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COMMUNICATION TO THE EDITOR

Chemical Modification of a Lignin Model Polymer via Arylboronate Ester Formation under Mild Reaction Conditions

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Lignin is the most abundant aromatic polymer on earth and, as such, represents a vast and renewable reservoir of latent polymeric materials or aromatic chemicals. The industrial conversion of wood to paper separates lignin from the cellulosic material and in the process generates ~50 million tons of lignin annually.[1−3] In addition to these already large quantities of technical lignins, biorefineries are expected to generate massive quantities of lignin en route to cellulosic ethanol and other biomass-based products.[4,5] Considering the current and future widespread availability of technical lignins, there is considerable interest in increasing the utilization of these materials in a wide assortment of specialty areas.[4]

Chemical modification of technical lignins is a well-established field of research that spans organic chemistry, wood chemistry, and polymeric materials chemistry.[6,7] By manipulating lignin's reactive functional groups, it is possible to adjust the physical and chemical properties of the material in order to achieve enhanced solubility, increased blend compatibility, and improved mechanical properties.[7−19] The heterogeneous polymeric structure of lignins is rich with alcohol and phenol functional groups; therefore, the majority of modification strategies have focused on esterification[8−10,15] or etherification[20,21] reactions.

In this Communication we report a new approach to the chemical modification of a lignin-like polymer based on the facile formation of arylboronate ester bonds (Figure 1). As a first step in developing this new modification strategy, we have synthesized and fully characterized a series of boron-modified synthetic lignin polymers with the long-term goal of applying this methodology to organosolv lignins. Our chemical modification strategy is based on the formation of arylboronate ester linkages between the 1,3-diols of the synthetic lignin and arylboronic acids. Surprisingly, despite the well-known reaction of arylboronic acids with 1,3-diols[22] *and* the presence of 1,3-diols in lignin's most prevalent structural subunit (β-O-4), the binding of arylboronic acids to lignin has not been systematically explored as a means of chemical modification.[23] Considering arylboronate ester formation can be mechanochemically[24,25] or thermally[26,27] induced, we envision future applications of our synthetic methodology in the development of lignin-based thermoplastics.

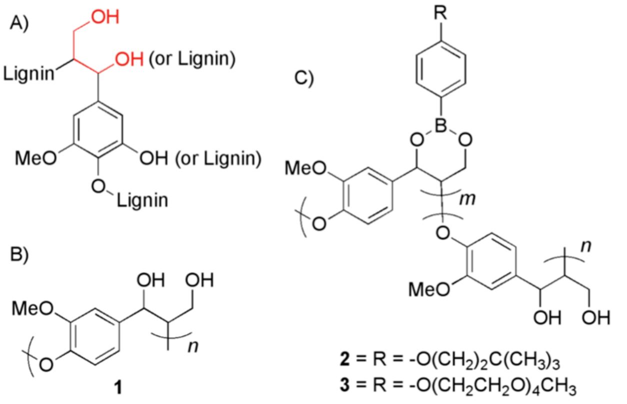

Figure 1. (A) Simplified representation of the lignin β-O-4 structural motif highlighting the 1,3-diol moiety (red). (B) Kishimoto et al.'s synthetic lignin polymer.[28−30] (C) Arylboronate ester-modified artificial lignins synthesized and characterized herein.

Polymer **1** was prepared and purified according to literature procedures.[28−30] Molecular weight characterization of polymer **1** was facilitated by acylation of the free hydroxy groups, as reported by Kishimoto et al., affording **4** quantitatively (Scheme 1).[30] Small molecule arylboronic acids **5** and **6** were prepared in good overall yield, and their synthesis is described in the Supporting Information. Arylboronic acid modifying agents were reacted with polymer **1** in a substoichiometric manner under mildly dehydrating conditions. The solubility profile of polymer **1** versus the borylated polymers **2** and **3** gives qualitative evidence that chemical modification has taken place. Whereas polymer **1** is completely insoluble in most organic solvents (except dimethyl sulfoxide), polymers **2** and **3** are freely soluble in a wide range of organic solvents including ethers, halogenated solvents, and aromatic solvents, making these materials more applicable to solution processing. There were two main reasons for targeting a substoichiometric loading of the arylboronic acid modifying agents. First, it is known that the β-O-4 structural motif comprises ~50% of the polymeric linkages in technical lignins such as organosolv.[3,28,31] Therefore, a substoichiometric loading of lignin model polymer **1** more closely mimics the loading achievable with actual technical lignins. Second, targeting a substoichiometric loading eliminates the need to purify the resultant polymers as the only other byproduct from the reaction (assuming quantitative arylboronate ester formation) is water.

Boron-modified polymers **2** and **3** were analyzed by ^{1}H, ^{13}C, and ^{11}B NMR as well as FT-IR spectroscopy in order to establish the spectroscopic signatures associated with the arylboronate ester linkage. Discrete monomeric arylboronate esters **7** and **8** were prepared from **5** and **6**, respectively, and characterized (Scheme 1, see also the Supporting Information) in order to provide comparative spectroscopic data and aid in characterizing the borylated polymeric materials. Under the substoichiometric reaction conditions, the arylboronate ester product is expected to dominate; however, side reactions were considered. One alternative reaction pathway for the arylboronic acid modifying agents is dehydration, but not covalent attachment, giving arylboroxine products. ^{1}H NMR is the most reliable means of differentiating arylboronic, side-chain appended arylboronate ester, and arylboroxine as aromatic protons *ortho* to the boron substituent are highly sensitive to the type of boron linkage present.[32−36] The ^{1}H NMR of both polymer **2** (see Figure 2) and **3** show characteristic arylboronate ester resonances at 7.8 ppm and lack resonances that would indicate the presence of arylboroxine (8.2 ppm) or unreacted arylboronic acid (7.6 ppm) in chloroform. FT-IR analysis further supports the presence of arylboronate ester linkages with diagnostic bands present at 1315 cm^{-1} (B−O stretch) and 640 cm^{-1} (B−O bend). Arylboroxines typically display a broad FT-IR band near 1350 cm^{-1}; however, this band was not observed in boron-modified polymers

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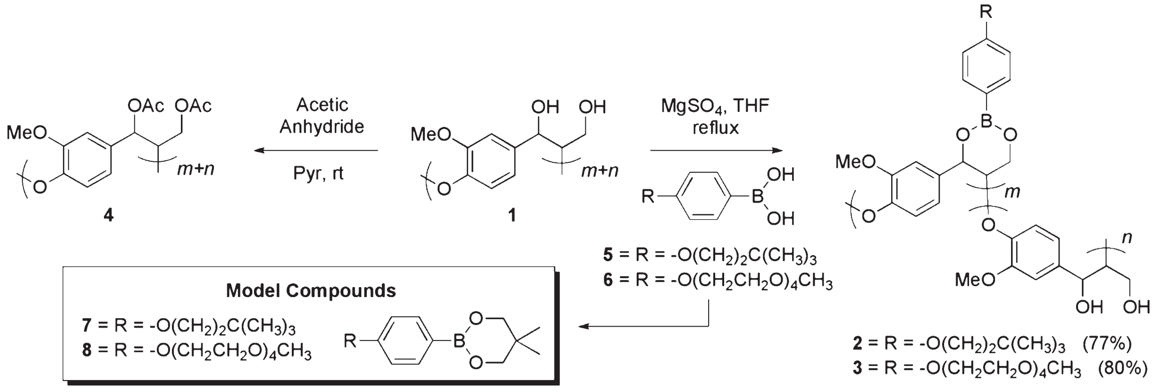
Scheme 1. Chemical Modification of Polymer 1 via Side-Chain Arylboronate Ester Formation under Mildly Dehydrating Reaction Conditions



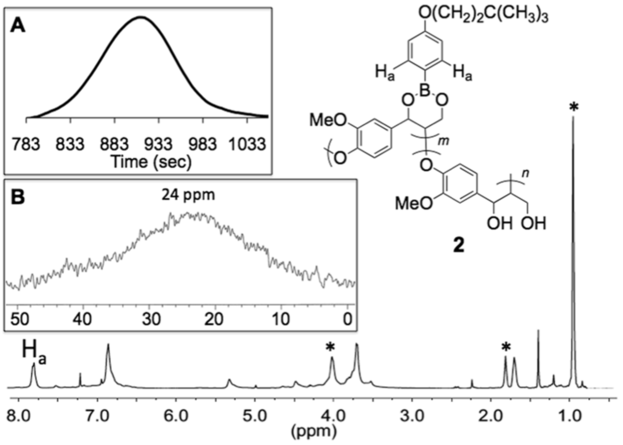


Figure 2. ^{1}H NMR (CDCl$_3$) of arylboronate ester-modified polymer **2**. The protons residing *ortho* to the boron substituent are labeled H$_a$, and their chemical shift is diagnostic of an arylboronate ester linkage. The asterisk (∗) identifies the alkyl protons also associated with the boron modifying agent. Polymer **2**'s GPC profile (THF) and ^{11}B NMR (CDCl$_3$) spectrum are shown in inset A and B, respectively.

2 and **3**.[37−39] ^{11}B NMR of polymers **2** and **3** also exhibit chemical shifts diagnostic of a trigonal boronate ester at 24 and 20 ppm, respectively. The ^{11}B chemical shift data for **2** and **3** compare well to model neopentyl glycol esters **7** and **8** which have ^{11}B chemical shifts of 26 ppm. The ^{11}B NMR chemical shift data for **2** and **3** also corresponds well with Lavigne's poly(dioxaborolane)s (20−24 ppm) where six-member arylboronate esters form in the main chain of the polymer.[40]

Polymers **2**−**4** were analyzed by gel permeation chromatography (GPC) in THF against polystyrene standards, and the results are summarized in Table 1. The acylation reaction providing polymer **4** proceeds quantitatively, and the molecular weight data acquired on this polymer were used for comparative analysis with polymers **2** and **3**. Although arylboronate ester bonds are best described as dynamic covalent, our THF-based GPC results (as well as other GPC studies involving arylboronate ester materials[27]) indicate that the key arylboronate ester linkages remain intact under the measurement conditions. Polymers **2** and **3** exhibit molecular weight increases in accordance with the targeted degree of functionalization.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were preformed on polymers **1**−**4** to examine their thermal behavior (see Supporting Information). Although polymers **1** and **4** were previously reported by Kishimoto et al., the thermal properties of these polymers were not disclosed. Side-chain modification of the hydroxyl-containing base polymer **1** resulted in significant decrease in the glass transition (T_g) for all chemically modified polymers (**2**−**4**). Comparing the three side-chain-modified polymers (**2**−**4**), borylated polymer **3** shows the largest decrease in T_g relative to the base polymer **1**. The T_g of polymer **3**, despite being only partially borylated, is even lower than the fully acylated polymer **4**, demonstrating the increased flexibility and plasticizing effect of **3**'s polyether groups. Although the T_g of **2** is lower than the base polymer, the T_g-lowering effect is not as dramatic as in the case of **3** given the same degree of borylation. The short alkyl tether of polymer **2**'s substituent increases flexibility of the polymer chains; however, the bulky tertiary butyl group of the substituent may stiffen the polymer chain and modulate the lowering of the glass transition temperature.[41] TGA analysis (see the Supporting Information) showed that functionalization of polymer **1**, either by acylation or by borylation, had no adverse affect on the modified polymers' thermal decomposition profiles with the major decomposition event(s) occurring at ~300 °C in an inert environment.

Table 1. Summary of Molecular Weight and Glass Transition Temperatures for Polymers 1−4

polymer	M_n[a] (g/mol)	M_w[a] (g/mol)	PDI	T_g[b] (°C)
1				156
2	4371	6598	1.51	101
3	4431	6067	1.36	43
4	3637	5462	1.50	59

[a] Determined by GPC in THF versus polystyrene standards. [b] T_g was determined using the inflection point of the third heating cycle.

In conclusion, we have established a novel means of chemically modifying a lignin model polymer using a mild arylboronate ester-forming reaction that produces water as the sole byproduct. The arylboronate ester chemical modifying approach enables one to adjust the thermal and solubility properties of the lignin-like material using structurally diverse arylboronic acid modifying agents and mild reaction conditions. Expanding the arylboronate ester chemical modification procedure to industrially available organosolv lignins and developing one-pot modification procedures that take advantage of solventless mechanochemical processing methods may ultimately impact the utilization of waste lignin. These complementary studies are underway in our laboratory.

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Supporting Information Available: A full experimental section detailing the synthesis and ^{1}H NMR, ^{13}C NMR, ^{11}B NMR, GPC, DSC, and TGA characterization of polymers **2**

and **3**; syntheses and characterization data of arylboronic acids **5** and **6** as well as model arylboronate esters **7** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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