

ADSORPTION OF CELLOBIOSE-PENDANT POLYMERS TO A CELLULOSE MATRIX DETERMINED BY QUARTZ CRYSTAL MICROBALANCE ANALYSIS

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Cellobiose-pendant polymers were synthesized by radical polymerization and their affinity for a cellulose matrix was investigated by quartz crystal microbalance (QCM). A 2-(methacryloyloxy)ethylureido cellobiose (MOU-Cel) macromer was synthesized by coupling cellobiosylamine with 2-(methacryloyloxy)ethyl isocyanate followed by polymerization in an aqueous radical reaction system. The interaction of the resulting poly(MOU-Cel) with a pure cellulose matrix in water was evaluated by QCM analysis. Poly(MOU-Cel) was strongly adsorbed to the cellulose substrate, whereas neither cellobiose nor MOU-Cel macromer exhibited an attractive interaction with cellulose. This specific interaction was not inhibited by the presence of ionic contaminants, suggesting that multiple cellobiopyranose moieties in each polymer molecule might cooperatively enhance its affinity for cellulose. Moderate insertion of acrylamide units into the polymer backbone improved the affinity for cellulose, possibly due to an increased mobility of sugar side chains. Polymers such as these, with a high affinity for cellulose, have potential applications for the surface functionalization of cellulose-based materials, including paper products.

Keywords: Cellobiose; Cellulose; Sugar-pendant polymer; Non-electrostatic interaction; Quartz crystal microbalance

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INTRODUCTION

Cellulose is the most abundant, renewable carbohydrate resource and has been widely used as a raw material in a variety of applications (Klemm et al. 2005). Paper products are a typical example of cellulose-based materials. In paper-manufacturing processes, various functionalizations are carried out according to consumer demands, using a diverse array of additives, in an aqueous reaction media named the “wet-end” process. Most papermaking additives adsorb to cellulosic pulp fibers via electrostatic interactions during the aqueous wet-end process, and therefore their retention behaviors are quite sensitive to the ionic conditions in the process (Zhang 1999). We have studied a new concept for improving wet-end interactions, using cellulose-anchoring molecules that do not depend on conventional electrostatic interactions. Carbohydrate-binding modules (CBMs) of enzymes (Kitaoka and Tanaka 2001; Yokota et al. 2008, 2009a) and a direct dye (Yokota et al. 2009b) have been proposed as promising cellulose-anchors.

Papermaking polymers containing such functional molecules exhibited both effective retention and good performance as paper-strengthening additives. However, some problems remain to be solved, e.g. the high cost and low production volumes of CBM-modified polymers, and the inhibition of dye-conjugated polymer retention by cationic multivalent ions (Yokota et al. 2008, 2009a, 2009b).

Recently, significant interest has been shown in carboxymethylcellulose (CMC) for versatile applications in practical paper-manufacturing processes, e.g. the treatment of pulp fibers with CMC during kraft pulping (Ekevåg et al. 2004) or oxygen delignification (Kontturi, E. et al. 2008), various surface modifications in wet-end systems (Laine et al. 2000; Watanabe et al. 2004; Blomstedt et al. 2007), and the prevention of vessel picking during printing (Rakkolainen et al. 2009). Concerning wet-end applications, anionic CMC molecules were reported to adsorb onto negatively-charged pulp fibers, regardless of electrostatic repulsion by adjusting the degree of substitution (DS) of CMC, and the pH of wet end (Laine et al. 2000; Blomstedt et al. 2007). CMCs with relatively low DS exhibit higher adsorptive property to pulp fibers, possibly involving specific interactions due to a structural homology with cellulose. Hence, cellobiose, which is a structural subunit of cellulose, is expected to be a cellulose-anchoring molecule candidate. In our previous study, β -D-cellobiosylamine was successfully conjugated with anionic poly(acrylamide) (A-PAM) via a condensation reaction (Yokota et al. 2009c). The A-PAM containing cellobiose residues (CB-A-PAM) was tightly adsorbed on the cellulose matrix, resulting in its good performance as a paper-strengthening agent. However, the performance of CB-A-PAM was sensitive to ionic conditions of wet end, possibly due to a negative effect of unmodified units in a polymer backbone, e.g. acrylic acid.

In the present work, synthetic polymers containing cellobiose moieties in their side chains were designed by a radical polymerization of nonionic polymerizable sugar macromers. The fundamental affinity of sugar-pendant polymers for cellulose in an aqueous system was investigated by quartz crystal microbalance (QCM) analysis.

EXPERIMENTAL

Materials

Cellobiose and glucose were purchased from Sigma-Aldrich Corp (St. Louis, MO, USA). Lignosulfonic acid sodium salt (LSA-Na, Sigma-Aldrich) and calcium chloride (CaCl_2 , Wako Pure Industries, Ltd., Osaka, Japan) were used as model contaminants of anionic trash and multivalent cations, respectively. Poly(diallyldimethylammonium chloride) (PDADMAC, Sigma-Aldrich) and poly(vinylsulfonate potassium) (PVSK, Wako) were utilized as standard polymers for colloid titration. 2-(Methacryloyloxy)ethyl isocyanate (MOI), acrylamide (AM) and other chemicals were of reagent grade, and were used as-purchased.

Synthesis of Glycosylamines

Cellobiosylamine was synthesized in a saturated aqueous ammonium solution (Kallin et al. 1989; Yokota et al. 2009c). D-Cellobiose (3.0 g) and ammonium hydrogen carbonate (1.5 g) were added to a 10% ammonia solution (20 mL) with stirring at 37°C

for 48 h. The cellobiosylamine obtained was purified by lyophilization and rehydration, repeated five times. Glucosylamine was prepared from D-glucose in a similar matter. ^{13}C -NMR (100 MHz, D_2O) Cellobiosylamine: δ 61.2; 61.6 (C-6, 6'), 70.5 (C-4'), 74.2; 75.1; 76.1; 76.5; 76.7; 77.0 (C-2, 3, 5, 2', 3', 5'), 80.0 (C-4), 85.9 (C-N), and 103.6 (C-1'). Glucosylamine: δ 61.3 (C-6), 70.1 (C-4), 72.5; 74.7; 76.2; 76.3; 77.0; 77.3 (C-2, 3, 5), and 83.4; 85.4 (C-N).

Synthesis of Polymerizable Sugar Macromers

Each glycosylamine (5.0 g) was dissolved in a 1.0 mM aqueous KOH solution (50 mL). 46 mL of MOI was added to the reaction medium and stirred at 3°C for 12 h. The precipitated by-product was removed by filtration. The filtrate was washed three times with diethyl ether to remove traces of unreacted MOI, and then the water phase was freeze-dried. The resultant 2-(methacryloyloxy)ethylureido sugar (MOU-sugar) was dissolved in an 80% methanol/ H_2O solution and purified by recrystallization from diethyl ether/acetone. ^{13}C -NMR (100 MHz, D_2O) MOU cellobiose (MOU-Cel): δ 18.4 ($-\text{CH}_3$), 39.6 ($-\text{CH}_2-\text{NH}-$), 61.6–103.5 (from sugar), 65.2 ($-\text{O}-\text{CH}_2-$), 127.9 ($\text{CH}_2=$), 136.8 ($-\text{C}=\text{C}$), 160.5 ($-\text{NH}-\text{CO}-\text{NH}-$), and 170.7 ($-\text{CO}_2-$). MOU glucose (MOU-Glc): δ 17.8 ($-\text{CH}_3$), 39.0 ($-\text{CH}_2-\text{NH}-$), 61.1–77.4 (from sugar), 64.7 ($-\text{O}-\text{CH}_2-$), 127.4 ($\text{CH}_2=$), 136.2 ($-\text{C}=\text{C}$), 159.9 ($-\text{NH}-\text{CO}-\text{NH}-$), and 170.1 ($-\text{CO}_2-$).

Synthesis of Sugar-pendant Polymers

Poly(MOU-sugar)

N,N,N',N'-Tetramethylethylenediamine (TEMED, 40 μL) and ammonium persulfate (APS, 20 mg) were added to deionized (DI) water (16 mL) containing an MOU-sugar (2.6 g). The mixture was stirred under a nitrogen atmosphere at 0°C for 2 h, then at room temperature for 12 h. The crude polymer obtained was purified by dialyzing with Spectra/Por[®] 3 (3500 molecular weight cut-off, Spectrum Laboratories, Inc., Rancho Dominguez, CA, USA) for 3 days. Finally, the product was freeze-dried.

Poly(MOU-Cel-co-AM)

Copolymers were synthesized from MOU-Cel and AM monomers. The molar ratio of MOU-Cel/AM dosage was adjusted to 10/1 (copolymer **1**), 5/1 (copolymer **2**), or 1/1 (copolymer **3**). Each mixture (2.6 g) was dissolved in DI water and polymerized similar to poly(MOU-sugar). The copolymers were dialyzed for 3 days using the Spectra/Por[®] 3 and the purified copolymers were then freeze-dried.

Characterization of Sugar-pendant Polymers

Charge densities (CDs) of synthesized polymers were determined by colloid titration (Tanaka and Sakamoto 1993). 10^{-4} N PDADMAC (CD 6.2 meq. g^{-1}) and 10^{-4} N PVS K (CD 6.2 meq. g^{-1}) were used as cationic and anionic standard polyelectrolytes, respectively. The end point was determined using acriflavine hydrochloride with a fluorescence spectrophotometer (Hitachi F-3010, Hitachi, Ltd., Tokyo, Japan). The excitation and emission wavelengths were 380 nm and 490 nm, respectively.

Size exclusion chromatography (SEC) measurements were carried out using an internal refractive index detector (RI-8022, Tosoh Corp., Tokyo, Japan) and two TSK gel

α -M columns (Tosoh Corp.) under the following conditions: eluent 10% (w/v) lithium chloride aqueous solution; flow rate 1.0 mL min⁻¹; temperature 40°C. Calibration curves for determining the molecular weight of synthesized polymers were obtained by using poly(ethylene oxide) (PEO) standards.

Measurement of Polymer Adsorption to Cellulose

A QCM instrument (AFFINIXQ, Initium Inc., Tokyo, Japan) with a 27 MHz AT-cut quartz crystal (gold coated) was used to quantitatively estimate the affinity of sugar-pendant polymers for a cellulose nanolayer formed on the gold surface of a QCM sensor chip. Cellulose nanolayers were prepared on the QCM sensor chip with a cellulose thiosemicarbazone (cellulose-TSC)/*N*-methylmorpholine-*N*-oxide/H₂O solution, following our previously published methods (Yokota et al. 2007). The frequency changes of the sensor chip crystal were monitored in a dilute aqueous solution of each polymer at 25°C, stirred at 2500 rpm. LSA-Na (10⁻⁶ wt%) or CaCl₂ (1 μ M) aqueous solutions were used as model contaminants to simulate those found in papermaking processes. The quartz probe parameters were as follows: density 2648 kg m⁻³; elastic shear modulus 2.947 \times 10¹⁰ kg m⁻¹ s⁻²; surface area of gold electrode 4.9 mm². In this system, 1 Hz of frequency change corresponded to 30 pg of weight change, calculated by Sauerbrey's equation (Sauerbrey 1959).

RESULTS AND DISCUSSION

Characterization of Synthetic Sugar-pendant Polymers

Various sugar-pendant polymers have been synthesized, and their fundamental characteristics and applications studied in the physicochemical and biomedical fields (Nagaoka et al. 2004; Hoshiba et al. 2006; Park et al. 2007; Kaneko et al. 2007; Enomoto-Rogers et al. 2009). In the present work, a cellobiose-pendant polymer was synthesized from cellobiose by a facile, three-step reaction as previously reported by Nagaoka et al. (Fig. 1).

Cellobiosylamine was first prepared by reductive amination of cellobiose (Kallin et al. 1989), followed by the synthesis of MOU-Cel by the mild reaction between cellobiosylamine and MOI. Crude poly(MOU-Cel), obtained via free-radical polymerization, was purified by dialyzing to remove unreacted residues. A poly(MOU-Glc) was synthesized as a control by a similar procedure. Table 1 lists the molecular weight and the CD value of the sugar-pendant polymers as determined by SEC and colloid titration, respectively.

The molecular weight and distribution of synthesized poly(MOU-sugar) samples were determined by SEC analysis using PEO standards. The molecular weight of poly(MOU-Cel) was significantly higher than that of poly(MOU-Glc), in agreement with the previous report (Nagaoka et al. 2004). The difference in the molecular weight of MOU-sugar polymers may be attributed to the specific conformation of each polymer, caused by the self-assembly of sugar side chains in the aqueous lithium chloride eluent. This unique molecular property implies the successful synthesis of the cellobiose-pendant

polymer. In addition, charge densities of the synthesized sugar-pendant polymers, which were measured by colloid titration, were little as to be neglected, i.e. neutral (nonionic).

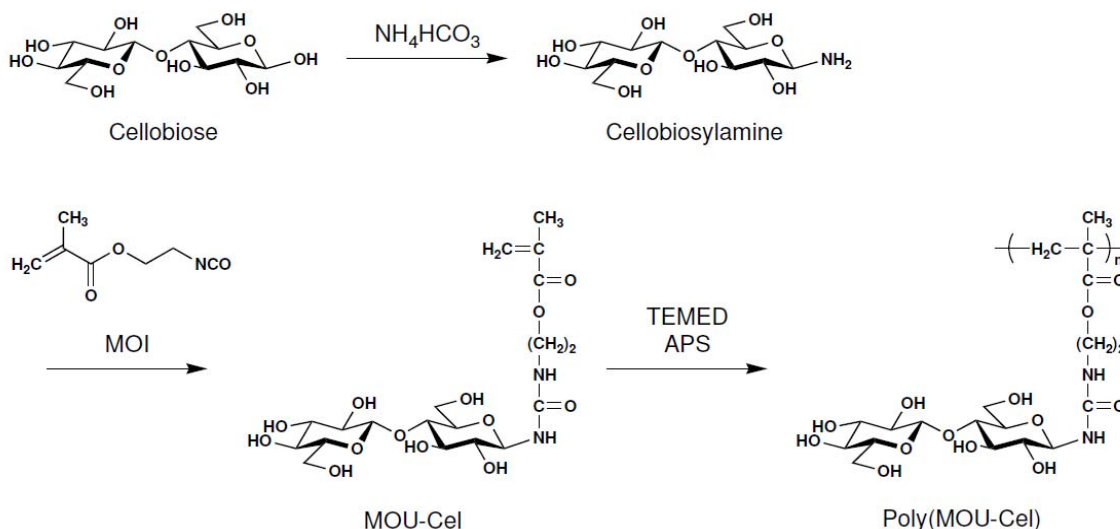


Fig. 1. Schematic representation of the synthesis of cellobiose-pendant polymer.

Table 1. Molecular Weight and Charge Density (CD) of Sugar-pendant Polymers

	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	M_w/M_n	CD (meq. g^{-1})
Poly(MOU-Cel)	1.49	0.62	2.40	0.00
Poly(MOU-Glc)	0.74	0.37	2.00	0.00
Copolymer 1	1.65	0.66	2.50	0.00
Copolymer 2	1.97	0.99	1.99	0.00
Copolymer 3	3.88	1.82	2.13	0.00

Affinity of Poly(MOU-sugar) for Cellulose

The affinity of poly(MOU-sugar) samples for cellulose was estimated from the mass of polymers adsorbed to a cellulose matrix surface in DI water. Adsorbed mass was measured by QCM, a sensitive tool that can precisely detect mass variations of the order of picograms. A model cellulose substrate was covalently immobilized onto a gold-coated QCM sensor chip by the self-assembling chemisorption of cellulose-TSC, following our previously reported method (Yokota et al. 2007). This self-assembled cellulose nanolayer has a crystal structure similar to native cellulose (cellulose I), and its surface comprises pure cellulose molecules with negligible ionic carboxyl groups (Yokota et al. 2007). MOU-sugar polymers and their precursors were subjected to QCM measurements. Figure 2 illustrates the typical QCM sensorgrams obtained using cellulose-modified QCM sensor chip in DI water. The resonance frequency of the sensor chip drastically decreased by the injection of poly(MOU-Cel), while negligible shift of QCM frequency was detected by adding free cellobiose or MOU-Cel macromer. This indicates that poly(MOU-Cel) had a strong affinity for the cellulose fixed on QCM sensor chip, although its chemical components, cellobiose and/or MOU-Cel macromer, had nearly no interaction with the cellulose matrix.

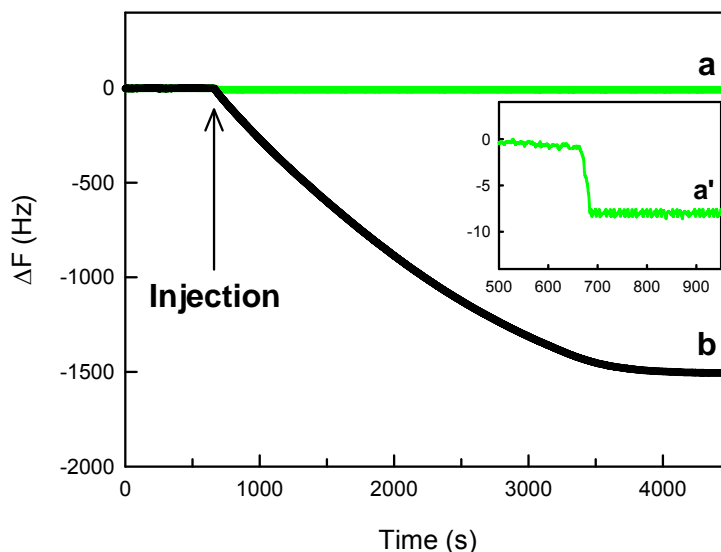


Fig. 2. QCM profiles for the adsorption of (a) cellobiose (or MOU-Cel macromer) and (b) poly(MOU-Cel) on a cellulose matrix in a DI water. (a'): the magnified sensorgram of (a).

The binding mass (mg m^{-2}) of MOU-sugar polymers and their precursors on a cellulose matrix was roughly estimated from the QCM frequency changes detected (Table 2). Neither free cellobiose nor MOU-Cel bound to the cellulose substrate. By contrast, significant adsorption of poly(MOU-Cel) to the cellulose matrix was detected.

Table 2. Mass of Sugar-pendant Polymers Bound onto the Cellulose Substrate

Sugar ligand	Binding mass (mg m^{-2})		
	Free sugar	MOU-sugar	Poly(MOU-sugar)
Cellobiose	0.02	0.02	16.77
Glucose	0.03	0.02	12.19

The adsorption behavior of papermaking polyelectrolytes onto slightly-charged cellulose films via electrostatic attractions was investigated in detail by QCM analysis with dissipation (Tammelin et al. 2006; Kontturi, K. S. et al. 2008; Enarsson and Wågberg 2009). On the other hand, in this study negligible adsorption of typical polyelectrolytes such as anionic PAM and cationic PDADMAC to the cellulose-modified QCM chip was confirmed, as shown in Fig. 3. Thus, the nonionic cellulose nanolayer fixed on QCM sensor chip is suitable for detecting only non-electrostatic interaction between sugar-pendant polymers and a cellulose matrix. QCM analysis presumably indicated that the multiple cellobiose moieties tethered on the polymer backbone interacted cooperatively with cellulose, leading to a high cellulose-affinity. This may be similar to the multivalent effect of sugar-sugar interactions that occurs on cell surfaces *in vivo* (Lee and Lee 2000; Schwarz et al. 2003). Glucose-conjugated polymers exhibited similar adsorptive behavior, but the total binding mass of poly(MOU-Glc) was significantly lower than that of poly(MOU-Cel). Cellulose is composed of β -1,4-linked

D-glucose units, with each adjacent unit taking a turn of 180 degrees. Therefore, cellobiose is a substantial unit of cellulose, resulted in the preferable adsorption of poly(MOU-Cel) to the cellulose matrix. Umemura and coworkers reported that cellohexaose packed more tightly than cellopentaose in water (Umemura et al. 2004), which suggests that the assembling ability of β -1,4 glucan is sensitive to chain length. Hence, for sugar-pendant polymers, the length of the sugar side-chain may be a key factor in determining their affinity for cellulose. Nonionic PEO, which can form hydrogen bonding with cellulose, showed slight affinity for the cellulose substrate (0.09 mg m^{-2}), as illustrated in Fig. 3. Thus the cellobiopyranose-ring structure would give rise to a strong attraction between sugar-pendant polymers and the cellulose matrix.

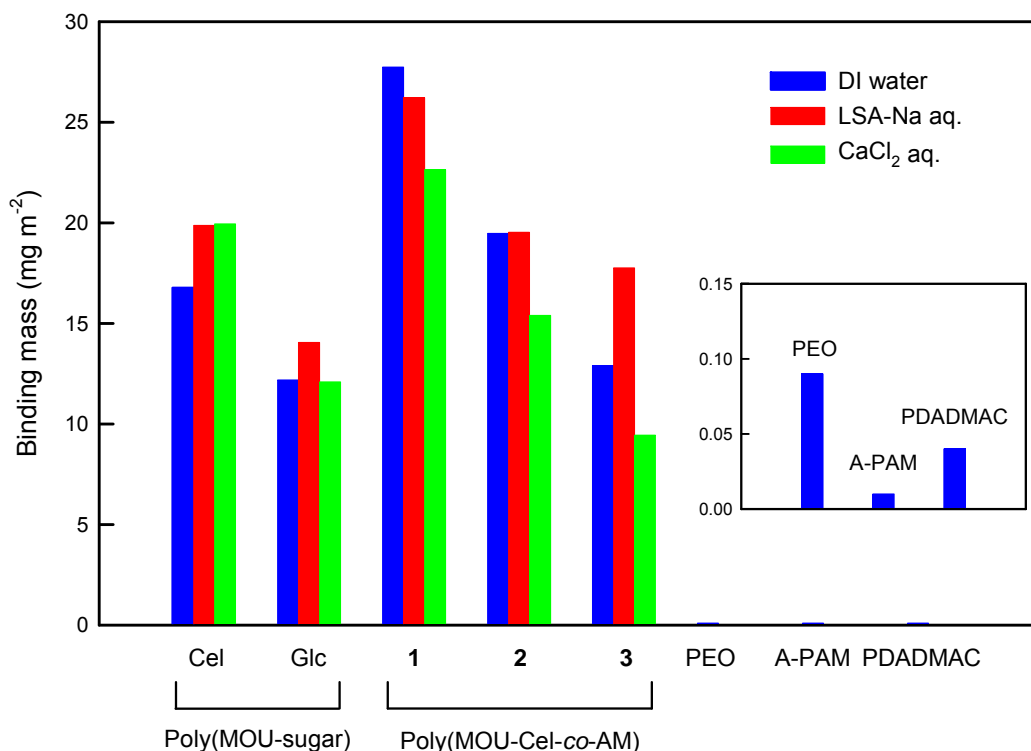


Fig. 3. Binding mass of sugar-pendant polymers and typical papermaking polymers bound onto the cellulose matrix in an aqueous system with or without ionic contaminants.

Affinity of Poly(MOU-Cel-co-AM) for Cellulose

Although it was confirmed in this study that poly(MOU-sugar) interacted strongly with a solid-state cellulose matrix, it was reported that MOU-Cel homopolymer formed spherical aggregates via intra- and intermolecular assembly in water (Nagaoka et al. 2004). Therefore, it is very likely that such polymers will have poor performance as paper-strengthening agents. Hence, MOU-Cel was copolymerized with an AM monomer to weaken the intra- and intermolecular assembly of cellobiose-pendant polymers. Three types of copolymers were synthesized by controlling the monomer ratios (MOU-Cel/AM) to 10/1 (copolymer **1**), 5/1 (copolymer **2**), and 1/1 (copolymer **3**), respectively. The synthesis approach used in this study, which is a simple free-radical polymerization from the mixture of MOU-Cel and AM monomers, possibly provided random copolymers;

however, the detailed chemical structures of obtained poly(MOU-Cel-co-AM)s are not clear at this stage. All polymers had zero electrostatic charge, being neutral (Table 1).

The density of cellobiose moieties conjugated with a polymer backbone must be a striking factor for the affinity of sugar-pendant polymers for cellulose. However, the binding mass of copolymer **1** was significantly higher than that of homopolymer (Fig. 3). This result suggests that a moderate insertion of AM units was effective for enhancing the affinity for cellulose, possibly due to higher molecular flexibility of cellobiose-pendant polymers. On the other hand, the lower binding mass of copolymer **3** than homopolymer was also confirmed, as shown in Fig. 3, suggesting poor affinity for cellulose because of less cellobiose content. Therefore, both flexibility and cellobiose density of polymers were of great importance for the functional design of high-performance cellobiose-pendant polymers. Several recent papers have indicated that the adsorption phenomena of water-soluble polymers are affected by the swelling behavior of cellulose substrates and by the viscoelastic characteristics of adsorbed polymers (Fält et al. 2003; Tammelin et al. 2006; Kontturi, K. S. et al. 2008). Hence, further analysis (e.g. QCM with dissipation) is required to elucidate unique adsorption behavior of cellobiose-pendant polymers, and it would provide precise information on the interaction between sugar-pendant polymers and a cellulose matrix in aqueous systems.

Cellulose-affinity of Sugar-pendant Polymer in Contaminated System

One of the most serious problems in papermaking is that charged contaminants, known to accumulate in the wet-end process, significantly interfere with the adsorption of ionic additives to pulp fibers (Zhang et al. 1999). Hence, the influence of contaminants on the adsorption of sugar-pendant polymers onto cellulose substrates was evaluated by QCM analysis. Papermaking polyelectrolytes act in a complicated manner in practical wet-end processes containing various charged contaminants; however in this study LSA-Na and CaCl_2 were used as model compounds of anionic contaminants and multivalent cations, respectively, for a simple, lab-level investigation. Figure 3 compares the binding mass of each polymer to the cellulose-modified QCM chip under the contaminant model conditions. Neither model contaminant significantly affected the affinity of sugar-pendant polymers for cellulose, though the binding mass of copolymers tended to be reduced by adding CaCl_2 . Cellobiose itself is unaffected by Ca^{2+} (Walzel et al. 1996). Therefore the negative effect of CaCl_2 addition on polymer adsorption might be attributed to coordination of the inserted AM units with Ca^{2+} ions (Jiraprasertkul et al. 2006). However, the mass of copolymer **1** bound remained sufficient and was higher than poly(MOU-Cel). Thus nonionic cellobiose-pendant polymers adsorbed stably to the cellulose matrix even under contaminated conditions, unlike common wet-end polyelectrolytes (Yokota et al. 2008) and previously-reported CB-A-PAM (Yokota et al. 2009c). In the case of CMC with a high DS, cationic electrolytes screen the electrostatic repulsion between anionic fibers and CMC (Laine et al. 2000). Therefore, the adsorption mechanism of sugar-pendant polymer is different from that of CMC, and possibly attributed to non-electrostatic interactions, based on the intermolecular assembly of structural carbohydrates. Such polymers would perform well as paper-strengthening agents, avoiding a number of problems in papermaking processes.

CONCLUSIONS

1. Nonionic sugar-pendant polymers with non-electrostatic cellulose-binding ability were successfully prepared by a radical polymerization of MOU-derivatized glyco-macromers.
2. Sugar-pendant polymers strongly adsorbed to a cellulose matrix surface even in the presence of ionic contaminants, whereas free sugars and sugar-macromers alone had negligible affinity for cellulose. The density of sugar moieties in and molecular flexibility of the polymer chain was an important factor for cellulose-affinity.
3. The sugar moieties in the polymer chains may interact cooperatively with cellulose via a unique molecular assembly of structurally compatible carbohydrates, resulting in an improvement in polymer adsorption, independent of conventional electrostatic interactions. This may open up new possibilities not only for papermaking applications but also for the functional design of glyco-materials via carbohydrate-carbohydrate interactions.

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