

Engineering Plastics from Lignin. I. Synthesis of Hydroxypropyl Lignin

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Synopsis

Hydroxypropylation of lignin in a batch reactor under alkaline conditions at 180°C was studied using propylene oxide (PO) by itself, and PO in combination with several ligninlike model compounds and with kraft lignin. While the PO homopolymerization rate increased rapidly at temperatures above 85°C, and was too fast to be determined accurately at 180°C, the addition of model compounds and lignin was found to delay homopolymerization in relation to the presence of ionizable functional groups. The observations are consistent with a reaction mechanism involving first order kinetics with regard to each alkoxide and PO concentrations. Where the reaction rates toward PO increase with increasing pK_a values, the reaction sequence proceeds in the order of declining basicity. Thus lignins with high acidity were found to be subject to greater degrees of modification than those with more neutral character. This explains the earlier observed beneficial effect of lignin carboxylation on the properties of lignin-PO reaction mixtures.

INTRODUCTION

Engineering plastics constitute a group of nonmetallic, solid materials "which possess physical properties enabling them to perform for prolonged use in structural applications, over a wide temperature range, under mechanical stress, and in difficult chemical and physical environments."¹ Engineering plastics have found widespread application in a wide range of materials. Major opportunities for further development in the engineering plastics field are seen in block copolymers, in sophisticated composites that are capable of withstanding high stresses and temperatures and which comprise both semicompatible polyblends and reinforced plastics, and in newer and easier processing techniques for high temperature polymers.²

Several of the envisioned applications, particularly those addressing impact and heat-resistant copolymers and composites, require properties of engineering plastics which are inherently similar to those of the natural polymer lignin.³ Lignin, the phenolic polymer matrix in which cellulose fibers are embedded in wood, is obviously "designed" as a high impact strength, thermally resistant thermoset polymer which performs best in combination with highly crystalline cellulosic fibers. The composite material, wood, consists of approximately 70% fiber component and 30% lignin.⁴

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It is the objective of this series of manuscripts to outline opportunities for employing lignin, the noncarbohydrate, nonfiber, polymer matrix component of natural (woody) plants, as a component in engineering plastics. These opportunities are to be evaluated in relation to technical limitations and constraints imposed by the polymeric nature of the starting material. This series is also to elucidate the relationships among chemical structure of lignin prepolymers, their thermodynamic properties, and their performance character in solid materials of various types. The first two manuscripts of this series deal with the synthesis, isolation, structure characterization, and several properties of hydroxypropyl derivatives of lignin in view of their utility for engineering plastics.

Hydroxyalkylation of lignin has been recognized⁵⁻⁷ as a promising technique for overcoming lignin's frequently observed adverse effects on mechanical properties of solid polymers³ and on viscosity and cure rate of resin systems. Chemical modification by oxyalkylation has been demonstrated to offer a route to reducing the brittleness of lignin-derived polymers and to improving viscoelastic properties in various end uses. Oxyalkylation results in a copolymer combining covalently high modulus lignin with a lower modulus aliphatic polyether phase.⁸

Hydroxyalkylation of lignin has been the subject of several prior reports. The reaction of various types of lignin and lignin analogs (tannins, etc.) with 1,2-oxides, 1,2-carbonates, and 1,2-sulfites has been accomplished with or without catalyst (alkali metal or alkali earth metal hydroxide or carbonate); at temperatures between 20°C and 250°C; in the presence or the absence of a solvent; with reactive (alcohols, amines) or unreactive (benzene, chlorobenzene) solvents; and in weight ratios between lignin and oxyalkylating agent between 3:1 and 1:100.^{9,10} The formation of liquid polyhydroxy compounds (polyols) from lignin and carboxylated (by reaction with maleic anhydride) lignin derivatives was achieved batchwise at temperatures in excess of 180°C.¹¹ Another approach employed reaction conditions involving incremental addition of alkylene oxides to the heated and stirred reactor content such that the reaction pressure was maintained at about 50 psig.¹⁰ Tarry polyols produced by batch reaction at temperatures above 180°C have recently been fractionated analytically and preparatively into liquid PO homopolymers and solid copolymers with lignin contents of around 60%.¹²

This paper deals with the synthesis of hydroxypropyl lignin derivatives by batch reaction at a temperature of 180°C (the approximate glass transition temperature of kraft lignin). These derivatives are viewed as prepolymers for thermoset engineering plastics with properties superior to those of unmodified lignins.

MATERIALS AND METHODS

Materials

Kraft Lignin. Commercial kraft lignin, Indulin ATR-C1 (Westvaco Corp., North Charleston, S. C.) was used throughout. This kraft lignin had a methoxyl content of 13.7%, a total and a phenolic OH content of 11.8% and 5.1%, respectively, and elemental analysis values of 61.3% C, 5.2% H, and 2.94% S. Ash and carbohydrate contents were less than 1% and 2%, respectively.

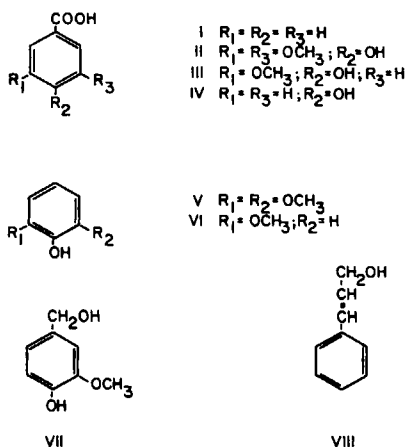


Fig. 1. Ligninlike model compounds.

Methylated Kraft Lignin. Methylation of lignin was achieved by reacting lignin with dimethyl sulfate at 60°C for 3 h. During methylation, sodium hydroxide was added to maintain a constant pH of 12.5. After the reaction was completed, the reaction mixture was acidified (pH 3) with HCl, filtered, and the solid precipitate was washed with water until neutral. The methoxyl content of this lignin was now 25.6%, and the phenolic OH content was <0.5%.

Model Compounds. The model compounds (Fig. 1) were all commercially available, and they were used as received.

Methods

Propoxylation Reaction. The reaction of propylene oxide (PO), of PO and model compounds, and of PO and lignin, was carried out in a 300-mL Parr reactor equipped with a heating mantle, mechanical stirrer, pressure gauge, cooling loop, safety valve, and thermocouple. The temperature curve was monitored via a potentiometric controller. The reactor was charged with 50 mL PO, to which 5–10-g model compound or lignin may have been added, and solid KOH.

After the reaction was completed (generally after 90 min), the reactor was cooled, and the pressure allowed to drop to near atmospheric. The reactor content was collected by dissolution in methanol or acetonitrile.

Isolation of Hydroxypropyl Lignin. The viscous reaction mixture dissolved in acetonitrile was poured into a liquid-liquid extractor with 500-mL capacity which was then charged with hexane. The extraction was carried out by refluxing hexane for 48 h. After extraction the acetonitrile layer was concentrated to a ca. 25% solution on a rotation evaporator, and the resulting syrup was precipitated into a large excess (ca. 20:1) of water. The precipitate was filtered, washed, and freeze-dried.

RESULTS

This research investigated the batch reaction of propylene oxide (PO) with lignin under alkaline (KOH) conditions and at 180°C ($>T_g$ of kraft lignin) in

terms of the reaction mechanism. This was evaluated by studying the homopolymerization of PO under the conditions chosen for lignin derivatization, by studying the behavior of appropriate ligninlike model compounds, and by conducting the reaction in the presence of lignin and methylated lignin. In the absence of a convenient and experimentally reliable procedure for sampling the reactor content at various time intervals, and to assay the reagent composition with regard to degree of reaction, reaction progress was monitored by means of a pressure-temperature-time (P - T - t) diagram. The use of the P - T - t diagram as a direct indicator of PO concentration in the reactor is an approximation which is based on the following assumptions:

1. Measurable vapor pressure in the reactor is contributed solely by PO (an assumption which is probably invalid for the final reaction stage in which some propylene glycol and low molecular weight propyl ethers may contribute to vapor pressure as well).
2. The ideal gas law applies to the conditions inside the reactor.
3. Pressure reductions are a direct indication of PO depletion inside the reactor.

Under these assumptions, the course of the oxyalkylation reaction was followed by determining the consumption of PO as a consequence of reaction. PO concentrations were normalized on the basis of vapor pressure and temperature data, and this was represented as percent of initial PO concentration. The slope of the normalized concentration vs. time curve represents the reaction rate. This method of approximating reaction kinetics was applied to the system PO-catalyst, PO model compound-catalyst, and PO-lignin (and a methylated lignin derivative)-catalyst.

Reaction Kinetics of Homopolymerization

Anionic homopolymerization occurs when PO is reacted with an alkaline catalyst, commonly KOH.¹³ The effect of the presence of KOH on the P - T - t diagram of a PO reaction is illustrated in Figure 2. Whereas there is neither an exothermic reaction nor a noticeable pressure drop (indicating PO consumption) in the absence of KOH, the temperature rises beyond control temperature (as

** Note added after review:* The expression of concentration of a reactant on the basis of pressure measurements is normally to be considered questionable practice, but it is acceptable and even most appropriate and safe in those special cases in which the contribution to vapor pressure of all components produced in the reaction remains negligible at all times, and does not distort the interpretation in relation to reagent concentration beyond the normal experimental error. The reaction of propylene oxide discussed here is such a special case. Analysis of the reaction products, partly presented in this paper (Fig. 8) and partly in the second paper of this series, indicates that approximately 90% of starting PO are converted into homopolymer and low molecular weight reaction products of which dimeric, trimeric, and oligomeric PO derivatives constitute the vast majority. A maximum of not more (worst case) than 20% PO results in a water-soluble mixture of low molecular weight products, primarily propylene glycol (bp 188.2°C) and possibly some unsaturated alcohols, such as allyl alcohol (bp 96.6°C). In the most unfavorable case, in which all of this lowest molecular weight fraction should consist of low-boiling allyl alcohol, all of it in the gas phase (and assuming the ideal gas law applies), its contribution to reactor pressure would give rise to a PO concentration error of <2%. This small error supports the validity of interpreting reactor pressure directly in terms of PO concentration.

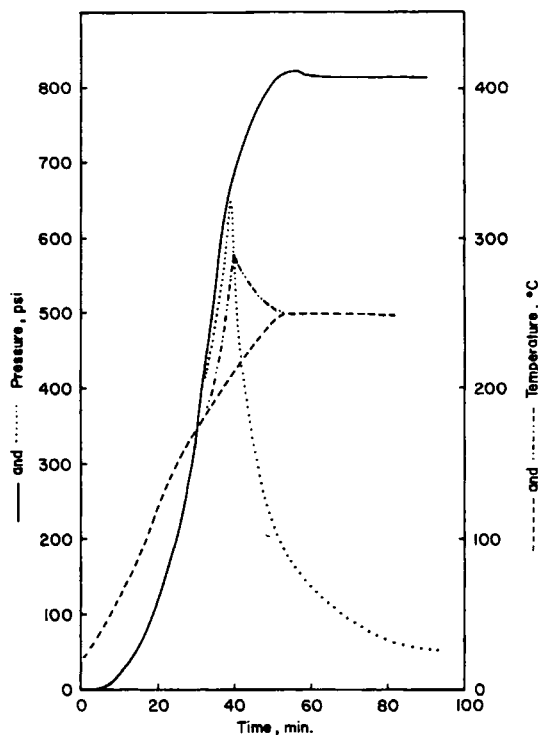


Fig. 2. Pressure-temperature-time (P - T - t) diagram of propylene oxide homopolymerization in relation to the presence of catalyst (KOH): (—, - - -) uncatalyzed; (· · · ·, · · · ·) catalyzed.

indicated by the temperature curve for the uncatalyzed sample, Fig. 2) in the presence of KOH, and the pressure declines rapidly once the exothermic reaction has commenced. No surface area effect of the catalyst was found when the KOH was added in the form of pellets or powder, and this agrees with earlier results by Steiner et al.¹⁴ No undissolved KOH was detected after the reaction.

Catalyst concentration was found to have a significant influence on reaction rate, on peak temperature, and on the viscosity of the reaction product. When catalyst concentration rose from 0 to 2.6 mmol/mol PO (Fig. 3), the reaction rate increased from close to zero to nearly instantaneous. Thus, catalyst concentration seems to be a rate-determining factor in PO homopolymerization under the reaction conditions chosen. However, no further increase in reaction rate was observed (nor could it have been detected) at KOH concentrations above 2.6 mmol/mol PO.

Homopolymer viscosities were measured in relation to KOH concentration, and a sharp increase was found up to 2.6 mmol KOH/mol PO, after which viscosity remained constant.

The relationship between reaction rate and reaction temperature was evaluated, and it was found that while the reaction rate is almost zero for $<85^{\circ}\text{C}$, the reaction is too fast to be measured at 150°C and above.

Although it is more common to perform oxyalkylation reactions in the presence of alkaline catalysts (anionically), acidic catalysts also are sometimes employed (cationic). The appeal of cationic reaction mechanisms lies in the formation

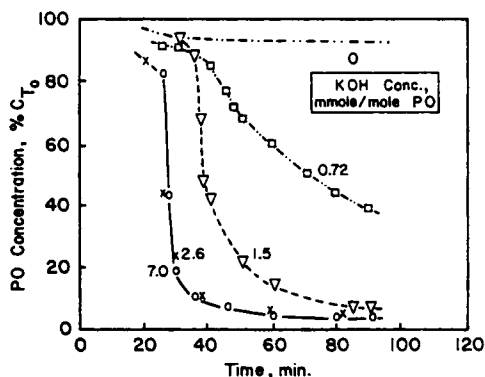


Fig. 3. Concentration-time ($c-t$) curves of propylene oxide (PO) homopolymerization in relation to KOH concentration.

of primary hydroxyl groups from propylene oxide and related alkylene oxides. For this reason, H_3BO_3 , Al_2O_3 , $AlCl_3$, ZnO , and KCl were tested as potential catalysts. However, variations in catalyst concentrations totally failed to effect homopolymerization behavior.

Reaction Kinetics of Model Compound Hydroxypropylation

Lignin is a complex polymer containing multiple functional groups and interunit linkages, and these complicate the study of reaction behaviors. It is therefore accepted practice to explore the reactions of lignin by the use of appropriate model compounds. The model compounds used in this study are presented in Figure 1. These compounds each contain at least one hydroxy or carboxy group.

The normalized concentration-time ($c-t$) curves of these compounds are shown in Figure 4. The very high residual PO concentration in the benzoic acid reaction indicates the absence of any homopolymerization. This suggests that KOH is initially (and very rapidly and completely) neutralized by the carboxy group of benzoic acid (in large stoichiometric excess) and that liberation of free KOH from the carboxylate—which occurs only after a sluggish esterification reaction is essentially complete—is long delayed. In contrast, several other model compounds, such as guaiacol (VI), vanillyl alcohol (VII), and cinnamyl alcohol (VIII), react with a rate too fast to be determined accurately. Since the compounds exhibiting rapid PO consumption are free of carboxylic functionality, the presence of acidic (ionizable) functional groups must be held responsible for the experienced time-delayed PO-depleting reaction. The reaction behavior of vanillic (III), syringic (II), and *p*-hydroxybenzoic acid (IV) differs from that of the other models by having two distinct reaction phases. The first reaction proceeds slowly and results in <10% consumption of monomeric PO. The second, rapid reaction consumes >90% of all PO. Onset time for the second phase reaction seems to be correlated with the phenolic pK_a value of these aromatic

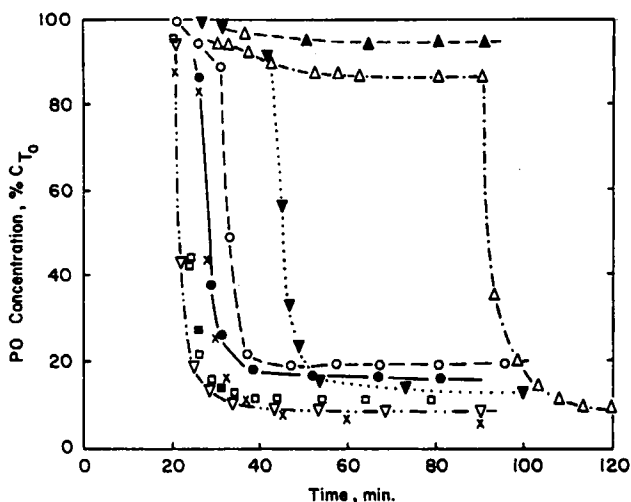


Fig. 4. Concentration-time curves of reactions of PO with model compounds: (▲) I; (△) II; (○) III; (▼) IV; (●) V; (■) VI; (□) VII; (▽) VIII; (×) homopolymer.

acids. The striking difference between the reaction rates of syringic (II), vanillic (III), and *p*-hydroxybenzoic acid (IV) indicates differences in reactivity of phenolic OH and/or carboxy groups, which in turn relate to how long it takes before the liberation of free KOH and the onset of rapid PO consumption due to homopolymerization begins. This may be rationalized either with differences in nucleophilicity of phenoxide anions related to the number and position of electronegative (OCH₃) substituents on the aromatic ring, or with steric hindrance.

Molar PO substitutions of model compounds were determined by H-NMR spectroscopy, and their averages were found to be always <2. Such low extents of substitution imply that only <10% of all available PO copolymerizes. The bulk of the reaction, as indicated by the rapid pressure drop in the second phase of the reaction, must be attributed to homopolymerization.

To confirm the sequence of homo- and copolymerization during the reaction, a series of reactions of syringic acid (II) were quenched at various reaction intervals. The percent of unreacted phenolic hydroxy and free syringic acid content were measured, and the results indicate a continuous decrease in both free syringic acid and phenolic hydroxy content. The final phenolic hydroxy content was 27%, and the syringic acid content was 0.25%. Since syringic acid is a difunctional compound, the disappearance of free syringic acid must be due to the reaction of either carboxy or phenolic hydroxy groups, or both.

The effect of KOH concentration on the hydroxypropylation reaction of 2,6-dimethoxyphenol (V) was explored, but no difference could be observed for the reaction rate or the reaction pattern for three different KOH concentration levels. In contrast, both the reaction rate and the reaction pattern of hydroxypropylation of benzoic acid (I) were found to depend largely on KOH concentration. The *P-t* diagrams of five experiments with benzoic acid are shown in Figure 5. Three reaction patterns are distinguished: (a) at a molar ratio of benzoic acid to KOH of 0.49, no homopolymerization is evident (no drop in

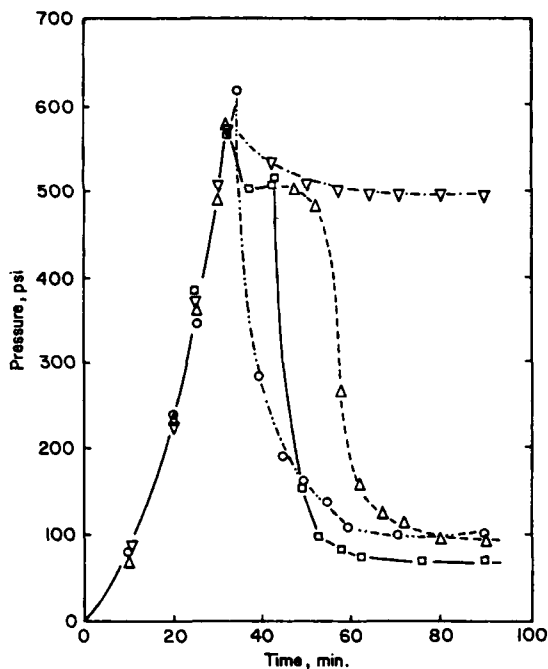


Fig. 5. Pressure-time diagram of hydroxypropylation reactions of benzoic acid (I) at various I/KOH molar ratios: (▽) 0.49; (Δ) 0.68; (□) 0.72; (O) 0.99.

pressure is observed within normal reaction time limits); (b) at a molar ratio of 0.99, a nearly instantaneous reaction is observed; (c) at molar ratios of 0.68 and 0.72, the reaction is characterized by two distinct reaction phases, the first phase representing a slow (copolymerization) reaction with a small pressure drop and the second phase the usual rapid (homopolymerization) reaction. Since constant amounts of KOH were used in these reactions (with model compound concentration being varied), variations in the onset of homopolymerization are related to the concentration of carboxy groups and carboxylate ions. No anionic species other than carboxylates can exist for as long as $\text{KOH}/(\text{RCOOH} + \text{RCOOK}) < 1.0$. As soon as esterification of carboxylates by PO allows the formation of other anionic species, homopolymerization commences. This agrees well with observations made with the homopolymerization experiments.

Reaction Kinetics of Lignin Hydroxypropylation

The reaction of PO with lignin is complicated by lignin's nature as a multi-functional polydisperse network polymer. The characteristics of (kraft) lignin have recently been reviewed elsewhere.¹⁵ Since many of (kraft) lignin's functional groups contain active hydrogen atoms, a multitude of reactions with PO may take place.

The pressure-time ($P-t$) diagram of the reaction of PO with lignins is shown in Figure 6. The result indicates a striking similarity to the model compound (benzoic acid) experiments where the molar ratio of carboxy functionality to

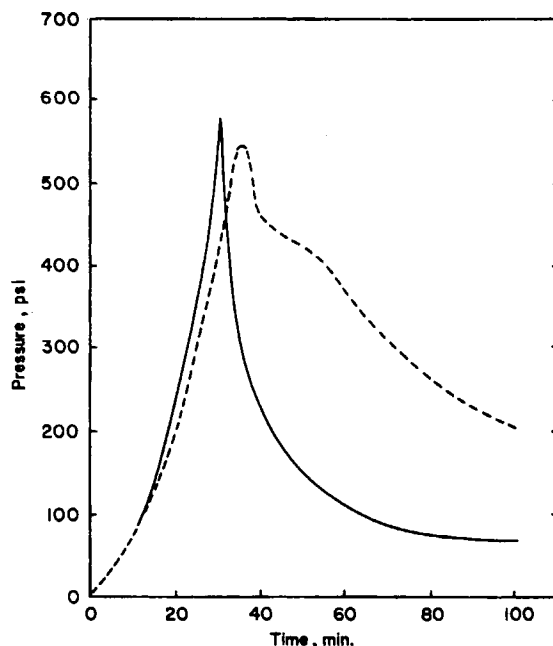


Fig. 6. Pressure-temperature-time diagram of the hydroxypropylation reaction of kraft lignin: (—) control (no lignin); (- - -) lignin.

KOH was around 0.7 (Fig. 5). Two distinct reactions, a minor initial slow, and a major subsequent rapid reaction suggest sequential slow co- and rapid homopolymerization of PO. Thus it becomes obvious that the presence of lignin (and specifically of lignin's acidic functionalities) drastically retards the onset of the homopolymerization reaction. In fact, the initial tardiness of PO consumption (Fig. 6) indicates that copolymerization is favored over homopolymerization until a sufficient number of acidic groups (carboxy and phenolic hydroxy groups) have been hydroxypropylated, and a significant concentration of homopolymerization catalyst (anions other than carboxylates and phenoxides) has been formed. This interpretation finds credence in two experiments employing (a) premethylated kraft lignin of significantly reduced acidity and (b) increasing amounts of KOH in the reaction medium.

Premethylating kraft lignin with DMSO_4 to a methoxy content of 25.6% (as compared to 13.7% for the control) causes a much more rapid PO consumption (Fig. 7) as compared to the control. Reduced degree of copolymerization is indicated by lower molar substitution and by residual phenolic hydroxy functionality (as determined by UV-difference spectroscopy, according to Goldschmid¹⁶) of the copolymer. Identical observations were made when the KOH concentration in the reaction medium was raised from 0.2 to 0.9 mmol/g lignin. Thus, a lignin with a high content of acidic functional groups appears to be better qualified for the copolymerization reaction with PO under alkaline conditions than one with a more neutral character.

The apparent dependence of the PO homopolymerization rate on KOH concentration at elevated temperatures makes it desirable (a) to perform the reaction at lower temperature and (b) to carry out the lignin copolymerization with

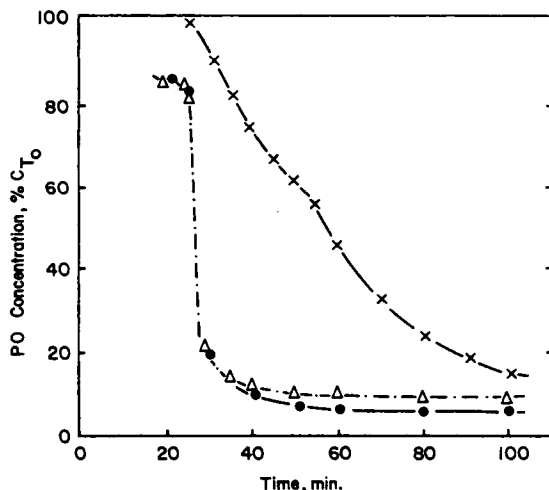


Fig. 7. Concentration-time curves of reactions of propylene oxide with several lignin preparations: (x) kraft lignin; (Δ) methylated lignin; (\bullet) control (no lignin).

minimal amount of PO rather than in excess PO (neat). (The initial copolymerization reaction converts lignin into a unifunctional derivative with only secondary OH groups, which are too nonacidic to effectively suppress homopolymerization.) Both scenarios have been tested.

Lignin batch reactions (neat) at control temperatures ranging from 125°C to 250°C were performed, and the reaction products were examined. At temperatures below 170°C, the reaction between PO and kraft lignin appeared incomplete as was indicated by the presence of residual, nonliquefied lignin in the reaction product mixture. A definite effect of the glass transition temperature on the reaction was established. This suggests that the reaction should be carried out at temperatures above the glass transition temperature of the particular lignin. A thermally expanded contact surface area is apparently necessary to enhance the reactivity of the lignin polymer. Increases in lignin's reactivity at temperatures above its T_g have been reported before.¹⁷ However, lignin hydroxypropylation has also been performed successfully in aqueous alkali at room temperature,⁸ although this was noted to have resulted in less uniform functionality.

Reactions of lignin with PO under conditions of limited PO availability have been completed with success in suspensions of toluene, acetone, and other solvents.^{10,18} (Acetone appeared somewhat less desirable as it gave rise to the formation of byproducts.) No significant differences in copolymer structure were noticed as long as PO content in the batch reactor exceeded 1.0–1.5 mL/g lignin.

Isolation of Copolymer

The reaction between lignin and PO in the presence of KOH as catalyst in either excess PO (neat) or in a solvent leads to a tarry mixture of homo- and copolymer. The composition of this mixture has recently been analyzed by gel permeation chromatography (GPC) with simultaneous detection by UV ab-

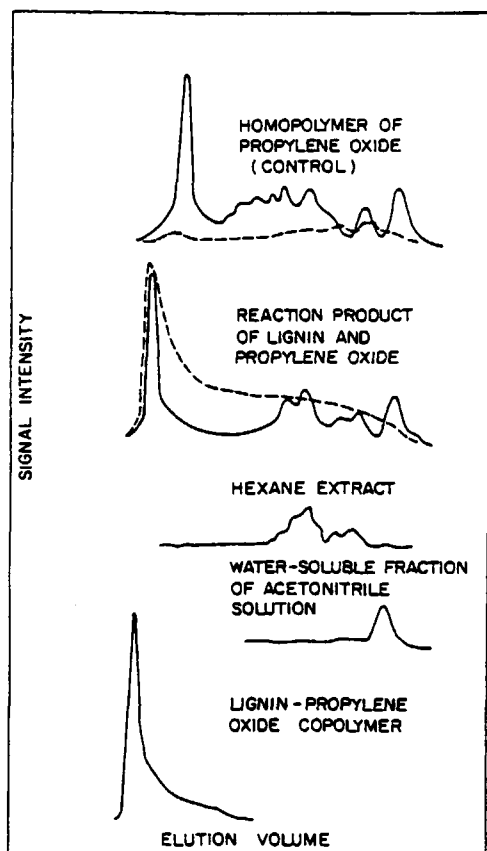


Fig. 8. Gel permeation chromatograms of hydroxypropylation reaction mixture of lignin, and of individual components on Sephadex LH-20. (Reproduced from Ref. 12 with permission of the authors.) (—) RI signal; (- -) UV signal.

sorption (UV) and refractive index (RI).¹² Results are illustrated in Figure 8. Preparative separation of the individual components contained in this mixture was achieved by liquid-liquid extraction of acetonitrile solutions with hexane and subsequent precipitation into water (containing a little HCl). Where the hexane extract is effectively separating homopolymer and homooligomer fractions, the water-soluble fraction removes any propylene glycol formed and the catalyst from the reaction mixture. The isolated and purified lignin-PO copolymer is a solid, yellow powder with good solubility characteristics. Its characterization in terms of its chemical structure, physical properties, and prepolymer utility will be the subject of forthcoming reports.

DISCUSSION

The observations concerning reaction kinetics of lignin hydroxypropylation are consistent with an overall kinetic equation for copolymerization given by

$$-\frac{d[\text{PO}]}{dt} = \sum_i k_i [\text{R}_i\text{O}^-][\text{PO}]$$

where $-d[\text{PO}]/dt$ is the rate of the overall propoxylation reaction and k_i is the rate of propoxylation of the R_iO^- anionic species. First-order rate dependences on anion concentrations establish the reaction sequence of the various functional groups on the basis of acid strengths. With pK_a values of 4.2, 10.0, 15.7, 17.0, and 17.5 for carboxy, phenolic hydroxy, water, primary and secondary hydroxy groups, respectively, the reaction rates towards PO rank in the order of

$$k_{\text{RALIO}^-} \approx k_{\text{OH}^-} > k_{\text{RAROO}^-} \gg k_{\text{RCO}_2^-}$$

Their reaction sequence is in the order of decreasing basicity, which, since they are all oxyanions, parallels decreasing nucleophilicity. This is in good agreement with results by Steiner et al.,¹⁴ who found that, at 30°C under solvent-free conditions, the polymerization of PO catalyzed by solid anhydrous KOH has the same mechanism as the homogeneous polymerization, and that the role of KOH is to convert hydroxy groups into alkoxide groups. And these results are also in accord with the findings of Mozheiko et al.,¹⁹ who observed that guaiacol reacted 35 times faster with PO than glycerol in the presence of sodium guaiacolate as catalyst and that this difference is to be attributed to the higher acidity of the phenolic hydroxy group.

CONCLUSIONS

1. The rate of PO homopolymerization under alkaline conditions (KOH) at a temperature of 180°C is too fast to be determined accurately.
2. Both homopolymerization and copolymerization take place during batchwise hydroxypropylation of ligninlike model compounds and lignin.
3. Reaction rate and reaction pattern depend on the molar ratio of acidic functional groups to KOH.
4. The retardation effect on the onset of PO homopolymerization by functional groups decreases in the order of $\text{COOH} > \text{phenolic OH} > \text{aliphatic OH}$.
5. Phenols without, or with only one electronegative substituent (OCH_3) in ortho position, cause a more expedient initiation of PO homopolymerization than those with two substituents of this type in ortho position.
6. Two distinct phases are observed during lignin propoxylation; these are a slow copolymerization to a unifunctional copolymer containing only secondary OH groups, followed by a rapid PO homopolymerization.
7. Isolation of a solid hydroxypropyl lignin derivative is possible by solvent-solvent extraction of acetonitrile solutions with hexane, followed by precipitation into water.
8. Batch propoxylation of lignin can be carried out in toluene containing as little as 1–1.5 mL PO/g lignin.

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