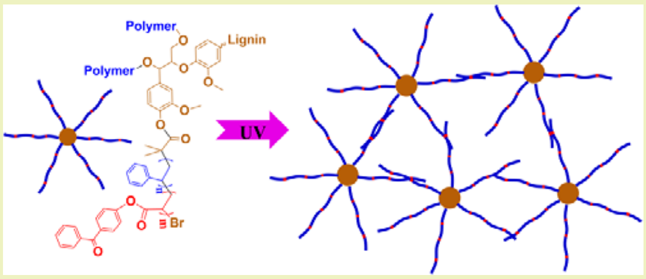
ACS Sustainable Chemistry & Engineering
Research Article
pubs.acs.org/journal/ascecg

UV Cross-Linkable Lignin Thermoplastic Graft Copolymers

Chao Wang and Richard A. Venditti*

Department of Forest Biomaterials, North Carolina State University, Raleigh, North Carolina 27695, United States

Supporting Information



ABSTRACT: This work highlighted a new method to prepare UV curable lignin thermoplastic copolymers, which are expected to show applications as functional materials (e.g., carbon fiber precursors) with improved thermal stability, solvent resistance and surface hardness. UV cross-linkable lignin graft copolymers were synthesized via activator regenerated by electron transfer (ARGET) atom transfer radical polymerization (ATRP) and characterized. By incorporating a photosensitive compound, acryloyl benzophenone (ABP), as a comonomer during the polymerization, lignin-*g*-poly(styrene-*co*-ABP) copolymers with 6−9% (mol %) of ABP moieties were obtained. The lignin graft copolymers showed similar glass transition temperature (~100 °C) as polystyrene. The carbon yields during pyrolysis decreased as the degrees of polymerization of the graft copolymers increased. Under UV irradiation, up to ~30 wt % of the lignin-*g*-poly(styrene-*co*-ABP) copolymers cross-linked to form polymer networks, whereas less than ~5 wt % of the lignin-*g*-polystyrene copolymers formed gelled structures.

KEYWORDS: *Lignin, Graft copolymer, Atom transfer radical polymerization, UV cross-linking, Thermoplastic*

INTRODUCTION

Lignin is a complex phenolic heteropolymer derived from woody tissues. As one of the most abundant renewable biopolymers, lignin accounts for about 30% of the nonfossil organic carbon in the biosphere.[1] Lignin is produced mainly as a byproduct from various pulping or biomass pretreatment processes. Traditionally, lignin is treated as a waste and usually combusted for energy. Recently, the transformation of lignin applications from low-value wastes to value-added products has attracted increasing interest. Great efforts have been made to investigate the utilization of lignin as building blocks for polymeric materials (e.g., polyurethanes and epoxy resins),[2−8] reinforcing fillers for polymer composites,[9−11] precursors for carbon materials (e.g., carbon fibers and active carbon)[7,12,13] and feedstocks for specialty chemicals (e.g., toluene and vanillin).[14−18]

As a natural polymer, lignin undergoes radical-induced self-condensation at high temperatures, which limits its thermal processability.[19,20] Additionally, technical lignin has relative low molecular weight, and lignin-based materials are usually brittle and thus exhibit poor mechanical properties. Blending or copolymerization with synthetic polymers usually improves the thermal and mechanical properties of lignin derivatives. Molecular modification of lignin via polymer grafting overcomes the incompatibility of lignin with synthetic polymers. The resulting lignin graft copolymers usually exhibit enhanced thermal processability and recyclability compared to the traditional lignin-based thermosetting polymer networks.[21−24]

Lignin graft copolymers have been prepared via both "grafting onto" and "grafting from" approaches. In a "graft onto" method, polymers are coupled to the hydroxyl or other functional groups of lignin via covalent bond formation, including diisocyanate[25,26] and boron[27] mediated coupling, and azide alkyne Huisgen cycloaddition (click chemistry).[28] On the other hand, monomers can be polymerized directly from the lignin cores via free radical polymerization,[23,29,30] ring opening polymerization[22,31,32] and chemo-enzymatic polymerization[33,34] in a "graft from" approach. Recently, atom transfer radical polymerization (ATRP) has shown potential as a powerful tool to prepare functional polymeric materials with well-defined molecular weights and architectures based on a variety of natural polymers, including lignin.[24,35−37]

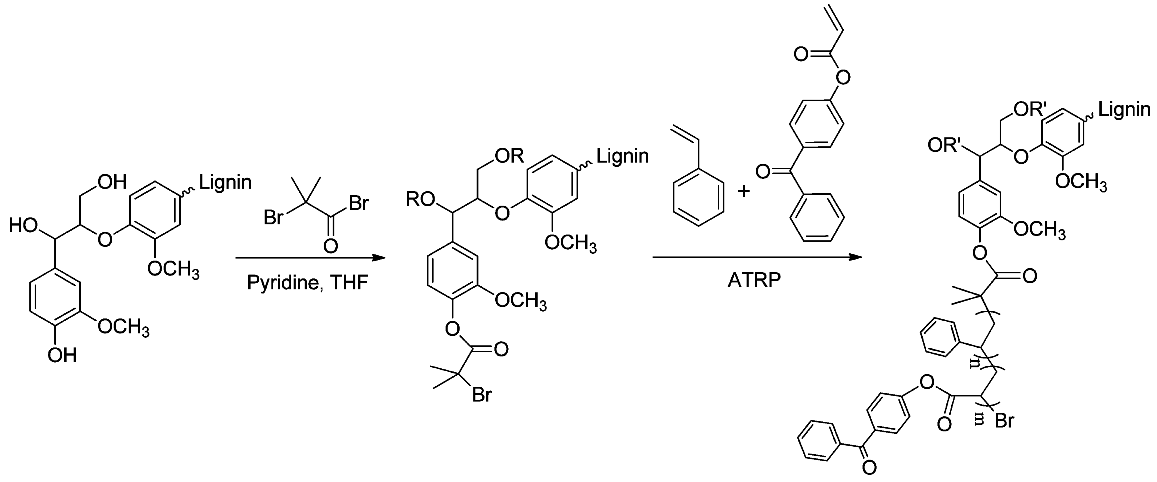
Postpolymerization modification, such as photo-cross-linking, provides a cost-effective, convenient and robust alternative to afford novel properties to polymeric materials.[38] By introducing photosensitive moieties into lignin derivatives, functional materials with improved surface hardness, solvent resistance and thermal stability, such as for coatings, hydrogels and carbon fiber precursors, are expected upon UV irradiation.

In this research, UV cross-linkable lignin graft polystyrene copolymers were synthesized via activator regenerated by electron transfer (ARGET) ATRP. A UV sensitive compound, acryloyl benzophenone (ABP), was incorporated as a comonomer during the polymerization. The structures, thermal and UV cross-linking properties of the resulting copolymers were investigated. This information is expected to provide a convenient method to make photo-cross-linkable lignin derivatives with well-defined structures.

Received: May 11, 2015
Revised: July 7, 2015
Published: July 10, 2015

DOI: 10.1021/acssuschemeng.5b00416

Scheme 1. Synthesis of lignin-Br and lignin-*g*-poly(styrene-*co*-ABP) Copolymers



EXPERIMENTAL SECTION

Materials. Hardwood kraft lignin (*Eucalyptus* sp.) was provided by Suzano Papel e Celulose (Brazil), and was purified following the procedure of Dong et al.[39] The purified lignin has ~0.55% of ash and pH = 5.1. Elemental composition was as follows: carbon = 56.6%, hydrogen = 5.8%, oxygen = 35.3%, nitrogen = 0.1% and sulfur = 2.2%. α-Bromoisobutyryl bromide (BiBB), acryloyl chloride, 4-hydroxybenzophenone, trimethylamine, Cu(II)Br_2, 2,2′-bipyridine (bpy), *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA), ascorbic acid and polystyrene (M_w = 230 kDa) were purchased from Sigma-Aldrich and used as received. Styrene was purchased from Sigma-Aldrich and purified by passing through a neutral alumina column before use. Pyridine, dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from Fisher Scientific and used as received. All other chemicals and solvents were obtained from Fisher Scientific and used as received.

Synthesis of Acryloyl Benzophenone (ABP). ABP was synthesized following a procedure reported elsewhere.[40] In general, 4-hydroxybenzophenone (12 g, 60 mmol) was added to 100 mL diethyl ether in a round-bottomed flask. Trimethylamine (6.8 g, 116 mmol) was added to the mixture, and a yellowish solution was obtained. Acryloyl chloride (9.1 g, 100 mmol) was added dropwise to the mixture under nitrogen protection. The mixture was stirred at room temperature for 5 h. 1 M HCl (100 mL) was added to the mixture to quench the excess acryloyl chloride. The organic layer was washed with 5% aqueous NaOH solution and water. The organic layer was collected and diethyl ether was removed under vacuum to give 14.2 g (93.8% yield) reddish crude product. The crude product was dissolved in hot ethanol and treated with activated charcoal. After recrystallization from ethanol, 13.9 g (91.9% yield) of a white crystal was obtained. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.90−7.30 (m, 9H, aromatic), 6.65−6.35 (m, 2H, vinyl), 6.25−6.15 (d, 1H, vinyl). m.p.: 49−50 °C.

Synthesis of Lignin Macroinitiator (lignin-Br). Lignin (2.0 g, 12.5 mmol hydroxyl content) was dissolved in 30 mL of pyridine in a round-bottomed flask, followed by the addition of 15 mL of THF. The solution was stirred under nitrogen for 1 h. BiBB (4.7 mL, 37.5 mmol) was added dropwise to the mixture at 0 °C. The reaction was allowed to stir for 24 h at room temperature, and 10 mL methanol was added to the flask to quench any unreacted BiBB. The mixture was then precipitated into 400 mL of an aqueous methanol (50% v/v) solution. The precipitate was collected by centrifugation at 10000 rpm for 10 min and washed with methanol in triplicate, followed by drying under vacuum at 50 °C overnight. The crude lignin-Br was redissolved in THF, and reprecipitated into 250 mL of an aqueous methanol (50% v/v) solution. 2.49 g (~65% yield) of a brownish purified lignin-Br was obtained after centrifugation and drying.

Synthesis of Lignin-*graft*-Polystyrene (lignin-*g*-PS) Copolymers. Lignin-Br (e.g., 0.5 g, 1.62 mmol Br) and ascorbic acid (e.g., 284 mg, 1.62 mmol) were dissolved in degassed styrene (e.g., 18.5 mL, 162 mmol) and DMF (e.g., 26.5 mL). The mixture was degassed by flushing with nitrogen. Cu(II)Br_2 (e.g., 36 mg, 0.162 mmol) and bpy (e.g., 252.2 mg, 1.62 mmol) were added to a dry 10 mL flask and degassed. 1 mL of degassed DMF was added to the flask, and the mixture was further degassed by three freeze−pump−thaw cycles. The Cu(II)/bpy complex was transferred to the reaction mixture. The reaction flask was then immersed in a preheated oil bath (95 °C). After the solution was stirred for 24 h, the reaction was diluted with DMF and passed through a neutral alumina column for the removal of the copper complex. The mixture was precipitated, filtered and washed with methanol. The pale brown lignin-*g*-PS copolymers were obtained after drying under vacuum at 50 °C overnight.

Synthesis of Lignin-*graft*-Poly(styrene-*co*-acryloyl benzophenone) (lignin-*g*-poly(styrene-*co*-ABP)) Copolymers (Scheme 1). Lignin-Br (e.g., 0.5 g, 1.62 mmol Br), ABP (e.g., 2.0 g, 8.1 mmol) and ascorbic acid (e.g., 284 mg, 1.62 mmol) were dissolved in degassed styrene (e.g., 17.5 mL, 154 mmol) and DMF (e.g., 25.5 mL), and the mixture was degassed by flushing with nitrogen. 1 mL of freshly made Cu(II)/bpy complex was transferred to the reaction mixture. The reaction was stirred at 95 °C for 24 h. The lignin-*g*-poly(styrene-*co*-ABP) copolymers were purified via a similar procedures as lignin-*g*-PS copolymers.

Characterization. ^{1}H and ^{31}P NMR were measured using a Bruker Avance 300 MHz spectrometer. For ^{1}H NMR measurements, ~5 mg sample was weighed and dissolved in 0.5 mL of DMSO-d_6 or dichloromethane-d_2. ^{31}P NMR was used to quantitatively analyze the aliphatic and phenolic hydroxyl group contents and was performed following a published procedure.[20] An accurately weighed amount of lignin or lignin-Br (40 mg) was dissolved in 500 μL of an anhydrous pyridine/$CDCl_3$ mixture (1.6:1, v/v). Chromium(III) acetylacetonate (50 μL) and endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide (200 μL) were added as relaxation reagent and internal standard. 2-Chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane (100 μL) was added as phosphitylating reagent prior to NMR acquisition. ^{31}P NMR was acquired using 256 scans, 12 000 Hz sweep width and 5 s delay time.

Gel Permeation Chromatography (GPC). The molecular weights of the lignin-Br and lignin graft copolymers were determined by GPC (Shimadzu, LC-20AD) equipped with two columns (HR-1 and HR-5E, Waters) and detectors (UV (280 nm) and refractive index). THF was used as the mobile phase (0.7 mL·min^{-1}) at 35 °C. The samples were dissolved in THF with an approximate concentration of 0.5 mg·mL^{-1} and then filtered through 0.25 μm microfilters. The columns were calibrated against polystyrene standards with molecular weights that ranged from 162−3 520 000 g·mol^{-1}.

Differential Scanning Calorimetry (DSC). All DSC measurements were performed on a TA Q100 instrument. All samples were dried under vacuum at 60 °C overnight prior to the DSC analyses. Approximately 7.5 mg of a sample was weighed directly into a DSC hermetic aluminum sample pan with a pinhole pierced on the lid. Samples were heated to 105 °C with a heating rate of 10 °C·min^{-1} (1st scan), isothermally conditioned for 10 min, cooled to 40 °C at 10 °C·min^{-1}, and heated to 230 °C (2nd scan) at 10 °C·min^{-1}. Glass transition temperature (T_g) was analyzed using Universal Analysis 2000.

Thermogravimetric Analysis (TGA). All TGA measurements were performed using a TA Q500 instrument. All samples were dried under vacuum at 60 °C overnight prior to the TGA measurements. Samples (approximate 10 mg) were heated to 105 °C with a heating rate of 10 °C·min^{-1} and maintained at this temperature for 10 min, followed by heating to 800 °C at the same heating rate under nitrogen atmosphere.

UV Cross-Linking and Gel Fraction Testing. Films of lignin-*g*-PS and lignin-*g*-poly(styrene-*co*-ABP) copolymers with a thickness of ~100 μm were casted from their THF solutions. The films were irradiated with a UV curing system (F300S UV lamp system, lamp power 120 W/cm, 1800 W total, and a LC6 benchtop conveyor, Fusion UV Systems Inc.) with indicated exposure time at 80 °C. The UV cross-linked films were swelled in THF for 24 h. After drying under vacuum at 50 °C overnight, the insoluble gel was weighed to obtain the mass fraction relative to the original mass of the film. Experiments were run in triplicate and reported values indicate averages ± one standard deviation.

■ RESULTS AND DISCUSSIONS

^{31}P NMR has proved to be a powerful tool for monitoring the hydroxyl-based functional groups in lignocellulosic biomass since the 1990s.[41] In this work, ^{31}P NMR was performed to quantitatively characterize the hydroxyl and carboxylic group contents in the hardwood kraft lignin and lignin-Br (Figure 1).

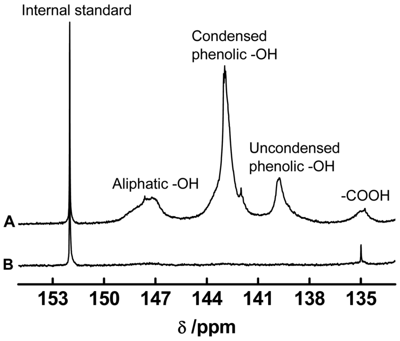


Figure 1. Quantitative ^{31}P NMR spectra of (A) hardwood kraft lignin and (B) lignin-Br.

The kraft lignin was determined to have 1.18 mmol·g^{-1} aliphatic hydroxyl group, 3.70 mmol·g^{-1} condensed phenolic hydroxyl group, 1.33 mmol·g^{-1} uncondensed phenolic hydroxyl group and 0.38 mmol·g^{-1} carboxylic group. The total amount of C_5 condensed structures, including β-5, 4-O-5 and 5-5 moieties, was determined to be 74% of the total phenolic hydroxyl group contents, which is much higher than the reported values (38–44%) for kraft lignin elsewhere.[42] In contrast, no appreciable amount of hydroxyl groups were observed for lignin-Br (Figure 1B), which indicated that all the free hydroxyl groups have been masked by bromoisobutyryl esters. Kadla et al.[35] found that phenolic hydroxyl groups were preferentially esterified when trimethylamine was used as a nucleophile, whereas both aliphatic and phenolic hydroxyl groups were readily esterified when pyridine was used, as seen in this work.

Representative ^{1}H NMR spectra for the kraft lignin, lignin-Br, lignin-*g*-PS and lignin-*g*-poly(styrene-*co*-ABP) are shown in Figure 2. ARGET ATRP utilizes nonradical forming reducing agents (e.g., glucose and ascorbic acid) to regenerate Cu(I) from Cu(II). Compared to traditional ATRP, ARGET ATRP has lower loading of copper catalyst and higher tolerance of oxygen and water.[43] ARGET ATRP has shown applications in the modification of natural polymers, such as cellulose.[44] In this work, ARGET ATRP was employed to synthesize the lignin graft copolymers using a constant lignin-Br/$CuBr_2$/ligand/ascorbic acid ([I]/[Cu]/[L]/[R] = 1:0.1:1:1) in DMF. Both PMDETA and bpy were tested as ligands in this work. However, PMDETA led to the formation of insoluble products even when the monomer volume fraction was lowered to 15%. This observation was supported by the results from Washburn et al.,[28] where Cu(I)/PMDETA complex resulted in gel formation in a few minutes when it was employed as a catalyst for lignin graft copolymerization. The bpy exhibited better control of the polymerization rate than PMDETA; however, the polymerization rate was relatively slow with a monomer conversion of ~20% after a 24 h reaction. This observation might be attributed to the much lower ATRP equilibrium constant for the Cu(I)/bpy complex than the Cu(I)/PMDETA complex (3.9×10^{-9} vs 7.5×10^{-8} in acetonitrile).[45] Thus, bpy was selected as the ligand in this work. Lignin graft copolymers were synthesized with monomer/initiator molar ratios of 20/1 and 100/1 (containing 5% ABP for lignin-*g*-poly(styrene-*co*-ABP) copolymers). Degrees of polymerization (DPs) of the resulting graft copolymers were calculated from ^{1}H NMR via the ratios between the vinyl protons of the polymer side chains and the methyl protons in the bromoisobutyryl ester, with the assumption that the proton ratios between the methoxyl group and the bromoisobutyryl ester are constant for both lignin-Br and the graft copolymers. The calculated DPs agree with the results estimated based on monomer conversions. The ratio between styrene and ABP in the lignin-*g*-poly(styrene-*co*-ABP) copolymers were calculated from ^{1}H NMR via the ratios between the aromatic protons of the styrene and ABP moieties. As summarized in Table 1, samples are identified as lignin-*g*-PS$_m$ and lignin-*g*-poly(styrene$_m$-*co*-ABP$_n$), where m and n are

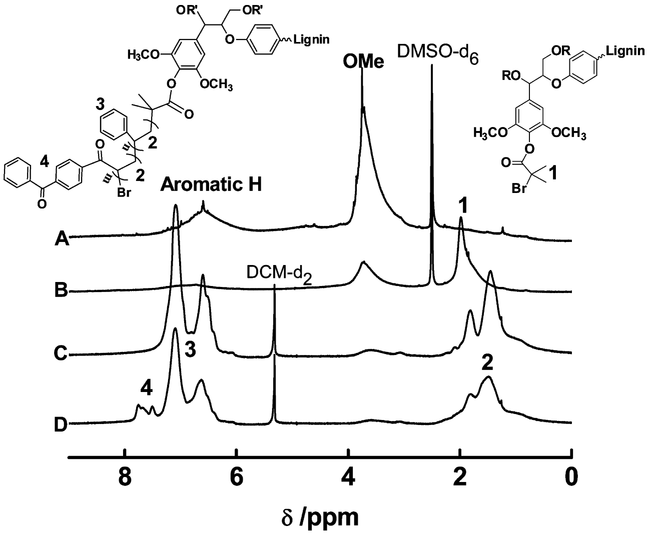


Figure 2. ^{1}H NMR spectra of (A) hardwood kraft lignin, (B) lignin-Br, (C) lignin-*g*-PS$_{22}$ and (D) lignin-*g*-poly(styrene$_{22.5}$-*co*-ABP$_{1.5}$).

Table 1. Molecular Weights of lignin-Br and Lignin Graft Copolymers

	[S]/[A]/[I]/[Cu]/[L]/[A][a]	M_n (kDa)	M_w (kDa)	M_w/M_n
lignin-Br	N/A	1.30	5.25	4.0
lignin-*g*-PS$_3$	20/0/1/0.1/1/1	5.20	11.6	2.3
lignin-*g*-poly(styrene$_{2.75}$-*co*-ABP$_{0.25}$)	19/1/1/0.1/1/1	6.03	13.0	2.2
lignin-*g*-PS$_{22}$	100/0/1/0.1/1/1	9.50	36.1	3.8
lignin-*g*-poly(styrene$_{22.5}$-*co*-ABP$_{1.5}$)	95/5/1/0.1/1/1	11.5	39.5	3.4

[a] [S]/[A]/[I]/[Cu]/[L]/[A] = [styrene]/[ABP]/[initiator]/[Cu(II)]/[bpy]/[ascorbic acid].

the average DPs of polystyrene and polyABP in the graft copolymers, respectively.

GPC was used to monitor the molecular weights and their distributions of the macroinitiator and the graft copolymers. The results are summarized in Table 1 and the representative GPC traces are shown in Figure 3. As shown in Table 1, all the graft copolymers exhibited higher molecular weights than lignin-Br and the molecular weights increased as the monomer/initiator ratio increased. Additionally, the graft copolymers showed relatively narrower molecular weight distribution compared to the macroinitiator, which indicated that the polymerization proceeded in a controlled manner. As seen in Figure 3, low-molecular-weight shoulders were observed in the GPC traces of the graft copolymers, indicating the poor initiation efficiency of the macroinitiator. Similar observations were reported when the monomer conversions were too low.[46−48] As the feeding ratio between monomer and initiator increased from 20 to 100, the shoulder diminished.

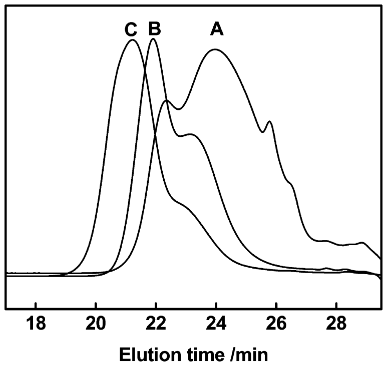


Figure 3. GPC traces for (A) lignin-Br, (B) lignin-*g*-poly(styrene$_{2.75}$-*co*-ABP$_{0.25}$) and (C) lignin-*g*-poly(styrene$_{22.5}$-*co*-ABP$_{1.5}$).

The glass transition temperatures of the hardwood kraft lignin, lignin-Br and the lignin graft copolymers were characterized by DSC (Figure 4). The kraft lignin showed a broad glass transition at 160−200 °C (Figure 4A), which is higher than many reported values for kraft lignin.[49−51] This exceptionally high T_g might be attributed to the high extent of condensation of the kraft lignin, as implied by the ^{31}P NMR results. As seen from Figure 4B, lignin-Br did not exhibit appreciable glass transition in the probed temperature range. As a comparison, both lignin-*g*-PS and lignin-*g*-poly(styrene-*co*-ABP) copolymers showed a single glass transition at ∼100 °C (Figure 4C−F), which was similar to the homopolymer of polystyrene (Figure 4G). The calculated heat capacity (ΔC_p) at glass transition was increased from 0.14 to 0.26 J·g^{-1}·°C^{-1} for lignin-*g*-PS$_3$ and lignin-*g*-PS$_{22}$. The relatively low T_g indicated the improved thermoplasticity of the lignin graft copolymers compared to the unmodified kraft lignin.

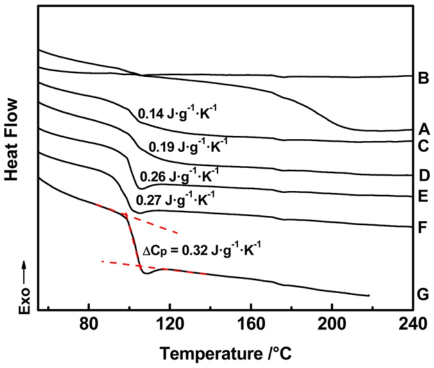


Figure 4. DSC curves for (A) lignin, (B) lignin-Br, (C) lignin-*g*-PS$_3$, (D) lignin-*g*-poly(styrene$_{2.75}$-*co*-ABP$_{0.25}$), (E) lignin-*g*-PS$_{22}$, (F) lignin-*g*-poly(styrene$_{22.5}$-*co*-ABP$_{1.5}$) and (G) polystyrene.

The thermal stability of the kraft lignin, lignin-Br and the graft copolymers were monitored by TGA. The TGA curves and the first derivative of the TGA curves (DTG) are shown in Figure 5. Lignin showed high residue yield (43%), which was attributed to the carbon formation during pyrolysis (Figure 4a). Lignin-Br exhibited a significantly decreased thermal stability with a two-stage decomposition (Figure 4b), due to the introduction of the bromoisobutyryl ester groups. The homopolymer of polystyrene (M_w = 230 kDa), on the other hand, decomposed completely without any carbon residue left (Figure 4g). The lignin graft copolymers showed a single-stage decomposition at 280−420 °C, and the carbon yield decreased as the weight fraction of lignin decreased in the graft copolymers (Figure 4c−f). The weight fractions of lignin in the macroinitiator and the graft copolymers can be estimated based on the carbon yield values, with the assumption that the carbon yield values for lignin and bromoisobutyryl ester/polymer fractions in the macroinitiator/graft copolymers are the same as those of unmodified lignin (43.5%) and polystyrene (0%). For instance, the calculated weight fraction values for the macroinitiator, lignin-*g*-poly(styrene$_{2.75}$-*co*-ABP$_{0.25}$) and lignin-*g*-poly(styrene$_{22.5}$-*co*-ABP$_{1.5}$) copolymers were 62.8%, 42.5% and 12.0%, respectively.

Benzophenone derivatives have been widely used as photoinitiators in UV curing applications.[52,53] A benzophenone acrylate derivative, ABP, was selected as a photosensitive comonomer in this work. The photosensitive moiety was expected to be incorporated quantitatively and uniformly in the copolymer chains compared to a simple blending. In a general photo-cross-linking mechanism, benzophenone is excited to a triple-state via a single-state by the absorption of a photon, and the excited triple-state benzophenone abstracts aliphatic hydrogens from neighboring polymer chains and thus generates radicals. The radicals couple to produce a cross-linked network or decay via side reactions.[54] In this work, the UV cross-linking properties of the lignin graft copolymers were investigated via

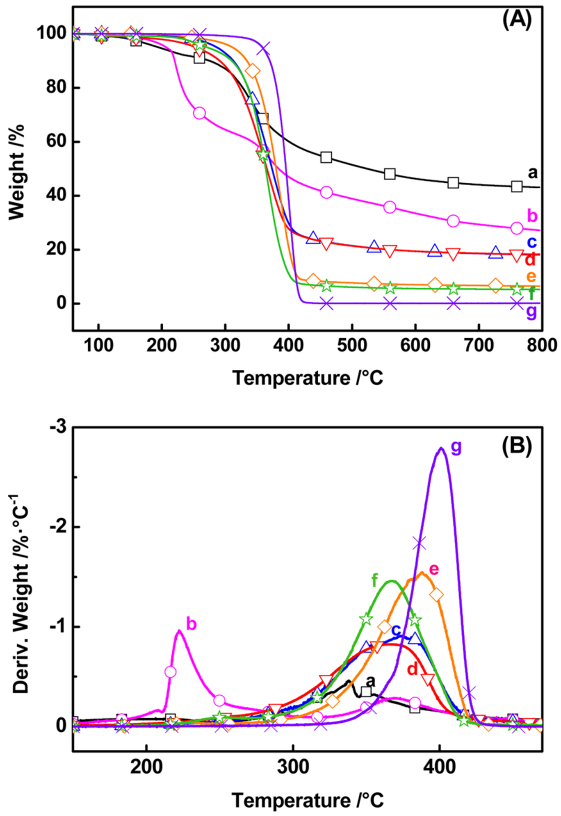


Figure 5. (A) TGA and (B) DTG curves for (a, □) lignin, (b, ○) lignin-Br, (c, Δ) lignin-*g*-PS$_3$, (d, ▽) lignin-*g*-poly(styrene$_{2.75}$-*co*-ABP$_{0.25}$), (e, ◇) lignin-*g*-PS$_{22}$, (f, ☆) lignin-*g*-poly(styrene$_{22.5}$-*co*-ABP$_{1.5}$) and (g, ×) polystyrene.

monitoring the mass fraction of the gelled network formed (Figure 6). As seen in Figure 6, lignin-*g*-poly(styrene-*co*-ABP) copolymers generated up to ∼30% of cross-linked insoluble polymer network, whereas the lignin-*g*-PS copolymers generally produced <5%. This observation indicated that UV curable lignin-based thermoplastic copolymers were obtained by incorporating the photosensitive moiety, ABP, as a comonomer. When polystyrene is irradiated under UV light, polystyryl radicals form via the elimination of a hydrogen atom from the excited polystyrene chains. The polystyryl radicals are readily attacked by oxygen in air to generate peroxyl radicals. Radicals couple with each other to form cross-linked networks, and chain scission also occurs simultaneously via carbon−carbon bond β-scission or photo-oxidation. In general, chain scission is the dominant process in air, whereas cross-linking is predominant in vacuo.[55,56] When benzophenone is present, both cross-linking and chain scission occur more efficiently than pure polystyrene owing to the enhanced radical initiation with the assistance of the excited benzophenone. Sakaguchi et al.[57] reported that it was more efficient to form cross-linking when benzophenone is covalently incorporated in the polymer chain (e.g., poly(styrene-*co*-4-vinylbenzophenone) copolymers) than simply blending with polystyrene.

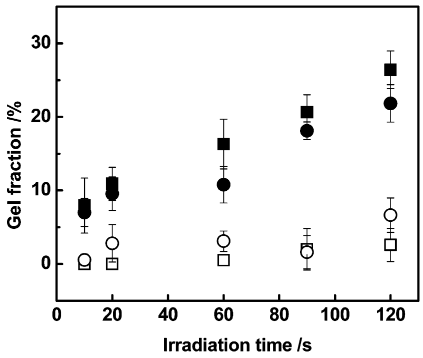


Figure 6. Gel fraction of (■) lignin-*g*-poly(styrene$_{22.5}$-*co*-ABP$_{1.5}$), (●) lignin-*g*-poly(styrene$_{2.75}$-*co*-ABP$_{0.25}$), (□) lignin-*g*-PS$_{22}$ and (○) lignin-*g*-PS$_3$ after UV irradiation.

McGrath and Ogale groups.[58,59] prepared a poly(acrylonitrile-*co*-methyl acrylate-*co*-ABP) copolymer as a melt processable and photo-cross-linkable carbon fiber precursor. The UV-assisted cross-linking provided adequate mechanical strength to the melt-processable precursor and thus prevented fiber fusion in the subsequent thermal stabilization. As a renewable natural material, lignin is potentially a precursor material for low-cost carbon fiber production owing to its high carbon yield.[12,13] By incorporating UV cross-linkable moieties to melt processable lignin materials, lignin fibers with improved thermal stability are expected.

■ CONCLUSIONS

In summary, UV curable lignin graft copolymers were prepared and characterized. Harwood kraft lignin based macroinitiator was synthesized by bromoisobutyryl esterification of both the aliphatic and phenolic hydroxyl groups. Lignin-*g*-PS and lignin-*g*-poly(styrene-*co*-ABP) copolymers were prepared via ARGET ATRP, and copolymers with different DPs were obtained by controlling the feed molar ratios between monomers and the macroinitiator. Relatively low monomer conversions were observed from the kinetic and GPC results. The enhanced thermoplasticity of the lignin graft copolymers was implied by the relatively lower glass transition temperature than the unmodified kraft lignin. The graft copolymers exhibited improved thermal stability compared to the macroinitiator, and the carbon yields during pyrolysis decreased as the DPs of the graft copolymers increased. Upon UV irradiation, up to ∼30% of the lignin-*g*-poly(styrene-*co*-ABP) copolymers cross-linked to form polymer network, whereas less than ∼5% was observed for lignin-*g*-PS copolymers. These results are expected to provide a convenient and robust alternative to prepare lignin-based functional materials with enhanced surface hardness, solvent resistance and thermal stability.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Estimation of DP of the lignin graft copolymers based on ^{1}H NMR spectra. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00416.

■ AUTHOR INFORMATION

Corresponding Author

*Richard A. Venditti. Phone: (919) 515-6185. Fax: (919) 515-6302. E-mail: richard_venditti@ncsu.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Southeastern Partnership for Integrated Biomass Supply Systems (IBSS) project within the Agriculture and Food Research Initiative Competitive Grant no. 2011-68005-30410 from the USDA National Institute of Food and Agriculture.

■ REFERENCES

(1) Boerjan, W.; Ralph, J.; Baucher, M. Lignin Biosynthesis. *Annu. Rev. Plant Biol.* **2003**, *54*, 519−546.

(2) Hatakeyama, H.; Hatakeyama, T. Lignin Structure, Properties, and Applications. In *Biopolymers*; Abe, A., Dusek, K., Kobayashi, S., Eds.; Springer: Berlin, 2010; Vol. *232*, pp 1−63.

(3) Stewart, D. Lignin as a base material for materials applications: Chemistry, application and economics. *Ind. Crops Prod.* **2008**, *27*, 202−207.

(4) Lora, J.; Glasser, W. Recent Industrial Applications of Lignin: A Sustainable Alternative to Nonrenewable Materials. *J. Polym. Environ.* **2002**, *10*, 39−48.

(5) Laurichesse, S.; Avérous, L. Chemical modification of lignins: Towards biobased polymers. *Prog. Polym. Sci.* **2014**, *39*, 1266−1290.

(6) Duval, A.; Lawoko, M. A review on lignin-based polymeric, micro- and nano-structured materials. *React. Funct. Polym.* **2014**, *85*, 78−96.

(7) Calvo-Flores, F. G.; Dobado, J. A. Lignin as Renewable Raw Material. *ChemSusChem* **2010**, *3*, 1227−1235.

(8) Chung, H.; Washburn, N. R. Chemistry of lignin-based materials. *Green Mater.* **2012**, *1*, 137−160.

(9) Thakur, V. K.; Thakur, M. K.; Raghavan, P.; Kessler, M. R. Progress in Green Polymer Composites from Lignin for Multifunctional Applications: A Review. *ACS Sustainable Chem. Eng.* **2014**, *2*, 1072−1092.

(10) Stiubianu, G.; Cazacu, M.; Cristea, M.; Vlad, A. Polysiloxane-lignin composites. *J. Appl. Polym. Sci.* **2009**, *113*, 2313−2321.

(11) Reza Barzegari, M.; Alemdar, A.; Zhang, Y.; Rodrigue, D. Mechanical and rheological behavior of highly filled polystyrene with lignin. *Polym. Compos.* **2012**, *33*, 353−361.

(12) Baker, D. A.; Rials, T. G. Recent advances in low-cost carbon fiber manufacture from lignin. *J. Appl. Polym. Sci.* **2013**, *130*, 713−728.

(13) Kadla, J.; Kubo, S.; Gilbert, R.; Venditti, R. Lignin-Based Carbon Fibers. In *Chemical Modification, Properties, and Usage of Lignin*; Hu, T., Ed.; Springer: New York, 2002; pp 121−137.

(14) Zakzeski, J.; Bruijnincx, P. C. A.; Jongerius, A. L.; Weckhuysen, B. M. The Catalytic Valorization of Lignin for the Production of Renewable Chemicals. *Chem. Rev.* **2010**, *110*, 3552−3599.

(15) Azadi, P.; Inderwildi, O. R.; Farnood, R.; King, D. A. Liquid fuels, hydrogen and chemicals from lignin: A critical review. *Renewable Sustainable Energy Rev.* **2013**, *21*, 506−523.

(16) Pandey, M. P.; Kim, C. S. Lignin Depolymerization and Conversion: A Review of Thermochemical Methods. *Chem. Eng. Technol.* **2011**, *34*, 29−41.

(17) Linger, J. G.; Vardon, D. R.; Guarnieri, M. T.; Karp, E. M.; Hunsinger, G. B.; Franden, M. A.; Johnson, C. W.; Chupka, G.; Strathmann, T. J.; Pienkos, P. T.; Beckham, G. T. Lignin valorization through integrated biological funneling and chemical catalysis. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 12013−12018.

(18) Ma, R.; Xu, Y.; Zhang, X. Catalytic Oxidation of Biorefinery Lignin to Value-added Chemicals to Support Sustainable Biofuel Production. *ChemSusChem* **2015**, *8*, 24−51.

(19) Cui, C.; Sadeghifar, H.; Sen, S.; Argyropoulos, D. S. Toward Thermoplastic Lignin Polymers; Part II: Thermal & Polymer Characteristics of Kraft Lignin & Derivatives. *BioResources* **2013**, *8*, 864−886.

(20) Sen, S.; Patil, S.; Argyropoulos, D. S. Methylation of softwood kraft lignin with dimethyl carbonate. *Green Chem.* **2015**, *17*, 1077−1087.

(21) Chen, M.-J.; Gunnells, D. W.; Gardner, D. J.; Milstein, O.; Gersonde, R.; Feine, H. J.; Hüttermann, A.; Frund, R.; Lüdemann, H. D.; Meister, J. J. Graft Copolymers of Lignin with 1-Ethenylbenzene. 2. Properties. *Macromolecules* **1996**, *29*, 1389−1398.

(22) Laurichesse, S.; Avérous, L. Synthesis, thermal properties, rheological and mechanical behaviors of lignins-grafted-poly(ε-caprolactone). *Polymer* **2013**, *54*, 3882−3890.

(23) Ayoub, A.; Venditti, R. A.; Jameel, H.; Chang, H.-M. Effect of irradiation on the composition and thermal properties of softwood kraft lignin and styrene grafted lignin. *J. Appl. Polym. Sci.* **2014**, *131*, DOI: 10.1002/app.39743

(24) Hilburg, S. L.; Elder, A. N.; Chung, H.; Ferebee, R. L.; Bockstaller, M. R.; Washburn, N. R. A universal route towards thermoplastic lignin composites with improved mechanical properties. *Polymer* **2014**, *55*, 995−1003.

(25) de Oliveira, W.; Glasser, W. G. Multiphase materials with lignin. 11. Starlike copolymers with caprolactone. *Macromolecules* **1994**, *27*, 5−11.

(26) de Oliveira, W.; Glasser, W. G. Multiphase Materials with Lignin. XIV. Star-Like Copolymers with Styrene. *J. Wood Chem. Technol.* **1994**, *14*, 119−126.

(27) Korich, A. L.; Fleming, A. B.; Walker, A. R.; Wang, J.; Tang, C.; Iovine, P. M. Chemical modification of organosolv lignin using boronic acid-containing reagents. *Polymer* **2012**, *53*, 87−93.

(28) Hoyong, C.; Amer, A.-K.; Newell, R. W. Lignin-Based Graft Copolymers via ATRP and Click Chemistry. In *Green Polymer Chemistry: Biocatalysis and Materials II*; American Chemical Society: Washtington, DC, 2013; Vol. *1144*, pp 373−391.

(29) Chen, M.-J.; Meister, J. J.; Gunnells, D. W.; Gardner, D. J. A process for coupling wood to thermoplastic using graft copolymers. *Adv. Polym. Technol.* **1995**, *14*, 97−109.

(30) Meister, J. J.; Chen, M. J. Graft 1-phenylethylene copolymers of lignin. 1. Synthesis and proof of copolymerization. *Macromolecules* **1991**, *24*, 6843−6848.

(31) Matsushita, Y.; Inomata, T.; Takagi, Y.; Hasegawa, T.; Fukushima, K. Conversion of sulfuric acid lignin generated during bioethanol production from lignocellulosic materials into polyesters with ε-caprolactone. *J. Wood Sci.* **2011**, *57*, 214−218.

(32) Hatakeyama, T.; Izuta, Y.; Hirose, S.; Hatakeyama, H. Phase transitions of lignin-based polycaprolactones and their polyurethane derivatives. *Polymer* **2002**, *43*, 1177−1182.

(33) Mai, C.; Milstein, O.; Hüttermann, A. Chemoenzymatical grafting of acrylamide onto lignin. *J. Biotechnol.* **2000**, *79*, 173−183.

(34) Corti, A.; Cristiano, F.; Solaro, R.; Chiellini, E. Biodegradable Hybrid Polymeric Materials Based on Lignin and Synthetic Polymers. In *Biodegradable Polymers and Plastics*; Chiellini, E., Solaro, R., Eds.; Springer: New York, 2003; pp 141−153.

(35) Kim, Y. S.; Kadla, J. F. Preparation of a Thermoresponsive Lignin-Based Biomaterial through Atom Transfer Radical Polymerization. *Biomacromolecules* **2010**, *11*, 981−988.

(36) Wang, J.; Yao, K.; Korich, A. L.; Li, S.; Ma, S.; Ploehn, H. J.; Iovine, P. M.; Wang, C.; Chu, F.; Tang, C. Combining renewable gum rosin and lignin: Towards hydrophobic polymer composites by controlled polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 3728−3738.

(37) Diao, B.; Zhang, Z.; Zhu, J.; Li, J. Biomass-based thermogelling copolymers consisting of lignin and grafted poly(N-isopropylacrylamide), poly(ethylene glycol), and poly(propylene glycol). *RSC Adv.* **2014**, *4*, 42996−43003.

(38) Gauthier, M. A.; Gibson, M. I.; Klok, H.-A. Synthesis of Functional Polymers by Post-Polymerization Modification. *Angew. Chem., Int. Ed.* **2009**, *48*, 48−58.

(39) Dong, D.; Fricke, A. L.; Moudgil, B. M.; Johnson, H. Electrokinetic study of kraft lignin. *Tappi J.* **1996**, *79*, 191−197.

(40) Carlini, C.; Gurzoni, F. Optically active polymers containing side-chain benzophenone chromophores. *Polymer* **1983**, *24*, 101−106.

(41) Pu, Y.; Cao, S.; Ragauskas, A. J. Application of quantitative 31P NMR in biomass lignin and biofuel precursors characterization. *Energy Environ. Sci.* **2011**, *4*, 3154−3166.

(42) Granata, A.; Argyropoulos, D. S. 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, a Reagent for the Accurate Determination of

the Uncondensed and Condensed Phenolic Moieties in Lignins. *J. Agric. Food Chem.* **1995**, *43*, 1538−1544.

(43) Matyjaszewski, K.; Dong, H.; Jakubowski, W.; Pietrasik, J.; Kusumo, A. Grafting from Surfaces for "Everyone": ARGET ATRP in the Presence of Air. *Langmuir* **2007**, *23*, 4528−4531.

(44) Hansson, S.; Östmark, E.; Carlmark, A.; Malmström, E. ARGET ATRP for Versatile Grafting of Cellulose Using Various Monomers. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2651−2659.

(45) Tang, W.; Kwak, Y.; Braunecker, W.; Tsarevsky, N. V.; Coote, M. L.; Matyjaszewski, K. Understanding Atom Transfer Radical Polymerization: Effect of Ligand and Initiator Structures on the Equilibrium Constants. *J. Am. Chem. Soc.* **2008**, *130*, 10702−10713.

(46) Zhu, L.-W.; Yang, W.; Wan, L.-S.; Xu, Z.-K. Synthesis of core cross-linked star polystyrene with functional end groups and self-assemblies templated by breath figures. *Polym. Chem.* **2014**, *5*, 5175−5182.

(47) Tasdelen, M. A.; Uygun, M.; Yagci, Y. Studies on Photoinduced ATRP in the Presence of Photoinitiator. *Macromol. Chem. Phys.* **2011**, *212*, 2036−2042.

(48) Mueller, L.; Jakubowski, W.; Tang, W.; Matyjaszewski, K. Successful Chain Extension of Polyacrylate and Polystyrene Macroinitiators with Methacrylates in an ARGET and ICAR ATRP. *Macromolecules* **2007**, *40*, 6464−6472.

(49) Dodd, A. P.; Kadla, J. F.; Straus, S. K. Characterization of Fractions Obtained from Two Industrial Softwood Kraft Lignins. *ACS Sustainable Chem. Eng.* **2014**, *3*, 103−110.

(50) Saito, T.; Perkins, J. H.; Vautard, F.; Meyer, H. M.; Messman, J. M.; Tolnai, B.; Naskar, A. K. Methanol Fractionation of Softwood Kraft Lignin: Impact on the Lignin Properties. *ChemSusChem* **2014**, *7*, 221−228.

(51) Sevastyanova, O.; Helander, M.; Chowdhury, S.; Lange, H.; Wedin, H.; Zhang, L.; Ek, M.; Kadla, J. F.; Crestini, C.; Lindström, M. E. Tailoring the molecular and thermo−mechanical properties of kraft lignin by ultrafiltration. *J. Appl. Polym. Sci.* **2014**, *131*.n/a10.1002/app.40799

(52) Christensen, S. K.; Chiappelli, M. C.; Hayward, R. C. Gelation of Copolymers with Pendent Benzophenone Photo-Cross-Linkers. *Macromolecules* **2012**, *45*, 5237−5246.

(53) Carbone, N. D.; Ene, M.; Lancaster, J. R.; Koberstein, J. T. Kinetics and Mechanisms of Radical-Based Branching/Cross-Linking Reactions in Preformed Polymers Induced by Benzophenone and Bis-Benzophenone Photoinitiators. *Macromolecules* **2013**, *46*, 5434−5444.

(54) Higuchi, H.; Yamashita, T.; Horie, K.; Mita, I. Photo-cross-linking reaction of benzophenone-containing polyimide and its model compounds. *Chem. Mater.* **1991**, *3*, 188−194.

(55) David, C.; Baeyens-Volant, D.; Delaunois, G.; Lu Vinh, Q.; Piret, W.; Geuskens, G. Photo-oxidation of polymers—III: Molecular weight changes in the photolysis and photo-oxidation of polystyrene. *Eur. Polym. J.* **1978**, *14*, 501−507.

(56) Torikai, A.; Takeuchi, T.; Fueki, K. Photodegradation of polystyrene and polystyrene containing benzophenone. *Polym. Photochem.* **1983**, *3*, 307−320.

(57) David, C.; Piret, W.; Sakaguchi, M.; Geuskens, G. Electron spin resonance study of polymer degradation, 2. Photolysis at 365 nm of polystyrene containing benzophenone. *Makromol. Chem.* **1978**, *179*, 181−187.

(58) Mukundan, T.; Bhanu, V. A.; Wiles, K. B.; Johnson, H.; Bortner, M.; Baird, D. G.; Naskar, A. K.; Ogale, A. A.; Edie, D. D.; McGrath, J. E. A photocrosslinkable melt processible acrylonitrile terpolymer as carbon fiber precursor. *Polymer* **2006**, *47*, 4163−4171.

(59) Naskar, A. K.; Walker, R. A.; Proulx, S.; Edie, D. D.; Ogale, A. A. UV assisted stabilization routes for carbon fiber precursors produced from melt-processible polyacrylonitrile terpolymer. *Carbon* **2005**, *43*, 1065−1072.