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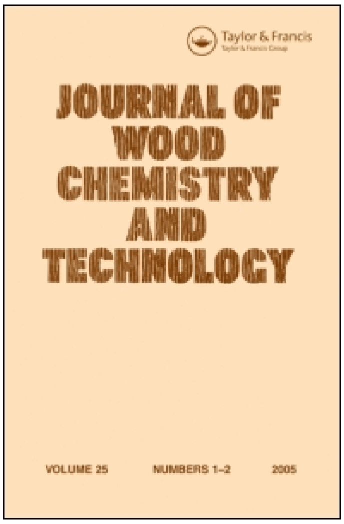

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INSOLUBLE LIGNIN MODELS (2): PREPARATION, CHARACTERIZATION, AND REACTIONS OF A POLYMER-BOUND β-ARYL ETHER LIGNIN MODEL

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ABSTRACT

A unique lignin model dimer, 2-(2-methoxyphenoxy)-1-(3-methoxy-4-hydroxyphenyl)-1,5-pentanediol (**8**), was attached to a macroreticular polystyrene resin by means of a trityl ether linkage. The extent of model loading was determined by gravimetric analysis and Zeisel methoxyl content. When reacted under simulated kraft pulping conditions, the polymer model, **8-TrP**, afforded moderate yields of guaiacol, a fragmentation product. The addition of 29% of *p*-dioxane or DMSO drastically depressed the yield of guaiacol from **8-TrP**. The polymer bound dimer model **8-TrP** and monomer model **6-TrP** were relatively unstable to the harsh, simulated pulping conditions. Some or all of the observed guaiacol fragmentation product could have come from degradation of polymer-released model.

INTRODUCTION

Lignin model compounds are designed to approximate the predominant structural units in lignin and their reactivity should mimic the basic, underlying chemistry of delignification. The model compounds are generally soluble in the reaction medium, are relatively easy to structurally characterize, and give rise to products that are relatively simple to define and measure.

Chemical reactions of native lignin, on the other hand, usually involve at least two dissimilar phases.[1] The phases during pulping consist of solid-liquid interfaces of lignin and pulping liquor.[2] The heterogeneous nature of lignin degradation reactions make studying rates and mechanisms very difficult; there is no straightforward method to quantify products and characterize the starting material.

The goal of chemical pulping is the selective removal of the insoluble native lignin. Studies of the chemistry of soluble lignin model compounds have, in general, suggested that the selective degradation and dissolution of lignin during alkaline pulping is controlled by the cleavage of several different types of alkyl-aryl ether bonds.[3]

However, the rates of reactions of polymeric materials might also be influenced by factors other than the inherent reactivity of certain bond types. Some such factors include (a) accessibility of reagents to lignin in different morphological regions,[4] (b) polyelectrolytic behavior of the degrading polymer, postulated by Schuerch as an "ion-exclusion" (Donnan equilibrium) effect,[5] (c) diffusion-, transport-, adsorption-, and desorption-phenomena,[1] (d) a loss in entropy on the reaction transition state,[6,7] and (e) temperature and solvent effects which impart greater flexibility to a polymer backbone and enhance the penetration of reactants to specific sites.[8]

Clearly, soluble lignin model compounds cannot fully mimic the various polymeric characteristics of a chemically reacting, insoluble native lignin. Therefore, we initiated an experimental program to synthesize, characterize, and study the reactions of insoluble (heterogeneous) lignin models. The insoluble polymer models possess a basic reactive unit of lignin attached to a polymer network and have the advantages of (1) a definable structure, which actual lignin does not, (2) heterogeneity, which soluble models lack, and (3) easily analyzable reaction products.

Design Criteria

The design of the insoluble model described herein will follow a polymer-bound protecting group methodology.[9] Premanufactured macroreticular polystyrene can be functionalized to a triphenylmethyl (trityl) chloride. Polymer-bound trityl chlorides preferentially form trityl ether linkages with primary alcohol groups.[10] Several lignin model dimers having propyl alcohol handles have been synthesized[11] and are considered appropriate substrates for binding to a polymer via a trityl ether linkage.

Polystyrene was chosen because insoluble, cross-linked polystyrene supports ("resins") are commercially available with a variety of physical characteristics, generally in a convenient bead form and with a thermal stability up to 220°C.[12] Also, polystyrene resembles lignin, superficially at least, in that it is a cross-linked, aliphatic-aromatic polymer.

Macroreticular polystyrene was chosen to maximize the solid-liquid interface of the insoluble model and cooking liquor. The definitive internal porous structure of macroreticular resins allows them to absorb significant quantities of virtually all solvents.[10,13,14] The structure of macroreticular resins can be envisioned as sponge-like, where the macropores are responsible for the absorption of liquid, and the gelular agglomerates of polymeric material will only be penetrated by a good polymer-swelling solvent.[12,13]

The choice of the trityl ether protecting group was in part based on its reported stability at $pH > 12$ and 150°C;[15] clearly, the model-polymer attachment should be stable to the conditions under which the insoluble model will be studied. Bulky trityl ethers probably will not react by S_N2 processes, so the addition of a nucleophilic additive (such as hydrosulfide in a kraft system) would not be expected to affect trityl ether stability.

RESULTS AND DISCUSSION

Polystyrene Support

The specific macroreticular polystyrene chosen for this study was Amberlite XE-305. The resin reportedly[16] has a large average pore diameter (1000 Å), which should ensure the transport of reagents and products in and out of the network, and has a low degree of cross-linking (4% divinylbenzene).[17] A multistage procedure[18,19] was employed to purify this industrial-grade resin.

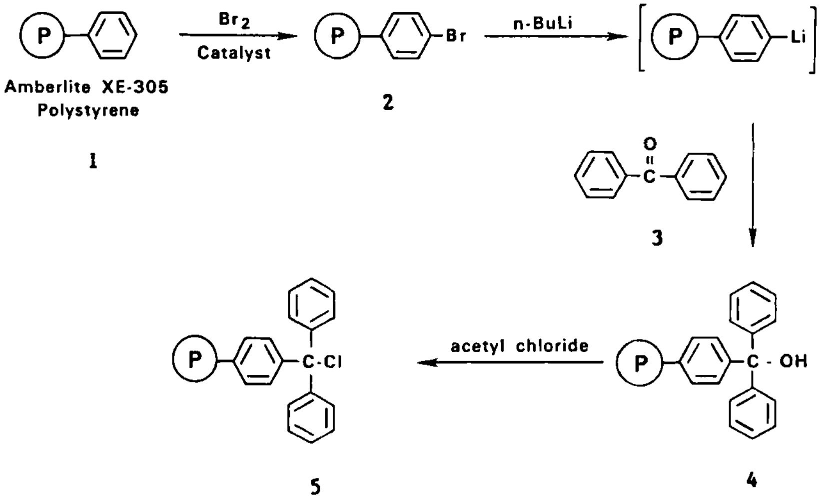
The stability of Amberlite XE-305 under high temperature alkaline conditions was confirmed in several ways. Portions of the polymer were subjected to aqueous 1N NaOH at 150°C for three hours, after which they were quantitatively recovered, thoroughly washed, dried under vacuum, and weighed; no loss in weight was observed. Each cooking liquor was extracted with ether and chloroform, and gas chromatographic analysis of the extracts showed no polystyrene degradation products. No macroscopically observable differences were observed between the thermally treated and untreated resin samples. Bovee[19] also found no significant microscopic differences between untreated resin and resin heated for seven days at 175°C, in 1N NaOH.

Amberlite XE-305 (1) was functionalized to a polymer-bound trityl chloride (5) employing the synthetic route shown in Scheme 1.[20] The elemental analyses of the various polymer products are presented in Table 1. The chlorine content of the final product 5 corresponds to 1 chlorine per 8.5 polystyrene aryl rings, and represents 60% of the theoretical maximum based on the original amount of bromine in 2.

From the elemental analysis (disappearance of Br) and the fact that the conversion of trityl alcohol to trityl chloride is typically quantitative,[21] the 60% conversion of 2 to 5 probably reflects only a modest success in the coupling of the lithiated intermediate with 3.

Lignin Models

The lignin models to be bound to the polymer were 6-8.[17] The simple compound 6 was to be used as a test substrate. The most desirable model for binding is 7 since the site of polymer attachment is far from the reactive α- and β-side chain carbons.



Scheme 1

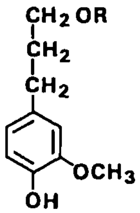
TABLE 1

Elemental analyses of purified Amberlite XE-305 (**1**) and functionalized polymer products **2**, **4**, and **5**.

Sample	% C	% H	% O	% Br	% Cl
1	91.47	7.75	1.36	--	--
2	77.78	6.47	1.93	14.67	--
4	89.48	7.36	2.99	0.67	--
5	88.12	7.22	1.63	--	3.22

However, **7** was difficult to tritylate. In contrast, both **6** and **8** were readily converted to trityl derivatives **6-Tr** and **8-Tr**.[17]

Several unsuccessful attempts to tritylate **7**, precursors of **7**, or similarly substituted molecules led to the conclusion that the phenolic hydroxyl group interfered with tritylation of the primary alcohol. Therefore, some indirect functionalization routes, utilizing protection group methodologies, were examined. Generally,



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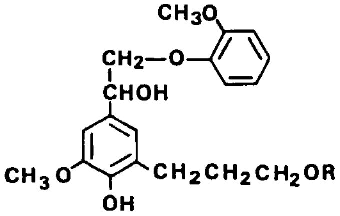

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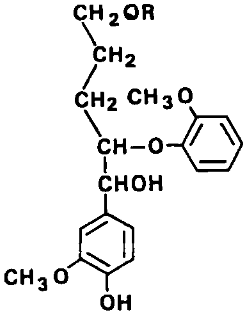
R = H, CH_2Ph (**Bn**), CPh_3 (**Tr**), CPh_3-polystrene (**TrP**)



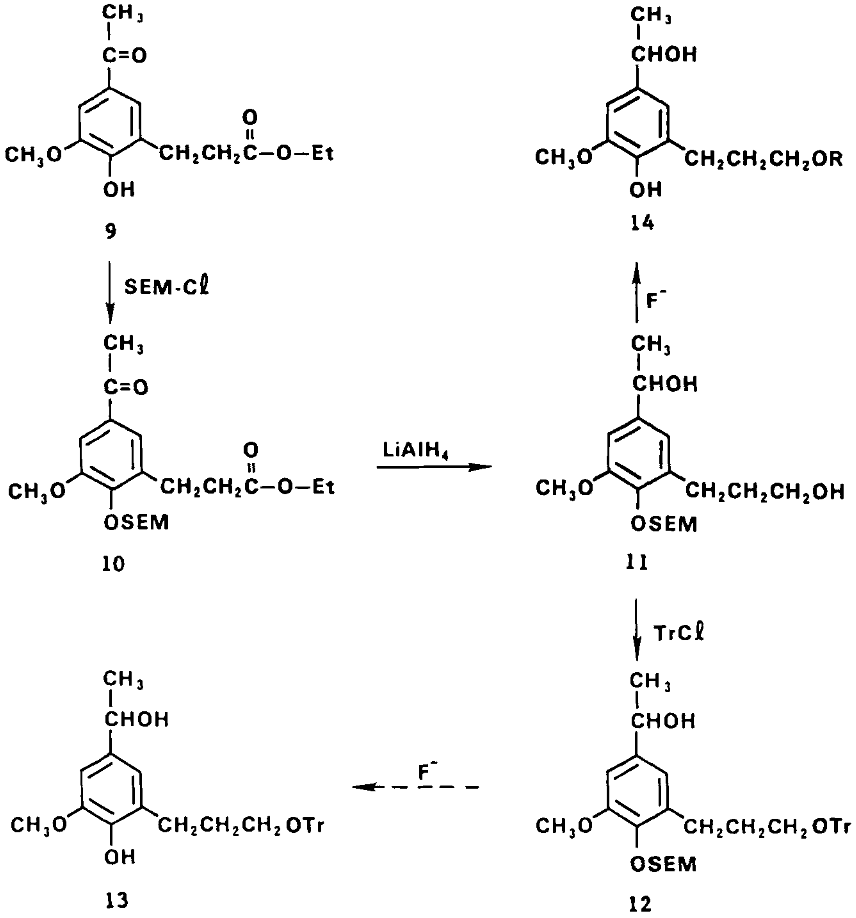
8

more readily available compounds (**9-14**) were used as substrates for examining these routes. Compound **9** is similar to the precursor used in preparing **7**.

Scheme 2 outlines an attractive route to specifically tritylate a propanol side chain. The phenolic hydroxyl is protected by a β-(trimethylsilyl)ethoxymethyl (SEM) group which later will be removed with n-Bu_4NF.[22] This route had appeal because the deprotecting agent (F^-) should not interfere with the acid sensitive trityl linkage. The sequence of steps was successful to the point of producing **12**. Difficulties were encountered, however, with removal of the SEM group.

A freshly prepared, "active" n-Bu_4NF apparently is required to remove SEM protecting groups.[23] We experienced problems in preparing such an "active" reagent. However, with a very large excess of freshly prepared n-Bu_4NF, we were able to deprotect **11**, thus preparing **14** (R=H). The procedure was not applied to compound **12**, for reasons to be explained later and because we felt that the deprotection would probably not be successful in a heterogeneous (polymer) case.

The complicated synthetic routes needed to bond model **7** to a polymer led us to abandon this model in favor of models **6** and **8**. Compound **8** has already been successfully tritylated[11] and **6** was tritylated, giving **6-Tr**, in 61% yield.



Scheme 2

Stability of Trityl Ether Models

Trityl ethers are reported to be stable at 150°C in 1N NaOH.[13,24] Nevertheless, we checked the stability of the tritylated monomer **6-Tr** under the kraftlike conditions to be employed in studying the lignin models. Portions of **6-Tr** were reacted for up to 2 hours at 150°C in a 0.11N NaOH/0.021N NaSH system; an aqueous medium employing 29% p-dioxane was used to ensure the solubility of **6-Tr**. No trityl ether cleavage was observed. Based on this result, a trityl model-to-polymer linkage should be stable to the planned kraft pulping conditions.

Preparation and Characterization of Polymer-Bound Monomer 6-TrP

A known weight of polymer bound trityl chloride (**5**) was slurried in pyridine with a 3-fold excess of guaiacylpropanol (**6**). The gain in weight displayed by the beads after thoroughly washing away the liquid phase (and drying) corresponded to a loading of 0.26 milliequivalents of **6** per gram.

Another method of determining model loading involved treating **6-TrP** with trifluoroacetic acid (TFAA) and analyzing for the **6** liberated into solution; this method relies on the fact that trityl ethers readily undergo acid hydrolysis.[25] The loading value obtained by the acid hydrolysis procedure was 102% of the value obtained by the gravimetric analysis, i.e., 0.26 meq./g.

Preparation and Characterization of Polymer-Bound Lignin Model Dimer 8-TrP

A known weight of polymer bound trityl chloride was slurried in 33% dry benzene/pyridine with a 6-fold excess of model dimer **8**. The benzene was added to assist in swelling the macroreticular polymer backbone and promote greater loading of **8** onto the beads. The gravimetric analysis indicated a loading of 0.41 milliequivalents of **8** per gram.

Reliable weight differences are difficult to obtain when working with polymer beads; quantitative delivery from vessel to vessel is awkward and complicated by the fact that functionalized polymer beads often take on a static electrical charge. Therefore, a specific analytical technique for determining the loading of model dimer on the beads was sought. The previously used TFAA method was considered to be too destructive in this case.

The only source of methoxyl groups in the insoluble model is from the attached lignin model (two methoxyls per dimer). The Zeisel methoxyl determination has proven to be reliable for a variety of insoluble substrates;[26,27] values are generally very reproducible in the range of the methoxyl content expected for insoluble model **8-TrP**. Methoxyl group analyses gave values of 2.67, 2.67, and 2.79% (triplicate determinations); this methoxyl content corresponds to a loading of 0.44 millimoles of dimer per gram of polymer product. Although this value is slightly higher than the value determined by weight difference, it is considered more reliable.

Additionally, the general degree of loading was confirmed by weight differences of a sample of **8-TrP** before and after an acid treatment (ca. 0.38-0.44 mmol/g of material could be hydrolyzed off the polymer using TFAA).[25] Also, a sample of **8-TrP** was treated with diazomethane to methylate the phenol of the attached dimer. The methoxyl content of the diazomethane treated product (with three methoxyls per dimer) was found to be 4.33%, which compares favorably to the theoretical value of 4.06%, based on the original methoxyl analysis. The excess methoxyl content of the diazomethane treated **8-TrP** may be due to the methylation of phenolic contaminants which are part of the functionalized polystyrene beads.

The loading value of 0.44 millimoles per gram represents a 51% conversion of trityl chloride groups (to trityl ethers) and corresponds to 1 model dimer per ca. 14 polystyrene aryl rings.

Although it seems unlikely that even a strongly adsorbed substrate would remain on the polystyrene following extensive Soxhlet extraction purification procedures (see Experimental), a control experiment was designed to rule out adsorption as a possibility. The polymer-bound trityl alcohol **4** does not have a reasonable mechanism for forming covalent bonds with a primary alcohol substrate but may absorb lignin models. Therefore, **4** was stirred with an excess of compound **8**, in a manner analogous to the preparation of **8-TrP**. After the workup/purification procedure, the polymer beads were dried in vacuo to a constant weight; the resultant beads showed no weight gain, confirming that adsorption was not occurring.

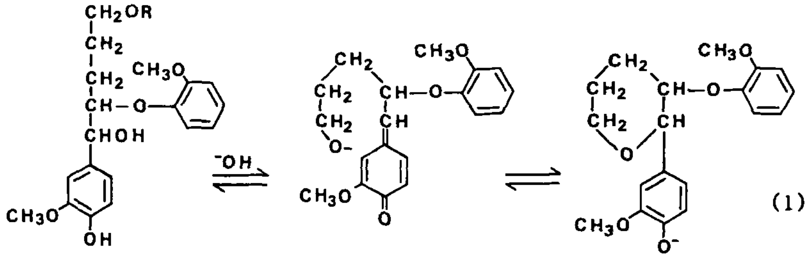
Model Degradation Reactions

Now, the critical question: how do the rates and product distributions change when comparing the reactions of alkali soluble models **8** and **8-Tr** with the insoluble polymer model **8-TrP**? The first problem to be addressed was which model **8** or **8-Tr** best represents the soluble analog of the polymer model? The answer seems obvious, **8-Tr**, since it more closely resembles **8-TrP**.

However, **8-Tr** appears to be insoluble at room temperature in aqueous alkali and probably has quite limited solubility at 150°C. Very little guaiacol (ca. 5%) was liberated when **8-Tr** was heated in 1N NaOH at 150°C; guaiacol production corresponds to β-aryl ether cleavage. In contrast, if either dioxane or DMSO is added as a 29% cosolvent to help solublize **8-Tr**, the guaiacol yield increases more than 10 fold (Fig. 1).[28] The low reactivity of **8-Tr** in pure water systems may be due to micelle formation in which there are polar phenoxide ions on the exterior and nonpolar side chains in inaccessible interior regions.

The fact that **8-Tr** and underivatized **8** display different reactivities at 150° in alkali, either in pure water or water organic mixtures,[28] argues that **8-Tr** is not hydrolyzed to **8** under these conditions. Again, another observation which appears to support the stability of the trityl ether linkage under simulated pulping conditions.

A problem associated with using **8** for comparative purposes is that it displays a unique chemistry - primarily because the propyl alcohol "handle" is not derivatized. The chemistry of **8** in 1N NaOH is dominated by a cyclization reaction which gives rise to compound **22** [Eq. (1)].[28]



8, 8-Tr, 8-TrP **22** (1)

We therefore anticipated that the most meaningful comparison between the soluble and insoluble models would be between **8-Tr** and **8-TrP** in a cosolvent system. Polymer model **8-TrP** was reacted in both water-only and water/p-dioxane under kraftlike conditions. Figure 1 depicts the production of guaiacol from each of these systems.

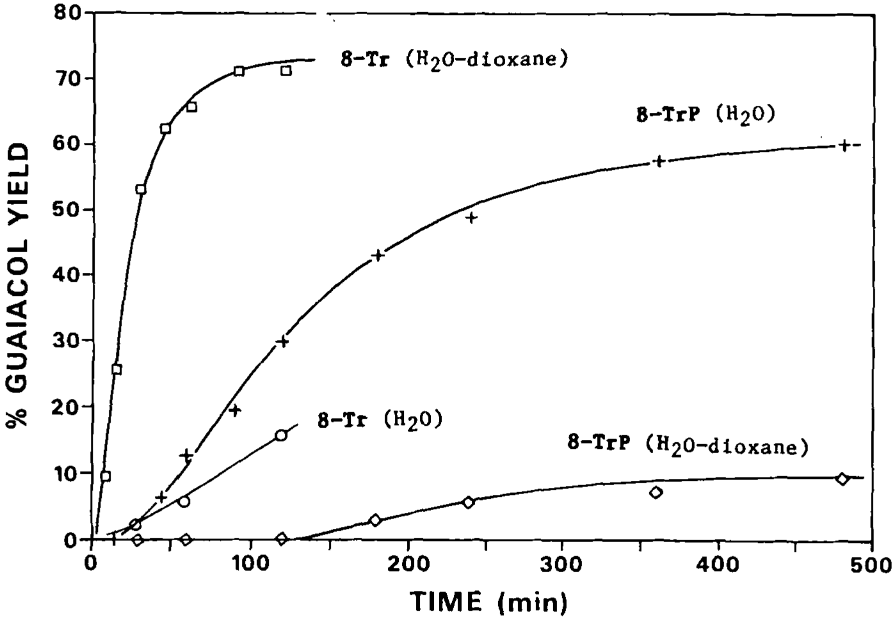


Figure 1. The relative yield of guaiacol from the kraftlike degradation of insoluble model **8-TrP** and **8-Tr** in aqueous and aqueous/29% *p*-dioxane systems.

The rate of guaiacol production from the insoluble model **8-TrP** in the _p_-dioxane system is unusually slow, _ca_. 9% after 8 hours. It is even lower in DMSO/H_2O, not reaching more than 1.5%. The dramatic effect of _p_-dioxane on the production of guaiacol from **8-TrP** was unexpected; possible explanations include phase separation of the reaction medium and/or collapse of the macroreticular network. Phase separation of _p_-dioxane/aqueous NaOH mixtures has been observed at high temperatures (90 to 170°C) by Obst.[29] If phase separation occurred during the reactions of **8-TrP**, and the organic layer penetrated and "surrounded" the polymer, then the accessibility of hydroxide and hydrosulfide to the reaction sites would have been limited.

Moreover, while macroreticular polystyrenes are generally considered "nonswelling,"[12] functionalized Amberlite XE-305 has been shown to swell moderately in _p_-dioxane.[30] The presence of _p_-dioxane in the kraftlike reactions could have swelled the polymer backbone of **8-TrP** and caused the macroreticular network to collapse. In this instance, the availability of the reactive sites would be restricted.

Stability of Polymer Bound Trityl Ether Models

A more important aspect of the polymer model's high temperature reactions is the observation of the cyclic compound **22** in the liquid phase of reaction samples. This signifies that the polymer-to-model trityl linkage is not stable to the reaction conditions! The guaiacol which was observed could have come either from a direct polymer model fragmentation reaction or from breakdown of **22** which was released into solution.[28] The extent of each pathway is unknown.

There are two reasonable ways for the cyclic compound **22** to be formed. First, the bound model might undergo a heterolysis (S_N1) reaction, giving rise to a relatively stable triarylmethyl carbonium ion and the conjugate base of **8**, which could cyclize as shown in Eq. (1). If this, however, were the case, why are the "soluble" trityl models apparently stable?

TABLE 2

Yields of **6** liberated from polymer-bound monomer **6-TrP**.

Time (min)	% 6 from **6-TrP(A)**[a]		% 6 from **6-TrP(B)**[b]	
	Kraft-135°C	Kraft-150°C	Kraft-147°C	Soda-147°C
15	4	14		
30	8	18		
45		21		
60	12	25	41	41
90	15	23		
120	15	24	59	
150				75
180			68	
240	17	25	78	75

---

[a] Kraft conditions employed 0.11N NaOH and 0.021N NaSH; the % **6** was determined by analyzing the amount of **6** liberated into solution using GC and an internal standard.

[b] Kraft conditions as above; soda conditions were 1N NaOH; the % **6** liberated was determined by methoxyl analysis of the resin.

A second pathway might be an attack of the C_α-O^- oxyanion on the terminal methylene, via a 6-membered ring S_N2 cyclic transition state, with the leaving group being $^-OCPh_2$-polystyrene. The reactions of polymer bound lignin model monomer **6-TrP** were therefore examined; **6-TrP** lacks an α-OH for an intramolecular S_N2 displacement of the polymer trityl ether and, consequently, may be expected to have a greater stability than **8-TrP**.

Two samples of **6-TrP** were examined. The samples had similar loading values, 0.26 and 0.22 mmol/g of resin, but differed in the solvent used in the coupling of the lignin model **6** to the polymer: sample A used pyridine, while sample B used a mixture of pyridine and benzene. Cleavage of the polymer-bound trityl ether bonds gave the yields of compound **6** shown in Table 2. Examination of these data shows that the fraction of cleaved ether bonds (a) is fairly high, (b) levels off with long reaction times, (c) is not very sensitive to the presence of NaSH, (d) is temperature dependent, and (e) differs significantly with the polymer substrate employed.

A possible explanation for the above behavior is that a fraction of polymer-bound trityl groups are intrinsically strained (being part of a cross-linked polymer), and form relatively weak trityl ethers with primary alcohol substrates. These weak ethers cleave more readily than a soluble trityl ether; the remaining fraction of polymer-bound ethers may be relatively unstrained and may maintain an alkaline stability similar to their soluble counterparts.

A second explanation is that there are a variable number (depending on the preparation) of bound models in environments conducive to heterolysis reactions. For example, regions which are exposed, or can be penetrated by the water and alkali, may experience model-polymer bond breakage (presumably via an S_N1 type mechanism in the case of **6-TrP**). Other regions, having principally an impenetrable "organic" environment are stable. A continuation of this theme argues that the "soluble" models were not really soluble, but formed impenetrable micelles, which protected the trityl bonds from cleavage reactions and provide the illusion that the molecules are inherently stable.

Lending support to these arguments, we observed different degrees of model loading, depending upon the solvent used in the coupling reactions leading to a polymer bound cellulose model.[19,31] Also, in this cellulose model case, the methods used to determine model loading did not always agree.[31] We suspect that the different solvents used in the reactions of the polymer, (i.e., coupling the model to the polymer and determining the loading) result in different degrees of polymer swelling and different degrees of reaction.

CONCLUSIONS

A propyl alcohol substituted lignin model monomer and dimer have been successfully attached to a polystyrene support. The linkage between the model and the polymer, a trityl ether type, does not, however, have good stability in aqueous alkali at 150°C. This lack of stability prevents these polymer models from being useful substrates in the study of pulping reactions. However, the trityl linked models may have value for studying heterogeneity effects under less severe conditions, such as exist in pulp bleaching or biodegradative reactions of lignin.

The large difference in trityl ether stabilities between simple models and polymer bound models is puzzling. Accessibility and solvent effects appear to play major roles in both the polymer bound models and the relatively water insoluble simple models. Our studies here suggest that a more stable model-to-polymer linkage, such as a benzyl ether linkage, is needed for producing a universally more useful heterogeneous lignin model.

Attempts to functionalize the propyl alcohol side chain of the A-ring model **7** met with difficulties. Apparently, the phenolic hydroxyl group interfers with direct derivatization of the nearby propyl alcohol. Even if an appropriate trityl ether linked model (**7-TrP**) could be prepared, it is highly likely that the stability under pulping conditions would be poor.

EXPERIMENTAL

The specific instrumentation, the performance of elemental analyses, and the reagents and solvents have been previously detailed.[11] Amberlite XE-305 (macroreticular polystyrene) was purchased from Polysciences, Inc., Warrington, Pennsylvania, as manufactured by Rohm and Haas Co., Philadelphia, Pennsylvania. The methoxyl analyses of the insoluble model were performed by Chem-Lig International, Inc., Schofield, Wisconsin.

The procedures for doing model degradation reactions at a 0.015 mmole level (either as a soluble model or corresponding amount of model bound to a polymer bead) and guaiacol analysis by methylation, followed by gas chromatography using p-isopropylphenol as an internal standard, have been previously described.[32] The cyclized product **22** from the degradation of **8-TrP** was characterized by methylation and GC/MS; it was identical to a previously prepared sample.[28]

Purification of Amberlite XE-305 resin followed the procedure outlined by Bovee.[19] The final steps in this purification, Soxhlet extraction with ethyl ether and with hexane for 8-10 hours and drying in a vacuum to a constant weight, were used with all polymer products. The preparation of polymer-bound trityl chloride (**5**, Scheme 1) followed the procedures outlined by Frechet and coworkers.[20,25] Polymer analyses are given in Table 1.

The reactions leading to and involving the p-methoxybenzyl compounds **17**, **18**, and **21** will not be described because of their dead-end nature and the lack of fully characterized products.

3-(3-Methoxy-4-hydroxyphenyl)-1-(polystyryltrityloxy)propane (6-TrP) - Procedure A. Polymer-bound trityl chloride (**5**), 4.6334 g (4.21 mmol chlorine content), was gently stirred (with a small magnetic stirbar) in 60 mL dry pyridine (under N_2) and 2.50 g (3 equiv) of 3-(3-methoxy-4-hydroxyphenyl)-1-propanol (**6**)[11] was added. The mixture was stirred for 5 days after which the polymer was washed successively with dry pyridine and dry Et_2O. The beads were placed in a cellulose thimble and Soxhlet extracted for 12 hr with Et_2O and hexane. The resultant beads were dried <u>in vacuo</u> at 40°C until a constant weight of 4.8118 g was achieved. The amount of material loaded, 0.2233 g, was calculated from the following equation:

$$[\text{model loaded (g)}] = \frac{[\text{weight gain of polymer product}]}{1 - \dfrac{[\text{MW of HCl}]}{[(\text{MW of model}) - 1]}}$$

The loading level, determined from this gravimetric analysis, was calculated to be 0.26 mmol/g. The quantity of compound **6** which could be liberated from **6-TrP** upon acid hydrolysis (as measured by GC) corresponds to 102% of the abovementioned loading.

Procedure B. A second batch of **6-TrP** was synthesized by suspending a second preparation of the trityl chloride (**5**), 5.05 g (2.61 mmol Cl), in 75 mL of a 1:3 (v/v) mixture of dry benzene:

dry pyridine solvent. The lignin model (**6**), 3.00 g (16.5 mmol), was added and the mixture stirred for 6 days at 45-50°C. The product was isolated as described above in Procedure A. Methoxyl analysis gave a loading of 0.22 mmol/g.

Model degradations of the procedure B product **6-TrP** were conducted under simulated soda or kraft conditions at 147°C for up to 4 hr. Once cool, the reacted model was isolated by filtration and washed successively with 3-5 mL of the following solvents: water, methanol-water (50% v/v), methanol, dichloromethane, and low boiling pet. ether. The model was then extracted with ethyl ether and hexane for 8 hr each and dried in vacuo at 45°C. Residual model loadings were determined by methoxyl analysis and compared with the methoxyl content before reaction to give the values reported in Table 2.

2-(2-Methoxyphenoxy)-1-(3-methoxy-4-hydroxy)-5-(polystyryltrityloxy)-1-pentanol (8-TrP). Into 50 mL of dry pyridine and 25 mL dry benzene was suspended 3.9121 g (3.55 mmol chlorine content) of **5**. To this was added 7.10 g (20.4 mmol) of compound **8**.[11] The reaction mixture was gently stirred at 45-50°C for 6 days and worked up as in the case of **6-TrP** to afford 4.4756 g of product. The amount of **8** loaded on **8-TrP** was calculated to be 0.630 g, which corresponds to 0.40 mmol/g. A more reliable estimate of loading, 0.44 mmol/g, was derived from methoxyl analyses; the latter value was used when calculating stoichiometries for the degradation studies.

Acid Hydrolysis of Polymer-Bound Models; General Procedure. Approximately 50-150 mg of insoluble model was suspended in 2 mL CH_2Cl_2 in a 60 mL separatory funnel (which had a plug of glass wool compressed into place just above the stopcock). To this suspension was added 0.5 mL of trifluoroacetic acid (TFAA) and the mixture was periodically swirled over 15 min. The mixture was then drained into another separatory funnel which contained an excess of saturated aqueous K_2CO_3; the K_2CO_3 neutralized excess TFAA and hydrolyzed any trifluoroacetates which may have formed.[31]

The overall process was repeated 2-3 times with the polymer beads, after which the resultant CH_2Cl_2 layer was separated, and its contents analyzed by GC, or GC/MS, compared to an internal standard. The weight of polymer, in the case of **8-TrP**, was compared before and after treatment.

Ethyl 5-Acetyl-3-methoxy-2-[β-(trimethylsilyl)ethoxymethoxy] dihydrocinnamate (10). A solution of 8.47 mL (3 eq.) of N,N-diisopropylethylamine in 25 mL of CH_2Cl_2 was prepared in dry glassware under a nitrogen atmosphere. To this was added successively, in rapid dropwise fashion, 5.73 mL (2 eq.) of β-(trimethylsilyl)ethoxymethyl chloride ("SEM-Cl")[22,33] in CH_2Cl_2 and then 4.31 g (16.2 mmoles) of ethyl 5-acetyl-3-methoxy-2-hydroxydihydrocinnamate (**9**)[11] dissolved in CH_2Cl_2; the final volume was roughly 150 mL. The solution was stirred overnight at 35°C, washed twice with dilute HCl and twice with water, dried (Na_2SO_4), filtered and evaporated to leave 6.1 g (95%) of **10** as a syrup: ^1H-NMR ($CDCl_3$) δ (referenced against the compound's internal Me_3S signal) 0.00 (s, 9, $SiMe_3$), 0.84-1.03 (m, 2, CH_2Si), 1.22 (t, 3, J = 7.0 Hz, CH_2CH_3), 2.54 (s, 3, $COCH_3$), 2.52-2.69 (m, 2, $ArCH_2$), 2.90-3.10 (m, 2, CH_2CO), 3.73-3.91 (m, 2, OCH_2CH_2Si), 4.10 (q, 2, J = 7.0 Hz, CH_2CH_3), 5.20 (s, 2, OCH_2O), and 7.40 (s, 2, aryl-H).

1-(3-Methoxy-4-[β-(trimethylsilyl)ethoxymethoxy]-5-[γ-hydroxypropyl]phenyl)ethanol (11). A slurry of 0.61 g (16 mmoles) of lithium aluminum hydride in 50 mL of freshly distilled THF was stirred vigorously while a solution of 2.5 g (6.3 mmoles) of **10** in 50 mL of THF was dripped in slowly over a 45 min period. Another 300 mL of THF was rinsed through the dropping funnel into the reaction mixture and the solution refluxed for 90 min and then stirred at room temperature overnight. A saturated aqueous solution of Na_2SO_4 was cautiously added until fizzing stopped; a white solid (aluminum salts) was present. The suspension was then filtered and the collected solids rinsed thoroughly with ether. The filtrate was dried (Na_2SO_4) and evaporated. An IR spectrum of the residue showed some carbonyl absorptions, indicative of starting material.

The residue was placed on a 40 x 2.5 cm column of silica gel packed in CH_2Cl_2 and eluted with progressively stronger concentrations of methanol in CH_2Cl_2 to give 1.8 g (ten combined collected fractions) of **11** as syrup: ^{1}H-NMR ($CDCl_3$) δ (relative to the compound's internal Me_3Si signal) 0.00 (s, 9, Me_3Si), 0.87-1.04 (m, 2, CH_2Si), 1.44 (d, 3, J = 6.5 Hz, α-CH_3), 1.82 (p, 2, J ≈ 6.5 Hz, β-CH_2), 2.75 (t, 2, J = 7.2 Hz, α-CH_2), 3.54 (t, 2, J = 6.1 Hz, γ-CH_2OH), 3.74-3.91 (m, 2, OCH_2CH_2Si), 3.81 (s, 3, OCH_3), 4.78 (q, 1, J = 6.5 Hz, benzyl-CHOH), 5.08 (s, 2, OCH_2O), 6.73 (d, 1, J = 1.8 Hz, C2-aryl-H), and 6.78 (d, 1, J = 1.8 Hz, C6-aryl-H).

1-(3-Methoxy-4-hydroxy-5-[γ-hydroxypropyl]phenyl)ethanol (14). In dry glassware, under nitrogen, 45 mg (0.12 mmoles) of **11** and 460 mg (10 eq.) of tetrabutylammonium fluoride[34] in 25 mL of dry THF were stirred for 36 hours. At this time, a TLC showed very little remaining **11**. The solution was diluted with $CHCl_3$ and extracted three times with $0.5\underline{M}$ NaOH. The combined base extracts were acidified and extracted three times with fresh $CHCl_3$. The latter extracts were combined, dried (Na_2SO_4), and evaporated to leave ~ 30 mg of **14** as an oil. An NMR spectrum of **14** produced in this way was identical to that of an authentic sample of **14**.[17]

1-(3-Methoxy-4-[β-(trimethylsilyl)ethoxymethoxy]-5-[γ-triphenylmethoxypropyl]phenyl)ethanol (12). In dry glassware, under nitrogen, 1.0 g (2.81 mmoles) of **11** in 15 mL of dry pyridine was added dropwise over an hour to a stirred solution of 1.58 g (5.7 mmoles) of freshly recrystallized triphenylmethyl chloride. The mixture was stirred for 24 hr at 45°C, cooled, diluted with 100 mL of water and the layers separated. The aqueous phase was extracted three times with toluene. The organic phase and toluene extracts were combined, washed with water (until the washes were neutral), washed with saturated NaCl solution, dried (Na_2SO_4), and evaporated. The gold colored liquid residue was applied to a 40 x 2.5 cm dry-packed alumina column and eluted with CH_2Cl_2 containing successively increasing amounts of methanol. The early collected fractions, which appeared by TLC analysis to be a mixture of **11**, trityl chloride, and some minor impurities, were column chromatographed again using only toluene as the eluent. The principal product **12** was observed in most collected fractions and appeared to be the only component in fractions 40-133: ^{1}H-NMR ($CDCl_3$) δ (relative to the compound's internal Me_3Si signal) 0.00 (s, 9, Me_3Si), 0.85-1.03 (m, 2, CH_2Si), 1.46 (d, 3, J = 6.3 Hz, $BnCH_3$), 1.70 (d, 1, J = 3.2 Hz, OH), 1.82-2.10 (m, 2, β-CH_2), 2.71-2.86 (m, 2, α-CH_2), 3.15 (t, 2, J = 6.4 Hz, γ-CH_2O), 3.74-3.91 (m, 2, OCH_2CH_2Si), 3.85 (s, 3, OCH_3), 4.72-4.84 (m, 1, CHOH), 5.10 (s, 2, OCH_2O), 6.73 (d, 1, J = 1.7 Hz, C2-aryl-H), 6.81 (d, 1, J = 1.7 Hz, C6-aryl-H) and 7.2-7.5 (m, 15, CPh_3); ^{13}C-NMR ($CDCl_3$) ppm -1.26 (q, Me_3Si), 18.2 (t, CH_2Si), 25.2 (q, $BnCH_3$), 27.3 (t, β-CH_2), 30.9 (t, α-CH_2), 55.6 (q, OCH_3), 63.4 (t, γ-CH_2O), 67.0 (t, OCH_2CH_2Si), 70.1 (d, CHOH), 86.3 (s, CPh_3), 96.9 (t, OCH_2O), 107.4 (d, C2), 118.7 (d, C6), 126.6, 127.5, 128.5 (d, trityl aryl-CH), 144.2 (s, trityl aryl C), 143.2, 152.0 (C4, C5) and 135.8, 141.4 (C1, C3).

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