Graft Copolymers of Lignin from Straw with 1-Ethenylbenzene: Synthesis and Characterization

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ABSTRACT: The synthesis of copolymers between lignin from steam-exploded straw and 1-ethenylbenzene is described. Beforehand, lignin from steam-exploded straw was fully characterized by using elemental analysis, ultraviolet spectroscopy, gel permeation chromatography (GPC), Fourier transform infrared (FTIR), and both ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Using a previously described procedure utilizing calcium chloride and hydrogen peroxide as reagents the synthesis of the copolymers was performed. FTIR of the copolymers showed the presence of both lignin and polystyrene. GPC analysis showed the presence of a fraction with high molecular weights. These results were confirmed from both viscosity data and differential calorimetry. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 72–79, 2001

Key words: lignin; straw; GPC; FTIR

INTRODUCTION

Straw is a residual biomass thoroughly diffused in the world and increasingly exploited for industrial applications. The low cost in the field can counterbalance the high transportation cost. The largest industrial use of straw is for pulp paper production but higher value niche markets have been proposed.[1]

Nearly any process of lignocellulosic exploitation requires a pretreatment step in order to disrupt the solid matrix and to separate cellulose from hemicellulose and lignin. Steam explosion is reported as one of the more interesting treatments in consequence of the morphological modifications induced in the vegetable fibers in addition to the hydrolytic bond cleavage. In particular, lignin solubility in solvents and alkaline solutions is greatly enhanced after steam explosion. However, the loss of lignin structure is only partial and the pieces in which it is broken are still macromolecular and they maintain almost all the complexity of the native material.

Recently, we reported that lignin can be efficiently degraded by the action of singlet oxygen.[2] Some years ago the synthesis of graft copolymers between 1-ethenylbenzene and lignin was described.[3,4] In those works the authors used Kraft pine lignin and yellow poplar lignin from steam explosion. Considering the wide diffusion of straw as a residual biomass rather than wood, in this paper we report our results in the copolymerization of lignin from steam-exploded straw and 1-ethenylbenzene. We found some different re-

Table I   Reagents for Copolymer Synthesis

Polymer	Reagents			Yields (g)
	$CaCl_2$ (mg)	H_2O_2 (mL)	DMSO (mL)	
PSL1	203	0.2	2	1.512
PSL2	203	0.3	2	1.530
PSL3	203	0.4	5	1.622
PSL4	202	0.4	5	1.640
PSL5	203	0.4	2	1.636
PSL6	210	0.3	2	0.503
PSL7	210	0.3	5	0.570

sults, in comparison with those reported with softwood and hardwood lignins, that appear of particular interest.

EXPERIMENTAL

The material used as source of lignin (straw) was mechanically reduced in pieces of about 1 cm of length and added with water to rise its initial content to the value of 50 wt %. Steam explosion runs were carried in a 101 batch reactor, loading about 0.5 Kg of material each cycle. Treatment conditions were 210°C and 4 min. The resulting severity parameter [] was log R_0 = 3.84. The raw material (100 g) was extracted two times with hot water (250–300 mL, 65 ± 5°C) in order to eliminate sugars and hemicelluloses. The extraction of lignin from exploded materials has been carried out by 1.5% sodium hydroxide solution (250 mL) at 90°C in 15 min for two times. Lignin in still warm solution was precipitated at pH 2 with 20% H_2SO_4, filtered, washed, and dried at 105°C.

Elemental analyses were obtained with a Carlo Erba Elemental Analyzer 1106.^{13}C NMR spectra were recorded with a Bruker 300 AM instrument. All the spectra were recorded in dimethyl sulfoxide (DMSO)-d_6. Gel permeation chromatography (GPC) analyses were performed on a Waters HPLC by using H-P Plgel 5 μ column. The lignin samples were acetylated before GPC analysis. Tetrahydrofuran (THF) was used as mobile phase. Spectrophotometric grade THF was used and distilled (oven LiAlH$_4$) before the use. The chromatograms were obtained using an ultraviolet (UV) detector at 280 nm. The conversion from elution time to molecular weight was performed by using a calibration obtained by using polystyrene samples.[5] Cary 2300 spectrophotometer was used for the UV spectra. Spectrophotometric grade dimethylformamide (DMF) was used as solvent.

Synthesis of the Copolymers

In an Erlenmayer flask lignin (200 mg) and CaCl$_2$ (Table I) were dissolved in dimethylsufoxide (Table I). The mixture was stirred for 5 min under nitrogen. Thirty percent hydrogen peroxide (Table I) was added and, after stirring for 20 min, 1-ethenylbenzene (1.876 g), previously bubbled with nitrogen for 10 min, was added under nitrogen. The Erlenmayer flask was maintained at 30°C under mechanical stirring for 48 hours. The mixture was treated with diluted hydrochloric acid solution (pH 2) (20 mL) and filtered on büchner. The filtered polymer was dried in an oven at 100°C overnight. The raw material was purified through extraction in benzene (200 mL) in a Soxhlet apparatus for 12 hours.

All the experiments were replicated three times. We have to note that lignin is not soluble in benzene at the reflux temperatura.

1-Ethylbenzene was purified to remove the stabilizer by washing the monomer three times with aqueous base at a ratio of 1g of ethenylbenzene to 1 mL of 2 N NaOH. The stabilizer-free monomer was washed with distilled water to pH 7 and dried with anhydrous calcium chloride for 2 days. It was then distilled in vacuo at 40°C and 20 mmHg pressure.

Intrinsic viscosity was determined in DMF as solvent. The thermal behavior was examined by a differential scanning calorimeter (DSC 7, Perkin Elmer), on 5 ± 0.25 mg samples of the benzene soluble extracts of copolymers, in a nitrogen atmosphere, at a scanning rate of 20°C min^{-1}. Scans were performed in the temperature range from 50 to 180°C. The data were analyzed through the software PYRIS running under Win-
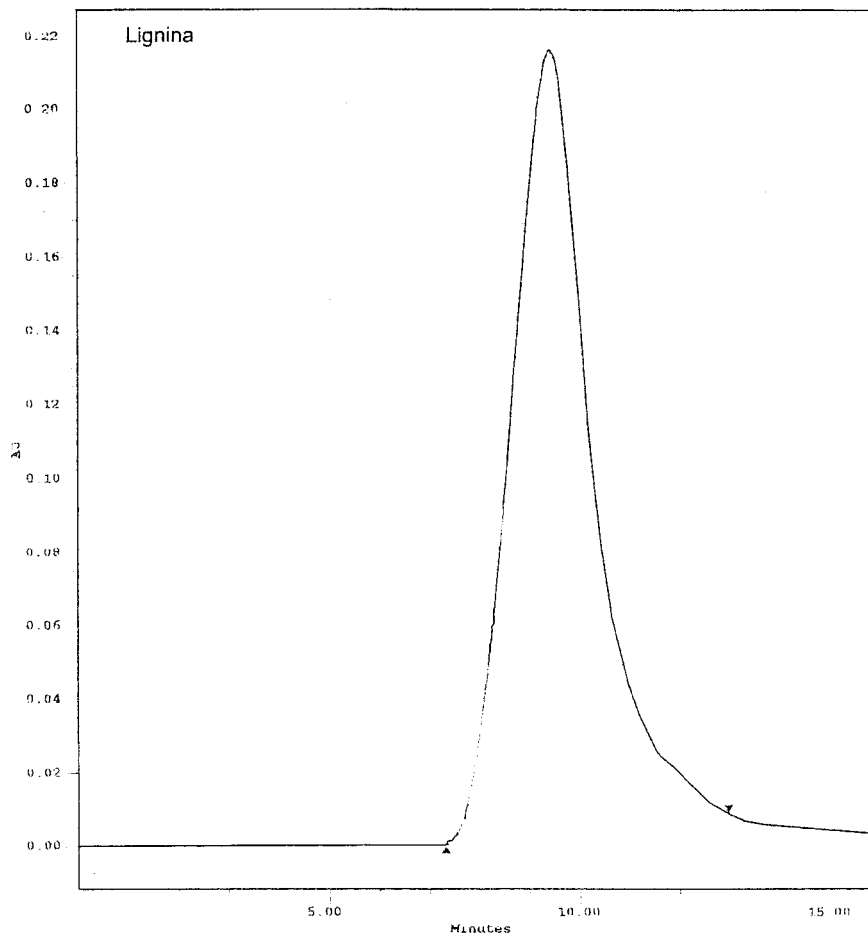
Figure 1   Gel permeation chromatography of lignin from steam-exploded straw.

dows NT 4.0 on a Compaq Prolinea 5133 computer. The glass transition temperature, T_g, has been taken, as usual, at the temperature corresponding to the point where half the increase of heat capacity has occurred.

Characterization of Lignins from Steam Explosion

The results of elemental analysis were C: 57.31, H: 5.56; N: 1.18; S, 0.00; O: 35.95%. We analyzed the presence of carbon and hydrogen in order to characterize the lignin, but also the presence of both nitrogen, as a marker of the presence of proteins in the lignin, and sulfur, as a marker of the presence of sulfate lignins. The presence of sulfur in our samples was not detected. The elemental analysis allows us to give the molecular weight of the lignin expressed in phenylpropanoid (C9) units. In our case the molecular formula was $C_9H_{10.47}O_{4.22}$ with a molecular weight of 186.

The distribution of acetylated lignin considering their molecular weights was obtained by using GPC. The results are depicted in the Figure 1. Most of the molecules of our sample show a molecular weight distribution in the range 100–100 000.
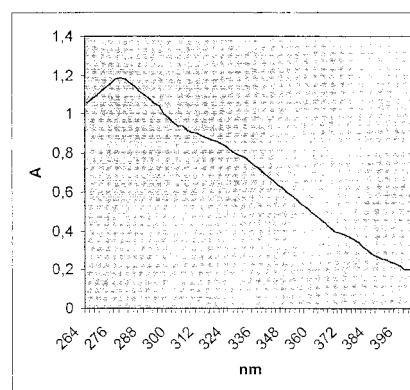


Figure 2   UV spectrum of the lignin.
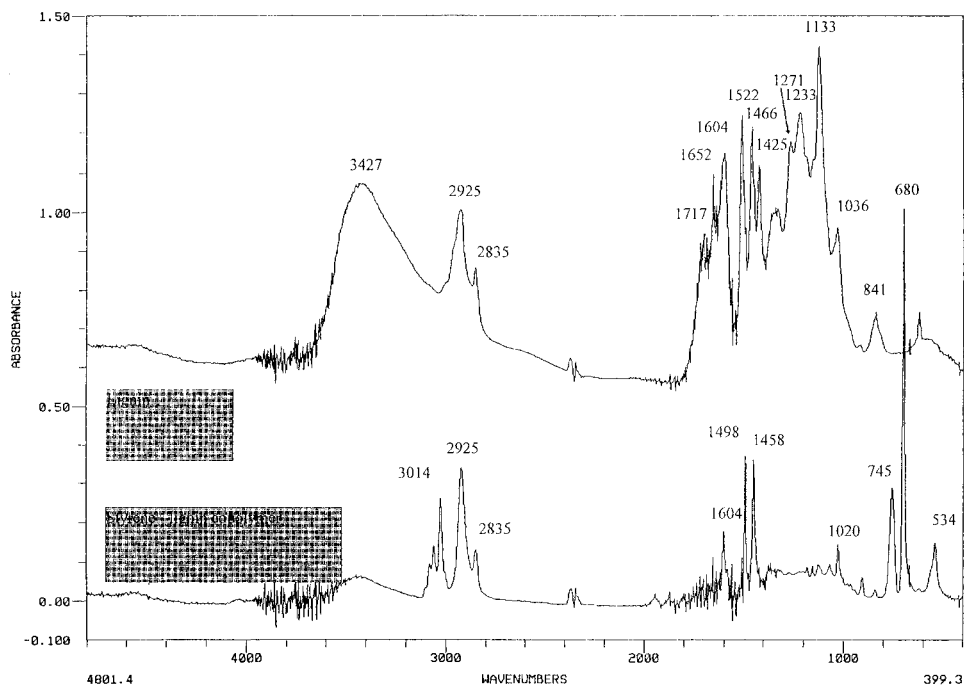
Figure 3 FTIR spectra of lignin from steam-exploded straw and 1-ethenylbenzene-lignin copolymer.

The UV spectra of our samples were recorded in DMF. The spectrum is reported in Figure 2. We observed two peaks at λ 278 (D = 21.60 lg^{-1}cm^{-1}) and 316 nm (D = 17.70 lg^{-1}cm^{-1}). We recorded also the differential spectra obtained carrying out the spectrum of the samples in 1 *M* NaOH vs. the standard solution in DMF. These data allow us to give the amount in mEq g^{-1} of some structural features in the lignin samples. In this case we can give the amounts of syringyl and guaiacyl phenols (Type I), the amounts of phenols containing conjugated double bonds (i.e., HO-Ar-CH=CH-CH$_2$OH, Type II), and the amounts of stilbenic phenols (Type IV). We found in our sample Type I (0.47 mEq/g) and Type IV structures (0.13 mEq/g).[6]
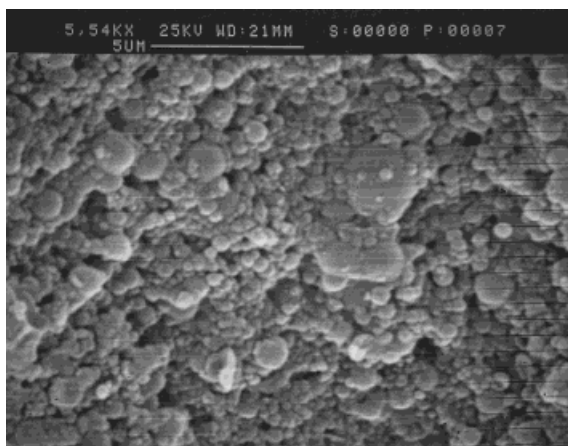
Finally, the characterization of the lignin used in this work was completed by using the ^{13}C and ^{1}H NMR spectroscopy. The signals observed in the ^{13}C
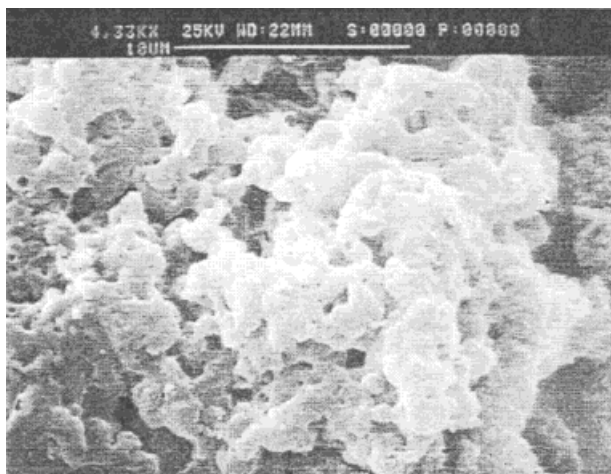
Figure 4 SEM of lignin from steam-exploded straw.



Figure 5 SEM of PSL1 copolymer.

Figure 6 SEM of PSL4 copolymer.

NMR spectrum with our sample were at 173, 153, 148, 145, 138, 135.5, 135, 131, 126, 121, 115, 112, 111, 106, 104,5, 87, 86, 72, and 55.5 ppm.[7,8] From these data we can observe the presence of guaiacyl and syringyl structures. These structures are both β-O-4 etherified and nonetherified. We observe the presence of both *threo* and *erithro* structures. We note the presence of structures of type cinnamaldehyde and stilbenes. The ^{1}H NMR spectrum of the acetylated lignin showed signals at 1.9, 2.0 (aliphatic acetates), 2.18, 2.35 (aromatic acetates), 3.81 (methoxyl), 6.60 (aromatic protons in syringyl structures), 6.92 (aromatic protons in guaiacyl structures), and 7.6 ppm (aromatic protons *ortho* to carbonyl groups).

RESULTS AND DISCUSSION

The styrene-lignin copolymers were obtained by using the procedure described in Meister and Chen.[3] We obtained seven polymers varying the amounts of calcium chloride, hydrogen peroxide
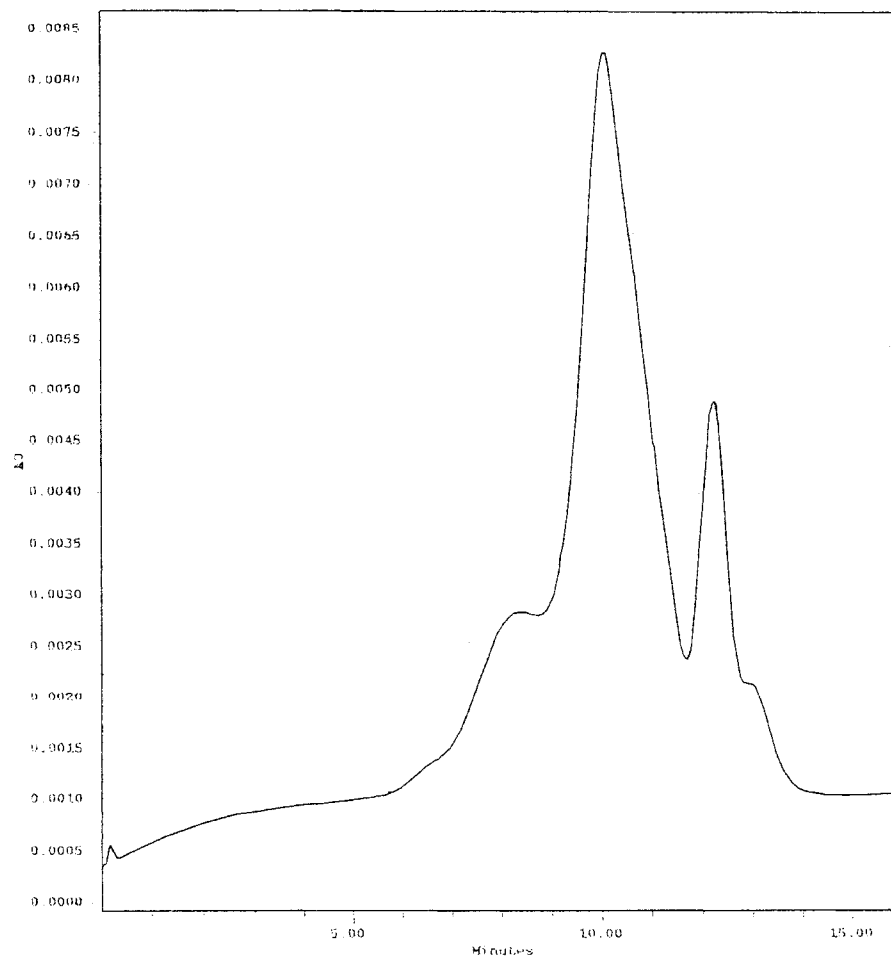
Figure 7 GPC of acetylated PSL1 copolymer.
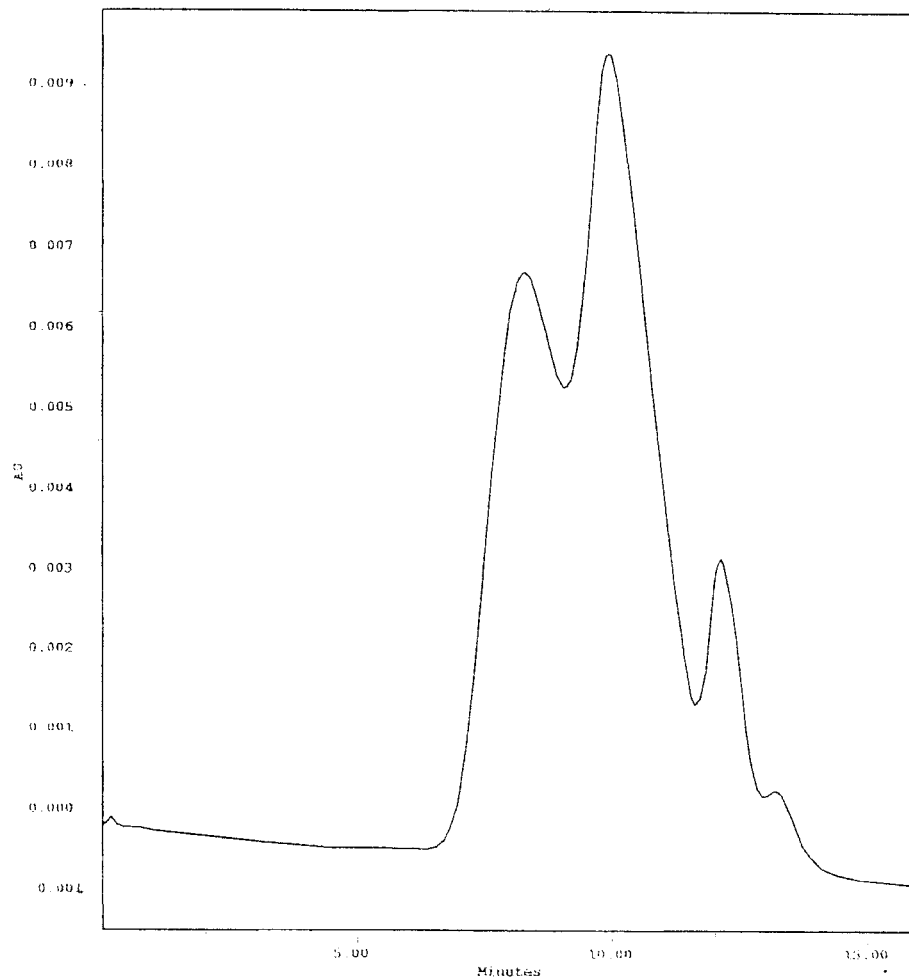
Figure 8   GPC of acetylated PSL6 copolymer.

and DMSO as described in Table I. The variation of the amounts of hydrogen peroxide or dimethyl sulfoxide does not alter the yields of the reaction (Table I). On the contrary, when the reaction is carried out in the presence of a little excess of calcium chloride (Table I, PSL6, PSL7), the yields of the reaction considerably lower. This result was not observed in the procedure described in Bonini et al.,[2] where the amount of calcium chloride was critical to optimize the yields, but no effect due to the presence of an excess of this reagent was observed.

It is noteworthy that the authors postulated the formation of a hydroperoxide chloride complex to induce the polymerization reaction. In this case, the presence of an excess chloride ion should shift towards the complex formation the equilibrium reaction between the hydroperoxide and chloride ion to form the complex.

The formation of the copolymer was confirmed by the Fourier transform infrared (FTIR) spectrum (Fig. 3). The presence of absorptions at 3014, 1498, 1458, 745, and 680 cm^{-1} are diagnostic for the presence of polystyrene chains in the materials, whereas the presence of the absorptions due to the hydroxyl groups at 34276 cm^{-1}, and the absorptions at 2925 and 2835 cm^{-1} are diagnostic for the presence of the lignin.

The formation of a new material can be obtained also by the analysis of the scanning electron microscopy (SEM) images. The SEM of the lignin used in these experiments is reported in Figure 4. We can see that it appears as superimposed plates. On the contrary, in the SEM of PSL3 copolymer (Fig. 5), this structure is lost and the formation of a granular structure is observed. In Figure 6 we reported the SEM photography of the PSL6 copolymer: In this case the granular

Table II   Intrinsic Viscosity and Degree of Polymerization

Sample	η [10^2 cm^3 g^{-1}]	DP$_v$
PSL1	0.20	405
PSL4	0.13	606
PSL6	0.05	1482

structure observed in the previous reported copolymer is lost and the formation of a homogeneous surface is observed.

In conclusion, the SEM analysis of the samples attests that the morphological properties of this material differ depending on the experimental conditions used in the copolymerization process.

Further information about the nature of the copolymer was obtained performing the analysis of the copolymers on acetylated samples (acetic anhydride in pyridine) by using GPC. The acetylation reaction was quenched by treatment with water and the water was then removed by several treatment of the mixture with toluene followed by distillation in vacuo. GPC was also reported in Bonini et al.[2] on the copolymers obtained using softwood and hardwood lignin but the chromatograms are not available. The chromatogram obtained on acetylated PSL1 copolymer is reported in Figure 7. We observed (i) the formation of a new peak at a retention time corresponding to at low molecular weight; this peak is due to the presence of ethenylbenzene in the polymer; (ii) a peak corresponding to lignin; and (iii) a third peak at higher molecular weights appeared.

These results were confirmed for all the polymer. In Figure 8 we report, for example, the results obtained for PSL6 copolymer.

Our hypothesis was confirmed by the determination of intrinsic viscosity (η) and, then, of the degree of polimerization (DP$_v$) of the polymers PSL1-PSL4-PSL6. In this case we observed an increase of the degree of polymerization in the

Table III   Glass Transition Temperatures T_g for Lignin and Graft Copolymers

Sample	Lignin (%)	T_g (°C)
Lignin	100	153.0
PSL1	90.2	153.7
PSL4		152.9
PSL6	100.7	152.8
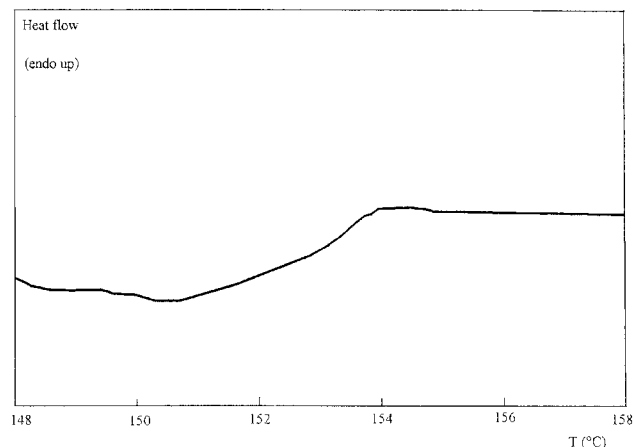
Figure 9   Thermogram of lignin.

PSL6 copolymer, whose GPC showed the presence of chains with high molecular weight (Table II).

The thermogram of neat lignin shows, at 152°C, a gradual increase of the specific heat, which can be easily attributed to the glass transition (Table III, Fig. 9). The thermogram of the sample PSL1 shows the same increase of the specific heat at nearly the same temperature, together with another one at about 90°C, which is likely to correspond to the glass transition of grafted polystyrene (Table III, Figs. 10 and 11). In contrast, the thermogram of sample PSL4 shows only the glass-transition of lignin at about 153°C (Table III). Lastly, the thermogram of the sample PSL6 presents the glass transition of lignin at about 153°C, whereas the glass transition of grafted polystyrene is shifted 10°C above those of the previously examined samples (Table III).
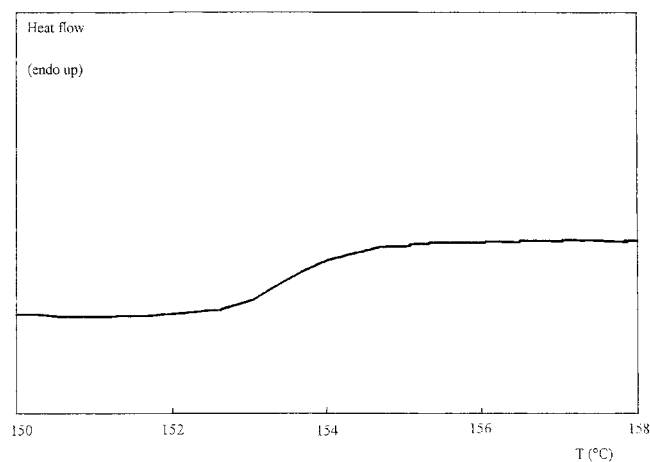
Figure 10   Thermogram of PSL1 copolymer.
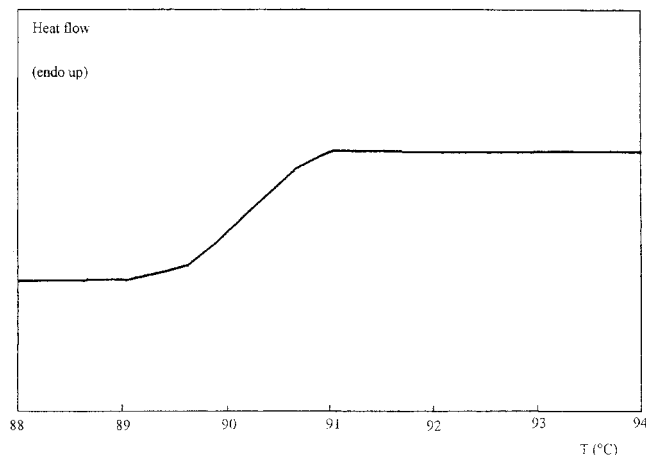
Figure 11 Thermogram of PSL1 copolymer.

These results are in agreement with the GPC analyses, which show an increase in molecular weight corresponding to the polystyrene segment, which has been, in turn, attributed to a cross-linking process, on passing from PSL4 to PSL1 and to PSL6. The DSC thermograms do not reveal the presence of grafted polystyrene in PSL4 (absence of the glass transition of polystyrene), whereas the longest polystyrene chains are present in PSL6 (highest T_g). Moreover, because Tg increases only for the polystyrene segment, whereas for lignin it remains constant, the cross-linking process is likely to involve mainly polystyrene.

An interesting comparison can be made between the DSC thermograms and the SEM observations.

It is well known that the measurement of the glass transition temperature is the most widely used test for the miscibility of two polymers, and a graft copolymer can be well considered as a blend. Then, the double glass transition behavior

points to a phase separation between lignin and grafted polystyrene. This result is in agreement with the morphology observed by SEM for PSL1 (Fig. 5) that shows a well-defined phase-separation. On the other hand, a more sensible measure of the component compatibility and the presence of phase separation, even if not evident in the microscopic observation, can be obtained by the calorimetric measurements, which clearly indicate at least a partial incompatibility at a molecular level also for this sample.

In conclusion, we have shown that steam-exploded straw can be used in the synthesis of copolymers with 1-ethenylbenzene. We have also shown that the copolymerization process induces the formation of long polystyrene side chains in the most of experiments.

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