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**Perspective on the controlled polymer-modification of chitosan and cellulose nanocrystals:
Towards the design of functional materials**

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Abstract

The development of reversible deactivation radical polymerization (RDRP) opened a vast number of possibilities for the synthesis of exotic macromolecular architectures with tailored properties for diverse applications. Given the advantages that RDRP provides, it is possible to obtain such architectures with good control over molecular weight distribution, morphology, composition, and functionality. A field of great interest for many research groups is the modification of natural polymers (or polysaccharides) with synthetic polymers via polymer grafting using RDRP approaches, such as atom transfer radical polymerization (ATRP), nitroxide-mediated polymerization (NMP), and reversible addition–fragmentation chain transfer polymerization (RAFT) since the properties of the resulting materials can be tailored. Two polysaccharides that stand out due to their properties and potential applications after polymer modification are chitosan and cellulose nanocrystals (CNC). Chitosan is a derivative of chitin, desirable for its biocompatibility, degradability, low toxicity, and ability to act as a chelating agent with potential applications in the biomedical and pharmacy fields or wastewater treatment. CNC are well known for their outstanding mechanical properties, such as high specific strength and modulus and high surface area. For both chitosan and CNC, however, their hydrophilic nature makes them incompatible with non-polar systems, limiting their potential applications. This feature article highlights the most recent development and our personal perspective of polymer grafting techniques on CNC and chitosan via RDRP for the design of different architectures, the design of responsive materials from such polysaccharides, potential water treatment applications, and our opinion of the future of this attractive research field.

KEYWORDS

polysaccharides. reversible deactivation radical polymerization, chitosan nanocrystals. cellulose nanocrystals, CNC

1 INTRODUCTION

Desirable properties of natural polysaccharides, such as biodegradability, biocompatibility, non-toxicity, relatively low cost, and abundance, have motivated their use and further development for the production of functional advanced materials for tailored applications and for replacing (to some degree) the use of petroleum-based polymers.^[1-3] Chitosan and cellulose nanocrystals are two natural polysaccharides that in particular have attracted the attention of industrial and academic researchers.

Chitosan (Figure 1A), produced from chitin which is based on poly(β -(1-4)-N-acetyl-d-glucosamine), is the second most abundant natural polymer on Earth after cellulose. It is present in living organisms such as insects, cell walls of fungi, and exoskeletons of crustaceans.^[1,2,4,5]

When the alkaline deacetylation of chitin reaches 50% or higher, the partially deacetylated chitin is referred to as chitosan. The partial (or complete) substitution of the chitosan acetyl group for a primary amine ($-\text{NH}_2$) in the second position changes its properties dramatically compared to native chitin. Chitosan, unlike chitin, can be solubilized under acidic conditions ($\text{pH} < 6$) by the protonation of the $-\text{NH}_2$ groups depending on the acid used (usually acetic acid or hydrochloride acid), degree of deacetylation, and/or degree of drying of the chitosan.^[5] Due to the presence of the $-\text{NH}_2$ group, chitosan is considered a natural polycation ($\text{pK}_a = 6.3$) and is a remarkable chelating agent, finding applications in wastewater treatment, cosmetics, agriculture, biopharmaceuticals, and the food packaging industry.^[1,2]

Cellulose nanocrystals (CNC) have generated enormous interest among the scientific community during the last 10 years (Figure 1B). CNC are obtained after the hydrolysis of cellulose, which removes the amorphous chains yielding crystals with nanodimensions of ~ 100 - 200 nm by ~ 10 nm.^[6-9] These nanocrystals possess high specific strength and modulus, and exhibit reinforcing, gas barrier, and unique optical properties.^[6-9]

Despite the fact that chitosan and CNC show such attractive properties for numerous applications, often chemical modification either with small molecules or polymer chains (via polymer grafting) is necessary in order to customize their properties for specific applications. Using polymer grafting via reversible deactivation radical polymerization (RDRP) approaches (atom transfer radical polymerization [ATRP], nitroxide-mediated polymerization [NMP], or reversible addition-fragmentation chain transfer polymerization [RAFT]) allows the preparation of chitosan or CNC with grafted polymer chains having a predetermined degree of

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polymerization, composition or functionality, as well as a narrow molecular weight distribution.^[10-12] In this feature article, we present a short review of the polymer graft modification of chitosan and CNC using RDRP approaches developed by our group and our perspective of how we developed specific polymer grafting techniques, design of CO₂ (pH)-responsive materials, water treatment applications, and our personal opinion on where we believe future opportunities lie for these renewable polymers.

2 REVERSIBLE DEACTIVATION RADICAL POLYMERIZATION

In 2010, the International Union of Pure and Applied Chemistry (IUPAC) adopted the terminology RDRP which, at that time, was referred to as controlled/living radical polymerization (C/LRP). This was recommended to avoid potential controversy and confusion since the terms controlled or living might have different meanings or refer to different aspects of a chemical process.^[13] Control refers to the narrowness of the molecular weight distribution, while livingness refers to the fraction of the polymer chains that have a mediating agent at the chain end and are therefore considered living. Ideally, but not necessarily, a polymerization exhibits both a high degree of control (low dispersity) and livingness. RDRP processes can be used to prepare well-defined polymers with narrow molecular weight distribution ($\mathcal{D} = M_w/M_n < 1.1-1.5$), predetermined degree of polymerization (DP_n), low percentage of terminated chains ($< \sim 10\%$), and specific functionalities and end-groups. When copolymers are synthesized, the arrangement of the monomers can be random, blocks, grafts, or stars. NMP was the first RDRP to be developed. The pioneering work on the use of nitroxide-based alkoxyamines presented by Solomon et al. and Moad and Rizzardo in the 1980s^[14,15] described the synthesis of polymeric architectures using vinyl monomer and the first concepts of what is today known as RDRP.^[14,15] The work published by Georges et al.^[16,17] in the early 1990s, that described the use of TEMPO (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl) and benzoyl peroxide for the polymerization of styrene, promoted the revolution of the radical polymerization field.^[14-17] The NMP mechanism is considered the simplest among the RDRP techniques and is based on a reversible deactivation equilibrium between active species (growing radicals) and nitroxide agents that act as growth mediators for the polymerization (Scheme 1).^[10,18] NMP can be carried out in solution or in bulk and has been successfully applied in various processes such as emulsion, miniemulsion, and suspension polymerization.^[19-21] NMP can effectively polymerize

styrenics or acrylates. Methacrylates can also be successfully polymerized if a controlling comonomer such as styrene or acrylonitrile is added to the system (~8-10 mol%).^[22,23] More recently, a new alkoxyamine was developed capable of polymerizing methacrylates without the presence of comonomer.^[24-26] The main disadvantage of NMP is that high temperatures are usually required (>80-100°C) for the polymerization to occur. Excellent reviews on NMP covering general aspects on the mechanism, kinetics, monomers, conditions, and so on by Nicolas et al.,^[10] Moad et al.,^[15] and Grubbs are available.^[18]

The ATRP mechanism is based on the formation of adducts of alkyl halides and alkenes catalyzed by transition metal complexes aided by a ligand (Scheme 2).^[11,27] In this process, radicals are produced via a reversible redox process which is catalyzed by the transition metal complex. It involves a one-electron oxidation process with the abstraction of the halogen atom present in the dormant species. Polymer chains grow by addition of monomer to the free radicals. In the deactivation step, the oxidized metal reacts with the propagating polymeric radicals, yielding dormant species. ATRP is very popular for several reasons: relatively low concentrations of catalyst (50-500 ppm) are required, a large number of monomers can be polymerized, a wide range of solvents can be used (low-high polarity), and initiators and transition metals ligands are commercially available.^[11,27] The main drawback of ATRP is that the transition metal may need to be removed from the polymer, depending on the concentration of catalyst used and the application.^[11,27] Interesting reviews about ATRP (mechanism, ligands, polymerization conditions, etc.) are available in the literature.^[11,27]

RAFT was developed by Moad, Rizzardo, and coworkers at CSIRO and has proven to be an important technique for the synthesis of complex and well-defined macromolecular architectures.^[12,28] The RAFT mechanism is different from NMP and ATRP mechanisms in that it is based on a degenerative transfer process based on chain transfer reactions. In this mechanism, a growing macroradical reacts first with a thiocarbonylthio compound, prior to the fragmentation of the intermediate radical, which produces a polymeric chain end-functionalized with the thiocarbonylthio compound, and a new propagating radical (Scheme 3).^[12] The equilibrium between the growing propagating radicals and thiocarbonylthio end-functionalized polymer chains allows the polymer chains to grow uniformly. Thiocarbonylthio compounds include dithioesters, dithiocarbamates, trithiocarbonates, and xanthates. The main drawbacks of RAFT are that the final materials may exhibit undesirable colour, odour, or possible toxicity due

to the dithioester groups and, therefore, removal could be necessary. More information about RAFT (covering general aspects on the mechanism, kinetics, monomers, conditions, etc.) is presented in comprehensive reviews by Moad et al.^[12,28]

3 POLYMER GRAFTING ONTO NATURAL POLYMERS VIA RDRP

One of the key advantages of RDRP is the ability to synthesize complex molecular architectures, including grafted copolymers. The polymer grafting process is usually carried out via grafting to, grafting from, or grafting through approaches. *The grafting to* approach is attractive since well-defined (molar mass, molecular weight distribution, functionality, or monomer arrangement), previously synthesized polymer chains are attached to the natural polymer by reacting functional groups on the natural polymer with the terminal RDRP functional group of the presynthesized polymers. The main disadvantage of this approach is that steric hindrance can limit the degree of grafting. In the grafting from approach, the natural polymer is modified with initiator moieties, alkoxyamines, or chain transfer agents (CTAs), and then polymers or copolymers grow from these initiating groups. This approach is recommended when high grafting densities are desired. Among the main disadvantages of this approach is that it is often difficult to accurately determine the degree of polymerization or the molecular weight distribution of the grafted chains, since cleavage of the grafted chains can be difficult.^[29] The grafting through approach has been the least used to date. In this approach, polysaccharides have to be modified with vinyl functionalities to act as macromonomers which are then copolymerized with monomer molecules to produce copolymers that are grafted from a natural polymer or a substrate.^[29]

3.1 Polymer graft modification of chitosan via nitroxide-mediated polymerization

In pursuit of the development of new chitosan-based materials, different research groups have modified chitosan with functional grafted polymer chains using RDRP (ATRP, RAFT, or NMP), anticipating new properties that would result from the synergy between chitosan and the corresponding polymeric chain.^[30-32]

The main challenge that has limited the development of chitosan is its poor solubility in organic solvents, which also limits the modification reactions that chitosan can undergo. As previously noted, chitosan can be solubilized under acidic conditions ($\text{pH} < 6.5$)^[1,2] or using ionic liquids.^[33] Efforts to make chitosan soluble in organic solvents have been reported. Lebouc noted that the protection of the primary $-\text{NH}_2$ of chitosan with phthalic anhydride makes chitosan soluble in

organic solvents such as dimethyl sulfoxide (DMSO) or dimethyl formamide (DMF); however, the yields upon deprotection (removing the phthalic functionalities from the -NH₂ group) were relatively low.^[34] It is very important to keep in mind that many of the unique properties of chitosan are due to the presence of -NH₂; therefore, the preservation of this functional group is of paramount importance.^[30,35,36] Also, it was reported that when an anionic surfactant such as sodium dodecylsulfate (SDS) was complexed with the amino group of chitosan, the material was soluble in DMSO, and the deprotection yields were high.^[37]

In our case, we chose to complex sodium dodecylbenzenesulfonate (SDBS) with chitosan, to make it soluble in organic media, while protecting the -NH₂ functionality. We observed that SDBS exhibited a higher thermal and chemical stability than SDS.^[30,35] We focused on the modification of chitosan with grafted polymers or copolymers using NMP, since NMP does not require the presence of metal-based catalysts that can potentially be adsorbed by the chitosan or complexed by the -NH₂ groups of the chitosan. We targeted the modification of chitosan using both grafting to and grafting from approaches. Our strategy relied on first attaching vinyl functionalities to the chitosan backbone chain using glycidyl methacrylate (GMA).^[38] Once chitosan modified with GMA was obtained, it was complexed with SDBS (CTS-SDBS-g-GMA), which can then be solubilized in DMSO. We used CTS-SDBS-g-GMA as precursor material for both grafting to^[30] and grafting from^[35] approaches. CTS-g-GMA was used when the graft modification could be carried out in aqueous media.^[36,39,40]

For the grafting from approach,^[35] the vinyl groups were functionalized with a corresponding alkoxyamine by an intermolecular 1,2 radical addition process. In this case, we studied two different alkoxyamines, TIPNO (2,2,5-Trimethyl-4-phenyl-3-azahexane-3-nitroxide) alkoxyamine (also known as the universal alkoxyamine) and SG1-alkoxyamine (known commercially as the BlocBuilder alkoxyamine), yielding two different macroalkoxyamines CTS-SDBS-g-GMA-UA (with TIPNO-alkoxyamine, see Scheme 4A) and CTS-SDBS-g-GMA-BB (with SG1-alkoxyamine, see Scheme 4B). With both alkoxyamines, we investigated the grafting polymerization of styrene and n-butyl acrylate (BA).

Using the CTS-SDBS-g-GMA-UA, the conditions of the reaction were 123°C for styrene and 115°C for BA. After 9 h of polymerization, the conversions for styrene and BA were approximately 7% and 3%, respectively. Next, we used a large amount of monomer relative to chitosan to promote the grafting reaction. Although the values of conversion were low, the ratio

of grafted polymer to chitosan using this specific macroalkoxyamine (TIPNO-alkoxyamine) were 65:35 wt% for polystyrene and 45:55 wt% for PBA. BA polymerization was slower compared to styrene, which was attributed to both the addition of free TIPNO (5 mol%) to the BA polymerizations (to improve control) and a lower polymerization temperature suppressing the polymerization rate. In acrylate polymerization reactions, low polymerization rates afford better control of the polymerization (avoiding termination and lower dispersity). For the polymerization of styrene, this is avoided due to the thermal generation of radicals that consume excess nitroxide moieties.

Using CTS-SDBS-g-GMA-BB, the conditions of the grafting polymerizations were 115°C for styrene and 110°C for BA. For the BA polymerization, we also added free SG1 (5 mol%) to suppress the rate of polymerization and avoid potential termination reactions during polymerization. Only ~4% conversion was attained after 9 h. For this system, we also used a high concentration of monomer to promote the grafting polymerization. Yet, despite the low conversion, the final amount of grafted polymer in the grafted chitosan was 55% after 9 h. Interestingly, for the polymerization of styrene, we observed termination reactions that promoted crosslinking between the growing chains and, as a result, the products precipitated out of solution. The loss of control that promoted termination and crosslinking was attributed to the rate of SG1-mediated polymerization, which was relatively high compared to other systems we investigated due to the higher polarity of the media (DMSO). It has been reported that polar solvents promote a slower deactivation of the radicals, the propagating radicals leading to a faster reaction rate and a greater propensity to termination reactions. Once the final materials were obtained, the SDBS was removed from the polymer-modified chitosan, making it insoluble in organic solvents again, but preserving the -NH₂ functionality. We could not measure the molecular weight distribution of the grafted chains as they could not be cleaved from the chitosan, since very strong acidic/basic conditions are necessary and not always successful (M_n was estimated based on conversion). From this study, we concluded that chitosan can be successfully modified with synthetic chains via NMP in homogenous media, achieving a high grafted polymer content. Complexing SDBS with the amino group of chitosan made it soluble in DMSO and facilitated its modification, while preserving the -NH₂ functionality. The amount of polymer present in the final material could be easily tailored simply by changing the reaction time.^[35]

We also studied the grafting from modification of chitosan in aqueous media. As stated previously, native chitosan is only soluble under acidic conditions; therefore, in the grafting polymerization, the monomer and resulting grafted polymer had to be soluble in water to maintain homogeneity and promote grafting reaction. We selected the monomer (poly(ethyleneglycol) methyl ether methacrylate) (PEGMA) to be grafted from chitosan backbone chain to produce CTS-g-GMA-PPEGMA. PPEGMA is a polymer soluble in water and in organic media. The introduction of polyethylene groups on chitosan (PEGylation) is often applied to develop materials for drug delivery systems.^[36] The PEGylation of chitosan using NMP had not been previously investigated. For the PEGylation of chitosan with PPEGMA via grafting from, we started with GMA-functionalized chitosan (CTS-g-GMA), which is soluble under acidic conditions. Vinyl groups of CTS-g-GMA were then functionalized with an alkoxyamine (N-tert-butyl-N-[1-diethoxyphosphoryl-2,2-dimethylpropyl] aminoxy)-N-propionyloxysuccinimide (NHS-BB) by intermolecular 1,2 radical addition under aqueous mild acidic conditions (pH~5.1), yielding CTS-g-GMA-NBB and converting chitosan into a macroalkoxyamine (Scheme 5). With this macroalkoxyamine, we performed grafting reactions of PPEGMA in the presence of styrene (10 mol%), yielding CTS-g-GMA-poly(PEGMA-co-S). Free nitroxide (SG1) was added to decrease the concentration of propagating radicals and prevent termination reactions. The grafting polymerization reactions were conducted at 90°C for 0.5, 1, and 2 h, achieving monomer conversion of between 2.0-3.0%. As previously discussed, we employed a large excess of monomer to promote the grafting reaction and, although the conversion was low, the chitosan:polymer ratios were in the range of 73:27-65:35 wt%.^[36] For the success of the grafting polymerization in aqueous media, it is important to maintain pH>5.0. At a lower pH, the nitroxide becomes protonated and is not effective. This work provided the first example for the grafting from polymerization of chitosan via NMP under aqueous conditions. In this approach, the composition of the resulting material was shown to be dependent on the reaction time.^[36]

In parallel, we investigated the modification of chitosan via the grafting to approach.^[30,36,39,40] The key factor for a successful grafting is to promote the reaction between the functionality in chitosan and the functionality in the polymer, which we performed in homogenous media. We used chitosan functionalized with GMA and complexed with SDBS (CTS-SDBS-g-GMA), which is soluble in DMSO (Scheme 6). The polymers grafted to chitosan included a series of

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polymers and copolymers (random and block) with different degrees of polymerization. We prepared poly(styrene) (PS), PBA, poly(acrylic acid) (PAA), poly(styrene)-*b*-poly(acrylic acid) (PS-*b*-PAA), and poly(styrene-*r*-acrylic acid) (PS-*r*-PAA) via NMP using the BlocBuilder alkoxyamine.

For a successful grafting to process via NMP, it is essential that a large fraction of the polymer chains is end-functionalized with the SG1. Our strategy for the grafting to process was based on the thermal (>75°C) dissociation of SG1 from the polymeric chains, producing two radicals: the SG1 nitroxide (stable radical) and an end-propagating radical of the polymeric chain (macroradical), which can react with the double bond of CTS-SDBS-*g*-GMA prior to being potentially deactivated by the corresponding nitroxide (see Scheme 7). After thermal dissociation, polymer chains can undergo termination reactions (combination or disproportionation) rather than reacting with vinyl groups present on chitosan, which can lead to a lower grafting efficiency. In order to promote grafting to reactions, we maintained a low concentration of macroradicals relative to GMA units (present on chitosan backbone chain), which prevented the macroradicals from terminating and promoted the reactions with GMA. The other factor that can be critical is the reaction temperature. At high temperature (>115°C), the dissociation rate constants are relatively high and might promote termination of the chains, whereas at lower temperature the dissociation rate constants are an order of magnitude lower, thereby avoiding excessive termination of the macroradicals. We noted an optimum reaction temperature in the range of 80-90°C^[30] and maintained a low concentration of macroradicals by feeding the polymers or copolymers in a semi-batch manner.^[30]

The primary advantage of the grafting to approach is that the syntheses of the polymers or copolymers to be grafted could be custom tailored. Therefore, the degree of polymerization of each polymer or copolymer and the composition could be determined. Combined with the fact that the materials were soluble, we could fully characterize the final grafted materials and determine the number of chains grafted per every 100 units of chitosan, as well as the grafting efficiencies, which varied between 25%-43%.^[30] The grafting efficiencies were determined by the ratio of number of chains grafted to the number of sites possible where chains could be grafted (GMA units).^[30]

We also attempted the polymer grafting to approach of chitosan in aqueous media. In this case, we grafted two aqueous soluble polymers, PPEGMA^[36] (see Scheme 5) and

poly(diethylaminoethyl methacrylate) (PDEAEMA) (see Scheme 8), to chitosan.^[40] PPEGMA is soluble at any pH and PDEAEMA is soluble under acidic conditions. In both cases, our starting material was chitosan functionalized with GMA, which is soluble under mild acidic conditions. Prior to grafting, both PPEGMA and PDEAEMA were synthesized via SG1-mediated polymerization, and therefore both polymers were end-functionalized with SG1 nitroxide. The average M_n for PPEGMA and PDEAEMA were approximately 10 900 and 9700 g/mol, respectively. For the chitosan modified with PPEGMA, we determined a grafting efficiency of ~64%, translating to approximately 7 chains of PPEGMA grafted for every 100 units of chitosan.^[36] For the modification with PDEAEMA, the grafting efficiency was approximately ~25%, indicating that approximately 2.7 of polymer chains were grafted for every 100 units of chitosan.^[40]

Our research group also investigated the modification of chitosan via grafting to and grafting from approaches with phosphonated polymers via NMP^[41] in a similar fashion as previously described.^[30,35,36] In this particular case, methacrylate dimethyl(methacryloyloxy)methyl phosphonate (MAPC1) was the monomer used. For the grafting to approach, CTS-g-GMA was firstly synthesized, and MAPC1 was polymerized via NMP using styrene as controlling comonomer. Once PMAPC1 was obtained, this was grafted to chitosan under mild acidic conditions (pH~5), yielding CTS-g-PMAPC1. PMAPC1 was silylated using TMSBr and subsequently hydrolyzed with methanol to obtain the grafted polymer with phosphonic acid groups (hPMAPC1), which was also grafted to CTS-g-GMA, yielding CTS-g-hPMAPC1 (see Scheme 9). The M_n of the grafted polymer was ~15 000 g/mol, and the average grafting efficiency was 8%. The relatively low efficiency was attributed to high M_n of PMAPC1, which limits the accessibility due to steric hindrance between the end groups, in this case, the double bond of CTS-g-GMA and BB of the polymer chain. The amount of grafted PMAPC1 was 33 wt% and 30 wt% for hPMAPC1. For grafting to approach, CTS-g-GMA was converted into a macroalkoxyamine by reacting the double bonds of GMA with BB alkoxyamine via 1,2-radical addition under mild acidic conditions, yielding CTS-BB. The grafting polymerization of MAPC1 or hMAPC1 (acidic version of the monomer) from CTS-BB was also carried out under mild acidic conditions (pH~5) for 24 h. However, after 14 h of reaction, the grafted chitosan precipitated, indicating possible crosslinking between the growing copolymer chains. The final amount of grafted PMAPC1 was 28 wt% and 35 wt% for PhMAPC1.^[41]

Using chitosan, we have also developed macroparticles modified with grafts of poly(4-vinylpyridine) (P4VP) using RAFT via grafting from approach. In this case, chitosan macroparticles were made first prior to being functionalized with a 4-(phenylcarbonothioylthio)pentanoic acid (CPA), which is a RAFT transfer agent. Once the macroparticles modified with CPA were obtained, the grafting polymerization was investigated at 10 and 40 h, yielding CTS-CPS-g-P4VP (see Scheme 10). Since it was not possible to cleave the grafted chains from the chitosan particles surface and determine their degree of polymerization, free CPA (sacrificial CTA) was added to the reaction mixture in order to estimate the molecular weight distribution to produce free polymer, assuming they will grow similarly to the grafted chains and have a rough estimate of the DP_n of the grafted P4VP. The analysis of the kinetics of the polymerization of the free chains showed the features of a classic RDRP polymerization, since both conversion versus time and M_n versus conversion were linear, and GPC traces indicated a clear evolution of the M_n . A grafting efficiency (number of P4VP chains/number of functionalized units of chitosan with CPA) of 30% was estimated. At 10 h, the ratio of grafted polymer was 12 wt% and at 40 h it was 21%. Finally, after yielding the macroparticles modified with P4VP, these were cross-linked with dialdehyde (producing XCTS-CPS-g-P4VP) in order to improve chemical and mechanical resistance for further applications.^[42]

3.2 Polymer grafting modification of CNC via reversible deactivation radical polymerization

CNC is currently a material of significant interest to the scientific community due to all the properties that a single material can present.^[8,29,44,45] The primary objective of our research was to modify the surface properties of CNC to make it compatible with more hydrophobic systems and/or stimuli-responsive. We explored the modification of CNC (made by acid hydrolysis) with grafted polymers via RDRP both via grafting from and grafting to approaches.^[46-50] This particular CNC possesses sulfur half-ester groups on the surface, giving the CNC a high surface negative charge, making the material dispersible only in very polar solvents such as water or DMSO.^[29] Our first reports involved the modification of CNC with poly(methyl acrylate) (PMA) via ATRP (Cu(0)-SET mediated polymerization)^[46] and with PMA and poly(methyl methacrylate) (PMMA) via NMP,^[47] both using grafting from approach. For the modification

using ATRP, CNC surface was transformed to a macroinitiator for ATRP by attaching Br functionalities using α -bromoisobutyric acid (BIBA) via carbonyldiimidazole (CDI)-mediated esterification in DMSO (see Scheme 11). Once the Br-functionalized CNC was obtained, the grafting polymerization was carried out in DMSO in the presence of Cu(II) bromide, Me₆TREN (tris[2-(dimethylamino)ethyl]amine) as the ligand, and copper wire (14 gauge) at room temperature. It was observed that the polymerization proceeded too quickly, achieving 30% monomer conversion in 30 min, which translates to six times the mass of PMA versus the mass of CNC. The advantage of using copper wire versus copper slats is that less copper is needed, yielding colourless reactions (colour is usually a disadvantage of ATRP systems). The PMA-modified CNC showed promising dispersity in common organic solvents including tetrahydrofuran (THF), chloroform (CHCl₃), DMF, and DMSO. [46]

For our initial report regarding the modification of CNC via NMP, we firstly transformed CNC into a macroalkoxyamine in order to be able to grow polymer from its surface. CNC was first modified with vinyl benzyl chloride, and then the vinyl groups were functionalized with the BlocBuilder alkoxyamine (CNC-BB) via 1,2 radical addition (Scheme 12). We demonstrated that, for the successful modification of CNC via NMP and grafting from, a good dispersion of CNC was of paramount importance. CNC-BB was never dried; hence, for the polymerization reactions, the corresponding monomers were added dropwise. Monomer conversions ranged from 0.4%-4% for PMMA and 0.3%-4.6% for PMA. For CNC-g-PMA and CNC-g-PMMA, the percentages of polymer grafted (of the total CNC-g-PMA or CNC-g-PMMA) were as high as 75 and 78 wt%, respectively. The amount of grafted polymer can be tailored simply by adjusting the reaction time. We observed that CNC modified with both PMA and PMMA were dispersible up to 1 wt% in organic solvents such as THF or acetone and, to a lesser extent, in toluene.

Interestingly, they were not dispersible in water, which confirms that the CNC surface properties were significantly altered. [47]

Following the same approach, we used CNC-BB to graft CO₂-responsive polymers (pH-responsive) such as poly(dimethylaminoethyl methacrylate) (PDMAEMA), poly(diethylaminoethyl methacrylate) (PDEAEMA) and poly(dimethyl aminopropyl methacrylamide) (PDMAPMAm), yielding CNC-g-PDMAEMA, CNC-g-PDEAEMA, and CNC-g-PDMAPMAm (see Scheme 13). [48] PDMAEMA, PDEAEMA, and PDMAPMAm are polymers containing tertiary amines that, in the presence of carbonic acid (formed when CO₂ is

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added to water), become protonated, making the polymers more hydrophilic.^[51] They can also be easily deprotonated by removing the CO₂ by sparging with N₂, Ar, or air or by applying gentle heat. When they are deprotonated, the polymers switch back to their hydrophobic state.^[51] Our goal was to make the CNC surface CO₂-switchable by making the surface highly hydrophilic when the corresponding polymer is protonated (forming stable dispersions in water), and hydrophobic when non-protonated, thereby yielding unstable dispersions in water. The grafting reactions of the CO₂-responsive polymers were conducted for 0.5 and 1 h in the presence of styrene as controlling comonomer (10 mol%). After 1 h, the conversion ranged from 45%-52%, yielding 49, 53, and 65 wt% polymer for CNC-g-PDMAPMAm, CNC-g-PDMAEMA, and CNC-g-PDEAEMA, respectively. The CO₂-responsiveness of CNC-g-PDMAEMA, CNC-g-PDEAEMA, and CNC-g-PDMAPMAm was evaluated by measuring the ζ -potential and pH of each material by using either alternating CO₂/N₂ atmospheres or alternating addition of glycolic acid and sodium hydroxide. Under CO₂ atmosphere or in an acidic environment, tertiary amines of the grafted polymers are protonated (low pH), and therefore the ζ -potential is positive. When deprotonated, under N₂ atmosphere or in a basic environment, the ζ -potential is reduced appreciably (the ζ -potential of unmodified CNC is \sim -43 mV). For the three different materials, it was that observed that under CO₂ or acidic conditions, the ζ -potential ranged from \sim 30-40 mV, which confirmed that both carbonic acid and glycolic acid could effectively protonate the tertiary amines. Under N₂, the ζ -potential ranged from 1-22 mV. The values were very different for every material, indicating the importance of the nature of the polymer. When sodium hydroxide was used to increase pH, ζ -potential values were considerably lower compared to N₂, suggesting that using liquid acid or base reduced mass transfer issues that can be present when gases are used for the protonation/deprotonation process. The three systems all exhibited better dispersion in aqueous solutions, indicating they were indeed more hydrophilic when protonated. When they were not protonated, unstable dispersions were observed, indicative of greater hydrophobicity. In general, we concluded that, using this approach, the surface of CNC could be modified and new properties such as CO₂-responsiveness could be obtained using NMP modification.^[48]

We have also developed a methodology to produce CNC CO₂-responsive materials by grafting PDEAEMA and PDMAEMA via grafting from and copper(0)-mediated polymerization (see Scheme 14).^[49] In this report, CNC was also transformed to a macroinitiator using BIBA, but before performing the grafting reactions, we studied polymerization kinetics of the

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corresponding monomers in order to determine the most suitable conditions (solvent and catalyst) of the homopolymerization to then perform the grafting polymerizations. Some issues were found to happen during the homopolymerization of DEAEMA and DMAEMA. Initially Me₆TREN was used as the catalyst, but low monomer conversions were observed, suggesting competition between the ligand with the copper, therefore HMTETA (1,1,4,7,10,10-hexamethyltriethylenetetramine) was used instead showing first-order kinetics, characteristic of ATRP. However, a rapid increase was observed for monomers in the Mn at very early stages of the polymerization, attributed to a low initiation efficiency caused by the interaction of the monomers with the copper catalyst affecting equilibrium (activation/deactivation). It was also determined that methanol (solvent used for the homopolymerization kinetics) has an important effect. Both monomers can self-catalyze their transesterification with methanol at room temperature, resulting in the formation of MMA during the polymerizations of DMAEMA (8 mol% of MMA) or DEAEMA (0.6 mol% of MMA). Despite this, it was decided to keep using methanol for the grafting polymerizations since it allows a decent dispersion of CNC macroinitiator, which is of paramount importance to obtain a good yield of the polymer-grafted CNC. The grafting polymerizations of DEAEMA and DMAEMA were carried out in methanol in the presence of HMTETA as the ligand and CuBr₂ as the catalyst (copper wires, 14 gauge), yielding CNC-g-PDEAEMA with polymer weight fraction of 14%-20% (and PMMA 14 wt%) and CNC-g-PDMAEMA with polymer weight fraction of 18%-26% (and PMMA 3-12 wt%). The CO₂-responsiveness of CNC-g-PDMAEMA and CNC-g-PDEAEMA was also evaluated under CO₂/N₂ cycles. Both products showed fully reversible CO₂-responsiveness over four switching cycles and no destabilization was observed.^[49]

Our group also modified CNC with CO₂-responsive polymers via a grafting to approach using NMP.^[45] CNC was firstly functionalized with vinyl groups using GMA in acidic media by reacting the epoxy groups of GMA with the primary hydroxyl groups on the CNC surface.^[50] Then, presynthesized PDEAEMA, PDMAEMA, and PDMAPMAm of different degrees of polymerization (made by NMP) were attached to the CNC surface by reacting the SG1 end group of the polymers with the GMA moieties in a similar fashion to the modification of chitosan via grafting to (see Scheme 15). As expected, the grafting to approach yielded lower grafting densities when higher molecular weight polymers were grafted due to steric hindrance. The amount of polymer grafted ranged between 7%-23%. A CNC CO₂-responsiveness was

confirmed as a result of the grafted PDEAEMA, PDMAEMA, and PDMAPMAM. When the materials were protonated, they showed affinity for polar systems such as water and when they were not protonated, they had affinity for less polar systems such as chloroform.^[50]

We also explored the grafting modification of CNC with CO₂-responsive polymers via RAFT, employing both grafting to and grafting from approaches (Scheme 16).^[52] For the modification via grafting to, it was necessary first to attach an anchor group to the CNC that could function as a link between the polymer chains and the CNC. In this case, GMA was also bound to the primary -OH groups on the CNC surface. Then, well-defined PDMAEMA, PDEAEMA, and poly(diisopropylaminoethyl methacrylate) (PDPAEMA) were synthesized via RAFT using 4-cyano-4-((phenylcarbonothioyl)thio)pentanoic acid (CTP) as the RAFT agent. Three different polymers of varying M_n ranging from ≈2500-8600 g/mol (Đ=1.1-1.2) were prepared. All polymers had high chain end-functionality with RAFT moieties and, therefore, readily reacted with the GMA groups present on the CNC surface. With this procedure it was possible to determine the number of chains per gram of CNC (grafting density), since the exact molecular weight of each polymer was known. It was observed that for each specific polymer, a higher grafting density was obtained with the lowest DP_n, attributable to the steric hindrance effect mentioned above. The polymer wt% in the final materials ranged from 6%-20%.

For the grafting from approach, CNC was first converted into a macro-chain transfer agent by functionalizing the CNC with CTP. Then, CTP-modified CNC was used for the grafting from polymerization of DMAEMA, DEAEMA, and DPAEMA. In this case, we expected to obtain higher grafting density; however, the actual M_n of each grafted polymer could not be determined and therefore it was not possible to determine the grafting density. The polymer wt% in the final product was higher than the products obtained via *grafting to*, ranging from 18%-28%.

The CO₂-responsiveness of these materials obtained via grafting to and grafting from was evaluated. In every case, it was observed that the ζ-potential of the polymer-modified CNC products changed as the pH changed. However, for the materials obtained via grafting to, the CO₂-responsiveness was surprisingly contrary to what was expected; aggregation or increased turbidity was observed under CO₂ (lower pH), and when CO₂ was removed by N₂ sparging (higher pH), the materials were re-dispersed, potentially due to the little amount of amine groups. The materials obtained via grafting from possess considerably more amine groups and are more basic, and therefore they produced stable dispersions under CO₂, and aggregated under N₂. In

general, it was observed that the properties of the final products could be readily tailored by adjusting the molecular weight of the grafts and/or the grafting density.^[52]

4 APPLICATIONS OF POLYMER MODIFIED POLYSACCHARIDES

We have successfully developed applications with two of our polymer-modified chitosan materials in the wastewater treatment area.^[39,40] Chitosan itself can capture either heavy metals or organic contaminants from wastewater. Based on this, we developed two polymer-modified chitosan materials that could enhance the properties of native chitosan. Chitosan modified with PDEAEMA (CTS-g-GMA-PDEAEMA) and chitosan modified with PPEGMA (CTS-g-GMA-PPEGMA), both synthesized as mentioned above, were used for the removal of nickel (Ni(II))^[40] and organic dye RO16, respectively, from water.^[39] In the case of CTS-g-GMA-PDEAEMA, the amine group of chitosan and of PDEAEMA act as the capture sites for the heavy metal following an ion-exchange process. The PDEAEMA chains add CO₂-responsiveness to the material; as such, CO₂ was used as a Ni(II) desorbing agent (or modified chitosan regenerating agent) rather than a liquid acid as is commonly used. We found that the capacity of the CTS-g-GMA-PDEAEMA was lower than native chitosan in its first use, but then after regeneration the adsorption capacity of CTS-g-GMA-PDEAEMA was improved considerably, likely because, when it was regenerated, the amine functionality became a quaternary amine, which made it a stronger base and more reactive for the ion-exchange process. CO₂ is an interesting option since it is a greener alternative to acid for these applications.^[40] Overall, the Ni(II) recovery was ~60% which is comparable to previous studies.^[40] These were initial and promising investigations and demonstrate that chitosan modified with CO₂-responsive polymers present a future greener alternative for removal of dissolved metals from water.^[40] CTS-g-GMA-PPEGMA was tested for the removal of the dye RO16.^[39] Contamination of water with synthetic dyes (or textile dyes) represents an important concern given their detrimental impacts on the environment and human health. In our study, we compared the adsorption capacity of CTS-g-GMA-g-PPEGMA with chitosan, 50/50 chitosan-PPEGMA, and PPEGMA. CTS-g-GMA-PPEGMA exhibited enhanced adsorption efficiency of RO16, over 33% higher. The physical mixture exhibited lower adsorption capacity and PPEGMA itself does not exhibit adsorption capacity. This demonstrated that the chemical binding of PPEGMA to chitosan provides an improvement on the native chitosan properties.^[39]

The use of XCTS-CPS-g-P4VP beads in wastewater treatment was also investigated. In this case, the adsorption of bisphenol (BPA) from water was studied.^[42] BPA presents significant hazards to human health and it has been used in the plastic industry and had been found in water for food for human consumption; therefore, its removal from water can be of significant importance. By adsorption kinetics studies, it was observed that modified XCTS-CPS-g-P4VP performed considerably better than native chitosan, especially the chitosan modified with larger P4VP chains. XCTS-CPS-g-P4VP maintained its ability after being cycled 7 times with 61%–62% of the initial adsorption retained after the seventh cycle.^[42] Modified chitosan with phosphorous groups also may be a promising candidate for applications in wastewater treatment, anticorrosion of coatings, or as flame retardancy material.^[41]

Our research group has also investigated applications for the modified CNC. CNC modified with PDEAEMA and PDMAPMAM produced via NMP and grafting to approach, was also used as Pickering emulsifier for the preparation of oil-in-water emulsions. It was observed that with a concentration of ≥ 0.35 wt% of the emulsifier, the shelf-life of the emulsions was about one month. The advantage of using these products was that the CO₂ and N₂ could be used to stabilize and destabilize the emulsions, respectively.^[53] The same materials were used as Pickering emulsifiers for the suspension polymerization of styrene and compared with native CNC. It was found that native CNC produced polymer particles of 5-9 μm , whereas the modified CNC produced larger particles in the range of 18-20 μm using oil-soluble radical initiators. In all cases, low monomer conversion was obtained; however, the solubility of the initiator has an important effect on the particle. Further experiments are necessary to understand the mechanism of nucleation in this polymerization process.^[54] We have developed applications with CNC modified with CO₂-responsive groups. In this case, CNC modified with 1-(3-aminopropyl)imidazole (APIm) capable of coagulating under N₂/water and redispersing under CO₂/water atmospheres was used.^[55] This can be advantageous since the APIm-modified CNC can harvest microalgae and actually be re-used by just switching atmospheres between CO₂ and N₂. Recovering and concentrating microalgae could be feasible for the production of bio-fuel (after anaerobic digestion, hydrothermal liquefaction, etc.), which represents a potential use of the CO₂-responsive CNC.^[56]

5 PRESENT AND FUTURE OUTLOOK

During the last decade, we have developed new procedures and modification techniques oriented towards the development of new and advanced chitosan and CNC-based materials using RDRP. The efforts were focused on improving the existing properties of these two natural polymers in order to find new applications or to expand their use in different fields. These techniques and procedures could potentially be applied to other polysaccharides such as starch, dextran, chitin, or other nanoparticles. It is important to highlight that NMP is a RDRP technique less commonly used since it is believed to be limited to specific monomers. However, we have demonstrated that a broad variety of functional monomers can be polymerized with the advantages of ease of use, robustness to impurities, and no requirement for post-reaction purification.

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Figure Captions

FIGURE 1 Structure of (a) chitosan (partially deacetylated) and (b) cellulose nanocrystals (CNC) produced via sulfuric acid hydrolysis

SCHEME 1 Mechanism of nitroxide-mediated polymerization (NMP)

SCHEME 2 General mechanism of atom transfer radical polymerization (ATRP)

SCHEME 3 General mechanism of reversible addition–fragmentation chain transfer polymerization (RAFT)

SCHEME 4 Synthesis scheme of the CTS-SDBS-g-GMA functionalization with (a) TIPNO alkoxyamine and (b) BB and subsequent graft polymerization reactions^[35]

SCHEME 5 Synthesis scheme of the PEGylation of chitosan via nitroxide-mediated polymerization (NMP) and grafting to and grafting from approaches^[36]

SCHEME 6 Synthesis scheme of the chitosan modification with graft (co)polymers copolymer via nitroxide-mediated polymerization (NMP) and grafting to approach^[30]

SCHEME 7 Grafting to mechanism of between a chain-end radical of a polymer chain and a double bond of CTS-SDBS-g-GMA^[30]

SCHEME 8 Synthesis scheme of the modification of chitosan with poly(diethylaminoethyl methacrylate) (PDEAEMA) via nitroxide-mediated polymerization (NMP) and grafting to approach^[40]

SCHEME 9 Synthesis scheme for the modification via grafting to and the grafting from of CTS with PMAPC1 and hPMAPC1 phosphonated polymers^[41]

SCHEME 10 Synthesis scheme to obtain functionalized chitosan (CTS-CPA), grafting from polymerization reactions of 4VP (CTS-CPA-g-P4VP), and crosslinking of the beads (XCTS-CPA-g-P4VP)^[42]

SCHEME 11 Synthesis scheme of the modification of cellulose nanocrystals (CNC) with α -bromoisobutyric acid (BIBA) and subsequent grafting polymerization of methacrylate (MA)

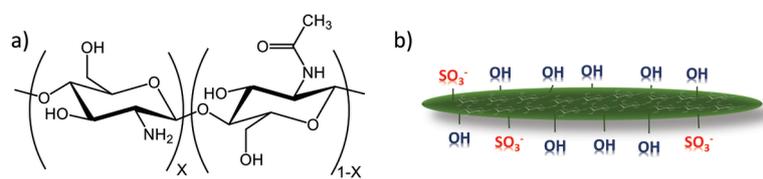
SCHEME 12 Synthesis scheme of the modification of cellulose nanocrystals (CNC) with BlocBuilder and subsequent grafting polymerizations of methyl methacrylate (MMA) and methacrylate (MA)^[47]

SCHEME 13 Synthesis scheme of the modification of cellulose nanocrystals (CNC) with BlocBuilder and subsequent grafting polymerizations of CO₂-responsive polymers^[48]

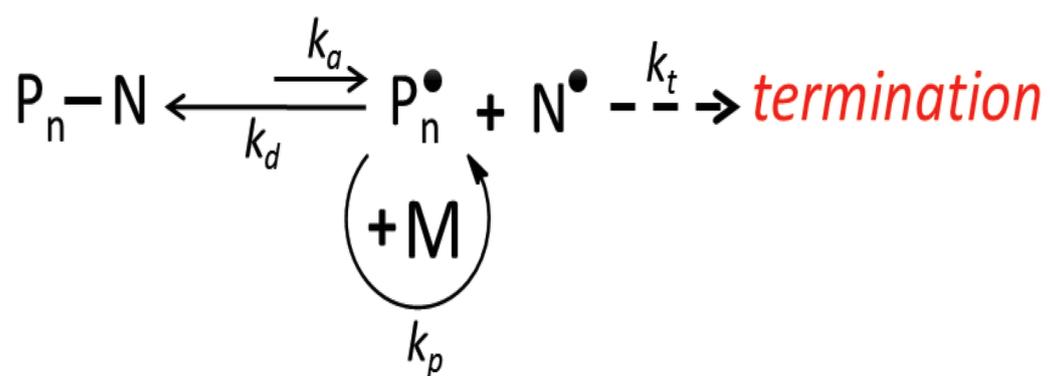
SCHEME 14 Synthesis scheme of the modification of cellulose nanocrystals (CNC) with α -bromoisobutyric acid (BIBA) and subsequent grafting polymerizations of CO₂-responsive polymers via atom transfer radical polymerization (ATRP)^[49]

SCHEME 15 Synthesis scheme of the modification of cellulose nanocrystals (CNC) via nitroxide-mediated polymerization (NMP) and grafting to approach^[50]

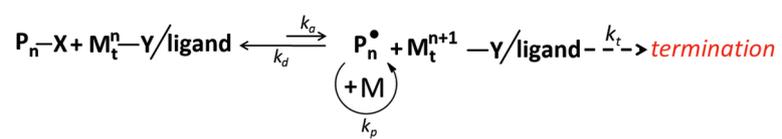
SCHEME 16 Cellulose nanocrystals (CNC) modification via reversible addition–fragmentation chain transfer polymerization (RAFT) using grafting from and grafting to approaches^[52]



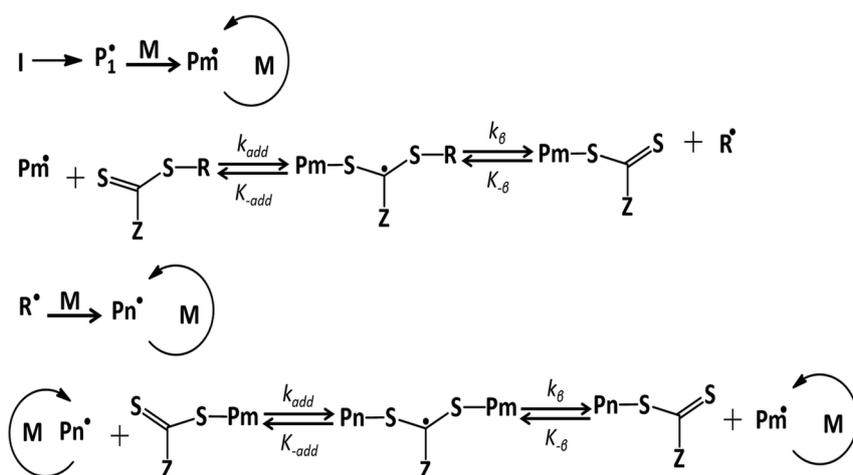
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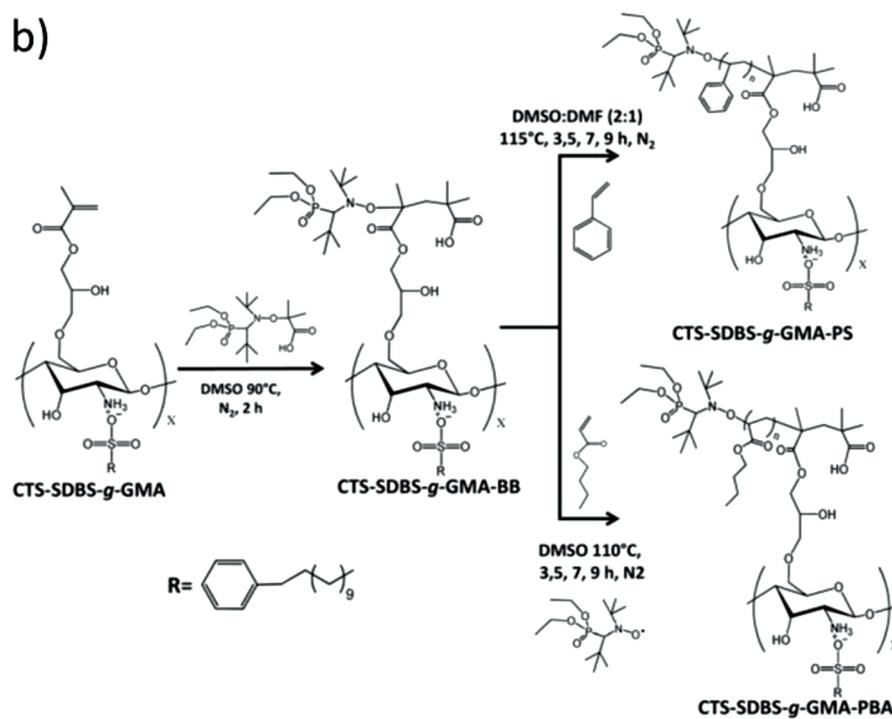
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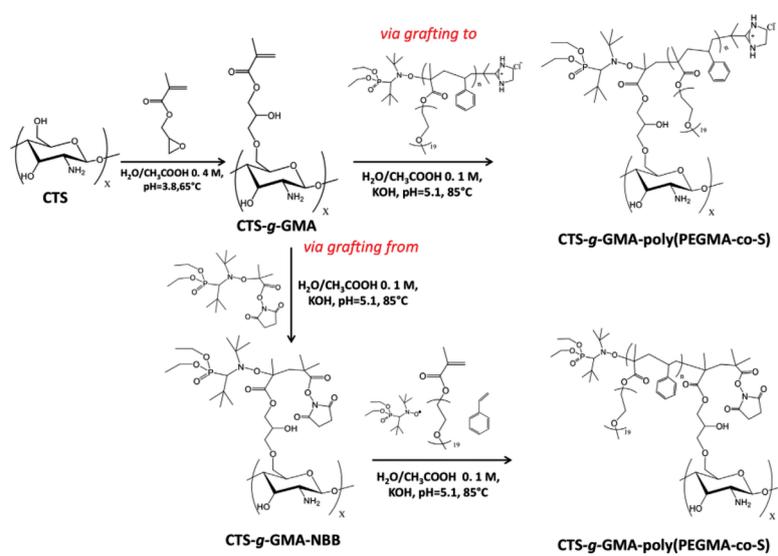
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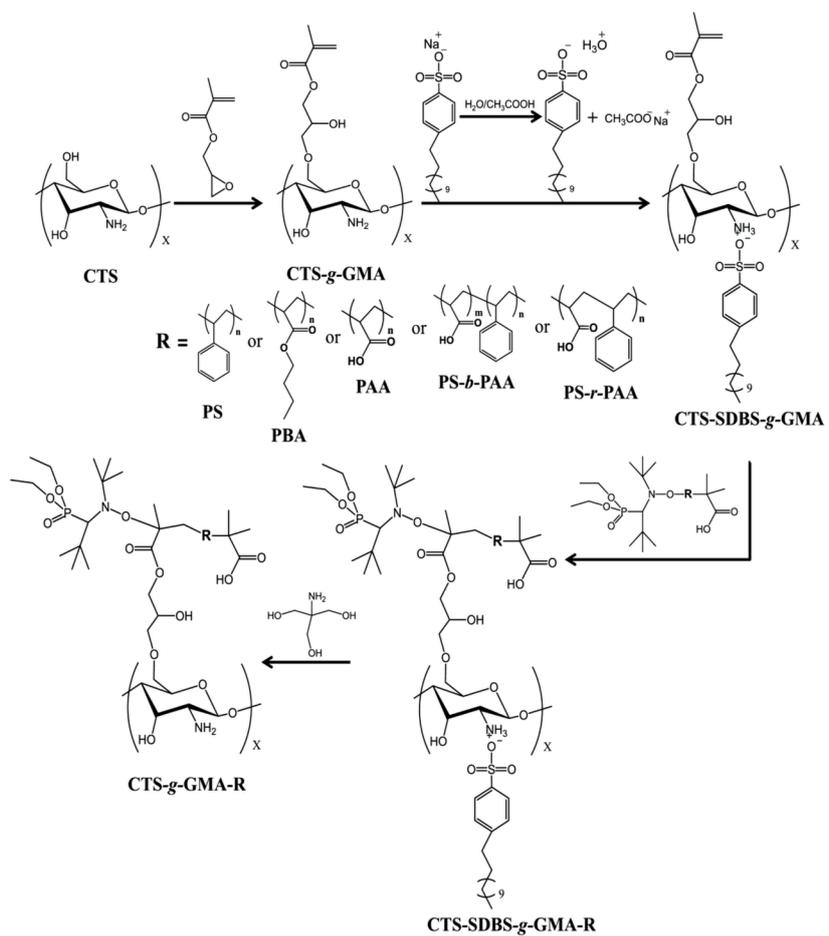
CJCE_24156_Scheme 3.tif



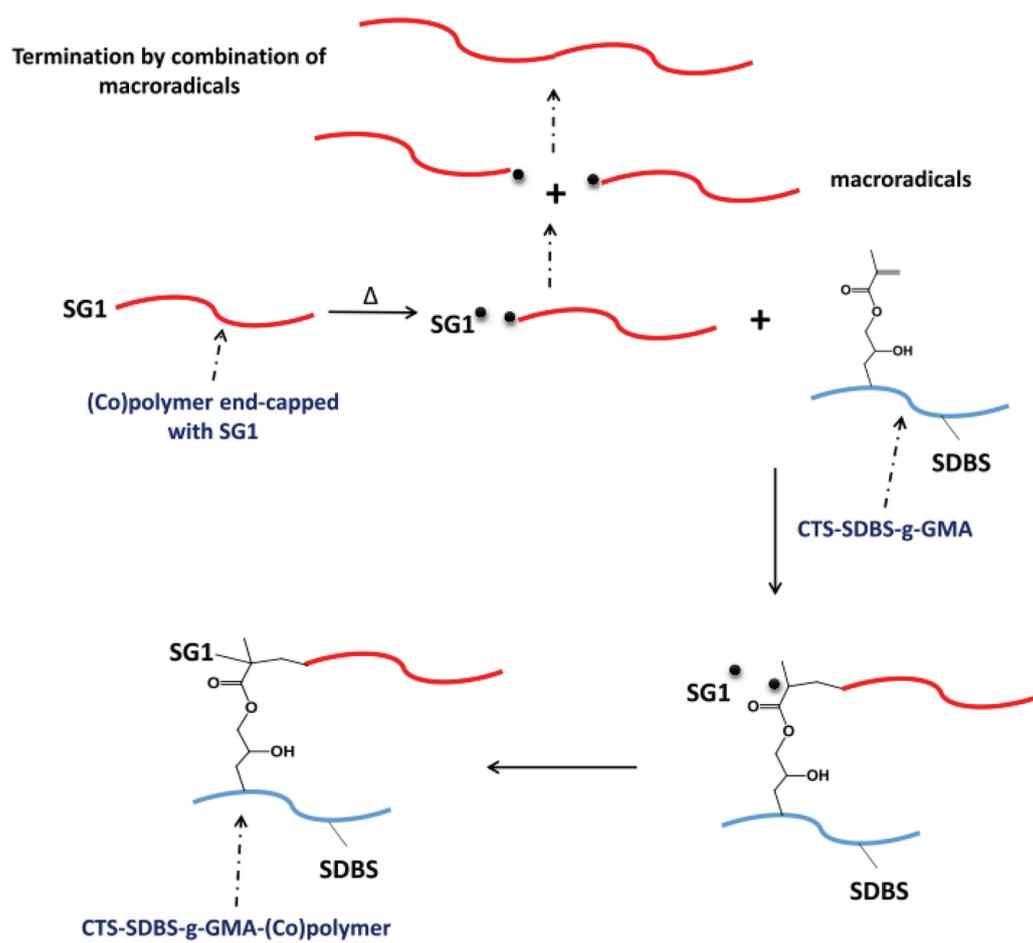
CJCE_24156_Scheme 4b.tif



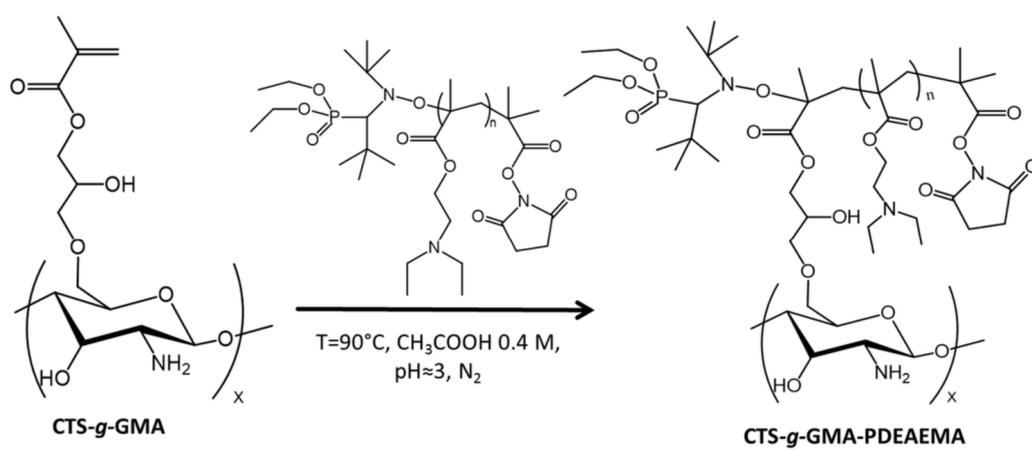
CJCE_24156_Scheme 5.tif



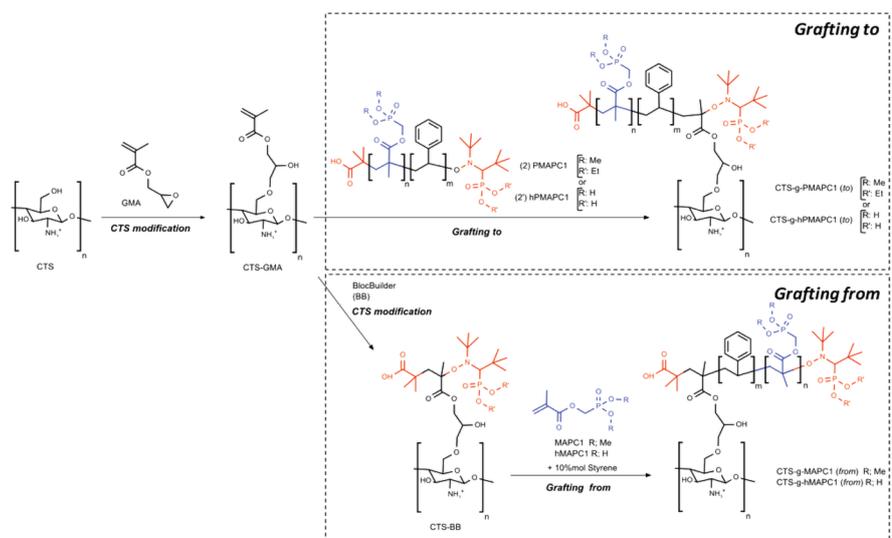
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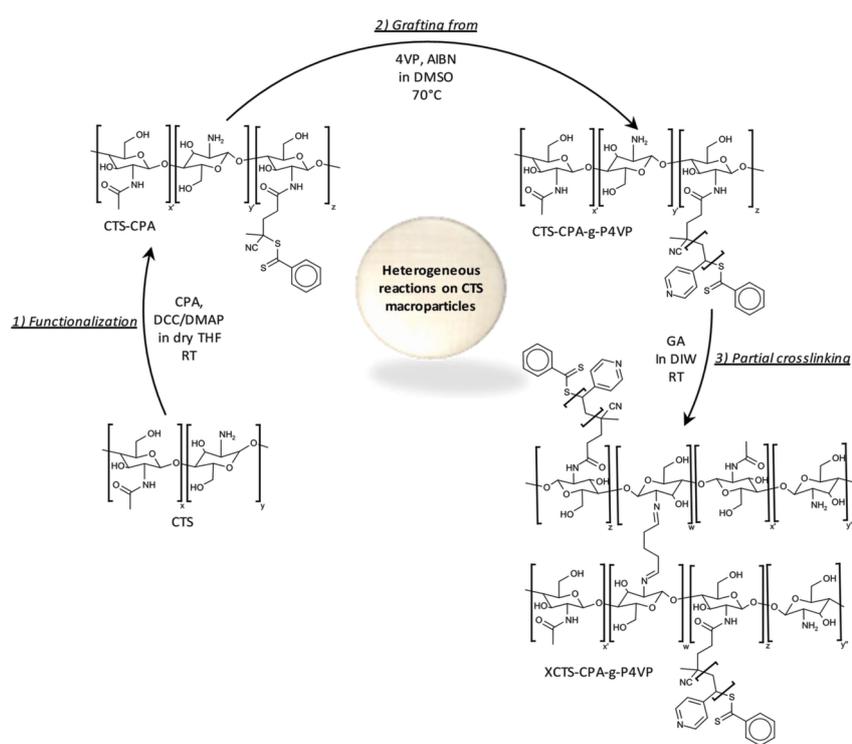
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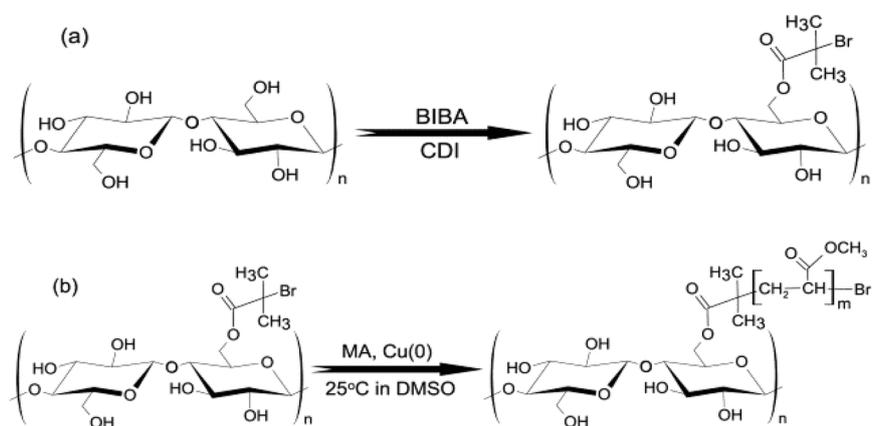
CJCE_24156_Scheme 8.tif



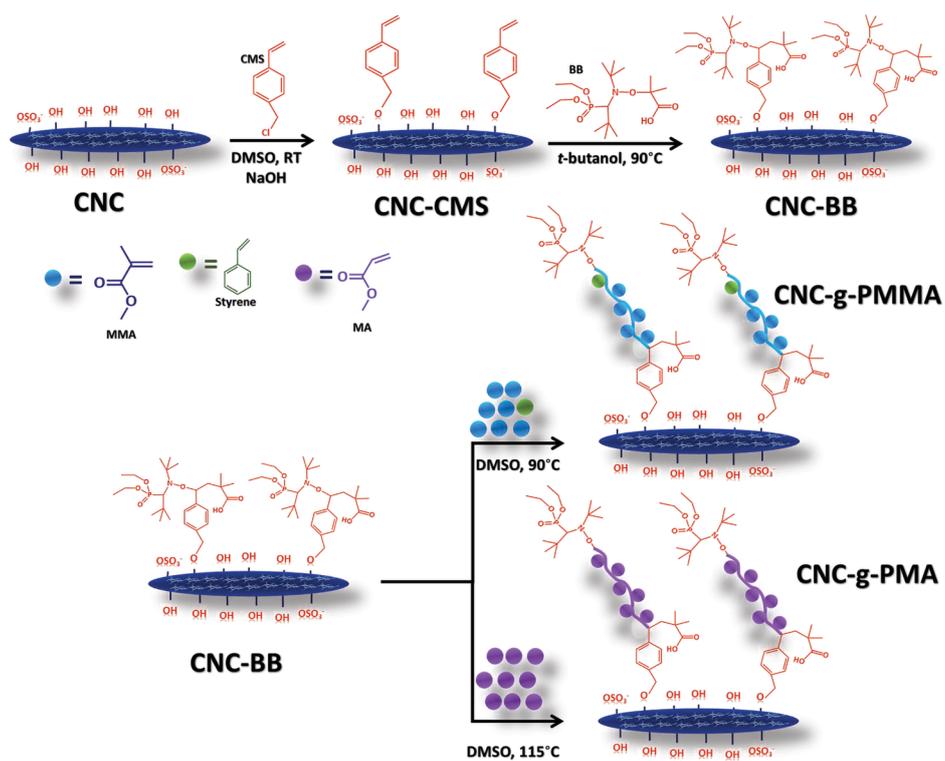
CJCE_24156_Scheme 9.tif



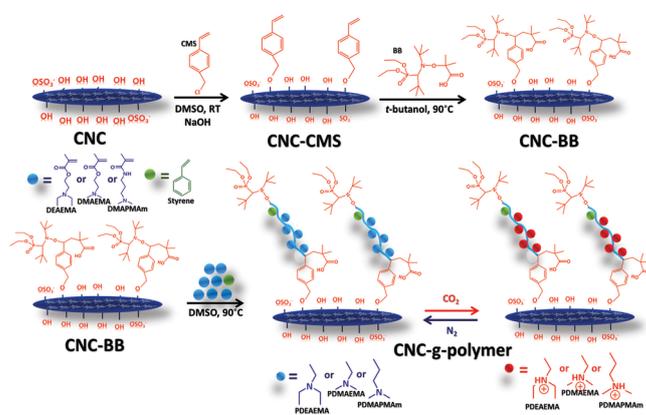
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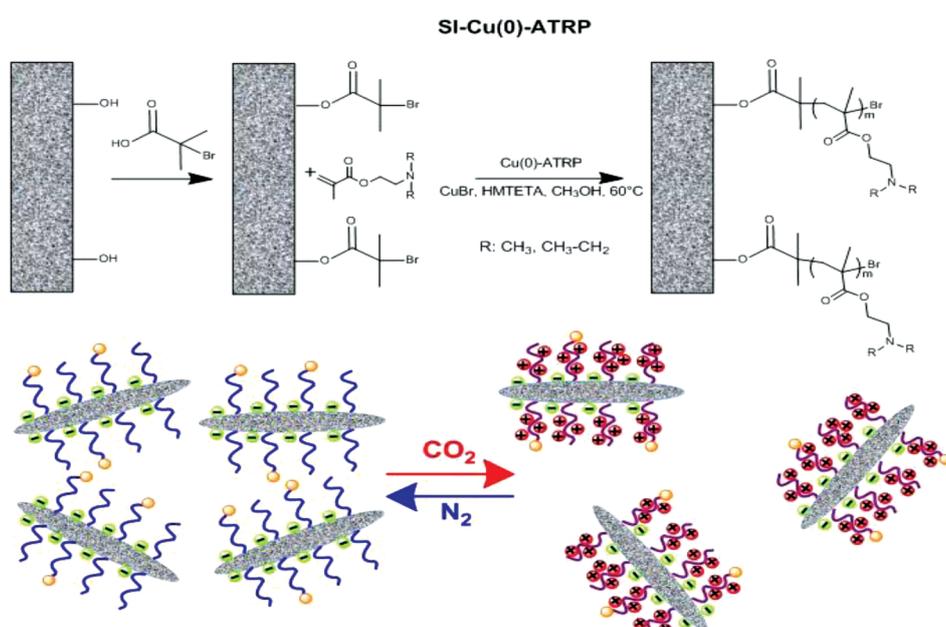
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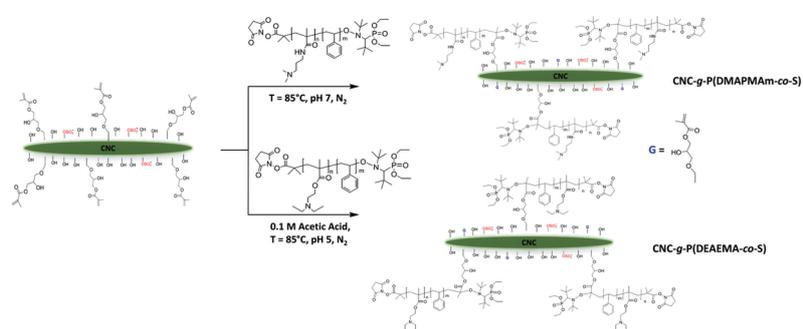
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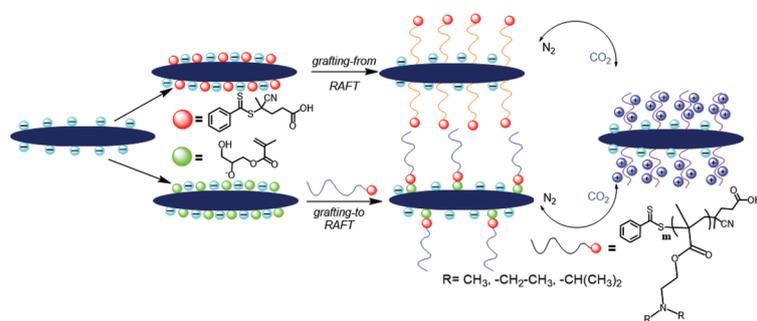
CJCE_24156_Scheme 13.tif



CJCE_24156_Scheme 14.tif



CJCE_24156_Scheme 15.tif



CJCE_24156_Scheme 16.tif