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Cellulose-Based Thermoplastics and Elastomers via Controlled Radical Polymerization

Feng Jiang, Fenfen Wang, Chenqian Pan and Yanxiong Fang

Abstract

This chapter is concerned with the recent progress in cellulose-based thermoplastic plastics and elastomers via homogeneous controlled radical polymerizations (CRPs), including atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization, and nitroxide-mediated polymerization (NMP). The first section is a brief introduction of cellulose and cellulose graft copolymers. The second section is recent developments in cellulose graft copolymers synthesized by CRPs. The third part is a perspective on design and applications of novel cellulose-based materials. The combination of cellulose and CRPs can provide new opportunities for sustainable materials ranging from thermoplastics to elastomers, and these fascinating materials can find a pyramid of applications in our daily life in the near future.

Keywords: cellulose, graft copolymers, controlled radical polymerization, thermoplastics, elastomers

1. Introduction

As the most abundant biomaterial on earth, cellulose has received enormous attention due to its wide applications in different fields, such as packaging [1], drug delivery [2], cosmetics [3], textiles [4], membranes [5], bioengineering [6], and electronics [7]. Cellulose has some outstanding advantages, including low cost, non-toxicity, good mechanical properties, and excellent biodegradability and biocompatibility [8]. However, cellulose is lack of thermoplasticity and shows poor dimensional stability and crease resistance. Due to the high crystallinity and presence of a large amount of intra- and inter-molecular hydrogen bonding, cellulose is difficult to be dissolved in common solvents [9]. Different solvent systems have been proposed to dissolve cellulose, including *N,N*-dimethylacetamide (DMAc)/lithium chloride (LiCl) [10], dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride (TBAF) [11], *N,N*-dimethylformamide (DMF)/dinitrogen tetroxide (N_2O_4) [12], *N*-methyl morpholine-*N*-oxide (NMMO) [13], alkali/urea aqueous [14], and ionic liquids [15]. The existence of three hydroxyl groups in each anhydroglucose repeating unit makes cellulose an active material to develop various derivatives via etherification [16], esterification [17], amination [18], carboxylation [19], carbanilation [20], acetylation [21], grafting [22], sulfation [23], and silylation [24]. It is worth noting that the hydroxyl group in the 6 position of cellulose is most

reactive, followed by the hydroxyl groups at 2 and 3 positions. The degree of substitution (DS) indicated the substituted number of hydroxyl group in anhydroglucose unit (AGU).

Cellulose graft copolymers, which combine cellulose and grafted side chains in one macromolecule can open new opportunities toward developing novel bio-based materials with tunable properties. Cellulose graft copolymers can be achieved with grafting-to, grafting-through, and grafting-from strategies [25]. Among these methods, the grafting-from strategy is the most effective route for designing cellulose graft copolymers from thermoplastics to thermoplastic elastomers. Atom transfer radical polymerization (ATRP) [26, 27], reversible addition-fragmentation chain transfer (RAFT) [28, 29] polymerization, and nitroxide-mediated polymerization (NMP) [30, 31] are well-established controlled radical polymerizations (CRPs) that can be performed to prepare cellulose-based copolymers with well-defined structures and narrow molecular weight distributions in both heterogeneous and homogeneous conditions. This chapter summarizes recent advances that have been made in cellulose-based thermoplastics and elastomers from native cellulose via homogeneous CRPs.

2. Cellulose graft copolymers via homogeneous CRPs

2.1 Atom transfer radical polymerization (ATRP)

ATRP is the most used grafting method to prepare graft copolymers with cellulose-based macroinitiators and transition-metal catalysts. In general, the macroinitiators can be prepared by substituting the hydroxyl groups on cellulose backbone with chlorine or bromine-contained compounds. As shown in **Figure 1**, the macroinitiators, cellulose 2-bromopropionate (Cell-Bp), cellulose 2-bromoisobutyrylate (Cell-BiB), and cellulose chloroacetyl (Cell-ClAc) can be synthesized by reacting cellulose with 2-bromopropionyl bromide, 2-bromoisobutyryl bromide, and chloroacetyl chloride in 1-allyl-3-methylimidazolium chloride (AMIMCl),

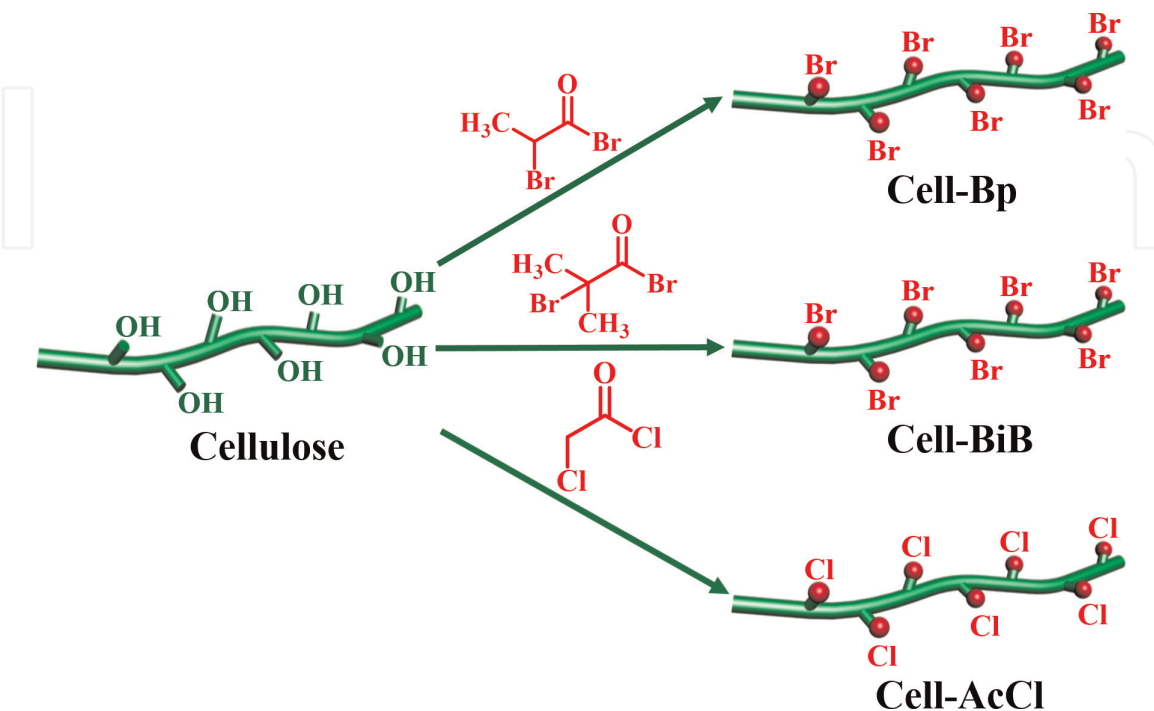


Figure 1.
Illustration for the synthesis of cellulose-based macroinitiators.

1-allyl-3-methylimidazolium chloride (BMIMCl) or DMAc/LiCl solution [32–37] under homogeneous conditions. The solubility of cellulose-based macroinitiator is strongly related to the DS of acylation, which can be adjusted by the molar ratio of acylating agent/AGU and reaction time [35, 38–40]. Therefore, it is flexible and convenient to prepare cellulose graft copolymers with controlled grafting density. Different solvents have been utilized as the media to synthesize cellulose graft copolymers via ATRP, including DMF, DMSO, 1,4-dioxane, AMIMCl, and BMIMCl. Moreover, varied catalyst systems, such as copper(I) chloride/2,2'-bipyridine (CuCl/bpy), CuCl/tris(2-(dimethylamino)ethyl)amine (CuCl/Me₆TREN), copper(I) bromide/bpy (CuBr/bpy), CuCl/N,N,N',N'',N''-pentamethyldiethylenetriamine (CuCl/PMDETA), CuBr/PMDETA, CuBr/ethylenediamine, and CuBr/diethylenetriamine (CuBr/DETA), have been reported to control the grafting polymerization initiated by cellulose macroinitiator. During polymerization, the attached bromine or chlorine groups on cellulose macroinitiators can undergo a reversible redox process with metal catalysts and thus form active radicals to react and propagate with monomers. The active radicals can capture the halide ions from the oxidized metal complex to form activators and dormant halide species which can be reactivated. When polymerization is finished, the resultant cellulose graft copolymer can be obtained by removing the metal catalyst and precipitating into a poor solvent.

ATRP can be performed to synthesize different kinds of thermoplastics and elastomeric polymers due to its high tolerance. As displayed in **Figure 2**, a variety of vinyl and acrylate monomers, including methyl methacrylate (MMA) [33, 35, 37, 41–44], *N*-isopropylacrylamide (NIPAM) [45–48], 2-methacryloyloxyethyl phosphorylcholine (MPC) [32], styrene (St) [35, 42], *n*-butyl acrylate (BA) [44], *tert*-butyl acrylate (*t*BA) [49, 50], 4-vinylpyridine (4-VP) [49, 51], acrylamide (AM) [40], 3-ethyl-3-methacryloyloxy-methyloxetane (EMO) [12], *N*,

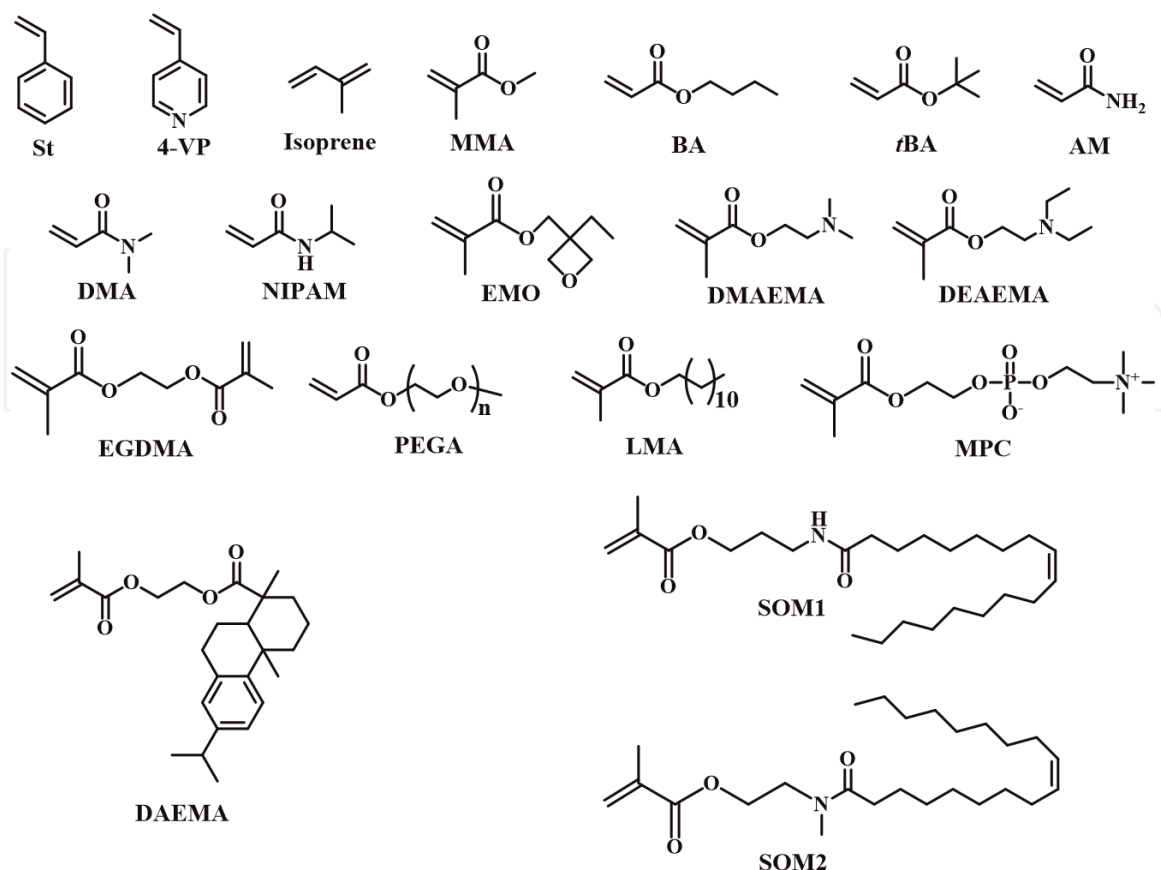


Figure 2. Monomers have been used to prepare cellulose graft copolymers via ATRP strategy in homogeneous conditions.

N-dimethylamino-2-ethyl methacrylate (DMAEMA) [34, 52], *N,N*-dimethylacrylamide (DMA) [40, 53–55], 2-(diethylamino)ethyl methacrylate (DEAEMA) [56], poly(ethylene glycol) methyl ether acrylate (PEGA) [57], isoprene [36, 58, 59], ethylene glycol dimethacrylate (EGDMA) [60], soybean oil-based methacrylates (SOM1 and SOM2) [61], lauryl methacrylate (LMA), and dehydroabietic ethyl methacrylate (DAEMA) [62], have been grafted from cellulose via homogeneous ATRP to develop novel cellulose graft copolymers.

Thermoplastics and elastomers are essential polymeric materials in our daily life, and they are commercially available and can be used in diverse areas, such as household goods, clothing, packaging, auto parts, electronics, sensors, drug delivery, seals, foods, and tissue engineering [63–73]. Cellulose is an interesting natural polymeric material with high strength and durability. The marriage of cellulose and synthetic polymers can promote the development of novel thermoplastics and elastomers with excellent thermal and mechanical properties. Cellulose chains can be used as rigid backbones to design high-performance elastomers. As shown in **Figure 3**, Cell-*g*-P(BA-*co*-MMA) copolymer thermoplastic elastomers (TPEs) or cross-linked Cell-*g*-PI brush polymer elastomers (CBPs) were fabricated in our group via activators regenerated by electron transfer for atom transfer radical polymerization (ARGET ATRP) or combination of ARGET ATRP and activators regenerated by electron transfer for atom transfer radical coupling (ARGET ATRC)

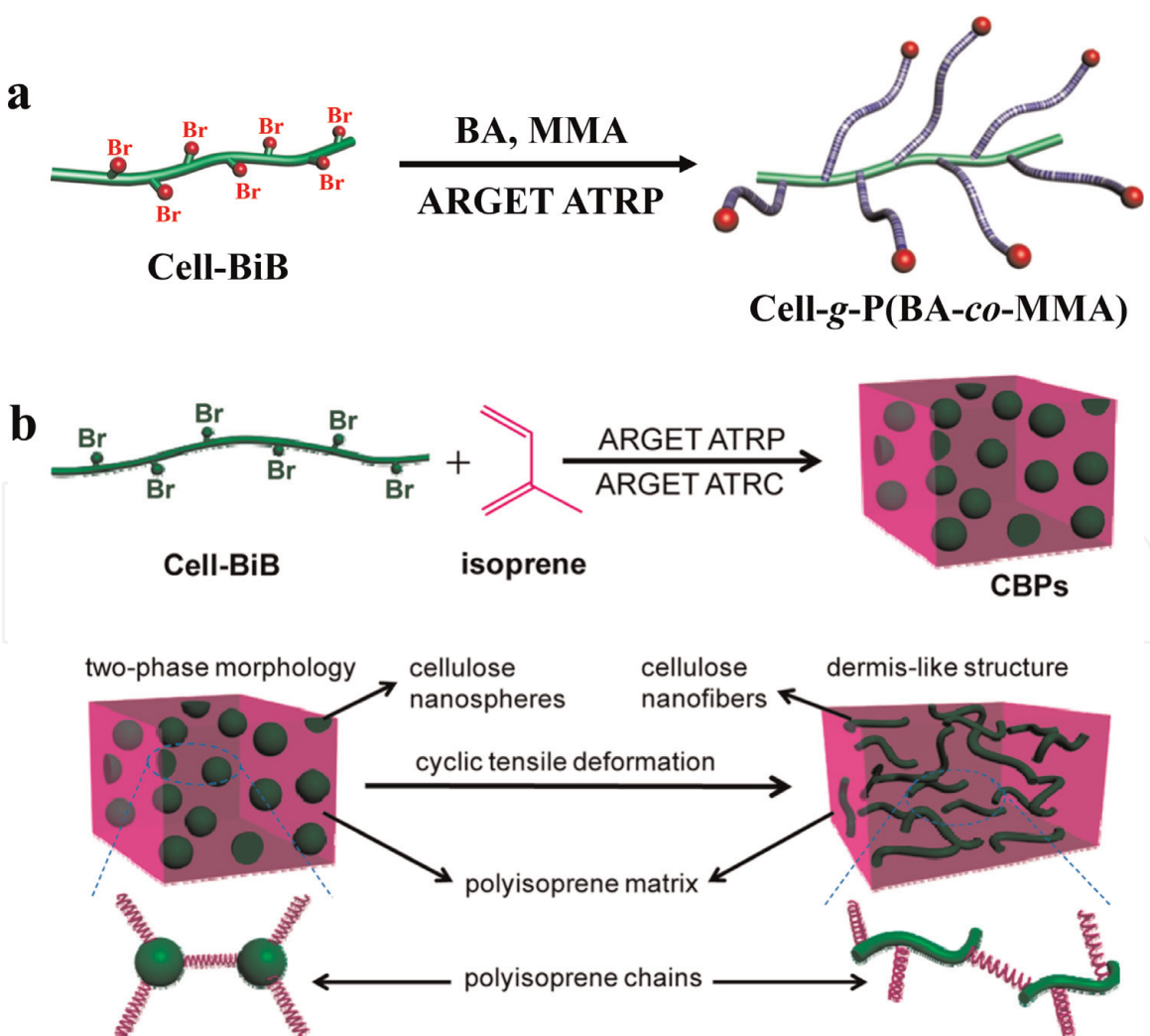


Figure 3.

(a) Illustration for synthesis of Cell-*g*-P(BA-*co*-MMA) as TPEs via ARGET ATRP (adapted with permission from Ref. [44]). (b) Design concept of CBPs via ARGET ATRP and subsequent ARGET ATRC (adapted with permission from Ref. [58]).

[44, 58]. The design concept of cellulose graft elastomers is to graft soft rubbery random polymer matrixes from cellulose backbones, and these rigid backbones can act as minority physical cross-linking points to significantly enhance the macroscopic mechanical properties of resultant elastomer materials. The tensile strength, extensibility, and elasticity can be systematically tuned by adjusting the composition and molecular weight of the grafted side chains during polymerization. ARGET ATRP was selected because of the relatively low catalyst concentration and simple purification process. Such kind of multigraft architectures can bring up huge impacts on developing new-generation sustainable thermoplastics and elastomers by elaborate molecular design with renewable resource derived monomers [74, 75].

Novel renewable polymers derived from resources have opened the door for sustainable science and engineering. Plant oils, which can be produced from different plants, such as palm, coconut, sunflower, olive, soy, and peanut, are typical natural resources for the chemical industry [76]. By reacting with (meth)acryloyl chloride or methacrylate anhydride, plant oils can be transformed into polymerizable monomers for free radical polymerization. Recently, two soybean oil-based sustainable monomers, SOM1 and SOM2, were designed and used by Wang and coworkers to produce Cell-*g*-P(SOM1-*co*-SOM2) copolymers via ATRP [61]. By changing the molar ratios of SOM1/SOM2 during grafting polymerization, the glass transition temperatures (T_g s) of resultant cellulose graft copolymers varied from 40.7 to -0.7°C . For comparison purpose, they also synthesized linear P(SOM1-*co*-SOM2) copolymers as counterparts via free radical polymerization. However, the T_g values are located in the range from -6.9 to 30.6°C , which were much lower than the values of corresponding graft counterparts. In cellulose graft copolymers, the chain mobility of P(SOM1-*co*-SOM2) side chains was significantly reduced due to the presence of rigid cellulose backbones and hydrogen bonding formed by hydroxyl groups on cellulose and amide groups on side chains. These transparent Cell-*g*-P(SOM1-*co*-SOM2) films show different mechanical behaviors from thermoplastics to elastomers, depending on the composition of grafted chains and cellulose content. The incorporation of cellulose as the backbone in graft copolymers could significantly enhance the tensile strength and Young's modulus, since the corresponding linear counterparts showed much poorer mechanical properties. The combination of two kinds of distinct natural resources, cellulose and soy oils, is a promising area for developing fantastic biomaterials. Moreover, cellulose graft copolymers can also be used as templates for the synthesis of diverse one-dimensional (1D) nanocrystals with precisely controlled dimensions and compositions, including plain nanorods, core-shell nanorods, and nanotubes. In this work, cellulose-based bottlebrush-like block copolymers synthesized by sequential ATRP were applied as amphiphilic unimolecular nanoreactors to develop well-defined nanorod materials, which can find various applications in electronics, optics, sensors, optoelectronics, catalysis, and magnetic technologies [49].

It is convenient to graft polymers with apparently opposite physical properties by grafting from strategy via ATRP and thus to form self-induced nanostructures in bulk or in solutions. As shown in **Figure 4**, cellulose-*g*-polyisoprene (Cell-*g*-PI) composed of flexible and hydrophobic polyisoprene (PI) grafts and rigid and hydrophobic cellulose backbone synthesized via ATRP can be self-organized into core-shell nanostructures by a simple solvent-evaporation process [36]. In the past two decades, stimuli-responsive molecular brushes composed of a backbone and densely grafted side chains, which are sensitive to small external changes, such as pH, temperature, and ionic strength, have received increased attention due to their unique stimuli-responsive properties [77]. Cellulose-based polymeric micelles can be applied in drug deliveries by introducing functional polymers with good environmental sensitivities, hydrophilicity, and biocompatibility, such as poly

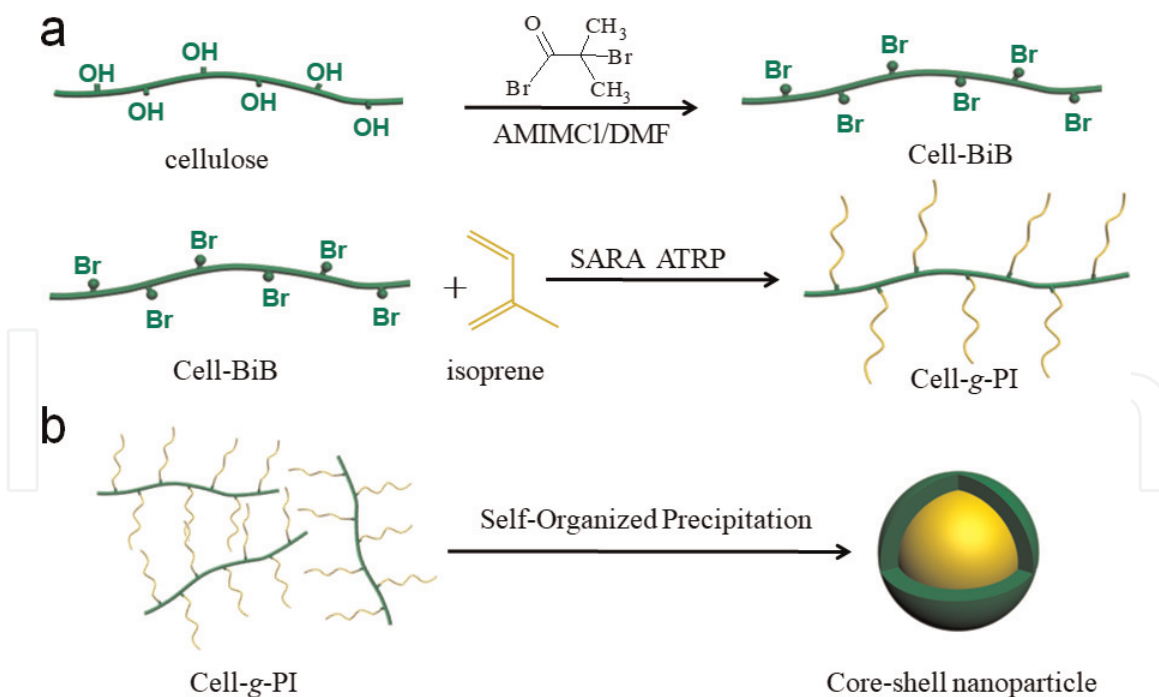


Figure 4. (a) Schematic illustration of the synthesis of Cell-g-PI by ATRP and (b) fabrication of Cell-g-PI core-shell nanoparticles with a PI core and cellulose shell (adapted with permission from Ref. [36]).

(*N*-isopropylacrylamide) (PNIPAM) [45–48], poly(4-vinylpyridine) (P4VP) [51], poly(*N,N*-dimethylamino-2-ethyl methacrylate) (PMDAEMA) [34], and poly(2-(diethylamino)ethyl methacrylate) (PDEAEMA) [56].

2.2 Reversible addition-fragmentation chain transfer (RAFT) polymerization

RAFT polymerization is an alternative method to synthesize well-defined and narrow distributed polymers with complex topological architectures by choosing a proper chain transfer agent (CTA). RAFT polymerization can be conducted without using any metal catalyst, and thus it is convenient and easy to purify the resultant polymers, which is the biggest advantage over ATRP. To date, only limited attention has been paid to cellulose graft copolymers through homogeneous RAFT polymerization in the literature [78–81]. The combination of cellulose and RAFT polymerization can provide new opportunities for graft copolymers, especially those that could not be synthesized directly via ATRP strategy. Recently, our group designed a novel cellulose-based macromolecular chain transfer agent by introducing a trithiocarbonate derivative with dodecyl as stabilizing group on cellulose backbone from Cell-BiB for the synthesis of Cell-*g*-P(BA-*co*-AM) copolymers as strong materials from thermoplastics to elastomers via RAFT polymerization [82]. As shown in **Figure 5**, the bromine groups on Cell-BiB can be substituted by reacting with 1-dodecanethiol, carbon disulfide (CS₂), and triethylamine (TEA) in DMSO. This Cell-CTA is versatile and suitable for a lot of monomers, and the DS of Cell-CTA can be manipulated by changing the molar ratios of above chemical reagents. AM and BA were chosen as the rigid and soft segments in the grafted side chains. PAM can provide reversible physical network structure in the cellulose graft copolymers. The N—H and C=O groups in AM units can form strong self-complementary hydrogen bonds, and they are distributed homogeneously in the polymer matrix, leading to the strong and tough elastomer materials. Inspired by this work, we propose that high-performance cellulose graft copolymer can be

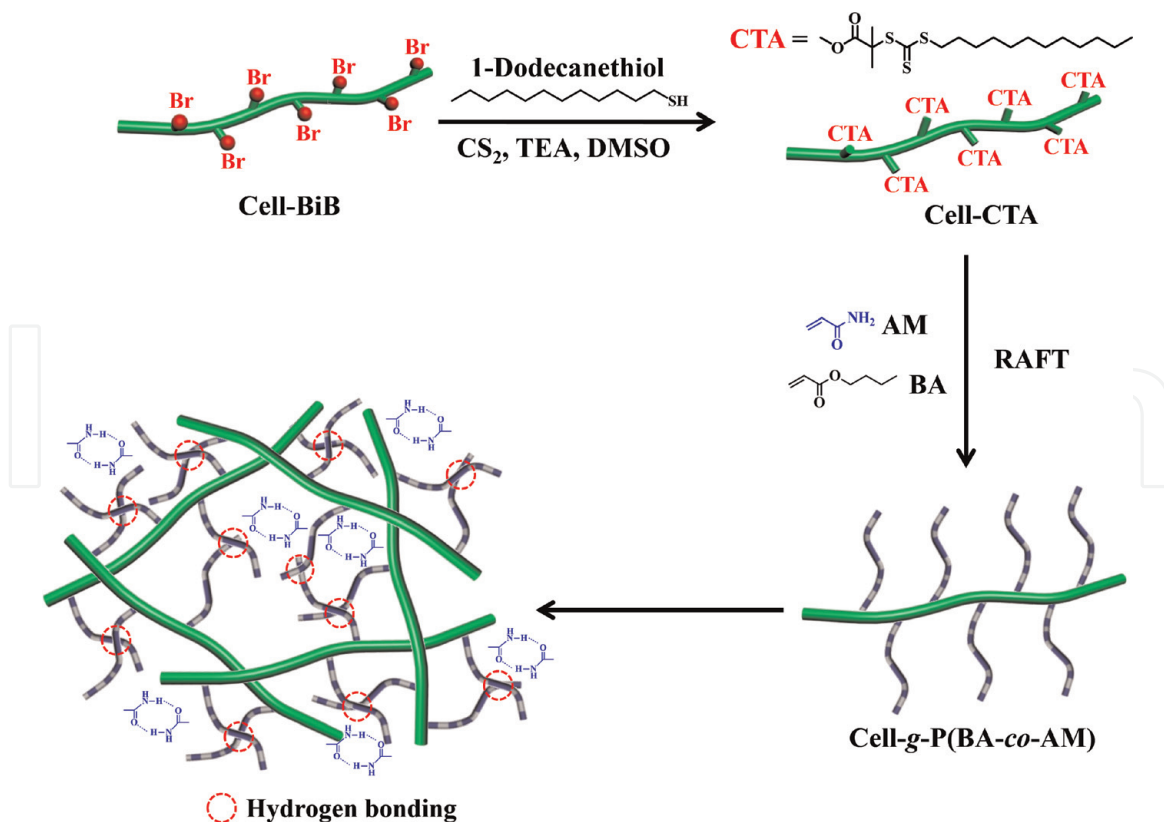


Figure 5. Illustrations for the synthesis of Cell-CTA, Cell-g-P(BA-co-AM) copolymer, and the self-complementary hydrogen bonding in the cellulose graft copolymer (adapted from Ref. [82]).

accessed by introducing other supramolecular interactions into the matrix as reversible physical networks, such as metal-ligand coordination, π - π stacking, and host-guest complexation.

2.3 Nitroxide-mediated polymerization (NMP)

NMP is the first and easiest CRP technology controlled by a reversible termination mechanism between the nitroxide moieties and growing propagating macroradicals. A wide range of monomers, including acrylates, styrene derivatives, vinylpyridines, acrylonitrile, acryl acid, acrylamide derivatives, cyclic ketene acetals, and miscellaneous, can be polymerized via NMP to develop well-defined polymers [31]. The primary advantage of NMP is the absence of post-treatment since no catalyst or bimolecular exchange is needed during the polymerization. However, the higher polymerization temperatures and lower polymerization rates limit the wide applications of NMP. To the best of our knowledge, only one study reported the synthesis of cellulose graft copolymers through homogeneous NMP strategy started from microcrystalline cellulose [83]. In this work, pretreated cellulose was dispersed in anhydrous tetrahydrofuran and reacted with 2-bromoisobutyryl bromide and pyridine to prepare Cell-BiB. As shown in **Figure 6**, Cell-BiB could react with 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) in DMF in the presence of sodium hydride (NaH) to obtain functionalized cellulose (Cell-TEMPO). At first, PS was grafted from cellulose backbone with Cell-TEMPO as macroinitiator in the absence of any catalyst to produce Cell-g-PS. Cell-g-(PMMA-*b*-PS) copolymer was synthesized by chain extension of above Cell-g-PS via the second NMP. Such kind of cellulose graft block copolymers may be applied as reinforcing agents, packing materials, and membrane materials. More efforts can be

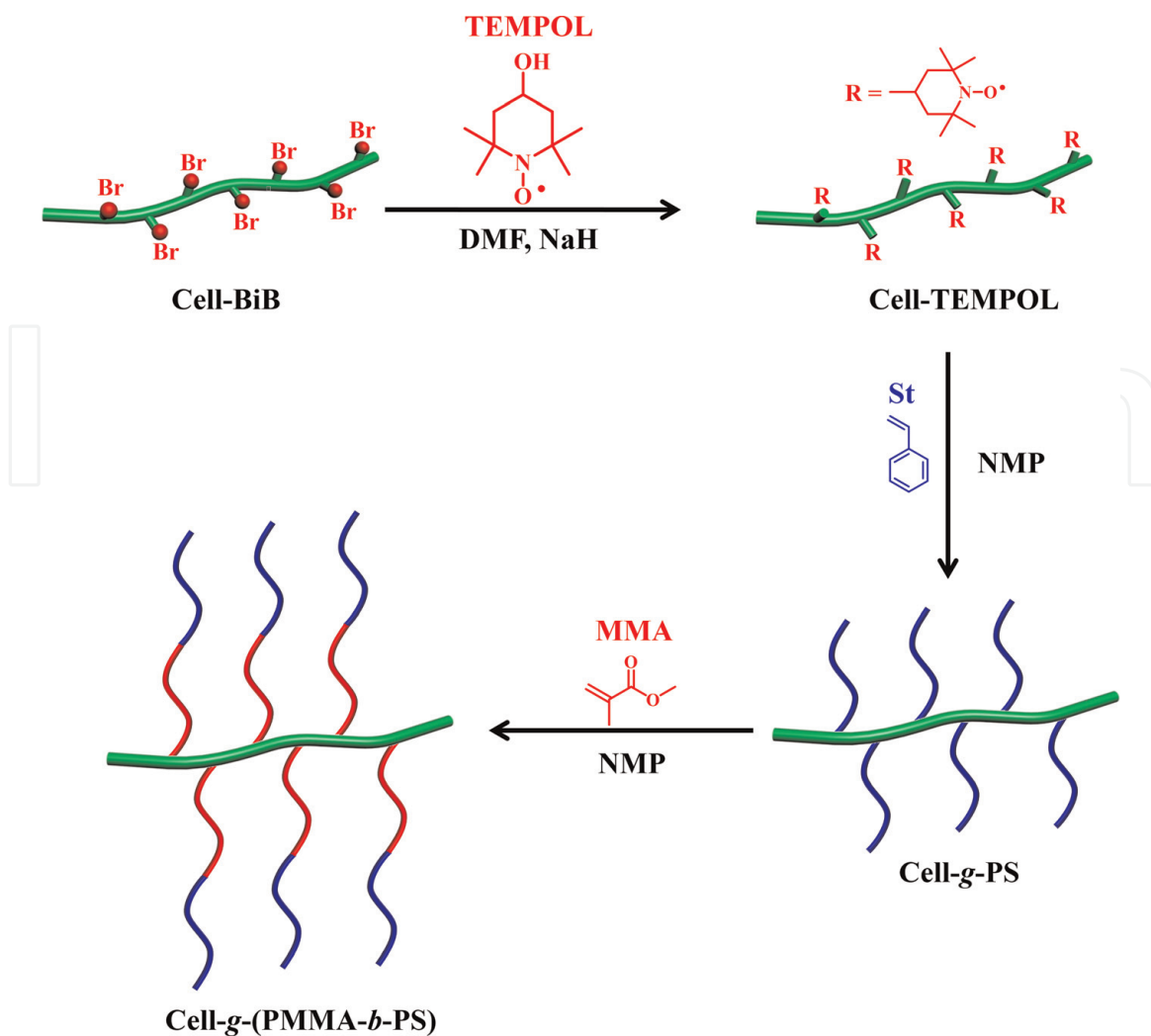


Figure 6. Schematic illustration for the synthesis of Cell-g-PS and Cell-g-(PMMA-b-PS) copolymers through NMP technique.

made in the future by grafting functional block polymers from cellulose via NMP to design novel stimuli-responsive hybrid materials with excellent macroscopic mechanical properties.

3. Perspective

CRPs are versatile and robust techniques to develop well-defined cellulose graft copolymers as novel thermoplastic and elastomers with desired properties for particular application demands. As the most adopted technique for cellulose graft copolymers, conventional ATRP suffers from the limitation of removing metal catalysts from the resultant products, which may cause undesired toxicity and coloration. Recently, new advances in ARTP have been reported, and metal-free ATRP has been developed to synthesize narrowly distributed polymers with well-defined structures by using photoredox organic catalysts under light irradiation instead of metal catalysts [84–86]. This new strategy can greatly promote the design and preparation of cellulose graft copolymers for different application fields. Cellulose graft copolymers show improved properties compared to the linear counterparts due to their unique molecular architectures, and the macroscopic performance of cellulose graft copolymers is affected by the degree of polymerization of cellulose

backbone, the grafting density (the average number of grafts per anhydroglucose unit), the degree of polymerization, and distribution of grafts. Various block and random copolymers have been grafted from cellulose via CRPs as described above. However, as exhibited in **Figure 7a**, heterograft and graft-on-graft architectures with cellulose as backbone remain unreported, and these interesting graft copolymers can be synthesized by the combination of RAFT polymerization and ATRP, ring-opening polymerization (ROP) and ATRP or ROP and RAFT polymerization.

Due to the increased attention paid on biomass-derived thermoplastics and elastomers, it becomes necessary and desirable to explore new monomers, which can be synthesized from bioresources, including lignins, terpenes, plant oils, rosin acids, and coumarins. For instance, bioresources, 7-hydroxyl-4-methylcoumarin, vanillin, guaiacol, and oleyl alcohol, can be used to synthesize sustainable monomers by reacting with acryloyl chloride, methacryloyl chloride or methacrylate anhydride as shown in **Figure 7b**. Among these monomers, 7-acryloyloxy-4-methylcoumarin (AMC), 7-methacryloyloxy-4-methylcoumarin (MMC), acrylated vanillin (AV), methacrylated vanillin (MV), acrylated guaiacol (AG), and methacrylated guaiacol (MG) can be utilized as rigid segments, while oleyl acrylate (OA) and oleyl methacrylate (OM) can be utilized as soft segments in the graft copolymers. Though there has been considerable progress, it is still challenging to

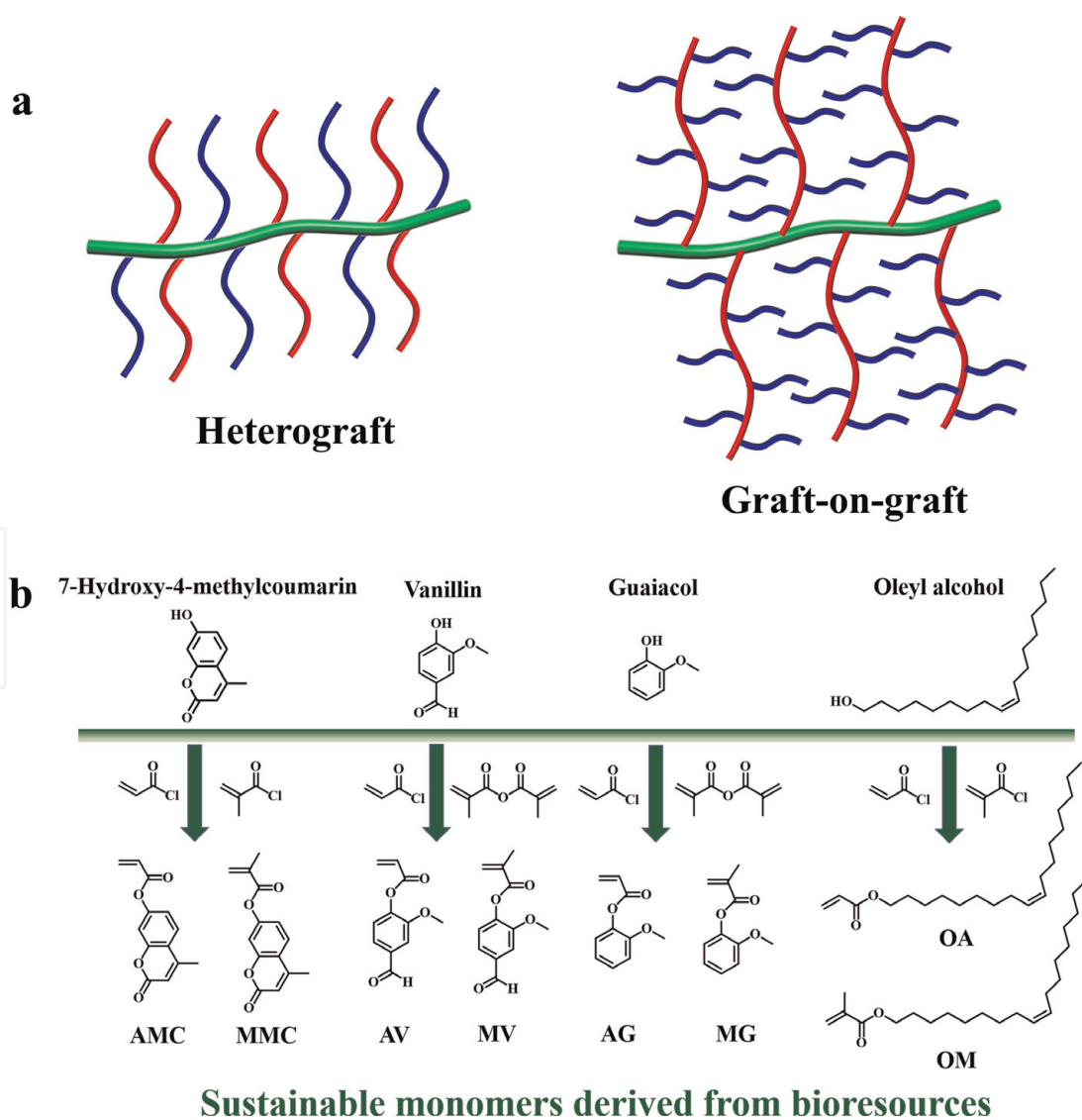


Figure 7. (a) Heterograft and graft-on-graft architectures of cellulose graft copolymers. (b) Sustainable monomers derived from different bioresources.

achieve breakthroughs for the development of cellulose graft copolymers with ultra-strong mechanical properties comparable to commercial petroleum-based products. The marriage of cellulose and novel bio-based monomers via CRPs can provide a variety of opportunities for sustainable materials ranging from thermoplastics to elastomers, and these fascinating materials can find a pyramid of applications in our daily life in the near future.

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Conflict of interest


The authors declare no conflict of interest.

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