Insoluble Lignin Models (3): Preparation of a Polymer-Bound Guaiacylpropanol Model

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INSOLUBLE LIGNIN MODELS (3): PREPARATION OF A POLYMER-BOUND GUAIACYLPROPANOL MODEL

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ABSTRACT

Guaiacylpropanol (4), has been attached at the gamma carbon through a benzyl ether linkage to a macroreticular polystyrene resin. The phenolic site of 4 was protected as an allyl ether when coupled to the resin. The amount of lignin model 4 which was attached to the polymer was determined by cleaving the benzyl ether linkage with iodotrimethylsilane (ITS) and quantifying the amount of released guaiacylpropanol. The ITS method was reproducible but not quantitative due to a high model loading (1.29 mmol/g). Both FTIR and ^{13}C-NMR were used to characterize the insoluble model.

INTRODUCTION

Recent work in our laboratory has centered on preparing, characterizing, and conducting simulated pulping experiments on polymer-supported lignin and carbohydrate models. The lignin[1] and carbohydrate[2] models were attached to a polystyrene support via trityl ether and benzyl ether linkages, respectively. The trityl ether linkage was sub-

233

sequently found to be unstable under pulping conditions;[1] the benzyl ether linkage, however, appeared to be relatively stable.[2, 3]

The work presented herein describes our efforts at preparing and characterizing a polymeric lignin model, which has guaiacylpropanol (4) attached to a macroreticular polystyrene resin _via_ a benzyl ether linkage. Macroreticular polystyrene, like lignin, is a crosslinked aliphatic-aromatic polymer. The heterogeneous model network will resemble lignin more closely in terms of its polyelectrolytic behavior if the resin has a high local concentration of ionizable lignin model units. An objective of this research was to prepare a resin with a high degree of lignin model incorporation. An incorporation of 1-3 phenolic rings per 10 phenyl rings of the polystrene resin would correspond to roughly the level of phenolic to nonphenolic aryl rings which exist in lignin during chemical pulping.

The lignin model is a simple one, representing only one structural feature of lignin -- (polymeric) phenol. The relative rates of "condensation" of the polymeric phenol and an analogous soluble phenol will be compared in the paper[4] which follows; the research addressses whether or not heterogeneous condensation reactions are occurring during pulping.

RESULTS AND DISCUSSION

Functionalization of the Polymer Support

The polymeric support used in previous studies in this laboratory[1, 2] has been Amberlite XE-305. Macroreticular resins of this type consist of agglomerates of microgels as shown in Figure 1.[5] The macropores, or interstices between the microgels, are accessible to all solvents.
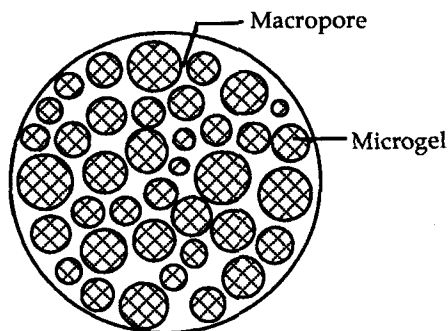
Figure 1. Cross-sectional view of a macroreticular polystyrene resin.[5]

The average diameter of the macroporous network in Amberlite XE-305 is 1400 Å.[6] Unlike the macropores, the interior regions of the microgel particles are accessible only in the presence of a good swelling agent. Amberlite XE-305, due to its light crosslinking (3-4%), swells in good organic solvents, a feature which is quite useful in synthesis.[7] The resin has been shown to be stable in 2.5$\underline{M}$ alkali at 170 °C for five days.[2]

A second macroreticular resin (Biobead SM-16) also was investigated for potential use. Table 1 compares the physical properties of the Amberlite XE-305 to those of the SM-16. As shown, the SM-16 is more highly crosslinked, which imparts limited swelling. A much smaller pore diameter (144 Å) results in the larger specific surface area (860 m²/g). It was envisioned that the SM-16 would provide a support that had a large concentration of attached model on the outer edges of the resin thus making the model more accessible to alkaline pulping reagents.

After being washed to remove surface impurities,[9] the two resins (1) were functionalized to benzyl iodides (Scheme 1). The iodides (3),

Table 1. Physical characteristics of polymeric supports.[6, 8]

	Amberlite XE-305	Biobead SM-16
Cross-link Ratio (%)	3-4	16
Ave. Pore Diam. (Å)	1400	144
Surface Area (m^2/g)	48	860
Swellability	Good	Limited
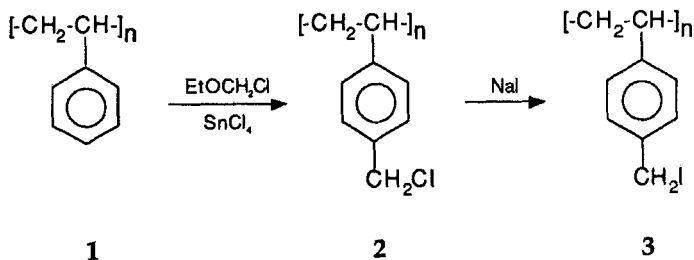
Scheme 1

which were prepared according to the Finkelstein reaction[10, 11] from the corresponding chlorides (2),[12] were sought to give greater S_N2 reactivity[13] during subsequent reactions. As shown in Scheme 1, para substitution is the dominant position of chloromethylation.[14] Elemental analyses of the various benzyl halide preparations are given in Table 2.

Depending on the catalyst and reaction conditions, several side reactions can occur during chloromethylation.[15-17] The most prominent are substitution at the backbone of the polymer or at the ortho position of the phenyl ring. Additional crosslinking can occur between the benzyl chloride residues and neighboring phenyl rings in the presence of a Lewis acid catalyst; cationic polymerization of unreacted vinyl

Table 2. Elemental analyses of the functionalized polystyrenes.[a]

	C	H	O	Cl	I	mmol/g[e]
Amberlite XE-305	91.25	7.67	1.64	------	------	------
PBnCl	75.56	6.65	2.16	16.30	------	4.60
PBnCl [b]	76.90	6.61	2.11	14.78	------	4.17
PBnI	54.47	4.62	1.48	0.00	39.24	3.09
PBnI [b]	63.17	5.37	1.31	0.00	31.06	2.45
SM-16 [c]	90.92	8.04	1.16	------	------	------
SBnCl [c]	79.64	7.62	3.65	9.54	------	2.69
SBnI [c]	73.51	6.98	3.34	2.08	13.89	0.59 (Cl)
						1.09 (I)
SBnI [c, d]	74.10	6.89	3.37	2.23	13.98	0.62 (Cl)
						1.06 (I)

[a] P = Amberlite backbone, S = SM-16 backbone, Bn = benzyl group.
[b] Batch No. 2. [c] Single analysis, all other values are averages of duplicates. [d] A second halide exchange performed on the previous entry. [e] Calculated degree of halide incorporation; does not reflect reaction yields since the polymer weight changes with substitution.

groups has also been observed. The crosslinking can be reduced by using pure grades of materials and good swelling solvents.[18, 19]

Concerning the SM-16 resin, Table 2 shows that the conversion from the chloride to the iodide is not quantitative; a second halide exchange reaction had no effect. The incomplete exchange could be due to vinyl chloride formation during the chloromethylation procedure or to limited reagent accessibility, since acetone is not a good resin swelling solvent. Vinyl groups are more prevalent in highly crosslinked resins due to incomplete polymerization. The resulting vinyl chlorides are less reactive toward further modifications than are the aromatic chloromethyl groups.[15]

Table 2 also shows that high benzyl chloride loadings were achieved in the Amberlite system; there is approximately 1 chlorine per 1.62 styrene units. The chloride groups were completely displaced during the Amberlite benzyl iodide preparations; although the yield of iodide replacement was approximately 92% for batch 1 based on the iodine elemental analysis data. The halide exchanges were readily discernible by Fourier Transform infrared spectroscopy (FTIR); the characteristic benzyl chloride signal at 1265 cm^{-1} was replaced by a benzyl iodide signal at 1155 cm^{-1}. Based on x-ray analyses (SEM-EDS), the cross-sectional distribution of Cl and I in the Amberlite benzyl halides was quite homogeneous. Similar results were observed by Belfer, et al.[20] The distribution is reportedly dependent upon the chloromethylation method employed.[21]

The highly crosslinked Biobead SM-16 resin was not studied further, primarily because of the low halide exchange yield. Highly crosslinked polymers have shown limited degrees of reactivity in other systems.[22] Unlike the SM-16, the more lightly crosslinked Amberlite XE-305 showed a high level of reactivity which should allow for the preparation of a resin with a high degree of model loading.

Protected Lignin Models

Preliminary work was conducted with a simple lignin model having both a propyl alcohol side chain and a phenolic hydroxyl group (4) to determine the conditions required to generate model-to-polymer benzyl ether linkages. As was previously encountered during the preparation of a trityl-linked model,[1] selectivity for reaction at a primary alcohol group[23] was not observed in the benzyl case. Treatment of guaiacylpropanol (4) with benzyl bromide (BnBr) in the presence of

NaH/DMSO did not give the anticipated propyloxybenzyl product **5**; rather benzylation occurred principally on the phenolic hydroxyl group (**6**). Product **6** was characterized as its acetate **7**.

This result suggested other possible protecting group methods. Guaiacylpropanol (**4**) was treated with p-methoxybenzyl iodide to give **8**; the latter was then benzylated, affording **9**. Attempts to specifically remove the p-methoxybenzyl group by treatment with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)[24] led to a complicated product mixture, rather than pure **5**. Apparently, the DDQ also oxidized the electron-rich ring of the model. This was further verified by the poor conversion of the p-methoxybenzylated phenol **10** to the simple phenol **11** with DDQ.

Methoxyethoxymethyl (MEM) ether was also investigated as a potential protecting group. Facile removal with trifluoroacetic acid
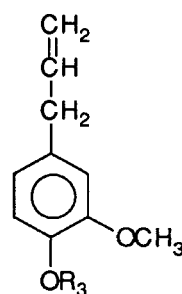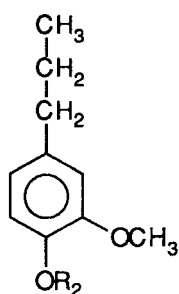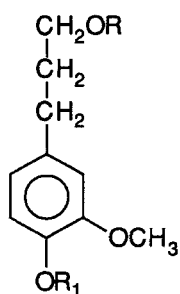
4, R=H, R$_1$=H	**10,** R$_2$=p-BnOMe	**13,** R$_3$=H
5, R=Bn, R$_1$=H	**11,** R$_2$=H	**14,** R$_3$=MEM
6, R=H, R$_1$=Bn		
7, R=Ac, R$_1$=Bn		
8, R=H, R$_1$=p-BnOMe		
9, R=Bn, R$_1$=p-BnOMe		
12, R=H, R$_1$=MEM		
15, R=H, R$_1$=allyl		
16, R=Bn, R$_1$=allyl		

makes the MEM ether attractive.[25] The MEM protected model **12** was prepared by first synthesizing the MEM ether of eugenol (**13**) and then hydrating **14** with disiamylborane/hydrogen peroxide. Difficulties were encountered, however, in benzylating the protected model **12** under the reflux conditions suggested by Corey, et al.[25] Analysis of the product mixture revealed that the MEM group was not completely stable since some free phenol was observed. Also, the MEM group did not completely remain attached to the phenolic OH during an attempted coupling reaction of the protected model (40-50 °C) with a polymer-bound benzyl halide. Milder conditions (room temperature) were not explored.

Bovee used allyl (-CH$_2$CH=CH$_2$) groups to protect hydroxyl groups of a disaccharide that was attached to a polystyrene support through a benzyl ether linkage.[2] Guaiacylpropanol was readily protected at the phenolic site with an equimolar amount of NaH and an excess of allylbromide to give **15**. The allyl protected model (**15**) was then benzylated, yielding **16**. The allyl group was quantitatively removed from **16** by isomerizing to a prop-1-enol with tris(triphenylphosphine)rhodium(I) chloride (TTPPR) and 1,4-diazabicyclo-[2.2.2]octane (Dabco), followed by acid catalyzed hydrolysis to give **5**.[26]

Complete isomerization of the phenolic allyl group required more than 24 hr at reflux, compared to 6 hr for primary or secondary hydroxyl groups.[26-28] Allyl isomerization _via_ potassium _t_-butoxide in DMSO was unsuccessful.[29] Cleavage of the prop-1-enol ethers by acetone/1$\underline{M}$ HCl was also sluggish, requiring reflux conditions. Triphenylphosphine and its oxide, which were observed in the isomerization product mixture, should be easily removed in the heterogeneous case by simply washing the resin.

Thus, the allyl group appeared to possess the required protecting group qualities: selective reaction at the phenolic OH, stability during benzylation of the aliphatic OH, and easily removed in the presence of a benzyl ether.

Preparation of Polymer-Bound Guaiacylpropanol

Initial attempts at coupling allyl-protected guaiacylpropanol (15) to the polymer-bound benzyl iodide (3) were performed in 25% benzene/DMF, using sodium hydride to deprotonate the primary alcohol (Scheme 2). Analysis of the resulting product (17) by FTIR showed strong hydroxyl and carbonyl absorbances, indicating that the DMF had sorbed onto the resin. Extended Soxhlet extraction of the resin did not remove the impurities. The coupling yield was presumably low since the FTIR spectrum did not show evidence of the allyl group.

Tetrahydrofuran, also a good swelling solvent for the resin, replaced DMF as the coupling solvent in a second attempt to bind model to the polymer. The FTIR spectrum of the coupled product (17) did not show any evidence of solvent absorption. An analysis of the liquor from the coupling reaction revealed starting material 15, thus confirming that the allyl group was stable under the prescribed reaction conditions.

The loading of the coupled material was apparently much higher than in the DMF case; infrared signals at 997 and 926 cm^{-1} (=C-H bend) attested to the presence of the allyl group. The benzyl iodide FTIR signal was still evident, however, indicating that the displacement was not quantitative. A rough estimate of the model loading was determined by the weight gain of the polymer following the coupling reaction;[1] this gravimetric analysis gave 1.57 mmol of model per gram of resin.
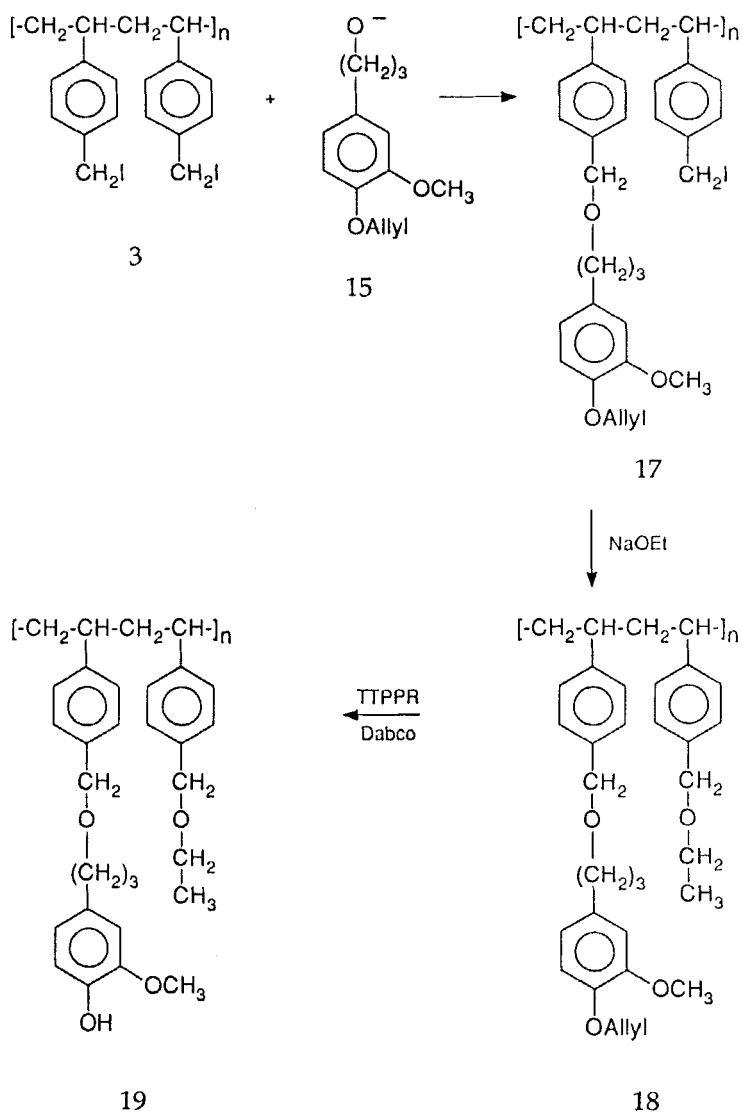
Scheme 2

The second step in preparing the heterogeneous model involved etherification of the remaining benzyl iodide groups. The residual benzyl iodide units (on **17**) were converted to nonreactive benzyl ethoxide groups (**18**) by treatment with sodium ethoxide in ethanol. An FTIR spectrum of the ethoxide treated resin showed that the initial benzyl iodide signal had been replaced by the corresponding benzyl ethoxide signal at 1097 cm-1. Model experiments under the above reaction conditions confirmed that the allyl protecting group was stable toward sodium ethoxide.

The final step in preparing the model involved removal of the allyl group with the TTPPR/Dabco/acid hydrolysis method to generate the free phenol **19**. The FTIR spectrum of the deprotected material **19** showed a strong hydroxyl absorbance indicating that some free phenol had been produced. The allyl signals were still evident, however, suggesting that the deprotection was incomplete. Two additional deprotection sequences were needed to remove the FTIR allyl absorbances.

A high resolution ^{13}C-NMR (CMR) technique[30] also was used to characterize selected resin samples (Fig. 2). The spectra, obtained using conventional methods by simply suspending the resin in $CDCl_3$, suffer from band broadening due to the heterogeneous nature of the substrate. In general, the spectra for the polymer-supported appendages were consistent with comparable soluble compounds.

The CMR spectrum of the iodomethylated polystyrene resin **3** (Fig. 2A) exhibited signals that were consistent with a polystyrene backbone.[31, 32] The signal for the heterogeneous benzyl iodide carbon, which for the soluble analog (a-iodo toluene) comes at 5.9 ppm,[33] was not readily apparent. The signal for the precursor benzyl chloride (**2**) carbon at 46 ppm was also not observed.[31, 32] This latter result confirms
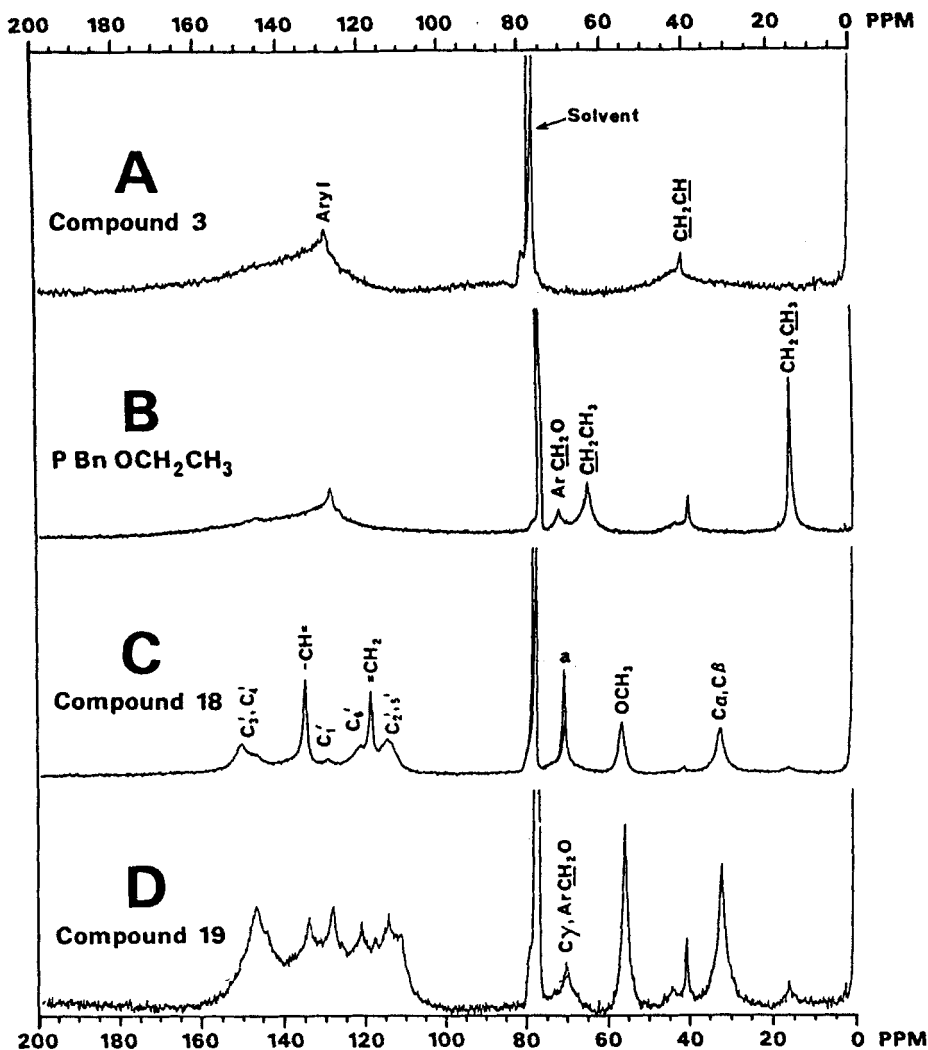
Figure 2. The ^{13}C-NMR spectra of selected resin samples; the area
between 78-80 ppm represents solvent signals (CDCl$_3$).
Signal "a" appears to be a combination of carbon types as
described in the text.

the elemental analysis of the iodide **3** (Table 2) in which no chlorine was detected.

Treatment of **3** with sodium ethoxide provided the corresponding ethoxymethylpolystyrene where the ethyl and benzyl signals were quite pronounced (Fig. 2B). It appears from this spectrum and the ones which follow that those carbons furthest removed from the polymer backbone display the strongest signal intensities. This phenomenon is related to differences in carbon relaxation times between nuclei close to the heterogeneous support, where motional freedom is restricted, and nuclei at the unbound end of the attached molecule, where rotation freedom is much higher.[30]

The CMR spectrum of polymer **18** (Fig. 2C) clearly showed the 4-O-allylguaiacylpropanol appendage. The allyl protecting group, which is the functional unit furthest removed from the polymer backbone, showed strong signals at 70, 117, and 135 ppm. The propyl carbons were indicated by signals at 30-35 and 70 ppm. The presence of an oxygenated aromatic ring in the resin was demonstrated by the methoxyl signal (56 ppm), together with the high field (135-150 ppm) signals for aryl-oxygen carbons and the low field (110-115 ppm) signal for aryl carbons which are ortho to aryl-oxygen substrates.

Finally, the spectrum of resin **19** (Fig. 2D), which exhibited a greater signal intensity than the other spectra, clearly showed that most of the allyl groups have been removed. Residual allyl signals were detected, however, at the resonances cited above. The oxygenated aryl ring, the methoxyl and the Cα/Cβ propyl carbons were again readily distinguished. The signals associated with the oxygenated methylenes of Cγ and the benzyl unit can not be clearly assigned; they appeared to be either part of the 70 ppm signal or overlapped with the strong sol-

Table 3. Elemental analysis (duplicates) of the compounds isolated
during the preparation of the heterogeneous lignin model.

Substrate	C	H	O	I	P	I loading (mmol/g)
17	76.43	7.28	9.50	6.15	---	0.48
18	79.36	7.65	11.18	1.41	---	0.11
19	78.09	7.42	12.47	0.11	0.29	<0.01

vent signal at 78-80 ppm. The relatively low signal intensity for the
ethoxy groups (15 and 66 ppm) in resins 18 and 19 indicate that most of
the polymer-bound benzyl iodide units were consumed by reaction
with guaiacylpropanol. A fourth deprotection sequence was not at-
tempted, since the remaining allyl groups appeared, by their inactivity,
to reside in inaccessible regions of the resin.

Table 3 summarizes the elemental analysis data of each inter-
mediate and the final product. The low iodine content of the initial
coupling product (17) provided more evidence that model-resin coup-
ling was extensive. The high conversion suggested that the distribu-
tion of the model was essentially that of the initial benzyl iodide. Phos-
phorus was detected in product 19, indicating that a small quantity of
triphenylphosphine residues had sorbed to the polymer. The phos-
phine residue, if covalently bonded to the resin, should be inert toward
the subsequent condensation reactions.

Model Loading Determination

Gravimetric and elemental analysis data, along with the FTIR
and ^{13}C-NMR spectra, showed that a sufficient quantity of model had

been covalently bound to the polymer _via_ a benzyl ether linkage. A method to quantify the amount of material on the resin was sought.

With the trityl-linked models, methoxyl analysis for the lignin-like units gave reproducible and quantitative results.[1] The methoxyl method was not applicable with the present benzyl-linked model since ethoxide groups, which were added to destroy the excess reactive benzyl iodide groups, are known to interfere with the determination.[34] Initially, a propyl group was investigated as an etherification reagent. Subsequent analyses of the polymer, which had bound propoxide groups and no attached model, gave positive methoxyl results; the same was found with an allyl etherified resin.

Another approach to quantification is to derivatize the polymer-bound phenol with a functional group that has an easily analyzed element. This approach was taken with heterogeneous model **19** using pentafluoropropionic anhydride and a pyridine catalyst.[35] The resulting pentafluoropropionate was found to be unstable over time giving inconsistent results. In contrast to what was observed with a soluble phenol, the heterogeneous derivatization in this case was incomplete.

Methods for quantitatively cleaving the heterogeneous benzyl ether bond, in order to isolate and analyze the amount of guaiacylpropanol liberated, were investigated. Benzyl ethers are readily cleaved by catalytic hydrogenation.[36] This method could not, however, be implemented due to the two insoluble phases.[37] Several other reagents were tested without success. These systems included boron trifluoride with ethanethiol,[38] acetolysis,[2] and anhydrous ferric chloride with acetic anhydride.[39]

A neutral reagent, iodotrimethylsilane (ITS), reportedly cleaves benzyl ether bonds quantitatively under mild reaction conditions

(room temp., 20 min).[40, 41] A similar reagent system, chlorotrimethyl-
silane in the presence of phenol, has been used effectively on polymer-
bound substrates.[42] Tests with benzylated allylguaiacylpropanol (16)
showed complete benzyl group removal in 20 min at room tempera-
ture. The allyl group was also cleaved but at a slower rate than the
benzyl group.

Iodotrimethylsilane proved to be an effective reagent with the
polymer system. Reaction of heterogeneous model 19 with ITS, fol-
lowed by acetylation of the cleaved product, yielded 20; the latter could
be quantified by GLC using an internal standard.

$$CH_2\text{-}R$$
$$|$$
$$CH_2$$
$$|$$
$$CH_2$$

OR$_2$

ÓR$_1$
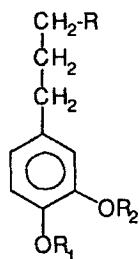
20, R=OAc, R$_1$=Ac, R$_2$=CH$_3$
21, R=I, R$_1$=Ac, R$_2$=CH$_3$
22, R=OAc, R$_1$=Ac, R$_2$=Ac
23, R=OAc, R$_1$=n-propyl, R$_2$=CH$_3$

Several minor compounds (21-23) were detected in the product
mixture. Combined, they accounted for less than 5% of the amount of
guaiacylpropanol present. The iodo compound 21 could result from
two routes. The most likely prospect is that excess ITS converts the
silated propyl alcohol function to the iodide after the model has been
cleaved.[41, 43] The other possibility is that the model is cleaved as the
iodide rather than as the alcohol. The literature reports that for soluble

models the cleavage is 100% for the benzyl iodide, giving the free alco-hol.[41] This may not be the case in the heterogeneous system.

The appearance of compound 22 indicated that a small amount of methyl aryl ether cleavage had occurred. Methyl ether cleavage dur-ing ITS treatment is known to be slow relative to that of the benzyl ethers and often requires harsher conditions.[44] Compound 23, which is observed in trace quantities, is believed to result from the reduction of residual allyl groups during the course of the synthesis. The propoxy group on 23 effectively prohibits the model from undergoing conden-sation reactions.

The ITS procedure for quantifying the model on the resin is sim-ple and reproducible, giving a loading of 1.29 ± 0.04 mmol/g. Quanti-tative results were, however, not obtained. A significant benzyl iodide signal in the FTIR spectrum of the ITS treated resin indicated that a majority of the model had been displaced; however, the spectrum also showed residual model. In some cases, a broad signal attributable to a silyl ether was observed; the signal could be removed with concomit-ant generation of the corresponding alcohol by treatment with citric acid in methanol.[45]

A product of the ITS reaction, as shown by FTIR, is polymer-bound benzyl iodide. A microscopic x-ray analysis (SEM-EDS) of the ITS-treated resin showed that iodine was present in the innermost re-gions of the bead at a uniform level; no gradient from the outer edge of the bead was observed. The iodine distribution indicates that the macroporous regions of the resin are accessible to the ITS during the 30 min reaction period.

The nonquantitative nature of the ITS procedure suggests that not all of the bound model is available for reaction. The inaccessible

model is presumably trapped within the microgel region of the resin. The loading value determined by the ITS method, however, may be a reasonable estimate for the amount of model on the polymer support that would be available for reaction during "pulping treatments."

The ITS loading value of 1.29 mmole/g of resin corresponds to roughly 1 guaiacylpropanol unit attached to every 4 styrene units, or a level of approximately 25% phenolic units to nonphenolic aryl rings. [See the Experimental Section for the calculation.] The loading value of 1.29 mmoles/g of resin is considered to be more accurate than the gravimetric loading value of 1.57.

CONCLUSIONS

A polymer-bound lignin model has been prepared with a high-loading using a benzyl ether model-to-polymer linkage. The lignin-like monomer, guaiacylpropanol, which was attached to the support through its primary alcohol, could be selectively protected at the phenolic site by several reagents. The allyl group proved to be the best protecting group tested in terms of stability during benzylation and high yield selective deprotection in the presence of benzyl ethers. Benzyl ether cleavage via iodotrimethylsilane was demonstrated to be a simple and reproducible method for determining the amount of accessible model (1.29 ± 0.04 mmol/g). However, this method was not quantitative for the highly loaded resin. Analysis by an x-ray method showed that the distribution of model throughout the resin was rather homogeneous and that the interior macroporous regions of the polymer network were accessible to ITS. Spectral characterization of the resin intermediates and products by FTIR and high resolution CMR con-

firmed the chemical analyses of the heterogeneous model. A highly crosslinked macroreticular resin, Biobead SM-16, showed limited synthetic reactivity and was therefore not suitable as a supporting matrix.

EXPERIMENTAL

Proton and ^{13}C-NMR were recorded on a Jeol FX100 spectrometer using TMS as an internal reference. High resolution ^{13}C-NMR spectra of the polymer-supported compounds in $CDCl_3$ were obtained by Spectral Data Services[46] on a 360 MHz instrument according to the method of Ford and co-workers.[30] Infrared spectra were recorded on a Perkin-Elmer Model 700 infrared spectrometer and standardized with polystyrene. Infrared spectra of the heterogeneous models were obtained as KBr pellets with a Nicolet 7199 Fourier Transform spectrometer. The x-ray data were recorded with a Tracor Northern TN-2000 energy dispersive spectrometer interfaced with a Jeol 35C scanning electron microscope.

Gas-liquid chromatography (GLC) was performed on a Hewlett-Packard 5890 instrument interfaced with a Hewlett-Packard 3392 integrator. Gas chromatographic analyses were performed on a glass column (6 ft. x 2 mm ID) packed with OV-17 (3%) on Supelcoport (80-100 mesh). The general operating conditions were as follows: inj. temp. 285 °C, det. temp. (FID) 300 °C, helium carrier gas at 20 mL/min, program 100 °C (1 min) to 285 °C (5-10 min) at 10-15 degrees/min. A Hewlett-Packard 5985 instrument was used for GLC mass spectroscopy (GC/MS). The GC/MS interface was maintained at 250 °C. Electron impact (EI) MS used helium as the carrier gas, a source temp. of 200 °C, and an ionization voltage of 70 eV.

Melting points were recorded on a Thomas-Hoover capillary apparatus and are uncorrected. Elemental analyses were performed by MicroTech Laboratories, Indianapolis, IN. The methoxyl analyses of the heterogeneous models were performed by Chem-Lig International, Schofield, WI.

Amberlite XE-305 was purchased from Polysciences, Inc., Warrington, PA. The Biobead SM-16 resin was obtained from Bio-Rad Laboratories, Richmond, CA. All solvents employed, unless indicated otherwise, were A.C.S. reagent grade. Reagents and starting materials were obtained from Aldrich Chemical Co., Milwaukee, WI.

Preparations involving the use of sodium hydride (97%) incorporated anhydrous solvents and were conducted under a dry nitrogen atmosphere in oven-dried glassware until the reaction was quenched. An overhead stirring apparatus was employed in all resin modification reactions to minimize mechanical damage to the polymer support. All column chromatography purifications employed silica gel 60 (70-230 mesh ASTM) as the stationary phase.

The reactions leading to and involving the p-methoxybenzyl (8-10) and MEM (12-14) compounds are described elsewhere.[47] The unsuccessful benzyl ether cleavage and phenolic derivatization methods for determining the loading of the heterogeneous model will not be described.

Polystyrene (1) - Both the Amberlite XE-305 and Biobead SM-16 (100 g each) were washed before use with 1 L volumes of the solvents employed by Farrall and Fréchet.[48] The resins were finally rinsed in a Soxhlet apparatus with ether and then hexane for 12 hr each before being dried under reduced pressure at 60 °C.

Polymer-supported benzyl chloride (2) - Chloromethylated poly-styrene (2) was prepared from both the Amberlite and SM-16 resins, according to the method of Hodge and Sherrington.[12] Elemental analysis data (Table 2) and FTIR data are given in the text.

Polymer-supported benzyl iodide (3) - The iodomethylated poly-styrene (3) was prepared from the chloromethylated resin 2 according to the method of Snyder.[11] The FTIR and elemental analysis data (Table 2) are given in the text. The high resolution ^{13}C-NMR spectrum of 3 (Fig. 2A) showed signals for the polystyrene backbone (P) that were consistent with the spectra reported by Ford, et al.[31, 32] However, no signal for the benzyl iodide carbon was evident. A signal (46 ppm)[31, 32] for the benzylic carbon of the chloromethylated precursor (PBnCl) was also absent, thus confirming the FTIR and elemental analysis data which showed that the chloride units had been quantitatively displaced.

3-(-4'-Hydroxy-3'-methoxyphenyl)-1-propanol (4) - Guaiacyl-propanol was prepared as described by Apfeld and Dimmel.[49] After vacuum distillation, the purified material crystallized on standing to give a white solid: mp 164-165 °C.

3-(-4'-Benzyloxyphenyl-3'-methoxy)-1-propanol (6) - Initially, 54.4 mg (2.3 mmoles) of sodium hydride were stirred in 5 mL of DMSO. After heating at 75 °C for 5 hr, the turbid green solution was cooled to room temperature. A solution of 200 mg (1.1 moles) of guaiacylpro-panol (4) in dry DMSO was added dropwise to the solution upon which the reaction mixture became yellow in color. After stirring for 15 min, 0.144 mL (1.2 mmoles) of benzyl bromide was added; the solution's color turned orange-brown. After stirring overnight, the solution was diluted with water and CHCl$_3$. The CHCl$_3$ phase was separated, washed thoroughly with water and 0.5$\underline{M}$ NaOH (to remove residual DMSO and

starting phenol), dried (Na_2SO_4), and evaporated to yield 150 mg of **6**: ^{1}H-NMR ($CDCl_3$) δ 1.6-1.8 (m, 2, β-CH_2), 2.5-2.6 (m, 2, $ArCH_2$), 3.43 (t, 2, J = 6.4 Hz, CH_2OH), 3.40 (s, 1, OH, exchangeable in D_2O), 3.75 (s, 3, OCH_3), 5.02 (s, 2, $PhCH_2O$), 6.6-7.0 (m, 3, Ar-H) and 7.2-7.4 (m, 5, Ar-H of benzyl).

The crude product (**6**) from above was acetylated by stirring with 0.11 mL (2 eq.) of acetic anhydride and 0.09 mL (2 eq.) of pyridine in 2 mL of $CHCl_3$ at 0 °C for 2 hr and then at room temperature for 2 hr. The reaction mixture was poured into water, and extracted with $CHCl_3$. The combined $CHCl_3$ extracts were washed successively with 3$\underline{M}$ HCl, sat. $NaHCO_3$, and water, dried (Na_2SO_4), and evaporated to give **7**: ^{1}H-NMR ($CDCl_3$) δ 1.7-2.0 (m, 2, β-CH_2), 2.00 (s, 3, $COCH_3$), 2.5-2.6, (m, 2, $ArCH_2$), 3.75 (s, 3, OCH_3), 3.99 (t, 2, J = 6.6 Hz, CH_2OAc), 5.02 (s, 2, $PhCH_2O$), 6.6-7.0 (m, 3, Ar-H), and 7.2-7.4 (m, 5, Ar-H of benzyl). The large shift of the terminal (C_γ) methylene (3.43 to 3.99) upon acetylation established that the primary hydroxyl group had not been benzylated in the first step.

3-(4'-Allyloxy-3'-methoxyphenyl)-1-propanol (15) - Guaiacyl-propanol (**4**) (15.8 g, 86.8 mmoles) was dissolved in 100 mL of a 50% (v/v) solution of benzene/DMF and added dropwise to a stirring mixture of sodium hydride (2.15 g, 86.8 mmoles) in 50 mL of benzene. After 30 min, 15.0 mL (174 mmoles) of distilled allyl bromide in 150 mL of benzene was added dropwise. Stirring was maintained for 10 hr after which 100 mL of 1$\underline{M}$ sodium methoxide was slowly added. After stirring for an additional 30 min, the reaction mixture was diluted with 50 mL of water and the resulting layers were separated. The organic layer was washed repeatedly with water. The aqueous washes were combined with the initial aqueous phase and acidified with 6$\underline{M}$ HCl. The

acidic solution was extracted with CHCl₃. The CHCl₃ extracts were com-
bined with the initial organic layer and dried over Na_2SO_4. The solu-
tion was evaporated first under reduced pressure (water aspirator) and
then under high vacuum, to remove the residual DMF. The crude pro-
duct was purified by column chromatography (eluent: 25 - 75% ethyl
acetate/toluene) yielding 18.2 g (94.3%) of a light gold oil: IR (cm⁻¹) 3600-
3100 (OH), 995, 910 (C=C-H); ¹H-NMR (CDCl₃) δ 1.60 (s, 1, OH, exchange-
able in D_2O), 1.79 (m, 2, β-CH_2), 2.64 (d of d, 2, J = 8.7 and 6.5 Hz, ArCH_2),
3.66 (t, 2, J = 6.5 Hz, CH_2OH), 3.85 (s, 3, OCH_3), 4.57 (d of t, 2, J = 5.4 and
1.5 Hz, ArOCH_2), 5.18-5.48 (d of d of q, 2, J = 16.5, 9.3, and 1.5 Hz, =CH_2),
5.89-6.27 (d of d of t, 1, J = 16.5, 9.3, and 1.5 Hz, -CH=), 6.65 (d, 1, J = 1.2
Hz, $C_{5'}$-H), 7.72 (s, 1, $C_{2'}$-H), 6.76 (d, 1, J = 1.2 Hz, $C_{6'}$-H); ¹³C-NMR
($CDCl_3$) ppm 31.6 (t, ArCH_2), 34.2 (t, β-CH_2), 55.8 (q, OCH_3), 61.9 (t,
CH_2OH), 70.0 (t, ArOCH_2), 112.2 (d, $C_{2'}$), 113.7 (d, $C_{5'}$), 117.4 (t, =CH_2),
120.0 (d, $C_{6'}$), 133.4 (s, $C_{1'}$), 134.8 (d, -CH=), 145.9 (s, $C_{4'}$), 149.1 (s, $C_{3'}$); MS
m/e (relative intensity) 222 (68, M⁺), 181 (72), 164 (12), 163 (100), 137 (18),
135 (17), 121 (10), 107 (43), 105 (17), 103 (27), 91 (28), 79 (18), 78 (11), 77 (24),
65 (11), 41 (11), 39 (11).

Anal. calcd. for $C_{13}H_{18}O_3$ (%): C, 70.2; H, 8.2; O, 21.6. Found: C,
70.5; H, 8.1; O, 21.6.

1-Benzyloxy-3-(-4'-allyloxy-3'-methoxyphenyl)propane (16) - To
a stirring mixture of 0.33 g (14 mmoles) of sodium hydride in 15 mL of
DMF was added, via a dropping funnel, 2.00 g (9.0 mmoles) of allyl-
protected guaiacylpropanol (15) dissolved in 20 mL DMF. After the
reaction mixture had stirred for 1 hr, 4.28 mL (36.0 mmol) of benzyl
bromide was added. Stirring continued for 5 days, after which meth-
anol (20 mL) was slowly added, followed by 40 mL of water. The result-
ing solution was extracted with $CHCl_3$ which was subsequently re-

moved under reduced pressure. Residual DMF was evaporated from the remaining organic phase under high vacuum. The crude product was purified by column chromatography (eluent: dichloromethane) yield-ing 1.81 g (64.4%) of a light yellow oil: IR (cm^{-1}) OH signal absent; ^{1}H-NMR (d$_6$-DMSO) δ 1.68-1.96 (m, 2, β-CH$_2$), 2.57 (d of d, 2, J = 8.3 and 6.5 Hz, ArCH$_2$), 3.43 (t, 2, J = 6.4 Hz, CH$_2$OBn), 3.73 (s, 3, OCH$_3$), 4.45-4.52 (m, 4, BnCH$_2$O, ArOCH$_2$), 5.13-5.46 (d of d of q, 2, J = 17.3, 10.3, and 1.5 Hz, =CH$_2$), 5.84-6.22 (d of d of t, 1, J = 17.3, 10.3 and 1.5 Hz, -CH=), 6.60-6.88 (m, 3, Ar-H), 7.32 (s, 5, Ar-H of benzyl); ^{13}C-NMR (d$_6$-DMSO) ppm 31.0 (t, ArCH$_2$), 31.3 (t, β-CH$_2$), 55.4 (q, OCH$_3$), 68.9 (t, CH$_2$OH), 69.2 (t, ArOCH$_2$), 71.7 (t, BnCH$_2$O), 112.5 (d, C$_{2'}$), 113.9 (d, C$_{5'}$), 116.7 (t, =CH$_2$), 119.8 (d, C$_{6'}$), 126.9 (d, C$_4$ of benzyl), 127.0 (d, C$_{3,5}$ of benzyl), 127.8 (d, C$_{2,6}$ of benzyl), 133.8 (s, C$_{1'}$), 134.5 (d, -CH=), 138.4 (s, C$_1$ of benzyl), 145.6 (s, C$_{4'}$), 148.9 (s, C$_{3'}$); MS m/e (rel. int.) 312 (20, M$^+$), 221 (5), 177 (5), 137 (7), 92 (8), 91 (100), 77 (5), 65 (6).

1-Benzyloxy-3-(4'-hydroxy-3'-methoxyphenyl)propane (5) - In 50 mL of an ethanol/benzene/water (7:3:1 v/v) mixture was dissolved 0.51 g (15 eq.) of the starting compound (16) along with (0.10 g, 1 eq.) of tris(triphenylphosphine)rhodium(I) chloride and 0.05 g (4 eq.) of 1,4-diazobicyclo[2.2.2]octane. The mixture was refluxed for 24 hr and then cooled. Water (25 mL) was added and the reaction mixture extracted with CHCl$_3$. The extracts were concentrated under reduced pressure and then dissolved in 60 mL of acetone/1M HCl (9:1 v/v). After re-fluxing for 1.5 hr, the reaction mixture was cooled, diluted with 50 mL of water, and extracted with CHCl$_3$. The combined CHCl$_3$ extracts were dried (Na$_2$SO$_4$), filtered, and concentrated in vacuo. A GLC analysis of the product mixture indicated that the allyl deprotection was incom-plete. The two procedures were repeated to achieve complete conver-

sion. The crude product, a dark oil, was purified by column chromato-graphy (eluent: 10% ethyl acetate-toluene) yielding a light yellow oil: MS $\underline{m}/\underline{e}$ (rel. int.): 272 (71, M$^+$), 181 (40), 164 (27), 151 (49), 137 (100), 122 (13), 119 (23), 119 (23), 91 (77), 77 (18), 65 (15).

Polymer-supported 4-O-allylguaiacylpropanol (17) - Allyl-protected guaiacylpropanol (**15**) (4.25 g, 19.1 mmoles) was dissolved in 50 mL of THF and added dropwise to 0.46 g (18.9 mmoles) of sodium hydride slurried in 25 mL of THF. The resulting mixture was stirred (overhead) for 60 min. Polymer-bound benzyl iodide (6.00 g, 14.7 mmoles) was then added to the reaction flask. Stirring continued for 114 hr, after which the resin was isolated in two batches by filtration and washed with 3x200 mL of THF each. The resin was further washed in a Soxhlet apparatus with THF followed by hexane for 12 and 11 hr, respectively. A yield of 7.03 g of coupled material (**17**) was obtained after the resin had dried in vacuo at 40 °C. Reported yields are ap-proximate values due to static losses on transferring operations. The FTIR spectrum of **17** exhibited signals assigned to the bound guaiacyl-propanol appendage at 1262 and 1229 (Ar-O-R), 1141 and 1101 (R-O-R), and at 997 and 926 (allyl =C-H) cm^{-1}. Signals at 1512 (Ar C=C) and 1419 (-CH$_2$-) cm^{-1}, which were also attributed to the bound model, were en-hanced relative to those observed in the spectrum of the precursor benzyl iodide (3). The elemental analysis data (Table 3) for compounds **17-19** are discussed in the text.

A sample of the reaction liquor was taken to dryness under re-duced pressure. The residue was dissolved in CHCl$_3$, diluted with an equal volume of water, and acidified with 6$\underline{M}$ HCl. The organic layer was separated, washed with water, dried (Na$_2$SO$_4$), and concentrated under vacuum. A GLC analysis of the resulting solution revealed the

presence of unmodified soluble model (15), thus confirming that the allyl group is stable under the specified coupling reaction conditions.

Polymer-supported 4-O-allylguaiacylpropanol/ethoxide (18) - The unreacted benzyl iodide units from the coupling reaction were converted into nonreactive benzyl ethoxide groups. The coupled material (17) (6.75 g) was slurried under nitrogen in 35 mL of THF to which an excess (165 mL) of $0.8\underline{M}$ sodium ethoxide in ethanol was added. The reaction mixture was stirred for 103 hr after which the resin was isolated by filtration. Washings were conducted with 6x100 mL portions of methanol, acetone, and THF. The resin product (18) was dried at 40 °C under reduced pressure, after being rinsed in a Soxhlet apparatus with hexane for 6.5 hr. A yield of 6.37 g was isolated. The polystyrene backbone signals in the high resolution ^{13}C-NMR spectrum of 18 were weak (Fig. 2C) but remained consistent with those reported by Ford.[31, 32] The benzyl ethoxide signals (15.8 ppm, BnO-$CH_2\underline{CH}_3$; and 65.6 ppm, BnO$\underline{CH}_2CH_3$) were also weak relative to the signals from the supported model. Weak benzyl ethoxide signals are consistent with the FTIR and elemental analysis data which indicated that the ethoxide loading was low due to an initially high displacement of iodide groups during the coupling reaction. Broad signals due to the supported model were observed as follows: ($CDCl_3$) ppm 31.8 ($ArCH_2$ and β-CH_2), 55.9 (OCH_3), 70.0 (PCH_2O, CH_2OBnP, and $ArOCH_2$), 113.5 (C_2 and C_5), 117.7 ($=CH_2$), 120.6 (C_6), 133.8 (C_1 and -CH=), 150.3 (C_4 and C_3).

Polymer-supported guaiacylpropanol/ethoxide (19) - The allyl protecting group was removed from the phenolic site of the bound model as follows. Tris(triphenylphosphine)rhodium(I) chloride (1.15 g, 1.25 mmoles) and 0.51 g (0.45 mmoles) of 1,4-diazabicyclo[2.2.2]octane were dissolved in 275 mL of a warm ethanol (absolute)/benzene/water

(7:3:1 v/v) solution. The ethoxide treated resin (18) (5.38 g) was added and the reaction mixture gently refluxed for 9.5 hr. Once cool, the resin was isolated by filtration and washed (5x100 mL) with $CHCl_3$, THF, and hexane before being dried under reduced pressure at 40 °C. The resin, which now supported the isomerized protecting group, was suspended in a mixture of 1.2$\underline{M}$ HCl (35 mL) and acetone (175 mL). After gently refluxing for 4 hr, the reaction mixture was allowed to cool. The resin was filtered and washed (5x100 mL) with acetone, THF, and hexane. The allyl deprotection sequence was repeated twice more. On the third trial, the acid reflux was extended to 6 hr. The final product was washed in a Soxhlet apparatus for 6 hr with hexane before being dried in a vacuum oven at 40 °C. The isolated yield of **19** was 4.86 g. High resolution ^{13}C-NMR signals for the supported model **19** (Fig. 2D) were observed as follows: ($CDCl_3$) ppm 31.8 (ArCH$_2$ and β-CH$_2$), 55.8 (OCH$_3$), 70.0 (PCH$_2$O and CH$_2$OBnP), 111.2 (C$_2$), 114.3 (C$_5$), 121.0 (C$_6$), 133.8 (C$_1$), 143.8 (C$_4$), 146.6 (C$_3$). The signals at 70.0 (ArOCH$_2$), 117.8 (=CH$_2$), and 133.8 (-CH=) were greatly reduced in relative area (<u>vs.</u> the spectrum of **18**) indicating that a substantial portion of the allyl groups were removed.

Polymer-supported benzyl ethoxide - Under a continuous stream of nitrogen, 2.50 g (6.13 mmol) of dried polymer-bound benzyl iodide was stirred (overhead) for 112 hr in 16 mL of freshly distilled THF and an excess (64 mL) of 0.9$\underline{M}$ sodium ethoxide in ethanol. The reacted resin was isolated by filtration and washed with 6x50 mL of methanol, acetone, and THF. The product was then extracted with hexane for 8 hr and dried under reduced pressure at 40 °C. Elemental analysis showed a residual iodide content of 0.21 mmol/g. To reduce the level of remaining iodide, a second ethoxide treatment was con-

ducted for 76 hr in an analogous manner. The FTIR spectrum of the final product showed a strong signal at 1098 cm^{-1} (C-O str.) in place of the original benzyl iodide signal at 1155 cm^{-1}. Elemental analysis gave the following: C, 82.1; H, 8.3; O, 8.7; I, 1.1 (0.09 mmol iodide per gram of resin). The ensuing assignments were made for the observed signals in the high resolution ^{13}C-NMR spectrum (Fig. 2B) of the polymer-bound benzyl ethoxide: ^{13}C-NMR (CDCl$_3$) ppm 15.4 (CH$_3$), 40.5 (backbone methine),[31, 32] 38-47 (backbone methylene), 65.6 (OCH$_2$), 72.8 (ArCH$_2$O), 126.5 (C$_4$), 128.3 (C$_{2, 3, 5, 6}$), 146.2 (C$_1$).

Polymer-supported propoxide - Sodium propoxide was prepared by dissolving freshly cut sodium metal in 1-propanol under a nitrogen atmosphere. Polymer-supported propoxide was prepared by stirring 1.00 g (3.09 mmoles) of polymer-bound benzyl iodide in 40 mL of 1M sodium propoxide in propanol and 15 mL of dry DMF for three days. The resin was isolated by filtration and washed successively with methanol and acetone (4x100 mL) followed by THF and hexane (3x100 mL). The washed resin was dried in a vacuum oven at 40 °C. An aliphatic ether stretch signal at 1097 cm^{-1} was observed in the FTIR spectrum along with additional C-H stretch signals at 2961 and 2878 cm^{-1}. An iodine loading of 0.35 mmol/g remained on the resin; a methoxyl content of 7.81% was also observed. The positive test for methoxyl units confirms that the propoxide group, and the allyl group as shown below, interfere with the methoxyl determination.

Polymer-supported allyloxide - The polymer-supported allyloxide was prepared in an analogous manner to the heterogeneous propoxide. The FTIR spectrum showed characteristic signals at 1097 (C-O str.), 991 and 923 (C=C-H str.) cm^{-1}. The resin had a methoxyl content of 5.73%.

Heterogeneous model loading by iodotrimethylsilane (ITS) -
Under a nitrogen atmosphere, 1.00 mL of dry acetonitrile was added to
a dark vial containing 20-25 mg of the dry heterogeneous model (**19**).
After the resin had soaked for 15 min, 0.035-0.040 mL (approx. 1.5-2.0 eq.
per oxygen atom) of ITS was added to the vial _via_ syringe. The vial was
sealed and shaken occasionally over a 30 min period. The reaction was
quenched by adding 0.50-0.75 mL of anhydrous methanol containing
internal standard (4-ethoxyphenol). The reaction liquor was pipetted
from the beads and added to 0.25 mL of pyridine. The resulting solu-
tion, along with 3x1 mL methanol rinses of the reacted resin, was con-
centrated under reduced pressure at a maximum of 40 °C Pyridine
(0.50 mL), acetic anhydride (0.75 mL), and anhydrous sodium acetate (30
mg) were then added to the resulting residue. After shaking for 24 hr,
the acetylation mixture was treated with 4x2.5 mL aliquots of cold water
and extracted with 2x5 mL of CH_2Cl_2. The organic extract was washed
with 5 mL of 1$\underline{M}$ HCl followed by 3x5 mL of water, then dried (Na_2SO_4)
and concentrated under reduced pressure with no applied heat. The
residual material was dissolved in 2 mL of CH_2Cl_2, stored in a dark vial
over Na_2SO_4, and analyzed by GLC. The MS, $\underline{m}/\underline{e}$ (rel. int.), for the
compounds (**20-23**) observed in the ITS product mixture were as
follows: **1-acetoxy-3-(4'-acetoxy-3'-methoxyphenyl)propane (20)**, 266
(12, M$^+$), 224 (83), 164 (100), 149 (40), 137 (79), 133 (25), 132 (22), 131 (15),
122 (10), 107 (10), 91 (15), 77 (11), 43 (28); **1-iodo-3-(4'-acetoxy-3'-methoxy-
phenyl)pro-pane (21)**, 334 (5, M$^+$), 292 (62), 155 (10), 137 (100), 43 (8); **1-
acetoxy-3-(3',4'-diacetoxyphenyl)propane (22)**, 294 (6, M$^+$), 252 (29), 210
(94), 150 (100), 149 (19), 133 (10), 132 (19), 131 (9), 123 (29), 122 (16), 91 (10),
77 (14), 43 (93); **1-acetoxy-3-(3'-methoxy-4'-propoxyphenyl)propane (23)**,
266 (84, M$^+$), 206 (6), 179 (7), 164 (94), 163 (19), 149 (34), 137 (100), 133 (28),
132 (18), 131 (18), 91 (20), 77 (18), 43 (57).

A loading value of 1.29 ± 0.04 mmol/g was obtained employing the conditions cited above. Increasing the reaction time to 90 min or the number of ITS equivalents (to approx. 5) lowered the loading values to 1.21 and 1.16 mmol/g, respectively. Raising the reaction temperature to 70 °C had a pronounced adverse effect as the loading level was reduced to 0.15 mmol/g. A loading of 1.35 ± 0.05 mmol/g was obtained by replacing acetonitrile with carbon tetrachloride. Use of carbon tetrachloride was not continued since the suspended beads tended to cling out of solution onto the walls of the vial. It was felt that the reproducibility over multiple samples would not be as high as the initial tests indicated.

The reacted resin was isolated by filtration and washed with 5x2 mL aliquots of the following solvents: methanol, ether, pet. ether, and hexane. The resin was dried in a vacuum oven at 40 °C before being analyzed by FTIR.

A portion (10 mg) of the isolated ITS-treated resin was powdered and shaken for 3.5 hr in 2 mL of $1\underline{M}$ citric acid monohydrate in methanol.[45] The resin was isolated by filtration and washed with the solvents used in the above isolation procedure. The FTIR spectrum was discussed in the text.

Loading calculations - For batch 1 the loading of the Cl groups in chloromethylated polymer **2** was 4.6 mmoles/g of resin (Table 2). This corresponds to 163.3 mg of Cl, 64.4 mg of CH_2, and 772.3 mg of polystyrene per 1 g of material. All calculations which follow assume that the only weight change which occurs is in the substituent.

In the case of Cl exchange for I, 163.3 mg is multiplied times the molecular weight change (126.9/35.5) and a factor 0.92 which represents the yield of the conversion to get 537 mg of iodine in the changed poly-

mer. The 537 is added to constant weight of 64.4 and 772.3 (associated with the CH_2 and polystyrene) to give 1373 mg. Dividing each unit weight by 1.373 provides the weight of each unit on a per gram scale. The weight of each unit on a per gram scale is then divided by the unit molecule weight to get the mmoles/g of resin (for the batch 1 iodo polymer this is 391 mg of I/g of resin/126.9 mg/mmole = 3.09 mmoles/g of resin). Knowing the mmoles/g of resin allows a back calculation to be done to estimate the yield (92% in the case of I replacement of Cl).

The above calculation is only approximate since the exact weight change associated with the unaccountable portion (8%) of the reaction is not known. We assumed for the calculation that this 8% was conversion of CH_2Cl to CH_3. The reaction could have been CH_2Cl to CH_2OH; the weight gained by having OH, instead of H, does not have a large effect on the calculations.

From the elemental analysis (Table 3) the amount of iodine left after the polymer-model coupling step corresponds to 19% of that present before reaction. Therefore, 81% reacted. If all 81% was model displacement, then the model loading value would be 81% of the iodine loading before reaction, or 1.78/ 0.81 = 2.17 polystyrene/model units. Considering the % CH_2I lost in conversion to CH_2OEt in the next synthetic step and the weight lost with removal of the allyl group in the last step, the calculations and assumptions described above predict that 2.17 polystyrene/protected model units would lead to 2.31 mmoles of deprotected model/g of resin. The observed value of 1.29 mmoles/g indicates that the coupling step is not 81% efficient and/or the next two synthetic steps are not quantitative. Factoring the observed with the calculated values leads to the estimate that 1 model is attached to roughly every 4th polystyrene unit.

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ADDENDUM

Paper 2 in this series (see reference 1) contained an error in Table 2. The column "Kraft-147°C" should read "Soda-147 °C"; likewise, the heading "Soda-147 °C" should read "Kraft-147 °C". This correction does not affect the conclusions drawn from Table 2.

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