Engineering Plastics from Lignin. II. Characterization of Hydroxyalkyl Lignin Derivatives*

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Synopsis

Several types of hydroxyalkyl lignin derivatives were synthesized from milled wood, organosolv, steam explosion, acid (H_2SO_4) hydrolysis, and kraft lignin with ethylene oxide, propylene oxide, and butylene oxide by either batch reaction in toluene at 180°C using KOH as catalyst, or in aqueous alkali at room temperature. The isolated derivatives were characterized in terms of their chemical structures by H-NMR and FT-IR spectroscopy. Thermal properties were determined by differential scanning calorimetry. Molecular weights were measured by gel permeation chromatography on polystyrene/lignin model compound calibrated high pressure μ-spherogel columns. Solubilities in various organic solvents spanning a solubility parameter (δ) range from 9.3 to 14.5 and a hydrogen bonding index (γ) range from 1.5 to 18.7 were tested using UV_{280} absorption of solutions of up to 20% concentration. Results indicate that hydroxyalkyl lignin derivatives are unifunctional products with degrees of substitution of between 1 and 2.6 (except for ethylene oxide derivatives which were higher) and with lignin contents of around 60%. The drastic reduction of glass transition temperature of between 50°C and 100°C is explained with increased free volume of the copolymer and with disruption of hydrogen bonds involving especially phenolic hydroxy groups. The greatly enhanced solubility in organic solvents indicates absence of the gel structure typical of network polymers. No molecular breakdown was observed as a consequence of oxyalkylation. The derivatives had molecular weights (M_w) of between 2000 and 50,000 at dispersity factors of between 2.5 and 25. The derivatives seem to constitute useful prepolymers for thermosetting engineering plastics.

INTRODUCTION

The utilization of polymeric lignin in solid material systems is constrained by the high modulus of most lignin types.[1] Chemical modification and derivatization involving the combination of a high modulus polyaromatic component with a low modulus substituent such as an aliphatic ether has been suggested as a promising route to tailoring viscoelastic properties of polymeric lignin derivatives for specific end uses.[2,3] Hydroxyalkylation has been described as a convenient method for producing such lignin derivatives.[4–6]

The previous paper in this series[7] has dealt with the synthesis of hydroxypropyl lignin derivatives in terms of the mechanism of homopolymerization and copolymerization with ligninlike model compounds and kraft lignin. Oxyalkylation and its reaction products with lignin, with wood, and with pulp fibers has also

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been studied in view of lignin reactivity,[8,9] in view of its effect on such wood properties as dimensional stability and biodegradability,[10–12] and in view of its effect on optical, strength, and permeability properties of pulp fibers and fiber mats.[13–15] It is the objective of this paper to discuss the characterization of hydroxyalkyl lignins in terms of their chemical composition and several of their physical properties. In addition, this characterization is to be applied to derivatives prepared from different oxyalkylating agents as well as from different lignin sources.

MATERIALS AND METHODS

Materials

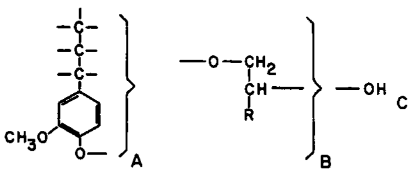
Tests were performed using six different lignin preparations. These were a milled wood lignin (MWL) of scarlet (red) oak (sapwood) an industrial kraft lignin (KL) from a Southern pine-based pulpmill (Indulin AT from Westvaco, Charleston, S. C.), a steam explosion lignin (SEL) obtained from aspen (Iotech Corp., Ottawa, Canada), organosolv lignins (OSL) from pine and from aspen (Biological Energy Corp., Valley Forge, Pa.), and an acid (H_2SO_4) hydrolysis lignin (AHL) from aspen (New York University, New York). The isolation and structural characterization of these lignins has been the subject of two earlier reports[16,17]; steam explosion lignins have also been evaluated by Marchessault et al.[18]

Methods

Derivatization Reaction. The derivatization was performed in toluene suspension with agitation at 180°C in a closed pressure reactor, or in aqueous medium at room temperature, using KOH as catalyst, as described previously.[3,7] Solid hydroxyalkyl lignin derivatives were obtained either by liquid–liquid extraction of an acetonitrile solution with hexane followed by precipitation into water (high-temperature product), or by precipitation with mineral acid.

Analysis. H-NMR spectra of the acetylated derivatives were taken in $CDCl_3$ solutions. FT-IR spectra were recorded using KBr pellets (1 mg lignin:200 mg KBr) or films cast on NaCl plates from THF solution, with a Nicolet MX-1 Spectrophotometer. Thermal analysis of lignins and lignin derivatives were done on a Perkin-Elmer DSC-4. Approximately 20 mg samples were scanned at 10°C/min under a dry nitrogen atmosphere. The glass transition temperature (T_g) was defined as one-half the total change in heat capacity (C_p). Gel permeation chromatography (GPC) was conducted with 0.1M LiBr solutions of DMF on 4 μ-spherogel columns (ALTEX) packed with polystyrene divinylbenzene resin of gel sizes 500, 1000, 10,000, and 100,000 Å.

Solubilities. Solubility tests of lignins and lignin derivatives were performed in various solvents by shaking 100 mg quantities of dry sample in 500 μL of solvent for 24 h at room temperature. After filtering the solution through a pad of glass wool, a 10 μL aliquot was taken and brought to 25 mL. Absorbances were measured on a Varian/Cary 219 UV-VIS Spectrophotometer at 280 nm.



B– Component:
R = H Ethylene Oxide
= CH_3 Propylene Oxide
= C_2H_5 Butylene Oxide

Fig. 1. Schematic structure of hydroxyalkyl lignin derivatives.

RESULTS AND DISCUSSION

Characterization Techniques

Chemical Structure

The reaction between alkylene oxides and lignin leads to the formation of a copolymer with a structure shown schematically in Figure 1. This copolymer contains a lignin component (A), an alkylene oxide component (B), and a hydroxy component (C), which is a primary hydroxy group in case of ethylene oxide copolymers and a secondary hydroxy group in case of higher carbon alkylene oxides. Chemical structure analysis of the hydroxyalkyl lignin derivatives has to address describing: the chemistry of lignin, component A; the type, the nature of attachment, and the number of alkoxy units in an alkylether chain, component B; and the frequency and type of hydroxy groups, component C. The analysis of the chemical structure of lignin has been the subject of extensive research in the past (for review, see Ref. 19). Various spectroscopic methods (UV, IR, H-NMR, ^{13}C-NMR, etc.), and chemical derivatization (i.e., methylation, acetylation) and depolymerization techniques in combination with chromatographic separation of degradation products, have found widespread application for this purpose. An approach combining data acquisition by experimental methods with data interpretation and structure modeling by computer techniques has been described recently.[20,21] The analysis of component B in wood pulp has been conducted by treatment with HI followed by gas chromatographic separation of the alkylene oxides.[22] Hydroxy contents may be analyzed by acetylation with acetic anhydride in pyridine followed by titrating unreacted acetic acid with base[20,23]; or they may be determined in the acetylated derivatives in analogy to the analysis of O-acetyl groups of cellulose acetate in a procedure employing aminolysis with pyrolidin.[24] A third, most widely used hydroxy determination method involves H-NMR spectroscopy of lignin acetates.[25,26] No indication is given in the literature that this acetylation remains incomplete; in fact, its completeness is supported by replicability[25,26] and by agreement with other analytical methods.[27] Although useful information may result from all three techniques, H-NMR spectroscopy was found to be a convenient and reliable analysis method, which was adopted for routine use in conjunction with this study. In addition, FT-IR spectroscopy was explored with good qualitative results. ^{13}C-NMR spectroscopy has been applied to lignins with success,[28,29] but quantitative interpretation of structural features has remained limited in

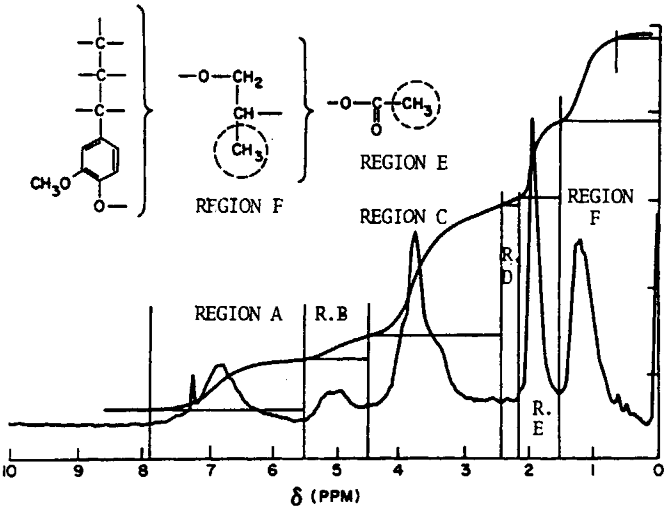


Fig. 2. Typical H-NMR spectrum, and assignment of acetoxy and methyl signal of acetylated hydroxypropyl lignin. (From Ref. 3 with permission of the publisher.)

scope[30] primarily because of lack of sensitivity.[31] This handicap may in the future be overcome by special pulse techniques,[30] or by the synthesis of ^{13}C-labeled lignin preparations.[31]

H-NMR Spectroscopy. Although hydroxyalkyl lignin derivatives are sufficiently soluble to be subject to direct H-NMR spectroscopy without prior chemical derivatization, the acetates proved to be more useful because their spectra exhibit a distinct quantitative acetoxy signal. A typical H-NMR spectrum of a lignin copolymer with propylene oxide is shown in Figure 2. This spectrum illustrates the existence of six distinct regions which allow for reasonably quantitative assessment of the distribution of hydrogen in the copolymer. These regions represent aromatic protons (region A), a multitude of aliphatic carbon-linked protons (region B), CH_2 and methoxy protons (region C), aromatic acetoxy protons (region D), aliphatic acetoxy protons (region E), and methyl protons (region F). Since no interference from overlapping protons is to be expected for regions E and F, these regions provide good quantitative information on the number of alkoxy units (component B) and hydroxy groups (component C) in the copolymer (Fig. 1). The ratio between region F and region E signals produces information as to the average number of alkoxy units linked chainlike to each other.

Spectra obtained with the acetates of three different hydroxyalkyl lignin derivatives, and of lignin, are illustrated in Figure 3. Further refinements of the method of subdividing H-NMR spectra into distinct ranges in accordance with the proposal of Ludwig, Nist, and McCarthy[25] becomes necessary. These revisions are summarized in Table I. Where hydroxyethyl lignins require the combination of ranges 2 and 3 (aromatic, vinylic, and benzylic protons), of ranges 6 and 7 (O-acetyl protons), and an extension of range 4 at the expense of range 5 as compared to unmodified lignin, hydroxypropyl, and hydroxybutyl lignin derivatives call for combinations also of ranges 4 and 5 (most aliphatic and methoxy protons), and for revision of range 8 to better account for the carbon-linked

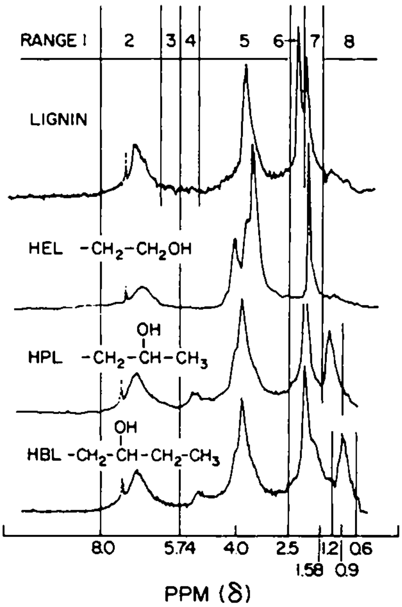


Fig. 3. H-NMR spectra of acetylated organosolv (pine) lignin and of the hydroxyethyl (HEL), hydroxypropyl (HPL), and hydroxybutyl (HBL) derivatives.

methyl group. The assignment of individual hydrogen atoms of respective alkyl substituents, and of the O-acetyl signal of the different hydroxy alkyl lignin derivatives, is summarized in Table II.

The NMR spectra clearly illustrate the complete absence of aromatic acetoxy groups in the lignin derivatives, and the nonphenolic nature of the lignin derivatives is verified by UV-difference spectroscopy.[32] The distinctly separated methyl group of the propyl and butyl substituents in range 8 (Fig. 3) provides a convenient quantitative tool for determining degree of derivatization.

The quantitative interpretation of primary H-NMR data in terms of alkoxy (component B) and hydroxy (component C) content of hydroxyalkyl lignin derivatives, and thus, in terms of the average degree of substitution and molar substitution, can be performed on the basis of the following three equations.

Total H/C_9 in Acetylated Lignin Derivatives:

$$H_{C_9} + 3{*}\mathrm{MeO} + B{*}H_s + C{*}3 = \sum H/C_9 \qquad (1)$$

whereby H_{C_9} = average number of aromatic and aliphatic C-bonded H per C_9 (between 6 and 8 in most lignins), MeO = number of methoxyl groups per C_9, H_s = number of H in alkoxy substituent (4, 6, or 8 in ethoxy, propoxy, and butoxy group, respectively), B = number of alkoxy groups per C_9, and C = number of acetoxy groups per C_9.

Ratio of Alkoxy to Hydroxy-H:

$$B/C = N{*}P_{R.X}/P_{R.6/7} \qquad (2)$$

whereby $N = 3/2$, 1, and $5/3$ for EtO, PrO, and BuO, respectively, $P_{R.X}$ = fraction of total integration of H-NMR spectrum in range X = 4, 8, and 8 for EtO, PrO, and BuO, respectively, in %/100, and $P_{R.6/7}$ = fraction of total integration of

TABLE I

Range Assignment for Chemical Shifts of Protons in Acetylated Lignins and Lignin Derivatives—in δ, ppm Values

Lignin and lignin derivative	Range 1	Range 2	Range 3	Range 4	Range 5	Range 6	Range 7	Range 8
Lignin	>8.0 Carboxylic, aldehydic	6.28–8.0 Aromatic, vinylic	5.74–6.28 Vinylic, benzylic	5.18–5.74 Benzylic	2.50–5.18 OCH_3, side chain	2.19–2.50 Aromatic OAc	1.58–2.19 Aliphatic OAc	0.38–1.58 Highly shielded
HEL	>8.0 Aldehydic	5.74–8.0 Aromatic, vinylic, benzylic		4.00–5.74 CH_2 of ethoxy	2.50–4.00 OCH_3, CH_2, side chain	1.58–2.50 O-Acetyl		0.38–1.58 Highly shielded
HPL	>8.0 Aldehydic	5.74–8.0 Aromatic, vinylic, benzylic		2.50–5.74 OCH_3, CH, CH_2, and side chain		1.58–2.50 O-Acetyl		0.90–1.58 CH_3
HBL	>8.0 Aldehydic	5.74–8.0 Aromatic, vinylic, benzylic		2.50–5.74 OCH_3, CH, CH_2, and side chain		1.20–2.50 CH_2 and OAc		0.60–1.20 CH_3

TABLE II
Range Assignment of Alkoxy (B) and Acetoxy (C) Group Protons of Copolymer (cf. Fig. 1) in H-NMR Spectrum

Alkoxy substituent (B)	Product designation	Range assignment
Ethoxy	HEL	2H of A in Range 4 2H of A in Range 5 3H of B in Range 6/7
Propoxy	HPL	3H of A in Range 4/5 3H of B in Range 6/7 3H of A in Range 8
Butoxy	HBL	3H of A in Range 4/5 3H of B and 2H of A in Range 6/7 3H of A in Range 8

H-NMR spectrum in ranges 6 and 7 (combined; cf. Table I), in %/100.

Sum of Alkoxy and Hydroxy-H:

$$\frac{3*C + H_s^*B}{\Sigma \mathrm{H}/\mathrm{C}_9} = P_{\mathrm{R}.6/7} + 2*P_{\mathrm{R}.X} \tag{3}$$

These three equations are based on: (a) knowledge of the chemical structure of the starting lignin material in terms of the H-distribution of the average C_9 unit; (b) on the ratio of alkoxy to O-acetyl groups as determined by H-NMR spectroscopy; and (c) on the sum of H in alkoxy and acetoxy groups, (% of total H) as revealed by NMR spectroscopy. By substitution, average acetoxy (hydroxy) groups (component C), can be computed according to eq. (4).

Solution for Hydroxy Content per C_9:

$$C = \frac{\mathrm{H}_{\mathrm{C}_9} + 3*\mathrm{MeO}}{\dfrac{3 + \mathrm{H}_s^*N*P_{\mathrm{R}.X}/P_{\mathrm{R}.6/7}}{P_{R.6/7} + 2*P_{\mathrm{R}.X}} - N*H_s^*P_{\mathrm{R}.X}/P_{\mathrm{R}.6/7} - 3} \tag{4}$$

Alkoxy groups (component B) result from eq. 2, degree of substitution (DS) is the greater of either, alkoxy or hydroxy group (per C_9) content, and molar substitution (MS) is the product of alkoxy divided by hydroxy group content, but this cannot be <1.0.

FT-IR Spectroscopy. FT-IR spectra of lignins and hydroxyalkyl lignin derivatives were taken with the objective of revealing structural features less clearly evaluated by H-NMR spectroscopy. The region in the IR spectrum which is of particular interest in this context is the 1800–1400 cm^{-1} range representing a variety of carbonyl, carboxy, and ester (1750–1650 cm^{-1}) vibrations. Appropriate sections from the FT-IR spectra of kraft and steam explosion (IOTECH) lignins, and of their hydroxypropyl derivatives, are shown in Figure 4. A distinct shift is noted for the 1720 cm^{-1} stretching as a consequence of hydroxypropylation. The absorption at 1720 cm^{-1} has been assigned to aliphatic carboxyl groups, although it has also been attributed to aromatic ester groups.[33,34] Studies on methanol-extracted steam explosion lignin from aspen[18] assigned these bands to unconjugated carbonyls or esters despite the fact that ^{13}C-NMR spectroscopy failed to reveal any signals around 200 ppm attributable to such groups. Studies

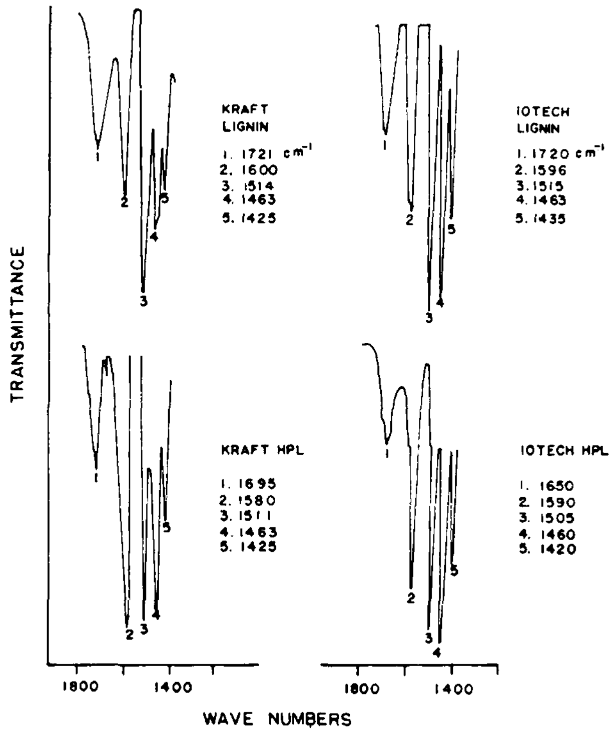


Fig. 4. FT-IR spectra (1800–1400 cm^{-1} range) of two lignins and hydroxypropyl lignin derivatives.

using model compounds showed the conjugated carboxylic acid groups of vanillic, veratric, and acetyl vanillic acid to absorb at 1677, 1672, and 1686 cm^{-1}, respectively, and the absorption bands varied with ring substitution pattern.[35] Despite the fact that the conjugated methyl esters of *p*-hydroxy benzoic, vanillic, and *p*-hydroxy cinnamic acid were found to absorb at 1694, 1699, and 1694 cm^{-1}, respectively,[36,37] (and thus at slightly greater wave numbers than their corresponding carboxylic acids), the distinctive shift of the 1720 cm^{-1} band towards 1695–1650 cm^{-1} following hydroxypropylation has to be interpreted with the formation of esters from carboxyl groups present in the starting materials. This is consistent with the assignment of the 1720 cm^{-1} band to aliphatic carboxyl groups and lower wave number peaks to aliphatic esters.[35] This interpretation is also consistent with that of Conrat and Olcott,[38] who have demonstrated that in slightly alkaline medium the esterification of carboxy groups is a predominant reaction during oxyalkylation and with that of Wu and Glasser,[7] who have attributed the initial propoxylation step at elevated temperature (180°C) in nonaqueous, catalyst-(KOH)-limited environment, to carboxy functional groups. This observation is also in accord with the finding that hydroxypropyl lignin derivatives produced at high temperature under alkali-limited conditions in nonpolar solvents have lower overall acidities than those generated in aqueous alkali at room temperature.[3]

The bands in the regions of 1605–1595 cm^{-1}, 1575–1505 cm^{-1}, and 1450–1420 cm^{-1} are readily assigned to aromatic skeletal vibrations and the one at 1460–1463 cm^{-1} to aliphatic C—H bending.

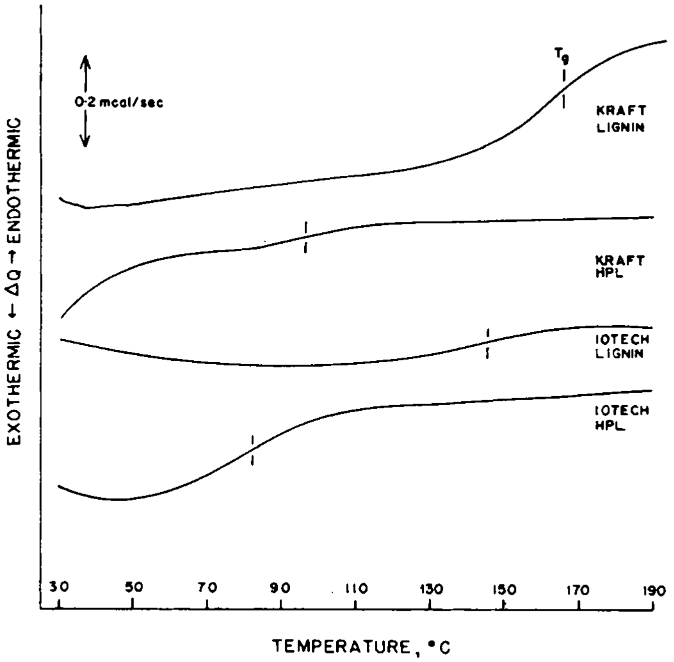


Fig. 5. DSC thermograms of two lignins and hydroxypropyl lignin derivatives.

Properties

Results of the thermal analysis by differential scanning calorimetry (DSC) of kraft and steam explosion lignin, and of the corresponding hydroxypropyl derivatives, are shown in Figure 5. These results illustrate a surprisingly large reduction (of ca. 50–100°C) in glass transition temperature (T_g) as a consequence of hydroxypropylation. This can either be explained by disruption of hydrogen bonds of phenolic hydroxy groups or by increased free volume. Phenolic hydroxy groups have in the past been held responsible for the formation of strong intra- and intermolecular hydrogen bonds,[1,38–40] which have a dramatic effect on the reactivity and solubility character of lignins.[14] Thus, methylation and acetylation have both been found to be responsible for reduced glass transition temperatures.[1] The conversion of phenolic into secondary or primary aliphatic hydroxy groups upon oxyalkylation seems to effectively eliminate these intramolecular H-bonds, thereby facilitating molecular motion and lowering the T_g. Variation of T_g in relation to molar and degree of substitution, however, suggests that there is an additional, and possibly overriding, effect on the free volume within the copolymer,[42] which increases with increasing degree of substitution by (bulky) substituents and thereby lowers the T_g.

Solubility Properties. The solubility character of lignins and lignin derivatives has been assessed by adding various solvents to dry, powderous lignin preparations with known absorptivity coefficients at 280 nm, and shaking these mixtures at room temperature for 24 h. These mixtures, solutions or suspensions, were then filtered through glass wool, and aliquots were diluted to a constant volume. Absorbences of UV light were determined for these solutions at 280 nm. Results are summarized in Table III. Organosolv lignins were soluble

TABLE III

Solubility of Lignins and Lignin Derivatives in Various Solvents (%)

	A_{280} (gL^{-1}·cm^{-1})	Methanol	DMF	Dioxane	90% aq dioxane	2-Butanone	Acetonitrile	THF	$HCCl_3$
Solubility parameter δ		14.5	12.1	9.9		9.3	11.9	12.1	9.3
Hydrogen bonding index γ		18.7	11.7	9.7		7.7	6.3		1.5
MW lignin (scarlet oak)	7.6[a]	3	>20	>20	>20	<3	3	8	Gel
HPL	16.6	>20	>20	>20	>20	>20	>20	>20	>20
HBL	15.0	Gel	Gel	Gel	Gel	2	<2	Gel	Gel
Kraft lignin	20.3	13	>20	>20	>20	18	4	>20	14
HPL	17.1	>20	>20	>20	>20	>20	11	>20	>20
HBL	13.7	>20	>20	>20	>20	>20	3	>20	>20
Acid hydrolysis L. (aspen)	21.4	14	>20	>20	>20	18	13	>20	14
HPL	13.4	>20	>20	>20	>20	7	3	>20	>20
HBL	13.6	>20	>20	>20	>20	>20	9	>20	>20
Steam explosion lignin	19.4	8	>20	>20	>20	9	6	>20	Gel
HPL	18.2	>20	>20	>20	>20	>20	>20	>20	>20
HBL	12.0	>20	>20	>20	>20	14	6	>20	>20
Organosolv lignin (aspen)	20.4	>20	>20	>20	>20	>20	>20	>20	>20
HPL	16.3	>20	>20	>20	>20	>20	>20	>20	>20
HBL	15.2	>20	>20	>20	>20	>20	10	>20	>20
Organosolv lignin (pine)	23.0	16	>20	>20	>20	>20	13	>20	Gel
HPL	18.4	>20	>20	>20	>20	18	6	>20	>20
HBL	16.7	>20	>20	>20	>20	>20	6	>20	>20

[a] Normal values are typically between 12 and 18 gL^{-1}·cm^{-1}; the low figure of 7.6 may reflect a higher than usual carbohydrate content for the unpurified MWL preparation.

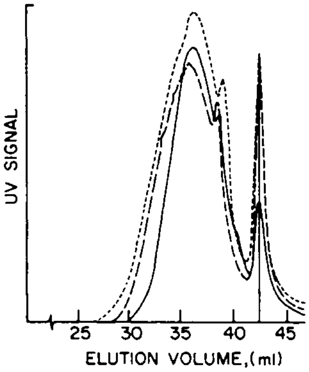


Fig. 6. GPC elution curves of organosolv lignin (OSL) (——) and of two hydroxyalkyl OSL derivatives (using vanillin as elution volume marker): (— — —) HPL; (- - -) HBL.

in concentrations of 20% or higher in more solvents than other lignins. Hydroxyalkylation raised the solubility of all lignins, with propoxylation being more efficient than butoxylation. Acid hydrolysis lignin and its derivatives were comparable to kraft lignin in its solubility characteristics. Milled wood lignin derivatives tended to form gels rather than solutions, probably owing to their higher molecular weights. High molar substitutions and higher methoxy contents seemed to beneficially influence solubility, as is illustrated by the difference between the pine and aspen organosolv lignin derivatives with molar substitutions of ca. 1 vs. >2, respectively.

Molecular Weight Properties. Molecular weights and molecular weight distributions of lignins and their hydroxyalkyl derivatives were determined by gel permeation chromatography (GPC) on high pressure polystyrene–divinyl benzene columns using electrolyte (LiBr) solutions of DMF. Solutions of lignin, to which vanillin was added as internal elution volume marker, were eluted from a series of four high pressure columns within about 50 min. Typical results obtained with lignin and hydroxyalkyl lignin derivatives are shown in Figure 6.

The GPC columns were calibrated with polystyrene molecular weight standards as well as with ligninlike model compounds. Since problems were encountered with (a) the solubility of polystyrene in DMF in the presence of LiBr and (b) the monitoring of polystyrene with a UV_{280} detector, a calibration curve was constructed on the basis of the elution behavior of lignin model compounds in the low molecular weight region and of polystyrene standards in the upper molecular weight range. This is illustrated in Figure 7. However, it should be noted that because of these difficulties the calibration was semiquantitative at best and molecular weights can only be expressed on a relative basis. However, no significant differences could be detected in the molecular weights between lignins and corresponding alkoxy lignin derivatives. On occasion, dispersity factors of the alkoxylated derivatives were found to have increased significantly.

Comparison of Different Lignins

Lignin is a polyphenolic plant component native to all perennial plants, contributing between 20% and 30% towards their total weight. Lignins differ from

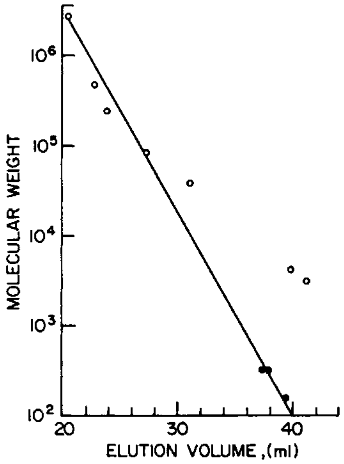


Fig. 7. GPC calibration curve: (○) polystyrene in DMF by RI; (●) model compounds in LiBr/DMF by UV.

each other in relation to their genetic origin as well as their method of isolation (for structural classification, see Ref. 16). Lignins are currently produced as byproducts of pulp and paper-making operations in the United States in quantities exceeding 20,000,000 t per year, and they may in the future be generated in industries producing chemicals from biomass.[43,44] While there are only two types of pulp and paper-derived lignin byproducts, kraft and sulfite (lignin sulfonates) lignins, there are many more different types of lignin from potential biomass-to-chemicals conversion processes. These include process schemes based on the involvement of mineral acid (acid hydrolysis lignin, AHL),[45] water and steam at various temperatures and pressures (autohydrolysis and steam explosion lignin, SEL),[46,47] and organic solvent mixtures, such as ethanol and water (organosolv lignin, OSL).[48] Milled wood lignins (MWL) constitute laboratory preparations isolated by extensive mechanical ball milling of solvent extracted sawdust, and subsequent lignin extraction and purification.[49] MWLs are presumed to be closely representative of native lignins in wood.

Copolymers of milled wood, kraft, acid hydrolysis, steam explosion, and two organosolv lignin types have been prepared with ethylene oxide (kraft lignin only), propylene oxide, and butylene oxide. These preparations were obtained in accordance with the synthesis and isolation technique described previously,[7] and they were characterized in regard to their chemical structure and thermal, solubility, and molecular weight properties. The results are summarized in Table IV.

It is apparent that the chemical composition of the various hydroxyalkyl derivatives is subject to only minor variation. The degree of substitution of 13 derivative preparations was between 0.9 and 2.6, and their molar substitutions* significantly exceeded 1.0 only in the case of the ethylene oxide copolymer. These low substitution levels imply that only between one and two functional groups per average phenylpropane lignin building unit (C_9) react with an alkylene oxide molecule, and that no chain extension occurs. From the synthesis studies[7] it is apparent that carboxy and phenolic hydroxy groups react prior to other

TABLE IV

H-Distribution by NMR and Structural Features of Lignins and Hydroxyalkyl Lignin Derivatives

Characteristics	Lignins	HEL	HPL						HBL					
		KL	MWL	KL	AHL	SEL	OSL, Aspen	OSL, pine	MWL	KL	AHL	SEL	OSL, aspen	OSL, pine
I. NMR spectrum (%)														
Range 1	0–1.7	—	—	—	—	—	—	—	—	—	—	—	—	—
Range 2	12.2–18.5	12.2	12.4	12.3	8.2	11.5	9.6	15.6	7.0	13.8	7.4	11.5	11.7	13.2
Range 3	2.3–4.4													
Range 4	1.6–6.1	20.0	44.2	41.5	44.3	44.6	44.4	45.1	46.1	33.3	37.8	40.1	37.9	40.4
Range 5	43.0–51.7	48.9												
Range 6	4.3–15.4	18.9	21.2	24.0	24.6	20.1	21.7	25.4	33.6	35.8	35.8	33.8	35.2	32.5
Range 7	13.9–23.9													
Range 8	1.4–2.3	—	22.1	22.2	23.0	23.1	24.4	13.9	13.3	17.1	18.9	14.7	15.2	14.0
II. Chemical structure														
$C\text{–}H/C_9$[a]	5.9–6.8	6.8	6.3	6.8	6.1	5.9	6.0	6.6	6.3	6.8	6.1	5.9	6.0	6.6
OCH_3/C_9[a]	0.77–1.39	0.81	1.39	0.81	1.28	1.13	1.03	0.77	1.39	0.81	1.28	1.13	1.03	0.77
Total H/C_9[a]	8.9–10.5	9.2	10.5	9.2	9.9	9.3	9.1	8.9	10.5	9.2	9.9	9.3	9.1	8.9
Alkoxy/C_9 (B)	—	2.2	2.2	2.1	2.6	2.1	2.4	0.9	1.3	1.8	2.4	1.3	1.4	1.1
Hydroxy/C_9(C)	1.1–1.6	1.4	2.1	2.3	2.7	1.9	2.2	1.6	1.9	2.3	2.8	1.8	2.0	1.6
Hydroxy (%)	10–12	7.1	10.0	11.4	12.3	8.7	9.8	9.9	10.4	11.9	11.8	10.0	10.6	9.8
DS	—	1.4	2.1	2.2	2.6	1.9	2.2	0.9	1.3	1.8	2.4	1.3	1.4	1.1
MS	—	1.6	1.0	1.0	1.0	1.1	1.1	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Lignin content (%)	>90	55	54	53	48	56	53	71	70	61	57	69	68	70
III. Polymer character[b]														
M_W ($\times 10^3$)[a]	1.5–13.5	3.2	13	3.2	—	3.8	2.3	1.5	13	3.2	—	3.8	2.3	1.5
M_N ($\times 10^3$)[a]	0.5–1.2	0.6	1.2	0.6	—	0.6	0.9	0.5	1.2	0.6	—	0.6	0.9	0.5
M_W ($\times 10^3$)		6	16	44	9.5	11	4.9	2.5	—	9.5	49	27	2.2	1.9
M_N ($\times 10^3$)		0.8	1.1	1.5	1.0	0.8	0.9	0.6	—	0.7	0.9	0.8	0.6	0.8
T_g (°C)	93–170	<50	65	77	69	81	59	83	65	subtle	subtle	subtle	66	43

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[a] Of starting material only; C—H represents aromatic and aliphatic H bound to C only; total H excludes OH, CO_2H, etc.

[b] Based on semiquantitative calibration discussed in text; data should be viewed as relative to each other only.

functional groups with active hydrogen atoms. Thus, homopolymerization seems to compete successfully with the alkoxylation of aliphatic hydroxy groups of lignin copolymers. The absence of phenolic hydroxy groups as evidenced by the absence of aromatic acetoxy signals in NMR spectra, and by the negative results of UV difference spectroscopy, indicates that a unifunctional copolymer has been formed, which consists of secondary hydroxy groups exclusively (except for ethylene oxide copolymers). These copolymers have lignin contents of between 50% and 70%. Hydroxyalkyl groups are attached to lignin predominantly via alkyl-aryl and dialkyl ether linkages, and, to a lesser extent, via ester linkages. The formation of ester linkages depends, of course, on the availability of carboxy groups in the lignin starting material.

The solubility character of lignins and of hydroxyalkyl lignin derivatives has been discussed earlier, and is summarized for the various lignin derivatives in Table III.

The influence of the alkoxy substituent type on derivative properties is unclear at this stage. It is recognized that ethylene oxide produces derivatives capable of chain extension due to the formation of more reactive primary hydroxy groups. Chain extension of the secondary hydroxy groups of hydroxypropyl and hydroxybutyl lignin derivatives, by contrast, does not occur to any significant extent. Other effects of the type and the number of alkoxy substituents on the properties and the behavior of lignin derivatives, and of their utility as prepolymers, will be the subject of continuing investigations.

CONCLUSIONS

1. Chemical characterization of copolymers of lignin with alkylene oxides can conveniently be performed by H-NMR spectroscopy of acetylated derivatives. The analysis yields information as to alkoxy, hydroxy, and lignin contents of the copolymer.
2. Thermal analysis by DSC has indicated that glass transition temperatures are in the range of <50°C to 100°C, and this is about 50–75°C lower than the T_g's of the parent lignins.
3. The solubility of hydroxyalkyl lignin derivatives in organic solvents increased dramatically following alkoxylation, allowing the preparation of solutions in excess of 20% in many organic solvents.
4. Molecular weights and molecular weight distributions of hydroxyalkyl derivatives were not found to be significantly different than those of the parent lignins.
5. Lignin derivatives with lignin contents between 50% and 70% resulted from the reaction with ethylene oxide, propylene oxide, and butylene oxide.
6. Degrees of substitution were between 1 and 2, and the formation of alkylether chains was observed only for ethylene oxide copolymers.
7. Chemical structure and polymeric character make these hydroxyalkyl lignin derivatives appear as promising prepolymers for thermosetting engineering plastics.

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* Defined according to Desmerais[50] as average number of moles of alkylene oxide per hydroxyl group.

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