained either in homogeneous or heterogeneous media. Most widely used methods for graft confirmation are FT-IR, NMR, TGA, SEM, TEM, XRD, and XRF. Monomer grafted on cellulose can give a hydrophilic or hydrophobic character to the new copolymer, which can pave the way to various applications. Reactions in homogeneous media usually show better controllability and yield to higher number of grafts per cellulose chain. CRP methods, such as ATRP, make it possible to obtain pre-designed copolymers, which make grafting a promising research area.

6. Abbreviations list

CRP: Controlled Radical Polymerization

ATRP: Atom Transfer Radical Polymerization

NMP: Nitroxide-Mediated Polymerization

RAFT: Reversible Addition–Fragmentation Chain Transfer Process

ATRA: Atom Transfer Radical Addition Reaction

SIP: Surface-Initiated Polymerization

ROP: Ring-Opening Polymerization

TEM: Transmission Electron Microscopy

AFM: Atomic Force Microscope

XPS: X-Ray Photoelectron Spectroscopy

SEC: Size Exclusion Chromatography

TGA: Thermal Gravimetric Analysis

DLS : Dynamic Light Scattering

GPC: Gel Permeation Chromatography

GPC: Gel Permeation Chromatography

LLS: Laser Light Scattering

$C_6H_{12}O_6$: D-glucose

EC: Ethyl Cellulose

MC: Methyl Cellulose

PC: Propyl Cellulose

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BC: Benzyl Cellulose

HPC: Hydroxypropyl Cellulose

HPMC: Hydroxypropyl Methyl Cellulose

HEC: Hydroxylethyl Cellulose

HEMC: Hydroxylethyl Methyl Cellulose

MHPC: Methyl Hydroxypropyl Cellulose

EHEC: Ethyl Hydroxylethyl Cellulose

CMC: Carboxymethyl Cellulose

CA: Cellulose Acetate

P_n: An Active Species

M^n-Y/L: Transition Metal Complex

X: Halogen

P_n-X: Initiator or a Dormant Species

CH_2=CH_2R_1: Active Species Initiate Monomers

X-M^{n+1}-Y/L: Oxidized Metal Complexes

k_a: Rate Constant of Activation Amit

k_d: Rate Constant of Deactivation

k_p: A Constant of Propagation

k_t: Termination Reactions

PMDETA: N,N,N$^{/}$,N$^{//}$,N$^{///}$–Pentamethyl Diethylene Triamine

TMEDA: Tetramethyl Ethylene Diamine

HMTETA: 1,14,7,10,10-Hexamethyl Triethylene Tetramine

Me_6-TREN: Tris [2-diamethylamino ethylamine]

o-phen: 1,10-phenanthroline

bpy: 2,2′-bipyridine

dNbpy: 4,4′-di-(5-nonyl)-2,2′-bipyridine

NPPMI: N-(n-propyl)pyridylmethanimine

NOPMI: N-(n-octyl)pyridylmethanimine

PMDETA: N, N, N′, N′′, N′′′-pentamethyldiethylenetriamine

HMTETA: 1,1,4,7,10,10-hexamethyltriethylenetetramine

TPMA: Tris[(2-pyridyl)methyl]amine

TPEN: N, N, N′,N′-tetrakis(2-pyridylmethyl)ethylenediamine

4NPA: N-(4-Nitrophenyl) acrylamide

NCA: N-Cyclohexylacrylamide

4VP: 4-Vinylpyridine

AM: Acrylamide

MAM: Methacrylamide

DAAM: Diacetone acrylamide

MMA: Methylmethacrylate

F–R: Fineman-Ross method

K–T: Kelen-Tüdos method

E–K–T: Extended Kelen-Tüdos method

I–F–R: Inverted Fineman-Ross method

Y–B–R: Yezrielev-Brokhina-Roskin method

DMF: N,N-Dimethylformamide

DMF: N,N-Dimethylformamide

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