Kraft Lignin Chain Extension Chemistry via Propargylation, Oxidative Coupling, and Claisen Rearrangement

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ABSTRACT: Despite its aromatic and polymeric nature, the heterogeneous, stochastic, and reactive characteristics of softwood kraft lignin seriously limit its potential for thermoplastic applications. Our continuing efforts toward creating thermoplastic lignin polymers are now focused on exploring propargylation derivatization chemistry and its potential as a versatile novel route for the eventual utilization of technical lignins with a significant amount of molecular control. To do this, we initially report the systematic propargylation of softwood kraft lignin. The synthesized derivatives were extensively characterized with thermal methods (DSC, TGA), 1H, 13C, and quantitative 31P NMR and IR spectroscopies. Further, we explore the versatile nature of the lignin pendant propargyl groups by demonstrating two distinct chain extension chemistries: the solution-based, copper-mediated, oxidative coupling and the thermally induced, solid-state, Claisen rearrangement polymerization chemistries. Overall, we show that it is possible to modulate the reactivity of softwood kraft lignin via a combination of methylation and chain extension providing a rational means for the creation of higher molecular weight polymers with the potential for thermoplastic materials and carbon fibers with the desired control of structure–property relations.

INTRODUCTION

Lignin is a natural polymer that together with hemicelluloses acts as a cementing matrix of cellulose fibers within the structure of plants and trees. It is one of the principal constituents of wood (around 25−35%) and is the second most abundant natural polymer after cellulose. Lignin is considered to have an amorphous, highly branched macromolecular network structure of aromatic nature with complex connectivity. The basic chemical phenylpropane units of lignin (primarily syringyl, guaiacyl, and p-hydroxy phenol) are bonded together by a set of linkages (mainly aryl alkyl ethers (β-O-4) and carbon−carbon bonds) to form a complex matrix. This matrix is comprised of a variety of functional groups, such as phenolic and aliphatic hydroxyl groups, methoxyl, carbonyl, and carboxyl groups in various amounts, depending on the origin and the isolation methods of this natural polymer. 3,4

An enormous amount of lignin is produced as the byproduct in the pulp and paper industries annually. However, only a small part of the isolated (about one million tons) byproducts are currently used as feedstocks for low molecular weight chemicals and other polymer applications. 5,6 Lignin is used as a polymer either by itself or following functionalization through the hydroxyl groups present in it. 7−11

The propargylation of phenolic hydroxyl groups using propargyl bromide through an aromatic nucleophilic substitution (SNAr) mechanism 12−15 is particularly important because of its potential to serve as a starting material to synthesize high molecular weight synthetic and natural polymers. Being a terminal alkyne, aryl propargyl ether moieties can be used as a prospective component for “click chemistry” along with an organic azide. 14,16−18 It has also been reported that, when aryl propargyl ether terminated monomers are heated around 220 °C, they first undergo a thermal sigmatropic Claisen rearrangement to form 2H-chromene or 2H-1-benzopyran. These intermediates possess reactive double bonds that can subsequently undergo thermal polymerization, generating polymers (Scheme 1). 15,19−26

Resins with these types of curable propargyl etherified phenolics possess enhanced thermal stability, high Tg, long-term high temperature durability, good dimensional stability, good durability, and good curing characteristics. 21,22 Another important polymerization reaction concerning aryl propargyl ether moieties is the metal-catalyzed oxidative coupling reaction (Glaser or modified Glaser−Hay reaction). 25−30 The reaction between triple-bonded monomers is known to produce a large variety of linear and hyperbranched polymers (Scheme 1). 25,29,31

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As such, the propargylation of relatively lower molecular weight lignin followed by oxidative coupling reaction or thermal polymerization via the Claisen rearrangement are potential techniques to proceed toward the preparation of biobased polymer materials and carbon fibers.32

Our work embarks, with a detailed report on the softwood kraft lignin fractionation aimed at obtaining a considerably more homogeneous (albeit of lower molecular weight) lignin fraction by dissolving it in acetone. Then the phenolic OHs of the acetone soluble kraft lignin (ASKL) fraction are propargylated in basic media using variable amounts of propargyl bromide, arriving at thoroughly characterized lignins with different degrees of substitution. We then describe our efforts toward copper-mediated oxidative coupling and thermal polymerization of the pendant alkynes. As anticipated, the multifunctional nature of the lignin soon causes it to arrive at a hyperbranched and cross-linked polymer, which is intractable and not suitable for further thermoplastic processing.33 This major limitation is addressed by appropriately reducing the degree of propargylation (75%) and masking the remaining (25%) phenolic –OHs by alkaline methylation with dimethyl sulfate. Our approach of modulating lignin reactivity via methylation was based on the principles we developed in earlier parts of our work.33,38

### MATERIALS AND METHODS

**Materials.** A sample of commercially available (Mead Westvaco) softwood kraft lignin (Indulin AT) was used as the starting material. All chemicals and reagents used in this study were purchased from Sigma-Aldrich and Fisher Chemical companies and used as received.

**Fractionation of Kraft Lignin.** The original softwood kraft lignin (Indulin) was suspended in acetone (1 g/10 mL) and extracted for 10 h at room temperature. The residue was removed by filtration (acetone insoluble kraft lignin) (AIKL). ASKL was recovered by evaporating the solvent in a rotary evaporator, followed by drying in a vacuum oven at room temperature. The functional group content and molecular weight of ASKL were determined by quantitative31P NMR and gel permeation chromatography (GPC), respectively. The yields of ASKL and acetone insoluble kraft lignin (AIKL) were 35% and 65%, respectively.

**Lignin Propargylation.** A total of 1.0 g of ASKL (Indulin) was dissolved in 20 mL of aqueous 0.5 N NaOH at room temperature. An appropriate amount of 0.25–2.5 mmol of propargyl bromide per each mmol of total phenolic –OH in the lignin was added to the reaction medium and heated at 75 °C for 2 h under continuous stirring. Next the reaction medium was cooled to room temperature and the product was precipitated by addition of 2 N HCl solution to pH = 2. The

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<th>N_{prop}/OH (mg)</th>
<th>mass of lignin in ASKL (mg)</th>
<th>% of aliphatic –OH remaining</th>
<th>% of noncondensed phenolic –OH remaining</th>
<th>% of DPM –OH remaining</th>
<th>% of DPE –OH remaining</th>
<th>% of BP –OH remaining</th>
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The reaction of propargyl bromide with the phenolic –OHs of the lignin will increase its molecular weight (38 g/mmol of –OH). For ASKL containing a total of 4.6 mmol of phenolic –OH, an increase of 15% of actual weight can be calculated for a fully propargylated sample. That is when 40 mg of propargylated lignin sample was taken for 31P NMR; it was actually 34 mg of lignin sample for a fully propargylated sample ([(40 – (1000 × 40)/(4.6 × 38 + 1000))] × 100/40). Accordingly, the actual weight of lignin present within each propargylated simple was calculated. DPM = diphenyl methane. DPE = diphenyl ether. BP = biphenyl(5′−5′) (see Figure 3).
product was washed with excess deionized water followed by drying in a freeze dryer. The details of the propargylation reaction are shown in Table 1. Initial characterizations of the product were carried out by 1H and 13C NMR and IR spectroscopies. The degrees of propargylation were measured by quantitative 31P NMR. The yield of the propargylated lignin varied between 91 and 96%, depending on the degree of propargylation.

**Coupling Reaction.** A 10 mol % of CuCl and 8 mol % of TMEDA per each mole of alkene group, present in the lignin sample (as calculated from 31P NMR), were dissolved in 2.5 mL of DMSO and stirred at predetermined temperatures in an open to air round-bottom flask until all of the CuCl was dissolved. A total of 0.5 g of propargylated lignin was added to the above reaction medium (keeping the concentration 20% by weight) and stirred at a predetermined temperature for a predetermined time, as stated in Table 2. Next the product was recovered by precipitation from methanol followed by acidification with HCl. The product was washed four times with excess methanol and dried under vacuum at room temperature. The product yield was 96% after precipitation and washing.

**Thermal Polymerization.** The thermal polymerizations were conducted within the crucible of a thermogravimetric analysis apparatus (TA TGA-Q500) because uniform and well-controlled heating conditions were obtained. Approximately 40 mg of the propargylated ASKL samples were heated within the chamber of TGA apparatus for predetermined times at predetermined temperatures (see Table 3) under a nitrogen atmosphere. The products were then characterized with spectroscopic methods and their molecular weights were determined after quantitative derivatization (acetobromination). The product yield was 95%.

**NMR Spectroscopy.** Quantitative 31P, 13C, and 1H NMR spectra were acquired using a Bruker 300 MHz spectrometer. The propargylation of the kraft lignins was monitored and analyzed by quantitative 31P NMR using published procedures. An accurately known amount (40 mg) of dried lignin sample was dissolved in 600 μL of anhydrous pyridine/CDCl3 mixture (1.6:1, v/v). A total of 200 μL of an endo-N-hydroxy-s-norbornene-2,3-dicarboximide solution (9.23 mg/mL) as the internal standard and 50 μL of a chromium(III) acetylacetonate solution (5.6 mg/mL) in the above pyridine/CDCl3 solvent as the relaxation reagent were added. Finally, 100 μL of phosphitylating reagent II (2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane) was added and transferred into a 5 mm NMR tube for subsequent immediate (within 10-15 mins) 300 MHz NMR acquisition.

**FT-IR Spectroscopy.** Spectra in the range of 4000 – 660 cm−1 were obtained with a resolution of 4 cm−1 by accumulating 64 scans using KBr.

**Thermogravimetric Analysis.** Thermogravimetric analyses were performed using 10–15 mg samples dried under vacuum overnight at 60 °C in a vacuum oven prior to the DSC analyses. Approximately 5 mg of a sample were weighed directly into a DSC hermetic aluminum sample pan, which was then covered by its lid and sealed by cold pressing and a small hole was carefully created on the lid. After being loaded into the TA-Q100, all samples were heated isothermally at 10 °C/min. They were then isothermally kept again for another 10 min. Finally, the DSC thermograms were recorded by increasing the temperature to 300 °C at a rate of 3 °C/min.

### RESULT AND DISCUSSION

During the last couple of decades, studies on lignin chemistry have shown that the main drawback for its application as a...
polymer is its heterogeneity, which leads to unpredictable and uncontrollable reactions. \textsuperscript{37–39} Previous reports regarding lignin fractionation through extraction from organic solvents show that a fraction with lower molecular weight and lower polydispersity can be obtained with promising application potential. \textsuperscript{40–42} Accordingly, in this work, we fractionated the as-received kraft lignin by dissolving it in acetone. Further derivatizations followed by polymerization were done on the acetone-soluble fraction (ASKL). About 35\% of the kraft lignin was dissolved in acetone. Molecular weight and polydispersity measurements ($M_w$/$M_n$) of the starting kraft lignin were about 6200 g/mol and 3.6, respectively. However, the ASKL was of a considerably lower molecular weight ($M_w = 1200$ g/mol) and of lower polydispersity ($M_w$/$M_n = 1.6$; all the molecular weights of the starting kraft lignin and ASKL were measured after acetobromination). Quantitative $^{31}$P NMR data for the fractionated sample showed that the ASKL contained 4.6 mmol/g of phenolic−OH and 2.4 mmol/g of aliphatic−OH, while the unfractionated starting lignin contained 3.9 and 2.4 mmol/g of phenolic and aliphatic −OHs, respectively.

**Lignin Propargylation.** A series of six propargylation reactions were conducted with varying molar ratios of propargyl bromide to the total phenolic −OHs present in the lignin ($N_{PrBr}/Ph−OH$), as stated in Table 1. Despite this being a two-phase reaction system, thorough mixing ensured the reaction of propargyl bromide with the phenoxide anions of the lignin. As anticipated, the hydrophobic pendant propargyl groups introduced on the lignin did cause some phase separation at higher degrees of reaction. However, no indication of unreacted lignin precipitating out was found. A reproducible and near quantitative phenolic−OH substitution (98\%, observed by $^{31}$P NMR) could be obtained using the same reaction conditions without the use of an organic cosolvent. All products were characterized using $^1$H, $^{13}$C, $^{31}$P NMR and FT-IR spectroscopies. The incorporation of the propargyl group onto the ASKL samples can evidently be seen from the broad peak in the alkyne region (between 4.3 to 4.9 ppm) of the $^1$H NMR spectrum (Figure 1A). Similarly the $^{13}$C NMR spectrum of the same sample shows two peaks between 77 to 82 ppm, which are attributed to the alkyne carbons (Figure 1B; the upfield resonance is due to the terminal carbon and the downfield resonance is due to the internal carbon).

**Quantitative $^{31}$P NMR Study.** During our earlier work we have examined the quantitative $^{31}$P NMR spectra of lignin in the presence of suitable internal standards and reported that the aliphatic and the phenolic −OHs present in the lignin can be thoroughly and accurately quantified. \textsuperscript{35,36,43,44} The same technique was used in this effort to measure the degree of propargylation as a function of the progress of the reaction, which illustrates that the level of propargylation of lignin can be controlled by varying the ratio $N_{PrBr}/Ph−OH$ (Table 1).

We have further exploited the quantitative $^{31}$P NMR spectral studies to comprehend the efficiency of the different functional −OHs present within the ASKL toward the propargylation chemistry (Figure 2). This study shows that the described propargylation chemistry can be specifically directed toward the phenolic −OHs leaving the aliphatic −OHs unaffected (Figure 3A). The higher ionization efficiency of the phenolic −OHs compared to their aliphatic counterparts is uniquely responsible for the observed selectivity. \textsuperscript{38}

Among the phenolic −OHs, the noncondensed moieties show rapid reduction with increasing $N_{PrBr}/Ph−OH$ representing a rapid increase in the degree of propargylation (Figure 3A). Almost 95\% of the noncondensed phenolic −OHs are substituted by propargyl groups at $N_{PrBr}/Ph−OH = 1.0$. This high reactivity trend of the noncondensed phenolic −OHs is thought to be due to their less sterically hindered environment. \textsuperscript{45}

However, the condensed phenolic −OHs show an exceptional reactivity trend toward propargylation (Figure 3A). Initially they are seen to rapidly react in a manner comparable to that of the noncondensed phenolic −OH groups. Beyond $N_{PrBr}/Ph−OH = 1.0$, their reactivity gradually slows down and almost reaches a plateau between $N_{PrBr}/Ph−OH = 1.0$−1.5. Interestingly, after this point, the condensed phenolic −OHs regain their reactivity slowly and show almost 100\% substitution on increasing the $N_{PrBr}/Ph−OH$ to 2.5. To explain this peculiar reactivity pattern, we further inspected the $^{31}$P NMR spectra of the condensed phenolic −OHs. Prominently, the condensed phenolic −OHs of softwood kraft lignin consist of three different structural units, namely, diphenyl ether moieties (DPE−OH), diphenylmethane moieties (DPM −OH), and biphenyl moieties (BP −OH) (Figure 4). The peaks corresponding to these three different structural units can be clearly identified in the $^{31}$P NMR spectra as shown in Figure

![Figure 1.](image1.png)  
**Figure 1.** (A) $^1$H NMR spectrum of propargylated lignin. The alkyne proton can be seen between 4.3 to 4.9 ppm. (B) $^{13}$C NMR spectrum of propargylated lignin. The alkyne carbons can be seen between 77 and 82 ppm (upfield signal for the terminal carbon and downfield signal for the internal carbon).
and ether (through the mesomeric effect) groups most likely increases the nucleophilicity of the phenoxide ions. As such it is likely that the combination of sterically and electronically favorable considerations makes DPE –OH and DPM –OH relatively reactive.\textsuperscript{45,46}

On the other hand, BP –OH shows a very distinct reactivity trend toward this substitution reaction (Figure 3B). At a lower level of propargylation, the reduction of BP –OH seems to be significantly less efficient than DPE –OH and DPM –OH. Later on, a sharp elimination in this type of condensed phenolic –OHs can be observed between N\textsubscript{PrBr/Ph} = 0.5 – 1.0. Beyond N\textsubscript{PrBr/Ph} = 1.0 almost a plateau is reached. However, the reactivity again increases slowly with increasing N\textsubscript{PrBr/Ph}. In addition to the sterically hindered environment, the unique molecular structure of the BP –OH moieties also contributes toward its low reactivity. Most likely BP –OH forms a seven-membered, hydrogen-bonded arrangement restricting it to rearrange to the required conformation needed to react with propargyl bromide.\textsuperscript{46,47} Increasing N\textsubscript{PrBr/Ph} beyond 0.5 (when major portions of the noncondensed phenolic –OH, DPE –OH, and DPM –OH are already substituted with propargyl groups), the BP –OHs are forced to react with the excess propargyl bromide added. As such, one may notice the rapid increase in the reactivity of the BP –OH units. Overall, at first the comparatively accessible BP –OHs are reacted slowly and thereby a decrease in the reaction progress is observed. However, increasing the propargyl bromide concentration further facilitates the reaction allowing an up to 95% substitution at N\textsubscript{PrBr/Ph} = 2.5.

At this point, it is rational to conclude that the reactivity of DPE –OH and DPM –OH governs the initial reactivity of the total condensed phenolic –OHs. As such, one may observe an initial rapid increase in the degree of propargylation. However, in the latter stages of the reaction (beyond N\textsubscript{PrBr/Ph} = 0.75) the BP –OH determines the reactivity of total condensed phenolic –OHs. Thereby, we can observe a decrease in the reaction progress, which however increases with an increase of the propargyl bromide concentration.

**FT-IR Spectroscopy.** The FT-IR spectra of the propargylated ASKL samples show two new peaks at 3260 and 2090 cm\textsuperscript{-1} (Figure 5), which correspond to the alkyne carbon hydrogen stretching and terminal alkyne carbon carbon triple bond stretching, respectively.\textsuperscript{31,48}

Lignin samples show a characteristic peak at 1515 cm\textsuperscript{-1} corresponding to the aromatic ring vibration. Each FT-IR spectrum is normalized with respect to this peak. The peak at 1515 cm\textsuperscript{-1} does not overlap with any of the alkyne peaks and its height can be quantified accurately (I\textsubscript{1515}). As such, in this effort we consider this peak as the internal standard to measure the increase in the height of the alkyne peak at 3260 cm\textsuperscript{-1} (I\textsubscript{3260}) as a function of increasing % of propargylation as

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Structures of different condensed phenolic –OHs present in softwood kraft lignin.
obtained from the $^{31}$P NMR studies. This study shows a linear increase in $I_{2350}$ with increasing degree of propargylation, which is expected as the progression in the substitution reaction incorporates higher amounts of propargyl groups in the ASKL samples. The figure is provided as Supporting Information (Figure S1).

**Thermal Stability.** The thermal stabilities of the ASKL samples with varying degrees of propargylation are examined using our thermogravimetric analysis apparatus (TGA; Figure 6A). The thermal stabilities are seen to improve significantly after 25% propargylation and keeps on improving (albeit marginally) with further increases in the degree of propargylation. Previously, the thermal curing of arylpropargyl ether terminated monomers has been examined in significant detail.\(^{15,19,20,49,50}\) These reports suggest that when the arylpropargyl ether terminated monomers are heated around 220 °C (in a nitrogen atmosphere in the absence of solvent and catalyst), they generally first undergo a thermal sigmatropic Claisen rearrangement to form 2H-chromenes or 2H-1-benzopyrans. These intermediates that possess reactive double bonds can subsequently undergo thermal polymerization (Scheme 1). Moreover, the aryl propargyl ether moieties can also undergo polymerization through ethynyl triple bond radical polymerization or ethynyl cyclotrimerization through double bond radical polymerization, generating a low molecular weight polymer. As such, in this work, we demonstrate that the aryl propargyl ether moieties of the propargylated ASKL samples also undergo similar rearrangement and polymerization chemistries when heated at moderate temperatures under a nitrogen atmosphere. Because the propargylated ASKL samples are multifunctional, they initially form chain-extended, higher molecular weight polymers, which eventually lead to cross-linked structures at higher temperatures. As such, one may observe a significant improvement in the thermal stability compared to the starting material upon heating. The frequency of the benzopyran structures and eventually the frequency of cross-linking increases with increasing degree of propargylation and therefore the slight improvements observed in the thermal stability of the polymers with increasing degree of propargylation can be rationalized. The details of the thermally induced polymerization chemistry of propargylated lignin will be discussed in latter parts of this paper.

Unlike the starting material, the DSC thermograms (Figure 6B) of the propargylated ASKL samples show broad exotherms with an onset and a maximum around 150 and 215 °C, respectively. These exotherms correspond to the heat generated during the intramolecular ring formation to form the 2H-chromene moiety and subsequent polymerizations. Furthermore, this data in combination with the enumerated analytical evidence provided additional support for the occurrence of these valuable transformations.

The reported onset and maximum temperatures are somewhat higher in previously reported similar polymers\(^ {15,20}\) synthesized by heating arylated propargyl moieties than our propargylated ASKL samples. The starting ASKL sample shows a distinct glass transition temperature at 117 °C and the 25% propargylated lignin shows a small $T_g$ around 133 °C. However, due to the thermal polymerization events enumerated above, higher propargylated lignin samples react during the DSC scans producing greater exotherms that precluded us from obtaining representative glass transition temperatures.

**Copper-Mediated Oxidative Coupling Reaction.** All the coupling reactions were conducted in DMSO medium in the presence of CuCl catalyst (10 mol % to the total phenolic −OH) and TMEDA base (8 mol % to the total phenolic −OH) with continuous bubbling of air (Scheme 2).\(^ {27−29,31,32}\) During
As anticipated, such heavily propargylated materials upon further coupling inevitably formed an intractable gel within 60 min due to the multiple functionality of lignin. Lowering the amount of CuCl (5 mol % to the total phenolic −OH) and TMEDA (4 mol % to the total phenolic −OH) was found to reduce and eventually eliminate the gel formation. However, even after 24 h no significant increase in the molecular weight was observed. This evidence indicates that certain minimal concentrations of CuCl catalyst and TMEDA base are necessary for the coupling reaction to take place. As such, we reduced the degrees of propargylation to 75% so as to reduce the incident of inter- and intramolecular cross coupling reactions eventually preventing and controlling the gel formation. Furthermore, the remaining phenolic −OHs were masked by methylation so as to protect them from thermal radical coupling reactions operating at elevated temperatures (known to occur under thermal processing). As such, ensuing coupling reactions were conducted using 25% methylated and 75% propargylated ASKL samples to protect extensive cross-linking and gel formation. The coupling reactions were conducted at different temperatures and for different periods of time, as shown in Table 2, offering the possibility to optimize the molecular weights of the chain extended polymers obtained.

The initial characterizations of the coupled, chain extended lignin based polymers were carried out by 13C NMR and FT-IR spectroscopies. It is quite clear from the 13C spectrum of the coupled products that a new broad signal is generated between 68 and 72 ppm (Figure 7A) in addition to the existing terminal alkylene carbon signals (between 77 and 82 ppm). The generation of a new upfield signal in the 13CNMR unequivocally indicates the conversion of the terminal alkynes to internal dialkynes. The 1H NMR spectrum (Figure S2) after the copper-mediated coupling reaction shows a signal in the alkyne region, confirming that a significant amount of alkyne groups still remain unreacted.

Throughout this work, the FT-IR spectra are normalized with respect to the peak at 1515 cm⁻¹. These show a significant reduction in the peaks at 3260 and 2090 cm⁻¹ after the oxidative coupling (Figure 7B). At the same time, a new peak is seen to be generated between 2200 to 2310 cm⁻¹, demonstrating the conversion of the terminal alkynes to internal dialkyynes.

Molecular Weight. The coupled samples were acetylated prior to the molecular weight determination. The number average molecular weight, weight average molecular weight and the distribution of molecular weight (polydispersity index, PDI) were calculated from the GPC traces and are reported in Table 2.

The molecular weight distributions of the lignin samples after the coupling reaction clearly shift toward higher molecular weights with an increasing temperature (Figure 8) showing a natural and controlled progression of the coupling chain extension reaction. The broad peak for sample 3 depicts that...
heating at 80 °C does not increase the molecular weight further but it initiates gelation significantly. This is because the onset of gelation chemistry is manifested when higher molecular weight species are distributed over a broad molecular weight range, displaying no apparent modality in the chromatogram.53−55 Cross-coupling of branched and highly functional molecular species typically leads to extensive polydispersity as manifested in the tailing along the high molecular weight end of the chromatograms. This has been experimentally demonstrated53,54 and theoretically modeled with synthetic polymer systems54,55. As such, our overall endeavors aim at creating chain extended polymers of uniform composition with reduced polydispersities. In this respect, the data of Figure 8 is well in accord with our objectives because no high molecular weight tailing was observed, indicative of augmented polydispersity.

**Thermal Properties of the Oxidative Coupled Polymers.** The thermal stability of the polymers formed after oxidative coupling were examined by TGA and the traces are provided in the Supporting Information (Figure S3). The chain extended polymers do not show any significant improvement in the thermal stability compared to the propargylated lignin starting material. This can be explained by the fact that the propargylated lignin itself forms a polymer during heating in the TGA apparatus as stated earlier in this paper, which improves the thermal stability of the starting material itself. As such, the additional thermal stability due to the chain extension polymerization cannot be observed.

**DSC.** The DSC thermograms of 25% methylated and 75% propargylated starting material and the polymers following the oxidative coupling reactions are shown in the Supporting Information (Figure S4). Each sample shows a broad exothermic peak between 150 and 280 °C. It is rational to conclude that these exothermic peaks are generated due to the Claisen rearrangement and subsequent polymerization of the remaining terminal alkynes after the coupling reaction. Based on 1H and 13C NMR we have found that significant amount of terminal alkynes still remain unreacted after the oxidative coupling reaction.22 The gradual decrease in the amount of heat evolved most likely depicts that lower amounts of alkyno groups remain unreacted when the coupling reactions are conducted at an elevated temperature with the concomitant increase in the degree polymerization. This data is in good agreement with our GPC results where the molecular weight of the polymers after the coupling reaction increases with increasing temperature. However, we were not able to determine a Tg for the coupled samples for the same reasons as discussed earlier for the simple propargylated liginns.

**Bulk Thermal Polymerization.** Due to the multifunctional structure of lignin and in an effort to avoid the onset of gelation we selected to conduct the thermal polymerizations in samples that contained 25% methylated and 75% propargylated phenolic −OH groups (as discussed earlier). While heating the aryl propargyl moieties of the propargylated ASKL samples, a thermal sigmatropic Claisen rearrangement is initially occurring forming 2H-chromene or 2H-1-benzopyran structures, which eventually polymerize through the ene-ene homopolymerization reaction of the reactive double bonds to produce high molecular weight polymers, as shown in Scheme 3.22−26,32

To further confirm our contentions, we subjected the isolated polymers to 13C NMR (Figure 9). The 13C NMR spectrum shows new signals at 75 ppm corresponding to the chromene −OCH2 group (signals 1, 2; Figure 9B) and between 48 and 49 ppm corresponding to the methine carbons generated during the opening of the double bonds (signals 3, 4; Figure 9B), as per relevant literature citations.23,24,26,32 Different structures in the lignin may be responsible for the appearance of two different 13C signals between 48 and 49 ppm.

![Scheme 3. Claisen Rearrangement and Subsequent Thermal Polymerizations of the Propargylated Lignin](image-url)

![Figure 9. 13C NMR spectra of (A) 25% methylated and 75% propargylated ASKL sample; (B) 25% methylated and 75% propargylated ASKL after the bulk thermal polymerization.](image-url)
However, signals between 77 and 82 ppm show the presence of substantial amounts of residual alkyne groups. This is most likely due to the mixing restrictions and the experimental limitations in our experimental design of the bulk polymerization. Future efforts are planned to carry out these reactions within a compounding extruder so as to ensure better control and reaction completion.

The thermal polymerization reactions were conducted at different predetermined temperatures and for predetermined periods of time, as shown in Table 3, offering the possibility to optimize the molecular weights of the polymers obtained.

**Molecular Weight.** The number and weight average molecular weights and the PDIs for the thermally polymerized polymers are calculated from the GPC traces (Figure 10) and are reported in Table 3. Apparently an increase in the polymerization temperature at around 150 °C causes the molecular weight distribution curves to shift toward higher molecular weights in a progressive manner.

However, exposing this 75% propargylated sample (25% methylated) at 170 °C for 20 min produced a gel that shows its distinct characteristic insolubility in THF (GPC eluent) even after acetobromination. Present efforts in our laboratory are aimed at further charting the thermal polymerization behavior of progressively propargylated fractionated technical lignin with the aim to explore the complete range of chain extended lignin polymers produced using this method.

In an effort to further define the chemistry that operates under thermal polymerization conditions within propargylated ASKL, we further examined the stability of the aliphatic −OHs under such conditions. To do this, a sample of 25% methylated, 75% propargylated ASKL was subjected to 1 h of thermal polymerization conditions at 150 °C under oxygen (so as to accentuate and emulate possible commercial operations). The amounts of the various −OH groups on the sample before and after heating were then quantitatively determined using 31P NMR spectroscopy (Figure S5). It was thus found that only 8.5% of the aliphatic −OHs were eliminated during the heating period. This data indicates that the aliphatic −OHs are quite capable of withstanding moderate thermal treatments within the propargylated lignin. This offers possibilities for additional modification chemistries being applied after the chain extension chemistry of the kraft lignin is first executed.

**Thermal Properties of Bulk Thermal Polymer.** The thermal stability of the polymers formed after thermal bulk polymerization were examined using the TGA apparatus and reported in the Supporting Information (Figure S6). The thermal stability is shown to be significantly improved from the starting ASKL to the propargylated ASKL, as discussed earlier. However, the chain extended polymers do not show any significant improvement in the thermal stability compared to the propargylated lignin material. This can be explained by the fact that the propargylated lignin itself forms a polymer during heating in the TGA as stated earlier, which improves its thermal stability. As such, the additional thermal stability due to the chain extension polymerization cannot be observed.

### CONCLUSION

The progressive propargylation of softwood kraft lignin has been demonstrated and the reactivity of the different types of phenolic −OHs present in the lignin toward this reaction has been elucidated. Propargyl bromide, under the described experimental conditions, selectively reacts with the phenolic −OHs in softwood kraft lignin while the aliphatic −OHs remain unaffected. Quantitative 31P NMR studies further show that there is significant reactivity differences among the various phenolic −OH groups and these are clarified in detail. The thermal stability of the propargylated lignin improves with increasing degree of propargylation. This is due to the initially occurring thermal rearrangement of the aryl propargyl ether moieties to form 2H-chromene or 2H-1-benzopyran structures, which eventually polymerize through an ene-ene homopolymization reaction of the reactive double bonds to produce high molecular weight polymers. This reaction upon further investigation showed potential for creating chain extended kraft lignin polymers. Furthermore, copper-mediated oxidative coupling reactions of propargylated kraft lignin were also demonstrated and another potential method for kraft lignin chain extension has been established.

Overall, the examined derivatization chemistry of the technical lignins offers a versatile novel route for their eventual utilization with a significant amount of molecular control. This is demonstrated by our approach of kraft lignin reactivity modulation via the combination of methylation and chain extension.

### ASSOCIATED CONTENT

#### Supporting Information

Figure S1, Linear relation between the increases of intensity of the alkyne CH stretching peak with % of propargylation. Figure S2, 1H NMR after the copper-mediated coupling reaction; Figure S3, TGA traces of the polymer product after Cu-mediated oxidative coupling; Figure S4, DSC traces of the polymer product after Cu-mediated oxidative coupling; Figure S5, Quantitative 31P NMR spectra of 25% methylated and 75% propargylated ASKL (A) before and (B) after thermal polymerization in bulk; Figure S6, TGA plots of the initial ASKL, the propargylated ASKL and the polymer (sample 3; see Table 3) formed after thermal polymerization in bulk. This material is available free of charge via the Internet at http://pubs.acs.org.