

Evaluation of the Contribution of Lignin Stilbene Phenol Units in the Photoyellowing of Peroxide-Bleached Lignin-Rich Pulps

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ABSTRACT: In order to assess and quantify the contribution of stilbene phenols in photoreversion of bleached high-yield pulps, a method to reduce the stilbene double bond and quantify the formed diphenylethane was developed on 4-benzyloxy-3,3'-dimethoxy-4'-hydroxystilbene, as lignin monomer model, and also on a more sophisticated lignin polymer constituted by a polystyrene framework containing 4,4'-dihydroxy-3,3'-dimethoxystilbene elements as pendent groups. The method used $\text{RhCl}(\text{PPh}_3)_3$ as soluble catalyst to get an efficient hydrogenation and AlCl_3 in benzene to liberate the diphenylethane from the polymer framework. For the first time a semi-quantitative evaluation of the content of the stilbene phenols formed from β -1 units was given for high-yield pulps. The value of 2 *p*-stilbene phenols for 1000 C_9 lignin units found indicates that they are present in very small quantities after the peroxide bleaching. UV irradiation of the polystyrene model adsorbed on solid cellulose matrix had revealed an efficient stabilization after the hydrogenation treatment. This was not the case for the peroxide bleached pulp showing that the *p*-stilbene phenols formed from β -1 units are not the main contributors of the rapid yellowing of bleached lignin-rich pulps. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2517–2531, 1998

Key words: lignin; stilbene; lignin model compound; photoyellowing

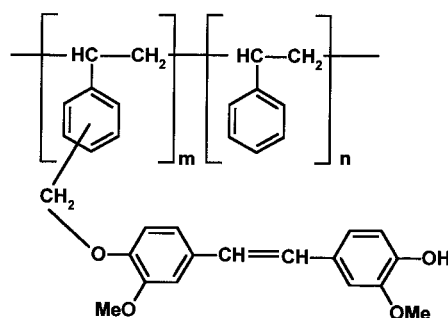
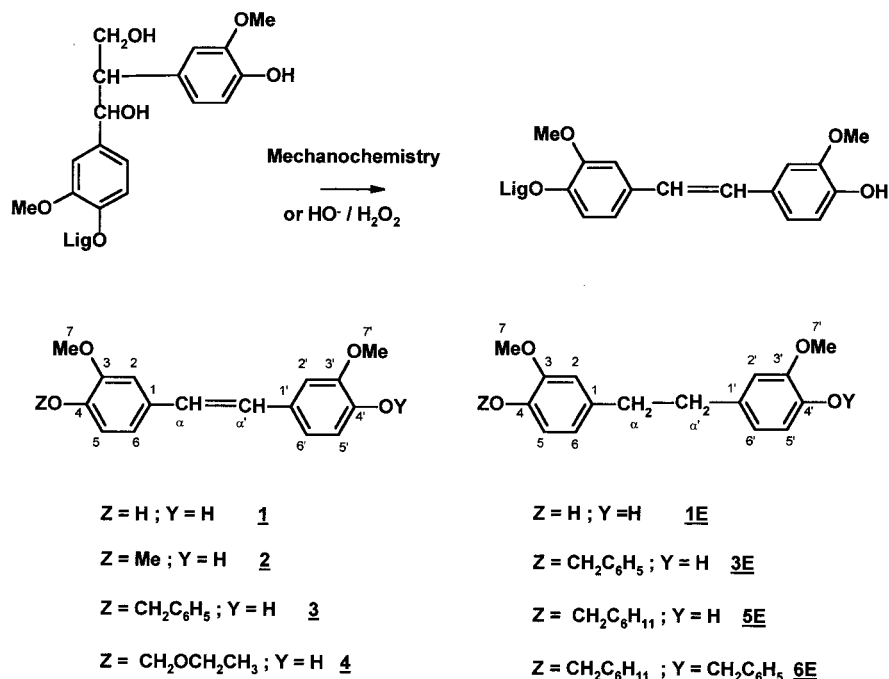
INTRODUCTION

One factor which seriously limits a more widespread utilization of highly bleached lignin-containing pulps is their susceptibility to yellow when exposed to daylight. The processes leading to yellowing are very complex and much of the discoloration is due to the presence of the lignin polymer which is oxidized by the UV component of the daylight.¹ Lignin is, after cellulose, the principal constituent of the woody structure of higher plants and is a highly branched structurally intricate polymer comprised of phenylpropane units.² The

bleaching of lignin-rich pulps usually consists in the action of hydrogen peroxide in basic medium ($\text{pH} \approx 11$), the hydroperoxyl anion reacting selectively with colored enone structures such as cinnamaldehydes, ortho and paraquinones transforming them into entities nonabsorbing in the visible.³ It is noteworthy that the bulk structure of lignin in high-yield pulps remains after the bleaching process in contrast to chemical pulps.⁴ Under UV irradiation, lignin undergoes a wide range of photochemical reactions^{1,5–8} among them phenols are readily oxidized to give a variety of products such as biaryls, quinones, and other colored species.^{1,5,6,9} The β -O-4 ether bonds are cleaved by UV light in aromatic carbonyl groups⁵ and by peroxy radicals in benzylic alcohol structures, giving phenoxy radicals and colored products.⁸

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Scheme 1

In 1990, Castellán et al.¹⁰ described qualitative results from the irradiation of several phenolic lignin model compounds of general type, stilbene, benzofuran, biphenyl, biphenylmethane, and alkenylphenyl adsorbed on filter paper. The two stilbene compounds **1** and **2** were proved to be very active (Scheme 1). For that reason, it was proposed that phenols absorbing above 300 nm were the main structures of the lignin polymer responsible for the yellowing of lignin-rich pulps.¹⁰ Later, Zhang and Gellerstedt^{11,12} isolated colored *o*-quinones and yellow nitrosostilbenes when they exposed filter paper containing *p*-hydroxystilbenes to daylight.^{11,12} In pulps, stilbenes are formed by degradation of lignin from β -1 diaryl-

propane units during grinding or disk refining¹³ and also through the hydrogen peroxide bleaching¹⁴ (Scheme 1). Some stilbene structures were isolated after mild acid hydrolysis of the pulp.¹⁵ Their concentration increased when the pulp was bleached, whereas the β -1 diarylpropane units were found in lower concentration.¹⁵ These observations supported the conclusion that light stability of bleached lignin-rich pulps was strongly dependent on the presence of stilbenes.^{16,17} Also, *o,p'*-dihydroxystilbenes are formed from *p*-hydroxyphenylcoumarans, but they are not necessarily associated with the formation of colored products because they may cyclize to benzofuran.¹⁸

A means to eliminate these very sensitive lig-

nin chromophores is to convert the stilbenes into diphenylethane by hydrogenation and so to bring a certain photostability to the pulp by stopping conjugation between two aromatic rings. This process was found efficient on isolated lignin.¹⁹ However, hydrogenation of pulp with either a soluble [RhCl(PPh₃)₃] or a heterogeneous (Pd/C), catalyst did not decrease the light-induced yellowing.²⁰ Also, hydroboration and reaction with diimide were equally ineffective.²⁰ The question arises regarding whether catalytic hydrogenation, hydroboration, or reduction with diimide can efficiently reduce stilbenic double bonds.

The present article, for the first time, brings new information on the role of stilbenes on the yellowing. The hydrogenation conditions were set up on a lignin-like polymer, constituted by a stilbenol grafted on a linear polystyrene, adsorbed on filter paper. Then the hydrogenation was performed on softwood bleached thermomechanical pulp; the pendent diphenylethane groups formed were liberated by mild acidolysis, characterized, and titrated by GC-MS. The kinetics of yellowing before and after efficient hydrogenation were established; some clear conclusions can be drawn.

EXPERIMENTAL

General

Melting points were measured with a Mettler FP62 heating block. NMR spectra were recorded on a Bruker DMP 200 (¹H, ¹³C, HMQC, HMBC) spectrometer (reference Me₄Si, solvent CDCl₃). The IR and UV absorption spectra were respectively performed on a Perkin-Elmer Paragon 1000 PC and a Hitachi U 3300 spectrometer. Mass spectra were obtained using a VG Micromass Autospec Q. Reflectance curves of handsheets were measured in the 350–700 nm range by means of the Hitachi U 3300 spectrophotometer equipped with an integrating sphere (diameter 15 cm).

The usual chemicals and chloromethylstyrene (ortho/para mixture ≈ 95/5) were obtained from Aldrich; they were used without further purification. The synthesized compounds were purified by column chromatography on silica gel 60 SDS (70–200 mesh) using the appropriate eluents. The solid products were crystallized after chromatography. Thioacidolysis and desulfurization experiments were realized according to the method described by Lapierre, Pollet, and Monties.²¹

Syntheses

4-Benzoyloxy-4'-hydroxy-3,3'-dimethoxystilbene (3)

4-Acetoxy-4'-benzyloxy-3,3'-dimethoxystilbene. A solution of 4-benzyl-3-methoxybenzyl-triphenylphosphonium chloride (5.0 g, 9.5 mmol), prepared from vanillin by conventional methods,²² in anhydrous DMF (60 mL) was treated with *t*-BuOK (1.17 g, 10.5 mmol) under nitrogen. The reaction mixture was stirred at room temperature for 3 h and then a solution of 4-acetoxy-3-methoxybenzaldehyde (1.85 g, 9.5 mmol) in anhydrous DMF (20 mL) was added. After being stirred for 20 h at room temperature, the DMF was removed under vacuum and the residue was dissolved in CH₂Cl₂ and hydrolyzed with hydrochloric acid (10%). The aqueous layer was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were washed with water, dried over MgSO₄, filtered, and concentrated. The residue was separated by chromatography (silica gel, eluent: CH₂Cl₂) giving the expected compound as a pale oil (yield 2.0 g, 53%). ¹H-NMR (CDCl₃): δ 2.25 (s, CH₃CO, 3H); 3.6 (s, OCH₃, 3H); 3.7 (s, OCH₃, 3H); 4.9 (s, OCH₂Ar, 2H); 6.2–6.9 (m, ArH and CH=CH, 8H); 7.1 (m, OCH₂ArH, 5H).

4-Benzoyloxy-4'-hydroxy-3,3'-dimethoxystilbene (3). 4-Acetoxy-4'-benzyloxy-3,3'-dimethoxystilbene (2.05 g, 5.07 mmol) in ethanol (250 mL) in presence of potassium carbonate (0.7 g, 5.07 mmol) was refluxed under nitrogen atmosphere for 3.5 h. Then, the reaction mixture was treated by a solution of hydrochloric acid (10%). The aqueous layer was extracted with CH₂Cl₂ (3 × 30 mL). The combined organic layers were washed with water, dried over MgSO₄, filtered, and concentrated. The residue was recrystallized from CH₂Cl₂/heptane, affording the expected stilbene phenol as white crystals (yield 1.6 g, 85%, mp 130°C). ¹H-NMR (CDCl₃): δ 3.7 (s, OCH₃, 3H); 3.8 (s, OCH₃, 3H); 5.1 (s, OCH₂Ar, 2H); 5.65 (s, OH, 1H); 6.7–7.4 (m, ArH and CH=CH, 13H). ¹³C-NMR (CDCl₃): δ 56.3 (C₇); 56.4 (C_{7'}); 71.4 (CH₂C₆H₅); 108.5 (C₂); 109.6 (C_{2'}); 114.4 (C₅); 115.0 (C_{5'}); 119.8 (C₆); 120.6 (C_{6'}); 126.7 (C_α); 127.4 (C_α); 127.7 (CH₂C₆H₅); 128.3 (CH₂C₆H₅); 129.0 (CH₂C₆H₅); 130.6 (C₁); 131.6 (C_{1'}); 137.5 (CH₂C₆H₅); 145.8 (C_{4'}); 147.2 (C₄); 148.2 (C₃); 150.2 (C_{3'}). MS: m/z 362 (M⁺, 100%); 361 (15); 272 (29); 271 (93). IR (KBr): 1025, 1140, 1275, 1520, 1605, 2940, 3450 cm⁻¹.

4-Benzoyloxy-4'-hydroxy-3,3'-dimethoxydiphenylethane (3E)

Hydrogenation of 3 (0.1 g, 0.28 mmol) in 50 mL of ethyl acetate containing RhCl(PPh₃)₃ (10 mg, 0.011 mmol) was accomplished by treating the mixture under hydrogen pressure (180 bars) for 7 h at room temperature. The solvent was removed under vacuum and the residue, dissolved in CH₂Cl₂, was chromatographed on silica gel column (eluent: CH₂Cl₂). The expected compound was obtained as a pale oil (yield 70 mg, 92%). ¹H-NMR (CDCl₃): δ 2.85 (s, CH₂—CH₂, 4H); 3.8 (s, OCH₃, 3H); 3.9 (s, OCH₃, 3H); 5.15 (s, OCH₂Ar, 2H); 5.6 (s, OH, 1H); 6.6–6.9 (m, ArH, 6H); 7.3–7.5 (m, ArH, 5H). ¹³C-NMR (CDCl₃): δ 37.8 and 37.9 (C_α, C_{α'}); 55.9 and 56.0 (C₇, C_{7'}); 71.6 (CH₂C₆H₅); 111.3 (C₂); 112.5 (C_{2'}); 114.2 (C₅); 114.3 (C_{5'}); 120.5 (C₆); 121.1 (C_{6'}); 127.4 (CH₂C₆H₅); 127.8 (CH₂C₆H₅); 128.6 (CH₂C₆H₅); 133.8 (C₁); 135.2 (C_{1'}); 137.5 (CH₂C₆H₅); 143.8 (C_{4'}); 146.3 (C₄); 146.4 (C₃); 149.5 (C_{3'}). IR (film): 1025; 1140; 1270; 1520; 2940; 3450 cm⁻¹.

4-Ethoxymethoxy-4'-hydroxy-3,3'-dimethoxystilbene (4)

4-Ethoxymethoxy-3-methoxybenzaldehyde. A solution of vanillin (6 g, 39.5 mmol) in DMF (100 mL) was treated with methylethylether chloride (8.0 mL, 86 mmol) and potassium carbonate (21 g, 152 mmol) under nitrogen. After being stirred at 80°C for 96 h the reaction mixture was cooled at room temperature and the DMF was removed under vacuum. Then the residue was dissolved in CH₂Cl₂ and treated with a solution of hydrochloric acid (10%). The aqueous layer was extracted with CH₂Cl₂ (3 × 30 mL). The combined organic layers were washed with water, dried over MgSO₄, and filtered. After evaporation the expected aldehyde was isolated as unique product as a pale oil (yield 7.8 g, 94%). ¹H-NMR (CDCl₃): δ 1.1 (t, CH₃CH₂, 3H); 3.7 (q, CH₃CH₂, 2H); 3.9 (s, OCH₃, 3H); 5.3 (s, OCH₂, 2H); 7.1–7.5 (m, ArH, 3H); 9.8 (s, CHO, 1H).

4-Acetoxy-4'-ethoxymethoxy-3,3'-dimethoxystilbene. A solution of 4-acetoxy-3-methoxybenzyl-triphenylphosphonium chloride (8.7 g, 18.2 mmol), prepared as for the other phosphonium salt, in anhydrous THF (100 mL) was treated with *n*-BuLi (10.5 mL, 26.2 mmol) under nitrogen at -40°C. Then a solution of 4-ethoxymethoxy-3-methoxybenzaldehyde (3.65 g, 17.4 mmol) in anhydrous THF (30 mL) was added. The reaction mix-

ture was stirred at -20°C for 1 h. After being stirred for 20 h at room temperature, the THF was removed under vacuum, the residue was dissolved in CH₂Cl₂ and treated with hydrochloric acid (10%). The aqueous layer was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were washed with water, dried over MgSO₄, filtered, and concentrated. The residue was purified by chromatography on silica gel (eluent: CH₂Cl₂) affording the expected stilbene as a pale oil (yield 4.2 g, 65%). ¹H-NMR (CDCl₃): δ 1.1 (t, CH₂CH₃, 3H); 2.25 (s, CH₃CO, 3H); 3.7 (q, CH₂CH₃, 2H); 3.97 (s, OCH₃, 3H); 3.99 (s, OCH₃, 3H); 5.25 (s, OCH₂O, 2H); 5.9–7.2 (m, ArH and CH=CH, 8H). IR (film): 1520, 1600, 1770, 2940 cm⁻¹.

4-Ethoxymethoxy-4'-hydroxy-3,3'-dimethoxystilbene (4). A solution of 4-acetoxy-4'-ethoxymethoxy-3,3'-dimethoxystilbene (3.42 g, 9.2 mmol) in ethanol (250 mL) under nitrogen atmosphere was treated with potassium carbonate (3.85 g, 27.6 mmol). After being stirred at room temperature for 4 h the reaction mixture was reacted with a solution of hydrochloric acid (10%). The aqueous layer was extracted with CH₂Cl₂ (3 × 30 mL). The combined organic layers were washed with water, dried over MgSO₄, filtered, and concentrated. The residue was purified by chromatography on silica gel (eluent: CH₂Cl₂/Et₂O : 95/5) affording the expected stilbene phenol as a pale oil (yield 2.6 g, 49%). ¹H-NMR (CDCl₃): δ 1.2 (t, CH₃CH₂, 3H); 3.8 (q, CH₃CH₂, 2H); 3.92 (s, OCH₃, 3H); 3.93 (s, OCH₃, 3H); 5.3 (s, OCH₂, 2H); 5.8 (s, OH, 1H); 6.8–7.2 (m, ArH, 8H). ¹³C-NMR (CDCl₃): δ 15.2 (C₁₀); 55.9 (C₇, C_{7'}); 64.4 (C₉); 94.2 (C₈); 108.2 (C₂); 109.2 (C_{2'}); 114.6 (C₅); 116.4 (C_{5'}); 119.4 (C₆); 120.3 (C_{6'}); 126.2 and 127.3 (C_α, C_{α'}); 130.1 (C₁); 132.2 (C_{1'}); 145.5 (C_{4'}); 146.2 (C₄); 146.8 (C₃); 149.8 (C_{3'}). MS: m/z 330 (M⁺ 100%); 300 (34); 273 (12); 272 (69); 271 (88); 211 (9); 59 (31); 31 (16). IR (film): 1510, 1600, 2950, 3420, 3550 cm⁻¹.

Synthesis of PS-1

Polystyrene PS. After being distilled, 10 mL of styrene (87 mmol) and 10 mL of chloromethylstyrene (70 mmol) in solution in toluene (40 mL) under nitrogen were polymerized in presence of 45 mg of AIBN (12 mmol). After being stirred at 70°C for 17 h the solvent was removed under vacuum and the residue was dissolved in CH₂Cl₂ and precipitated in 500 mL of methanol. The white precipitate obtained was filtered and

washed with methanol to give 14 g of polystyrene. $^1\text{H-NMR}$ (CDCl_3): δ 1.2–2.2 (m, $\text{CH}_2\text{-CH}$, 3H); 4.3–4.7 (m, CH_2Cl , 2H); 6.2–7.4 (m, ArH, 9H). $^{13}\text{C-NMR}$ (CDCl_3): δ 40.6 ($\text{CH}_2\text{-CH}$); 40.5–46 (CH_2CH); 46.6 (CH_2Cl); 125.9 (CH ar.); 127.8 (C Ar); 128.2 (C Ar); 134.9 (C Ar); 137.1 (C Ar); 145.6 (C Ar). IR (KBr): 700, 760, 1265, 1450, 1490, 1600, 2920, 3025, 3440 cm^{-1} . SEC $M_n = 16,800$; $M_w = 34,000$, $I_p = 2.0$.

Polystyrene PS-4. A solution of **4** (2.0 g, 6.06 mmol) treated with KOH (0.42 g, 7.5 mmol) in DMF (40 mL) at 100°C was added to a solution of polystyrene PS (1.1 g, 4.07 mmol) in DMF (60 mL) at 130°C under nitrogen. After being stirred at 130°C for 15 h, a second solution of phenate prepared from **4** (1.0 g, 3.03 mmol) and KOH (0.21 g, 3.75 mmol) was added. After being stirred at 130°C for 3 days, the DMF was removed under vacuum and the residue was dissolved in CH_2Cl_2 and precipitated in 1400 mL of cold methanol. The precipitate was filtered and reprecipitated in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to yield 1.98 g. $^1\text{H-NMR}$ (CDCl_3): δ 1.1–2.3 (m, CH_2CH , 3H); 1.2 (t, $\text{CH}_3\text{CH}_2\text{O}$, 3H); 3.4–4.1 (m, $\text{CH}_3\text{CH}_2\text{O}$, OCH_3 , 8H); 5.28 (s, OCH_2O , 2H); 4.7–5.7 (s, ArCH_2O , 2H); 6.1–7.3 (m, ArH, $\text{CH}=\text{CH}$, 17H). $^{13}\text{C-NMR}$ (CDCl_3): δ 15.2 (C_{10}), 40.4 (CH-CH_2), 40–48 (CH-CH_2), 55.9 (C_7 , $\text{C}_{7'}$), 64.4 (C_9); 71.0 ($\text{C}_{8'}$); 94.1 (C_8); 109.2 (C_2 , $\text{C}_{2'}$); 113.8 (C_5); 116.3 ($\text{C}_{5'}$); 119.5 (C_6 , $\text{C}_{6'}$); 126.6 and 127.1 (C_α , $\text{C}_{\alpha'}$); 124–129 (CH Ar polystyrene); 130.9 (C_1); 132.1 ($\text{C}_{1'}$); 136–146 ($\text{C}_{4'}$ and C Ar polystyrene); 146.3 (C_4); 148.2 (C_3); 149.8 ($\text{C}_{3'}$). IR (KBr): 700, 990, 1130, 1240, 1260, 1510, 1585, 1600, 2925, 3430 cm^{-1} . SEC $M_n = 16,600$, $M_w = 32,700$, $I_p = 2.0$.

Polystyrene PS-1. A solution of PS-4 (300 mg) in CH_2Cl_2 (100 mL) were treated with 0.7 mL of trifluoroacetic acid under nitrogen. After being stirred at room temperature for 4 h a large part of the solvent was removed under vacuum at room temperature. Then the product was precipitated in cold Et_2O and centrifuged at 8000 tr/min for 15 min to yield 300 mg of polystyrene PS-1. $^1\text{H-NMR}$ (CDCl_3): δ 1.1–2.3 (m, CH_2CH , 3H); 3.3–4.1 (m, OCH_3 , 6H); 4.9–5.1 (s, ArCH_2O , 2H); 5.7 (s, OH, 1H); 6.1–7.3 (m, ArH, $\text{CH}=\text{CH}$, 17H). $^{13}\text{C-NMR}$ (CDCl_3): δ 40.5 (CH-CH_2); 40–48 (CH-CH_2), 55.3 and 56.0 (C_7 , $\text{C}_{7'}$); 71.1 ($\text{C}_{8'}$); 108.2 and 109.3 (C_2 , $\text{C}_{2'}$); 114.0 (C_5); 114.8 ($\text{C}_{5'}$); 119.6 and 120.3 (C_6 , $\text{C}_{6'}$); 126.4 and 127.0 (C_α , $\text{C}_{\alpha'}$); 124–129 (CH Ar polystyrene); 130.3 (C_1); 130.7 ($\text{C}_{1'}$); 136–147 (C Ar polystyrene, C_4 , $\text{C}_{4'}$); 148.1

(C_3); 149.8 ($\text{C}_{3'}$). IR (KBr): 700, 1030, 1270, 1450, 1460, 1515, 1600, 2925, 3500 cm^{-1} . SEC $M_n = 20,300$, $M_w = 40,100$, $I_p = 2.0$.

4-Benzyloxy-4'-(1-cyclohexylmethoxy)-3,3'-dimethoxydiphenylethane (**6E**)

4-Benzyloxy-4'-(1-cyclohexylmethoxy)-3,3'-dimethoxystilbene. A solution of **3** (500 mg, 1.38 mmol) was treated with K_2CO_3 (280 mg, 2 mmol) and methylcyclohexyl bromide (0.28 mL, 2 mmol) under nitrogen in DMF (40 mL). After being stirred at 90°C for 14 h the solvent was removed under vacuum. The residue, dissolved in CH_2Cl_2 , was treated with a solution of hydrochloric acid (10%), the aqueous layer was extracted with CH_2Cl_2 (3 \times 30 mL) and the combined organic layers were washed with water, dried over MgSO_4 , filtered, and concentrated under vacuum. The residue was purified by chromatography on silica gel (eluent: CH_2Cl_2) affording the expected product as a white solid (yield 410 mg, 65%, mp 174°C). $^1\text{H-NMR}$ (CDCl_3): δ 1.0–2.0 (m, C_6H_{11} , 11H); 3.8 (d, OCH_2 , 2H); 3.95 (s, OCH_3 , 3H); 4.0 (s, OCH_3 , 3H); 5.2 (s, OCH_2Ar , 2H); 6.8–7.1 (m, ArH and $\text{CH}=\text{CH}$, 8H); 7.3–7.5 (m, ArH, 5H). IR (KBr): 1265, 1515, 1605, 2845, 2925 cm^{-1} .

4-Benzyloxy-4'-(1-cyclohexylmethoxy)-3,3'-dimethoxydiphenylethane (6E**).** Hydrogenation of 4-benzyloxy-4'-(1-cyclohexylmethoxy)-3,3'-dimethoxystilbene (300 mg, 0.654 mmol) in ethyl acetate (100 mL) containing 30 mg of $\text{RhCl}(\text{PPh}_3)_3$ (0.032 mmol) was accomplished by treating the mixture under hydrogen pressure (180 bars) for 5 h at 100°C. The mixture, after filtration on a silica gel to removed the catalyst afforded a white solid, compound **6E** as unique product (yield 290 mg, 96%, mp 95°C). $^1\text{H-NMR}$ (CDCl_3): δ 1.0–2.3 (m, C_6H_{11} , 11H); 2.9 (s, $\text{CH}_2\text{-CH}_2$, 4H); 3.85 (s, OCH_3 , 3H); 3.9 (s, OCH_3 , 3H); 4.0 (d, OCH_2 , 2H); 5.2 (s, OCH_2Ar , 2H); 6.7–6.9 (m, ArH, 6H); 7.3–7.5 (m, ArH, 5H). $^{13}\text{C-NMR}$ (CDCl_3): δ 25.8 ($\text{CH}_2\text{C}_6\text{H}_{11}$); 26.6 ($\text{CH}_2\text{C}_6\text{H}_{11}$); 30.0 ($\text{CH}_2\text{C}_6\text{H}_{11}$); 37.6 ($\text{CH}_2\text{C}_6\text{H}_{11}$); 37.7 and 37.8 (C_α , $\text{C}_{\alpha'}$); 56.0 (C_7); 56.1 ($\text{C}_{7'}$); 71.2 ($\text{CH}_2\text{C}_6\text{H}_5$); 74.7 ($\text{CH}_2\text{C}_6\text{H}_{11}$); 112.5 (C_2); 112.7 ($\text{C}_{2'}$); 113.3 (C_5); 114.2 ($\text{C}_{5'}$); 120.4 (C_6); 120.5 ($\text{C}_{6'}$); 127.3 ($\text{CH}_2\text{C}_6\text{H}_5$); 127.8 ($\text{CH}_2\text{C}_6\text{H}_5$); 128.5 ($\text{CH}_2\text{C}_6\text{H}_5$); 134.4 (C_1); 135.2 ($\text{C}_{1'}$); 138.2 ($\text{CH}_2\text{C}_6\text{H}_5$); 147.1 ($\text{C}_{4'}$); 148.3 (C_4); 150.1 (C_3); 150.8 ($\text{C}_{3'}$). IR (KBr): 810, 850, 1140, 1220, 1270, 1515, 2860, 2920 cm^{-1} .

4-(1-Cyclohexylmethoxy)-4'-hydroxy-3,3'-dimethoxydiphenylethane (**5E**)

A solution of **6E** (400 mg, 0.88 mmol) was treated with a solution of HBr in acetic acid (10 mL) at room temperature for 3 h. After being hydrolyzed with water, the product was extracted with CH₂Cl₂ (3 × 30 mL). The combined organic layers were washed with water, dried over MgSO₄, filtered, and concentrated. The residue was purified by chromatography on silica gel (eluent: CH₂Cl₂) affording **5E** as a white solid (yield 290 mg, 90%, mp 158°C). ¹H-NMR (CDCl₃): δ 1.0–2.0 (m, C₆H₁₁, 11H); 2.9 (s, CH₂-CH₂, 4H); 3.80 (s, OCH₃, 3H); 3.85 (s, OCH₃, 3H); 3.9 (d, OCH₂, 2H); 5.8 (s, OH, 1H); 6.6–7.0 (m, ArH, 6H). ¹³C-NMR (CDCl₃): δ 25.8 (CH₂C₆H₁₁); 26.6 (CH₂C₆H₁₁); 30.0 (CH₂C₆H₁₁); 37.5 (CH₂C₆H₁₁); 37.8 (C_α, C_{α'}); 55.9 and 56.1 (C₇, C_{7'}); 74.7 (CH₂C₆H₁₁); 114.2 (C₂); 114.6 (C_{2'}); 119.6 (C₅); 120.2 (C_{5'}); 121.0 (C₆); 126.6 (C_{6'}); 143.7 (C₁); 145.3 (C_{1'}); 146.2 (C₄); 146.7 (C_{4'}); 148.6 (C₃); 149.6 (C_{3'}). IR (KBr): 810, 850, 1030, 1130, 1160, 1225, 1275, 1520, 2850, 2925, 3420 cm⁻¹. MS on the trimethylsilyl derivative m/z 442 (M⁺ 29%), 233 (13); 210 (16); 209 (100); 179 (145); 137 (51); 73 (24); 55 (18).

Peroxide Bleaching of TMP Pulp

Unbleached softwood thermomechanical pulp, kindly provided by Dr. Petit-Conil (Centre Technique du Papier, Grenoble), (20 g) was treated in a polyethylene bag with the bleaching liquor (200 mL) constituted by hydrogen peroxide (3% oven dry pulp, odp), NaOH (1.5% odp), MgSO₄·7H₂O (0.5% odp), sodium silicate (3.5% odp) and DTPA (0.25% odp) at 60°C for 4 h. Then the pulp was filtered and bleached for a second time in the same conditions with fresh liquor (200 mL). At the conclusion of the bleaching, the pulp was washed with distilled water and dilute hydrochloric acid to pH 4.5. The sheet preparation procedure has been described elsewhere.²³

Hydrogenation

Hydrogenation of 3 on filter paper. A solution of **3** (15 mg) in ethyl acetate (1 mL) was spread on a filter paper sheet (4 cm × 4 cm) and the solvent evaporated with a gentle air stream. Then a solution of RhCl(PPh₃)₃ (1.5 mg) in ethyl acetate (1 mL) was added to the paper and the sheet was put in a stainless steel reactor to perform the reaction under hydrogen pressure (180 bars). Ethyl ace-

tate (3 mL) was added to the reactor and direct contact between the paper and the liquid solvent was avoided by the presence of a piece of metal. The reaction was performed at 60°C for 4 h. After cooling the reactor to room temperature, the paper was washed with ethyl acetate and CH₂Cl₂ to extract the organic products. The reacting mixture was filtered on silica gel to remove the catalyst and then analyzed by gas chromatography after silylation with N,O-bis(trimethylsilyl)-trifluoroacetamide (BSFA) (50 μL), pyridine (10 μL) in THF (50 μL).

Hydrogenation of PS-1 on filter paper. The same procedure as used for **3** was employed for the hydrogenation of PS-1 (15 mg) on filter paper sheet (4 cm × 4 cm) using RhCl(PPh₃)₃ (1.5 mg). The polymer was extracted from the paper sheet with ethyl acetate and CH₂Cl₂. The solution was evaporated to the 1 mL and then the polymer was precipitated in Et₂O giving after centrifugation a white solid corresponding to the hydrogenated polystyrene PS-1H (yield 14 mg, 93%).

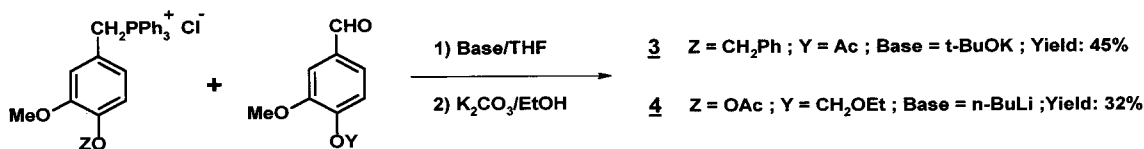
Hydrogenation of BTMP. Hydrogenation of bleached thermomechanical pulp (300 mg) impregnated with a solution of RhCl(PPh₃)₃ (15 mg) in ethyl acetate (3 mL) was accomplished under 180 bars of hydrogen for 4 h at 60°C in presence of 3 mL of ethyl acetate as described for the hydrogenation of compound **3**. After cooling the reactor, the sheet was washed with ethyl acetate, methanol, and CH₂Cl₂ to remove the catalyst and then washed with water and dried at 40°C.

Acidolysis with AlCl₃

Pulp (100 mg) (or 15 mg of polystyrene) in benzene (30 mL) were treated with 10 mg of AlCl₃ at 90°C for 12 h, then the reacting mixture was hydrolyzed with water and extracted with CH₂Cl₂. The organic phase was dried with magnesium sulfate concentrated under vacuum and silylated with (BSFA) (50 μL), pyridine (10 μL) in THF (50 μL) at room temperature. The silylated mixture was analyzed by GC-MS using docosane as internal standard.

Irradiation of PS-1 and PS-1H (Adsorbed on Cellulosic Matrix) and TMP Paper

Two paper sheets (3 cm × 3 cm) made from a Kraft pulp (30 g/m²) were separately impregnated with PS-1 (5.0 mg) and PS-1H (5.0 mg) in CH₂Cl₂ (1 mL) and dried with a nitrogen stream. The paper sheets were irradiated with a 3 black



Scheme 2 Synthetic scheme of compounds **3** and **4**.

light UV lamps (Mazdafluor TFWN 18) emitting mainly in the 350 nm wavelength range. The distance between the lamp and the sheets was 20 cm. The temperature of the irradiation setup was maintained at 25°C by a fan. The reflectance of the sheets was measured at appropriate time intervals and the K and S values of the Kubelka–Munk theory were calculated using the Microsoft Excel software and the formulas given in the Discussion section. The nonhydrogenated and hydrogenated papers were irradiated using the procedure described for the polystyrene samples.

RESULTS AND DISCUSSION

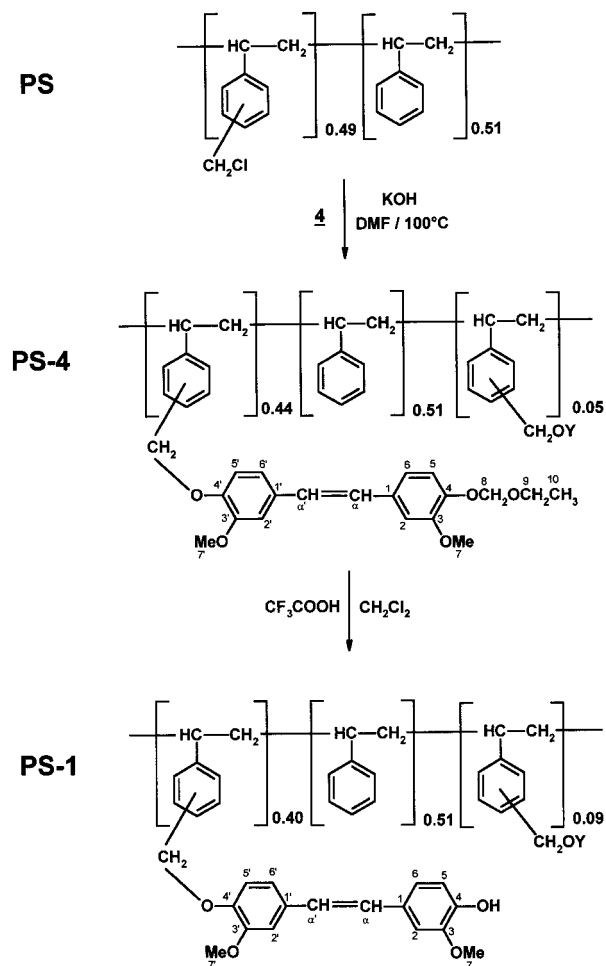
Syntheses of Stilbene Lignin Models and Stilbenol Grafted on Polystyrene

Our first concern was to set up appropriate conditions to hydrogenate stilbenols in peroxide bleached thermomechanical pulp (BCTMP) with the Wilkinson catalyst [RhCl(PPh₃)₃] which is soluble in ethyl acetate. The efficiency of the reaction will be assessed by the detection and titration of the diphenylethane **1E** formed after mild acidolysis of the hydrogenated pulp. In that respect, 4-benzyloxy-3,3'-dimethoxy-4'-hydroxystilbene **3** was selected as the simplest model because it has a phenolic end and the benzyl group mimics the chain between the stilbene group and others units of the lignin polymer (Scheme 1). A more sophisticated model was also designed; it is constituted by a linear polystyrene backbone including stilbenol units as pendent groups (Scheme 1). It might be considered more representative of lignin because it is an aliphatic-aromatic polymer and so it displays the specific properties of a polymer.

Compounds **3** and **4** were synthesized using the Wittig reaction. Substituted benzyltriphenyl phosphonium chloride derivatives were treated with potassium *t*-butoxylate or *n*-butyllithium to generate the corresponding ylides which were further reacted with the appropriate benzaldehyde compound. After mild saponification compounds **3** and **4** are obtained in their *trans* form (Scheme 2).

4,4'-Dihydroxy-3,3'-dimethoxystilbene **1** was chosen to be grafted to polystyrene. Given the symmetry of this molecule, it was necessary to differentiate the two hydroxyl groups to obtain a monofunctional linkage and therefore a linear polymer. So the monoprotected stilbenol **4**, synthesized according to Scheme 2, was grafted to a linear chloromethylpolystyrene prepared by radical copolymerization of chloromethylstyrene (para/ortho mixture ≈ 95/5) and styrene in presence of AIBN as initiator (Scheme 3).

The structure of the grafted polystyrene and



Scheme 3 Synthetic scheme of PS-1.

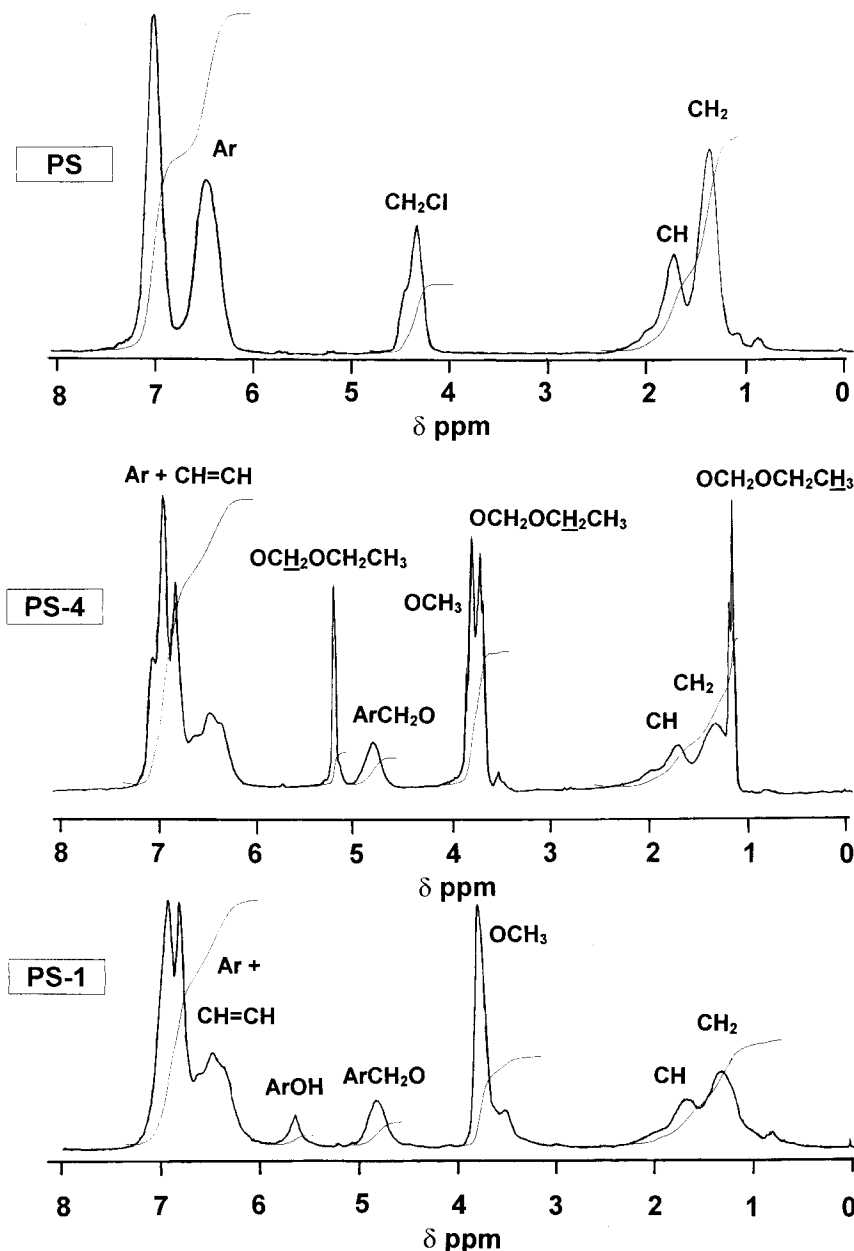


Figure 1 ^1H -NMR spectra of chloromethylpolystyrene (PS), PS-4 and PS-1.

the grafting rates were established mainly by NMR spectroscopy. The ^1H -NMR spectra (Fig. 1) show the different assignments of the starting polystyrene (PS), the protected stilbene grafted on polystyrene (PS-4), and the polystyrene with the stilbenols as pendent groups (PS-1). It is noticeable that the grafting of the stilbene was not quantitative (90%) and some benzylic cleavage occurred during the treatment with trifluoroacetic acid during the deprotection. The presence of a peak at 3.6 ppm might be due to the formation of

some diphenylmethane type structure formed by intramolecular condensation. In Figure 2 are indicated the ^{13}C -NMR spectra of PS, PS-4, PS-1, and also the spectrum of the monoprotected stilbenol 4 to differentiate the peaks due to a stilbene which includes a phenolic hydroxyl and an ethoxymethyl protecting group. The assignments of the ^{13}C -NMR spectra, given in Figure 2 and in the Experimental section, were supported by DEPT experiments and by comparison with the spectra of other lignin model molecules.²⁴ The ^{13}C -NMR

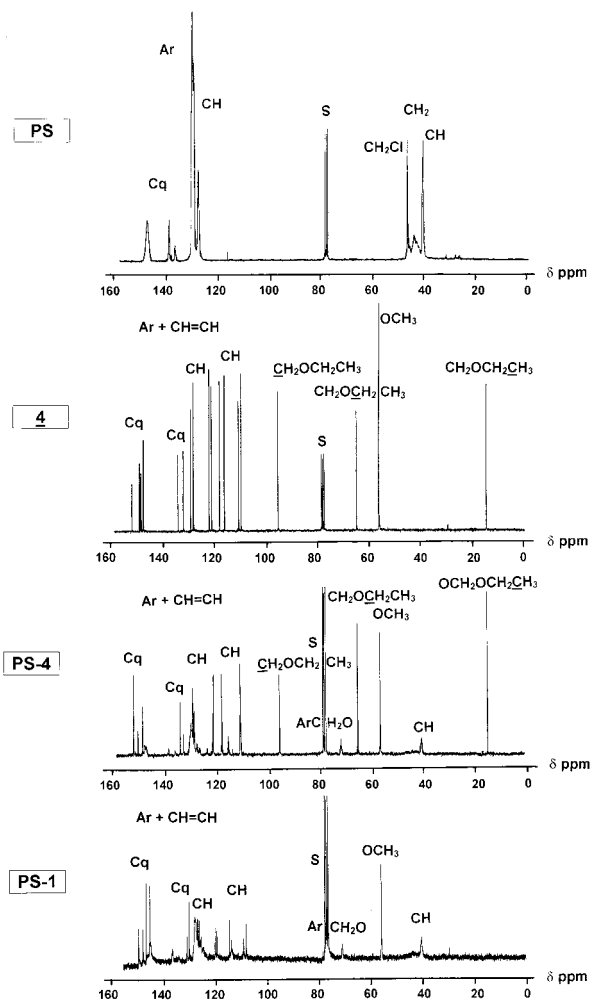


Figure 2 ^{13}C -NMR spectra of chloromethylpolystyrene (PS), PS-4 and PS-1.

technique was not sensitive enough to unambiguously assign the nature of the Y substituent (Scheme 3) in PS-4 (5%) and PS-1 (9%) which probably belongs to the bulk structure of the polystyrene framework.

Analysis of the stilbenol polystyrene PS-1 by size exclusion chromatography revealed a quite large mass distribution ($M_w/M_n = 2$ and $M_n = 20,300$) traducing the presence of various chain lengths.

Hydrogenation of Stilbene Lignin Models, Stilbenol Grafted on Polystyrene, and Peroxide Bleached TMP

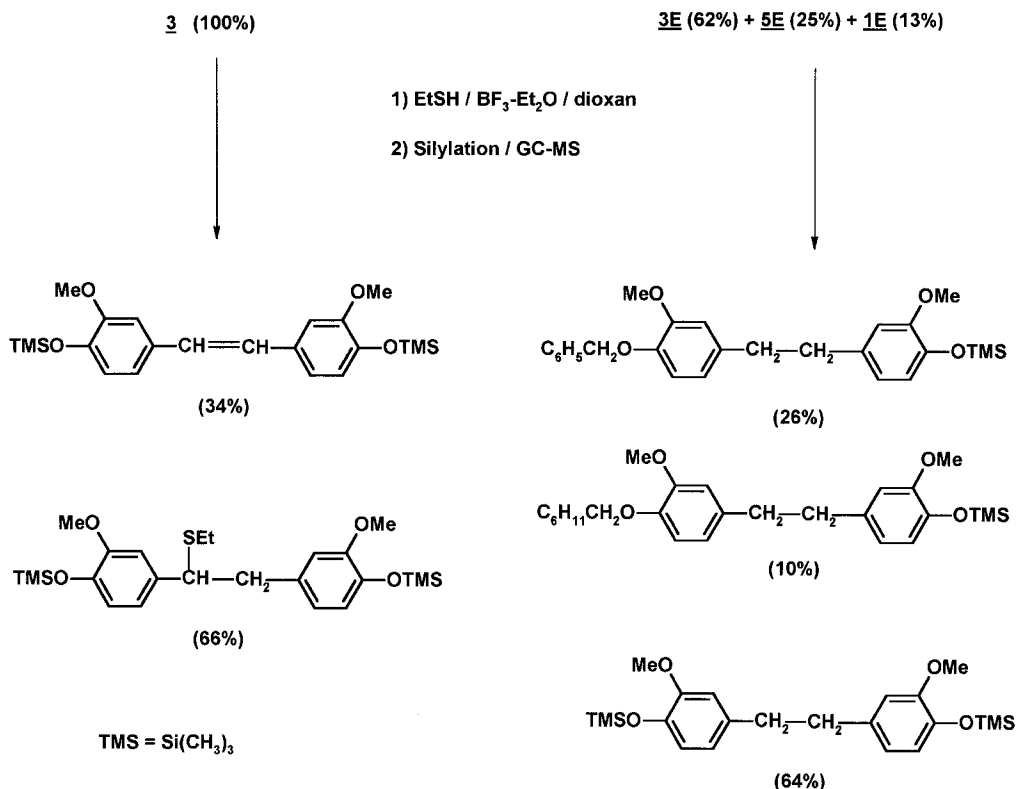
Hydrogenation of the stilbene double bond must be selective, in particular hydrogenolysis of the benzylic group must be avoided. Stilbene **3**, designed to optimize the experimental conditions, was hydrogenated with the Wilkinson's catalyst

$\text{RhCl}(\text{PPh}_3)_3$, prepared from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and PPh_3 according to the procedure of Osborn et al.²⁵ Among the hydrogenation conditions tested on compound **3** adsorbed on filter paper (cellulose) in presence of $\text{RhCl}(\text{PPh}_3)_3$, the best results were obtained for a temperature of 60°C and for a hydrogen pressure of 180 bars. Special care was taken to avoid the paper contacting the liquid ethyl acetate solvent. It was observed that heterogeneous hydrogenation of **3** yields three products: **3E** (62%), **5E** (25%), and **1E** (13%), whereas hydrogenation of **3** in solution yields only two of these products: **3E** (87%) and **1E** (13%). In both cases, some debenzilation was observed. The carbohydrate matrix seems to induce favorable stereorearrangement to facilitate the reaction of the benzene ring with the hydrogen gas in presence of the soluble rhodium catalyst. Aromatic hydrogenation of lignin models was also observed by Hu, James, and Lee²⁶ using colloidal rhodium catalyst.

The *p*-stilbene phenols formed from β -1 units during alkaline peroxide bleaching of high-yield pulps are localized as end groups in the lignin polymer. To characterize and titrate the diphenylethane formed after hydrogenation it is necessary to liberate them by acid catalyzed solvolysis.

The thioacidolysis technique developed by Lapiere, Pollet, and Monties,²¹ which consists in an acidolysis of the benzylarylether bonds of lignin by EtSH in presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in dioxan, was found very powerful to analyze lignin structural elements in lignocellulosic materials. We have applied this method to compound **3** and to a mixture (**3E** + **5E** + **1E**) resulting from the hydrogenation of this compound adsorbed on cellulosic matrix. The results, reported in Scheme 4, show that debenzilation of the stilbene derivative **3** is total, the sulfur derivative being formed by EtSH addition on the double bond, whereas the thioacidolysis on the hydrogenated mixture is not conducive to complete deprotection of the phenol.

The deprotection of both cyclohexylmethyl and benzyl groups was established on compound **6E** using AlCl_3 in refluxing benzene for 12 h. Compound **1E** (trimethylsilyl derivative) was isolated and characterized by GC-MS as single deprotected product; nevertheless, the extraction procedure allows only 35% yield in detected product. Hydrogenation of PS-1 was carried out using the same procedure as for stilbene **3**. The resulting hydrogenated compound was then treated with AlCl_3 in refluxing benzene. It gives compound **1E** (trimethylsilyl derivative) as unique deprotected



Scheme 4 Thioacidolysis of compound $\underline{3}$ and of the mixture of $\underline{3}$ hydrogenated on cellulose paper.

product, the yield of isolated compound (13%) being lower than for compound $\underline{6E}$. The polymeric nature of the model is probably one of the causes of the low yield in the work-up procedure. It is noteworthy that no stilbene phenol $\underline{1}$ has been detected after the AlCl₃ treatment, and in accordance with the photoyellowing kinetic, as we shall see later, the hydrogenation appears quite complete.

Peroxide bleached softwood thermomechanical pulp was hydrogenated using the same procedure as for PS-1 adsorbed on filter paper. Then, the pulp was thioacidolyzed with EtSH/BF₃-Et₂O in dioxan to break down the lignocellulosic structure (cellulose, hemicelluloses and lignin),²¹ the organic extract was desulfurized with Raney nickel and then treated with AlCl₃ in benzene. GC-MS analysis of the mixture allowed the detection of compound $\underline{1E}$ as TMS derivative: 4.15×10^{-7} mol g⁻¹ of pulp. The same experiment without the thioacidolysis stage gave the same quantity of compound $\underline{1E}$ (4.08×10^{-7} mol g⁻¹ of pulp); this result confirms that the stilbene phenols are localized as end groups in the lignin polymer, and are very accessible to the chemical reagents. Ac-

ording to the data established on PS-1 we might expect, using our experimental conditions, an almost complete hydrogenation of the stilbene phenols of the pulp formed from the β -1 structures, and so an estimation of their content using the yield of diphenylethane found for the grafted polystyrene PS-1. A value of 2 stilbenes for 1000 C₉ units of the lignin polymer was obtained. It is the first time that the proportion of stilbene can be semiquantitatively evaluated in bleached high yield pulps. The number found indicates that *p*-stilbene phenols are present in very minute quantities and it suggests that the rapid photoyellowing of lignin rich pulps might not only be attributed to these chromophores.

UV Irradiation of Stilbenol Grafted on Polystyrene (PS-1) and Peroxide Bleached TMP

PS-1

UV-irradiations of stilbenol-bound polystyrene PS-1 and PS-1 hydrogenated (PS-1H) were studied. These two compounds were deposited on a cellulose paper sheet to use the Kubelka-Munk the-

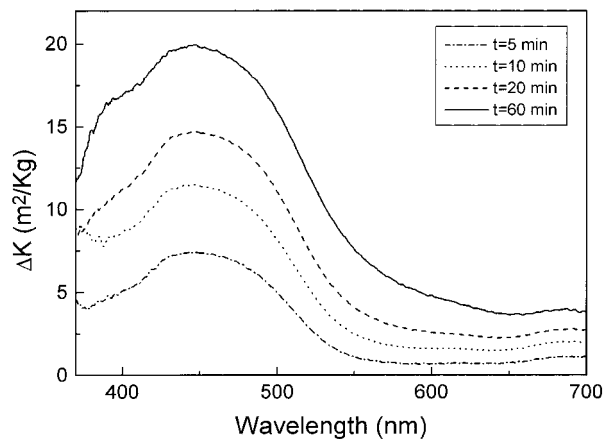


Figure 3 Formation of colored species when PS-1, adsorbed on cellulose matrix, was irradiated with UV light. The color formation was expressed by the difference of absorption coefficients ΔK (Kubelka Munk theory, see Results section) between irradiated sample and nonirradiated one versus irradiation times.

ory.²⁷ This method involves measurement of R_w , reflectance over a white background as well as R_o , reflectance over a black background. The following equations were used to calculate the absorption coefficient K , which is proportional to the chromophore concentration.

$$(R_\infty + 1)/R_\infty = R_w + [(R_o - R_w + R_b)/(R_o R_b)]$$

$$S = (1/\alpha)$$

$$\times [R_\infty/(1 - R_\infty^2)] \log[R_\infty(1 - R_\infty R_o)/(R_\infty R_o)]$$

$$K/S = (1 - R_\infty)^2/(2R_\infty)$$

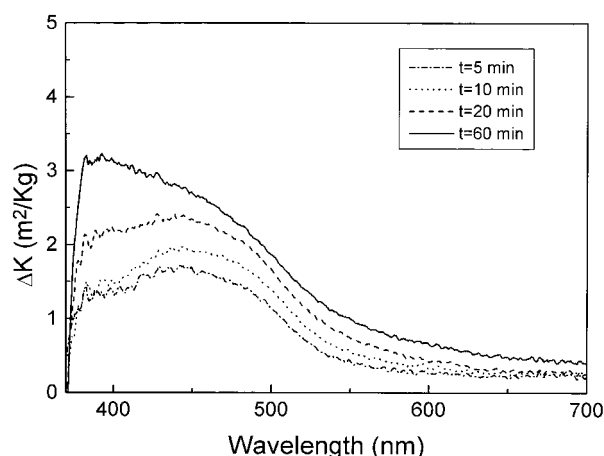


Figure 4 Formation of colored species when hydrogenated PS-1 (PS-1H), adsorbed on cellulose matrix, was irradiated with UV light (see legend to Fig. 3).

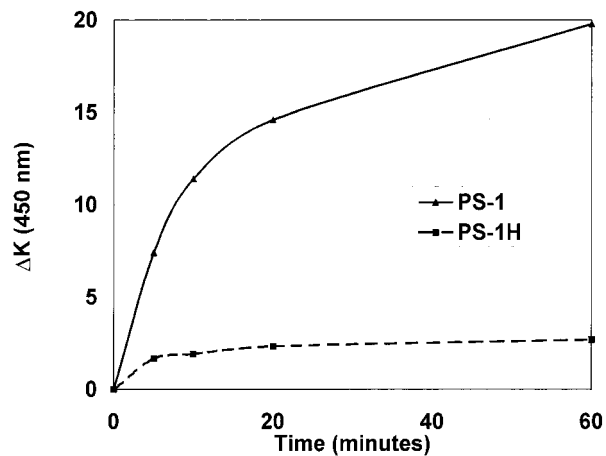


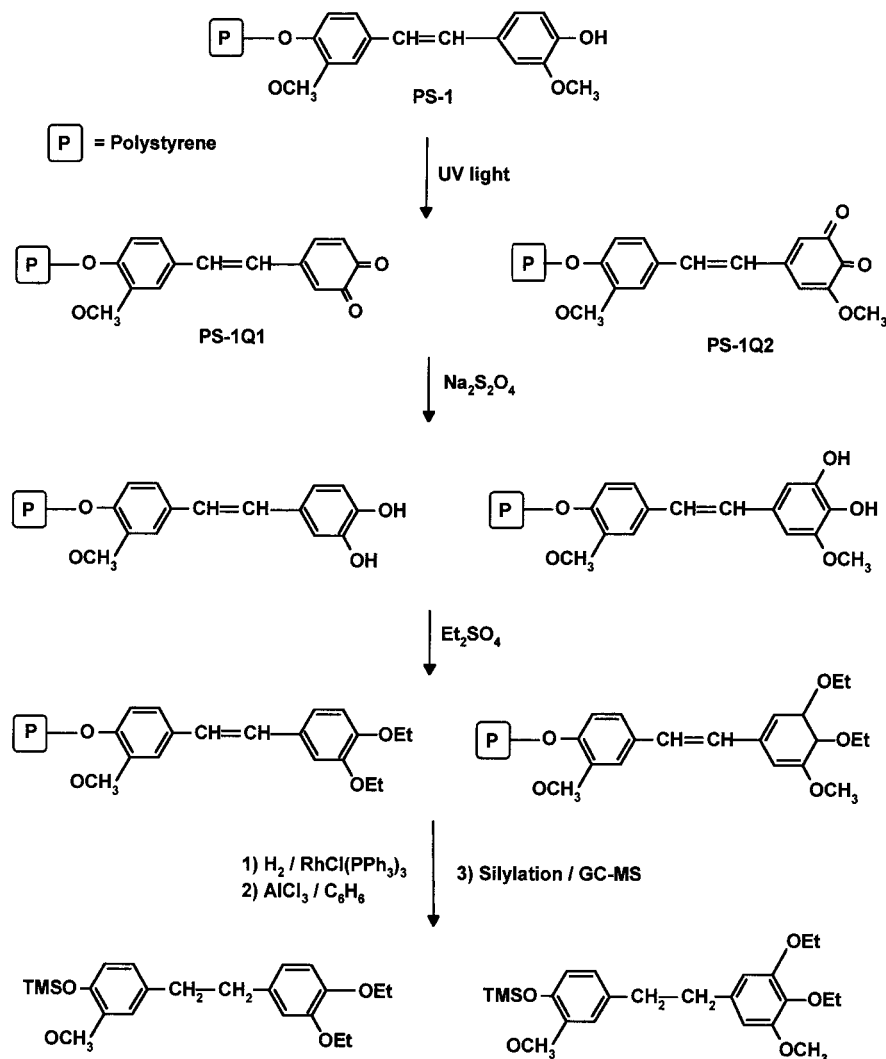
Figure 5 Comparison of the kinetics of formation of colored species, expressed by ΔK measured at 450 nm, for PS-1 and PS-1H.

where K is the absorption coefficient; S is the scattering coefficient; R_b is reflectance of the white background (BaSO_4); and α is the basis weight in kg m^{-2} .

Figures 3 and 4 show the difference of absorption coefficient ΔK for PS-1 and PS-1H adsorbed on cellulose paper before and after irradiation with UV light ($\lambda \approx 360$ nm) ranging from 5 to 60 min. Variations of ΔK are less important for PS-1H than for PS-1, so a photostabilization effect is observed thanks to hydrogenation (Fig. 5). The remaining yellowing of the hydrogenated stilbene is due to the ability of the nonconjugated phenol to be photooxidized as previously observed on phenolic lignin monomer models.¹⁰

After irradiation it was difficult to remove the polymer PS-1 from the paper; a grafting of the polymer to the cellulosic matrix was probably occurring. This might be due to the formation of radicals in the cellulose framework as observed previously for coniferyl alcohol models²⁸ and for hydroquinones.²⁹ The irradiation of PS-1 was also done on glass support, which is chemically more inert than cellulose. In those conditions, even with just a minute of UV light, a great part of the polymer becomes insoluble in all solvents (THF, CH_2Cl_2 , benzene). SEC analysis of the irradiated mixture was not conclusive due to the great insolubility of the polymer in THF. This insolubility is probably ascribable to the oxidative coupling usually found for phenols and/or to $2\pi + 2\pi$ photodimerization as observed for monomer stilbenol by Leigh et al.¹⁷

As it was indicated in the Introduction, chemical products obtained by UV irradiation of stil-



Scheme 5 Tentative characterization of the quinones formed by UV irradiation of PS-1.

benzene phenols are *ortho*-quinones, so two photoproducts were expected from PS-1: PS-1Q1 and PS-1Q2 (Scheme 5). It is noticeable that the absorption maximum observed in Figures 4 and 5 situated at 450 nm is in favor of a structure of type 3-methoxy-1,2-benzoquinone instead of a simple 1,2-benzoquinone structure.³⁰ Three methods were attempted to show the formation of *ortho*-quinones from polystyrene-stilbene by irradiation. The first one was the detection by GC-MS of specific structures after cleavage of the ether bond linking the pendent group to the polymer. In this order, the irradiated polymer was reduced with $\text{Na}_2\text{S}_2\text{O}_4$ and then ethylated by Et_2SO_4 (Scheme 5) before to be hydrogenated by H_2 with $\text{RhCl}(\text{PPh}_3)_3$. The cleavage was accomplished by a treatment with AlCl_3 in benzene. The GC-MS

analysis of the mixture did not show presence of the expected diphenylethane products. Fluorescence spectroscopy seems to be a good means to study quinone formation because of its high sensitivity, even when small amounts of *ortho*-quinones are formed. Quinones are generally non-fluorescent; therefore they need to be derivatized to be detectable. Recently, Zhu, Olmstead, and Gray³¹ have shown that *ortho*-quinone and 1,2-phenylenediamine react to form phenazine which, in its hydrated form, has a characteristic fluorescence. We have applied this technique to PS-1 irradiated with UV light but it was very difficult to attribute unambiguously a signal to the formation of any *ortho*-quinone. Konya and Scaiano³² using the same technique have shown that high-intensity photodecomposition of 2-methoxyph-

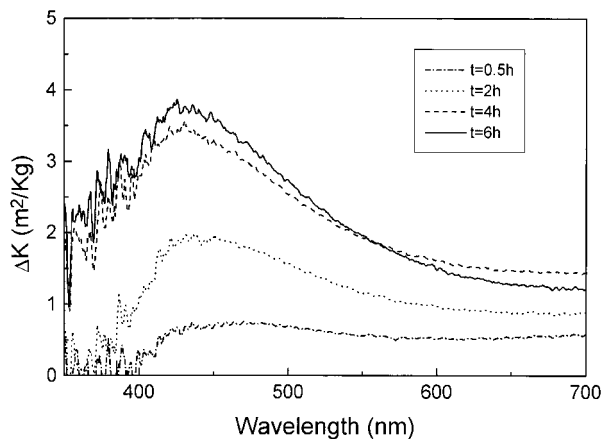


Figure 6 Formation of colored species when bleached TMP paper (BTMP) was irradiated with UV light (see legend to Fig. 3).

nols generates some *ortho*-quinones through the intermediary of phenoxyl radicals. Prakash, Krishnamurti, and Olah³³ reported the selective trifluoromethylation of carbonyl-containing compounds by using trifluoromethyltrimethylsilane (Ruppert's reagent) in the presence of catalytic amounts of tetraalkylammonium fluoride. The intermediate trimethylsiloxy adducts were then converted to their corresponding alcohol. Ahvazi and Argyropoulos³⁴ demonstrated that such a method can be an analytical tool using ¹⁹F-NMR spectroscopy for the detection and quantification of quinonoid groups in lignin. We applied this technique to detect the quinones after irradiation of polymer PS-1. We detected small peaks respec-

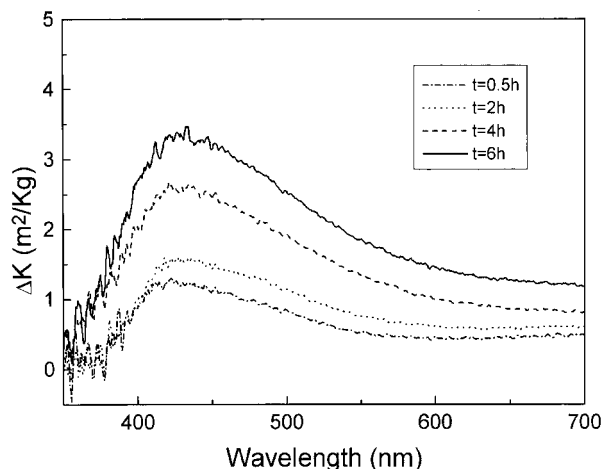


Figure 7 Formation of colored species when hydrogenated bleached TMP paper (BTMPH) was irradiated with UV light (see legend to Fig. 3).

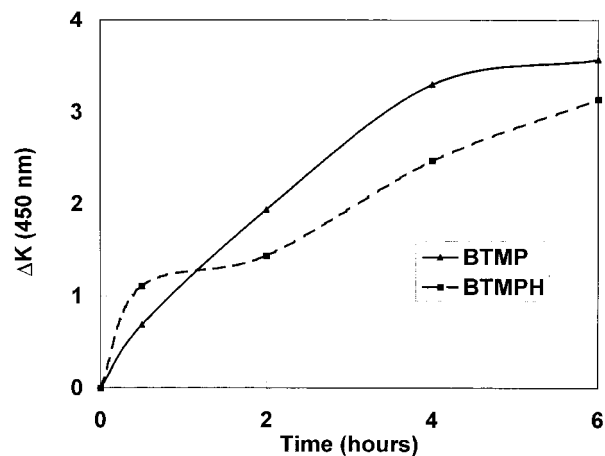


Figure 8 Comparison of the kinetics of formation of colored species, expressed by ΔK measured at 450 nm, for BTMP and BTMPH.

tively at -83.1 and -84.3 ppm. Their presence appears to be more in favor of a *para*-quinone type structure than an *ortho*-quinone one. The difficulty to characterize such *ortho*-quinonoid structures is apparently due to their high thermal and photochemical reactivity toward other unsaturated double bonds present in the polymer.³⁵

Peroxide Bleached TMP (BTMP)

Figures 6 and 7 show the difference absorption coefficient ΔK for the softwood peroxide-bleached TMP with and without an hydrogenation treatment (*vide infra*) before and after irradiation with UV light. The absorption maximum is located at 430 nm for both pulps. This is in accordance with what was observed by Schmidt, Kimura, and Gray³⁰ on borohydride reduced mechanical pulps. This absorption is probably due to a mixture of 3-methoxy-1,2-benzoquinone and 1,2-benzoquinone as suggested in ref. 30. The kinetic curves of formation of colored species (450 nm) for BTMP and BTMPH are given in Figure 8. The hydrogenation treatment designed to be efficient on pulp does not bring any stabilization for the first hour of UV irradiation. For a longer period of irradiation time, only a slight reduction ($\approx 20\%$) of the formation of colored species was observed. This result indicates unambiguously that the *p*-stilbene phenols formed from β -1 units are not the major contributors of the rapid photoyellowing of peroxide bleached lignin-rich pulps. Among the chromophores able to give the rapid yellowing developed under UV irradiation of the pulps some *para*-hydroquinone structures, which were shown to be

very reactive and prone to form strong colored species with UV light in the 300–400 nm wavelength range,²⁹ appear to be very good candidates.

CONCLUSIONS

The contribution of the *p*-stilbene phenol units to the photoyellowing of peroxide-bleached thermomechanical pulps was assessed by efficiently converting the stilbene structures into the diphenylethane ones using RhCl(PPh₃)₃ (Wilkinson catalyst) which is soluble in ethyl acetate. The hydrogenation conditions were set up on a simple model: 4-benzyloxy-3,3'-dimethoxy-4'-hydroxystilbene and a more elaborated lignin-like model (PS-1) constituted by a polystyrene framework containing the 3,3'-dimethoxy-4'-hydroxystilbene entity as pendent group. For the first time a semiquantitative evaluation of the content of the *p*-stilbene phenols, formed from the β-1 lignin structural element, had been possible in pulp. A very small quantity of this chromophore (2 for 1000 C₉) was found for bleached softwood TMP. The irradiation of PS-1 showed that the stilbenols, even included in a polymeric structure, are very photoreactive and give colored species, probably *ortho*-quinones. It has not been possible to characterize them due to their high ability to react and crosslink the polymer in a very insoluble material. Upon hydrogenation, the polymer showed a very strong decrease of the photoproduction of colored species, the nonconjugated phenol, not absorbing above 300 nm, being at the origin of the remaining color formation. In contrast, the same conclusion does not apply to the bleached TMP where no or slight stabilization was observed after efficient hydrogenation of the conjugated stilbene double bond. This indicates that the *p*-stilbene phenols formed from the β-1 units are not the main contributors of the photoyellowing of the bleached lignin-rich pulps. This result is of major significance for the stabilization of the brightness of bleached high-yield pulps. A chemical treatment based on hydrogenation of the pulp should not be only able to saturate the conjugated double bond of the stilbenes but also to hydrogenate the aromatic rings to remove the benzenic character of the lignin polymer. This appears to be the direction of recent studies presented by Hu, James, and Lee.²⁶ Our findings indicate that further studies are still needed to determine the main chromophore at

the origin of the rapid photoyellowing of bleached high-yield pulps.

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