ARTICLE

OBC
www.rsc.org/obc

Easy synthesis of β-*O*-4 type lignin related polymers

Takao Kishimoto,* Yasumitsu Uraki and Makoto Ubukata
Laboratory of Wood Chemistry, Research Group of Bioorganic Chemistry, Division of Applied Bioscience, Graduate School of Agriculture, Hokkaido University, Sapporo, 060-8589, Japan.
E-mail: takao@for.agr.hokudai.ac.jp; Fax: +81-11-716-0879; Tel: +81-11-706-3871

Received 3rd November 2004, Accepted 28th January 2005
First published as an Advance Article on the web 15th February 2005

The β-*O*-4 structure is the most abundant substructure in lignin. Lignin related polymers composed of only the β-*O*-4 structure were prepared using simple aromatic compounds as starting materials. Acetophenone derivatives were brominated, polymerized in the presence of K_2CO_3 and reduced with $NaBH_4$ to give the lignin related polymers. These are linear polymers which resemble natural lignins in their structures, although they do not have a γ-hydroxymethyl group. The number average degree of polymerization (DP_n) was determined with peracetate of the polymers by gel permeation chromatography. The DP_n of guaiacyl type polymers ranged from 15.2–21.4, where the value for the syringyl type was 11.3 and for the *p*-hydroxyphenyl type 16.9. The Guaiacyl type polymer was very soluble in usual lignin solvents such as 1, 4-dioxane–water (96 : 4, v/v) and DMSO, but only slightly soluble in acetone–water (9 : 1, v/v).

Introduction

Lignin is one of the main cell wall components in woody plants. It is considered to be the second most abundant biopolymer after cellulose. There are three precursors of lignin; coniferyl alcohol, sinapyl alcohol and *p*-coumaryl alcohol as shown in Fig. 1. These precursors are called monolignols and contribute to guaiacyl, syringyl and *p*-hydroxyphenyl propane units in lignin, respectively. Softwood lignin is produced mainly from coniferyl alcohol and hardwood lignin is made mainly from coniferyl alcohol and sinapyl alcohol. In addition to these two monolignols, *p*-coumaryl alcohol contributes to lignin in herbaceous plants. These monolignols are considered to be polymerized *via* a random dehydrogenative reaction mechanism to produce the complicated biomacromolecule, lignin.[1,2] The main interunit linkages are called β-*O*-4, β-β, β-5, β-1, 5-5, 4-*O*-5 linkages and so on. Among these linkages, the β-*O*-4 linkage is the most abundant and probably the most important substructure in lignin, which greatly affects both the chemical and physical properties of lignins (Fig. 2).

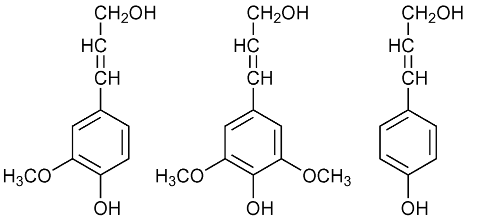


Fig. 1 Lignin precursors: coniferyl alcohol, sinapyl alcohol and *p*-coumaryl alcohol.

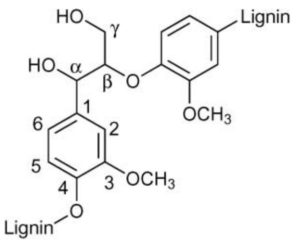


Fig. 2 Most abundant substructure (β-*O*-4 linkage) in lignin.

The purpose of this investigation is to prepare well defined linear polymers composed of the β-*O*-4 structure. We planned to produce the polymer from simple aromatic compounds which can be prepared from lignin degradation products. This would be a great help in the development of new utilization methods of lignin. Thermal and other properties would be improved with the linear structure. New functional groups may be introduced easily if simple compounds are used as starting monomers. Artificial biopolymers, such as artificial suberin, can be produced by introduction of ω-hydroxy acid into the polymers. The linear lignin related polymer would be useful to gain a better understanding of the relationship between the structure and properties of lignin.

Several methods have been reported for the synthesis of β-*O*-4 type oligomeric lignin model compounds.[3–5] When we started to prepare this paper we noticed that an attempt to synthesize polyether, related to lignin, had been reported.[6] However, molecular weights of the obtained carbonyl polymers were quite low. Recently, a new procedure for the preparation of a β-*O*-4 type oligomeric lignin model compound was reported by Katahira *et al.*[7] By using an addition polymerization method, they prepared a non-phenolic β-*O*-4 type lignin model oligomer from vanillin with three reaction steps. However, the degree of polymerization was limited to an oligomeric level in this case as well.

In this investigation we developed an easy preparation procedure for lignin related polymers composed of only β-*O*-4 structures. Three kinds of lignin related polymers, namely guaiacyl, syringyl and *p*-hydroxyphenyl type polymers, were prepared. These are linear polymers which resemble natural lignins in their structures, although they do not have a γ-hydroxymethyl group. Similar dimers and trimers have been synthesized by Erdtman and Leopold.[8] However, the method is a stepwise synthesis which requires activation of methylene carbons and deprotection of aromatic hydroxyl groups before each coupling reaction. We propose a facile preparation method of β-*O*-4 type lignin related polymers with a much higher degree of polymerization. Synthesis of β-*O*-4 type lignin polymers with a three-carbon side chain is our ongoing project.

Experimental

Materials

4-Hydroxy-3-methoxy-acetophenone, 4-hydroxy-3,5-dimethoxy-acetophenone and 4-hydroxy-acetophenone were purchased

DOI: 10.1039/b416699j

from Wako Pure Chemical Industry or Tokyo Kasei Kogyo Co., Ltd. Anhydrous DMF (organic synthesis grade) was purchased from Aldrich.

Measurements

^{1}H- and ^{13}C-NMR spectra were recorded with a JEOL JNM EX-270 FT-NMR (270 MHz) or a Bruker AMX500 FT-NMR (500 MHz) spectrometer. HMQC and HMBC NMR spectra were recorded with a Bruker AMX500 FT-NMR (500 MHz) spectrometer. Chemical shifts (δ) and coupling constants are given in δ-values (ppm) and Hz, respectively. Average molecular weights were analyzed by gel permeation chromatography (GPC) in tetrahydrofuran. A HITACHI Liquid Chromatograph L-6200 with a UV detector, L-4000 (Hitachi, 280 nm) and a RI detector (JASCO RI-2031 Plus) were used. Shodex GPC packed columns KF-803l and 802 (30 cm × 8.0 mm) were connected in a series and molecular weight was calibrated with standard polystyrene (tetrahydrofuran, flow-rate: 0.5 ml min^{-1}, 40 °C).

Preparation of monomers 1–3

To a stirred solution of acetovanillone (26 g) in anhydrous 1,4-dioxane–diethyl ether (3 : 4, v/v) (700 ml), bromine (25 g) was added dropwise under nitrogen over 2 h at 0 °C. The reaction mixture was kept at 0 °C for 1 h. The reaction mixture was diluted with ether and washed with iced water and brine. The solution was dried over anhydrous Na_2SO_4 and concentrated to dryness *in vacuo* below 30 °C. The obtained crude crystalline was treated with activated carbon powder and recrystallized from ether–hexane to afford monomer **1** (76 mol%). Monomer **1** was further recrystallized from the same solvents for polymerization in order to remove impurities completely. Monomers **2** and **3** were synthesized according to the method used for monomer **1**. Monomer **1**: mp 82.3–82.8 °C (lit. 81 °C),[6] monomer **2**: mp 127.0–127.5 °C, monomer **3**: mp 130.3–130.9 °C (lit. 129–130 °C).[6]

Polymerization

Prior to polymerization, starting monomers and glassware were dried under a vacuum over P_2O_5. To a stirred solution of monomer **1** (500 mg, 2.0 mmol) in anhydrous DMF (2.5 ml) was added finely powdered K_2CO_3 (422 mg, 3.0 mmol). The reaction mixture was kept under nitrogen at 50 °C for 3 h. The clear solution became clouded and gradually produced a precipitate. After 3 h, the reaction mixture was poured into iced water (100 ml) to precipitate a polymer. The polymer was filtered and washed with water and methanol. The polymer was dried over P_2O_5 under a vacuum to give polymer **4** (315 mg, 94 mol%). Polymers **5** and **6** were prepared from monomers **2** and **3**, respectively, according to the procedure used for polymer **4**.

Reduction of polymers 4–6

To a stirred suspension of polymer **4** (200 mg) in dimethyl sulfoxide (DMSO) (10 ml) was added $NaBH_4$ (230 mg). The reaction mixture was kept at 50 °C for 24 h. The suspension gradually became a clear solution. The reaction mixture was poured into iced water (200 ml) and was acidified to pH 3.0 with 2 N HCl. The obtained precipitate was filtered, washed with water and dried *in vacuo* over P_2O_5. The precipitate was dissolved in 1,4-dioxane (distilled over Na, 2 ml) and poured into diethyl ether (50 ml) to remove low molecular weight compounds. The precipitate was filtered and then dried *in vacuo* to give polymer **7** (180 mg). Polymers **8** and **9** were prepared from polymers **5** and **6**, respectively, according to the same procedure used for polymer **7**.

Polymer **7**: ^{1}H-NMR (DMSO-d_6): δ 1.28 (d, J = 6.4, CH_3), 3.76 (s, 3H, OCH_3), 3.90–3.98 (m, 2H, Cβ-H), 4.84 (m, 1H, Cα-H), 5.49 (d, 1H, J = 4.7, Cα-OH), 6.90 (s, 2H, C5-H, C6-H), 7.06 (s, 1H, C2-H); ^{13}C-NMR (DMSO-d_6): δ 55.5 (OCH_3), 70.7 (α), 74.1 (β), 110.7 (2), 113.1 (5), 118.3 (6), 135.2 (1), 147.1 (4), 148.5 (3). Polymer **8**: ^{1}H-NMR (DMSO-d_6): δ 1.31 (d, J = 6.4, CH_3), 3.76 (s, 6H, OCH_3), 3.81–3.85, 3.94–3.97 (m, 2H, Cβ-H), 4.77 (m, 1H, Cα-H), 5.22 (d, 1H, J = 3.2, Cα-OH), 6.72 (s, 2H, C2-H, C6-H); ^{13}C-NMR (DMSO-d_6): δ 55.9 (OCH_3), 71.7 (α), 78.2 (β), 103.7 (2,6), 135.6 (1), 137.5 (4), 152.1 (3,5). Polymer **9**: ^{1}H-NMR (DMSO-d_6): δ 1.27 (d, J = 6.4, CH_3), 3.95 (br. s, 2H, Cβ-H), 4.80 (br s, 1H, Cα-H), 5.51 (br s, Cα-OH), 6.92 (d, 2H, J = 8.5, C3-H, C5-H), 7.32 (d, 2H, J = 8.5, C2-H, C6-H); ^{13}C-NMR (DMSO-d_6): δ 70.4 (α), 73.1 (β), 113.9 (3,5), 127.4 (2,6), 134.3 (1), 157.7 (4).

Acetylation of polymer

Polymer **7** (30 mg) was acetylated by acetic anhydride–pyridine (1 : 1, v/v, 4 ml) at room temperature for 12 h. After 12 h ethanol (2 ml) was added and the mixture was evaporated to 2 ml. The reaction mixture was poured into water (50 ml) to precipitate a polymer. The polymer was filtered and dried *in vacuo* over P_2O_5. Polymers **8** and **9** were acetylated according to the same procedure used for polymer **7**.

Polymer **7** (acetate): ^{1}H-NMR ($CDCl_3$): δ 2.09 (s, 3H, $OCOCH_3$), 3.84 (s, 3H, OCH_3), 4.14–4.31 (m, 2H, Cβ-H), 6.07 (m, 1H, Cα-H), 6.76–7.02 (m, 3H, aromatics); ^{13}C-NMR ($CDCl_3$): δ 21.3 (OCO*C*H_3), 56.1 (OCH_3), 72.1, 73.8, 111.4, 114.8, 119.3, 130.9, 148.1, 149.9, 169.9 (O*C*OCH_3). Polymer **8** (acetate): ^{1}H-NMR ($CDCl_3$): δ 2.08 (s, 3H, $OCOCH_3$), 3.81 (s, 6H, OCH_3), 4.10–4.36 (m, 2H, Cβ-H), 5.99 (m, 1H, Cα-H), 6.57 (s, 2H, C2-H, C6-H); ^{13}C-NMR ($CDCl_3$): δ 21.2 (OCO*C*H_3), 56.2 (OCH_3), 74.9, 104.0, 133.1, 136.5, 152.9, 170.0 (O*C*OCH_3). Polymer **9** (acetate): ^{1}H-NMR ($CDCl_3$): δ 2.08 (s, 3H, $OCOCH_3$), 4.07–4.32 (m, 2H, Cβ-H), 6.07 (m, 1H, Cα-H), 6.88 (d, 2H, J = 8.4, C3-H, C5-H), 7.32 (d, 2H, J = 8.4, C2-H, C6-H); ^{13}C-NMR ($CDCl_3$): δ 21.2 (OCO*C*H_3), 70.3, 73.4, 114.7, 128.1, 129.5, 158.4, 169.9 (O*C*OCH_3).

Solubility test of polymer 7

A small amount of polymer **7** (25 mg) was shaken in various solvents (0.5 ml) at room temperature and examined for the presence of undissolved material. In some cases the amount of solvent was increased to 1.0 ml.

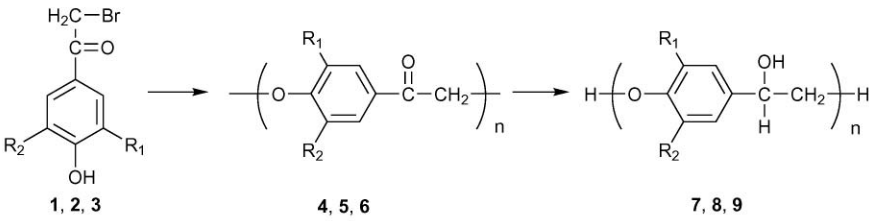
Results and discussion

Preparation of monomers 1–3

Three brominated 4-hydroxy-acetophenone derivatives, 2-bromo-1-(4-hydroxy-3-methoxyphenyl)ethanone (**1**), 2-bromo-1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone (**2**) and 2-bromo-1-(4-hydroxyphenyl)ethanone (**3**), were selected as starting monomers for preparation of lignin related polymers composed of the β-*O*-4 structure using a solution polymerization method (Fig. 3). The monomers correspond to three structural units of lignin; guaiacyl, syringyl and *p*-hydroxyphenyl propane units, respectively. Monomers **1–3** were prepared from commercially available 4-hydroxy-3-methoxy-acetophenone, 4-hydroxy-3,5-dimethoxy-acetophenone and 4-hydroxy-acetophenone, respectively, using a procedure similar to the reported method.[9] Special attention was paid to the purity of the starting monomers in order to obtain the polymer with high molecular weights, because a conversion ratio of monomer very much affects the molecular weight of polymer in polycondensation. The obtained monomers were treated with activated carbon powder and recrystallized twice from ether–hexane and the purity was checked by thin layer chromatography. Melting points of monomers **1** and **3** were higher than the reported data,[6] which suggests the higher purity of the monomers.

Polymerization of monomers 1–3 and characterization of polymers

Polymerization of monomer **1** was carried out with K_2CO_3 in anhydrous DMF. Reaction conditions were similar to those reported by Hirose *et al.*[6] However, in our hands, the molecular

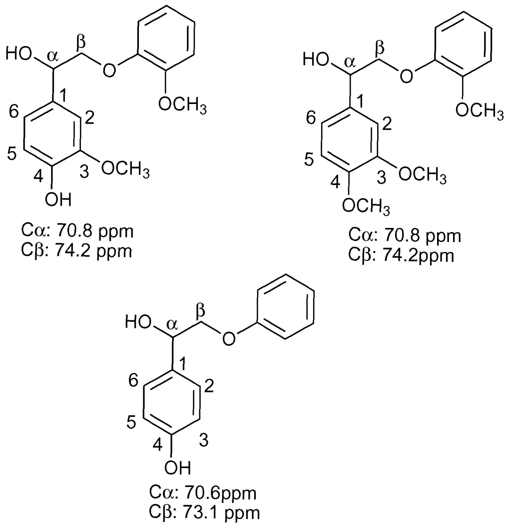


1, 4, 7: $R_1 = OCH_3$, $R_2 = H$,
2, 5, 8: $R_1 = OCH_3$, $R_2 = OCH_3$
3, 6, 9: $R_1 = H$, $R_2 = H$

Fig. 3 Synthesis of polymers **7**–**9** from monomers **1**–**3**.

weight of the the obtained polymer was much higher than that reported so far, as described below. The polymer was insoluble in usual solvents at room temperature. We first tried to introduce a hydroxymethyl group at the β-carbon in polymer **4** in order to obtain the polymer that represents the protolignin structure more precisely. Several methods for the hydroxymethylation of this type of structure have been reported.[3,9,10] However, a regular polymer with a distinct structure was not obtained by hydroxymethylation of polymer **4**. In contrast, reduction of polymer **4** was conducted successfully with $NaBH_4$ in DMSO at 50 °C to give polymer **7**. A suspension of polymer **4** in DMSO gradually became a clear solution with the increasing amount of hydroxyl groups. DMSO often promotes reduction with $NaBH_4$. Reduction of alkyl bromide to alkane can be achieved by $NaBH_4$ in DMSO.[11]

^{13}C-NMR spectrum of guaiacyl type polymer **7** is shown in Fig. 4. The distinct sharp signals of all carbons indicate that the polymer has a highly regulated structure, although the polymer actually exists as a mixture of many isomers which have a chiral center at the α-positon. C-alkylation seems to be negligible, which is sometimes a serious side reaction with aromatic Williamson ether formations. The side chain signals appearing at 70.7 and 74.1 ppm were compared with those reported for β-*O*-4 dimer model compounds as shown in Fig. 5.[12] Both signals are almost the same as those for lignin model dimers. A partial HMBC spectrum of polymer **7** is shown in Fig. 6. The distinct cross-signal at δ_H/δ_C 3.94/147.1 ppm shows the correlation between H_β and C_4 in β-*O*-4 linkages. These results clearly indicate that polymer **7** has β-*O*-4 linkages. Carbonyl signals corresponding to ketones can not be seen in Fig. 4, which indicates that reduction at the α-position with $NaBH_4$ was successfully conducted under the conditions used. All carbons were assigned by HMQC and HMBC spectra and the comparison with similar model compounds.[12]



Cα: 70.8 ppm
Cβ: 74.2 ppm

Cα: 70.8 ppm
Cβ: 74.2ppm

Cα: 70.6ppm
Cβ: 73.1 ppm

Fig. 5 ^{13}C-NMR spectral data for lignin dimer model compounds in DMSO-*d*$_6$ (ref. 12).

Acetylation of polymer **7** was easily achieved by conventional procedures. This suggests that various functional groups may be introduced into hydroxyl groups in the polymers. ^{1}H-NMR spectrum of acetylated polymer **7** is shown in Fig. 7. Number average of degree of polymerization (DP_n) was estimated to be 14.7 from the comparison of the signal area of methyl protons in acetyl groups, which is much higher than the carbonyl polymer **4** reported by Hirose *et al.* ($DP_n = 3.2$).[6] Number and weight average molecular weights of acetylated polymer **7** were further analyzed by gel permeation chromatography (GPC) and were $M_n = 3120$ and $M_w = 7310$, respectively, as summarized in

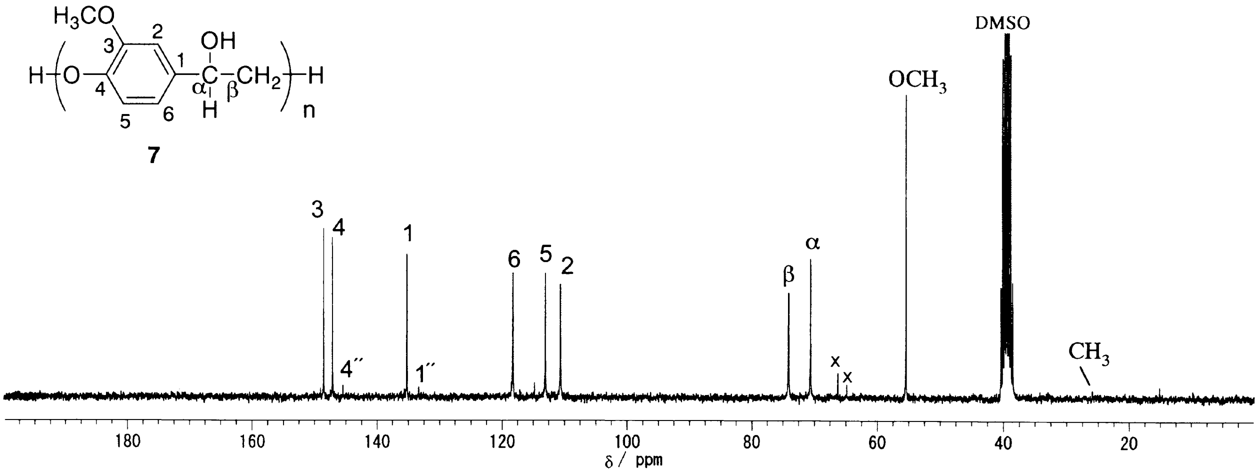


Fig. 4 ^{13}C-NMR spectrum of polymer **7** in DMSO-*d*$_6$. CH_3 (β′): non-phenolic end units; 1″, 4″: phenolic end units.

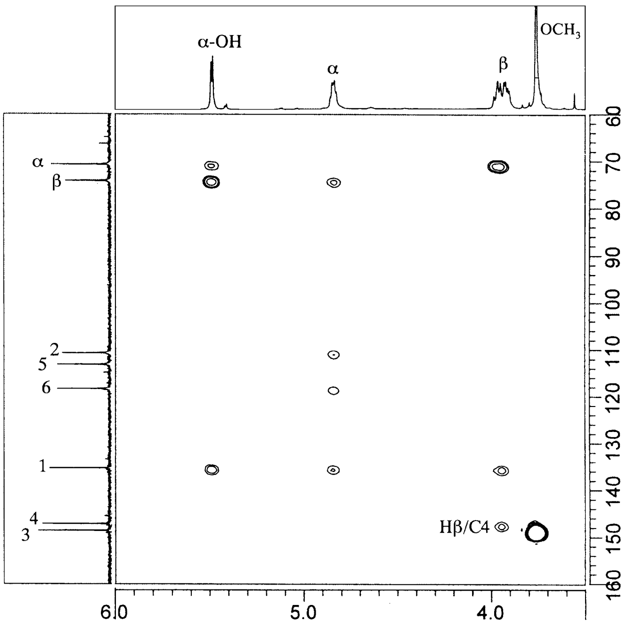


Fig. 6 HMBC spectrum of polymer **7** in DMSO-d_6.

Table 1. These correspond to $DP_n = 15.2$ and $DP_w = 35.1$, respectively. DP_n measured by GPC was in good agreement with that determined by ^{1}H-NMR spectrum.

Syringyl type polymer **8** and *p*-hydroxyphenyl type polymer **9** were successfully prepared from monomers **2** and **3**, respectively, by the same procedure used for guaiacyl type polymer **7**. ^{13}C-NMR spectra of polymers **8** and **9** are shown in Fig. 8 and Fig. 9, respectively. Signals at 71.6 and 78.2 ppm in Fig. 8 correspond to C_α and C_β in polymer **8**, respectively. Signals at 70.4 and 73.1 ppm in Fig. 9 were assigned to C_α and C_β in polymer **9**, respectively, and are almost the same as those for model dimer at 70.6 and 73.1 ppm (Fig. 5). HMBC spectra of polymers **8** and **9** also showed the correlations between H_β and C_4 in β-*O*-4 linkages. These results indicate the presence of β-*O*-4 linkages in both polymers. In addition to the main signals corresponding to repeating units, several signals corresponding to end units can be seen both in Fig. 8 and Fig. 9.

Number average polymerization of syringyl type polymer **8** ($DP_n = 11.3$) was smaller than *p*-hydroxyphenyl type polymer **9** ($DP_n = 16.9$) as shown in Table 1. A yield of syringyl type polymer **8** was also lower than polymer **9**. The polymerization of monomer **2** might have been retarded by the steric hindrance of two methoxy groups. The molecular weights of these polymers were comparable to those of technical lignins. GPC profile of acetylated polymers **7–9** are shown in Fig. 10. Molecular weight distributions of polymers **8** and **9** show several peaks with high and low molecular weights, although polymer **7** shows a single peak. The fractions with lower molecular weight decreased the average molecular weights of polymers **8** and **9**, although it is unclear why the fractions were formed with polymers **8** and **9**.

Table 1 Preparation of polymers **7–9** from monomers **1–3**, respectively

Monomer	Yield^a (%)	M_n (DP_n)	M_w (DP_w)	M_w/M_n
1	84.7	3120 (15.2)	7310 (35.1)	2.31
2	68.1	2690 (11.3)	4970 (20.9)	1.85
3	86.0	3010 (16.9)	5300 (29.8)	1.76

^{a} Yields are total yields of polymers **7–9** from monomers **1–3**, respectively.

Table 2 Effect of catalysts on the polymerization of monomer **1**

Catalyst	Yield^a (%)	M_n (DP_n)	M_w (DP_w)	M_w/M_n
No	84.7	3120 (15.2)	7310 (35.1)	2.31
n-Bu$_4$NI	80.1	4140 (19.9)	7780 (37.4)	1.88
18-Crown-6	87.1	3760 (18.1)	7880 (37.9)	2.10
KI	87.6	4170 (20.0)	7860 (37.8)	1.89

^{a} Yields are total yields of polymer **7** from monomer **1**.

Polymers **7–9** were further analyzed with unacetylated forms by MALDI-TOF-MS (Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry). The peaks corresponding to sodium and potassium adducts were successfully observed for all polymers as illustrated in Fig. 11. Molecular masses were found to be given by 166*n* + 2 + Na/K (guaiacyl), 196*n* + 2 + Na/K (syringyl) and 136*n* + 2 + Na/K (*p*-hydroxyphenyl) (*n* is degree of polymerization). This indicates that the polymers have regular structures and reduction of carbonyl groups at α-position were successfully conducted under the conditions used. Bromine at the end group was also removed by the reduction with NaBH$_4$.

Effects of catalysts, temperature and concentration on polymerization

It is not easy to adjust molecular weight or molecular weight distribution when polymers precipitate during polymerization. However, several factors affected the degree of polymerization as summarized in Table 2. A crown ether (18-crown-6), potassium iodide (KI) and tetrabutylammonium iodide (*n*-Bu$_4$NI) were

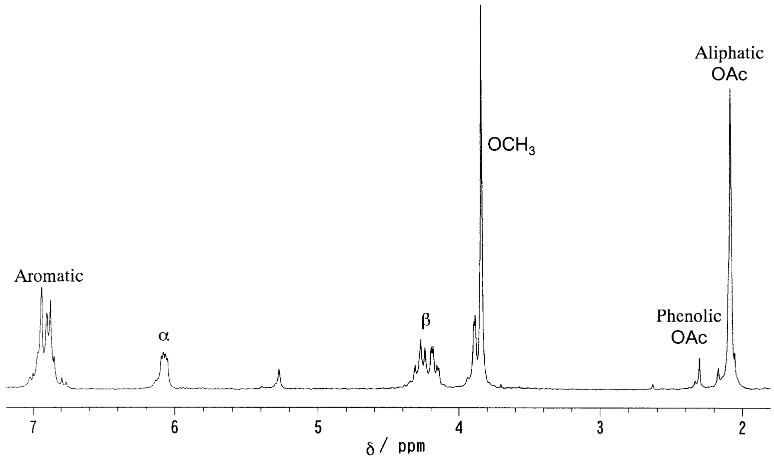


Fig. 7 ^{1}H-NMR spectrum of acetylated polymer **7**.

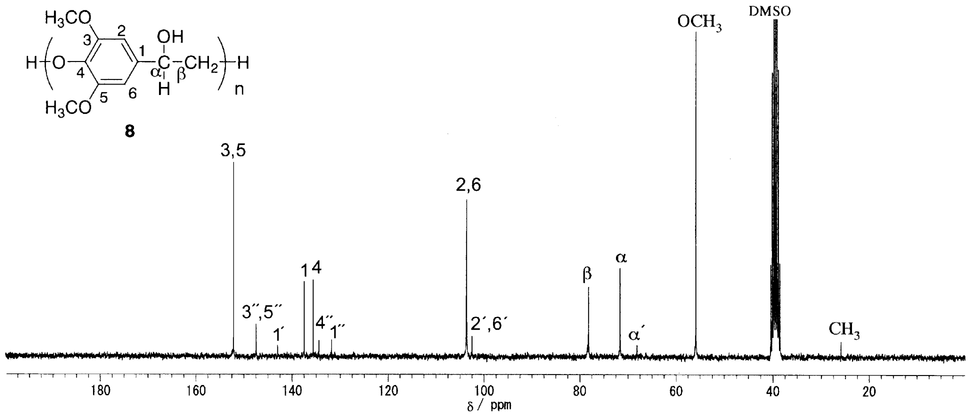


Fig. 8 ^{13}C-NMR spectrum of polymer **8** in DMSO-d_6. 1′, 2′, 6′, α′, CH_3 (β′): non-phenolic end units; 1″, 3″, 4″, 5″: phenolic end units.

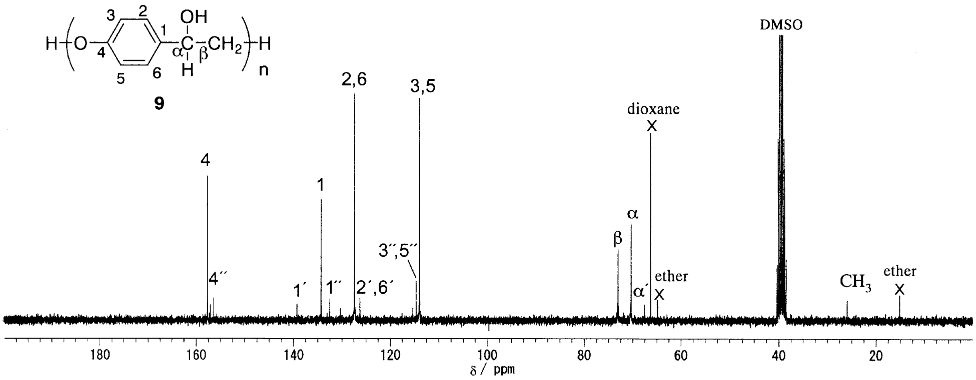


Fig. 9 ^{13}C-NMR spectrum of polymer **9** in DMSO-d_6. 1′, 2′, 6′, α′, CH_3 (β′): non-phenolic end units; 1″, 3″, 4″, 5″: phenolic end units.

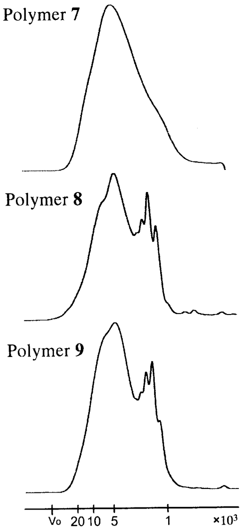


Fig. 10 Molecular weight distributions of polymers **7–9** determined by gel permeation chromatography.

selected as catalysts to promote polymerization of monomer **1**. These catalysts are often used to improve *O*-alkylation of phenol by Williamson reactions. All catalysts were effective in increasing number average molecular weights. Total yields of polymer **7** from monomer **1** were over 80% in all cases. Polydispersity ranged from 1.88 to 2.31. Among these, potassium iodide was the best catalyst for increasing the degree of polymerization.

Concentration of the starting monomer is also one of the most important factors to affect the degree of polymerization. Lowering the monomer concentration resulted in an increase in DP_n as shown in Table 3. This is probably because the amount of solubilized polymer **4** increased in the diluted solution during polymerization. The effects of reaction temperature were also investigated. DP_n increased when reaction temperature was changed from 50 °C to 100 °C. Increasing reaction temperatures increased the solubility of polymer **4** and avoided undesirable precipitation during polymerization. However, the color of the polymer obtained turned to light orange. Some side reactions may have been involved in this case. Contrary to our expectations, the best result was obtained when the reaction temperature decreased to room temperature and the reaction

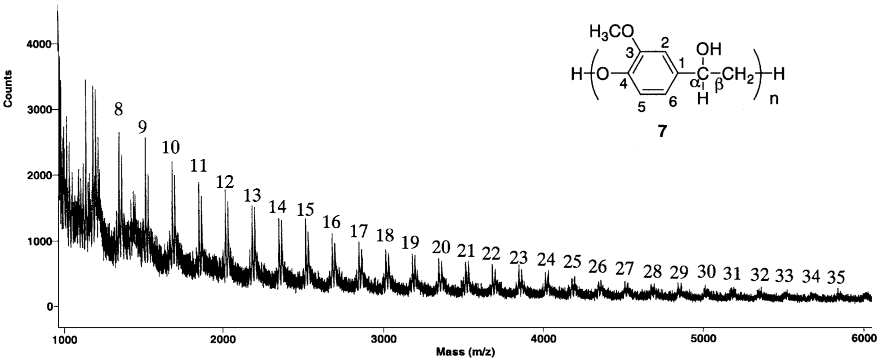


Fig. 11 MALDI-TOF-MS of polymer **7**.

Table 3 Effects of reaction temperature and concentration of monomer **1**

Conc./M	Temp./°C	Time/h	Yield[a] (%)	M_n (DP_n)	M_w (DP_w)	M_w/M_n
0.82	100	3	85.2	3860 (18.6)	7960 (38.2)	2.06
0.82	50	3	80.7	3120 (15.2)	7310 (35.1)	2.31
0.82	rt	24	88.4	4450 (21.4)	9830 (47.2)	2.21
0.41	50	3	91.2	3780 (18.2)	8660 (41.6)	2.29

[a] Yields are total yields of polymer **7** from monomer **1**.

Table 4 The solubility of polymer **7** in various solvents[a]

Solvents	Solubility parameter[b]/(cal per cm^3)$^{1/2}$	Solubility	Native spruce lignin[b]	Kraft pine lignin[b]	Soda hardwood lignin[b]
Diethyl ether	7.4	Insol	Insol	Insol	Insol
THF	9.5	Part	—	—	—
Diglyme	—	Part	—	—	—
Acetone	10.0	Insol	Sol	Part	Part
Acetone–water (9 : 1)	—	Sli	—	—	—
Acetone–water (4 : 1)	—	Part	—	—	—
Dioxane	10.0	Sol	Sol	Sol	Sol
Dioxane–water (96 : 4)	—	Sol	—	—	—
Pyridine	10.7	Sol	Sol	Sol	Sol
Methyl cellosolve	10.8	Sol	Sol	Sol	Sol
Diethylene glycol monomethyl ether	—	Sol	—	—	—
DMF	12.1	Part	—	—	—
DMSO	12.9	Sol	—	—	—
DMAc	—	Sol	—	—	—
Sulfolane	—	Sol[c]	—	—	—
HMPA	—	Sol[c]	—	—	—
Ethanol	12.9	Insol	—	Sli	Sli
Ethylene glycol	14.2	Insol	Sol	Sol	Sol
Water	23.4	Insol	Insol	Insol	Insol

[a] Solubility of polymer **7** (25 mg) was tested in 0.5 ml of each solvent. Sol = soluble, part = partially soluble, sli = slightly soluble, insol = insoluble. [b] Data are sited from ref. 13. [c] Partially soluble in 0.5 ml of the solvent but soluble in 1.0 ml of the solvent.

time was prolonged to 24 hours. DP_n and DP_w reached 21.4 and 47.2, respectively.

Solubility of polymers in various solvents

Solubility of the lignin related polymers in solvents is one of their most important properties. Ordinary solvents could not dissolve carbonyl polymers **4–6** at room temperature. The solution NMR spectroscopic analysis of the polymers could not be conducted. However, lignin related polymers **7–9** could be dissolved in several solvents. Pyridine dissolved them and acetylation could be carried out using conventional procedures. A wide variety of functional groups can be introduced into the polymers if a suitable solvent is found.

It has been reported that the ability of solvents to dissolve or swell a variety of isolated lignins increases as the hydrogen-bonding capacities of the solvents increase and as their solubility parameters approach a value of around eleven.[13] Solubility parameter is defined as the square root of a substance's cohesive energy density. Polymers are usually soluble in solvents with a close solubility parameter to their own. Solubility of polymer **7** in several solvents is summarized in Table 4. The results were compared with those reported for isolated lignins.[13] It is obvious that polymer **7** is most soluble in solvents, with solubility parameters of 10–13. The behavior was basically similar to isolated lignins. DMSO and 1,4-dioxane dissolved polymer **7** very well. Dioxane–water (96 : 4) which is often used for isolated lignins, also dissolved the polymer. However, acetone–water (9 : 1) dissolved it only slightly. The solubility in acetone was increased when acetone–water (4 : 1) was used, but the solution was still clouded slightly.

Conclusion

Three lignin related polymers composed of only a β-*O*-4 structure were successfully prepared from simple aromatic compounds. The degree of polymerization was comparable to isolated lignins. The solubilities of these polymers in various solvents were similar to those of reported isolated lignins. The polymers would be useful for aiding in our understanding of the relationship between the structure and properties of lignins. These polymers would be useful as polymeric lignin model compounds in some cases. New lignin related polymers having functional groups may also be produced from the polymers.

Acknowledgements

We are grateful to Dr Kamitakahara and Dr Nakatsubo, Kyoto University, Japan for their kind help regarding MALDI-TOF-MS.

References

1 K. Freudenberg, *Angew. Chem, Int. Ed. Engl.*, 1956, **68**, 508.
2 K. V. Sarkanen, *Lignins, -Occurrence, Formation, Structure and Reaction*, ed. K. V. Sarkanen and C. H. Ludwis, Wiley-Interscience, New York, 1971, p. 150.
3 E. Adler, B. O. Lindgren and U. Saedlen, *Sven. Papperstidn.*, 1952, **55**, 245.
4 F. Nakatsubo, in *Methods in Enzymology Vol. 161. Lignin, Pectin and Chitin*, ed. W. A. Wood and S. T. Kellogg, Academic Press, San Diego, CA, 1988, p. 57.
5 S. Cofi-Baffoni, L. Banci and A. Brandi, *J. Chem. Soc., Perkin Trans. 1*, 1998, 3207–3217.

6 S. Hirose, T. Hatakeyama and H. Hatakeyama, *Cellul. Chem. Technol.*, 1978, **12**, 713.

7 R. Katahira, H. Kamitakahara, T. Takano and F. Nakatsubo, *J. Wood Sci.*, 2003, **49**, 553.

8 H. Erdtman and B. Leopold, *Acta Chem. Scand.*, 1949, **3**, 1358–1374.

9 S. Hosoya, K. Kanazawa, H. Kaneko and J. Nakano, *Mokuzai Gakkaishi*, 1980, **26**, 118.

10 T. Umezawa and T. Higuchi, in *Plant Fiber, Modern Methods of Plant Analysis New Series*, ed. H. F. Linskens and J. F. Jackson, Springer-Verlag, Berlin, 1989, vol. 10, p. 161.

11 J. March, *Advanced Organic Chemistry, -Reactions, Mechanisms, and Structures*, Wiley-Interscience, New York, 5th edn., 1992, p. 439.

12 S. A. Ralph, J. Ralph and L. L. Landucci, http://www.dfrc.wisc.edu/software.html, 2004.

13 C. Schurch, *J. Am. Chem. Soc.*, 1952, **74**, 5061.