

Toward Thermoplastic Lignin Polymers. Part 1. Selective Masking of Phenolic Hydroxyl Groups in Kraft Lignins via Methylation and Oxypropylation Chemistries

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S Supporting Information

ABSTRACT: This work offers a comprehensive understanding of the conditions required for the selective masking of the phenolic hydroxyl groups in technical kraft lignins, which is pivotal in determining their subsequent chemical and thermal reactivity. To this effect, we have examined the chemistry and developed the conditions for the facile, mild, and selective masking of the phenolic hydroxyl groups in softwood and hardwood kraft lignins. We have compared two series of methylated softwood kraft lignins synthesized using different methylation chemistries. Our data show that (when used as specified) dimethyl sulfate in aqueous NaOH selectively converts the phenolic hydroxyl groups of kraft lignin to its methylated derivatives without apparent side reactions. In contrast, methyl iodide (in the presence of excess K_2CO_3 in *N,N*-dimethylformamide) was found to be rather ineffective and unselective. Various milder methylation conditions were also examined for both softwood and hardwood kraft lignins using dimethyl sulfate, and the details of this work are documented. In addition, a series of oxypropylation reactions were also carried out using propylene oxide in aqueous NaOH. Propylene oxide was shown to selectively add (at room temperature, 0.5 M NaOH, 18 h) less than two units on average per phenolic hydroxyl group without significant additional polymerization or other side reactions.

1. INTRODUCTION

Lignin is the second most abundant natural polymer in woody and nonwoody plants. It is considered to have an amorphous, highly branched network structure of an aromatic macromolecule with complex connectivity. However, a recent account points to milled wood lignin being a linear oligomer.^{1,2} Its physical and chemical properties are determined by the original wood species, the technical process to which the wood was exposed, and the isolation method that was applied to arrive at a given lignin sample.^{3,4} Chemically, native lignin is composed of a carbon–oxygen framework that extends to a variety of functional groups, namely, methoxyl, phenolic, aliphatic, carbonyl, and carboxyl moieties.

Large amounts of technical lignin are generated as by-products in the modern pulp and paper industries. This material represents an integral component of the actual paper manufacturing process because it is incinerated to recover energy and chemicals. Such technical lignin sources, however, represent potential market opportunities because of their aromatic nature and their vast daily supply. Only a small part of it is isolated from the spent pulping liquor and eventually commercialized at a scale of about 1 million tons per year.⁵ In contrast to native lignins, the phenolic hydroxyl groups are among the most abundant functional groups in kraft lignins, determining its augmented chemical reactivity and, consequently, its stability toward technical utility.

Lignin utilization as a polymer has been previously attempted in various fields, and such endeavors have occurred either with the direct use of lignin or by derivatization of its hydroxyl groups.⁶ Treating lignin under conditions of extreme pH and temperature is considered undesirable because of its structural

complexity and thermal instability. For example, subjecting lignin to elevated temperatures converts the material to a condensed, rigid, unreactive, and insoluble material.⁷ Such issues are major drawbacks for lignin utilization in polymer applications. Efforts for improving such processing characteristics for lignin lead to a variety of chemical modifications.

Among the most well-known chemical modification reactions attempted on lignin is its reaction with propylene oxide.^{8–11} Initially aimed at preparing engineering thermoplastics and polyurethane foam, this modification resulted in the formation of lignin poly(propylene glycol) derivatives (lignopolyols),¹² which showed improved solubility and uniformity. Oxypropylated lignins are generally prepared by dispersion of the solid lignin into neat propylene oxide in the presence of a base (usually KOH) at 150–200 °C for 1–2 h. Through an anionic ring-opening polymerization mechanism, the phenolic hydroxyl groups are extended with poly(propylene glycol) chains, possessing only one secondary hydroxyl group at each chain end.¹³ The average chain length of the grafted poly(propylene glycol) determines the molecular weight, glass transition temperature (T_g), and functionality of the final lignin derivatives.^{8,14,15} As far as structure–property relations are concerned, oxypropylation of lignin with a controlled amount of added propylene oxide will induce less uncertainty; therefore, the mild oxypropylation reaction of lignin in aqueous sodium hydroxide (NaOH) was examined during this work.

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In addition, we focused our attention on the understanding of lignin methylation chemistries.^{8,16} Most citations in the area, unfortunately, were not the main goal of the published efforts, and as such, no detailed literature analyses have been offered. The selective methylation of the phenolic hydroxyl groups in lignin may offer important advances toward this material being used in polymer applications because the lignin phenolic hydroxyl group will be converted to a significantly less reactive phenyl methyl ether. In addition, a carefully monitored and controlled methylation reaction of lignin may offer a means of reducing and modulating its reactivity, which, when coupled with its heavily branched nature, may offer additional possibilities toward subsequent polymerization and/or copolymerization efforts as well as high-temperature treatments.¹⁷

Consequently, the objective of this paper is to systematically address the detailed chemistries of the enumerated methods aimed at an eventual comprehensive understanding of the conditions for the selective masking of the phenolic hydroxyl groups in technical kraft lignins.

2. EXPERIMENTAL SECTION

2.1. Materials and Chemicals. A sample of commercially available (Mead Westvaco) softwood kraft lignin (Indulin AT) was used as the starting material. The hardwood lignin was isolated from a black liquor (300 mL), supplied by Mead Westvaco, which was purged with sufficient CO₂ until pH 10.0 was reached; the solid precipitate was isolated by centrifugation and further washed with a 2 M KCl aqueous solution (200 mL × 3) and a 0.01 M HCl aqueous solution (200 mL × 2); the recovered solid product was then freeze-dried, followed by vacuum drying in a vacuum oven set at 40 °C for 48 h. Quantitative ³¹P NMR analyses on the softwood kraft lignin sample showed that the amounts of condensed and noncondensed phenolic and aliphatic hydroxyl groups were 1.6, 2.2, and 2.4 mmol/g, respectively; for the hardwood kraft lignin sample, the amounts of condensed and noncondensed phenolic and aliphatic hydroxyl groups were 2.2, 1.0, and 1.1 mmol/g, respectively (the methodology and integration ranges applied, for these determinations have been published elsewhere).^{18–20} All chemicals and reagents used in this study were purchased from Sigma-Aldrich and Fisher Chemical companies and used as received.

2.2. Methylation and Oxypropylation of Kraft Lignins.

2.2.1. Methylation of Softwood Kraft Lignin with Dimethyl Sulfate. A total of 1.0 g of softwood kraft lignin was dissolved in 15 mL of aqueous 0.7 M NaOH at room temperature. An appropriate amount of 0.25–2.5 mmol of dimethyl sulfate per each 1 mmol of total phenolic hydroxyl groups was added, and the solution was stirred for 30 min at room temperature. Then the mixture was heated to 80 °C for an additional 2 h (Scheme 1, I). Detailed information of these methylation reactions is shown in Table 1.

When high degrees of methylation were required, special care was taken to maintain the reaction pH between 11.0 to 11.5 so as a homogeneous mixture is present and no precipitation is observed by the continuous addition of an aqueous 0.7 M NaOH solution. After the reaction, the mixture was acidified (pH 2.5) with 2 M HCl and the solid precipitate was washed with excess deionized water and freeze-dried.

At relatively milder reaction conditions, additional methylation experiments with dimethyl sulfate for softwood kraft lignin were conducted in order to gain an in-depth understanding for lignin methylation chemistry using dimethyl

sulfate. Detailed information of these methylation reactions is shown in Table S1 in the Supporting Information (SI).

2.2.2. Methylation of Softwood Kraft Lignin with Methyl Iodide. A total of 1.0 g of softwood kraft lignin was dissolved in 15 mL of anhydrous *N,N*-dimethylformamide (DMF) containing finely dispersed potassium carbonate as per procedures for the methylation of simple phenols.²¹ An appropriate amount of methyl iodide was then added, and the mixture was vigorously stirred for 18 h at room temperature (Scheme 1, II). Finally, the reaction mixture was acidified (pH 2.5) with 2 M HCl, and the solid precipitate was washed with deionized water and freeze-dried.

2.2.3. Methylation of Hardwood Kraft Lignin with Dimethyl Sulfate. A variety of methylation experiments for hardwood kraft lignin using dimethyl sulfate under milder reaction conditions were conducted, and the detailed reaction information is shown in Table 2.

2.2.4. Oxypropylation of Softwood Kraft Lignin. Appropriate amounts of propylene oxide (as per the desired degree of functionalization) were reacted with the lignin solution in 0.5 M aqueous NaOH (10 mL/g of lignin) at 40 °C for 18 h (Scheme 1, III). Finally, the mixture was acidified (pH 2.5) with 2 M HCl, and the solid precipitate was washed with deionized water and freeze-dried. The degrees of oxypropylation were measured by quantitative ³¹P NMR.

2.3. Quantitative ³¹P NMR. Methylation and oxypropylation of kraft lignins were monitored and analyzed by quantitative ³¹P NMR using published procedures.^{18–20} An accurately known amount of 40–45 mg of a dried lignin sample was dissolved in 500 μL of anhydrous pyridine/CDCl₃ mixture (1.6:1, v/v). A total of 200 μL of an *endo-N*-hydroxy-5-norbornene-2,3-dicarboximide solution (9.23 mg/mL) as the internal standard and 50 μL of a chromium(III) acetylacetonate solution (5.6 mg/mL) in the above pyridine/CDCl₃ solution as the relaxation reagent were added. Finally, 100 μL of phosphitylating reagent II (2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane) was added and transferred into a 5-mm NMR tube for subsequent NMR acquisition. NMR spectra were acquired using a Bruker 300 MHz spectrometer equipped with a Quad probe dedicated to ³¹P, ¹³C, ¹⁹F, and ¹H NMR acquisition.

2.4. ¹H NMR. ¹H NMR spectra were acquired using a Bruker 300 MHz spectrometer and deuterated dimethyl sulfoxide (DMSO)-*d*₆ as the solvent. The ¹H NMR was typically used to monitor the degree of addition of propylene oxide to lignin during the oxypropylation reaction.²² A standard solution containing pentafluorobenzaldehyde (PFB) in DMSO-*d*₆ was prepared by carefully weighing PFB (33.0 mg) and diluting it with 0.40 mL with DMSO-*d*₆. To each lignin sample (20.0 mg) in DMSO-*d*₆, an aliquot of the standard solution (0.10 mL) was added prior to the NMR experiment. The relaxation delay was set to 10 s.

2.5. Gel Permeation Chromatography (GPC). GPC measurements were carried out at 35 °C on a Waters instrument using a UV detector whose wavelength was set at 280 nm. Tetrahydrofuran (THF) was used as the eluent using a flow rate of 0.6 mL/min. Two styragel linear columns linked in series (Styragel HR 1 and Styragel HR 5E) were used for the measurements. A series of monodisperse polystyrene standards were used for calibration.

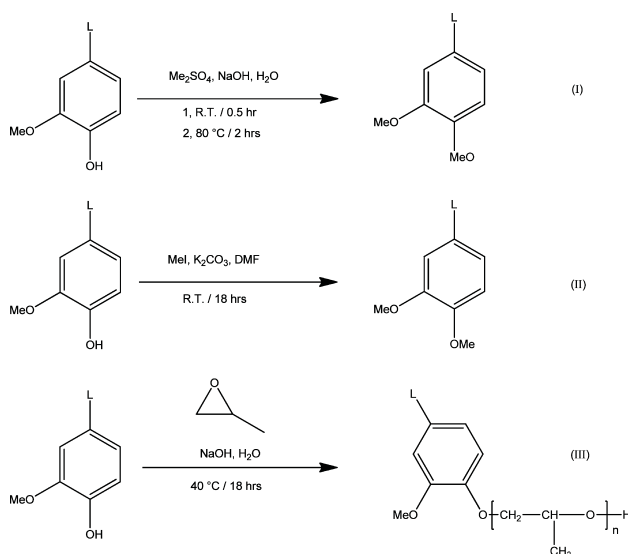
2.6. Acetobromination Derivatization prior to GPC. A total of 5 mg of a dried lignin sample was mixed in 2 mL of a glacial acetic acid/acetyl bromide mixture (92:8, v/v). The

mixture was stirred at room temperature for about 2 h or until its complete dissolution. Finally, the solvents were completely removed at room temperature using a rotary evaporator connected to a cold-trap-protected vacuum pump. Acetobromination was applied to all GPC samples to ensure complete solubilization in the THF mobile phase.

3. RESULTS AND DISCUSSION

The main objective of this work was to develop facile, mild, and selective methodologies for masking of the phenolic hydroxyl groups in technical lignins. Consequently, our efforts focused on the methylation and oxypropylation procedures (see Scheme 1).

Scheme 1^a



^aMethylation of softwood kraft lignin by using dimethyl sulfate in aqueous NaOH (I) and methyl iodide in DMF in the presence of excess K_2CO_3 (II). Oxypropylation of softwood kraft lignin by using propylene oxide in aqueous NaOH (III).

3.1. Lignin Methylation. Two different reagents, dimethyl sulfate and methyl iodide, at specific reaction conditions (Scheme 1, I and II) were used for softwood kraft lignin methylation. For each methylation reagent, we attempted to prepare a series of six samples whose degree of methylation varied by varying the mole ratios of the methylating reagent to the total phenolic hydroxyl present (Table 1). The hydroxyl content analysis data shown in Table 1 were obtained using quantitative ^{31}P NMR analyses in the presence of a suitable internal standard. Representative quantitative ^{31}P NMR spectra (Figure 1) and the corresponding data of Table 1 support the theory that dimethyl sulfate can afford the selective methylation of the phenolic hydroxyl groups in softwood kraft lignin in a controlled fashion. Alternatively, the aliphatic hydroxyl groups in softwood kraft lignin remained unaffected. At a mole ratio of 2.5 (dimethyl sulfate to phenolic hydroxyl groups), the conversion is nearly quantitative. The observed selective methylation of dimethyl sulfate toward the phenolic hydroxyl groups can be rationalized on the basis of the relatively large $\text{p}K_a$ differential of the aliphatic hydroxyl groups of lignin compared to their phenolic counterparts. We attempted to conduct calculations to estimate the concentrations of the

Table 1. Hydroxyl Group Content Analysis Data for Initial and Methylated Softwood Kraft Lignins

sample entry	R/L ^b	hydroxyl groups (mmol/g of lignin) ^a			
		total phenolic	condensed phenolic	noncondensed phenolic	aliphatic
kraft lignin		3.8	1.6	2.2	2.4
methylation with $(\text{CH}_3)_2\text{SO}_4$	0.25	3.1	1.3	1.8	2.3
	0.5	2.3	1.0	1.3	2.4
	1	1.8	0.9	0.9	2.3
	1.5	1.3	0.7	0.6	2.3
	2	0.5	0.4	0.1	2.3
methylation with CH_3I	2.5	0.03	0.03	0.0	2.3
	0.5	3.5	1.4	2.1	2.3
	1	2.9	1.3	1.6	1.9
	1.5	2.4	1.0	1.4	1.8
	2	1.8	1.0	0.9	1.6
	2.5	1.6	0.8	0.8	1.6
	3	1.5	0.8	0.7	1.5

^aAverage of two experiments. ^bMole ratio of the methylation reagent to the total phenolic hydroxyl in the softwood lignin.

different ionic species at the beginning of the methylation reactions at room temperature. The relatively low $\text{p}K_a$ of 15.4 for benzyl alcohol was selected to represent the different aliphatic hydroxyl groups. The $\text{p}K_a$ values of methanol, ethanol, and isopropyl alcohol are all actually higher than 15.4, so that the calculation will preclude the underestimation of the ionization efficiency of the aliphatic hydroxyl groups in lignin. The $\text{p}K_a$ value of 9.65 for 3-methoxyphenol was selected for the calculation because it may resemble the guaiacyl structural unit in softwood lignin and is of lower $\text{p}K_a$ than phenol ($\text{p}K_a = 9.94$), thus avoiding an overestimation of the ionization efficiency of the phenolic hydroxyl groups in lignin. These calculations showed that the ionization efficiency of the phenolic hydroxyl group is about 80 times higher than that of their aliphatic counterparts in 0.7 M NaOH (the highest NaOH concentration used in this work). These large ionization differences between the two types of hydroxyl groups offer support for our observations that the aliphatic hydroxyl groups were methylated to an unnoticeable degree under our methylation conditions. While the hydrolysis rate of dimethyl sulfate would also be increased when elevated pH and temperature (80 °C) values were used, such conditions did not alter the calculated selectivity. When higher degrees of methylation were the goal, higher amounts of dimethyl sulfate were used. Under those circumstances, a quick drop in the pH (due to hydrolysis of dimethyl sulfate) was apparent. This had to be manually compensated for by the slow addition of a base for the remaining of the reaction time.

In contrast to the remarkable effectiveness of dimethyl sulfate, the data of Table 1 also demonstrate that methyl iodide was significantly less reactive toward the different phenolic hydroxyl groups in softwood kraft lignin. It was found that the methylation leveled off at about 60% when mole ratios (methyl iodide to phenolic hydroxyl groups) above 2.5 were used. Furthermore, methyl iodide was also shown to methylate the aliphatic hydroxyl groups within the lignin. When methyl iodide was used in 3 mol equiv (based on phenolic hydroxyl groups), 38% of the aliphatic hydroxyl groups and 61% of the phenolic hydroxyl groups were methylated (Figure 2).

It was also found, especially at the lower mole ratios (Table 1), that the non-condensed phenolic hydroxyl groups were

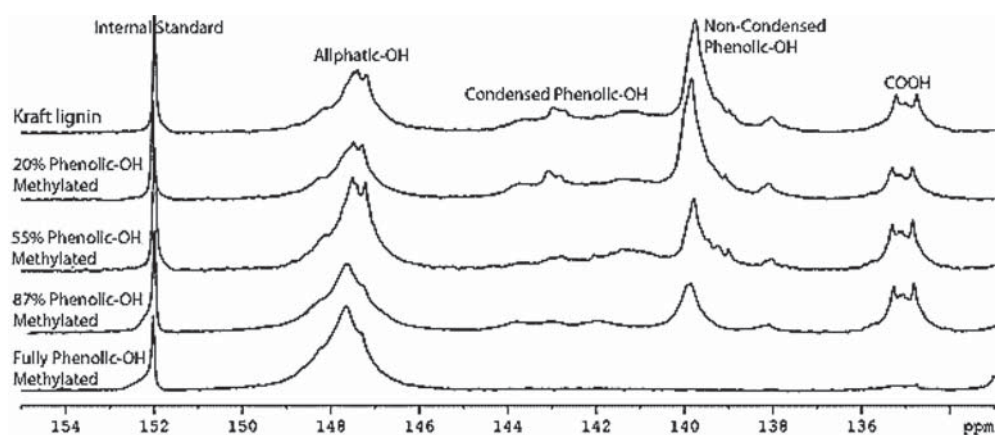


Figure 1. Quantitative ^{31}P NMR spectra of methylated softwood kraft lignins at variable degrees of methylation by using dimethyl sulfate in aqueous NaOH.

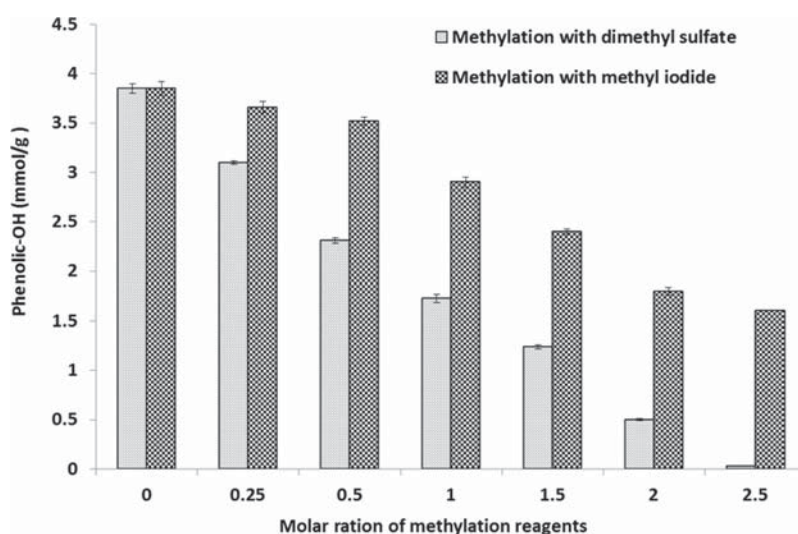


Figure 2. Effectiveness of methylation toward the various phenolic hydroxyl groups in softwood kraft lignin using different methylation reagents under the determined optimum reaction conditions.

more susceptible to methylation than those containing substituents in the C5 position, termed the “condensed” phenolic hydroxyl groups.

A variety of additional methylation experiments were also carried out at milder reaction conditions. These were all valuable for an in-depth understanding of the methylation chemistry of softwood kraft lignin in basic aqueous media. These details are provided in Table S1 in the SI.

For example, the hydrolytic decomposition of dimethyl sulfate is seen to always be associated with methylation. To fully methylate all phenolic hydroxyl groups present in lignins, excess dimethyl sulfate is needed. Because sulfuric acid will be generated from the hydrolysis reaction of dimethyl sulfate, excess NaOH is needed. At this point care needs to be exercised so that the pH is moderate enough to avoid ionization of a comparable amount of aliphatic hydroxyl groups. In this work, 0.7 M NaOH was found not to alter the reaction selectivity toward softwood kraft lignin. Efforts at lowering the concentration of the base resulted in the formation of precipitates (Table S1 in the SI). This dilemma can be solved by using reaction solutions of reduced pH and increased

volume, which, however, will inevitably lower the lignin concentration in the reaction system.

The reaction entry labeled C4, selected from one of the reactions in Table 1, can be viewed as a standard to evaluate the effectiveness of the different reaction conditions examined. Prior to being heated to 80 °C, the reaction C4 had been stirred for 30 min at room temperature, which was found to be very important to obtain complete methylation. For reaction entry C3 (Table S1 in the SI), an identical reaction solution was immersed in a hot oil bath set at 60 °C. As a result, the degree of methylation was only 63% after 1 h. The reaction entry C2 is very similar to C3 with the exception that a relatively lower base concentration was used; consequently, the degrees of methylation of these two runs were actually almost identical. The initial room temperature stage in C4 can be expected to partly alleviate the hydrolysis of dimethyl sulfate as the methylating agent reacts with the phenolic hydroxyl groups of lignin quickly. Moreover, the continuous addition of base as the reaction is heated will keep the base concentration at a level high enough to maintain the reaction homogeneity and sufficiently ionize the phenolic hydroxyl groups in order to be methylated. As an example, at the same lignin concentration,

Table 2. Experimental Details of Methylation of Hardwood Kraft Lignin at Different Reaction Conditions

sample entry	reaction conditions					hydroxyl groups (mmol/g of lignin)			
	R/L ^a	NaOH (mol/L)	Lignin (g/mL)	time (h)	T (°C)	total phenolic	condensed phenolic	noncondensed phenolic	aliphatic
hardwood kraft lignin						3.2	2.2	1.0	1.1
D1	7.4	0.30	0.01	8	25	0.4	0.3	0.1	1.1
D2	1.8	0.7	0.05	2	80	2.2	1.5	0.7	1.1
D3 ^b	2.0	0.15	0.02	14	25	0.6	0.4	0.2	1.1
E1	0.4	0.7	0.03	10	25	2.9	2.0	0.9	1.1
E2	0.9	0.7	0.03	10	25	2.8	1.9	0.9	1.1
E3	1.3	0.7	0.03	10	25	2.5	1.7	0.8	1.1
E4	2.5	0.7	0.03	10	25	2.1	1.4	0.7	1.1
E5	3.4	0.7	0.03	10	25	1.9	1.2	0.7	1.1
E6	4.2	0.7	0.03	10	25	1.7	1.1	0.6	1.1

^aMole ratio of dimethyl sulfate to the total phenolic hydroxyl in the hardwood lignin. ^bDuring the reaction, a NaOH solution (0.15 M) was continuously added to maintain a pH above 11 during the first 3 h.

Table 3. Hydroxyl Group Contents for the Initial and Oxypropylated Softwood Kraft Lignins

sample entry	R/L ^b	hydroxyl groups (mmol/g of lignin) ^a				
		total phenolic	condensed phenolic	noncondensed phenolic	aliphatic	new aliphatic
softwood kraft lignin	0	3.8	1.6	2.2	2.4	0
oxypropylated softwood kraft lignin	0.25	3.6	1.5	2.1	2.4	0.2
	0.5	3.4	1.4	2.0	2.4	0.5
	1.0	1.8	0.8	1.0	2.4	1.9
	1.5	1.0	0.4	0.6	2.4	2.8
	2.0	0.5	0.3	0.2	2.4	3.3
	2.5	0.05	0.05	0.0	2.4	3.8

^aAverage of two experiments. ^bMole ratio of the methylation reagent to the total phenolic hydroxyl in the lignin.

the room temperature reaction, C5, was found to precipitate quickly because of the decrease in the pH when no special care of the continuous addition of base was exercised. As a result, only 89% methylation was obtained in reaction entry C5 using more than 5.5 equiv of dimethyl sulfate to phenolic hydroxyl groups. In some other reactions of lower base concentrations from 0.1 to 0.3 mmol/mL and also a lower lignin concentration of 0.01 g/mL, the highest degrees of methylation that could be attained were about 85% by using 2.5 equiv of dimethyl sulfate. In the reaction entry B1, 84% methylation was obtained when 0.1 mmol/mL of base were used at 60 °C. The reaction quickly became cloudy, but dimethyl sulfate still demonstrated fairly good effectiveness toward the phenolic hydroxyl groups at elevated temperatures. This may indicate that using appropriately elevated temperatures can enhance the effectiveness of the methylation reaction so that one may reduce, in a controlled manner, the use of the toxic dimethyl sulfate during practical applications. As an example, in the reaction entry B3, room temperature and a relatively higher base concentration of 0.15 g/mL were adopted to prolong the homogeneous reaction period; however, a lower degree of methylation (74%) than that of the reaction entry B1 was attained.

On the basis of the knowledge accumulated from the methylation of softwood kraft lignin, we have also made efforts toward understanding the hardwood kraft lignin methylation chemistry. This series of methylation reactions using dimethyl sulfate are shown in Table 2.

Upon comparison of the series of reaction entries labeled as D in Table 2, it becomes apparent that reaction entry D3 attained 81% methylation despite the fact that it was conducted at room temperature. This impressive result can be attributed to the continuous addition of base (0.15 M aqueous NaOH) to

maintain an ionizing pH level toward the phenolic hydroxyl groups in the hardwood kraft lignin. Only 2 equiv of dimethyl sulfate to phenolic hydroxyl groups was used in reaction entry D3. However, such conditions offered degrees of methylation similar to those of reaction entry D1, which used more than 7.4 equiv of dimethyl sulfate to phenolic hydroxyl groups. The methylation at 80 °C in reaction entry D2 was not very efficient. This again may be due to the absence of a room temperature reaction period at the early reaction stage. The methylation of hardwood kraft lignin was also verified to be a selective reaction in a controlled fashion. A series of reaction entries, labeled as E, were carried out in order to examine the selectivity and effectiveness of dimethyl sulfate toward hardwood kraft lignin methylation. In a manner different from that of the corresponding softwood kraft lignin methylation, room temperature conditions were used. The aliphatic hydroxyl groups (Table 2) were not affected as anticipated. The total phenolic hydroxyl groups were found to be gradually reduced upon an increase in the dimethyl sulfate feeding ratio. However, only about 50% methylation was attained under these mild conditions when using more than 4 equiv of dimethyl sulfate, as shown in reaction entry E6. This can be interpreted by the relatively low reactivity of the chemical characteristics of the phenolic hydroxyl groups present in hardwood kraft lignin.

3.2. Lignin Oxypropylation. In earlier work, in efforts to tailor-make lignin polyols suitable for the preparation of polyurethane materials and other polymeric materials,^{8,23,24} the reaction of lignin with propylene oxide was explored, often requiring elevated temperatures and high pressures (because of the highly volatile nature of propylene oxide) in the presence or absence of solvent.^{6,25} Almost unavoidably under such

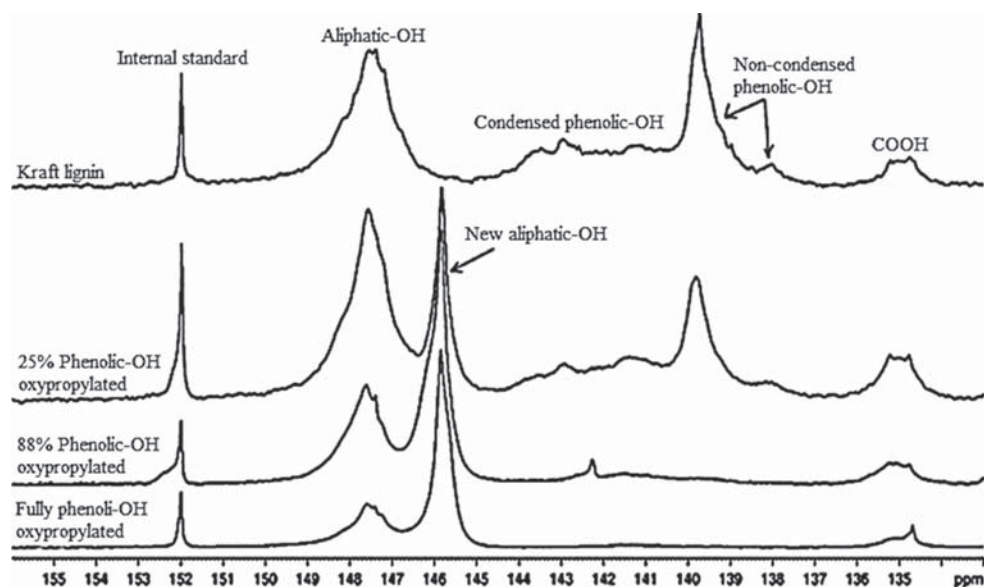


Figure 3. ^{31}P NMR spectra of softwood kraft lignin samples of different oxypropylation levels.

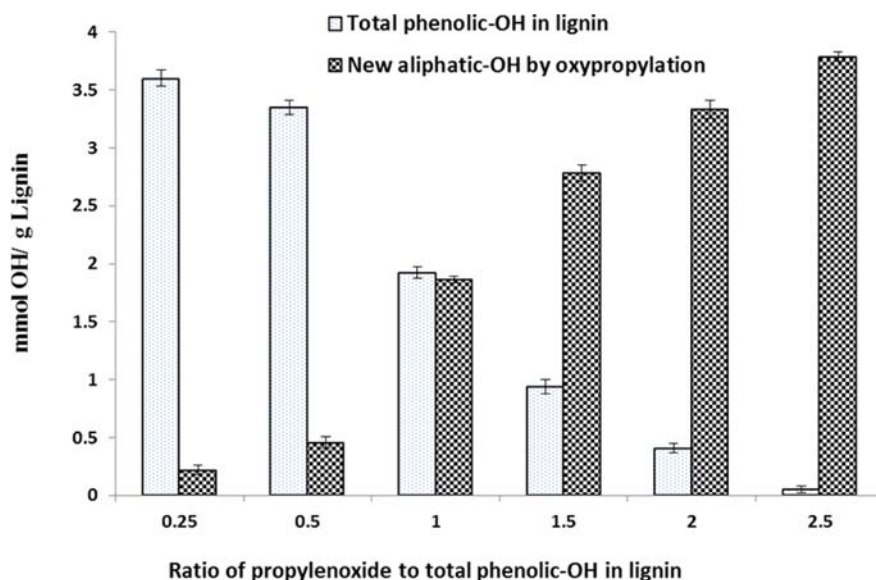


Figure 4. Selective conversion of phenolic hydroxyl groups into new aliphatic groups by oxypropylation.

conditions, ring-opening polymerization was induced through secondary nucleophilic reactions.

In contrast to earlier efforts, we aimed at selectively masking the phenolic hydroxyl groups of lignin using oxypropylation chemistry under mild conditions, preventing polymerization. A series of six samples were prepared at different mole ratios of propylene oxide to phenolic hydroxy groups in 0.5 M NaOH solutions at room temperature for 18 h (Scheme 1, III). The chemistry and extent of oxypropylation was monitored by quantitative ^{31}P NMR.

As shown in Figure 3, two distinct broad signals appear in the aliphatic region of the ^{31}P NMR spectra evident at between 144.5 and 149.5 ppm, respectively. While the broad peak at around 147.5 ppm is responsible for the typical primary and secondary aliphatic hydroxyl groups originally present in lignin, the relatively sharper peak observed at around 145.8 ppm is attributed to the new secondary aliphatic hydroxyl groups

formed by the ring-opening attachment of propylene oxide¹² (Scheme 1, III).

The hydroxyl content analytical data for the initial and oxypropylated samples are shown in Table 3, as obtained by quantitative ^{31}P NMR (Figure 3). A close examination of the data of Table 3 and the spectra of Figure 3 reveals a quantitative correlation in the reduction of the total phenolic hydroxyls with the concomitant increase of the new secondary hydroxyl groups as they emerge from the ring-opening reaction and the attachment of propylene oxide onto lignin (Scheme 1, III). In contrast, the original aliphatic hydroxyl groups were actually not affected. This evidence supports our contention that the selected mild reaction conditions for lignin oxypropylation are selective toward the phenolic hydroxyl groups of the softwood kraft lignin (Figure 4). Moreover, the oxypropylation reactions examined here have also demonstrated that under these reaction conditions the relatively smooth derivatization of the

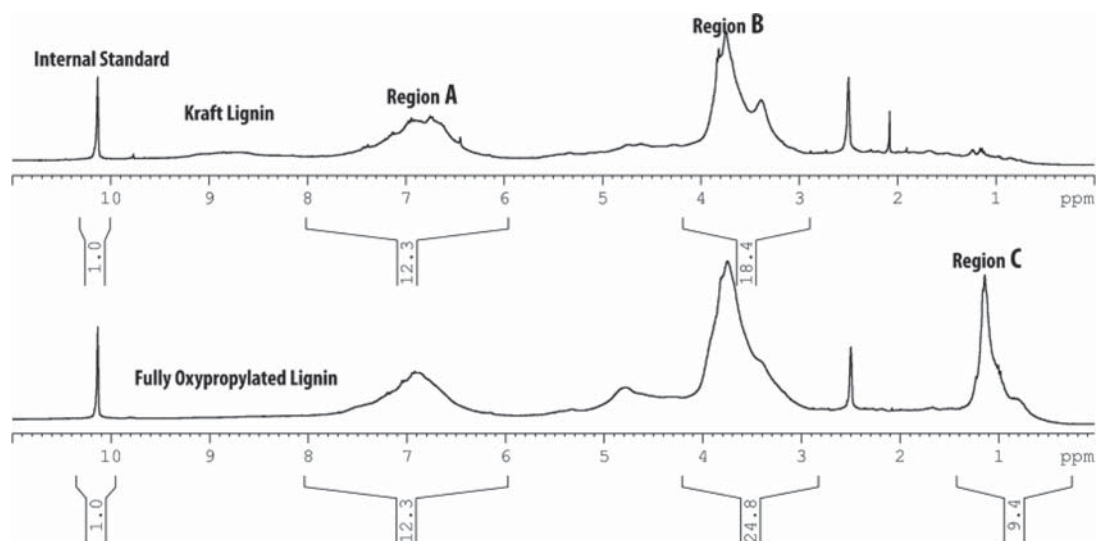


Figure 5. ^1H NMR spectra of the initial and fully oxypropylated softwood kraft lignins.

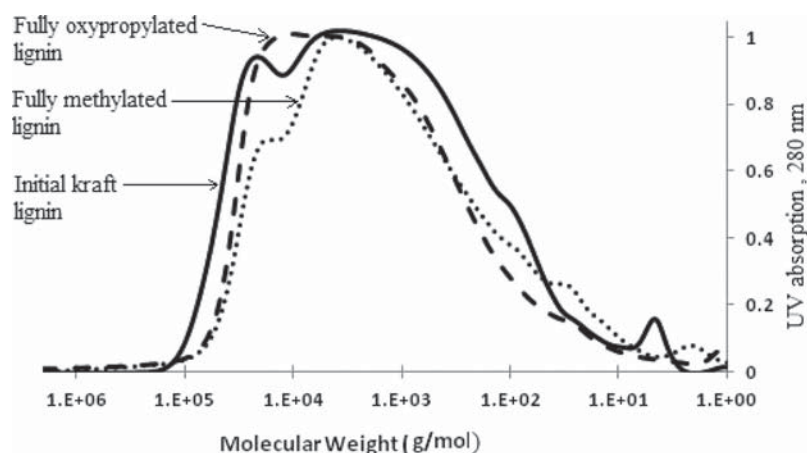


Figure 6. Molecular weight distributions of the initial and fully oxypropylated and methylated (by dimethyl sulfate) softwood kraft lignins.

phenolic hydroxyl groups in softwood kraft lignin can be attained progressively by increasing the feeding ratio of propylene oxide to phenolic hydroxyl groups. About 99% of the phenolic hydroxyl groups were oxypropylated by using 2.5 equiv of propylene oxide based on the total phenolic hydroxyl groups.

In an effort to accurately estimate the maximum average addition number of propylene oxide to each phenolic hydroxyl group under the selected reaction conditions, quantitative ^1H NMR spectra were acquired to compare the initial and fully oxypropylated softwood kraft lignin in the presence of an internal standard, PFB (Figure 5). The spectrum of the fully oxypropylated sample illustrates three distinct regions, which allow for the quantitative assessment of the distribution of various protons in the product.²² These regions represent aromatic protons (region A, 6.0–8.0 ppm), methylene and methoxy protons (region B, 2.8–4.2 ppm), and new aliphatic methyl protons (region C, 0.2–1.5 ppm) formed by oxypropylation. Because the aliphatic hydroxyl groups in the lignin were not affected by the oxypropylation reaction (based on the ^{31}P NMR data), the new methyl protons are therefore considered to be formed by the ring-opening attachment of propylene oxide onto phenolic hydroxyl groups. Because 3.8

mmol/g of phenolic hydroxyl groups was present in the initial softwood kraft lignin, as determined by quantitative ^{31}P NMR, 6.8 mmol/g of methyl groups was estimated to be formed based on quantitative ^1H NMR analyses for the fully oxypropylated softwood kraft lignin (Figure 5). Consequently, the average addition number of oxypropylene repeating units in the fully oxypropylated softwood kraft lignin sample was calculated as approximately 1.8.

3.3. Molecular Weight. Molecular weight distributions of fully derivatized lignin samples, including the fully methylated softwood kraft lignin using dimethyl sulfate as the methylation reagent and the fully oxypropylated, were examined using GPC. The chromatograms of the initial softwood kraft lignin and its two derivatives are shown in Figure 6. These analyses confirm the conclusions of our quantitative ^1H NMR work that showed a nearly stoichiometric and nonpolymerized propylene glycol being grafted onto the lignin. This was most likely due to the intentionally mild oxypropylation reaction conditions used in this work. Despite some minor (and yet unexplained) changes in the modality of these chromatograms, the molecular weight distributions of the initial and modified softwood kraft lignins are nearly identical, as anticipated.

4. CONCLUSIONS

In this work, we have developed mild and facile conditions for the selective masking of the phenolic hydroxyl groups of softwood kraft lignin through either methylation using dimethyl sulfate or oxypropylation. Under the developed and optimized conditions, the degree of derivatization can be varied at will by varying the mole ratio of the derivatization reagent to the total phenolic hydroxyl groups present in the lignin. Complete derivatization of all lignin phenolic hydroxyl groups can be achieved by using about 2.5 equiv of each derivatization reagent to phenolic hydroxyl groups under the specified reaction conditions. No apparent substitution effects on the aliphatic hydroxyl groups of the lignin were observed for both derivatization chemistries. In contrast, methylation using methyl iodide was not as selective and as effective. Hardwood kraft lignin was also methylated using dimethyl sulfate based on the accumulated understanding from our work with its softwood counterpart. This work verified that the methylation of hardwood kraft lignin using dimethyl sulfate (under the described reaction conditions) is selective toward the phenolic hydroxyl groups, allowing for a progressive methylation that can be adjusted by varying the feed ratio of dimethyl sulfate to the phenolic hydroxyl groups. The hardwood kraft lignin also seemed to be relatively less reactive than its softwood counterpart, which can be anticipated because of the significantly different chemical characteristics of the phenolic hydroxyl groups in the hardwood kraft lignin.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental details for methylation of softwood kraft lignin at different reaction conditions (Table S1). 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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