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Feature article

Graft modification of cellulose: Methods, properties and applications

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ABSTRACT

In this feature article, the recent progresses in the synthesis of cellulose graft copolymers with well-defined architecture were reviewed. The graft modification of cellulose using living/controlled polymerization methods was summarized. The properties of the cellulose graft copolymers can be adjusted by the cellulosic backbones and the chemical structure, graft density and length of the side chains. The stimuli-responsive properties of cellulose graft polymers are summarized and the stimuli-induced assemblies of cellulose graft copolymers can be used as carriers for drug and gene delivery. The graft modified cellulose materials can be applied in varies fields, including smart materials, adsorbents, and antibacterial materials and protein adsorption resistant materials.

1. Introduction

Cellulose is the most abundant, renewable, biodegradable natural polymer resource on earth. The discovery of cellulose goes back to 1838, when cellulose was first discovered and isolated by Anselme Payen. Cellulose have been extensively studied [1], including its biosynthesis [2,3], structure analysis [4–10], chemical modification [11], regeneration of cellulosic materials [12–14], applications in various fields [15,16]. Cellulose is one of the key research subjects during the foundation of polymer science. The enthusiasm on the research of cellulose had once been lost with the renaissance fossil resourced polymeric materials. However, the environmental problems and the exhausting fossil resources made the interests in the researches of cellulose recover. Cellulose has been well overviewed by Klemm et al. [17]. The recent progresses on new cellulose solvents for preparation of regenerated cellulose materials [12,18–21], cellulose functional materials [22–24], nanocellulose [25–29], and surface modification of cellulosic materials [30–32] have been reviewed. In this review, the recent progresses on the synthesis and applications of cellulose graft copolymers are focused.

Cellulose is a polysaccharide and its molecular weight depends on its sources as well as the extraction conditions for the purification. The molecular chain is composed of β-1,4-linked anhydro-D-glucose units in which every unit is corkscrewed 180° with respect to its neighbors, and the repeat segment is frequently taken to be a dimer of glucose, known as cellobiose (Scheme 1) [27]. Cellulose is highly crystalline and generally insoluble, due to the intramolecular hydrogen bond networks extending from the O(3′)-H hydroxyl to the O(5) ring oxygen of the next unit across the glycosidic linkage and from the O(2)-H hydroxyl to the O(6′) hydroxyl of the next residue. Nowadays the main uses of cellulose are for papers or cardboards, membranes, tissues, explosives, textiles and construction materials. An extensive scope of applications of cellulose is limited for insoluble in common solvents and by the lack of properties inherent to synthetic polymers. Significant efforts have been paid to the chemical modification of cellulose [11] to improve resistance to heat or abrasion [33–35], mechanical strength [36,37], water or oil repellency [38–40], or antibacterial activity [41]. One convenient route introducing new chemical and physical properties to cellulose is the graft modification.

Three approaches are generally used for synthesis graft copolymers (Scheme 2). “Grafting onto” involves the reaction between functional groups on two different polymers. “Grafting from” involves a polymer with functional groups (macro-initiator) that initiates the polymerization of vinyl monomers. “Grafting through” involves (co)polymerization of macromonomer(s) [42]. In

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Abbreviations

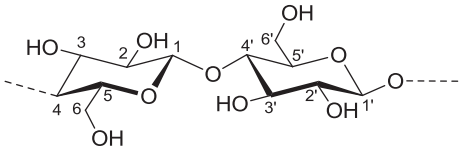
AAm acrylamide;
AA(-Na) acrylic acid (sodium);
AcM acrylomorpholine;
ACPA 4,4′-azobis(4-cyanopentanoic acid);
AEDA 2-acryloyloxyethyl dehydroabieticcarboxylate;
AEM 2-aminoethylmethacrylate hydrochloride;
AEMA 2-aminoethylmethacrylamide hydrochloride;
AEFC 2-acryloyloxyethyl ferrocenecarboxylate;
AHDA acryloyloxyhexyl dehydroabieticcarboxylate;
AIBN azobisisobutyronitrile;
AMIMCl 1-allyl-3-methylimidazolium chloride;
ARGET activators regenerated by electron transfer;
AsAc ascorbic acid;
ATRP atom transfer radical polymerization;
(*t*)BA (*tert*-)butyl acrylate;
bis-MPA 2,2-bis(methylol)-propionic acid;
BMA butyl methacrylate;
BMIMCl 1-butyl-3-methylimidazolium chloride;
BPDF benzyl pyridine-2-yldithioformiate;
BPy bipyridine;
BrIB 2-bromoisobutyryl bromide;
BSPA 3-benzylsulfanylthiocarbonylsufanylpropionic acid chloride;
BSPAC 3-benzylsulfanylthiocarbonylsulfanyl-propionic acid;
CA cellulose acetate;
CDA cellulose diacetate;
CNCs cellulose nanocrystals;
CPDA cumyl phenyldithioacetate;
CPADB 4-cyanopentanoic acid dithiobenzoate;
CPDB 2-cyanoprop-2-yl dithiobenzoate;
CRPs controlled/living radical polymerizations;
CTAs chain transfer agents;
DCACl dichloroacetyl chloride;
DDMAT 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid;
DDMATC S-1-dodecyl-S'-(α,α'-dimethyl-α''-acetic acid) trithiocarbonate;
DEAEMA 2-(diethylamino)ethylmethacrylate;
DEGMA di(ethylene glycol)methyl ether methacrylate;
DMAAm *N*,*N*-Dimethylacrylamide;
DMAc dimethylacetamide;
DMAEMA 2-(*N*,*N*-dimethyl amino)ethyl methacrylate;
DMF *N*,*N*-dimethylformamide;
DMMSA 2-(methacryloyloxy ethyl)ethyl-dimethyl-(3-sulfopropyl)-ammonium;
DMVSA *N*,*N*-dimethyl-*N*-(*p*-vinylbenzyl)-*N*-(3-sulfopropyl) ammonium;
dnBpy 4,4′-dnonyl-2,2′-bipyridine;
DPE 1,2-dipiperidinoethane;
DMSO dimethyl sulfoxide;
EA ethyl acrylate;
EBiB ethyl 2-bromoisobutyrate;
EBP ethyl 2-bromopropionate;
EC ethyl cellulose;
ECPDB 2-(ethoxycarbonyl) prop-2-yl dithiobenzoate;
EC-*g*-PAA ethyl cellulose-*graft*-poly(acrylic acid);
EC-*g*-PDEAEMA ethyl cellulose-*graft*-poly[2-(diethylamino) ethylmethacrylate];
EC-*g*-PHEMA ethyl cellulose-*graft*-poly(2-hydroxyethyl methacrylate);
EC-*g*-P(PEGMA) ethyl cellulose-*graft*-poly[poly(ethylene glycol) methyl ether methacrylate];
EC-*g*-PS ethyl cellulose-*graft*-polystyrene;
EDTA ethylenedinitrilo tetraacetic acid solution;
EECX *O*-ethyl *S*-(1-ethoxycarbonylethyl) xanthate;
EHEC ethyl hydroxyethyl cellulose;
EMO 3-ethyl-3-methacryloyl oxymethyloxetane;
GMA glycidyl methacrylate;
HEC hydroxyethyl cellulose;
HEC-*g*-PAA hydroxyethyl cellulose-*graft*-poly(acrylic acid);
HEMA 2-hydroxyethyl methacrylate;
HiPC hydroxyisopropyl cellulose;
HMA hostasol methacrylate;
HMTA hexamethylenetetramine;
HMTETA 1,1,4,7,10,10-hexamethyl-triethylenetetramine;
HPC hydroxyl propylcellulose;
HPC-*g*-PDMAEMA hydroxyl propylcellulose-*graft*-poly[2-(*N*,*N*-dimethyl amino)ethyl methacrylate];
HPC-*g*-P4VP hydroxyl propylcellulose-*graft*-poly(4-vinylpyridine);
IBA isobornyl acrylate;
MA methyl acrylate;
MADIX macromolecular design *via* interchange of xanthate;
MAEDA 2-methacryloyloxyethyl dehydroabieticcarboxylate;
MAHDA methacryloyloxy-hexyl dehydroabieticcarboxylate;
MAm methacrylamide;
MC methyl cellulose
MCC microcrystalline cellulose
MCPDB *S*-methoxycarbonylphenylmethyl dithiobenzoate;
MCPMT *S*-methoxycarbonylphenylmethyl methyltrithiocarbonate;
Me_4Cyclam 1,4,8,11-tetraazacyclotetradecane;
MeDMA 2-(methacryloyloxy) ethyl-trimethylammoniumchloride;
Me_6TREN tris[2-(dimethylamino)ethyl]amine;
MMA methyl methacrylate;
MMAzo 6-[4-(4-methoxy phenylazo)phenoxy]hexyl methacrylate;
MP *N*-methylpyrrolidone;
MPC 2-methacryloyloxyethyl phosphorylcholine;
NaAsc sodium ascorbate;
NASS sodium 4-styrenesulfonate;
NIPAAm *N*-isopropylacrylamide;
NMP nitroxide-mediated polymerization;
11OCB-MA 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate;
OEGMA oligo(ethylene glycol)methyl ether methacrylate;
PAA poly(acrylic acid);
P(AA-Na) poly(acrylic acid sodium);
PABTC propionic acidyl butyl trithiocarbonate;
PBMA poly(butyl methacrylate);
PBS poly(butylenes succinate);
PBuA poly(butyl acrylate);
PCL polycaprolactone;
PDEGMA poly[di(ethylene glycol) methyl ether methacrylate];
PDMAAm poly(*N*,*N*-dimethylacrylamide);
PDMAEMA poly[2-(*N*,*N*-dimethylamino)ethyl methacrylate];
PDMMSA poly[2-(methacryloyloxyethyl) ethyl-dimethyl-(3-sulfopropyl)-ammonium];
PEG poly(ethylene glycol);
PEGMA poly(ethylene glycol)methyl ether methacrylate;
PETA pentaerythritol triacrylate;
PGMA poly(glydicyl methacrylate);
PHEMA poly(2-hydroxyethyl methacrylate);
PLLA poly(L-lactic acid);
PMDETA *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine;

P(MEO_2MA-*co*-OEGMA) poly[2-(2-methoxyethoxy)ethyl methacrylate-*co*-oligo(ethylene glycol) methacrylate];
PMMA poly(methyl methacrylate);
PMMAZO poly[6-[4-(4-methoxyphenylazo)phenoxy] hexyl methacrylate]
POEGMA poly[oligo(ethylene glycol)methyl ether methacrylate];
PMA-*b*-PHEMA poly(methyl acrylate)-*block*-poly(2-hydroxyethyl methacrylate);
PPEGMA poly[poly(ethylene glycol) methyl ether methacrylate];
PPETA poly(pentaerythritol triacrylate);
PS polystyrene;
P*t*BA poly (*tert*-butyl acrylate);
P4VP poly(4-vinylpyridine);
P4VP-*b*-PNIPAAm poly(4-vinylpyridine)-*block*-poly(*N*-isopropylacrylamide);
RAFT reversible addition-fragmentation chaintransfer;
RC regenerated cellulose
ROP ring-opening polymerization;
R.T. room temperature;
SARA supplementary activator and reducing agent;
SET-LRP single electron transfer-living radical polymerization;
SG1 acyclic β-phosphorylated nitroxide *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethyl propyl)-*N*-oxyl;
SI-ATRP surface-initiated atom transfer radical polymerization;
SS sodium 4-styrenesulfonate;
St styrene;
SMP 3-sulfopropyl methacrylatepotassium salt;
TEMED *N,N,N′,N′*-tetramethylethylenediamine;
TEMPO 2,2,6,6-tetramethyl-1-piperidinyloxy;
TFEMA 2,2,2-trifluoroethyl methacrylate;
THF tetrahydrofuran;
TPMA tris(2-pyridylmethyl)amine;
VAc vinyl acetate;
VBC 4-vinylbenzyl chloride;
VBTAC (arvinylbenzyl)trimethylammonium chloride
4VP 4-vinylpyridine.

the case of synthesis of cellulose graft copolymers, "grafting onto" and "grafting from" approaches are generally used. The "grafting onto" approach generally has low reaction efficiency due to the low activity of macromolecular reactions [43]. Therefore, "grafting from" is a more expected synthetic approach. In "grafting from" approach, reactive sites along the main chain can be simply created by chemical treatment or irradiation followed by addition of monomer to generate graft copolymer.

"Grafting from" approach in the synthesis of cellulose graft copolymers has been extensively investigated, involving the growth of polymer grafts directly from the cellulose backbone in a conventional free radical polymerization process. Radicals can be conveniently generated along cellulose backbones in the presence of chemical initiators [44–46] or by applying irradiation [47,48]. However, this grafting is always accompanied with the formation of homopolymer, uncontrolled graft density as well as molecular parameters of the grafts, degradation of cellulose backbone and impossible generation of block copolymer grafts, which limits the applications of the resultant cellulose graft copolymers. The above mentioned disadvantages of the traditional free radical graft copolymerization for preparing cellulose graft copolymers have been tried to overcome by using anionic and cationic controlled polymerization [49]. However, the specific strict reaction conditions of ionic polymerizations, as well as the tedious procedure, had not made ionic polymerization be widely accepted in both scientific and industrial aspects.

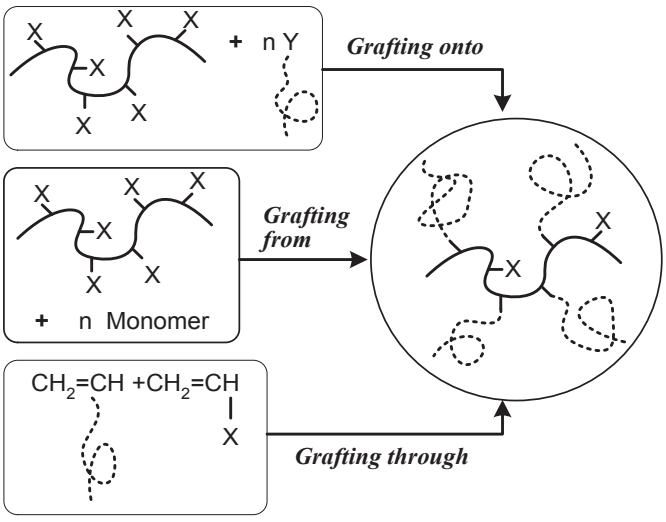
During the last two decades, CRPs techniques [50], such as ATRP [50–55], RAFT [56,57], or NMP [58], contained recently developed SET-LRP [59,60], have been erupted in polymer science for the synthesis of polymers with well-defined architectures. The above listed CRPs are tolerant to moisture and compatible with a large range of functional groups and have been applied for the synthesis of polymers with various architecture and chemical properties. Recently, IUPAC has recommended the denomination of reversible-deactivation radical polymerizations [61,62]. The inherent characteristics of the CRPs techniques include the reducing in the concentration of propagating radical chain ends in order to minimize the occurrence of irreversible termination reactions and the formation of 'dead' polymer chains, which is elegantly achieved by addition of species that ensure the reversible trapping of the 'active' propagating radical species as 'dormant' species through reversible termination or reversible transfer.



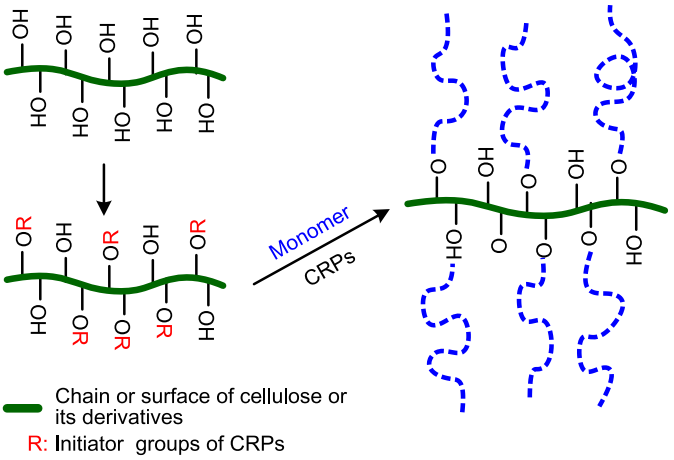
Scheme 1. Schematic representation of cellulose structure.

2. Living/controlled graft polymerizations of cellulose

Cellulose is a natural resource polymer with the molecular weight depending on its sources and purification conditions. The molecular weight distribution of cellulose is generally wider than that of synthetic polymers prepared by CRPs or anionic polymerization. Herein this review, the well-defined architecture of cellulose graft copolymers is referred to the side chains. Cellulose graft



Scheme 2. Methods for synthesis of graft copolymers.



Scheme 3. Grafting from approach for the graft modification of cellulose.

copolymers or surface graft modification of cellulosic materials can be prepared by using free radical polymerization, CRPs, and ROP. The application of traditional free radical polymerization for the graft modification of cellulose is well known and the ROP from cellulosic materials has been reviewed recently[31]. Carlmark [30,63] and Tizzotti et al. [64] also reviewed the development modification of cellulose fibers and polysaccharides through CRP, respectively. In this review, modification progresses of using CRPs on the cellulosic materials, composed of cellulose bulks, cellulose derivatives and natural materials contained cellulose composition, specifically on cellulose graft copolymers are focused in detail. Meanwhile, some promising applications of cellulose graft copolymers were also reviewed for further developing this strategy material. In synthesis cellulose graft copolymers using "grafting from" method via CRPs, active groups for CRPs initiation must be first linked onto the surface or chains of cellulose, which is generally achieved via esterification and etherification of hydroxyl groups on cellulose (Scheme 3).

2.1. ATRP of cellulose

ATRP is one of the most popular living/controlled polymerization since it was discovered in 1995 [52,65]. The general mechanism for ATRP [66–68] is that the radicals, or the active species, are generated through a reversible redox process complex (M_t^n–Y/Ligand, where Y may be another catalyzed by a transition metal ligand or the counterion) which undergoes one electron oxidation with concomitant abstraction of a (pseudo) halogen atom, X, from a dormant species, R–X. In ATRP, the initiators are usually compounds with halogen atoms that are activated by α-carbonyl, phenyl, vinyl or cyano groups. The reactivity of these initiators

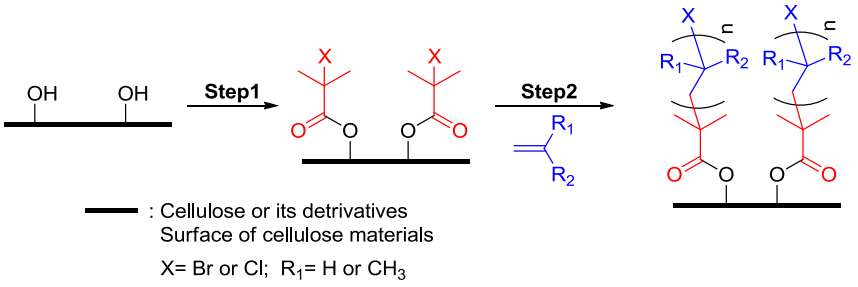
Table 1
Effects of the reactive conditions on the degree of substitution of bromoisobutyryl groups [73–75].

Cellulose derivatives	Solvent	Ratio of reactant[a]	Reaction time (h)	DS_{Br}[b]
CDA	THF	1:2	12	0.43
CDA	THF	1:2	24	0.506
CDA	THF	2:1	12	0.499
CDA	THF	2:1	24	0.508
EC	THF	1:5	48	0.0414
EC	THF	1:1	48	0.3689
EC	THF	1.5:1	48	0.4606
EC	THF	3:1	48	0.5159
EC	THF	6:1	120	0.5273
HPC	DMAc	0.5:1	12	0.10
HPC	DMAc	1:1	12	0.15
HPC	THF	0.5:1	12	0.21
HPC	THF	0.5:1	24	0.30

[a] Mole ratio of bromoisobutyl bromide to the hydroxyl groups on cellulose derivatives as indicated.
[b] Degree of substitution of bromoisobutyryl group estimated by ^{1}H-NMR.

depends on the bond dissociation energies of alkyl halide [69]. Several rules pertaining to initiator structure that govern activation rate constants have also emerged from recent studies about initiators [70]: (1) activity depends on the degree of initiator substitution (primary < secondary < tertiary), (2) on the leaving atom/group (for methyl 2-halopropionates: Cl < Br < I), and (3) on the radical stabilizing groups (−Ph ~ −C(O)OR << −CN).

In the case of synthesis of graft copolymers using ATRP, macroinitiators have been used by the preparation of various cellulose attached ATRP initiators via surface modification of cellulosic materials under heterogeneous condition or solution reaction under homogeneous condition (Scheme 4, step 1). The applications of ATRP for surface graft modification of cellulosic materials were first reported by Carlmark and Malmstom [71,72]. Meanwhile, the linkage of ATRP initiators onto the backbone of cellulose derivatives in homogeneous conditions has been carried out in our groups [73–75]. The reaction conditions and the substitution degree of the bromoisobutyryl groups of the cellulose based macro-initiators for ATRP are summarized in Table 1. In general, the increase in the molar ratio of 2-bromoisobutyryl bromide to the hydroxyl groups on cellulose derivatives or the extension of the reaction time corresponds to a higher degree of substitution of the bromoisobutyryl groups. Moreover, THF, in which many cellulose derivatives can be dissolved, is preferred to be used as the solvent. The degree of substitution of bromide groups is generally higher than using other solvent such as DMAc as the reaction media. The resultant cellulose–X (halide) initiator is commonly used in many graft polymerizations by ATRP (Scheme 4, step 2). The degree of the substitution of alkyl halide for the hydroxyl group determined the density of the branch chains of graft copolymers. Besides the single substitution of hydroxyl group with the alkyl halide groups, HPC linked bis-MPA dendron initiator for ATRP graft copolymerization was also reported [76].



Scheme 4. The formation process of graft copolymers on cellulose, cellulose derivatives, or the surface of cellulose materials by ATRP.

Table 2
Surface modification of cellulose materials by ATRP.

Start materials	Initiator[a]	Monomer	Catalyst	Solvent	Temp. (°C)	Refs.
Filter paper	−Br	MMA, St, GMA	$CuBr_2$/PMDETA/AsAc	Anisole	30,100,0	[96]
		*t*BA	$CuBr_2$/PMDETA/EBiB	Acetone	60	[97]
		GMA	CuCl/$CuBr_2$/PMDETA	Toluene	30	[98,99]
		MA	CuBr/Me_6TREN	Ethyl acetate	R.T.	[71,100]
		11OCB-MA	CuBr/PMDETA	Toluene	100	[32]
	−Br, −Cl	NIPAAm, 4VP, GMA	CuCl/$CuCl_2$/Me_6TREN	MeOH/H_2O	R.T.,30,50	[78]
			CuCl/$CuBr_2$/PMDETA	2-propanol, toluene		
Cotton	−Br	AA-Na	CuBr/$CuBr_2$/HMTETA,	DMF	45	[94]
		GMA	CuBr/$CuBr_2$/PMDETA	H_2O	30	
		EA	CuBr/$CuBr_2$/PMDETA	Anisole	90,100	[101]
		St		In bulk		
Cellulose fiber	−Br	MA, HEMA	CuBr/Me_6TREN, CuCl/$CuCl_2$/BPy	Ethyl acetate, H_2O	R.T.	[72]
		MeDMA	CuBr/BPy	H_2O	20,40,70	[102]
Ramie fiber	−Br	MMA	CuBr/$CuBr_2$/PMDETA/EBiB	THF	30	[103]
		DMAEMA	CuCl/1,10-phenanthroline	Acetone/H_2O	30	[104]
Bamboo fiber	−Br	PEGMA	CuBr/BPy	H_2O	30	[93]
Jute fiber	−Br	St	CuBr/PMDETA	Xylene	110	[95]
Lyocell fiber	−Br	MA	CuBr/Me_6TREN	Ethyl acetate	R.T.	[100]
Cellulose microfibril	−Br	BA	CuBr/BPy, CuBr/PMDETA	DMF, toluene	90	[79,80]
MCC	−Br	MA	CuBr/Me_6TREN	Ethyl acetate	R.T.	[100]
		isoprene	$CuBr_2$/Me_6TREN/Cu^0	DMF/dioxane	130	[105]
			$CuBr_2$/PMDETA/Cu^0			
			$CuBr_2$/BPy/Cu^0			
CNCs	−Br	St	CuBr/HMTETA	In bulk	110	[89]
		St	CuBr/PMDETA	Anisole	100	[90]
		AEM, AEMA	CuBr/PMDETA	H_2O/MeOH	–	[106]
		DMAEMA	CuBr/HMTETA	MeOH	55	[91]
		NIPAm	CuBr/PMDETA	MeOH/H_2O	R.T.	[107]
Cellulose	−Cl	St, MMA, MAm, AcM	CuBr/DPE	DMF	130	[77]
Cellulose membrane	−Br	AA	NaOH/NaCl/CuCl/bpy	H_2O	R.T.	[108]
		NIPAm	CuCl/bpy			
		PEGMA	CuCl/$CuCl_2$/bpy	H_2O	R.T.	[87]
		AA	NaOH/NaCl /CuCl/Me_4Cyclam	H_2O	R.T.	[109]
		DMAEMA	CuCl/BPy	DMSO	R.T.	[110]
		DMAEMA	$CuCl_2$/HMTEMA/AsAc	2-propanol	40	[111]
		NASS	CuBr/BPy	MeOH/H_2O	30	[112]
		MA	CuBr/Me_6TREN	Ethyl acetate	R.T.	[100]
		NIPAm, DEAEMA	CuBr/BPy/Cu^0	MeOH	40	[113]
		GMA	CuCl/BPy	2-propanol	40	[114]
		DMVSA, DMMSA, MPC	CuBr/BPy	MeOH/H_2O	R.T.	[82]
		DMAEMA	$CuBr_2$/PMDETA/AsAc	MeOH/H_2O	25	[115]
		AA	CuCl/BPy	H_2O	45	[84]
		GMA	CuBr/BPy	DMF, H_2O	R.T.	[85]
		DMVSA	CuBr/BPy	MeOH/H_2O	25	[81]
CA membrane	−Br	HEMA	$CuCl_2$/TPMA/AsAc	MeOH/H_2O	R.T.	[83]
Chitosan/CA blend membrane	−Br	SMP	CuBr/$CuBr_2$/BPy	MeOH/H_2O	R.T.	[86]
Wood pulp	−Br	EA	CuBr/Me_6TREN/EBP	Ethyl acetate	R.T.	[116]
Wood	−Br	MMA	$CuBr_2$/PMDETA/AsAc	Anisole	30	[117]

[a] −Br and −Cl are the initiating groups for ATRP that linked to the surface of cellulose materials.

The ATRP of different vinyl monomers were initiated by cellulose−X initiators and catalyzed with copper salts in the presence of various amine-type ligands. The details for the surface modification of cellulose materials and the synthesis of cellulose graft copolymers via ATRP are summarized in Table 2 and Table 3, respectively. In the synthesis of cellulose graft copolymers via ATRP, the formation of homopolymers can be effectively avoided due to that the anchored haloacyl groups are the only initiating sites in the system. In synthesis cellulosic graft materials via ATRP, both heterogeneous and homogeneous reaction media were used in literatures, depending on the solubility of cellulose−X initiators. The surface modification of cellulose materials, such as fibers, membranes or nanocrystals, via ATRP is generally carried out in heterogeneous media. The so called surface-initiated ATRP (SI-ATRP) is important for the preparation of materials with well controlled surface properties in the cases of biomaterials, microelectronics, and fiber composites. SI-ATRP provides a versatile technique for preparing graft surface functionalized materials with high-density graft chains with the controllable molecular weight and narrow molecular weight distribution. The reaction conditions are less stringent in comparison with living anionic/cationic polymerization. Since the first report of the surface modification of cellulose fibers (paper) via the ATRP graft copolymerization of MA by Carlmark et al. [71], various monomers, including St [77], MMA [77], 4VP, NIPAAm [78], BA [79,80], as well as liquid crystalline monomer [32], have been used for the graft surface modification of cellulosic materials using ATRP. The living/controlled features of ATRP allow the further polymerization via ATRP of other monomers initiated by the bromides at the chain ends, which allows modifying the surface of cellulosic materials by block copolymer with special properties. Typical examples are the surface modification of cellulosic materials with hydrophobic/hydrophilic copolymer PMA-*b*-PHEMA [72] and pH/thermal stimuli-responsive copolymer P4VP-*b*-PNIPAAm [78]. Some RC or CA membranes were modified on the surface using SI-ATRP [81–86]. Zwitterionic polymers were grafted from cellulose membrane using SI-ATRP for improving blood compatibility, resistance to

Table 3
Cellulose graft copolymers synthesized by ATRP.

Backbone	Initiator[a]	Monomer	Catalyst	Solvent	Temp. (°C)	Refs.
Cellulose	–Br	NIPAM	CuBr/PMDETA	DMF	R.T.	[118]
		DMAam	CuCl/PMDETA	DMSO	80	[119,120]
		*t*BA	CuBr/PMDETA	DMF	75	[121]
		DMAEMA	CuBr/PMDETA	DMF	60	[122]
		MMA, St	CuCl/BPy	DMF, butanone, DMF/H_2O, dioxane, butanone/toluene	40–110	[123]
		MPC	CuBr/BPy	DMSO/MeOH	40	[124]
	–Cl	MMA	CuBr/BPy	BMIMCl	90	[125]
		EMO, MMA	CuBr(CuCl)/TEMED	DMF	130, 70	[126]
		MMA	$CuBr_2$/TEMED/AsAc	DMAc	50–70	[127]
		NIPAm	CuCl/Me_6TREN	DMF/H_2O	80	[128]
CDA	–Br	MMA	CuBr/PMDETA	Dioxane	70	[73,129]
		MMA, BA, St	CuCl/$CuCl_2$/HMTETA CuCl/PMDETA	Dioxane, anisole	70,110	[130]
		MMA	CuBr/PMDETA	MP	70	[131]
	–Br, –Cl	MMA, BA, *t*BA	Cu/PMDETA, Cu/Me_6TREN	Dioxane, DMSO	60	[132]
		St, BA, MMA	CuCl/$CuCl_2$/HMTETA CuCl/PMDETA/Cu^0	Dioxane, acetone	110	[133]
HPC	–Br	OEGMA300, DEGMA	$CuBr_2$/BPy/AsAc	Anisole, MeOH	40	[134]
		*t*BA	CuBr/PMDETA	Chloroform	100	[135]
		DMAEMA	CuCl/HMTETA	MeOH/H_2O	60	[75]
		4VP	CuCl/Me_6-TREN	2-propanol	30	[136]
		AEFC	CuBr/PMDETA	DMF	35	[137]
		*t*BA	CuBr/$CuBr_2$/PMDETA	MeOH/H_2O	70	[138]
		MMA	CuBr/$CuBr_2$/PMDETA	Toluene	80	[76]
		*t*BA			70	
EC	–Br	St, MMA, *t*BA	CuBr/PMDETA	Toluene	70–110	[74,139,140]
		PEGMA	CuCl/dnBPy	Toluene	60	[141]
		DEAEMA	CuBr/BPy	DMF	20	[142]
		DMAEMA	CuBr/PMDETA	THF	60	[143]
		HEMA	CuCl/BPy	MeOH/cyclohexane	30	[144]
		MMAzo	CuBr/PMDETA	Anisole	85	[145]
		NIPAAm	CuBr/PMDETA	DMF	R.T.	[118]
		MAEDA, AEDA, AHDA, MAHDA	CuBr/PMDETA	THF	55	[146]

[a] –Br and –Cl are the initiating groups for ATRP that linked to the cellulose backbone.

nonspecific protein adsorption and platelet adhesion [81,82]. RC membranes graft modified by PAA are pH sensitive, by which the permeability of the membranes can be modulated by pH [84]. To remove boron in aqueous solution, grafting PGMA from a RC membrane and further introducing polyhydroxyl groups through ring-opening reactions with *N*-methylglucamine on the membrane [85]. PPEGMA was grafted from RC membrane by ATRP in order to control over water flux and improve antifouling properties, meanwhile in which the pore size of the membrane decreased with the PPEMA chain length [87]. CNCs are hydrolysis products of natural cellulose materials with rod-like shape [88], which are highly reactive and ready for surface functionalization. Through SI-ATRP, functional polymer chains, such as PS [89,90], PDMAEMA [91], and PMMAZO [92], have been used for surface modification of CNC to improve the poor dispersibility in common solvents, lack of thermo plasticity, and poor dimensional stability. Unfortunately, analysis of successful ATRP was not clearly demonstrated in any of their reports. Besides pure cellulose materials, some natural cellulose materials were also graft modified using SI-ATRP [93–95], such as cotton graft P(AA-Na) and PGMA for adsorption of Cu^{2+} and Pb^{2+} ions [94], bamboo fibers grafted PPEGMA for improving the mechanical properties of PBS [93], and jute fibers grafted PS to improve the compatibility with PS [95].

Recently, graft modification of native cellulose in homogeneous state have been achieved [122], which is due to the finding of ILs as the direct solvent for cellulose [147]. Generally, cellulose based macro-initiators for ATRP were first synthesized in ILs and then graft copolymerization can be performed in ILs [125] or normal organic solvents [122,123]. The classic cellulose solvent DMAc/LiCl was also used as the media for synthesis cellulose macro-initiators for ATRP in homogenous state [118,124,126,127].

Cellulose derivatives are widely applied in many fields due to their dissolution in commonly organic solvents. Functionalized cellulosic materials can be prepared via graft polymerization from cellulose derivatives. The remained hydroxyl groups in cellulose derivatives can be used to synthesize the macro-initiators of ATRP (Table 1). The cellulose graft copolymers synthesized via ATRP could be multiple functionalities, such as hydrophilic, hydrophobic, amphiphilic, environmental responsive or polyelectrolyte according to the side chains, such as PS [74], P(M)MA [129], PHEMA [144], P*t*BA(AA) [140], PPEGMA [141], PDMAEMA [75], P4VP [136]. Solvents are important for the controlled/living process for synthesis cellulose graft copolymers via ATRP. An idea solvent should dissolve the macro-initiators, monomers and catalysts [73,133,144]. It was previously reported that the catalysts became more active when the Cu^{II} state of the catalyst was better stabilized by the ligand [148,149]. In general, the activities of complexes with various ligands decrease in the following order: alkyl amine ≈ pyridine > alkyl imine > aryl imine > aryl amine. They also decrease as the number of nitrogens in the ligand decreases [149]. In the cellulose graft polymerizations through ATRP, ligands were selected mainly according to the polarity of monomers to be polymerized. The molecular weight and polydispersity of the side chains of cellulose graft copolymers, such as EC-*g*-PS and EC-*g*-PMMA, were determined through hydrolysis of the cellulose backbone. The molecular weight of the side chains of both PS and PMMA increased linearly with the monomer conversion and resulted narrow molecular weight distribution of the side chains [74,139].

Furthermore, combing ATRP with other polymerization method (e.g. "click" or ROP), cellulose graft copolymers with complex architectures, such as dual-, block-, or centipede-like graft [130,133,138,143,150–152] can be synthesized. Yuan et al. [152] have reported a novel amphiphilic EC brush polymers with mono and dual side chains of P(MEO_2MA-*co*-OEGMA) and PDMAEMA by the combination of ATRP and click chemistry. The molar ratio of P(MEO_2MA-*co*-OEGMA) and PDMAEMA was varied through changing the feed ratio of these polymers and the coupling efficiency of click chemistry is relatively high.

For maintaining a high polymerization rate, the catalyst concentrations in ATRP are traditionally greater than ppm [153], which limits the applications of the obtained polymers. With the aim to be "greener" procedures, a new generation of ATRP methods were developed, such as ARGET ATRP [154,155] and SARA ATRP [156,157]. In ARGET ATRP, a sufficient amount of reducing agent tin^{II} 2-ethylhexanoate [158] or ascorbic acid [159] was added to reduce the complex of Cu^{II}/L to the Cu^{I}/L state. The amount of copper used was significantly reduced in ARGET ATRP and the reaction can performed with limited amount of air [160]. Zerovalent metals (Cu, Fe, Zn, Mg, etc.) act as supplemental activators and reducing agents are generally used in SARA ATRP [161]. Redox reaction between reducing metal and the deactivator Cu^{II}/L, taking place at the surface of zerovalent metals, generates the activator Cu^{I}/L and the ions of a reducing metal. The activator diffuses away from the surface of the metal and triggers polymerization [50]. SARA ATRP works well in organic solutions and ensures good control over polymerization. Cellulose functional materials have been successfully synthesized by using ARGET and SARA ATRP [83,96,105,111,115,117,162].

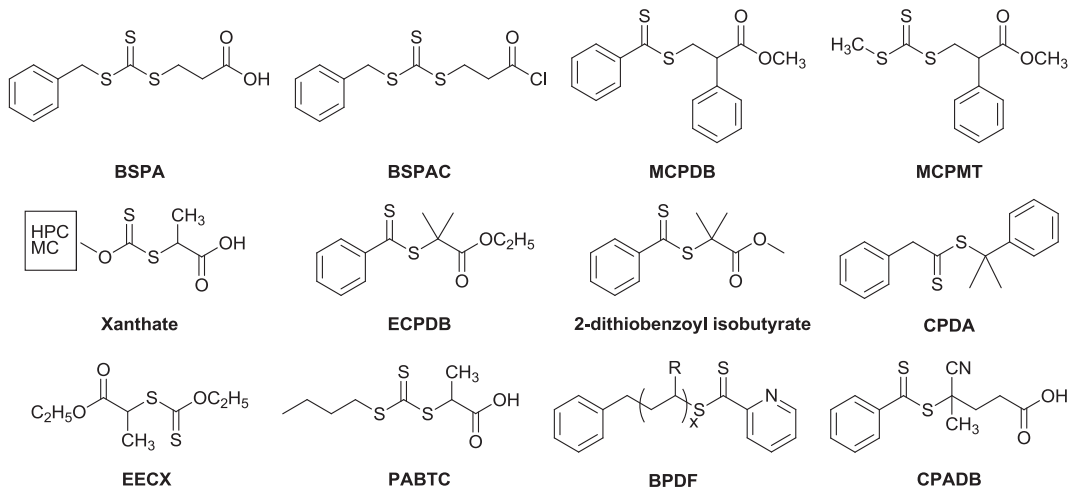
2.2. RAFT of cellulose

RAFT polymerization was first reported by Chiefari et al. [56] and was also reported as MADIX polymerization by Charmot et al. [163]. In both cases, a small amount of dithioester was introduced as CTA in the classic free radical system. RAFT agents are organic compounds that contains a thiocarbonylthio moiety. The **R** group initiates the growth of polymeric chains, while the **Z** group activates the thiocarbonyl bond toward radical addition and then stabilizes the resultant adduct radical. In RAFT mechanism, the propagating radical adds to the C=S moiety of the RAFT agent to form an intermediate radical that will either fragment back to the original propagating radical or to a new carbon-centered radical. The transfer of the CTA between growing radical chains (present at very low concentration) and dormant polymer chains (present at higher concentration) can effectively regulate the growth of the molecular weight and limit the termination reaction. Typical CTAs for RAFT polymerization contain a dithioester, dithiocarbonate, dithiocarbamate, or xanthate group [164–166], allow the control over molecular weight and molecular weight distribution. The CTAs that used for the synthesis cellulose graft copolymers by RAFT graft copolymerization are shown in Scheme 5. The details of the reaction parameters for the RAFT graft copolymerization of cellulose are listed in Table 4.

When using RAFT polymerization for the grafting monomer from cellulose backbone, the preliminary step is to attach the CTA groups onto cellulose. CTAs with carboxyl group are generally used for preparing cellulose-based CTA [191]. Depending on the location of carboxyl group, the CTAs can be attached via esterification to the polysaccharide backbone through fragmenting covalent bond (**R**–group) [192–194] or through non-fragmenting covalent bond (**Z**–group) [166,183–185,195,196], corresponding to the 'grafting from' and 'grafting onto' polymerization mechanisms, respectively.

In the **Z** approach, the cellulose backbone acts as the **Z**-group of the CTA. The growth of the grafts occurs at the nexus of the backbone and the grafts, and as a consequence as the grafts build up, static congestion around the thiocarbonyl thio functions, restricting the access of growing macro-radical to the C=S bonds, may induce a loss of control and low graft densities. Since Stenzel et al. [183] first reported the synthesis of HPC-*g*-PS using **Z** approach by RAFT, many graft polymerizations on different cellulose derivatives have proved this approach carry the broad polydispersity of molecular weight in branch chains [184–187].

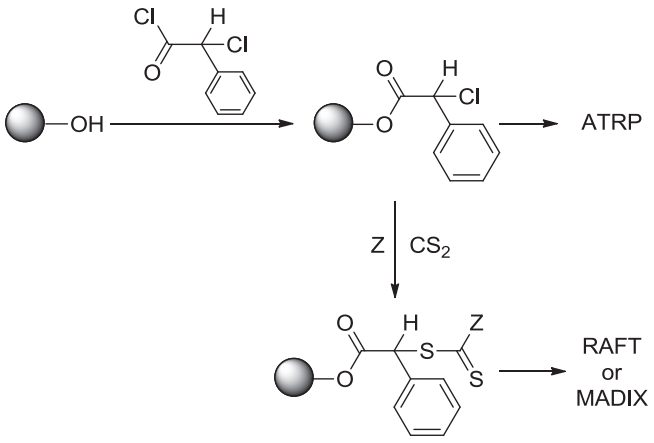
Using the **R**-group approach, the chains are grown directly from the cellulose backbone and the thiocarbonyl thio function can be found either attached to the end of the polymer grafts or attached to free chains in solution. The presence of the propagating species onto the cellulose backbones may also promote the generation of comb–comb coupled products from radical termination reactions via combination. **R** group have shown a high rate of propagation when polymerizing monomers by RAFT [175,197,198]. An important effect of the **R** group is its use to either introduce chain-end functionalities into polymers or design various polymeric architectures. The disadvantage of such CTAs is the tedious synthetic process. Perrier et al. [170,171,173,187] ever synthesized two CTAs with phenyl or methanethiol group, and they offered good control over the living polymerization of St, MA, DMA and MMA polymerization, by comparison to more classic RAFT agents such as cumyl



Scheme 5. Representative CTAs in RAFT of cellulose.

Table 4
The graft copolymerization conditions of cellulose by RAFT.

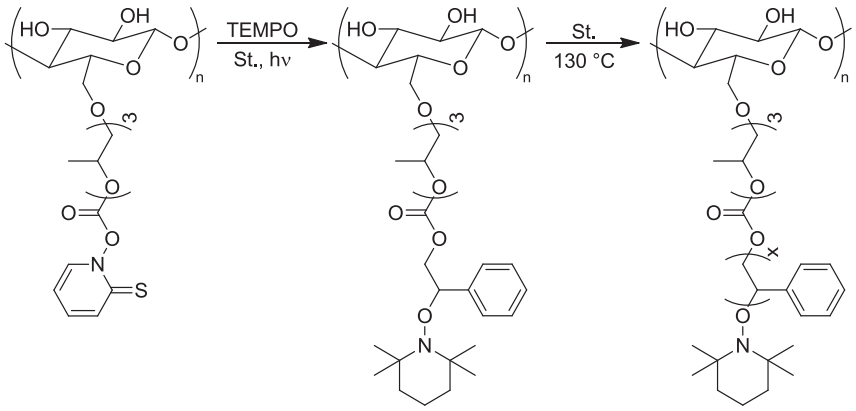
Start materials		CTAs	Monomer	Initiator	Solvent	Temp (°C)	Refs.
Surface modification	Filter paper	BPDF	IBA	AIBN	$CHCl_3$/THF	R.T.	[167]
		CPDA	St	γ-ray	EtOH, toluene, dioxin/H_2O	R.T.	[168]
		CPADB, BSPAC	SS	ACPA or γ-ray	H_2O/EtOH	70	[169]
		MCPDB	DMAEMA	AIBN	EtOH	R. T.	[170]
		MCPDB	DMAEMA, St	AIBN	Toluene	60	[171]
		CPDB	GMA	γ-ray	DMF	–	[172]
	Cotton	MCPDB	St	AIBN	Toluene	60	[173]
	Cotton fabric	MCPDB	St, MMA, MA, DMA	AIBN	In bulk	60	[174,175]
	Ramie fibers	ECPDB (free CTA)	MMA,MA, St, *p*-chlorostyrene	AIBN	THF	60	[176,177]
			TFEMA	AIBN	Supercritical CO_2	70	[178]
	Wood fibers	EECX	VAc, St, VBC	AIBN	In bulk	90	[179]
	CA nanofibers	CPADB (free CTA)	VBTAC	ACPA	Buffer	70	[180]
	CNCs	DDMAT	NIPAm, AA	AIBN	Dioxane	70	[181]
	Cellulose membrane	CPADB	DMAPS	AIBN	MeOH	70	[182]
Graft copolymers	Filter paper	BSPA	St	AIBN	MP	–	[183]
		BSPAC	St, HEMA	AIBN	MP	60	[184]
	HPC, MC	*S*-sec propionic acid xanthate	VAc	AIBN	DMF	68	[185]
	EHEC	BSPA	AAM	ACPA	DMSO	70	[186]
	HPC	PABTC	NIPAAm, EA	AIBN	Dioxane, DMAc	60	[187]
	Cellulose	DDMATC	amino acid acrylate, (A-(L)Ala-OH, A-(L)Pro-OH, A-(L)Glu-OH)	AIBN	DMAc/THF	80	[188]
		ECDPB	MMA	AIBN	BMIMCl	60	[189]
		Trithiocarbonate	NIPAm, DEAAm	AIBN	DMF	70	[190]



Scheme 6. The synthesis cellulose based macro-initiators for ATRP and/or chain transfer agent for RAFT and MADIX polymerization. Reproduced with permission from Refs. [173–175].

dithiobenzoate and cyanoisopropyl dithiobenzoate. They further used cellulose as backbone to reaction by RAFT [173–175]. The detailed process is shown in Scheme 6. Firstly, the hydroxyl groups of a cotton fabric were treated with 2-chloro-2-phenylacetyl chloride to form the corresponding 1-alkoxycarbonyl-1-phenyl methyl and then form the corresponding dithiobenzoate (cellulose-MCPDB) or trithioester (cellulose-MCPMT) CTA, respectively. The cotton supported polymerizations of MMA, MA, and St were undertaken in bulk, up to full conversion. After hydrolyzed in acidic conditions to collect the grafted PMMA, PS, and PMA chains, PS and PMA showed a molecular weight very close to that theoretical M_n with lower PDI, and PMMA had a lower molecular weight than that of theoretical M_n with higher PDI. They also used MCPDB-functionalized cellulosic substrates to the polymerization of DMAEMA [170,171]. After the establishment of the RAFT equilibrium, a near to linear increase of PDMAEMA with time and monomer conversion was observed. However, the polymerization process was not controlled with the broad PDI and dissimilar molecular weight of free and immobilized chains. To maintain an appropriate concentration of thiocarbonyl thio groups in solution and impart a controlled character to the solution and graft polymerization processes, free MCPDB was incorporated into the system. The introduction of MCPDB considerably improved the control over the polymerizations by the good agreement between theoretical and experimental M_w and the narrow PDI. Indeed the introduction of a CTA in solution could prevent the occurrence of 'radical hopping' and thus enhance the 'living' character of the graft polymerization. Practically, surface RAFT polymerization on many substrates containing cellulose composition, such as native ramie [176–178], or wood fibers [179] needed extra addition of a free CTA to enhance the control of the polymerization of both grafted and free polymer chains, and monitor the macromolecular features of the growing chains.

Among the various RAFT polymerizations, the thermal decomposition of radical initiators AIBN is the widely adopted initiation due to its commercial availability. The γ-radiation is another source of initiation for a RAFT polymerization. Barsbay et al. [168] reported a simple and promising approach to achieve controlled graft polymerization from non-functionalized cellulose surfaces. In this study the authors investigated the application of γ-irradiation in conjunction with the RAFT process to induce graft polymerization of St from cellulose. Practically, cellulose was initially pretreated with an aqueous basic solution to break hydrogen bonding between hydroxyl groups, opening up the ordered region and consequently enhancing the graft ratio. γ-Radiation (^{60}Co) was then applied to the deoxygenated polymerization solution (St, solvent, cumyl phenyl dithioacetate and cellulose) to create radicals both on the cellulose surface and in the monomer solution that initiated the growth of immobilized and free PS chains. Controlled polymerization and satisfying graft ratios (max. 39% graft) were observed. The PS grafts grown from the surface were cleaved by acidic hydrolysis of the cellulose substrate. The free (non-grafted) PS chains and the cleaved graft PS chains had almost the same M_n (nearly theoretical M_n) and PDI. The M_n of the grafted as well as the non-grafted PS chains increased linearly with monomer conversion and the polydispersities (<1.25) were narrow. After that, RAFT graft polymerization of SS from CPADB functionalized cellulose in



Scheme 7. Route to cellulose-*g*-PS by NMP. Reproduced with permission from Ref. [200].

aqueous media was achieved under γ-irradiation [169]. The graft frequency was found to be higher in the RAFT mediated graft polymerizations compared to the conventional graft copolymerization. However, the RAFT graft polymerization conditions needed optimization to obtain higher graft ratios and graft frequency.

2.3. NMP of cellulose

NMP is mainly based on the use of a stable nitroxide radical, such as TEMPO, which is the more commonly used nitroxides. In this method, the propagating species ($P_n^{\bullet}$) reacts with a stable radical ($X^{\bullet}$) to form dormant species (P_n–X). Thus, deactivation of propagating radicals occurs. The resulting dormant species can then reversibly cleave to reform the free radicals. Once $P_n^{\bullet}$ forms, it can propagate by reacting with a monomer (M) or it can terminate with other growing radicals [199]. NMP only requires the addition of an appropriate alkoxyamine to the polymerization system. Polymerization is usually undertaken at high temperatures.

The synthesis of cellulose-based comb copolymers using a nitroxide-mediated grafting process under homogeneous conditions was first reported by Daly et al. [200]. In their approach, Barton carbonates (carbonates of *N*-hydroxypyridine-2-thione) was first immobilized onto HPC backbones (Scheme 7) and subsequently irradiated the polysaccharide derivatives in the presence of an excess of TEMPO and St to form St–TEMPO adducts promoting the preparation of HPC-*g*-PS graft copolymers by NMP. An increase in grafted polymeric chain length with increasing polymerization time was observed. The polydispersity of the PS grafts ranged from 1.3 to 1.5. However, the grafting was limited to St monomer only and required the use of high temperatures (130 °C). Due to strong hydrogen bonds inter– or intra– chains, cellulose commonly dissolves in complicate solvent systems, such as DMAc/LiCl or ionic liquid. Homogeneous polymerization of cellulose is the aim going after all the time. Recently, some authors tried to investigate the stability of nitroxides in DMF(or DMAc)/LiCl(or LiBr), such as TEMPO and SG1, which were clearly of crucial importance to perform the graft polymerization of cellulose by NMP. And then they tried to used glucose and cellobiose as model of cellulose for graft polymerization of PS by NMP in DMF/LiCl [201].

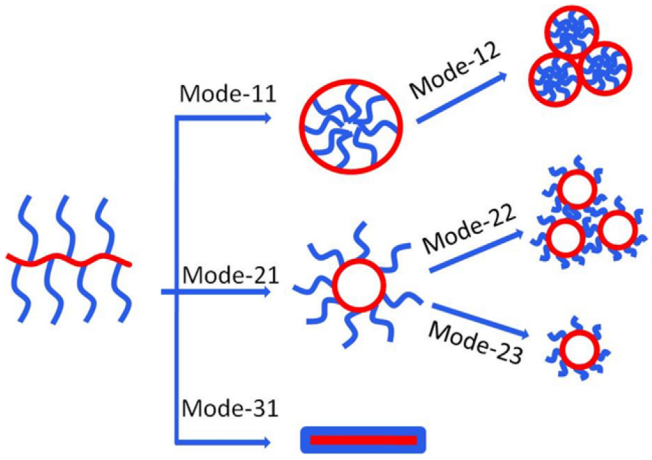
2.4. SET-LRP of cellulose

Recently, a novel method of controlled polymerization, named SET-LRP has been developed where dormant chains (or initiator) are activated via the outer-sphere electron-transfer [202]. In SET-LRP, the initiating system contains halide-type initiator (sulfonyl halides, haloacid esters, etc.), similar to those for ATRP, zero-valent copper in the form of fine powder or thin wire and appropriate ligand, like PMDETA or Me_6TREN, in various solvents [59]. The differences between SET-LRP and ATRP are derived from the low activation energy in an outer-sphere electron transfer mechanism and the rapid disproportionation of Cu^{I} with *N*-containing ligands in polar solvents [203]. It has been demonstrated by Percec et al. that Cu^{I}X can disproportionate into Cu^{0} and $Cu^{II}X_2$ species in polar solvents in the presence of *N*-containing ligands [59]. This disproportionation leads to rapid living radical polymerization via the outer-sphere single-electrontransfer mechanism. Clearly, it has been shown that Cu^{I}-mediated ATRP of *N*-isopropylacrylamide proceeded via Cu^{0}-mediated SET-LRP, and not ATRP [204]. Especially, a choice of reaction medium is crucial, because deactivating complex salt of Cu^{II} originates from the disproportionation of the Cu^{I} salt, the rate of which substantially depends on the solvent used [203,205]. So far, polar solvents such as DMSO, DMF, and methanol are generally used in SET-LRP. The graft modification of cellulose using SET-LRP and the corresponding synthesis conditions are listed in Table 5.

Table 5
Reaction conditions of cellulose graft polymerization by SET-LRP.

Cellulose materials	Initiator[a]	Monomers	Catalyst	Solvent	Temp. (°C)	Refs.
CDA, CBA		MMA, BuA, *t*-BuA	Cu^{0}/PMDETA	1,4-dioxane, DMSO	30, 60	[132]
	–Br, –Cl		Cu^{0}/Me_6TREN			
Cellulose	–Br	AAm or DMAAm	CuCl/PMDETA	DMSO	80	[120]
EC	–Br	NIPAm	CuCl/Me_6TREN	THF/MeOH	50	[204]
CNCs	–Br	NIPAm	CuBr/PMDETA	H_2O/MeOH	R. T.	[206]
CNCs	–Br	*t*BA, AA	CuBr/PMDETA	DMF	75	[121]
Softwood	–Br	DMAam	CuCl/PMDETA	DMSO	80	[119]
Cotton fiber	–Br	BMA,PETA	Cu^{0}/HMTA	DMF	75	[207]

[a] –Br, –Cl are the initiating groups that linked to the cellulose backbone or the surface of cellulose materials including fibers, and nanocrystals.



Scheme 8. Self-assembly of cellulose graft copolymers.

3. Applications

3.1. Micelles and drug release

Cellulose graft copolymers with well-defined architecture have been synthesized, combining the properties of both the cellulose backbone and side chains for the purpose of using the graft copolymers in many fields. The stimuli-responsive properties of the cellulose graft copolymers can either tailored by the cellulose backbone or the chemical structure of the side chains. The cellulose graft copolymers can be self-assembled into single- [140–143] or multi-stimuli [75,136,208,209] responsive micelles in selected solvents depending on the components of the graft copolymers, which have the potential applications as carriers for drug and gene delivery and controlled release [142,143,210]. On the basis of polymer topology and morphology, comb-type cellulose graft copolymers are classified into single-, dual-, block-, centipede- and dendritic-like grafts [19]. The multiple functions of cellulose graft copolymers, such as hydrophilic, hydrophobic, amphiphilic, environmental responsive or polyelectrolyte, can be synthesized by designing the chemical structures of both the cellulosic backbone and the side chains. The abundance architectures of cellulose graft copolymers offer the versatile self-assembly behaviors and the structures of the resultant assemblies (Scheme 8), depending on the media and the chemical structure of the side chains. EC-*g*-PS can self-assemble into spherical unimolecular micelles in acetone (Mode-11, Scheme 8), due to the fact that acetone was a relatively good solvent for EC [211]. The micelles had a core–shell structure with the EC rich shell and PS rich core. The size of the micelles increased with the increasing copolymer concentration and length of PS side chains. Moreover, the cellulose graft copolymers could self-assemble into multimolecular micelles at relatively high polymer concentration (Mode-12, Scheme 8). EC-*g*-PHEMA copolymers showed different self-assembly behaviors in water from those of EC-*g*-PS in acetone. The hydrophobic EC backbones collapsed in water and formed the core of the micelles, and the hydrophilic PHEMA chains stayed at the shell of the micelles to stabilize the micelles (Mode-21, Scheme 8) [144]. EC-*g*-PAA showed various self-assembly behaviors in THF/water, according to the length and density of the branch chains [212]. The structure of the micelles was as same as that of EC-*g*-PHEMA in water. The core of the micelles was rich in EC backbones and the shell was rich in PAA chains. Unimolecular and multimolecular spherical micelles can be obtained from the graft copolymers with longer and shorter side chains, respectively. For EC-*g*-PAA copolymers with the high graft density, the conformation transition happened from coil-like to extended straight rod-like conformation in methanol (Mode-31, Scheme 8) [213]. Amphiphilic EC-*g*-P(PEGMA) copolymers could self-assemble into spherical micelles in water (Mode-21, Scheme 8) [141]. The size of the micelles increased with the increasing side chain length. P(PEGMA) is a thermo-sensitive polymer. Therefore, the micelles showed thermo-sensitive properties with LCST around 65 °C, which was almost independent on the graft density and the side chain length. Above LCST, the micelles prepared from EC-*g*-P(PEGMA) would aggregate (Mode-22, Scheme 8). The process was totally reversible. The pH-sensitive EC-*g*-PDEAEMA copolymers could self-assemble into micelles in acidic aqueous solution [142]. The micelles would shrink at pH 6.0 (Mode-23, Scheme 8) and aggregate at pH > 6.9 (Mode-22, Scheme 8).

To mimic the physiological environment, many works focused on fabricating functional materials with the combination of pH and thermal sensitivities. Novel dual-hydrophilic cellulose graft copolymers based on HPC, HPC-*g*-PDMAEMA [75] and HPC-*g*-P4VP [136] copolymers, have been synthesized. HPC backbones were thermal sensitive, while the side PDMAEMA or P4VP chains were pH sensitive, which offered the dual stimuli responsive properties of the graft copolymers in aqueous solution. The LCST of $HPC_{0.1}$-*g*-$PDMAEMA_{20}$ shifted to lower temperature with the increase in pH, which was due to the deprotonation of the PDMAEMA side chains at higher pH (Fig. 1). At low pH (*e.g.* 3.0), the HPC backbone of the copolymer first collapsed to form the core of micelles stabilized with protonated PDMAEMA side chains upon heating. At medium pH (*e.g.* 8.1), both HPC backbone and PDMAEMA side chains collapsed upon heating to form unstable aggregates. At high pH (*e.g.* 12.3), the PDMAEMA side chains first collapsed to form the core of micelles stabilized with HPC chains upon heating. Further

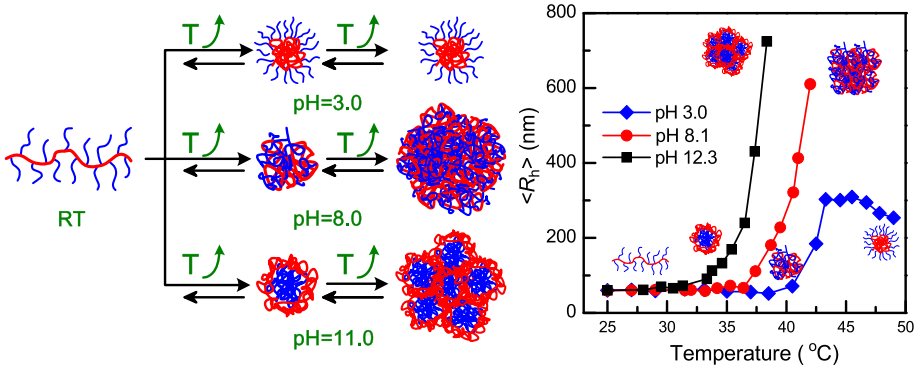


Fig. 1. Thermal-induced self-assembly of $HPC_{0.1}$-*g*-$PDMAEMA_{20}$ copolymer in aqueous solution at different temperature. Reprinted with permission from Ref. [75].

heating the micellar solution leaded to the aggregation of the micelles due to the collapse of the HPC chains at the surface of the micelles. The above mentioned thermal sensitivity of the HPC-*g*-PDMAEMA copolymers was reversible (Fig. 1). Similarly, HPC-*g*-P4VP copolymers can self-assemble into core–shell micelles induced by pH or temperature [136].

Jiang et al. prepared pH-sensitive polymeric nanospheres and nano-vesicles from HEC-*g*-PAA copolymers, and the reversible transition between nanospheres and nano-vesicles was achieved via the adjusting the pH of the media [214–216]. At high pH, both HEC backbones and PAA grafts were dissolved in water. At pH < 3, carboxyl groups of PAA were completely protonated and thus formed hydrogen bonds with HEC to form insoluble complexes. Meanwhile, due to the low degree of grafting, parts of HEC chains remained soluble. Therefore, HEC-*g*-PAA can self-assemble into micelles with the HEC/PAA complex core, and free HEC shell. Then, the micellar structure was efficiently locked by crosslinking PAA with diamine. Thus, pH-sensitive polymeric nanospheres were obtained. After the acidic solution of the nanospheres was dialyzed against water to remove impurities and increasing pH, the carboxyl groups of PAA dissociated and lost the ability to complex with HEC. In this case, the nanosphere cores disintegrated and the crosslinked copolymers swelled substantially to form polymeric hollow spheres (Fig. 2). The hollow spheres of crosslinked PAA and HEC-*g*-PAA both showed size-ionic strength (the concentration of NaCl) dependence, which was due to the shielding effect of ions on the charge. Besides, it was found that the medium pH strongly affected the size-ionic strength dependence of the PAA hollow spheres. Specifically, as the salt concentration increased, the hydrodynamic diameter ($<D_h>$) of PAA hollow spheres increased in the acid medium but decreased in the basic medium. In the neutral medium, there was a little change in $<D_h>$ with the salt concentration (Fig. 2).

The stimuli-responsive polymer based nanomaterial in aqueous solution, are of great interest in recent years because of their singular properties and potential applications [217]. Various structures and properties of stimuli-sensitive polymers can be finely tuned by altering the molecular structure parameters or environmental conditions, such as pH, temperature, ionic strength, light, photochemical processes, etc. [218–231]. The stimuli-responsive polymer based nanomaterials in aqueous solution may have the potential applications in biomedicine and biotechnology. The drug loading and sustained release behaviors of the EC-*g*-PPEGMA with different graft density and graft length were investigated using pyrene as the fluorescence probe and model of the poor water-soluble drug [210]. It was found that a low graft density of the copolymers corresponded to a higher drug loading efficiency and a higher loading capacity of drug in the micelles. The release rate of the loaded pyrene depended on both the length of the side chains and the loading capacity of pryene in the micelles. A shorter side

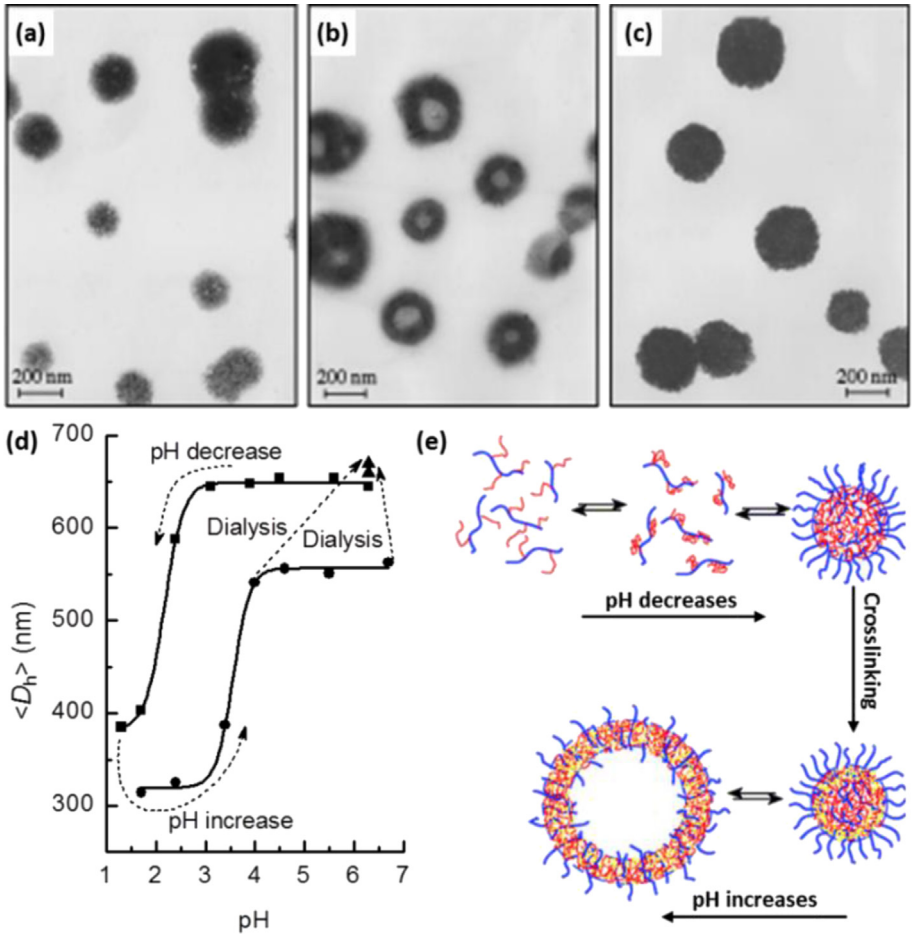


Fig. 2. The pH dependent self-assembly of HEC-*g*-PAA. TEM image for the HEC-*g*-PAA copolymer micelles (a) formed at pH 1.3; (b) the hollow spheres after cross-linking and dialysis, and (c) the micelles of obtained by adjusting the acidity of the cross-linked and dialyzed the solution to pH 1.3; (d) Average hydrodynamic diameter $<D_h>$ of the aggregates as a function of pH during the transition from micelle to hollow sphere; (e) scheme of the pH-dependent micellization and transition of HEC-*g*-PAA from micelle to hollow sphere. Reprinted with permission from Ref. [215].

chain of the copolymer and a higher ratio of the copolymer to the pyrene in the micelles corresponded to a lower release rate. Furthermore, by using rifampicin (RIF) as the model drug, the loading and controlled release of drugs of EC-*g*-PDEAEMA copolymers in the micelles was investigated that cumulant release in the buffer solution at pH 6.6 higher than that at pH 7.4 [142].

3.2. Adsorbents

Removal of toxic ions, including heavy metal ions (*e.g.* Pb^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}) and toxic anions (*e.g.* F^-, CrO_4^{2-}, AsO_4^{3-}, AsO_3^-) from both waste and natural waters have gained increasing attentions to solve or minimize the industrial and ecological waste problems. Adsorption has been recognized as an effective, efficient, and economic approach in water decontamination and analytical separation [232]. Nowadays, adsorbents based on naturally-occurring support materials gained increasing emphasis due to their availability in large quantities, relatively cheap, and facile chemical modification to introduce specific functional groups for enhanced metal binding ability. Cellulose, the most abundant naturally-occurring polymer with abundant hydroxyl groups along its chain, is an idea raw material for the fabrication of absorbents for the removal of toxic ions. Both derivation and graft modification can be used for the introduction of functional groups that can chelate the toxic ions onto cellulosic materials. Specifically, surface modifications are generally used. The preparation and properties of cellulose based adsorbents for removal of toxic ions have been reviewed [233,234].

The surface graft modification of cellulosic materials (*e.g.* pure cellulose, wood, cellulose acetate) using monomers containing $-COOH$, $-COO^-$, $-SO_3H$ or $-NH_2$ groups could be used as the adsorbents for the removal of divalent metal ions from water [235–239]. The carboxyl groups had two lone pairs of electrons on the oxygen atoms, by which divalent metal ions, *e.g.* Cu^{2+}, Ni^{2+}, Pb^{2+}, Hg^{2+} and Cd^{2+} could be chelated. While the amino groups had a lone pair of electrons on the nitrogen atom and might form a covalent bond with the metal, especially showing selective sorption for Hg^{2+} [239]. The absorbents can be reused after desorption of the chelated metal ions.

The protonation of amine groups such as $-NH_2$, $-NRH$, and $-NR_1R_2$ results positive groups of $-NH_3^+$, $-NRH_2^+$, and $-NR_1R_2H^+$, which can adsorb the toxic anions in aqueous solutions through electrostatic interaction. Cellulose materials modified by surface grafting of the monomers with amine groups could be used as the adsorbent for the removal of toxic anions such as F^-, AsO_2^-, AsO_4^{3-}, and CrO_4^{2-} from water [240]. Native cellulose fibers surface modified by PDMAEMA showed high efficiency in the removal of F^-, AsO_2^- and AsO_4^{3-} from aqueous solutions. The adsorption kinetics showed that the adsorption equilibrium could be reached within 1 min. The adsorption process followed Langmuir model, and the adsorption capacity was in the order of $AsO_4^{3-} >> AsO_2^- > F^-$ [240].

Graft acrylonitrile or vinyl acetate and copolymers of acrylonitrile and vinyl acetate are of considerable interest because both acetate and nitrile groups could be hydrolyzed by using different chemical reagents to give a variety of functional groups [241]. Cellulose graft polyacrylonitrile or polymethacrylonitrile materials had the low adsorption efficiency for metal ions due to the low affinity of nitrile groups to metal ions for complex formation [242]. However, the cyano groups ($-C\equiv N$) could be transformed into carboxyl group by sodium hydroxide treatment [243,244] or amidoxime group in alcoholic hydroxylamine solution [245–248], which was used as the adsorbent. Specifically, the amidoxime group has both acidic and basic parts and for the coordination two lone pairs of electrons are available on the oxygen and one lone pair on each nitrogen atom, which has been used for the removal of heavy mental ions from aqueous system. More recently, it was found that both cationic and anionic toxic ions could be adsorbed by amidoxime group [248].

3.3. Resistance to protein adsorption

Cellulose and its derivatives have been widely used in biomedical fields. The biocompatibility (especially the blood compatibility) of the raw cellulose is inadequate and needs to be improved before use. Anti-protein adsorption of cellulose is importance through surface modifications. Protein adsorption on biomaterials' surfaces is thought to be the first step of many undesired bio-reactions and bio-responses [249], followed by platelet adhesion and activation of coagulation pathways, leading to thrombus formation [250]. Several efforts had been taken to solve these problems, such as modification of the surface of the membrane with PEG or oligo(ethylene glycol), zwitterionic molecules, and biologically active heparin [251]. PEG have been identified as a synthetic nonfouling and nonthrombogenic materials [252], by the repelling of protein molecules from the surface [253].

Three vinyl monomers, DMVSA, DMMSA, and MPC, are generally used for the synthesis zwitterionic polymers. On the surface of the zwitterionic polymers modified materials, the zwitterions formed a hydration layer via electrostatic interactions in addition to hydrogen bonding and could bind a significant amount of water molecules [254], which generated a strong repulsive force to protein at specific separation distances or made the protein contact with the material surface in a reverse manner without a significant change in conformation [81,255]. The surface modification of cellulosic materials using zwitterionic monomers have been achieved by traditional free radical graft copolymerization [256–258], polycondensation [259], and ATRP [81,82,124,254,260]. The surfaces of zwitterionic polymers modified cellulosic materials have the good resistance to protein and platelet adhesion.

3.4. Antimicrobial

Antibacterial properties of materials are important for the applications of food packages, sanitary materials, household, medical, and military items [261]. Antimicrobial surfaces can be obtained by incorporating antimicrobial species either through covalent bonding or via noncovalent interactions on the surface. The covalent immobilization of the antimicrobial agents on the surface could result effective and durable antimicrobial properties. The surface graft modification has been successively used for the construction antibacterial surfaces by using the monomers with the functional groups such as antibiotics [262], phenol derivatives [263,264], polypeptide mimics [265,266], *N*-halamines [267,268], quaternary ammonium and phosphonium salts [269–273]. Living/controlled polymerization endows uniform and high concentration of polymer chains on the surface of cellulose matrix, which can show good antibacterial activity. Tertiary amine polymers, *e.g.* PDMAEMA[170], P4VP [274], were grafted from filter paper by ATRP [261] or RAFT[170] to produce a polymer brush. After quaternized using an alkyl halide, the surface with a large concentration of quaternary ammonium groups showed effective antibacterial activity.

3.5. Other applications

Microporous films with regular patterned structure have the potential applications for filter membranes, optical materials, catalysts, templates, cell culture substrates, transparent and super hydrophobic polymer films [275–283]. Microporous films can be prepared from cellulose graft copolymers *via* “breath figure”

method [183,184]. For example, the microporous films can be prepared from EC-*g*-PS copolymers *via* "breath figure" method and the morphology of the microporous films depended on the length of the side PS chains [284].

In case of conjugating the redox Os(bipyridine) groups onto side P4VP chains on HPC-*g*-P4VP copolymers (HPC-*g*-P4VP-Os(bpy)), the resultant polymer can be used for the fabrication of biosensors with a wider working window. HPC-*g*-P4VP-Os(bpy) copolymers provide a good environment for enzyme activity to enhance the sensitivity of the modified electrode for glucose detection [285].

Rod-like CNCs can be modified via SI-ATRP to result hairy rods. For example, PEG-grafted CNCs can form a chiral nematic mesophase through a phase separation as that of the unmodified CNCs [286]. The PEG-grafted CNCs showed drastically enhanced dispersion stability even at high solid content and the ability to redisperse into either water or chloroform from a freeze-dried state. CNCs surface grafted poly(PMMAZO) can be stable dispersed in organic solvents [287]. The poly(PMMAZO) modified CNCs showed both lyotropic and thermotropic liquid crystalline properties. Moreover, the surface graft modified CNCs can be used as the reinforced additives to prepare reinforced composites [288–294]. The grafting chains on the CNCs surface are generally used for the improving the interface interactions between CNCs and the polymer matrix.

4. Conclusions and perspectives

Cellulose is the most abundant, renewable biomass energy. However, strong hydrogen bonds inter- or intra-macromolecules seriously restrict its widely applications. Modification doesn't only destroy the hydrogen bonds but also endows cellulose many functionalities. Among many modification methods, the living/controlled polymerizations have shown especial advantages, introducing well-defined side chains of synthesized polymers with controlled structures, molecular weight, molecular weight polydispersity and multiple functions onto cellulose backbones, overcoming a lack of control such as degradation of cellulose backbone and generation of homopolymers by traditional radical polymerization. Well-defined architecture of cellulose graft copolymer makes cellulose materials potential applications in wider fields. In this review, we briefly introduced the mechanism of different living/controlled polymerizations. The factors that influence the controlled grafting reactions through different process in living/controlled polymerizations were also discussed. Examples for the applications of cellulose grafting copolymers were summarized, including micelles and drug carriers, adsorbents, resistance to protein adsorption, and antibacterial.

Although living/controlled polymerizations show much superiority in grafting techniques, in spite of an enormous ingenious research, no large-scale commercial exploitation of the method has developed. The main disadvantage of living/controlled polymerizations is the low efficiency and high cost, which is due to that the living/controlled processes of CRPs are generally achieved by sacrificing the polymerization rate. In the case of using ATRP for cellulose modification, the molecular weight distribution will be broadened if less copper was used, which may result the loss of the functionalities of the graft chains. Moreover, cellulose graft materials with residual copper in ATRP are not suitable for being used in medical fields. The modification of cellulose via RAFT graft copolymerization is generally unfavorable due to its complex reaction steps and the color of the final products. The above mentioned disadvantages of CRP still remain challengers in polymer science.

The extension of graft method for cellulose extensively enriches the properties and possible applications of cellulose. Thus, the application of cellulosic materials can be extended far beyond the traditional application areas. It should be noted that the comprehensive understanding of the structure-function correlations, as well as the structure-polymerization method connections for various cellulose graft copolymers are still necessary to be investigated in details. Specially, cellulose-based smart materials with the grafted stimuli-responsive side polymer chains have potential applications, such as active packaging, biosensors, tissue engineering, antimicrobial surfaces, separation and detection, smart clothing. Moreover, the methods of the graft modification of cellulosic materials can be extended to the graft modification of other natural resourced polymers, such as dextran [295–297] and keratin [248,298,299] for various applications.

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