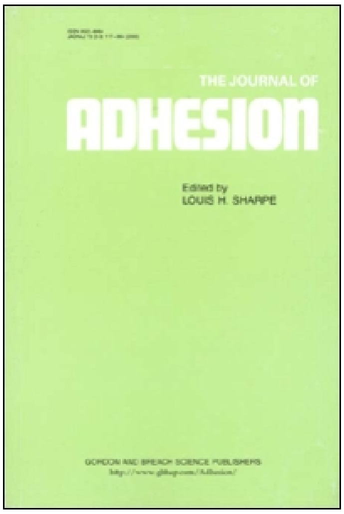

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Engineering Plastics from Lignin. VIII. Phenolic Resin Prepolymer Synthesis and Analysis

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Engineering Plastics from Lignin. VIII. Phenolic Resin Prepolymer Synthesis and Analysis

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A sequential derivatization of lignin with formaldehyde and phenol was investigated as a means of enhancing lignin's reactivity in phenol-formaldehyde resins. Kraft lignin (KL) and two novel bioconversion lignins, steam explosion (SEL) and acid (H_2SO_4) hydrolysis lignin (AHL), were chemically modified by sequential reaction with formaldehyde and phenol. The results with regard to the chemical structure of the phenolic resin prepolymers showed that the ability to hydroxymethylate and phenolate is related to lignin structure. KL from pine proved to be more amenable to chemical modification with formaldehyde and phenol than was either SEL from aspen or AHL from pine. Degrees of substitution were determined by H–NMR spectroscopy and by oxidative analysis with alkaline permanganate. H–NMR spectroscopy revealed degrees of phenolation of 0.42, 0.29 and 0.21 per average C_9-unit for KL, AHL, and SEL, respectively; and permanganate oxidation illustrated that approximately 90%, 60%, and 60% of all available unsubstituted phenolic guaiacyl units in KL, AHL and SEL, but none of the corresponding non-phenolic or syringyl entities, had become derivatized.

INTRODUCTION

Phenol-formaldehyde resins are finding widespread use in diverse

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markets ranging from insulation materials to foundry resins to wood adhesives, with a total market volume of over two billion pounds per year (1982)[1]. The forest products industry is the single largest consumer of phenolic resins with 37% of the total U.S. production being used in plywood applications[2]. Base catalyzed (NaOH) phenolic resins, or resoles, are the preferred adhesive in plywood production due to their low cost and high adhesive strength, especially in exterior applications where durability against high moisture contents is crucial.

The chemistry involved in phenol-formaldehyde resins has been the subject of extensive research[3-9]. The complex crosslinked nature of phenolics in the later stages of cure has obscured a detailed understanding of the mechanisms and chemical structures involved. Recently, research has focused on the important interaction of formulation parameters with chemical structure and their effect on bond performance[10-12]. This work optimized synthesis schedules and formulation parameters, in terms of cooking time-temperature profiles and mole ratios of ingredients, to determine their effect on condensed polymer structure and adhesive performance.

The opportunity to incorporate lignin, an abundant polyphenolic pulping residue very similar in structure to a phenolic resin, into a phenol-formaldehyde adhesive has interested researchers since the early part of this century. Contemporary pulp production is dominated by the kraft process with total U.S. lignin co-generation reaching over twenty million tons per year[13]. All but about 35,000 t/yr of the lignin in kraft black liquors produced is used as an in-house fuel source[13]. At a fuel value of <4¢/lb, this represents an underutilized material with promise in high value polymer applications[13-16]. Previous studies in this series have explored opportunities for lignin to serve in various polymeric applications[17-19], and to contribute to the economics of various chemicals-from-biomass process schemes[13].

An area of demonstrated lignin utility is in the adhesives field, and this has recently been the subject of a comprehensive review by Nimz[20]. Most early attempts to incorporate lignin into thermosetting phenolics were limited to low replacement levels. Higher incorporation levels often resulted in unsatisfactory chemical and physical properties. Differing reasons were given as to what limited high lignin contents. Thus, work was conducted to enhance either the chemical reactivity or the physical properties of lignin fractions to be used as prepolymers in phenolic resins. Reactivity was improved by hydroxymethylation with formaldehyde to provide methylol functionalities[21-24]. Both kraft lignin and lignin sulfonates have been derivatized with phenol to provide a reactive prepolymeric resole which can either be used as an extender or as the sole component in phenolic resins[25-27]. The degree of phenolation is dictated by reaction conditions. "Karatex", a lignin based phenolic resin, has received attention as a plywood adhesive[28] in which the utility of the lignin is improved by ultrafiltration. Use is made of the high molecular weight fraction, and this has resulted in replacement levels between 40 and 70%.

This work adopts various aspects of previous research in an approach to modify lignin chemically to achieve high incorporation levels. These are necessary to resolve the effects of lignin structure on adhesive performance. Hydroxymethylation was chosen to modify the lignins initially since the condensation of lignin and phenol is greatly enhanced by the methylol substituents in lignin [4,6]. Subsequent phenolation of the hydroxymethylated adduct provides a material capable of crosslinking with phenol and formaldehyde. As a result, lignin can be incorporated into the crosslinked phenolic network structure.

MATERIALS AND METHODS

I. Materials

Kraft Lignin (KL): The kraft lignin used in this study was the commercially available product Indulin AT(R) from Westvaco, Charleston, SC. The softwood (mixed pine)-based material was purified by dissolution in aqueous alkali, acid precipitation and washing by centrifugation in distilled water. This preparation may differ from other kraft lignin preparations in relation to wood source, pulping conditions and isolation procedure.

Acid Hydrolysis Lignin (AHL): Lignin from white pine chips was obtained from a continuous cellulose-to-glucose acid hydrolysis pilot plant at New York University. In this process, biomass is fed into a twin screw extruder heated by superheated steam (232°C) under high pressure (500 psi). Sulfuric acid heated to 220°C at a concentration of 2% is injected into the slurry near the outlet. Reaction times approach 20 seconds[29]. The solid residue was separated by centrifugation and shipped moist in plastic containers. Lignin residues were further purified by extraction in alkali, filtration and acid precipitation.

Steam Explosion Lignin (SĒL): Lignin from steam exploded aspen wood chips was obtained from a pilot plant operated by Iotech Corp. of Ottawa, Canada[30]. The process involves steam hydrolysis (240°C) at 600 psi followed by explosive decompression and extraction by aqueous alkali. Lignin preparations were received as dry brown powders and were further purified by acid precipitation from an alkaline solution prior to use.

The chemistry of these three lignins has been the subject of an earlier publication[31].

II. Methods

Hydroxymethylation: A slurry consisting of purified lignin (50 g) and distilled water (125 g) was prepared in a 500 ml. Erlenmeyer flask. To this slurry is added 2N NaOH (125 ml) followed by the addition of a 37% formalin solution (48.6 g). Hydroxymethylation was performed at room temperature for 72 hours or at 70°C for 20 hours in an agitated water bath. After reaction, the mixture was acid precipitated and centrifuged with distilled water to remove free acid. The solid material was then freeze dried.

Phenolation: In a 600 ml stainless steel Parr reactor, hydroxymethylated lignin (50 g) was combined with distilled water (200 g), NaOH (107.5 g), and phenol (84.3 g at 89%). The reactor was equipped with pressure gauge, mechanical stirrer and automatic heat control. The reaction schedule consisted of a 15 minute warm up period followed by 2 hours at the phenolation temperature (170°C). After 2 hours, the reaction mixture was cooled to room temperature followed by acidification with dilute HCl and centrifugation. After removal of the supernatant, purification was conducted by successive washings with ethyl ether, followed by freeze drying to a brown powder.

H-NMR Spectroscopy: Lignin samples were acetylated overnight at room temperature in a 1:1 mixture of pyridine and acetic anhydride. The acetylated lignins were precipitated into dilute HCl, filtered, washed with distilled water, and freeze dried. Spectral analysis was conducted on acetylated lignins dissolved in deutero chloroform ($CDCl_3$) with 1% TMS.

Permanganate Oxidation: Lignin preparations were subjected to sequential ethylation with diethylsulfate ($DESO_4$), oxidative depolymerization with cupric oxide (CuO), methylation with dimethylsulfate ($DMSO_4$), oxidation by alkaline permanganate followed by treatment with H_2O_2, and methylation with diazomethane in accordance with a procedure reported earlier[31,32]. The degradation product mix was analyzed by gas chromatography.

RESULTS AND DISCUSSION

I. Lignin Analysis Methodology

H–NMR Spectroscopy: Lignin analysis by H–NMR spectroscopy was pioneered by Ludwig *et al.*[33–35] and by Lenz[36]. Peak assignments and range boundaries were established through the use of monomeric and oligomeric ligninlike model compounds. The eight ranges suggested by Ludwig *et al.*[35] and commonly adopted by others[31,32,36] are illustrated in Figure 1. These are for carboxylic and aldehydic protons (range 1); for aromatic protons (range 2); for vinylic and other minor aliphatic protons in the sidechains of lignin's phenylpropanoid units (ranges 3 and 4); for methylene (CH_2) and methoxy (OCH_3) protons (range 5); for aromatic (range 6) and aliphatic (range 7) acetoxy protons; and for various highly shielded protons (range 8).

Changes in lignin structure in response to chemical modification, such as derivatization with formaldehyde and/or phenol, can be modelled quantitatively to allow for the determination of degrees of substitution. The methylene protons in a methylol substituent added to lignin during hydroxymethylation gives rise to a new peak, within range 4, in the H–NMR spectrum. Range 4a is designated for this CH_2-peak. Abstraction of aromatic protons during electrophilic substitution by formaldehyde enables modelling of the relationship between H–NMR signal response in range 2 and degree of substitution by formaldehyde. The increase in aromatic protons and in phenolic hydroxy groups from phenolation allows for the modelling of the relationship between H–NMR signal response in ranges 2 (aromatic protons) and 6 (aromatic acetoxy-H) and degree of phenolation. These models can be used in a spectral determination of structural changes arising from lignin derivatization with formaldehyde and phenol.

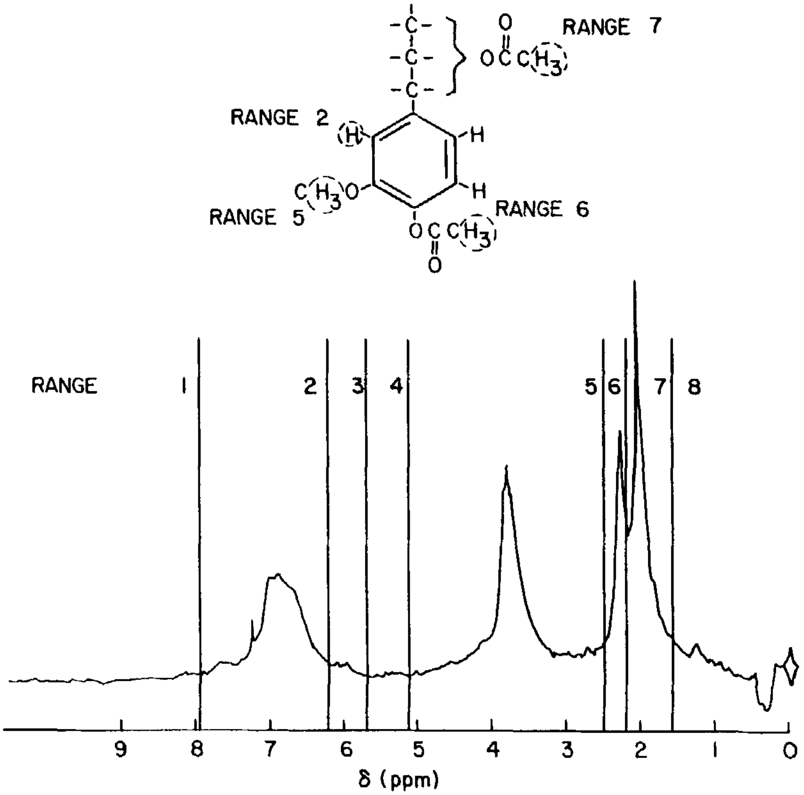

FIGURE 1 Typical H-NMR spectrum for KL with range assignment for protons on a C_9 unit.

Permanganate Oxidation: Degradative permanganate oxidation is a technique for primary chemical analysis which has shown great utility as a means for generating quantitative information on the nature of macromolecular lignin[37–41,31,32]. Ethylated, depolymerized, and methylated lignin is degraded into a mixture of monomeric and dimeric aromatic acids. Subsequent analysis of the reaction product mixture by gas chromatography reveals intimate details regarding interunit linkages and repeating unit (C_9) structure[31,32,42].

The addition of phenol to a C_9-unit can be monitored by permanganate oxidation. Phenolation can be expected to result in substantial yields of unsubstituted ethoxy methyl benzoate. Since phenolation occurs primarily at an unsubstituted 5-position of a guaiacyl nucleus following methylolation, there should be a concommitant decrease in the proportion of 3-methoxy-4-ethoxy methyl benzoate present in the degradation product mix.

II. Synthesis of Lignin Derivative Prepolymer

Hydroxymethylation: The successful derivatization of lignin with formaldehyde requires the presence of both phenolic hydroxy functionality and a free (unsubstituted) ortho or para position on a C_9-unit. Hydroxymethylation can also occur adjacent to an α-carbonyl on the alkyl sidechain due to the reactivity of an activated hydrogen. Depending on lignin type (i.e. KL, SEL, or AHL), these structural features will be present in varying quantities. Thus the ability to hydroxymethylate can be related directly to lignin structure.

The reaction between formaldehyde and lignin, in aqueous alkaline solution, results in an ortho- (or para-) substituted hydroxymethylated lignin derivative[43] whose chemical nature has been altered to provide material more crosslinkable with a phenol-formaldehyde resin.

Results by H–NMR analysis for the hydroxymethylated and phenolated lignins are shown in Table I. The data reveal that the ability

TABLE I
H–NMR analysis results for several acetylated lignins and lignin derivatives—in percent of integration by ranges according to Ludwig *et al.*[34]

	Signal response (% integration)									
	Range									
Lignin type	1	2	3	4	4a	5	6	7	6 + 7	8
Kraft Lignin	0	20.4	2.0	1.0	1.9	36.7	11.2	23.5	34.7	3.1
KL–F[1]	0	15.5	2.6	1.7	6.0	36.2	8.6	26.7	35.3	2.5
KL–FP[2]	0	27.1	0.7	0	0	35.4	16.0	18.7	34.7	2.1
Steam expl. L.	0	16.2	4.1	1.5	3.5	44.7	11.2	17.3	28.5	1.5
SEL–F[3]	0	15.6	1.4	0	4.1	42.8	8.2	25.9	34.1	1.4
SEL–FP[4]	0	21.3	1.6	0.8	0	40.2	13.1	18.8	31.9	2.5
Acid hydrol. L.	0	19.4	4.0	2.4	5.6	37.1	8.9	20.2	29.0	2.4
AHL–F[5]	0	20.3	2.5	0.8	2.5	38.1	11.0	22.9	33.9	1.7
AHL–FP[6]	0	25.4	1.7	1.1	0	37.3	14.1	18.6	32.7	1.7

[1] Hydroxymethylated kraft lignin
[2] Phenolated kraft lignin
[3] Hydroxymethylated steam explosion lignin
[4] Phenolated steam explosion lignin
[5] Hydroxymethylated acid hydrolysis lignin
[6] Phenolated acid hydrolysis lignin

to derivatize lignin with formaldehyde is indeed dependent on lignin type. The lack of a characteristic methylene proton peak for both hydroxymethylated AHL (AHL–F) and hydroxymethylated SEL (SEL–F) in range 4a, and a non-discernible change in response in range 2, provide direct evidence for the inability to achieve substantial degrees of hydroxymethylation with these two bioconversion lignins. This is related to the structural features inherent in these lignins[31]. Hardwood (aspen) SEL has a high methoxyl content (18.23%) due to the presence of syringyl units. As a consequence, the relative number of available 5-positions (ortho to phenolic OH) is decreased[31]. AHL has undergone structural modification during processing by acid condensation involving the aromatic ring. Although this reaction consumes predominantly free 6-positions (as indicated by an increase of appropriate phthalic acid derivatives in permanganate oxidation), it can be expected to limit the reactivity of available 5-positions by

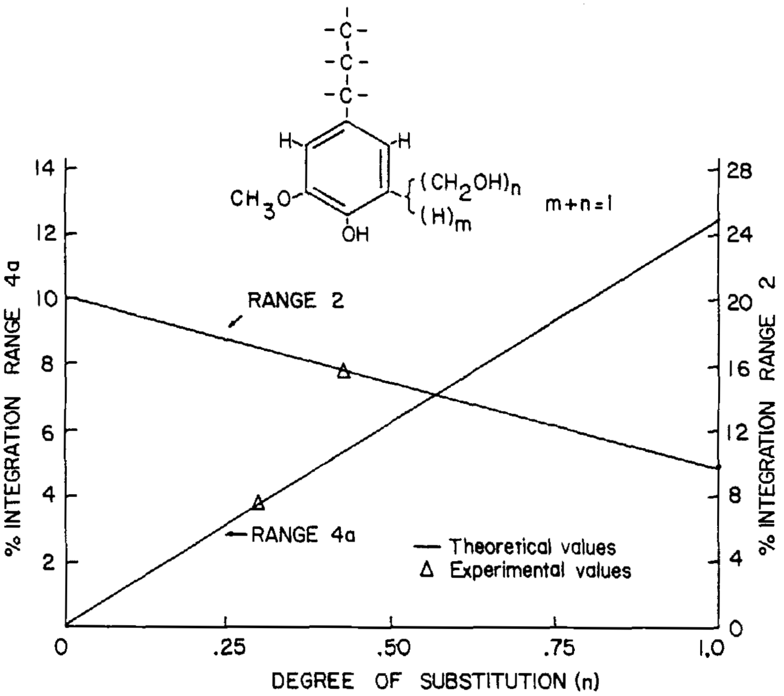

FIGURE 2 Relationship between H-NMR signal intensity (percent integration in ranges 2 and 4a) and degree of substitution for hydroxymethylated KL.

crowding. The interunit linkage distribution for AHL shows a very high content of condensed carbon-to-carbon linkages with a concommitant depletion of alkyl aryl ether linkages[31].

By plotting the values for percent integration in both ranges, 2 and 4a, as determined by H–NMR spectroscopy, and by determining the position of these values on the lines of a theoretical model shown in Figure 2, the degree of substitution for KL is determined to be about 0.35. This figure agrees well with previous reports on the reaction between kraft lignin and formaldehyde[21,44].

Despite indistinct trends in ranges 2 and 4a, the H–NMR spectra for hydroxymethylated SEL and AHL show that lignin structure has been modified during the reaction with formaldehyde. By summing the signal response in ranges 6 and 7, total hydroxy (as acetoxy signals) content is seen to increase by 15–20%. This suggests that formaldehyde is indeed incorporated into these two lignins as hydroxymethyl groups, but not as aromatic substituents reactive with other phenol-formaldehyde resin prepolymers.

Phenolation: The purpose of the addition of a hydroxymethyl group onto lignin was to provide functionality capable of promoting condensation between phenol and the methylolated lignin species. As shown in Figure 3, this condensation proceeds *via* a typical Lederer–Manasse type reaction. The nucleophilic attack by phenol on the hydroxymethyl

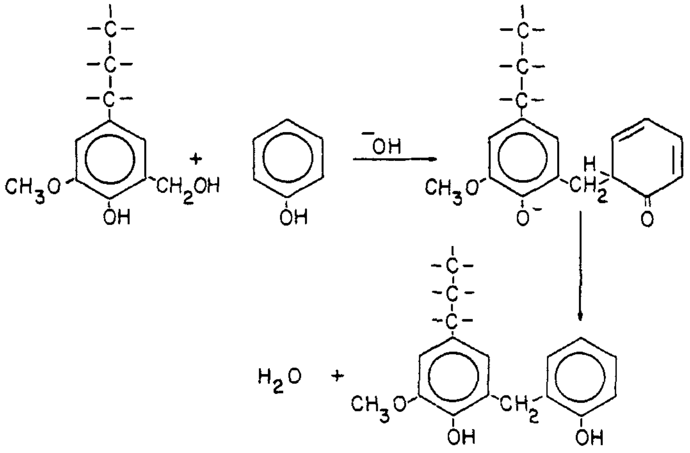

FIGURE 3 Reaction of phenol with methylol lignin.

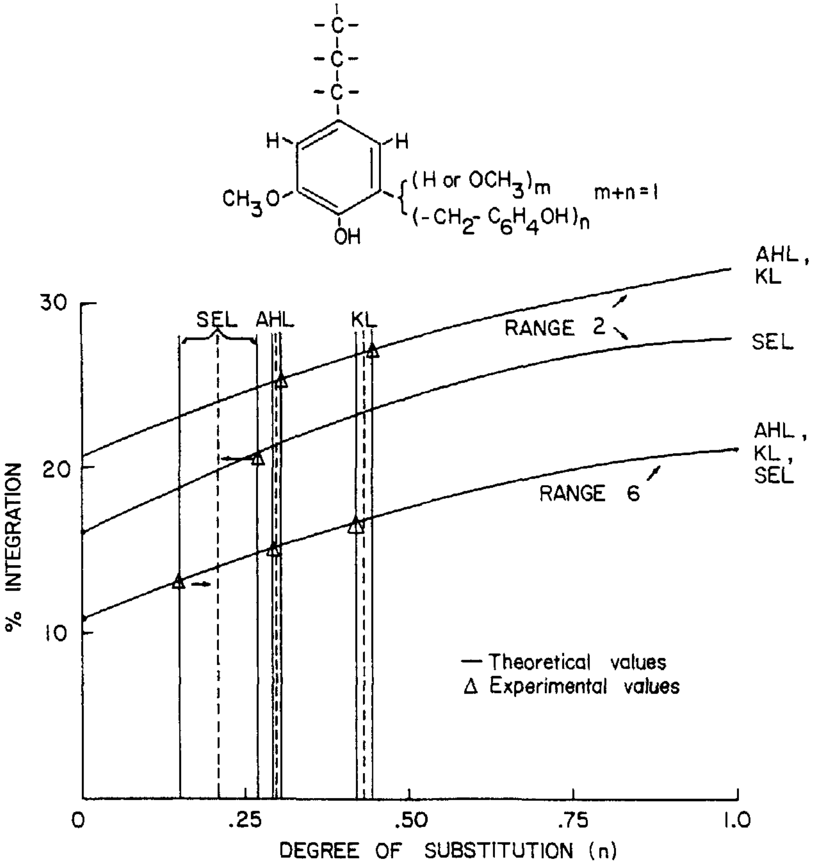

FIGURE 4 Relationship between H-NMR signal intensity (percent integration) and degree of phenolation for KL, SEL and AHL.

group of lignin produces a methylene bridge between the two phenolic nuclei. Rearomatization of phenol is the driving force for the reaction which produces water as a by-product.

The reaction was performed in aqueous alkali at a constant temperature of 170°C under pressure. These were found to be suitable conditions by Foster[27], who studied phenolation of lignin sulfonates over a temperature range between 134 and 245°C. No attempt was made to explore other, potentially adequate phenolation conditions.

The derivatization of lignin with phenol can be monitored by observing the H-NMR signal response in two ranges. The addition of an aromatic ring to lignin leads to an increase in range 2 from the added aromatic protons, and the increased phenolic hydroxy content can be detected in range 6. Through a theoretical model of the relationship between signal intensity (percent integration) in ranges 2 and 6 and degree of substitution, the amount of phenol added per C_9 unit can be calculated. Figure 4 illustrates this relationship for KL, SEL and AHL. Experimentally derived values for percent integration in ranges 2 and 6, shown in Table I for all three lignins were plotted on the theoretical curves displayed in Figure 4 to determine degrees of substitution. From this model, degrees of phenolation for KL, SEL and AHL were 0.43, 0.21 and 0.29, respectively.

The degree of phenolation is related to chemical functionality. In comparison to KL, SEL and AHL had relatively low degrees of hydroxymethylation. Since the successful condensation between phenol and lignin depends in large part on the presence of reactive methylol substituents on the aromatic ring, it is not surprising that hydroxy-

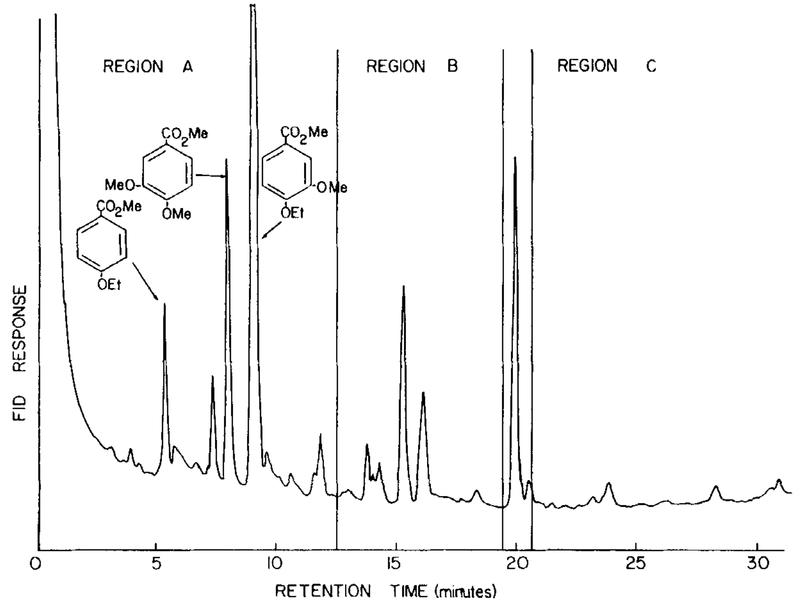

FIGURE 5 Gas chromatogram of permanganate oxidation product mixture for nonderivatized KL.

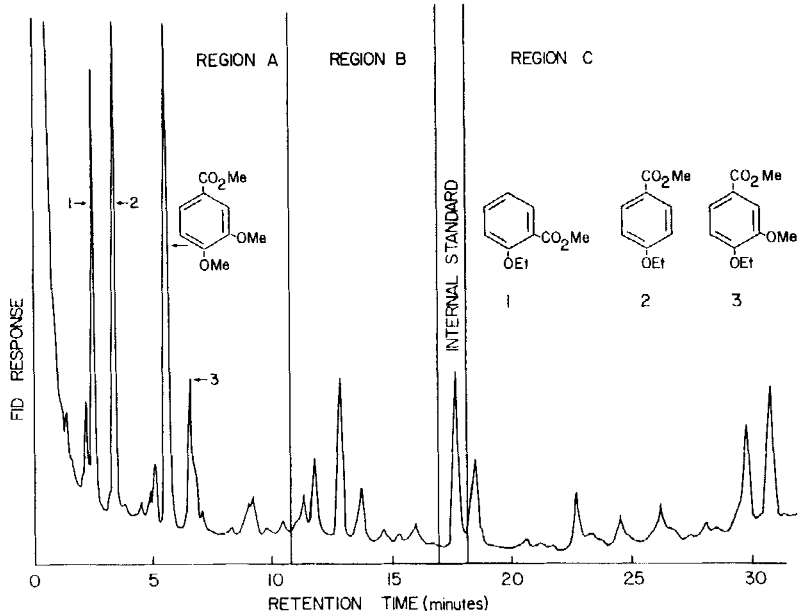

FIGURE 6 Gas chromatogram of permanganate oxidation mixture for phenolated KL.

methylated KL is more amenable to derivatization with phenol than either the SEL or the AHL derivative.

Degradative analysis by permanganate oxidation was performed on all lignins and all phenolated lignin derivatives. The gas chromatogram of the KL and the hydroxymethylated and phenolated KL derivative preparation are shown in Figures 5 and 6, respectively. Region A represents the monomeric monocarboxylic acids; region B contains the moneric di- and multi-carboxylic acids; and region C constitutes a multitude of dimeric compounds. Peak assignments for the various degradation products have been made by the use of authentic compounds. Degradation products which are used to monitor changes in lignin structure after phenolation are designated in region A. The ortho- and para-isomers of ethoxy methyl benzoate, compounds 1 and 2 in Figure 6, are the degradation products from bound phenol. Phenolic, unsubstituted guaiacyl-units giving rise to the 3-methoxy-4-ethoxy benzoic acid peak in the chromatogram of Figure 5 (compound 3 in Figure 6) are greatly diminished in the chromatogram of Figure 6,

TABLE II

Permanganate oxidation results for authentic and derivatized (formaldehyde and phenol) lignins

	KL		AHL[5]		SEL	
Structural feature	Authentic	Prepolymer	Authentic	Prepolymer	Authentic	Prepolymer
I. Distribution of degradation products[1] (in wt. % of total monomers and dimers)						
—Region A	39	45	44	67	69	58
—Region B	15	13	30	14	9	12
—Region C	17	40	25	18	21	30
II. Yield of degradation products (in mmol/C_g)[2]						
—Cmpd. 1	—	80	—	105	—	65
—Cmpd. 2	40	145	53	95	25	170
—Cmpd. 3	271	27	88	95	62	21
—Total unsubstituted guaiacyl units	330	95	104	280	340	192
—Total o and p-OH phenyl units	40	225	53	200	25	235
III. Measure of Condensation						
—GUA (+SYR)/Dimers (wt)[3]	3.4	1.4	0.6	2.7	4.9	1.5
—GUA (+SYR)/(ISO-) Phthalic Acid[4]	1.8	0.6	0.3	1.5	3.4	1.2

[1] According to the divisions shown in Figures 5 and 6.

[2] Yield of benzoic acid derivatives after yield correction according to the method of Larsson and Miksche.

[3] Weight ratio of unsubstituted guaiacyl (softwood) and guaiacyl-syringyl (hardwood) monomeric monocarboxylic acids to the four (softwood) and six (hardwood) most prominent dimers.

[4] Molar ratio of unsubstituted guaiacyl (softwood) and guaiacyl-syringyl (hardwood) monomeric monocarboxylic acids to phthalic and isophthalic acid derivatives.

[5] The increase in monomeric degradation products, in total unsubstituted guaiacyl units, and in the measures of condensation for the AHL preparation as a consequence of derivatization must be explained with selective fractionation. Considering however that the molar ratio of cmpd. 3 to total unsubstituted guaiacyl units changes from 0.85 to 0.34, an approximately 60% derivatization degree can be computed for unsubstituted, phenolic guaiacyl units.

illustrating their consumption by derivatization. The increase in ortho- and para-ethoxy methyl benzoate content (compounds 1 and 2 in Figure 6) as a result of chemical modification supports the H–NMR spectroscopy results. No change is seen either in the amount of degradation products from alkyl–aryl ether linked non-phenolic guaiacyl units or from the syringyl moieties (in SEL), which all remain unreactive with formaldehyde.

The permanganate oxidation results for the prepolymer preparations are given in Table II. The results illustrate changes in the degradation product distribution (monocarboxylic and dicarboxylic monomers and dimers in regions A, B and C, Figures 5 and 6, respectively), in the yields of monomeric, monocarboxylic degradation products, and in condensation. The yields of phenol-derived compounds 1 and 2, Figure 6, increase from <20 to 200–235 mmol/C_9, and compound 3, Figure 6, representing phenolic unsubstituted guaiacyl units decreases expectedly from 280 to between 21 and 95 mmol/C_9 for the three phenolated lignin samples. This indicates that $>90\%$ of the available 5-positions ortho to a phenolic hydroxy group of uncondensed guaiacyl units in KL have been derivatized in the formaldehyde-phenol reactions, but only 60% in both the AHL and SEL preparations, respectively; and that none of the corresponding alkyl–aryl ether-linked guaiacyl units and none of the syringyl units in SEL, have been consumed by the reaction. The 200–235 mmol/C_9 of compounds 1 and 2, Figure 6, stipulate a degree of substitution by phenol of only between 45 and 100% of that indicated by H–NMR; however, both condensation and degradation product distribution suggest that a significant amount of phenol leads to the formation of dimeric and higher oligomeric permanganate oxidation products. Thus, the structure analysis by permanganate oxidation supports the H–NMR data and suggests the lignin can indeed be derivatized with formaldehyde and phenol although to different extents, in reactions consistent with those described for formaldehyde and depicted in Figure 3.

It should also be noted that number average molecular weight (M_N) determinations indicate that KL exists, on the average, as a polymeric fragment with 7 C_9 units, and SEL and AHL both with about 4[31]. At a degree of substitution of 0.43, 0.21 and 0.29 for KL, SEL, and AHL, respectively, >2, <1, and about 1 phenolic units are attached to a number-average KL, SEL, and AHL fragment, respectively. Recognizing that at least 2 phenolic units per average prepolymer fragment are necessary for this to become an integral part of a network structure (*i.e.* linked with more than one repeating unit), KL holds an apparent edge over SEL and AHL in terms of PF-prepolymer qualification. A forthcoming paper will evaluate the performance characteristics of these lignin derivative prepolymers as wood bonding agents.

CONCLUSIONS

The derivatization of lignin by sequential hydroxymethylation and phenolation provides a means for upgrading lignin's potential utility as a prepolymer for use in phenol-formaldehyde resin systems. The degree of chemical modification is not uniform but depends on the structural characteristics of a specific lignin. Using the apparent degree of derivatization as a criterion for polymer value, lignins can be ranked in terms of end-use potential. (Softwood) KL was found to be amenable to a higher degree of hydroxymethylation and phenolation than were either (hardwood) SEL or (softwood) AHL. The resistance to chemical modification of these two bioconversion lignins can be related directly to structural features found in the polymers. SEL contains a substantial number of syringyl (di-methoxyphenyl) units, hence its reactivity with phenol and formaldehyde is diminished. And AHL has undergone acid condensation during processing which has resulted in a highly cross-linked material with low reactivity.

Degree of substitution by phenol is >2 per (number-) average molecular species for KL and <1 or about 1 for the corresponding entities of both SEL and AHL. This is expected to influence the performance of the phenolated lignin prepolymers in the preparation of resole resins.

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