Use of Xyloglucan as a Molecular Anchor for the Elaboration of Polymers from Cellulose Surfaces: A General Route for the Design of Biocomposites

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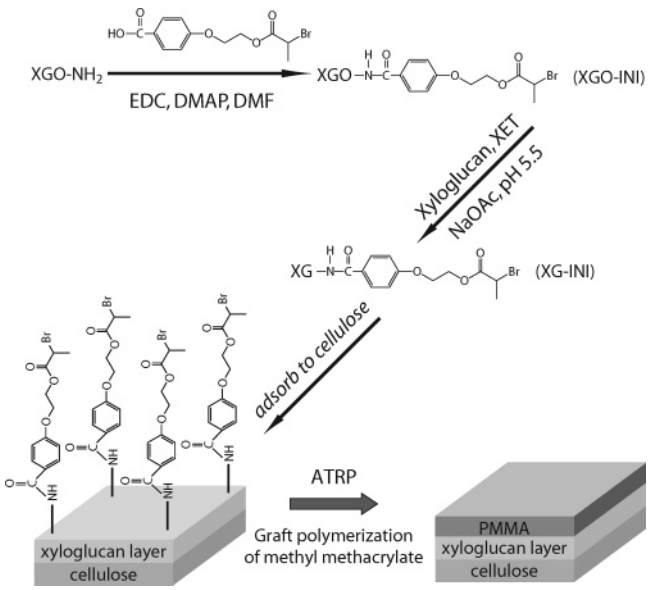
Introduction. In plastic composites with natural fibers as reinforcing elements, the hydrophilic nature of cellulose results in high moisture absorption and leads to weak interfacial interactions between the natural fibers and the matrix polymer.[1] A variety of chemical surface modification techniques have thus been devised to improve cellulose fiber−matrix adhesion.[2] In particular, growth of tethered (co)polymers from surface-anchored initiators, i.e., the "grafting from" technique, is an attractive method to tailor surface properties such as wetting, adhesion, compatibility, and antimicrobial activity.[3] Atom transfer radical polymerization (ATRP),[4] one of the most successful methods for controlled/"living" radical polymerization, has previously been utilized for "grafting from" processes on silicon,[5] gold,[6] and silica particle[7] surfaces. Recently, this technique has been extended to cellulose fibers through O-acylation with the initiator 2-bromoisobutyryl bromide and subsequent ATRP of methyl acrylate, 2-hydroxyethyl methacrylate, and 2-(dimethylamino)ethyl methacrylate.[3] However, such approaches require mild reaction conditions for the chemical immobilization of initiators onto cellulose fiber surfaces to preserve their native structure, morphology, biodegradability, and good mechanical properties.[8]

We have previously described a general chemo-enzymatic method for the efficient incorporation of chemical functionality onto cellulose surfaces without disruption of individual fibers or fiber networks.[9] This surface-specific modification relies upon the use of a transglycosylating enzyme, xyloglucan endotransglycosylase (XET, EC 2.4.1.207), to introduce chemically modified xyloglucan oligosaccharides (XGOs) into the plant polysaccharide xyloglucan (XG), which has a naturally high affinity for cellulose. To demonstrate the versatility of this method to tailor surface properties without impairing the inherent properties of cellulose fibers, we now report the controlled graft polymerization of methyl methacrylate (MMA) on cellulose fibers through a combination of the XET and ATRP techniques.

Scheme 1 illustrates our experimental approach for the preparation of poly(methyl methacrylate) (PMMA)-grafted cellulose filter papers. 4-[2-(2-Bromopropionyloxy)ethoxy]benzoic acid,[10] which bears both an excellent ATRP initiator moiety and a convenient chromophoric tag, was coupled to aminoalditol derivatives of XGOs ($XGO\text{-}NH_2$) and subsequently incorporated into XG with the XET enzyme. The small size of the $XGO\text{-}NH_2$ (ca. M_r 1200) allows for precise synthetic and analytical chemistry to ensure complete derivatization, followed by a specific, controllable enzyme reaction to tailor XG chain length.[9] Subsequent adsorption of initiator-bearing XG (XG-INI) to cellulose effectively tethers the initiator to the surface via a polyvalent interaction. (XGOs and derivatives do not themselves bind to cellulose; a XG chain >20 Glc units is required.) For the present work, Whatman Grade 1 qualitative filter paper was chosen as a convenient, high-purity cellulose fiber sheet, although the method is directly applicable to a wide variety of wood pulps and regenerated cellulose (ref 9 and unpublished data). Graft polymerization of MMA on the initiator-laden filter paper under appropriate ATRP conditions yields fibers that have altered surface properties.

Scheme 1. Principle of the Use of Xyloglucan as a Molecular Anchor for Elaborating Polymers from Cellulose Surfaces[a]



[a] Initiator-modified xyloglucan oligosaccharides (XGO-INI) are incorporated into xyloglucan (XG) by xyloglucan endotransglycosylase (XET) activity to produce initiator-modified xyloglucan (XG-INI). Adsorption of XG-INI to cellulose under mild conditions and subsequent atom transfer radical polymerization can be used to radically alter cellulose surface properties.

Results and Discussion. Immobilization of the initiator onto the cellulose surface with the XET technique were performed as follows. Initiator-modified XGOs, XGO-INI, was obtained by reductive amination of XGOs[9] and subsequent carbodiimide-mediated N-acylation with 4-[2-(2-bromopropionyloxy)ethoxy]benzoic acid (Supporting Information). A sample containing a 1 mL mixture of XG (1 g/L), XGO-INI (0.5 g/L), and XET (10 units)[9] in sodium acetate buffer (20 mM, pH 5.5) was incubated at 30 °C for 24 h. The reaction was terminated by heating at 75 °C for 10 min, and the denatured XET was removed by centrifugation at 12000*g* for 20 min. The initiator-modified XG (XG-INI) produced in this

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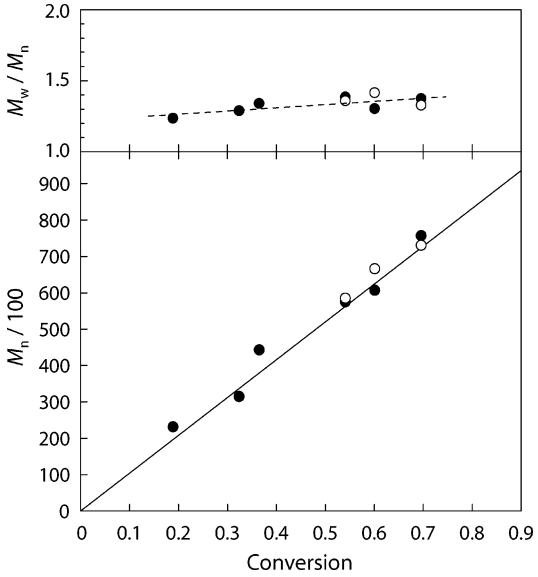

Figure 1. M_n and M_w/M_n of the free (solid circles) and cleaved polymers (open circles) as a function of monomer conversion for the ATRP of MMA at 90 °C. $[MMA]_0 = 4.7$ M (diphenyl ether solution); $[CuBr]_0 = 10$ mM; $[dHbipy]_0 = 20$ mM; $[MBP]_0 = 4.5$ mM. The solid line represents the theoretical M_n as a function of conversion; the dashed line represents a linear least-squares fit to M_w/M_n vs conversion data.

manner had a weight-average molecular mass (M_w) of 2.2×10^4 and a polydispersity index (M_w/M_n, where M_n is the number-average molecular mass) of 2.0.[11] A filter paper disk (Whatman Grade 1, Φ 1.5 cm, average mass 15 mg) was added to the supernatant and incubated at 25 °C for 24 h with orbital shaking. The cellulose disk was then removed and washed with water (3 × 5 mL) in an end-over-end mixer and dried under vacuum at 60 °C for 48 h. The amount of XGO-INI incorporated into XG and subsequently bound to the filter paper disk was 0.06 μmol, as determined from the amount of XGO-INI ($\epsilon_{250nm} = 11\,000$ cm^{-1} M^{-1} in H_2O) remaining in the wash solutions. Although only a single loading density was used in the present study, a key feature of the method is the ability to alter the amount of functional group on the cellulose surface by controlling the M_w and/or added amount of the chemo-enzymatically derivatized xyloglucan.[9]

Initiator-laden filters were then placed into Schlenk reaction tubes containing a homogeneous solution of MMA (2.0 mL, 19 mmol), methyl 2-bromopropionate (MBP, 2.0 μL, 18 μmol), CuBr (5.7 mg, 0.04 mmol), 4,4′-di-*n*-heptyl-2,2′-bipyridine[12] (dHbipy, 28.2 mg, 0.08 mmol), and diphenyl ether (2.0 mL, as solvent and internal standard) for graft ATRP. Following degassing by three freeze−pump−thaw cycles, the individual tubes were heated at 90 °C for 20, 40, 60, 120, 180, and 240 min with stirring (magnetic stir bar). The solution quickly turned reddish brown, and the mixture gradually turned viscous as the polymerization proceeded. The addition of methyl 2-bromopropionate as a sacrificial initiator in solution brought about well-controlled polymerization, with negligible contributions from transfer and termination reactions. As shown in Figure 1, the M_n of the free polymer[13] produced in solution increased linearly vs the conversion of MMA with a slope comparable to the theoretical value calculated from the initial ratio between the feed concentration of the monomer and free initiator. (The amount of xyloglucan-immobilized initiator on the surface was negligible relative to the sacrificial initiator in solution.) Additionally, the polydispersity index (M_w/M_n) was relatively low (Figure 1). Analysis of the grafted polymer after cleavage from the cellulose surface[13] indicated that the molecular mass distribution of the free polymer reflected that of the graft polymer (Figure 1), as has been previously observed for silicon oxide substrates.[7]

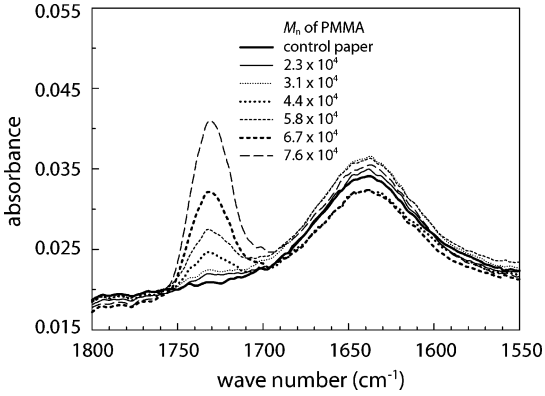

Figure 2. Reflectance FTIR spectra[14] of PMMA-grafted filter papers as a function of the M_n of PMMA. The control sample contained unmodified XG instead of XG-INI and was subjected to polymerization reaction conditions for 240 min.

The filter papers were washed repeatedly with chloroform after polymerization to confirm that the polymer chains were chemically anchored onto the cellulose fibers and not simply adsorbed from solution. Because of difficulties with using standard surface analysis techniques such as atomic force microscopy and ellipsometry on rough filter papers, further evidence for the surface grafting of PMMA was based on the appearance of the carbonyl peak ($\upsilon_{C=O}$) at 1732 cm^{-1} in ATR FTIR spectra,[14] the intensity of which increased with increasing M_n of the grafted PMMA (Figure 2). PMMA-grafted filter papers from reactions where the free polymers had $M_n < 5 \times 10^4$ (DP < 500) absorbed water very slowly, while no water adsorption could be detected for samples from reactions yielding $M_n > 5 \times 10^4$. The advancing angles (θ_a) for these highly hydrophobic cellulose papers were 120 ± 6°, 126 ± 5°, and 131 ± 5° for samples with graft polymers of M_n 5.8×10^4, 6.7×10^4, and 7.6×10^4, respectively. Control paper, which contained unmodified xyloglucan instead of XG-INI, exhibited no water repellant properties and no carbonyl absorption peak at 1732 cm^{-1} (Figure 2) when subjected to identical polymerization and extraction conditions.

Controlled ATRP carried out using an initiator specifically immobilized on cellulose fibers via the XG/XET system provides a new route for the generation of biocomposite materials. Attachment of the initiator by adsorption occurs under mild conditions that completely preserve fiber sheet (and therefore individual fiber) structures. Furthermore, the choice of initiators that can be bound in this fashion is essentially unlimited and, correspondingly, so is the range of accessible polymerization reactions. Extension of the method to biodegradable polymers such as poly(lactic acid) and poly(caprolactone), using appropriate initiators and polymerization methods (e.g., ring-opening polymerization), may provide a new route to environmentally friendly materials with predefined structures and properties. As such, the present method provides a novel approach for the immobilization of polymerization initiators on cellulose, which is complementary to previously established chemi-

cal routes. In an industrial process, however, it may be a significant advantage that the initiator is attached to a carrier molecule instead of directly to cellulose; preparation of carriers with various initiators can be easily achieved in separate, cost-efficient processes that are easier to control than the direct modification of cellulose.

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Supporting Information Available: Experimental procedures for the synthesis of XGO-INI. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Measured on a Waters 616 HPLC system with TSKgel G5000H_{HR} (7.8 mm × 30 cm, pore size 1 × 10^5 Å, particle size 5 μm) and G3000H_{HR} (7.8 mm × 30 cm, pore size 1500 Å, particle size 5 μm) columns and evaporative light scattering detection (Polymer Laboratories, PL-ELS 1000) versus pullulan M_w standards (Polymer Laboratories). Eluent: dimethylsulfoxide (DMSO), 1 mL/min; column temperature, 60 °C.
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(13) M_n and M_w/M_n of the free and graft polymers were measured on polystyrene-calibrated SEC with two TSKgel GMH_{HR}-M columns (7.8 mm × 30 cm, pore size 500−1 × 10^6 Å, particle size 5 μm) coupled to a Viscotek TDA model 301 detector, a VE 5200 GPC autosampler, a VE 1121 GPC solvent pump, and a VE 7510 GPC degasser, using tetrahydrofuran (THF) as the mobile phase. Graft polymers were cleaved from filter papers by acid hydrolysis in 1 mM $HCl_{(aq)}$ (1 mL) overnight. The solution was concentrated to dryness in vacuo, and the residue was dissolved in THF (500 μL) for SEC analysis. Limited recovery of material from papers with graft polymers of DP < 500 precluded precise analysis on these samples. Monomer conversion was determined from the concentration of residual monomers measured by ^{1}H NMR on a Bruker AM400 instrument using $CDCl_3$ as the solvent.
(14) Infrared spectra were recorded on a Perkin-Elmer Spectrum 2000 FTIR equipped with a MKII Golden Gate, single reflection attenuated total reflectance (ATR) system (Specac Ltd., London, U.K.) The ATR crystal was a MKII heated diamond 45° ATR top plate.

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