ACS Sustainable Chemistry & Engineering

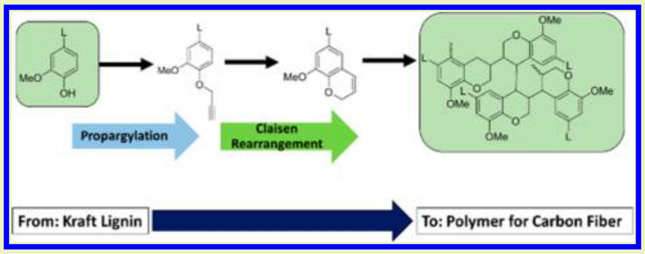
Research Article

pubs.acs.org/journal/ascecg

Toward Carbon Fibers from Single Component Kraft Lignin Systems: Optimization of Chain Extension Chemistry

Hasan Sadeghifar,[†] Sanghamitra Sen,[§,†] Shradha V. Patil,[§,†] and Dimitris S. Argyropoulos*[,†,‡]

[†]Organic Chemistry of Wood Components Laboratory, Departments of Forest Biomaterials and [‡]Chemistry, North Carolina State University, 2820 Faucette Drive, Raleigh, North Carolina 27695-8005, United States



ABSTRACT: Single component softwood kraft lignins have been sought after as precursors to carbon fibers. This noble goal can be achieved by adding carbon onto lignin via propargylation. The reactivity of propargylated lignins may then be modulated via methylation, thus eliminating the onset of gelation via phenoxyl radical initiated random polymerization. This article demonstrates that properly installed propargyl groups of an acetone soluble kraft lignin (ASKL) fraction can be thermally polymerized to high molecular weights in a controlled manner. In order to create single component chain extended softwood kraft lignin systems for carbon fiber applications, one needs to regulate the amount and the positioning of the propargyl groups on the lignin. This became possible, and it is now demonstrated that the propargylation of lignin needs to occur first, followed by methylation and not the other way around. Such a sequence offers substantial benefits for the onset of a Claisen rearrangement to occur between the propargyl groups and the free C5 positions of the softwood lignin. Furthermore, once in position, the created benzopyrans can effectively further polymerize in a controlled manner offering chain extended kraft lignin products of sufficient molecular weight so as to apply subsequent stabilization and carbonization steps to it.

KEYWORDS: *Softwood kraft lignin, Claisen rearrangement, Thermal polymerization, Methylation, Propargylation, ^{31}P NMR, DSC, Phenolic−OH*

■ INTRODUCTION

Lignin is a naturally occurring biopolymer with an amorphous and branched polyphenolic network structure.[1,2] Large amounts of this biopolymer are produced daily as a byproduct of pulp and paper industry via the kraft process (also known as the sulfate process).[3]

Lignin is composed of aromatic rings and has considerable potential to replace a variety of fossil based aromatic polymers. As such, it opens up a new arena of alternative sustainable chemistry along with the opportunity for significant financial ramifications. Kraft lignins are of relatively low molecular weight, high polydispersity, and of variable functional group content.[4,5] Currently, the main use of kraft lignin is the generation of energy for the pulp and paper industry. However, currently only 2% of the isolated lignin is being used for processes other than incineration.[2,6] The abundant presence of phenolic structures in kraft lignins has directed a number of investigations toward utilizing it as a phenolic polymer in its native or derivatized form.[7−10]

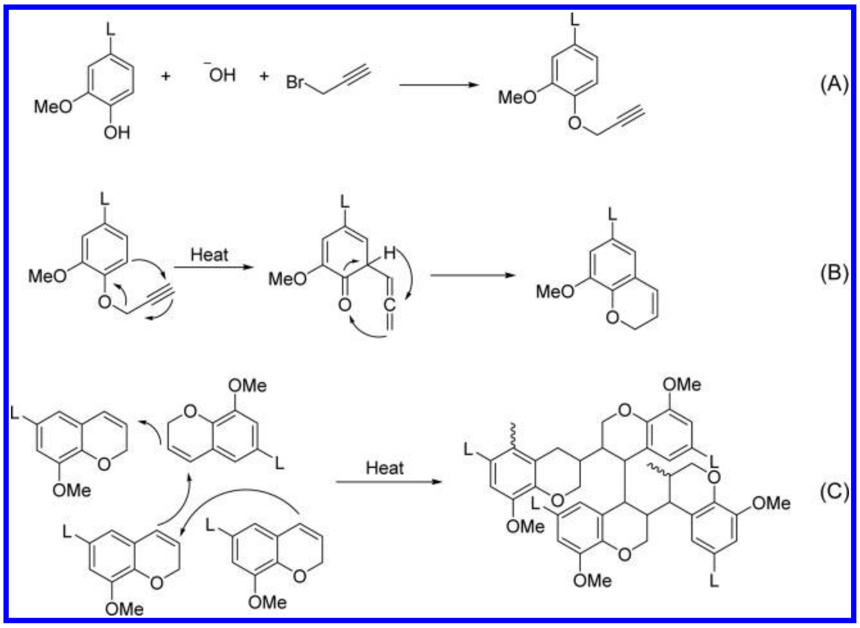
Additionally, researchers have directed efforts toward an intense investigation for exploring the use of lignin as a precursor to carbon fibers (CF's)[11−15] because this may satisfy many of the requirements for skillfully exploiting this naturally available resource.[16,17] CFs display high stiffness and strength which along with their low density makes them extremely valuable reinforcing materials for polymer composites. These materials are currently manufactured from polyacrylonitrile (PAN), an expensive polymer, thus limiting their use to specialty applications, such as automotive, aerospace, and sporting goods. The use of lignin as a precursor could contribute to a 2-fold reduction of the final cost of carbon fibers according to the estimations of the US Department of Energy cited in a recent review by Baker and Rials.[18] However, the molecular weight of technical lignin is low, and it has a glass transition temperature (T_g) far below the temperatures required for carbonization; therefore, it must be pretreated to prevent softening during carbonization.[19,20] Consequently, lignin derivatization becomes essential if one is to prepare CF precursors from it to prevent softening. Air oxidation is a simple and cost-effective method of thermal stabilization. During the production of lignin based CFs, the omission of the thermal stabilization process is anticipated because lignin contains a large amount of oxygen.[13] However, its low molecular weight and in particular its T_g, being well below the temperatures required for carbonization and stabilization, offers severe limitations to the material. Reactions occurring during such thermal treatments increase its T_g, but at heating rates realistic to actual commercial production rates, the thermal stabilization reactions are not able to maintain a high

Special Issue: Lignin Refining, Functionalization, and Utilization

Received: April 23, 2016
Revised: June 13, 2016

DOI: 10.1021/acssuschemeng.6b00848
ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX

Scheme 1. Sequence of Reactions That Involves Lignin Propargylation (A) Followed by Claisen Rearrangement (B) and Thermal Polymerization (C)



enough T_g,[16,21] and the material devitrifies rendering it unsuitable, limiting its utility in CF production.[19,20] As such, derivatization of this natural polymer becomes essential to prepare CF precursors from lignin.

In our earlier effort,[9,41] we have embarked in describing and discussing the importance of propargylation chemistry on lignin so as to synthesize macromonomers for click chemistry,[22,23] metal mediated oxidative coupling (Glaser or modified Glaser–Hay reaction),[24,25] and thermal polymerization via Claisen rearrangement.[26] We have also discussed that the molecular weight and glass transition temperatures of the thermally polymerized lignin improves significantly relative to the starting material. The intricate polymer structure created within lignin as a result of the benzopyran double bond thermal polymerization chemistry (see Scheme 1C) is offering a regular covalently linked framework from which, after carbonization, a regular carbon fiber material could be envisaged to emerge. As such, thermally polymerized propargylated softwood lignin can be explored as a prospective material for the synthesis of biobased CF precursors.

In this effort, an in-depth investigation of such chemistry on fractionated softwood kraft lignin is reported. In this study, the phenolic–OHs of acetone soluble kraft lignin (ASKL) fractions are propargylated in basic media using variable amounts of propargyl bromide, arriving at thoroughly characterized lignins with various degrees of substitution. Then, efforts toward inducing a thermal-mediated Claisen rearrangement reaction (Scheme 1B) and the ensuing thermal polymerization chemistry (Scheme 1C) of the pendant alkynes are described.[9] As anticipated, the multifunctional nature of the lignin causes it to arrive at a hyper-branched and cross-linked polymer, which is intractable and not suitable for further thermoplastic processing. This major limitation is addressed by appropriately reducing the degree of propargylation and masking the remaining phenolic–OHs by alkaline methylation with dimethyl sulfate. This is a novel approach for the simultaneous systematic modulation of the functionality and the reactivity of lignin developed in earlier parts of our work.[7,27]

MATERIALS AND METHODS

Materials. A sample of softwood (Southern Pine) kraft lignin supplied by Domtar Corporation was isolated via the Lignoboost process[28] and used as the starting material.

Acetone Soluble Fraction of Kraft Lignin. The original kraft lignin was fractionated into two high and low molecular weight fractions based on its solubility in acetone (1g/15 mL).[4,41] The lignin was mixed with pure acetone (1g/10 mL) at room temperature for 10 h. The dissolved acetone soluble fraction (ASKL) was separated from the residue by filtration and recovered by evaporating the solvent in a rotary evaporator followed by drying in a vacuum oven at room temperature for 12 h. The functional groups and the molecular weight of ASKL were determined using quantitative ^{31}P NMR[29,30,32] and gel permeation chromatography (GPC),[9] respectively.[29−32]

Lignin Methylation[40−42] and Propargylation.[9] A 1 g sample of ASKL was dissolved in 15 mL of aqueous 0.5 N NaOH at room temperature. Depending on the required degree of methylation, an appropriate amount of dimethyl sulfate (DMS) ranging from 0.25 to 2.00 mmol per each mmol of the total phenolic–OH groups present in the sample was added and the reaction medium stirred for 30 min at room temperature followed by heating at 75 °C for an additional 2 h. The final product was recovered after cooling the mixture to room temperature. Finally, the pH of the solution was adjusted to around 2 by the addition of 2 N HCl. The precipitated sample was washed with enough water and freeze-dried overnight. The level of methylation was determined using ^{31}P NMR spectroscopy.[29,30,32] The remaining phenolic–OHs in the washed methylated lignin samples were further propargylated with excess propargyl bromide in 0.5 M of NaOH at 75 °C for 2 h under continuous stirring.[9] Excess propargyl bromide was used for complete functionalization of the lignin sample. The clean final product was recovered with acidification. The final product was obtained by washing the lignin sample with water followed by freeze-drying overnight. Complete propargylation was examined using ^{31}P NMR spectroscopy.[29,30,32] The second series of samples were first propargylated (using 0.20 to 2.00 equiv of propargyl bromide compared to the total amount of phenolic–OH present in the lignin sample), and then, the remaining phenolic–OH groups were methylated using excess DMS (for complete functionalization) using the procedure described earlier.

Thermal Polymerization in DMSO. ASKL (20 g) samples, which were either first propargylated and then methylated or first methylated and then propargylated, were dissolved in dimethyl sulfoxide (DMSO)

(100 mL) and transferred within a glass lined Parr reactor equipped with a mechanical stirrer. Two reaction temperatures, 150 and 180 °C, and three reaction times (45, 60, and 180 min) were examined. After completion of the reaction, the mixture was allowed to cool to room temperature and then acidified with 2 N HCl to precipitate the lignin. The precipitated lignin was washed with water and then freeze-dried overnight followed by drying in a vacuum oven at 40 °C.

Thermal Polymerization in an Extruder. A laboratory scale extruder (DSM Xplore Micro 15 cm^3 Twin Screw Compounder) of 15 mL capacity was used for the dry thermal polymerization runs. Thirteen grams of a lignin sample (first methylated then propargylated) was injected into the extruder using a manual feeder. The temperature of the barrel was set at 170 °C, and the actual mixing took place for 25 min at a screw rotating speed of 100 rpm.

^{31}P NMR Spectroscopy. The methylation and propargylation levels of the kraft lignin samples examined were determined using quantitative ^{31}P NMR on a Bruker 300 MHz spectrometer as per the earlier parts of our work.[29,30,32] An accurately weighed amount (40 mg) of a dried lignin sample was dissolved in 600 μL of anhydrous pyridine/$CDCl_3$ mixture (1.6:1, v/v). A total of 200 μL of an endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide solution (9.23 mg/mL) served as the internal standard, and 50 μL of a chromium(III) acetylacetonate solution (5.6 mg/mL) served as the relaxation reagent. These were added to the above pyridine/$CDCl_3$ solution. Finally, 100 μL of the phosphitylating reagent II (2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane) were added and transferred into a 5 mm NMR tube for subsequent NMR acquisition using 256 scans, 12,000 Hz sweep width, and 5 s delay time.

Acetobromination.[31] A lignin sample (10 mg) was weighed into a predried reaction vessel, where 2.3 mL of glacial (anhydrous) acetic acid was added. The reaction mixture was stirred for 30 min, and then, 0.25 mL (3.38 mmol) of acetyl bromide was added. The reaction mixture was finally stirred at room temperature for 4 h. Acetic acid and excess of acetyl bromide were evaporated with an efficient rotary evaporator followed by high vacuum drying at 25−30 °C for 30−45 min. The acetobrominated lignin products were completely soluble in the GPC mobile phase (THF).

Gel Permeation Chromatography (GPC). GPC measurements were carried out using a Waters GPC instrument equipped with UV (set at 280 nm) and RI detectors using tetrahydrofuran (THF) as the eluent at a flow rate of 0.7 mL/min at 35 °C. An injection volume of 50 μL and a sample concentration of 0.3 mg/mL were used. Two ultra styralgel linear columns (Styragel HR2 and Styragel HR 5E) were linked in series. A series of polystyrene narrow standards were used for calibration purposes (the actual series was of M_w 820, 2330, 3680, 18 700, 31 600, 44 000, 212 400, 382 100, 570 000, 994 000, and 1 860 000 g/mol).

Differential Scanning Calorimetry (DSC). A TA-Instruments model TA-Q100 was used for the DSC analyses. All samples were dried at 60 °C for 12 h in a vacuum oven prior to the DSC analyses. Approximately 5 mg of a sample were weighed directly into a DSC hermetic aluminum pan. Then, the pan was covered by its lid and sealed by cold pressing and a small hole (around 1 mm diameter) was carefully created on the lid. An empty pan was prepared as the control. After being loaded into the TA-Q100, all samples were heated up to 105 °C at a rate of 1 °C/min. They were then isothermally conditioned at this temperature for 20 min prior to being quenched to 20 °C, where they were 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.

RESULTS AND DISCUSSION

The main objective of this research program was to develop a systematic understanding that could facilitate the steps that involve the Claisen rearrangement (Scheme 1B) and the thermally induced polymerization (Scheme 1C) of propargylated softwood kraft lignin (Scheme 1A) to form higher molecular weight polymers.

A number of studies have shown that one of the main constraints on lignin from readily becoming a versatile feedstock for a variety of applications is its heterogeneity which leads to unpredictable and uncontrollable reactions.[4,28,33] Consequently, we have examined this issue here by making sure that the PDI of our samples is actually narrow so that we minimize this variable before proceeding to a more complex polydisperse system. Reports regarding lignin fractionation via the use of extraction protocols with organic solvents of varying polarity and/or dielectric constant show that a fraction with lower molecular weight and lower polydispersity can be obtained with promising application potential.[34−36] Our recent work, however, has shown that the use of a multitude of solvents for such endeavors is not necessary but that these issues can be addressed by a fractional precipitation protocol using acetone and hexane.[4] Accordingly, in this work we fractionated the as received kraft lignin by dissolving it in acetone following an even more simplified version of the earlier devised process.[4] About 70% of the dry kraft lignin was dissolved in pure acetone. The weight-average molecular weight (M_w) and polydispersity index (M_w/M_n) of the starting kraft lignin was about 6300 g/mol and 6.6, respectively. However, the ASKL was of a considerably lower molecular weight (M_w = 3800 g/mol) and of lower polydispersity (M_w/M_n = 4.3) (all of the molecular weights of the starting kraft lignin and ASKL were measured using our in house developed acetobromination method[31] (see the Materials and Methods section). Quantitative ^{31}P NMR data for the fractionated sample also showed that the ASKL contained 5.83 mmol/g of phenolic−OH and 1.93 mmol/g of aliphatic−OH, while the unfractionated starting lignin contained 4.6 mmol/g and 2.2 mmol/g of phenolic and aliphatic−OHs, respectively. In this respect, the material used in the study was much better defined in terms of functional group distribution and consequent chemical reactivity.

It is important to state at this point that a detailed structure for softwood kraft lignin does not exist and that all the structural explanations of lignin are made on the basis of known chemistry occurring during the kraft delignification process. Since softwood kraft lignin most likely contains phenolic−OHs of variable structure and consequently pK_a values,[37] the reactivity of the phenolic−OHs is expected to be very diverse toward the substitution reactions and is anticipated to depend on their electronic and steric environments.

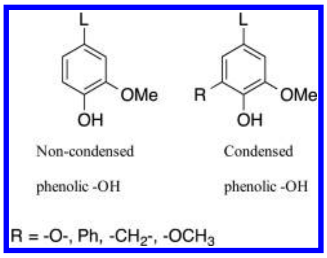
The selectivity of propargylation toward the phenolic−OH groups of lignin was studied and verified in detail in our earlier work using propargyl bromide on purified ASKL.[9] There is ample literature precedent that shows that when aryl propargyl ether terminated monomers are heated at temperatures above 150 °C, they first undergo a thermal sigmatropic Claisen rearrangement to form a 2*H*-chromene or 2*H*-1-benzopyran (Scheme 1B). These intermediates possess reactive double bonds that can subsequently undergo thermal polymerization, generating polymers (Scheme 1C). Resins with these types of curable propargyl etherified phenolics possess enhanced thermal stability, high T_g, long-term high temperature durability, good dimensional stability, good durability, and good curing characteristics.[38,39]

As stated earlier, lignin comprises phenyl propane units, and based on the substitution pattern of the C_5 position (especially true for softwood kraftlignins), the phenyl propane units can be categorized as belonging to condensed or uncondensed units. Condensed phenolic−OHs in lignin are defined, as those that belong to aromatic groups that have a substituent in the 5

DOI: 10.1021/acssuschemeng.6b00848
ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX

position of the aromatic ring, while noncondensed phenolic−OHs have no such substituents (Scheme 2).

Scheme 2. Structures of Condensed and Noncondensed Phenolic Units Present in Lignin



On the basis of the information depicted in Schemes 1 and 2, it is quite clear that only the propargyl groups that are located on the noncondensed phenolic−OHs can participate in the Claisen rearrangement followed by thermal polymerization. In softwood kraft lignin, about 55% of the phenolic−OHs are noncondensed which are able to contribute in the Claisen rearrangement.[40] For the purposes of this study and in view of the objectives of this program, we will define propargyl groups present on noncondensed phenolic units as "active propargyl groups". Consequently, all of the data reported in this effort will be based on the amount of active propargyl groups present in a given sample as it is calculated from the ^{31}P NMR spectra in mmol/g.

The reaction of propargyl bromide (3.8 mg/mmol of −OH) with the phenolic−OHs of the lignin has been shown to increase its molecular weight.[9] For ASKL, which contains a total of 5.8 mmol of phenolic−OH, an increase of 18% of actual weight can be calculated for a fully propargylated sample, altering the gram value of our samples when we express our NMR data on the basis of mmol/g. Consequently, one may calculate the functional groups present per each gram of lignin, allowing one to arrive at the weight gain as induced by the presence of the propargyl groups in it. These calculations showed that the maximum weight gain was18%. However, we could not calculate the weight gain for intermediate propargylation levels. For this reason and since we have invariably used multiple propargylation levels, we used an average value of 7.5% weight gain for all samples to correct and calculate the level of propargylation in mmol/g. On the basis of this approach, our values will contain a maximum error of 7.5%.

On a number of instances, our earlier work[9,41,42] has shown that the noncondensed phenolic−OHs are more reactive than the condensed ones. Both steric and electronic factors may account for these reactivity variations. Furthermore, the multifunctional nature of lignin dictated that extreme care should be paid to polymerization considerations so as to avoid the onset of gelation.[7,10,46,47] As such, in all our published lignin polymerization work we have selected to conduct thermal[41] or step growth,[7,41] polymerizations with partially propargylated[9,41] or otherwise derivatized[7,41] lignin samples. This approach has been found to be very useful to modulate the multifunctional character of lignin.[41]

Furthermore, since our earlier work[9,41,42] has shown that lignin may undergo thermally induced polymerization chemistry initiated via the free phenolic−OHs, it was essential that all available free phenolic−OH be masked via methylation. This was an essential operation inherent in allowing for proper polymer growth in the absence of random phenoxyl radical initiated polymerization. Accordingly in this report, we explore two regimes. We initially explore a variety of ASKL samples where we partially first mask (via methylation) and then propargylate the remaining phenolic−OHs followed by thermal polymerization. In other words, initially we masked the most reactive phenolic−OHs with methyl groups and then propargylated the less reactive remaining phenolic−OHs.

In a second set of experiments, we initially propargylated at various levels the phenolic−OHs of ASKL, followed by methylation of the remaining phenolic−OHs. In the second set of experiments, it is anticipated that the propargyl groups will be installed on more reactive phenolic centers offering for more possibilities of Claisen rearrangement (Scheme 1B) and thermal polymerization events (Scheme 1C). Both of these sets of experiments are aimed at a systematic investigation aimed at understanding and optimizing these reactions toward inducing sufficient chain extension chemistry within the softwood kraft lignin precursors prior to oxidative carbonization.

Methylation Prior to Propargylation. In our initial efforts to chart the reactivity of masked (methylated) propargylated ASKL, we used methylated ASKL, and then, we propargylated it with different levels of active propargyl groups. These samples were heated, as DMSO solutions, at 150 °C and at 180 °C for 1 h and for 3 h.

Not surprisingly, the molecular weights of the resulting polymers were found to increase with increasing degrees of active propargyl groups present and with increasing duration of reaction time and temperature (Figure 1A). All polymer samples produced were soluble in DMSO and acetone showing no signs of stochastic radical initiated self-polymerizations of the lignin creating three-dimensionally cross-linked structures. The absence of gelation type of reactions is also apparent from the shape of the plots of polydispersity as a function of active propargyl groups shown in Figure 1B. The heterogeneity as indicated by the ratio of M_w/M_n is known to be exponentially increasing as a gelation reaction proceeds especially beyond the gel point.[43−45]

For all cases examined, the data in Figure 1A shows that irrespective of the reaction time or temperature, a ceiling in the molecular weight is reached. Despite the apparent 3-fold increases in the M_w values (Figure 1A) from about 4K to about 12K, this is certainly not enough to cause for significant chain extension chemistry that may eventually allow for fiber pulling prior to carbonization. It is likely that the reason for the observed ceiling in the attained molecular weight is that there were not enough propargyl groups present in any of these reactions, capable of promoting a hyper-branched structure creating the sought polymeric character.

For these reasons, another series of thermal polymerization reactions were carried out at 180 °C using a more augmented range of active propargyl groups. While the data of Figure 1 spanned from 0 to 0.8 active propargyl groups, more samples were produced ranging in active propargyl groups from 1.6 to 2.5 mmol/g[4]. Again, it is to be noted that methylation was applied prior to propargylation for the synthesis of these series.

After thermal polymerization at 180 °C for 3 h, as DMSO solutions, the data of Figure 2 shows practically no molecular weight increase when the active propargyl group content ranged from 1.6 to 2.1 mmol/g. In effect, this range of active propargyl groups manifests itself in minor increases in molecular weights similar to the M_w levels attained as per the data of Figure 1A (M_w increased up to 11 000 g/mol). The persistent lack of molecular weight increase beyond a value of

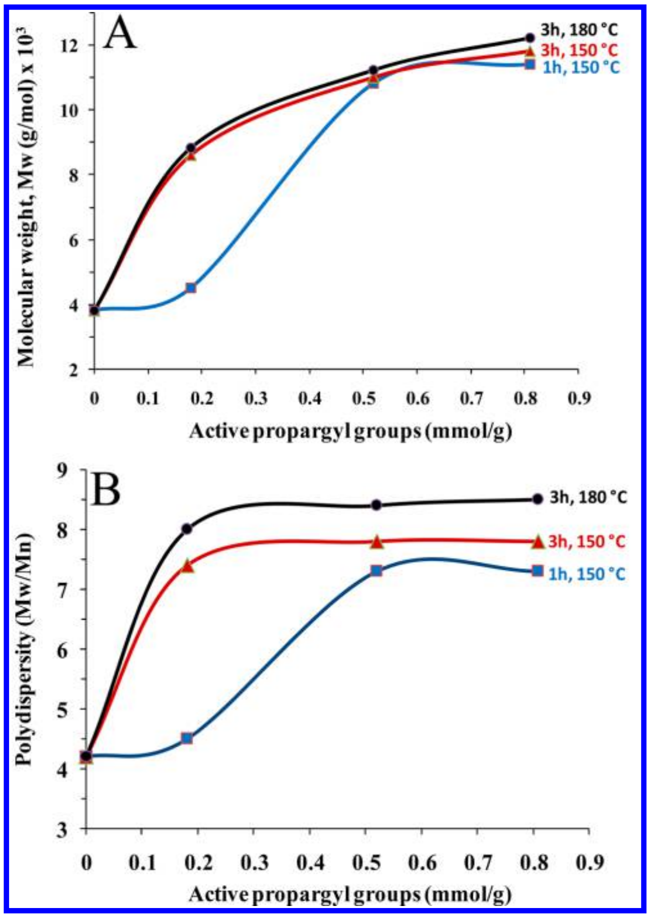


Figure 1. Effect of active propargyl groups and reaction time on (A) the weight-average molecular weight (M_w) and (B) the polydispersity of ASKL at 150 °C and at 180 °C. All lignin samples depicted here were first methylated prior to propargylation.

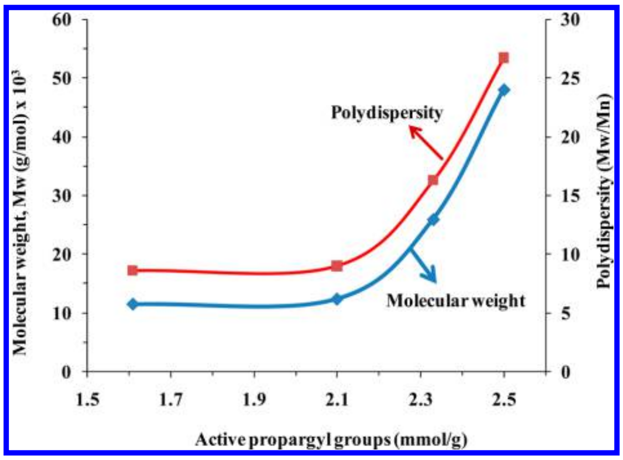


Figure 2. Effect of active propargyl groups on molecular weight and polydispersity of ASKL at 180 °C for 3 h of reaction. All lignin samples depicted here were first methylated prior to propargylation.

about 11–12 000 g/mol is very likely due to the fact that the molecular weight of the starting lignin was rather low (about 4000 g/mol). At a qualitative, molecular level, the data seem to validate the traditional Flory–Stockmayer polymer view that smaller preformed chains need a larger number of cross-linking events to create a network.[46,47]

It is likely that the small starting molecular weight of ASKL requires a larger number of functional points, in the form of active propargyl groups, to promote molecular weight increase. This event could not take place until the amount of active propargyl groups reached 2.1 mmol/g and beyond (see Figure 2).

The shape of the M_w versus active propargyl group content plot, depicted in Figure 2, is indicative that the polymerization reactions occurring via Claisen rearrangement (Scheme 1B) followed by radical polymerization (Scheme 1C), following gelation statistics. This is apparent because beyond an active propargyl group content level of 2.1 mmol/g, small increases in active propargyl group content (e.g from 2.1 To 2.5) manifest themselves in larger increases in M_w (from about 11 000 g/mol to about 50 000 g/mol), and the PDI increases from about 8 to 27. Admittedly, the reaction is still well before the gel point even at active propargyl group levels of about 2.5 mmol/g.

At this point, it is important to point out that beyond the enumerated polymerization statistical considerations, additional reactivity considerations are also likely operating. Conducting methylation prior to propargylation masks all the easily available and most reactive phenolic–OHs of lignin. As the degree of methylation is increased, more and more sterically hindered phenolic–OHs are left behind for further propargylation with limited reactivity for subsequent Claisen rearrangement and thermal polymerization. This reactivity variable also offers difficulties in attaining high molecular weights, and as such, it needs to be further examined. A thorough examination of this variable is conducted in the section below.

Propargylation Prior to Methylation. The reactivity considerations already enumerated were addressed by a series of experiments where initially ASKL was propargylated, thus occupying all readily accessible and highly reactive phenolic–OHs, followed by methylation of the remaining phenolic OHs to limit phenoxy radical induced thermal polymerization. All of the polymerization reactions were conducted by heating the samples at 180 °C for 3 h, and the corresponding molecular weights and distributions were determined.

Figure 3 shows the development of M_w and polydispersity (M_w/M_n) after thermal polymerization as a function of active propargyl group content ranging from 0.4 to 2.6 mmol/g.

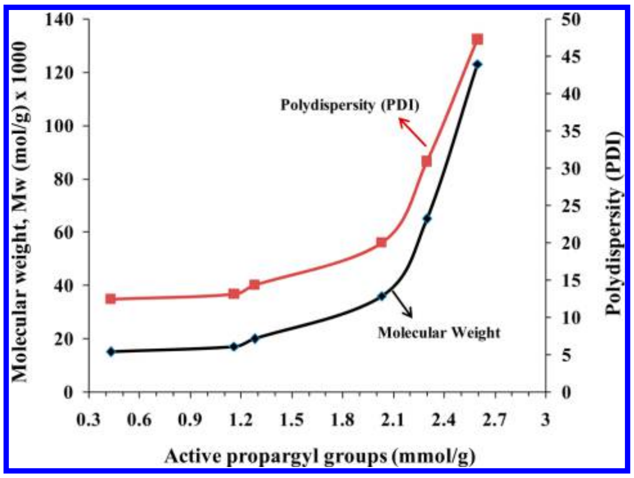


Figure 3. Effect of active propargyl groups on the molecular weight and polydispersity of ASKL at 180 °C for 3 h of reaction for samples that were propargylated first prior to methylation.

As anticipated, the installation of the propargyl groups in more reactive positions, more readily prone to Claisen rearrnagnent and thermal polymerization events, offered much better developed molecular weights. The shape of the overall plot in Figure 3 is exponential, indicative of molecular weights exceeding 130 000 g/mol at the extreme end of active propargyl group content (2.6 mmol/g). Similarly, the extreme heterogeneity of the sample as evidenced by the ratio of M_w/M_n approaching nearly a value of 50 is an undisputed indication that gelation statistics are operational. The fact that all thermally polymerized samples were soluble in acetone and/or DMSO indicates that using the specific starting sample of ASKL (M_w of about 4,000g/mol) and within the examined range of active propargyl groups (0.4–2.6 mmol/g), the reaction conditions were such that the gel point had not yet been reached or exceeded. Overall, our experiments validate our contention that both gelation statistics and significant reactivity issues are the underlying considerations that define the progress of thermally induced polymerization chemistry on propargylated lignin samples.

Solvent-Free Claisen Rearrangement and Thermal Polymerization. For the purposes of the accurate control of the reaction conditions, the thermal polymerization work described so far was conducted in a sealed Parr reactor in DMSO solutions. As already discussed, however, the developed chemistry is seeking knowledge that could be eventually extended toward creating stable chain extended unimolecular systems that could be used as carbon fiber precursors. It is therefore imperative that the lignin polymerization reactions be conducted in bulk in the absence of solvent. To this effect, we used a laboratory twin screw compounding extruder where the propargylated lignin samples were injected and thermally compounded for 25 min at 180 °C. The extruder temperature and rotation speed were selected so as to promote thorough mixing of the precursor lignin oligomers via the shearing forces exerted by the screws, aiming at inducing thermal polymerization for the creation of high molecular weight chain extended lignin based carbon fiber precursors.

In a manner similar to the polymers synthesized in the Parr reactor, the molecular weight of the polymers synthesized in the extruder showed only a small and gradual increase in the molecular weight. After 25 min of actual compounding at 180 °C and at an active propargyl group content of 0.8 mmol/g, only a doubling of the molecular weight could be attained. This data, when coupled with the data of Figures 2 and 3 points to the following two factors as being responsible for the lack of molecular weight development. The one factor being the relatively low degree of active propargyl groups being present and the second being the fact that the propargylation was conducted after methylation. It is thus planned that these experiments be repeated with ASKL samples that are first propargylated with active propargyl groups exceeding the range of 1.5 to 3 mmol/g followed by methylation. It is to be noted that the experimental arrangements used in this work allow and have actually resulted in extruded fibers that are currently under investigation for their strength properties after the necessary additional steps. As stated above, however, and in accordance with our systematic approach, more work is currently being carried out to ensure that we carefully proceed in answering fundamental chemical enquiries in the design and execution of these subsequent steps.

Monitoring the Thermal Polymerization Events Using Differential Scanning Calorimetry (DSC). Scheme 1B depicts the intramolecular ring formation to form the 2*H*-chromene moiety, while Scheme 1C depicts the thermally initiated polymerization reactions of these unsaturated moieties. Both of these reactions are of an exothermic nature,[48,49] especially the latter one since each addition of a double bonded segment to the growing polymer chain involves the conversion of π bonds into σ bonds. Consequently, it was thought appropriate to use DSC to monitor the progress of the reaction and if possible correlate it to the sought molecular weight increase events during future efforts. It is to be noted that the measurements discussed in this section were conducted on ASKL samples that were initially methylated and then propargylated. DSC thermograms of all methylated and then propargylated ASKL samples show broad exotherms developing between 150 to 215 °C (Figure 5 (Lower) and not due to the reactions depicted in Schemes 1B and 1C).[48,49]

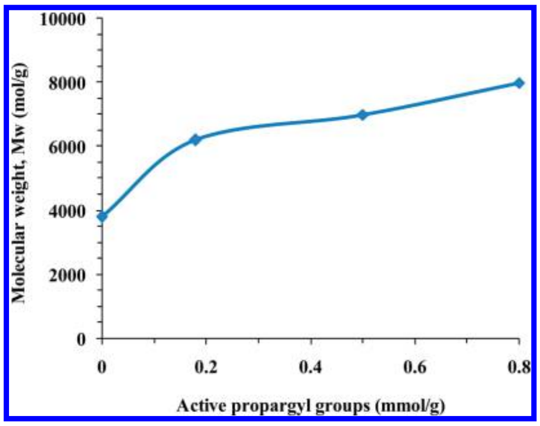


Figure 4. Development of M_w as a function of active propargyl groups of ASKL. (Thermal polymerization was conducted in a laboratory twin screw extruder at 180 °C at compounding time = 25 min. The lignin samples were first methylated and then propargylated.)

Figure 5 shows that the total amount of heat evolved during the Claisen rearrangement and thermal polymerization of the starting methylated propargylated sample containing 0.81 mmol/g active propargyl group is 138 j/g. Once this sample was subjected to thermal polymerizations treatments at 150 °C and at 180 °C for 3 h, the amount of heat evolved was only 38 j/g and 8 j/g, respectively. The reduction in heat evolved with increasing polymerization temperature is because at higher temperatures more active propargyl groups actually participate in 2*H*-chromene formation via the Claisen rearrangement (Scheme 1B) and then proceed to thermal polymerization (Scheme 1C). As such, fewer amounts of active propargyl groups are left behind when the polymerization is conducted at 180 °C compared to 150 °C offering the development of lower amounts of heat during the DSC scans. These data also signify that indeed higher temperatures are beneficial for the development of molecular weight.

Another useful example of the application of DSC toward understanding the progress of these reactions was provided when samples from the experiments of Figure 4 were examined. The DSC scans showed that a small reduction in heat evolution occurred for samples subjected to thermal polymerization via the extrusion approach. This indicates that most of the active propargyl groups remained unreacted during the solvent-free thermal polymerization. As such, there seems to be plenty of room available for further optimizations of this reaction aimed

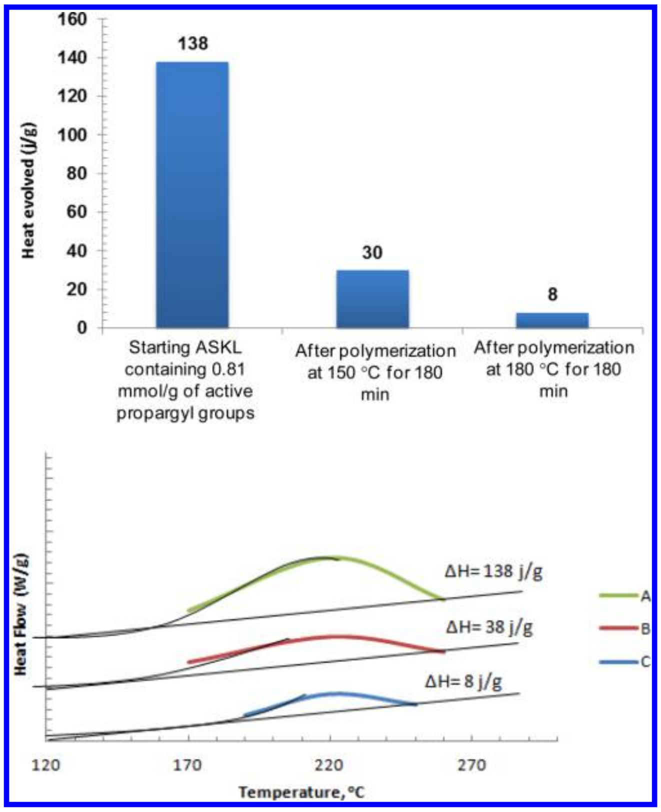


Figure 5. (Upper) Amount of heat evolved (j/g) during a DSC scan for three samples. (A) The starting ASKL (containing 0.81 mmol/g active propargyl group) and (B) a post-polymerized sample heated at 150 °C (for 3 h) and (C) heated at 180 °C for 3 h. (Lower) Actual DSC traces of (A) ASKL containing 0.81 mmol/g of the active propargyl group (B) after polymerization at 150 °C for 180 min and (C) after polymerization at 180 °C for 180 min and the heat evolved.

at creating a financially feasible scheme for the utilization of softwood kraft lignin as a single component precursor to carbon fibers.

Overall, such measurements in combination with the already discussed molecular weight evidence are envisaged to provide additional support for the accurate monitoring of these valuable transformations.

■ CONCLUSIONS

Various thermal polymerizations and Claisen rearrangements were conducted on propargylated ASKL samples. The amounts of active propargyl groups present were thoroughly quantified using ^{31}P NMR. The temperature, reaction time, and amount of active propargyl groups present in the samples showed correlations with the sought increases in the molecular weights of the polymers. Moreover, once an adequately large range of propargyl groups was installed within the lignin the molecular weights (and PDI's) of the resultant polymers were found to increase exponentially when thermally polymerized. Efforts to offer better control on the progress of these reactions led to a close examination of the actual chemistry involved that eventually allowed us to properly design the chemistry that needs to be conducted on the precursor lignin. ASKL samples on which propargylation was conducted, prior to methylation, resulted in polymers with higher weight-average molecular weights compared to lignin samples on which methylation was conducted prior to propargylation. This was anticipated since steric obstructions could operate on the propargyl groups inhibiting thermally induced polymerization when propargylation was carried out after the methylation step. A series of polymerization reactions were also conducted in bulk and solvent-free conditions in a twin screw extruder. These experiments showed that bulk polymerization conditions require higher amounts of active propargyl groups to be present for the proper development of the required molecular weight. Efforts to form carbon fibers from the described chemistry are currently in progress and will be the subject of subsequent publications.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 919-515-7708. Fax: 919-515-6302. E-mail: dsargyro@ncsu.edu.

Author Contributions

§S.S. and S.V.P. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Sette, M.; Wechselberger, R.; Crestini, C. Elucidation of lignin structure by quantitative 2D NMR. *Chem. - Eur. J.* **2011**, *17*, 9529−9535.

(2) 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.

(3) Froass, P. M.; Ragauskas, A. J.; Jiang, J. Chemical structure of residual lignin from kraft pulp. *J. Wood Chem. Technol.* **1996**, *16*, 347−365.

(4) Cui, C.; Sun, R.; Argyropoulos, D. S. Fractional Precipitation of Softwood Kraft Lignin: Isolation of Narrow Fractions Common to a Variety of Lignins. *ACS Sustainable Chem. Eng.* **2014**, *2*, 959−968.

(5) Ropponen, J.; Rasanen, L.; Rovio, S.; Ohra-aho, T.; Liitia, T.; Mikkonen, H.; van de Pas, D.; Tamminen, T. Solvent extraction as a means of preparing homogeneous lignin fractions. *Holzforschung* **2011**, *65*, 543−549.

(6) Wang, J.; Manley, R. S. J.; Feldman, D. Synthetic polymer-lignin copolymers and blends. *Prog. Polym. Sci.* **1992**, *17*, 611−646.

(7) Argyropoulos, D. S.; Sadeghifar, H.; Cui, C.; Sen, S. Synthesis and Characterization of Poly(arylene ether sulfone) Kraft Lignin Heat Stable Copolymers. *ACS Sustainable Chem. Eng.* **2014**, *2*, 264−271.

(8) Hofmann, K.; Glasser, W. G. Engineering plastics from lignin. 21. Synthesis and properties of epoxidized lignin−poly(propylene oxide) copolymers. *J. Wood Chem. Technol.* **1993**, *13*, 73−95.

(9) Sen, S.; Sadeghifar, H.; Argyropoulos, D. S. Kraft Lignin Chain Extension Chemistry via Propargylation, Oxidative Coupling, and Claisen Rearrangement. *Biomacromolecules* **2013**, *14*, 3399−3408.

(10) Wu, L. C. F.; Glasser, W. G. Engineering plastics from lignin. I. Synthesis of hydroxypropyl lignin. *J. Appl. Polym. Sci.* **1984**, *29*, 1111−1123.

(11) Baker, D. A.; Gallego, N. C.; Baker, F. S. On the characterization and spinning of an organic-purified lignin toward the manufacture of low-Cost carbon fiber. *J. Appl. Polym. Sci.* **2012**, *124*, 227−234.

(12) Kubo, S.; Kadla, J. F. Lignin-based carbon fibers: Effect of synthetic polymer blending on fiber properties. *J. Polym. Environ.* **2005**, *13*, 97−105.

(13) Kubo, S.; Uraki, Y.; Sano, Y. Preparation of carbon fibers from softwood lignin by atmospheric acetic acid pulping. *Carbon* **1998**, *36*, 1119−1124.

(14) Sudo, K.; Shimizu, K. A new carbon-fiber from lignin. *J. Appl. Polym. Sci.* **1992**, *44*, 127−134.

(15) Zhang, M.; Ogale, A. A. Carbon fibers from dry-spinning of acetylated softwood kraft lignin. *Carbon* **2014**, *69*, 626−629.

DOI: 10.1021/acssuschemeng.6b00848

(16) Kadla, J. F.; Kubo, S.; Venditti, R. A.; Gilbert, R. D.; Griffith, A. L. Lignin-based carbon fibers for composite fiber applications. *Carbon* **2002**, *40*, 2913−2920.

(17) Maradur, S. P.; Kim, C. H.; Kim, S. Y.; Kim, B.-H.; Yang, W. C. K. K. S. Preparation of carbon fibers from a lignin copolymer with polyacrylonitrile. *Synth. Met.* **2012**, *162*, 453−459.

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

(19) Braun, J. L.; Holtman, K. M.; Kadla, J. F. Lignin-based carbon fibers: Oxidative thermostabilization of kraft lignin. *Carbon* **2005**, *43*, 385−394.

(20) Lin, J.; Koda, K.; Kubo, S.; Yamada, T.; Enoki, M.; Uraki, Y. Improvement of Mechanical Properties of Softwood Lignin-Based Carbon Fibers. *J. Wood Chem. Technol.* **2014**, *34*, 111−121.

(21) Uraki, Y.; Kubo, S.; Nigo, N.; Sano, Y.; Sasaya, T. *Holzforschung* **1995**, *49*, 343−350.

(22) Chung, H.; Al-Khouja, A.; Washburn, N. R. Lignin-Based Graft Copolymers via ATRP and Click Chemistry. In *Green Polymer Chemistry: Biocatalysis and Materials II*; ACS Symposium Series; American Chemical Society: Washington, DC, 2013; Vol. *1144*, Chapter 25, pp 373−391.

(23) Cohrt, A. E.; Jensen, J. F.; Nielsen, T. E. Traceless Azido Linker for the Solid-Phase Synthesis of NH-1,2,3-Triazoles via Cu-Catalyzed Azide−Alkyne Cycloaddition Reactions. *Org. Lett.* **2010**, *12*, 5414−5417.

(24) Hay, A. S. Polymerization by oxidative coupling: Discovery and commercialization of PPO® and Noryl® resins. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 505−517.

(25) Lin, J.; Lam, J. W. Y.; Tang, B. Z. Acetylenic polymers: Syntheses, structures, and functions. *Chem. Rev.* **2009**, *109*, 5799−5867.

(26) Wang, M.; Yang, L. Lignin Functionalized by Thermally Curable Propargyl Groups as Heat-Resistant Polymeric Material. *J. Polym. Environ.* **2012**, *20*, 783−787.

(27) Sen, S.; Patil, S.; Argyropoulos, D. S. Methylation of Softwood Kraft Lignin with Dimethyl Carbonate. *Green Chem.* **2015**, *17*, 1077−1087.

(28) Tomani, P. The Lignoboost Process. *Cellulose Chem. Technology* **2010**, *44*, 53−58.

(29) Argyropoulos, D. S. Quantitative Phosphorus-31NMR Analysis of Lignins, a New Tool for the Lignin Chemist. *J. Wood Chem. Technol.* **1994**, *14*, 45−63.

(30) Argyropoulos, D. S. ^{31}P NMR In Wood Chemistry: A Review of Recent Progress. *Res. Chem. Intermed.* **1995**, *21*, 373−395.

(31) Asikkala, J.; Tamminen, T.; Argyropoulos, D. S. Accurate and Reproducible Determination of Lignin Molar Mass by Acetobromination. *J. Agric. Food Chem.* **2012**, *60*, 8968−8973.

(32) 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.

(33) Baumberger, S.; Lapierre, C.; Monties, B. Utilization of pine kraft lignin in starch composites: Impact of structural heterogeneity. *J. Agric. Food Chem.* **1998**, *46*, 2234−2240.

(34) Gosselink, R. J. A.; Van Dam, J. E. G.; de Jong, E.; Scott, E. L.; Sanders, J. P. M.; Li, J.; Gellerstedt, G. Fractionation, analysis, and PCA modeling of properties of four technical lignins for prediction of their application potential in binders. *Holzforschung* **2010**, *64*, 193−200.

(35) Leger, C. A.; Chan, F. D.; Schneider, M. H. Fractionation and characterisation of technical ammonium lignosulphonate. *Bioresources* **2010**, *5*, 2239−2247.

(36) Thring, R. W.; Vanderlaan, M. N.; Griffin, S. L. Fractionation Of Alcell® Lignin By Sequential Solvent Extraction. *J. Wood Chem. Technol.* **1996**, *16*, 139−154.

(37) Ragnar, M.; Lindgren, C. T.; Nilvebrant, N.-O. pKa-values of guaiacyl and syringyl phenols related to lignin. *J. Wood Chem. Technol.* **2000**, *20*, 277−305.

(38) Agag, T.; Takeichi, T. Novel Benzoxazine Monomers Containing p-Phenyl Propargyl Ether: Polymerization of Monomers and Properties of Polybenzoxazines. *Macromolecules* **2001**, *34*, 7257−7263.

(39) Chang, H. C.; Lin, C. H.; Lin, H. T.; Dai, S. A. Deprotection-free preparation of propargyl ether-containing phosphinated benzoxazine and the structure-property relationship of the resulting thermosets. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 1008−1017.

(40) Sadeghifar, H.; Cui, C.; Argyropoulos, D. S. Toward Thermoplastic Lignin Polymers. Part 1. Selective Masking of Phenolic Hydroxyl Groups in Kraft Lignins via Methylation and Oxypropylation Chemistries. *Ind. Eng. Chem. Res.* **2012**, *51*, 16713−16720.

(41) Argyropoulos, D. S. High Value Lignin Derivatives, Polymers, & Copolymers & Use Thereof in Thermoplastic, Thermoset, Composite and Carbon Fiber Applications. US Patent US 20130255216 A1, 2013.

(42) Cui, C.; Sadeghifar, H.; Sen, S.; Argyropoulos, D. S. Towards thermoplastic lignin polymers; Part II: Thermal & polymer characteristics of kraft lignin & derivatives. *BioResources* **2012**, *8*, 864−886.

(43) Argyropoulos, D. S.; Berry, R. M.; Bolker, H. I. Polymerization beyond the gel point. I. The molecular weight of sol as a function of the extent of reaction. *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *25*, 1191−1202.

(44) Argyropoulos, D. S.; Berry, R. M.; Bolker, H. I. Polymerization beyond the gel point, 2. A study of the soluble fraction as a function of the extent of reaction. *Makromol. Chem.* **1987**, *188*, 1985−1992.

(45) Argyropoulos, D. S.; Berry, R. M.; Bolker, H. I. Species distribution within the soluble phase beyond the gel point. *Macromolecules* **1987**, *20*, 357−361.

(46) Flory, P. J. Molecular Size Distribution in Three Dimensional Polymers. I. Gelation. *J. Am. Chem. Soc.* **1941**, *63*, 3083−3090.

(47) Stockmayer, W. H. Theory of Molecular Size Distribution and Gel Formation in Branched Polymers II. General Cross Linking. *J. Chem. Phys.* **1944**, *12*, 125−131.

(48) Chernykh, A.; Agag, T.; Ishida, H. Novel benzoaxazine monomer containing diacetylene linkage: An approch to benzoxazine thermosets with low polymerization temperature without addedinitiators or catalysts. *Polymer* **2009**, *50*, 3153−3157.

(49) Nair, C. P. R.; Bindu, R. L.; Krishnan, K.; Ninan, K. N. Bis propargyl ether resins: synthesis and structure-thermal property correlations. *Eur. Polym. J.* **1999**, *35*, 235−246.