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Synthesis and Characterization of Poly(arylene ether sulfone) Kraft Lignin Heat Stable Copolymers

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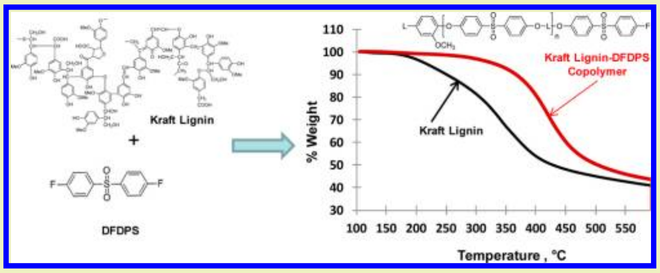
Ⓢ *Supporting Information*

ABSTRACT: In this effort 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′-diflourodiphenyl sulfone (DFDPS). This has been done by careful ^{31}P 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. Overall, this effort provides the foundations for creating lignin copolymers of controlled and modulated characteristics exhibiting augmented thermal stability. Such thermal properties and uniform molecular weight distributions of lignins and copolymers produced from commercial lignins provides a means for beneficially modulating the properties of an otherwise intractable biopolymer.



KEYWORDS: *Polyarylene ether sulfone, Softwood kraft lignin, Glass transition temperature, Thermogravimetry analysis, Characterization, Difluorodiphenyl sulphone*

■ INTRODUCTION

Lignin is the second most abundant natural polymer (after cellulose) on the planet, which is primarily obtained from the plant cell walls. It has a branched and irregular chemical structure composed primarily of phenyl propane (C_6-C_3) units[1] along with phenolic hydroxyl and methoxy substitutions in varying amounts depending on the botanical source of the material. The different phenyl propane (C_6-C_3) units of lignin are connected by ethers, carbon−carbon bonds of variable substitution patterns. The other functional groups present in lignin are aliphatic-hydroxyls, carbonyls, and carboxyls again with a varying frequency depending on its origin.[1,2]

The aromatic rich structure of lignin makes it a good choice for the replacement of fossil based materials as well as for polymers with sustainable alternatives. A large amount of lignin is obtained as the byproduct from the pulp and paper industry annually. The structure of native lignin is altered significantly by chemical fragmentation and condensation during the industrial kraft pulping processes, and the resultant lignin is known as technical lignin or kraft lignin. As such, technical lignins are of relatively low molecular weight, high polydispersity, and of a variable functional group content.[3] Still to date kraft lignin is mainly used to fulfill the energy and chemical recovery demands of the pulp and paper industry. Despite the fact that kraft and other industrial lignins offer significant challenges in being utilized (because of their random structure and reactivity), their enormous economic potential when coupled with societal and environmental imperatives are major motivating factors for ensuring their utilization.[4−6] However, enhanced solubility, uniformity, and lower glass transition temperatures of lignin make it a good substitute of polyols in polyurethane production.[7−9] The direct site-specific attachment of telechelic synthetic polymers to lignins has also been recently reported[10] while coupling methodologies for the production of lignin-containing phenolic resins have seen more extensive utility employing formaldehyde cross-linking chemistry.[11]

Conventional poly(arylene ether sulfone)s are tough and ductile engineering thermoplastics with many desirable properties including durability, high temperature stability, hydrolytic, and dimensional stability. As such, they are used to create several important commercial products.[12] These polymers are generally synthesized by the base catalyzed stepwise copolymerization of biphenols (with bisphenol A predominating) with 4,4′-dichlorodiphenyl sulfone (DCDPS) or 4,4′ difluorodi-

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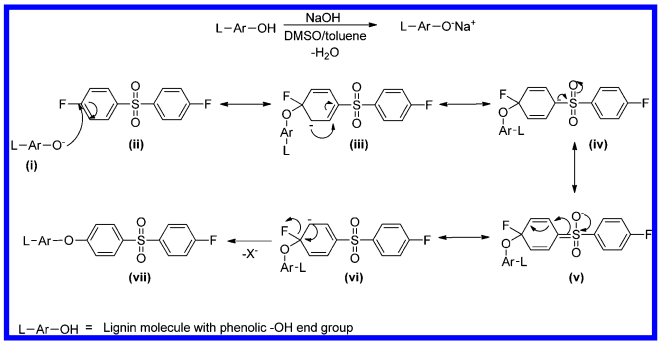
phenyl sulfone (DFDPS) in an aprotic solvent at elevated temperatures via nucleophilic aromatic substitution (SNAr) reactions.[13−16] This reaction is composed of two steps as depicted in Scheme 1: initial generation of resonance stabilized carbanions (iii, iv, v, vi) (Meisenheimer complex[13]) via the nucleophilic attack of the phenoxide (i) on the halide substituted carbon (ii) and next the rearomatization of the phenyl ring (vii) by elimination of the halide ion. Factors that influence the resonance stabilization of the Meisenheimer complex include the nature of the leaving group, the nature of the nucleophile, the activating group, and the solvent used.[13,27]

Scheme 1. Mechanism of Formation of Lignin DFDPS Copolymer by the SNAr Reaction



Usually, SNAr reactions used for the synthesis of poly(arylene ether sulfone)s, can proceed in the presence of either a strong base (e.g., sodium hydroxide) or a weak base (e.g., potassium carbonate) involving similar mechanisms that initially require the formation of a phenolate (with weak base) or a diphenolate anion (with strong base). The diphenolate formation with the strong base is much faster than the corresponding mono-phenolate formation with the weak base. As such, a much shorter reaction time is required in the case of strong base than the weak base.

In this effort, 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 acetone-fractionated softwood kraft lignin whose phenolic hydroxyl groups have been systematically protected in order to avoid gelation during the copolymerization with 4, 4′-diflourodiphenyl sulfone (DFDPS). We thus describe the progress of these copolymerizations by a careful ^{31}P 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, their molecular weight averages, their distributions, their glass transition temperatures, and thermal stability profiles are documented, providing an integrated picture of the scientific and technological ramifications of this work.[38,39]

EXPERIMENTAL SECTION

Materials and Methods. A commercially available (Mead Westvaco) softwood kraft lignin (KL), Indulin AT, was used in our work. Quantitative ^{31}P NMR analyses on the original KL showed that the amounts of condensed and noncondensed phenolic and aliphatic hydroxyl groups were 1.6, 2.2, and 2.4 mmol/g, respectively.[17,18] The term of "condensed phenolic −OH" is designated to those phenolic hydroxyl units being substituted in the C5 position either via direct carbon−carbon, methylene, or ether linkages to another phenolic unit. Molecular weight characteristics (M_w = 6200 g/mol, M_n = 1700 g/mol, and PDI = 3.6) were determined by using gel permeation chromatography (GPC) for the original KL sample. Toluene solvent was freshly dried and distilled over CaH_2 before use. Anhydrous dimethyl sulfoxide (DMSO) (≥99.9%) and all other chemicals and reagents used in this work were purchased from Sigma-Aldrich and Fisher Chemical companies and used as received.

NMR Analyses. All NMR spectra were acquired using a Bruker 300 MHz spectrometer equipped with a Quad probe dedicated to ^{31}P, ^{13}C, ^{19}F, and ^{1}H acquisitions. ^{1}H and ^{13}C NMR spectra of each sample were collected using DMSO-d_6 as the solvent. NOE effects were eliminated by the application of the inverse gated decoupling technique. Typical spectral parameters for quantitative ^{31}P NMR studies were as follows: 90° pulse width, sweep width of 12200 Hz. The spectra were accumulated with a delay of 5 s between successive pulses. Line broadening of 4 Hz was applied, and a drift correction was performed prior to Fourier transform. Chemical shifts were expressed in parts per million from 85% H_3PO_4 as an external reference.

^{1}H NMR spectra were collected with 3300 Hz sweep width, 1 s delay time, and 128 scans. ^{13}C NMR spectra were collected with 18 800 Hz sweep width, 3 s delay time, 20 000 scans.

The degrees of methylation of the softwood kraft lignin samples and the extents of reactions of their various hydroxyl groups, in the copolymerizations with 4,4-difluorodiphenylsulfone (DFDPS), were determined using a quantitative ^{31}P NMR procedure developed in our laboratory[17−19] More specifically, 40 mg of a dried sample was weighted into a NMR tube, to which, 500 μL of anhydrous pyridine/$CDCl_3$ mixture (1.6:1, v/v), 200 μL of endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide (e-NHI) solution (9.23 mg/mL as the internal standard), and 50 μL of chromium(III) acetylacetonate solution (5.6 mg/mL as a relaxation reagent) were then added. The solutions of the internal standard and relaxation reagent were both prepared using an anhydrous pyridine/$CDCl_3$ mixture (1.6:1, v/v). Subsequently, 100 μL of phosphitylating reagent (2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane) were transferred into the NMR tube, the reaction mixture was vigorously shaken, and subjected to immediate ^{31}P NMR analyses.

GPC. GPC measurements were carried out using a Waters GPC instrument equipped with UV (set at 280 nm) and RI detectors using tetrahydrofuran (THF) as the eluent at a flow rate of 0.7 mL/min at 35 °C. An injection volume of 50 μL and a sample concentration of 0.3 mg/mL were used. Two ultra styryl gel linear columns (Styragel HR 1 and Styragel HR 5E) were linked in series. A series of polystyrene narrow standards were used for calibration (the molecular weights of the polystyrenes used for the calibration were the following: 820, 2330, 3680, 18 700, 31 600, 44 000, 212 400, 382 100, 570 000, 994 000, and 1 860 000 g/mol).

Acetobromination Derivatization prior to GPC. Due to the variable solubilities displayed by lignin samples in THF, all samples examined in this work were subjected to a fast and reliable room temperature derivatization procedure developed in our laboratory.[16] A 5 mg portion of dried lignin or lignin copolymer sample were mixed in 2 mL of glacial acetic acid/acetyl bromide mixture (92:8, v/v). The mixture was stirred at room temperature for 2 h. Finally, the solvent and excess acetyl bromide were completely removed at room temperature using a rotary evaporator connected to a cold trap-protected high vacuum pump.

Differential Scanning Calorimetry (DSC). All glass transition temperature determinations were performed on a TA-Instrument model TA-Q100 using a temperature range of 30−250 °C. All samples were dried at 40 °C for 12 h in a vacuum oven prior to the DSC analyses. Approximately 5 mg of each sample were weighed directly into a DSC hermetic aluminum sample pan, which was then covered by its lid and sealed by cold pressing; a small hole was subsequently made on the lid. After being loaded into the TA-Q100, all samples were heated up to 105 °C at a rate of 5 °C/min and then isothermally conditioned for 40 min prior to being quenched to 30 °C and isothermally kept for 5 min. Finally, the DSC thermograms were recorded by increasing the temperature to 250 °C at a rate of 10 °C/min.

Thermogravimetric Analysis (TGA). All thermogravimetric analyses were carried out on a TA-Instrument model TGA-Q500 using a temperature range of 40−600 °C and a nitrogen flow rate of 60 mL/min. The sample size for each analysis was approximately 15 mg. The samples were initially heated to 105 °C with a heating rate of 10 °C/min and maintained at this temperature for 20 min before being heated to 600 °C with a heating rate of 10 °C/min.

Fractionation of Softwood Kraft Lignin. The KL was suspended under mild agitation in acetone (1 g/10 mL) for 6 h at room temperature. The insoluble residue (AIKL) was then filtered and isolated. The acetone was then removed from the soluble fraction (ASKL) by rotary evaporation at room temperature. Both fractions were dried in a vacuum oven set at 40 °C. The yields of ASKL and AIKL were about 30% and 70%, respectively. GPC results of the acetone soluble fraction show M_n = 612 g/mol and M_w = 980 g/mol. ^{31}P NMR spectra of the same show that the amounts of condensed, noncondensed phenolic, and aliphatic hydroxyl groups are 2.04, 2.56, and 1.8 mmol/g, respectively.

Methylation. A 1.0 g portion of ASKL was dissolved in 15 mL of aqueous 0.7 M NaOH at room temperature. Depending on the required degree of methylation, an appropriate amount of dimethyl sulfate (DMS) ranging from 0.25 to 2.5 mmol per mmol of the total phenolic −OH groups was added and the reaction medium was stirred for 30 min at room temperature and then heated at 75 °C for an additional 2 h.[20] In the case of higher degrees of methylation, special care was taken in order to maintain reaction homogeneity by continuous addition of sodium hydroxide aqueous solution (0.7 M). The product was recovered by addition of 2 M HCl (pH = 2.5), and the solid precipitate was washed with excess deionized water followed by freeze-drying.[20]

Lignin Copolymer Synthesis. A 5 mL portion of anhydrous DMSO and 3 mL of dried toluene were mixed in a two-necked round-bottom flask equipped with a Dean−Stark condenser under nitrogen and heated in an oil bath to 80 °C. An equivalent amount (to the total phenolic−OH groups present in the sample) of finely powdered dry NaOH was added into the solvent mixture. A 1 g portion of ASKL was added into the mixture, which was stirred at 80 °C for 1 h and then at 160 °C to remove toluene azeotropically. The azeotropic distillation was repeated three times with 4 mL dry toluene. Subsequently, 0.5 equiv (to the total phenolic−OH groups present in the sample) of DFDPS dissolved in dry toluene (4 mL) was transferred into the reaction medium and heating was continued at 160 °C for an additional 2 h. The reaction medium was finally cooled to room temperature and acidified to pH = 2.5 with 2 N HCl to obtain a dark brown solid precipitate, which was collected by centrifugation. After washing with ethanol (100 mL) and excess water (100 mL × 3), the solid product was freeze-dried and eventually dried in a vacuum oven at 40 °C.

Control Experiments. To examine the effect of solvent, base, and temperature on the copolymerization reaction, we examined a control reaction under the same conditions without DFDPS (DMSO/NaOH, 160 °C for 2 h). After the control reaction, we compared the molecular weight distributions and functional group contents of the control sample with the starting lignin. Quantitative ^{31}P NMR and GPC analyses indicated that the copolymerization condition adopted in this work did not alter the molecular characteristics of the lignin starting materials. Thus, any variations of the lignin samples upon their copolymerizations with DFDPS can be confirmed to be derived from the covalent linkage between lignin and DFDPS. However, the ^{13}C NMR study after the control reaction showed that the amount of aliphatic −OH reduced significantly and unsaturation in the side-chain (between 123 and 138 ppm) structures within ASKL increased dramatically. This is most likely due to side-chain elimination reactions occurring that involve the aliphatic −OH groups in ASKL. Current efforts in our laboratory further explore the details of this reaction aimed at understanding and capitalizing on its potential effects.[38]

■ RESULT AND DISCUSSION

Lignin Fractions and Their Properties. The inherent heterogeneity of technical lignins offers unpredictable and uncontrollable reactivity.[3,21−24] Efforts to fractionate technical lignins using organic solvents of variable polarities have been reported and the resulting fractions have shown to vary based on molecular weight and functional group distributions.[25,26] In our efforts to provide a platform of lignin-based polymeric materials with consistent and reliable reactivity, we examined a simple fractionation scheme with tangible commercial potential. This involved extracting the softwood kraft lignin (weight average molecular weight and PDI were 6200 g/mol and 3.6 respectively) with acetone offering two distinct fractions, an acetone soluble (ASKL) and an acetone insoluble fraction (AIKL), with considerable variations in their overall molecular and polymeric characteristics. The molecular weight distributions of these two fractions were found to be significantly different (Figure 1). AIKL was found to be of much higher weight average molecular weight (M_w = 12 200 g/mol) and PDI (M_w/M_n = 5.4), while ASKL was found to be of a much lower molecular weight (M_w = 980 g/mol) and of a much smaller PDI (M_w/M_n = 1.6; see Figure 1). These findings are in agreement with previously reported values[26,29] Moreover, other physical properties of KL, ASKL, and AIKL (provided in Table 1) show considerable differences regarding overall molecular and polymeric characteristics.

The quantitative ^{31}P NMR data of these samples show that the ASKL contains significantly higher amount of total phenolic hydroxyl groups (4.6 mmol/g) and lower amount of aliphatic hydroxyl groups −OH (1.8 mmol/g) compared to the AIKL (3.1 and 3.1 mmol/g of phenolic and aliphatic hydroxyl groups respectively, Table 1).

In relation to their thermal properties, Table 1 shows that the T_g of the initial unfractionated kraft lignin was determined to be 150 °C which is comparable with previous reports.[3,25,28] The T_g

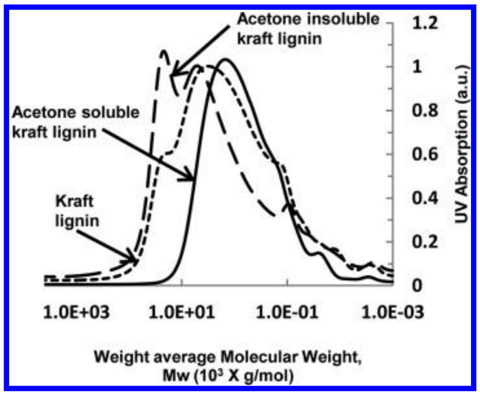


Figure 1. Molecular weight distributions of KL and its acetone fractions, ASKL and AIKL.

of the ASKL is about 90 °C while the T_g of the AIKL is as high as 210 °C. The large difference between these two fractions is indicative of an extreme heterogeneity being present within the initial KL in terms of polymeric characteristics and molecular weights that eventually are reflected in the thermal properties of the material as per earlier accounts related to lignin samples.[3,26,29]

Copolymerization of Acetone Soluble Kraft Lignin (ASKL) with Difuorodiphenyl Sulfone (DFDPS). Nucleophilic aromatic substitution reactions are normally carried out in polar aprotic solvents because these solvents do not solvate the nucleophile[14,15,2730] During the early stages of this reaction where the sodium phenolate anions of the lignin are created, water forms as a byproduct. Typically, the presence of water causes several major problems to the SNAr reactions. Water not only solvates the nucleophile but also can act as a nucleophile hydrolyzing DFDPS, which ultimately leads to low molecular weight polymers due to losses in stoichiometry. To prevent the side reactions, we used dry toluene to assist in the removal of water from the reaction medium (see experimental) azeotropically.

The complex and labile structure of lignin precluded us from selecting the weak base approach during the SNAr reactions due to the possibility of structural alterations during the prolonged polymerization periods at elevated temperatures required as discussed earlier. As such, we selected the stronger base NaOH (required reaction time 2−3 h) over the weaker and most popular base for the SNAr reactions, potassium carbonate (required reaction time 24 h and more), for these reactions.

The copolymerization of the difunctional reagent (DFDPS) with a multifunctional phenol (ASKL) is known to lead to the formation of a network structure inevitably. However, our approach to avoid gelation was by modulating the reactivity of the ASKL by partial masking of the phenolic hydroxyl groups through methylation prior to the copolymerization reaction.[20,31,38] At this point it is worth mentioning that unfractionated kraft lignin whose molecular weight distribution is rather broad (PDI = 3.6, Table 1), when subjected to copolymerization with DFDPS offered copolymers with wide molecular weight distributions. The extended tailing in the high molecular weight end of these polymers was evidently due to the network-like materials present in the system. Such molecular weight distributions in the resulting copolymers are better to be avoided to circumvent weak mechanical and other physical properties in the copolymer.

On the other hand, when the ASKL was copolymerized with DFDPS at various degrees of methylation, considerably more uniform/narrow molecular weight distributed copolymers were obtained. The more homogeneous structure and narrower molecular weight distribution (PDI = 1.6) of the ASKL compare to the starting kraft lignin is responsible for producing more uniform copolymers. Furthermore, as anticipated the molecular weights of the final products progressively increased with decreasing degree of methylation (Figure 2).

The molecular weight (M_w) of the copolymer synthesized with a completely nonmethylated ASKL and DFDPS reached up to 20 000 mol/g, which represents a 20-fold increase in the M_w from the starting ASKL.

Spectroscopic Evidence for the Formation of Copolymers. As anticipated, the quantitative ^{31}P NMR spectra of the copolymer (Figure 3) show a dramatic reduction in the phenolic −OH content compared to the starting ASKL. The total phenolic −OH was decreased from 4.6 to 1.1 mmol/g after the copolymerization (for the nonmethylated lignin sample). The higher ionization efficiency of the phenolic −OHs compared to their aliphatic counterparts is uniquely responsible for the observed selectivity.

In an effort to better understand the way the different types of ASKL phenolic OHs react during the copolymerization, we examined in detail their progressive elimination as it occurred in copolymer samples of variable methylation levels (Figure 4).

Apparently, the slope characterizing the decrease of the noncondensed phenolic hydroxyl groups is steeper than that of its condensed counterparts. Such differences in the reactivity are most likely a combination of pK_a (basicity) and steric considerations for the different condensed and noncondensed phenolic hydroxyl moieties present within the softwood kraft lignin. Data by Ragnar et al. showed that the pK_a values of different multifunctional noncondensed and condensed typical lignin phenols vary based on which phenolic −OH ionizes first.[32] Overall, the data supplied by Ragnar et al. indicates that about 50% of the phenolic hydroxyl groups within condensed lignin moieties react easily and fast while the remaining 50% react slowly. As such one anticipates observing a similar trend with the phenolic hydroxyl group reactivity present in ASKL.

Table 1. Functional Group Distributions, Molecular Weight and T_gs of the Softwood Kraft Lignin and its Acetone Fractions, ASKL and AIKL

	molecular weight, g/mol						
samples[a]	M_w	M_n	PDI	T_g[b], °C	aliphatic−OH, mmol/g	noncondensed phenolic−OH, mmol/g	condensed phenolic−OH, mmol/g
KL	6200 ± 186	1700 ± 123	3.6	153 ± 4	2.4 ± 0.06	2.31 ± 0.06	1.52 ± 0.05
ASKL	980 ± 95	620 ± 69	1.6	90 ± 5	1.8 ± 0.05	2.56 ± 0.08	2.04 ± 0.07
AIKL	12200 ± 680	2200 ± 112	5.4	210 ± 3	3.1 ± 0.05	1.6 ± 0.04	1.5 ± 0.02

[a] Experiments repeated three times. [b] Average of two experiments.

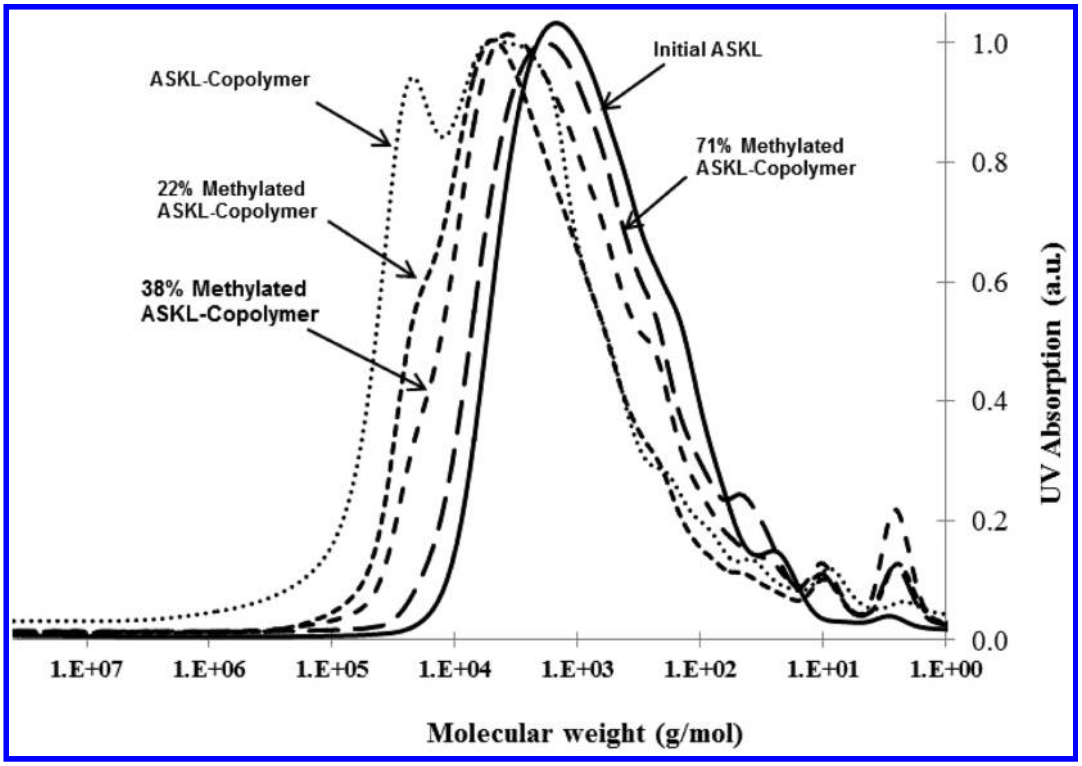


Figure 2. Molecular weight distribution of acetone soluble kraft lignin after copolymerization with DFDPS at different levels of phenolic−OH methylation .

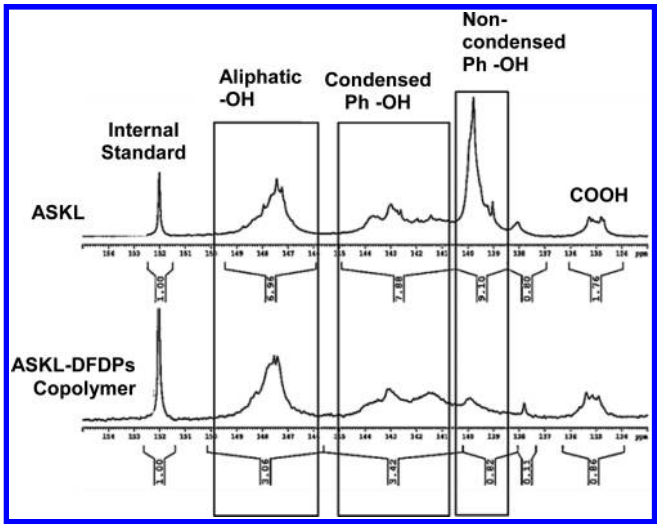


Figure 3. Quantitative ^{31}P NMR of acetone soluble kraft lignin before and after copolymerization with DFDPS. The noncondensed phenolic −OH content is seen to be reduced dramatically. Significant reductions in the condensed phenolic −OH and aliphatic −OH are also apparent.

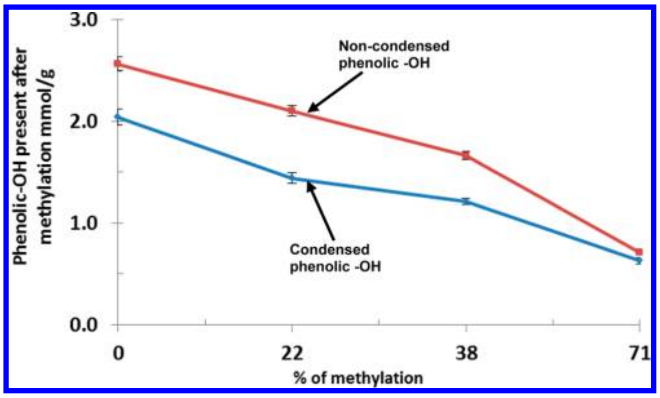


Figure 4. Plots depicting the relative decrease in condensed and noncondensed phenolic −OH's as a function of % methylation within ASKL after copolymerization with DFDPS.

Furthermore, the noncondensed phenolic hydroxyl groups are less sterically hindered than the condensed phenolic OH's, which possess bulky neighboring groups. Consequently, one anticipates that with increasing degree of methylation greater numbers of noncondensed (and more reactive) phenolic hydroxyl groups are masked leaving behind the less reactive condensed ones for subsequent copolymerization.

However, surprisingly the quantitative ^{31}P NMR spectra of the product always show significant reduction in the aliphatic hydroxyl content too. For example, the quantitative ^{31}P NMR spectrum of the copolymer synthesized by reacting the original, nonmethylated ASKL with DFDPS shows 63% and 27% reduction in total phenolic −OH and aliphatic −OHs, respectively. The reduction in phenolic hydroxyl groups is definitely the result of copolymerization with DFDPS based on the spectroscopic evidence. However, we have no definitive ^{13}C or other NMR spectroscopic evidence that points to a reaction between DFDPS and aliphatic −OH during these copolymerizations. Furthermore, there are no literature accounts regarding reactions between aliphatic alcohols and halogenated diphenyl sulfones. To this effect we examined the quantitative ^{13}C NMR spectra of ASKL subjected to control reactions (DMSO and NaOH at the same temperature and time profiles as the actual copolymerizations) as provided in the supplementary data section (S1). This data shows that upon such a treatment a dramatic increase in unsaturated side-chain

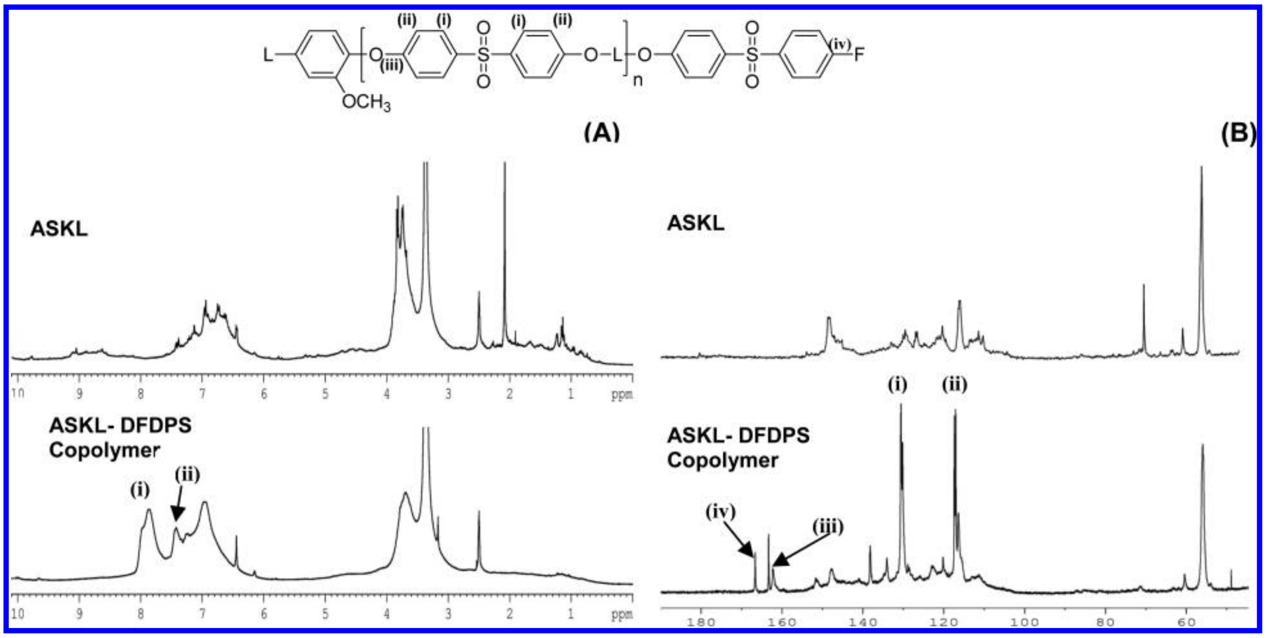


Figure 5. ^1H NMR (A) and ^{13}C NMR (B) spectra of the acetone soluble kraft lignin (ASKL) copolymer with DFDPS.

(between 123 to 138 ppm) structures occurred within ASKL. This is most likely due to side-chain elimination reactions occurring that involve the aliphatic OH groups in ASKL.[33] Current efforts in our laboratory further explore the details of this reaction aimed at understanding and capitalizing on its potential effects.

The ^1H NMR spectra of the reprecipitated, well washed, and purified copolymers show a new distinct broad peak between 7.0 to 8.1 ppm (Figure 5A) which corresponds to the aromatic region of the diphenyl sulfone moiety (proton signals labeled as ii and i). Moreover, the ^{13}C NMR spectra show two peaks at 117 and 131 ppm (Figure 5B), which correspond to the aromatic carbons of the diphenyl sulfone moiety (carbon signals labeled as ii and i). In addition, the new broad signal at 162 ppm is attributed to the fully coupled diphenyl sulfone linkers in the final copolymer (carbon C_4 in DFDPS connected to the phenolic oxygen in the lignin after copolymerization, labeled (iii) in the copolymer structure). At this point, the sharp signal at around 163 ppm is still of an unknown origin but it could be due to lignin phenolic moieties linked with DFDPS bearing some yet unknown substituents or geometries. These signal assignments are based on literature accounts for similar reactions and environments as well as our own calculations and observations of the spectra of the starting materials.[34,35] As such at this point, it is rational to conclude that the ^1H and ^{13}C spectra of the products verify the incorporation of the diphenyl sulfone moiety onto the lignin after the copolymerization reaction.

Overall, ^{13}C NMR spectroscopy has been rather useful in further probing the detailed coupling reactions between lignin and DFDPS. For example the downfield ^{13}C NMR signal labeled iv in Figure 5B, located at 168 ppm, can be attributed to the para carbon still containing intact its fluorine substitution present in the original diphenyl sulfone molecule. The reason for this inefficiency may be steric crowding as imposed by the branched character of the ASKL molecules or due to stoichiometry imbalances preventing higher molecular weight formation. Quantitative estimations of the degree of incorporation of DFDPS within the lignin are currently carried out using quantitative ^{13}C NMR with internal standards.[36] This data, coupled with the selection of other less sterically hindered monomers is aimed to be used in subsequent efforts to further optimize these reactions.

Thermal Stability and Glass Transition Studies of the Copolymers. Since the thermal stability of the targeted copolymer is also one of the main objectives of this work, thermogravimetric analyses (TGA) were carried out for the starting material and the copolymer samples under a N_2 atmosphere (Figure 6).

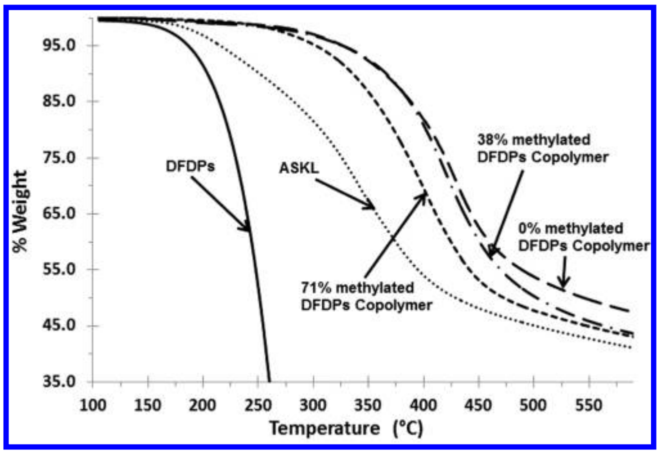


Figure 6. Thermogravimetric analyses of DFDPS, ASKL, and related copolymers.

TGA traces show a single decomposition step for all copolymers. Overall it is apparent that all ASKL samples copolymerized with DFDPS show a very significant improvement in their thermal stability. The effect becomes more pronounced for the copolymers with lower degree of methylation and consequently greater degree of DFDPS incorporation. For example, the $T_{5\%}$ (the specific temperature for a 5% weight loss) of ASKL and DFDPS are 216 and 184 °C respectively while, the $T_{5\%}$ for non-methylated ASKL-DFDPS copolymer and 71% methylated ASKL-DFDPS copolymer were found to be 327 and 303 °C, respectively. These findings are in accordance with our expectations in a similar way to that displayed by conventional poly(arylene ether sulfone) copolymers.[37] The char residue at 600 °C for ASKL-DFDPS was about 48%, which in actual fact is 7% more than the starting ASKL (41%).

Finally, the glass transition temperatures of ASKL and its copolymers with DFDPS are shown in Table 2. In order to eliminate thermal history, the samples were annealed at 105 °C for 40 min and cooled rapidly to 40 °C. It is apparent that the T_g increases with the increasing molecular weight of the sample. The copolymer synthesized by reacting non-methylated ASKL with DFDPS shows the highest T_g (172 °C; Table 2) while the ASKL copolymer samples produced with partially methylated phenolic −OHs show lower molecular weights and lower T_g's. The variation in T_g with molecular weight is a well-known phenomenon.[25] In this case as the degree of methylation decreases the amount of DFDPS in the copolymer increases offering higher molecular weights, which effectively contributes at the creation of a more rigid backbone on the polymer with more restricted segmental motion and higher T_g.

Table 2. Variation of Glass Transition Temperature with the Molecular Weight Distribution of the Copolymer

sample	M_w, g/mol	M_n, g/mol	T_g, °C
ASKL	1212	669	90
0% methylated ASKL−DFDPS polymer (ASKL content 63 wt %)	20280	1820	172
22% methylated ASKL−DFDPS polymer (ASKL content 69 wt %)	7016	1512	170
38% methylated ASKL−DFDPS polymer (ASKL content 74 wt %)	6041	1384	167
71% methylated ASKL−DFDPS polymer (ASKL content 86 wt %)	2057	864	147

CONCLUSIONS

This effort has provided an initial detailed understanding of using the phenolic hydroxyl groups of technical softwood kraft lignin for replacing the difunctional phenolic component required for the synthesis of heat stable poly(arylene ether) sulfones. As anticipated, the multifunctional nature of lignin, upon copolymerization with a difunctional monomer, soon causes it to arrive at a hyperbranched and cross-linked polymer, which is intractable and not suitable for further thermoplastic processing. This major limitation was addressed by appropriately reducing the phenolic functionality of kraft lignin by masking them via methylation with dimethyl sulfate in alkaline aqueous solution. Furthermore, the use of acetone-fractionated softwood kraft lignin provided a starting material of a narrow molecular weight distribution. The characterized copolymers showed the covalent, progressive incorporation of DFDPS in the lignin structure with concomitant increases in the molecular weight averages, their distributions, their glass transition temperatures and thermal stability profiles. Overall, we show that it is possible to modulate the reactivity of softwood kraft lignin via a combination of methylation and fractionation providing a rational means for the creation of modest molecular weight polyarylene ether sulfone lignin copolymers.

It is envisaged that the present effort demonstrates the potential of using technical kraft lignin as a phenolic precursor for the creation of heat stable thermoplastic materials with the desired control of structure−property relations.

ASSOCIATED CONTENT

Supporting Information

Figure S1. (A) ^{13}C NMR of the starting ASKL sample. (B) ^{13}C NMR of the ASKL after control reaction (heating at 160 °C for 2 h). The signals between 123 and 138 ppm, due to unsaturated environments in lignin, are seen to increase dramatically. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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