

## Effect of Irradiation on the Composition and Thermal Properties of Softwood Kraft Lignin and Styrene Grafted Lignin

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**ABSTRACT:** Lignin is an abundant, underutilized natural resource that has potential to be used as a biomaterial but is currently hampered in its use by not being uniform in structure and composition and is thermally unstable due to phenolic group. To address these issues and modify its thermal properties, softwood kraft lignin was modified using  $\gamma$ -irradiation at low doses with and without styrene present and characterized. Irradiation of kraft lignin alone with  $\gamma$ -radiation shows an initial decrease in molecular weight due to chain scission up to about 10 kGy followed by an increase in molecular weight due to crosslinking. NMR results indicate a decrease of about 15% in the OH content of the lignin with 30 kGy irradiation. Thermal properties such as  $T_g$ , free volume and  $\Delta C_p$  follow accordingly. Irradiation at very low dosages was determined to facilitate the grafting of styrene monomer to lignin, decreasing the OH content by 23%. This effect increased the hydrophobicity of the material, depressed the value of  $T_g$ , increased the  $\Delta C_p$ , increased the mobility in the liquid state, and made the material more thermally stable relative to the lignin alone, thus improving its processability at high temperatures. Both the irradiation of lignin alone and the grafting of styrene to lignin increased the yield of mass during pyrolysis and the activation energy for mass loss relative to untreated lignin alone. This work has demonstrated that the application of low dosages of  $\gamma$ -irradiation is a promising method to attach functional molecules onto lignin for use in various applications. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39743.

**KEYWORDS:** cellulose and other wood products; biomaterials; crosslinking; irradiation; lignin; glass transition temperature

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### INTRODUCTION

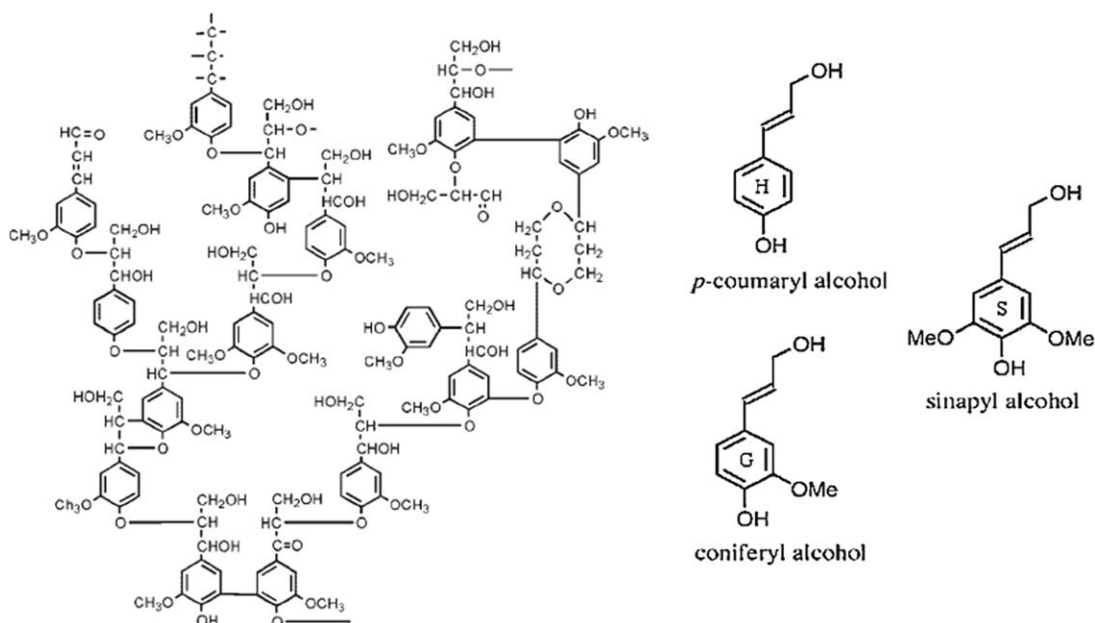
Lignin is one of the most abundant macromolecules existing in the plant kingdom and the second major component of biomass.<sup>1</sup> The chemical structure of lignin varies according to its origin. In contrast to cellulose, which is a linear polymer, the lignin structure is complex and forms a three-dimensional network, as shown in Figure 1.<sup>2</sup> To form the network, mainly three types of monolignols are linked together by different ether and carbon–carbon bonds, Figure 1. As the phenyl-propane units (including *p*-hydroxyl- guaiacyl-, and syringyl-propane units) constitute the basic chain unit of lignin molecules, lignin may roughly be categorized as a hydrophobic polymer. However, a certain portion of the hydroxyl groups attached to phenyl-propane units does facilitate a limited interaction with water.

Hardwood lignins are mainly derived from two monolignolic precursors; coniferyl alcohol and sinapyl alcohol, whereas softwood lignin is derived mainly from coniferyl alcohol. Approximately two thirds of the linkages are ether linkages and

approximately one third is carbon–carbon linkages.<sup>3</sup> The carbon–carbon bonds as well as diaryl ethers are generally more stable as compared with the other ether bonds and are often resistant to processes such as chemical pulping. Because of the differences in the chemical structure of softwoods and hardwoods, the hardwood structure is more linear and less branched.<sup>4</sup>

From an academic point of view, lignin has gained interest as a source of fuel and new materials.<sup>5–10</sup> The main reasons for this trend are due to its renewability, the enormous amount produced as a byproduct of the pulp and paper industry and the growing concern for more sustainability, which results in an increased usage of renewable materials to replace petrochemicals.<sup>11–13</sup> It has long been viewed as potential carbon fiber source and biopolymer for engineering materials.<sup>14,15</sup>

Today, in the paper industry, the kraft lignin in black liquor is used as a fuel in the recovery boiler at the mill.<sup>16</sup> However, the utilization of lignin as a fuel may not be economically optimum; the value equivalent of lignin used as fuel is \$0.18/kg



**Figure 1.** Fragment of the softwood lignin model and the monolignol precursors.<sup>2</sup> The structure of lignin is very complicated and the phenylpropanoid unit is believed to be a main component.

whereas the approximate value of lignin used in chemical conversion can be as high as \$1.08/kg.<sup>17</sup> The conversion of lignin into valuable products is one way to add value to an existing wood processing process, a biorefinery.

Utilization of technical lignin as high value added applications is limited currently. There are several factors restricting the use of lignin namely: a non-uniform structure, unique chemical reactivity, and the presence of various organic and inorganic impurities. Moreover, difficulties exist in the recovery of lignin from the product streams. However, many isolation processes have been approved to use lignin as fuel in thermal power stations or upgraded to more value-added products.<sup>18</sup> In this context, the most interesting value-added product is to make thermoplastic materials and carbon fiber from lignin.<sup>19–22</sup>

The behavior of kraft lignin during heat treatment is important for making new products that are processable and have the correct final properties. Lignin is an amorphous macromolecule, which means that a melting point cannot be obtained for it.<sup>22</sup> The main desirable processing requirement of lignin is to be able to generate a softened or flowable lignin in a temperature window between the softening and decomposition/degradation temperatures.

The phenolic hydroxyl groups and the methoxyl groups are functional groups in lignin, which are important for the reactivity of the lignin. Without modification, the decomposition of softwood kraft lignin has been reported to start at temperatures as low as 120°C, indicated the formation of formaldehyde.<sup>23</sup> In addition, thermally and mechanically generated free radicals are known to exist within lignin.<sup>24</sup> So far, research efforts using milder thermal processing have centered on blending lignin with other synthetic polymers.<sup>15</sup> For example, polyethylene glycol was mechanically blended with hardwood kraft lignin to

improve its extrusion processing characteristics prior to carbon fiber preparation. For this reason, the objective of this work was to develop a method of masking phenolic hydroxyl groups with the aim of reducing its chemical reactivity above its  $T_g$  and by consequence improving its thermal stability.

Due to its technical and environmental advantages over traditional solvent-based treatments, the processing of polymers under ionizing radiations has known increasing industrial developments for the past 20 years, in particular in the field of synthetic coating cross-linking.<sup>25</sup> The radiation-based modification of biopolymers is also a feasible method either to produce material or to tailor their usage properties.<sup>26,27</sup> From a molecular point of view,  $\gamma$ -irradiation was shown to generate free radicals in polymers and then induce various reactions such as scission or crosslinking depending upon both the environmental conditions and the radiation dosage.<sup>28,29</sup>

In this study,  $\gamma$ -irradiation was applied in low dose to different samples of softwood kraft lignin containing different concentrations of styrene to evaluate the potential of such a treatment to block the reactive phenol groups. In a previous study, the grafting of styrene to lignin with high  $\gamma$ -irradiation (50–200 kGy) in the presence of methanol as a solvent was shown but no thermal characterizations of the products were reported.<sup>30–33</sup> This article takes a different approach in which low dosages of irradiation are applied to a solvent-less system with high concentrations of lignin and lower concentrations of styrene. The first aim of this article is to characterize changes in the chemical and physical properties after the styrene grafting process. The secondary objective is to examine the thermal behavior under pyrolysis conditions of unmodified and modified lignin and to identify the kinetic parameters of the thermal reaction.

## MATERIALS AND METHODS

### Materials

Kraft Lignin (Biochoice™) was provided by Domtar Company July 2012 from North Carolina. Specifications about BioChoice™ are as follow: Pure Lignin = 98.3%; Arabinan = 0.2%; Galactan = 0.7%; Glucan = 0.1%, Xylan = 0.4%, Ash = 0.73%; Molecular Weight = 5500 g mol<sup>-1</sup>; pH = 4.1; Glass transition temperature = 148°C; Methoxyl content = 12.3%; Carbon = 64.4%; Hydrogen = 6.24%; Oxygen = 27.9%; Nitrogen = 0.36%; Sulfur = 1.36%; Molecular formula = C<sub>9</sub>H<sub>9.08</sub>O<sub>2.48</sub>(OCH<sub>3</sub>)<sub>0.73</sub>S<sub>0.079</sub>; Inorganic Element [Na = 1089 mg kg<sup>-1</sup>; K = 105 mg kg<sup>-1</sup>; Ca = 157 mg kg<sup>-1</sup>; Si = 5313 mg kg<sup>-1</sup>]; Concentration of OH groups in lignin: Aliphatic phenol = 2.11 mmol g<sup>-1</sup>; Condensed phenol = 1.63 mmol g<sup>-1</sup>; Carboxylic acid groups = 0.53 mmol g<sup>-1</sup>.

The materials were stored in the refrigerator at 5°C after washing with deionized water and centrifuged several times to obtain a final pH ~ 5.4. All chemicals and reagents used in this study were purchased from Sigma-Aldrich and Fisher Chemical companies and used as received.

### γ-Irradiation

Irradiation was performed by the Department of Nuclear Engineering, North Carolina State University, USA on the kraft lignin samples with and without styrene, using a 2 × 10<sup>6</sup> Ci <sup>60</sup>Co source, (Atomic Energy of Canada Limited, AECL, Canada), under an air atmosphere at ambient temperature. The samples were stored at -20°C to prevent the recombination of the free radicals before characterizing. Final doses ranged from 5 to 50 kGy with a precision of ±5%. The measurement of free volume was performed on these irradiated samples using a positron annihilation lifetime (PAL) spectrometer. The PAL spectrometer consists of a fast coincidence system using KL236 plastic scintillator coupled to a RCA-8575 photomultiplier assembly as detector and has a time resolution of 340 ps.

### Radiation Grafting of Styrene onto Lignin

Lignin (5 g) was charged into a glass vial. Styrene was added to lignin so that the styrene content of the mixture was either 13 or 33%. To make a homogenized paste, 1 mL of water was added to the mixture gradually and stirred manually for 15 min. After stirring, the mixture was irradiated by gamma rays to various total doses ranging from 5 to 50 kGy at a dose rate of 0.36 kGy h<sup>-1</sup>. A suspension of 2 g of irradiated mixture of lignin and styrene in 20 mL of toluene was mixed for 3 h at room temperature. The solid was removed by filtration, washed with water and ethanol, and dried at 37°C for 72 h. The solid sample was weighed and used for further studies.

The percentage reaction of styrene grafted to lignin, Y%, was calculated from the following equation, after an extraction step with toluene to remove the styrene not reacted to lignin:

$$Y(\%) = \frac{W_2 - W_1}{W_3} \times 100 \quad (1)$$

where  $W_1$  is the original weight of lignin,  $W_2$  is the weight of products after extraction, and  $W_3$  is weight of styrene monomer added.<sup>34</sup> The resulting weight percent styrene in the product, X%, is calculated as follows:

$$X(\%) = \frac{W_2 - W_1}{W_2} \times 100 \quad (2)$$

### Acetobromination

Due the variable solubility that lignin samples display in THF, all samples examined in this work were subjected to a fast room temperature derivatization procedure, the feasibility and reliability of which has been reported.<sup>23</sup> A quantity of 5 mg of a dried lignin sample was mixed in 2 mL of a glacial acetic acid/acetyl bromide mixture (92 : 8, v/v) and stirred at room temperature for 2 h. The solvents were completely removed at room temperature using a rotary evaporator connected to a cold trap-protected vacuum pump.

### Gel Permeation Chromatography (GPC)

The molecular weight of the lignin and derivatives were determined by gel permeation chromatography (GPC). The acetobrominated samples were dissolved in Tetrahydrofuran (THF) at a concentration of 0.1%, and a 200 μL sample in solution was injected. GPC measurements for molecular weight calculation were carried out with a Waters GPC 510 pump equipped with UV (270 nm) and RI detectors using THF as the eluent at a flow rate of 0.6 mL/min at room temperature. Two Ultrastaygel linear columns linked in series (Styragel HR 1 and Styragel HR 5E) were used for the measurements. Standard mono-disperse polystyrenes with molecular weight ranges from 0.82 to 1860 kg/mol were used for the calibration. The number- and weight-average molecular weights were calculated using Millenium software of Waters.

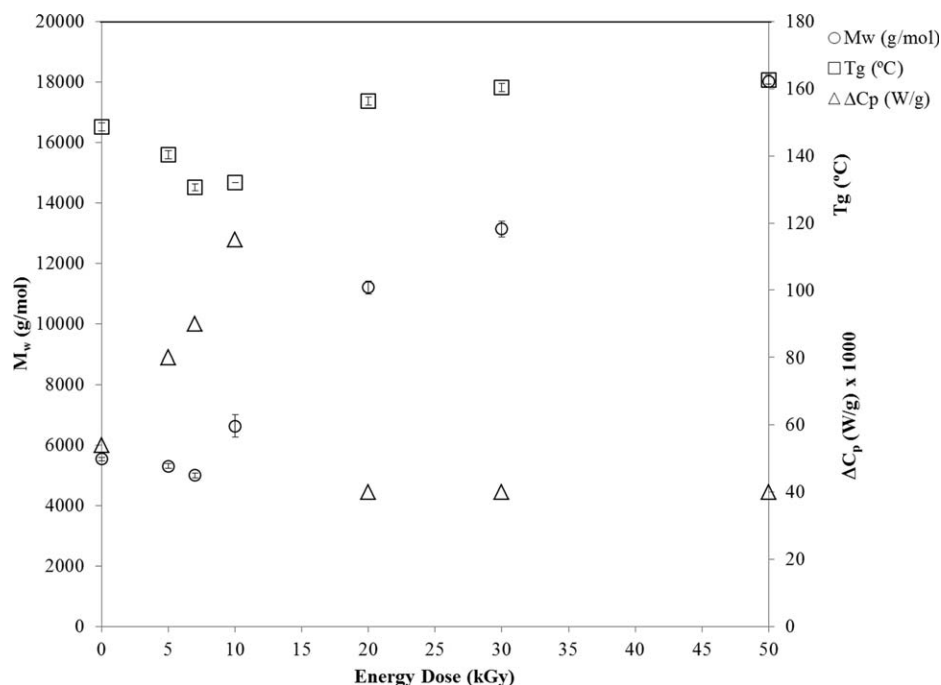
### FTIR and <sup>31</sup>P NMR Analysis

The Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a NEXUS 670 FTIR spectrophotometer (Thermo Electron Corp., Madison, WI) using KBr disc containing 2% (mg/mg) finely ground sample particles. All the spectra were obtained by accumulation of 256 scans, with resolution of 4 cm<sup>-1</sup>, at 400–4000 cm<sup>-1</sup>.

The effect of the irradiation on kraft lignin without and with styrene were determined using quantitative <sup>31</sup>P Nuclear Magnetic Resonance (NMR) to determine various hydroxyl groups quantitatively, following published procedures.<sup>35</sup> Lignin (40 mg OD) was dissolved in 500 μm of an anhydrous pyridine/CDCl<sub>3</sub> mixture (1.6 : 2, v/v). Two hundred μm of endo-N-hydroxy-5-norbornene-2,3-dicarboximide (e-NHI) solution (9.23 mg/mL as the internal standard and 50 μm of chromium (III) acetylacetonate solution (5.6 mg/mL) in the above pyridine/CDCl<sub>3</sub> solution) as a relaxation reagent were then added. Finally, 100 μm of phosphitylating reagent (2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane) was added prior to NMR acquisition. NMR spectra were acquired using a Bruker 300 MHz spectrometer equipped with a Quad probe dedicated to <sup>31</sup>P acquisition.

### Thermal Analysis

The thermal transitions of the samples were studied using differential scanning calorimetry (DSC). The instrument used was a DSCQ100 (TA, New Castle, DE) with a hermetic pan (T 090127) under nitrogen purge with an empty pan as reference. Approximately 5 mg of a sample were weighed directly into a DSC aluminum sample pan with a pinhole created in the lid. Samples were subjected to 10°C/min temperature ramp. The thermal



**Figure 2.** Glass transition of kraft lignin and its molecular weight as a function of irradiation energy. The experiments were done in triplicate and the standard deviations are shown with error bars.

history of the samples in the DSC was the following: (1) sample was heated from 40 to 105°C at a rate of 10°C/min, (2) isothermally conditioned for 10 min, (3) jumped to 10°C using liquid nitrogen, and (4) ramped to 200°C at a heating rate of 10°C/min. The glass transition temperature ( $T_g$ ) for each sample was determined as the midpoint of the change of the heat capacity associated with the glass transition. In some cases, the thermal history procedure was repeated to monitor changes in thermal behavior upon repeated cycling above the  $T_g$ .

Thermal gravimetric analysis (TGA) was performed with a Q500 instrument (TA, New Castle, DE) on 10 mg of samples in a nitrogen atmosphere. Samples were heated at 10°C/min to 105°C, maintained for 10 min, and then heated at 10°C/min to 600°C. Each sample was repeated three times and the average of the results reported.

#### Water Contact Angle Measurement

Contact angle measurements were performed with a NRL Contact Angle Goniometer by Rame Hart (model 100–00). A drop of deionized water (mass ~ 35mg) was placed on the top of the film. The contact angles on two sides of the drop were measured immediately and the average reported.

## RESULTS AND DISCUSSION

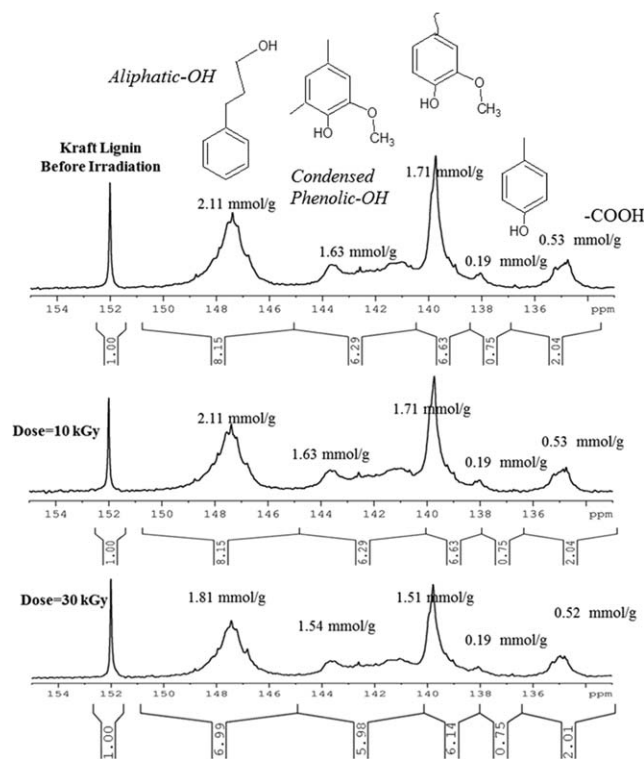
### Effect of Irradiation on Lignin

Reaction mechanisms induced by irradiation of lignin and lignin model compounds have been extensively described. Irradiation energy absorbed by the lignin changes the electronic energy of the molecule resulting in the transitions of valence electrons causing various physical and chemical processes. Radiation from  $\gamma$ -sources has sufficient energy to cleave bonds in many polymers, thereby producing free radicals.<sup>28</sup> The radicals so pro-

duced can initiate further reactions such as crosslinking. The most prominent reactive species generated are pendant or end groups such as hydrogen or phenol as examples. It has been well established that structural and chemical properties change with irradiation. Crosslinking enhances mechanical stability while scission degrades mechanical strength. The exact effect produced in a polymer depends on the structure of the polymer and on the dose and intensity of the irradiation.

The weight averaged molecular weight decreases slightly with irradiation energy up to an energy dose of 10 kGy and then increases with further irradiation, Figure 2. This indicates that chain-scission leading to free radical formation is the dominant process in the early stage of  $\gamma$ -irradiation. A recombination of reactive species in a crosslinking reaction later causes the average molecular weight to increase, Figure 2.

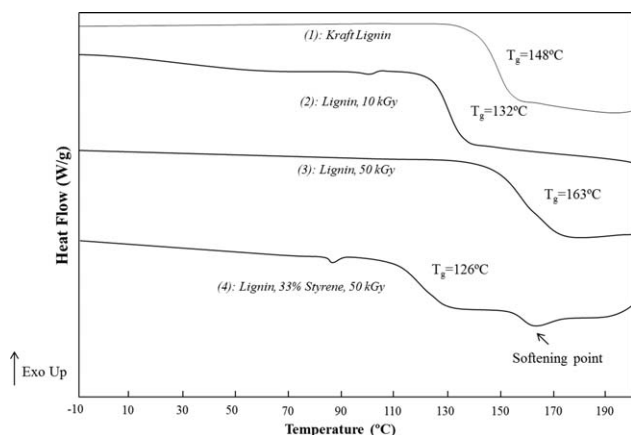
The changes in chemistry of the irradiated lignin were followed by <sup>31</sup>P NMR since the variation of various hydroxyl groups can be elucidated. In Figure 3, the <sup>31</sup>P NMR spectrum of samples with 0, 10, and 30 kGy are shown. The integration of the peaks of different OH groups on aliphatic, condensed and non-condensed phenolic hydroxyl groups, and acid groups all show decreases in concentration with irradiation at a 30 kGy level. Under the irradiation conditions, the phenoxy radicals can be generated via a hydrogen abstraction process. These radicals ( $R^\cdot$ ) can interact with other pendants and initiate chemical modifications of the macromolecule. Thus, the measured decreases in phenolic groups are consistent with the ultimate increases in the molecular weight of the lignin after an initial period dominated by scission. The chemistry of degradation of lignin has been studied; however, the mechanism of such behavior is still under debate because most of the previous studies



**Figure 3.**  $^{31}\text{P}$  NMR spectrum of kraft softwood lignin before irradiation and after irradiation at 10 and 30 kGy.

were done under different exposure conditions.<sup>24,29</sup> Lignin irradiated at 10 kGy or less doses not show any significant differences in any hydroxyl group content, compared to the non-irradiated sample. This and the molecular weight data suggest that chain scission and not recombination of radicals is dominant in the early stages of irradiation (Figures 2 and 3).

The glass transition temperature ( $T_g$ ) is a transition upon heating from glass to a liquid or rubbery state. The transition is associated with the energy required to allow segmental motions to occur such that individual molecules can move independently. The value of  $T_g$  is known to generally increase with increased molecular weight and crosslinking density, both phenomena gen-



**Figure 4.** DSC curves of unmodified and modified kraft softwood lignin, heating rate =  $10^\circ\text{C}/\text{min}$ . (The sample with 33% charged styrene has 19% styrene content.)

erally causing a decreased molecular mobility. The value of the  $T_g$  of the untreated lignin was  $148^\circ\text{C}$ , Figure 4. The value of  $T_g$  decreased to  $132^\circ\text{C}$  in the lignin up to 10 kGy and then increased to  $160^\circ\text{C}$ , Figures 2 and 4. This behavior is consistent with the observed net molecular weight decreases up to 10 kGy followed by molecular weight increases with increased irradiation, Figure 2. In fact, the  $T_g$  was determined to have a weak linear correlation with the molecular weight with an equation of  $T_g$  ( $^\circ\text{C}$ ) =  $0.0022M_w(\text{g}/\text{mol}) + 127$ ;  $R^2 = 0.8$ , data not shown.

The free volume, unoccupied space in an amorphous material that allows for segmental motions to occur, has been widely used to explain the glass transition. Wang et al.<sup>36</sup> proposed a semi-empirical relation that can be used to evaluate the fractional free volume,  $F(\%)$ :

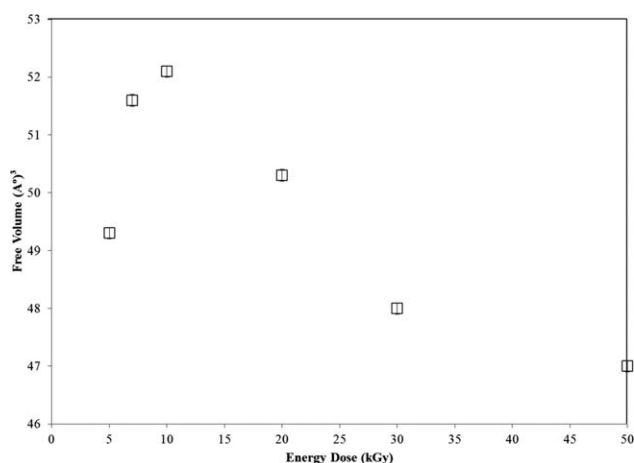
$$F(\%) = A \times I_3 \times V \quad (3)$$

where  $V$  ( $\text{\AA}^3$ ) =  $4\pi R^3/3$  is the size of the nanoscale free-volume hole.  $A = 0.0014$  is the normalization constant,  $I_3$  is the intensity in % attributed to the pickoff annihilation of o-Ps in the nanoscale free volume holes and  $R$  ( $\text{\AA}$ ) value is taken from the following relation based on a simple quantum mechanical model:

$$\frac{0.5}{\tau_3} = \left[ 1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + \Delta R}\right) \right] \quad (4)$$

where  $\tau_3$  (%) is the measured o-Ps lifetime and  $\Delta R = 1.656 \text{ \AA}$  which is an empirical parameter obtained through the fitting of the measured lifetimes cavities of a known size.

Materials with increased free volume have increased mobility and thus lower  $T_g$ . The free volume was measured on samples with different levels of irradiation at room temperature using PAL. The free volume is shown to increase up to 10 kGy and then decrease with further irradiation (Figure 5), consistent with the  $T_g$  dependence on irradiation. The change in heat capacity at the glass transition temperature ( $\Delta C_p$ ) reflects the differences in mobility between the glassy and liquid rubbery state and the  $\Delta C_p$  versus irradiation dose data showing a



**Figure 5.** Free volume at room temperature a function of energy dose for kraft softwood lignin. (Error bars indicate  $\pm$  one standard deviation for three measurements.)

**Table I.** The Percentage of the Initial Styrene Reacted to Lignin  $Y$  (%) and the Resulting Weight Percent of Styrene in the Grafted Lignin,  $X$  (%)

Dose (kGy)	Styrene charge (%)	$Y$ (%)	$X$ (%)
0	13	0	0
5	13	91	10
7	13	96	11
10	13	79	9
20	13	80	9
30	13	70	8
50	13	73	9
0	33	0	0
5	33	79	21
7	33	79	21
10	33	77	20
20	33	71	19
30	33	68	18
50	33	69	19

maximum at 10 kGy (Figure 2) is in agreement with the free volume maximum at 10 kGy.

Investigations with polystyrene and  $\gamma$ -radiation<sup>37</sup> and aromatic polycarbonate and UV- radiation<sup>38</sup> also showed a similar behavior regarding the glass transition temperature and free volume versus irradiation. Moreover, Ramani and Ranganathaiah<sup>39</sup> in a viscosity measurement on irradiated polycarbonate reported a minimum in molecular weight versus irradiation due to chain scission and partial crosslinking.

#### Effect of Styrene Grafting to Lignin

During the irradiation of a mixture of styrene and lignin, the absorption from ionizing radiation is expected to be scattered over the components. The electrons are taken by the lignin molecules to produce radicals within the lignin chains. Hydroxyl radicals in the macromolecule are the reactive species of lignin irradiated. Then the most probable mechanism is the addition of a styrene molecule to the lignin-based radical, follow by styrene polymerization. These reactions cause formation of grafted styrene or short chains of oligo-styrene onto lignin.

Mixtures of styrene and lignin were exposed to  $\gamma$ -irradiation and the percentage of styrene reacted with lignin and the weight percentage of styrene on lignin was determined, Table I. The styrene and oligomeric polystyrene not reacted to lignin was removed from the product by solubilizing in toluene; the grafted lignin was insoluble in toluene. The amount of styrene monomer and the dose of irradiation showed significant effects on the percentage of styrene reacted with lignin,  $Y$  (%). The lower styrene content charge of 13% led to the highest yields, which is consistent with another study using styrene and starch as the polymer.<sup>34</sup> In general, there will be an optimum monomer concentration for each system because too low of a concentration of styrene leads to a decrease in the length of grafted chains and too high a concentration leads to more homopolymerization of styrene. The lower doses of irradiation resulted in a higher percentage of styrene reacted with lignin for both the 13 and 33% levels. The

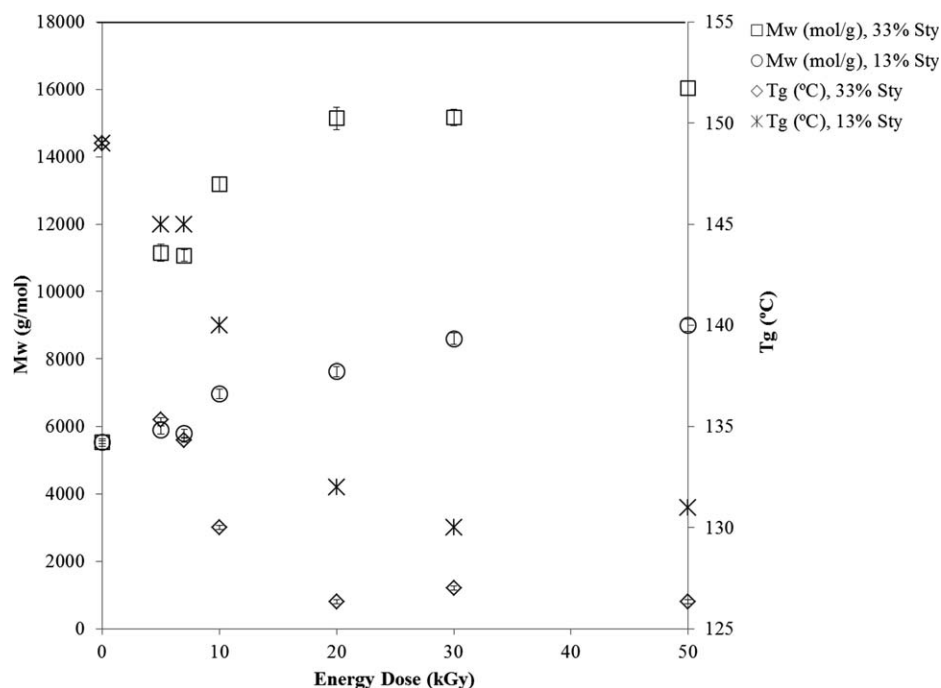
polymerization is a complex process which exhibits a number of anomalous behaviors with respect to the reaction kinetics and mechanism: initial auto-acceleration followed by auto-deceleration due to the termination process controlled by reaction diffusion. This causes drastic variations of the reactive species mobility and will ultimately lead to a premature ending of the chain reaction. In this study, the higher dose has increased the termination process of the grafting and this was demonstrated by the limitation of increasing of the molecular weight. The weight % of styrene in the product was around 20% for the 33% styrene charge and around 10% for the 13% styrene charge. The weight % of styrene trended with the percentage of styrene reacted with the lignin, as expected.

The molecular weight increases with the dose of irradiation and concentration of styrene, Figure 6. Note that this behavior does not show the initial decrease in molecular weight as did the lignin alone in Figure 2. This may be due to radicals on the lignin preferentially reacting with styrene rather than participating in scission or condensation reactions. The value of the  $T_g$  decreases on styrene grafting, Figures 4 and 6. The decreases in  $T_g$  with increased irradiation are consistent with the styrene monomer replacing OH groups on the lignin decreasing the intermolecular forces and thus allowing more mobility. The grafted styrene is acting as a self-plasticizer, the  $T_g$  of polystyrene is around 105°C. The  $T_g$  of the systems charged with 33% styrene with a styrene weight percentage of product around 20% was lower than the  $T_g$  of the systems with 13% charged with a styrene weight percentage of around 10%, as would be expected with increased self-plasticizer concentration. The results showed that the  $\Delta C_p$  increased to 0.1 W/g with grafting at 33% styrene and 50 kGy, relative to the ungrafted lignin at 0.056 W/g.

Detailed analyses of the various hydroxyl-bearing functional groups present in the untreated and irradiated kraft lignins with styrene was carried out using quantitative <sup>31</sup>P NMR in the presence of an internal standard, Figure 7. The amounts of aliphatic and non-condensed phenolic and condensed phenolic hydroxyl groups were reduced by 25%, 26%, and 22%, respectively.

Infrared spectrum of a sample (33% styrene, 10 kGy) in comparison with kraft lignin and a polystyrene spectrum are shown in Figure 8. The lignin modified after irradiation with styrene (33%) at 10 kGy contains all the characteristics absorption peaks of lignin containing, 3500–3000  $\text{cm}^{-1}$ , 2930  $\text{cm}^{-1}$ , for the O–H stretching, C–H stretching, and C–O stretching, respectively. Moreover, absorption peaks including 3024  $\text{cm}^{-1}$  (1600, 1490, 760, 700  $\text{cm}^{-1}$ ), and 2000–1700  $\text{cm}^{-1}$  for the aromatic C=C stretching, respectively, are all observed in the grafted lignin. These results confirm the styrene and lignin grafting reaction due to irradiation.

The grafting of the styrene onto the lignin resulted in significant changes in the physical properties of the material. The contact angle with water increased from  $64 \pm 3^\circ$  on the untreated lignin (cast from dioxane) to  $78 \pm 5^\circ$  on the styrene grafted lignin (30 kGy, 33% styrene charge, 19% styrene grafted by weight, cast from THF). The measured contact angle for polystyrene was  $83 \pm 1^\circ$ , somewhat above the styrene grafted lignin. The contact angles indicate that polar groups are being reacted with

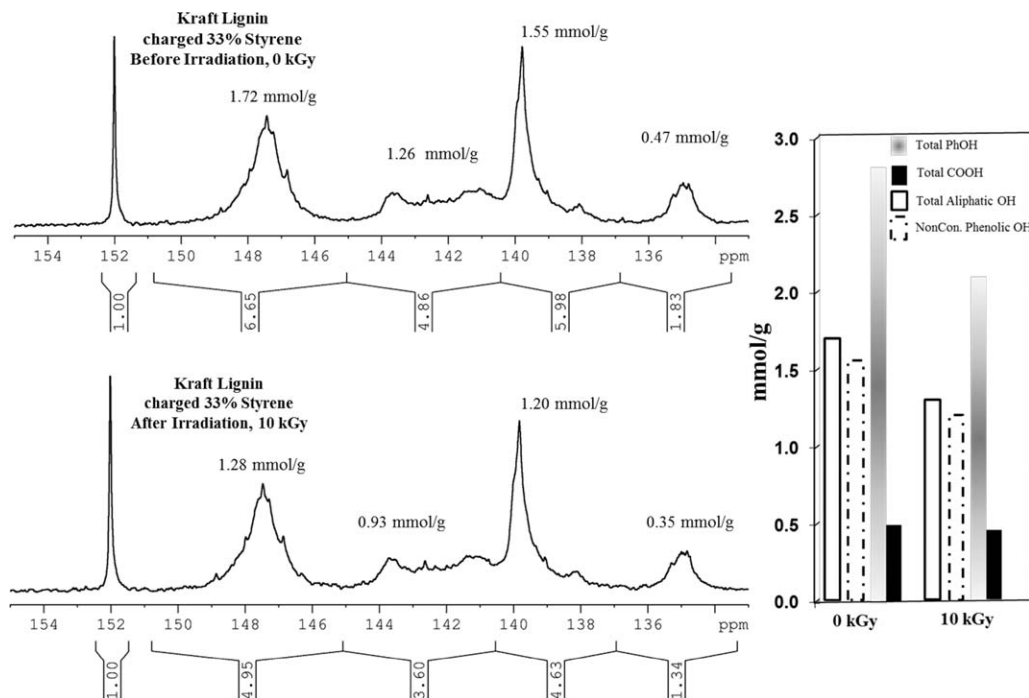


**Figure 6.** Glass transition and molecular weight of kraft lignin with 13 and 33% of charged styrene versus irradiation energy. The experiments were done in triplicate and the standard deviations are shown with error bars.

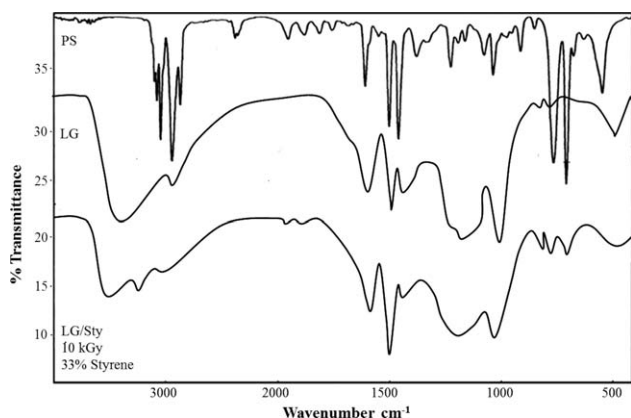
styrene, making the material more hydrophobic. Further, the thin films of styrene grafted lignin solvent cast from THF onto glass slides had a much lower adhesion to the glass film than did lignin films cast from dioxane, supposedly due to the chemical modification of OH groups in the lignin.

To further investigate the changes in the thermal properties of lignin after irradiation and after grafting with styrene, thermogravimetric analysis on heating at 10°C/min to 600°C under nitrogen was conducted, Figure 9 and Table II. A first gradual weight loss occurred in the ranges of 162–270°C for all lignin containing materials. This weight loss is not present in polystyrene, so is attributed to changes in the lignin fraction of the material. Increased amounts of styrene grafted onto the lignin decrease the mass loss in this temperature range, again reflecting

changes in the lignin fraction of the material. Increased amounts of styrene grafted onto the lignin decrease the mass loss in this temperature range, again reflecting



**Figure 7.**  $^{31}\text{P}$  NMR spectrum of kraft lignin before and after irradiation and styrene grafting at dose = 10 kGy.



**Figure 8.** FTIR spectrum of polystyrene (PS), lignin (LG), and lignin/styrene (33% charged styrene, 10 kGy).

that the styrene is promoting heat stabilization of the lignin. This may be due to a simple dilution of the lignin with grafted styrene material or other reason. Irradiation of the lignin without styrene present also decreases weight loss in this temperature range, indicating a more stable structure, presumably due to free radical crosslinking of the lignin during irradiation, consistent with the molecular weight behavior in Figure 2 and the NMR data for lignin alone, Figure 3.

At higher temperatures above 270°C, continued mass loss is observed. Irradiation of the lignin at 30 kGy decreases the mass loss up to 600°C by 7% (of the original mass) relative to the non-irradiated lignin. Irradiation of lignin up to 10 kGy showed similar weight loss behavior as the non-irradiated lignin, Table II. Styrene grafted lignin shows even lower mass losses than the irradiated lignin alone. This indicates that the styrene grafted lignin is more thermally stable than the lignin alone. A drastic mass loss is not observed for the styrene grafted to lignin in the temperature range in which PS decomposes, around 400°C,

which suggests that large phase separated macromolecules of polystyrene are not present in the material.

To further explore the ability of grafting styrene to produce a more stable thermoplastic material for processing, repeated cycling of the materials between room temperature and 200°C was performed in a DSC and the  $T_g$  and  $\Delta C_p$  was tracked, Figure 10. The value of the  $T_g$  of the lignin alone increased with each ramp to 200°C with smaller increases in subsequent ramps. The  $\Delta C_p$  decreased for each ramp also. Both of these can be attributed to lower mobility of the lignin due to chemical reactions such as crosslinking. The styrene grafted lignin also showed an increase in  $T_g$  upon the second ramp to 200°C but no further increases on the third and fourth ramps. However, for the styrene grafted lignin the  $\Delta C_p$  did not decrease significantly as did the lignin alone sample, further evidence that the chemical reactions above  $T_g$  are reduced when styrene is grafted. There also appears to be a weak endothermic peak for the styrene grafted lignin around 170°C that is repeatable.

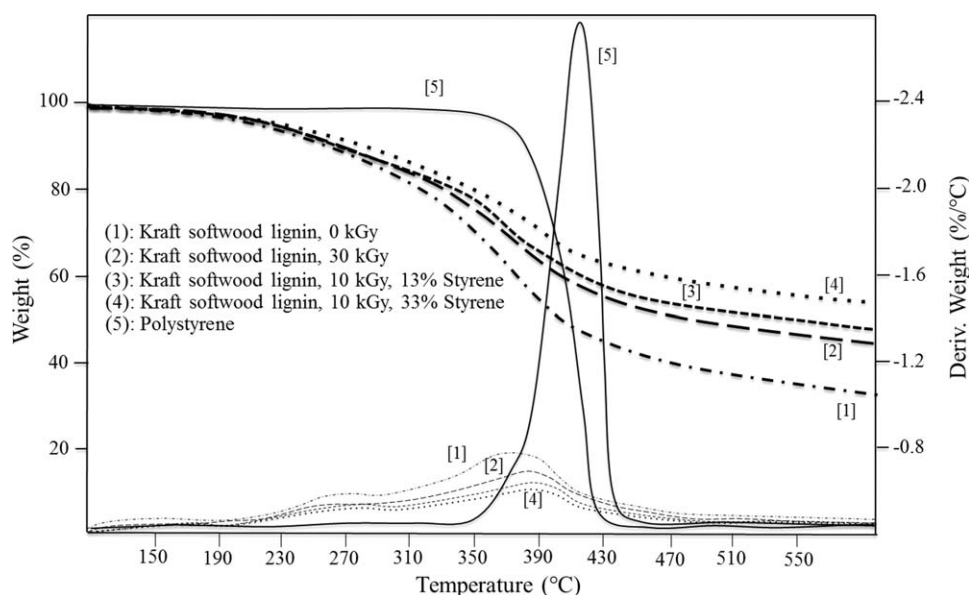
Modeling of the degradation reactions during pyrolysis that cause mass loss has been performed according to Murugan et al.<sup>40</sup> for a non-isothermal process with a linear heating rate. It is assumed that heat transfer is instantaneous and no temperature gradient exists within the sample. Under these conditions, the reaction kinetics can be modeled with the following general equation:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (5)$$

here,  $\alpha$  is the fraction reacted in time  $t$  and is equal to:

$$\alpha = (m_i - m) / (m_i - m_f) \quad (6)$$

where  $m_i$  is the initial mass of the sample,  $m$  is the mass at time  $t$ , and  $m_f$  is the final mass of the sample;  $n$  = order of



**Figure 9.** TGA and dTGA curves for untreated (1), modified lignin (2–4), and polystyrene (5).



**Table II.** Activation Energy ( $E$ ) for the Different Ranges of Temperatures from the Plot of  $\ln \left[ \frac{-\ln(1-\alpha)}{T^2} \right]$  Versus ( $1/T$ ) for Untreated and Modified Kraft Softwood Lignin

Sample	CS (%)	Dose (kGy)	X (%)	ML% $T = 270^\circ\text{C}$	ML% $T = 600^\circ\text{C}$	$E$ ( $\text{kJ mol}^{-1}$ ) $110^\circ\text{C} < T < 150^\circ\text{C}$	$E$ ( $\text{kJ mol}^{-1}$ ) $175^\circ\text{C} < T < 265^\circ\text{C}$	$E$ ( $\text{kJ mol}^{-1}$ ) $270^\circ\text{C} < T < 450^\circ\text{C}$
KL	0	0	0	12	59	29	49	26
KL	0	5	0	12	59	29	49	26
KL	0	10	0	12	59	29	49	26
KL	0	30	0	11	52	30	54	32
KL	13	10	9	11	51	35	52	49
KL	33	10	20	8	39	39	61	58
PS	-	-	-	1	100	n/a	n/a	172

KL = kraft lignin; PS = polystyrene; CS = % charged styrene; X% is the weight percent of styrene in the grafted lignin, ML = mass loss.

reaction and  $k$  = rate constant that obeys the Arrhenius relationship given by the expression:

$$k = A \exp(-E/RT) \quad (7)$$

where  $A$  = pre-exponential factor,  $E$  = activation energy of the reaction in J/mol,  $R$  is the universal gas constant, 8.314462 J/(mol·K), and  $T$  is the absolute temperature in K.

For a constant heating rate of  $\beta$

$$\beta = \frac{dT}{dt} \quad (8)$$

Combining eqs. (5), (7), and (8), rearranging and integrating, we get:

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \int_0^T e^{-E/RT} dT \quad (9)$$

By following Murugan et al.<sup>40</sup> methods, for  $n = 1$ , eq. (9) becomes

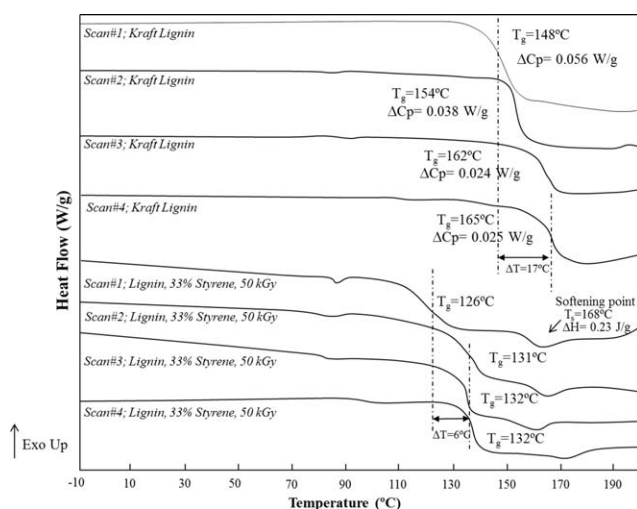
$$\ln \left[ \frac{-\ln(1-\alpha)}{T^2} \right] = \ln \left[ \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (10)$$

The value of  $E$  is calculated from the plot of  $\ln \left[ \frac{-\ln(1-\alpha)}{T^2} \right]$  versus ( $1/T$ ). Note, it is assumed that  $2RT/E$  is much less than 1 in equation (10).

The fit of the model to the data was very good, indicating three events with activation energies with  $R^2$  values all above 0.87, Table II. The activation energy of mass loss increased for lignin alone with irradiation relative to non-irradiated lignin. Also, the activation energy for styrene grafted lignin was higher than lignin alone. The activation energy for lignin alone and polystyrene alone is similar to those in the literature.<sup>40</sup> These results indicate a higher stability of lignin after irradiation and after grafting of styrene, in agreement with some combination of increased blocking of reactive phenolic OH groups, crosslinking and molecular weight.

## CONCLUSIONS

Kraft lignin irradiated by  $\gamma$ -sources produced an initial decrease in molecular weight due to chain scission up to about 10 kGy followed by an increase in molecular weight due to crosslinking. A decrease of about 14% in the OH content of the lignin has been indicated by <sup>31</sup>P NMR with a dose of 30 kGy. The glass transition temperature,  $\Delta C_p$  and free volume follow accordingly. The reaction between lignin and styrene monomer under  $\gamma$ -irradiation from 5 to 50 kGy led to the formation of a lignin grafted styrene. Irradiation at very low dosages was determined to facilitate the grafting of styrene monomer to lignin. The <sup>31</sup>P NMR showed a decrease in OH content of 23% with the styrene grafting to lignin. This effect increased the hydrophobicity of the material, increased the  $\Delta C_p$ , increased the mobility in the liquid state, and made the material more thermally stable relative to the lignin alone, thus improving its processability at high temperatures. Both the irradiation of lignin alone and the grafting of styrene to lignin increased the yield of mass during pyrolysis and the activation energy for mass loss relative to lignin alone. This type of research is one of the first steps in modifying renewable lignin so that it is a more consistent and reliable precursor for material applications. Irradiation is a



**Figure 10.** DSC curves of unmodified and modified kraft softwood lignin after repetitive scans to 200°C at 10°C/min. (The sample with 33% charged styrene has 19% styrene content).

promising green tool in this respect and optimized/alternative methods to utilize irradiation to improve lignin as a precursor in a cost effective manner should be pursued.

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