

Towards Thermoplastic Lignin Polymers; Synthesis & Characterization of Poly(aryl ether sulfone) Kraft Lignin Heat Stable Copolymers

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Abstract

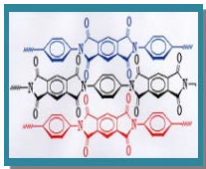
During this presentation, we aim at documenting our understanding of using the phenolic hydroxyl groups of technical softwood kraft lignin in replacing the multifunctional phenolic component required for the synthesis of poly(arylene ether) sulfones. To do this we use a two-pronged approach that uses fractionated softwood kraft lignin whose phenolic hydroxyl groups have been systematically protected in order to avoid gelation when copolymerized with 4, 4'-difluorodiphenyl sulfone (DFDPS). We will thus describe the progress of these copolymerizations for unfractionated and fractionated kraft lignin. This has been done by careful ³¹P NMR profiling of the various hydroxyl groups present in the lignin as a function of the degree of phenolic hydroxyl group protection. For all copolymers, weight average molecular weights (M_w), polydispersity indices (PDI), glass transition temperatures (T_g) and thermal stability profiles (TGA) were obtained, providing an integrated picture of the scientific and technological ramifications of this work.

Introduction

Lignin is the second most abundant biopolymer on the plant, next only to cellulose. Most efforts to utilize lignin have been limited by various factors that impart in it characteristics that define it as an unreliable precursor to polymer production. This is because lignin (and more specifically technical lignin) offers relatively unpredictable polymerization characteristics, depending upon its source and the degree of delignification to which the plant materials were subjected. More specifically, the highly functional character of lignin (i.e., rich in phenolic and aliphatic OH groups, as well as reactive benzylic carbons) induces a variety of potential polymerization sites and heat instability in such materials. Both factors promote gelation processes under polymerization conditions or when the temperature increases close to and/or above the glass transition temperature (T_g). In addition, the relatively low molecular weight (a few thousands) for lignin derived from commercial pulping and biorefinery operations makes lignin unsuitable for higher end applications, such as, high performance, heat stable engineering thermoplastic applications.

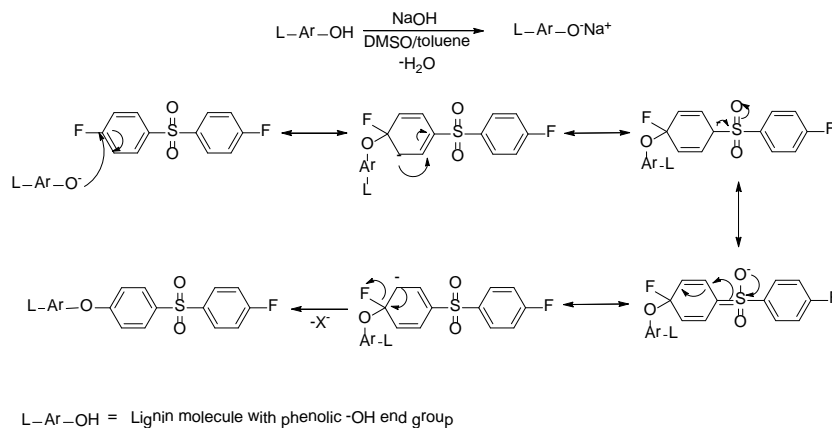
Results & Discussion

During this presentation, the fundamental work of our group will be described aimed at creating reactive lignin precursors that are stabilized and rendered better suited for industrial applications. Specifically, our work provides methods for creating lignins of controlled and modulated characteristics exhibiting thermal and polymerization stabilities. Such thermal properties and stable molecular weight distributions of lignins and copolymers produced from commercial lignins provides a means for beneficially modulating the properties of an otherwise intractable bio-polymer.



STEPI 9
Polyimides & High Performance Polymers
 3-5 June 2013
 Montpellier, France

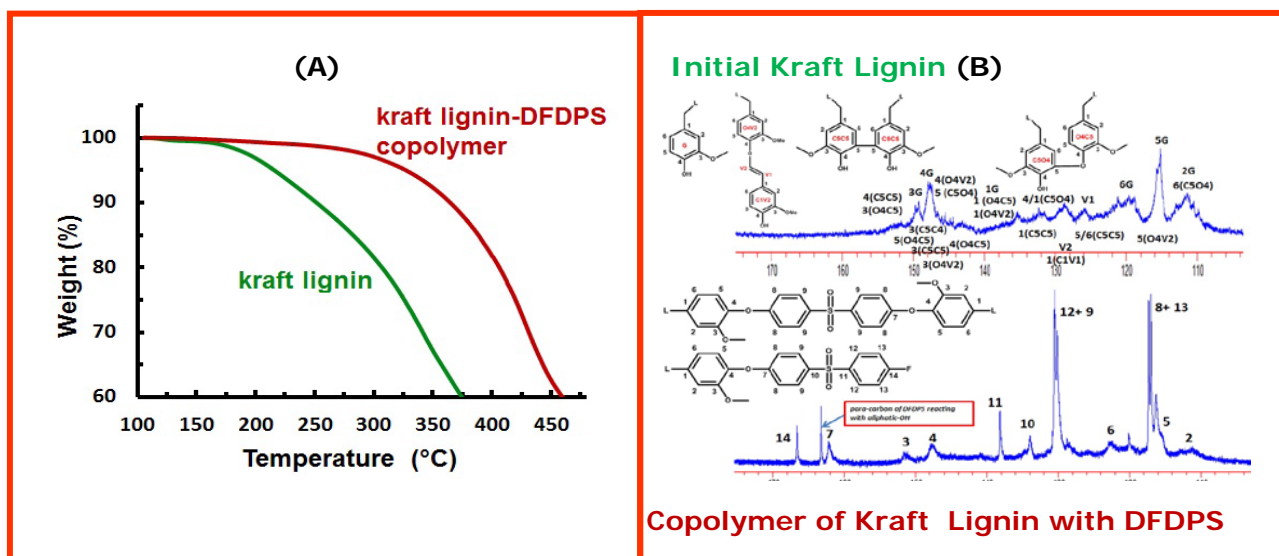
More specifically, our paper will describe the synthesis and characterization of polyarylene (ether sulfone)-kraft lignin copolymers synthesized by a base catalyzed stepwise copolymerization of suitably functionalized, fractionated kraft lignin with 4,4'-difluorodiphenyl sulfone (DFDPS) in an aprotic solvent at elevated temperatures (Scheme 1).



Scheme 1. Copolymerization of kraft lignin with difluorodiphenyl sulfone (DFDPS).

Detailed gel permeation chromatographic analyses, of the initial kraft lignin and its narrow fractions before and after copolymerization provided the details of the molecular weight development during these co-polymerizations. The 1H NMR spectra of the copolymers showed (amongst others) a downfield signal due to the meta-protons of DFDPS (7.4 ppm), signifying the conjugation between DFDPS and lignin. Furthermore the ^{13}C NMR spectra of the copolymers were found to be very revealing displaying distinct signals and clearly resolved signals for the aromatic carbons after the incorporation of the DFDPS (Figure 1B). For example specific signals (130, 117 ppm) due to the ortho- and meta- carbons of the DFDPS conjugated to lignin and of the ipso-carbons of DFDPS (138 ppm) were apparent as well as many other features (Fig. 1B).

Figure 1. A) TGA of kraft lignin and its DFDPS copolymer; B) ^{13}C NMR of kraft lignin and its DFDPS copolymer.



The benefits of incorporating DFDPS within kraft lignin are apparent in the TGA thermograms of the copolymer shown in Figure 1A.