



Chemical modification of organosolv lignin using boronic acid-containing reagents

Andrew L. Korich^d, Andrew B. Fleming^a, Amanda R. Walker^a, Jifu Wang^{b,c}, Chuanbing Tang^b, Peter M. Iovine^{a,*}

^a Department of Chemistry and Biochemistry, University of San Diego, 5998 Alcalá Park, San Diego, CA 92110, USA

^b Department of Chemistry and Biochemistry and Nanocenter, University of South Carolina, Columbia, SC 29208, USA

^c Institute of Chemical Industry of Forestry Products, Chinese Academy of Forestry, Nanjing 210042, China

^d Department of Chemistry, Grand Valley State University, 1 Campus DR, Allendale, MI 49401, USA

ARTICLE INFO

Article history:

Received 19 August 2011
Received in revised form
21 October 2011
Accepted 29 October 2011
Available online 22 November 2011

Keywords:

Biopolymers
Graft copolymers
Star polymers

ABSTRACT

Organosolv lignin was chemically modified with boron-containing reagents using a novel “graft-to” approach. The newly synthesized graft copolymers were prepared by covalently linking boron end-functionalized polycaprolactone (PCL) macromolecular reagents with organosolv lignin via reversible covalent bonds. Using a combination of ¹H, ¹³C, ¹⁹F, and ¹¹B NMR, it has been shown that arylboronate ester bonds are involved in the key linkages between the polyester grafts and the lignin core. Using a straightforward synthetic procedure and altering both the PCL graft density and the PCL molecular weight, a selection of compositions were studied. The newly prepared lignin-g-PCL copolymers were analyzed by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The Lignin-PCL₅₂₀₀ series shows an increase in PCL crystallinity with an increase PCL graft density. However, the crystallinity of the PCL in the lignin-g-PCL₉₁₀₀ set of materials remained constant throughout the series. TGA analysis for all lignin-g-PCL copolymers prepared herein show thermal decomposition near 300 °C.

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1. Introduction

Technical lignins are abundant waste products of both the pulp and paper industry and the burgeoning biorefinery industry. Lignin byproducts are generally considered low value and have limited commercial potential. Increasing lignin utilization, therefore, is an important goal in improving the economic viability of current and future biomass processes. Generally speaking, lignin utilization research can be broken into two limiting approaches. Break-down strategies seek to degrade lignin's complex polymeric structure into monomeric building blocks [1]. Ideally, the low molecular weight degradation products can be funneled into the existing commodity chemicals market [2]. A second approach seeks to build-up lignin's macromolecular structure in order to enhance the mechanical properties or modify its solution properties [3–6]. The research presented herein represents a build-up strategy as it involves grafting preformed synthetic polymer chains onto the lignin macromolecular structure. The novelty of this work, compared to other “graft-to” approaches resides in the covalent

linkage tethering the arms to the macromolecular structure. Reversibly formed arylboronate ester bonds are used to chemically modify (i.e. build-up) lignin and adjust its physical properties including glass transition temperature and solubility profile.

“Graft-to” and “graft-from” strategies have been used extensively en route to chemically modified lignins [7]. For example, the groups of Glasser and Kadla have shown that lignin-based copolymers are a viable route to preparing new classes of lignin-core star polymers [8,9]. Glasser's group has demonstrated that hydroxypropylated lignin can initiate ring-opening polymerization (ROP) of ϵ -caprolactone [9]. The resulting copolymers show suppressed glass transition states (T_g) relative to the starting lignin. More recently, Kadla and co-workers used ATRP to synthesize thermoresponsive lignin-based polymers [8]. Lastly, Wang et al have recently prepared rosin-lignin copolymers as a new class of highly hydrophobic materials [10].

Our group has previously demonstrated the chemical modification of a lignin model polymer using reversible covalent arylboronate ester bond formation [11]. In the current paper, we apply the same boron-based synthetic method to the chemical modification of industrially relevant organosolv lignin (Fig. 1).

Several structurally distinct arylboronic acid modifying agents were used in this study including boron end-functionalized

* Corresponding author. Tel.: +1 619 260 4028; fax: +1 619 260 2211.
E-mail address: piovine@sandiego.edu (P.M. Iovine).

macromolecular reagents as well as low molecular weight mono-arylboronic acids. The results of this study indicate that arylboronate ester bond formation provides a straightforward way to tune the physical properties of organosolv lignin. We present spectroscopic evidence that supports the existence of arylboronate ester bonds as the key linkage bridging the organosolv lignin and the grafting agent.

2. Materials and procedures

Organosolv lignin was obtained from Lignol Corporation and was used without further purification. Anhydrous 1,2-dichloroethane (1,2-DCE) was purchased from Sigma–Aldrich and used without further purification. ^1H NMR data was acquired on either a 400 MHz Varian Mercury or a 500 MHz Varian INOVA system. ^1H NMR of Lignin-PCL copolymers were taken in CDCl_3 that had been stored over 4 Å molecular sieves and referenced to residual solvent peak. ^{19}F NMR spectra were acquired in CDCl_3 and referenced to fluorotrichloromethane. Polymer molecular weights were determined on a Polymer Laboratories (now Agilent Technologies) GPC-120 equipped with two PL gel 5 μm MIXED-D columns and refractive index detection. THF was used as a mobile phase with a flow rate of 1.0 mL/min at 40 °C and samples were compared with polystyrene standards. A polymer concentration of 2 mg/mL was used for all GPC experiments. Attenuated total reflection IR (ATR-IR) spectra were obtained using a Jasco FT-IR-480 plus. Thermal gravimetric analysis (TGA) was operated on a TGA Q500 apparatus (TA instruments), ramping from 30 °C to 1000 °C at a rate of 10 °C/min and maintained at 1000 °C for 5 min under nitrogen gas at a flow rate of 100 mL/min. Differential scanning calorimetry (DSC) was performed on a TA Instrument Q20 with a ramp rate of 20 °C/min from –90 °C to 125 °C. The reported glass transition temperatures (T_g), temperature of melting (T_m), and heat of fusion (ΔH_f) were based on data associated with the second heating cycle. Crystallinity (X_c) was determined using Eq. (1):

$$X_c = \frac{\Delta H_f}{\Delta H_f^0} \quad (1)$$

where ΔH_f is the normalized heat of fusion (J/g) and ΔH_f^0 is the heat of fusion for an ideal PCL polymer (137.5 J/g) [12]. The preparation of arylboronic acid end-functionalized PCL are reported elsewhere ((HO) $_2$ B-Alkoxy [11] and (HO) $_2$ B-PCL-OAc [13]).

2.1. Determination of lignin hydroxyl content [14,15]

The organosolv lignin hydroxyl content was determined by the well established ^1H NMR method. In brief, organosolv lignin was acylated using a mixture of acetic anhydride and pyridine at 50 °C. After work-up, the acyl groups were quantified by ^1H NMR and compared with an internal standard (1,3-dinitrobenzene). Using this method it was determined that the batch of organosolv lignin used in these studies had a total hydroxyl content of 1.6 mmol g^{-1} .

2.2. General procedure for the chemical modification of organosolv lignin by arylboronic acids

Organosolv lignin was stirred in 1,2-DCE (10 mL per 100 mg of lignin) for 1 h. Arylboronic acid binding agent was added to give the desired loading value (loading percentages are relative to the total hydroxyl content of lignin). MgSO_4 (50 mg of MgSO_4 per 100 mg of lignin) was also added to the mixture. The solution was heated to 65 °C for 17 h before being cooled to room temperature. The MgSO_4 was removed by filtration through celite. The filtrate was concentrated under reduced pressure to afford the desired product without further purification.

2.3. General procedure for the preparation of lignin/PCL blends

The synthetic procedure used to prepare the lignin/PCL blends was identical to the preparation of the chemically modified organosolv lignin. Lignin was stirred as a heterogeneous mixture for 1 h in 1,2-DCE (1 mL DCE per 100 mg of lignin). The boronate ester end-functionalized PCL polymer (Bpin-PCL $_x$ -OAc) was mixed in solution with lignin so that the final weight percent of PCL matched the composition of the 50% covalent adduct. MgSO_4 (50 mg per 100 mg of lignin) was added and the solution heated to 65 °C for 17 h before being cooled to room temperature. The MgSO_4 was removed by filtration through celite. The celite was washed with a minimal amount of anhydrous THF. Finally, the filtrate was concentrated under reduced pressure leaving a dark brown solid.

3. Results and discussion

3.1. Arylboronic acid-lignin binding considerations

It was hypothesized that arylboronic acid modifying agents would bind mainly to the β -O-4 linkage (a 1,3-diol) in lignin due to

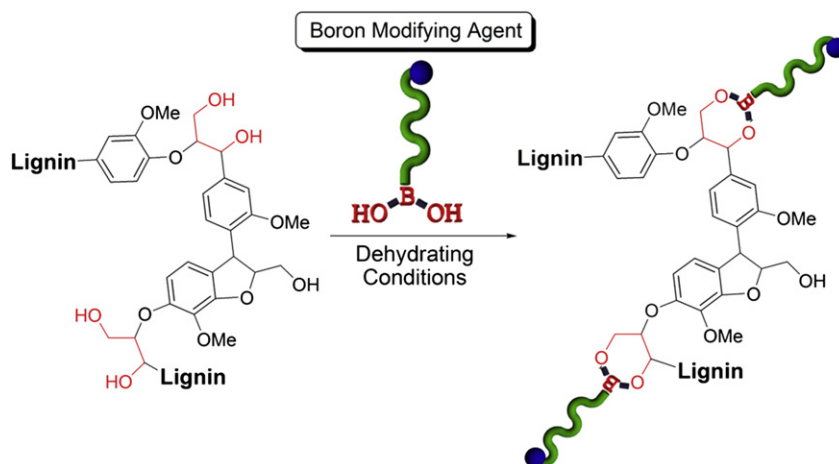


Fig. 1. “Graft-to” chemical modification of organosolv lignin using arylboronic acid end-functionalized polymers and low molecular weight mono-arylboronic acids.

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