

**Enabling high-quality carbon fiber through transforming lignin into an
orientable and melt-spinnable polymer**

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Abstract

Red oak derived crude lignin bio-oil (LB) containing mostly phenolic oligomers were synthesized to acrylate polymers based on a two-step functionalization method followed by reversible addition–fragmentation chain-transfer (RAFT) polymerizations. The LB was first partially acrylated and then subsequently acetylated to control radically polymerizable sites, while suppressing radical inhibitory effect of residue phenolic hydroxyls. It has shown that both the molecular weights and yields of the acrylate polymers increase as either the degree of acrylation or AIBN concentration increases. On the other hand, a chain transfer agent (CTA) was needed during the radical polymerization to suppress gelation of the LB sample with a high degree of acrylation. It was also found that the LB has several intrinsic properties that are not found in other monomers and their mixtures commonly used in RAFT polymerizations, which affected the polymerization process. Acrylation among different phenolic compounds in the LB was non-uniform, and multi-hydroxyl oligomers were preferentially acrylated. The crude LB could be polymerized in the presence of AIBN even without acrylation, although the molecular weight of the non-acrylated polymer was much lower compared to those of acrylated polymers. The LB also contains intrinsic free radicals and their concentration decreased as the AIBN concentration increases, implying the free radicals either consume the AIBN radical initiators or prematurely terminate chain growth by coupling with chain propagation radicals. In the present study, the T_g of the LB-derived acrylate polymers ranged from 93.7 °C to 160.6 °C, increasing as the degree of

acrylation or AIBN concentration increased. There was a linear relationship between the number average molecule weight (M_n) and the T_g s of the polymers. All polymers exhibited similar decomposition profiles during the TGA in N_2 atmosphere. However, under the air atmosphere, the polymers with lower acrylation degrees had much better thermal stability. The polymers with lower degree of acrylation or lower AIBN concentration also had improved viscoelastic properties and melt processability.

Keywords: Lignin bio-oil, acrylation, acetylation, polymer, RAFT polymerization

1. Introduction

Lignin is the second most abundant natural polymer on earth, next to cellulose. It is also the major byproduct from pulping industries and cellulosic bio-refineries, available in large quantities and low cost¹. Therefore, successful lignin valorization can greatly contribute to the development of bio-renewable products and green environment. To date, extensive research has been conducted to convert lignin into biofuels, chemicals, polymers and composites². The synthesis of lignin-inspired polymers has also been frequently demonstrated using lignin-derived model monomers^{3,4}. For instance, biobased bisphenol was prepared by reacting guaiacol and vanillyl alcohol⁵, and bisepoxide was synthesized using syringaldehyde as starting material⁶. In addition, vanillin, ferulic acid, syringol, ethyl or methylsyringol were also used to synthesize bio-polymers^{3,7}. While most of the above studies demonstrated the syntheses using commercially available synthetic monomers, a few studies also used the monomers isolated from real biomass or lignin. Koelewijn et al. developed polycarbonates and cyanate ester resins using propylguaiacol isolated from softwood lignin⁸, and Wang et al. used poplar wood-derived 4-propylsyringol and 4-propylguaiacol to synthesize an adhesive material⁹. Nevertheless, the synthesis routes using monomers as feedstocks were often straightforward in most of the previous studies. For example, only mono-hydroxyl monomers were chosen as the starting materials, and rigorously linear thermoplastic polymers were synthesized based on a single-step methacrylation and subsequent radical polymerization^{3,7}. Since molecular structures and feedstock

compositions were well-defined as they are for any other mono(meth)acrylate system, it was also possible to evaluate the structure-property relationships between the feedstocks and the resulting polymers⁴. While the previous studies demonstrated the properties of polymers and copolymers derived from the well-defined monomeric components of lignin, unfortunately, the practicality of economically obtaining these monomers at the requisite purity and scale from lignin is prohibitive based on current technologies^{10,11}. Due to its amorphous, randomly cross-linked macromolecular structure, lignin usually depolymerizes to yield a complex mixture containing hundreds of different phenolic compounds^{12,13}. Although novel catalysts, solvents, hydrogen and/or high reaction pressures have been used to improve lignin depolymerization¹⁴, selectivity producing high-yield monomers and isolating them from the rest of the mixtures remains technically challenging and cost-prohibitive. Since crude bio-oils are mixtures of various compounds, some studies manually mixed a few model monomers to mimic crude bio-oil⁴; however, these bio-oil mimics are too ideal. Real crude bio-oil is far different compared to the bio-oil mimics both on the compositions and their intrinsic properties. Usually, the lignin-derived bio-oils are extremely heterogeneous mixtures, consisting of monomers and oligomers with various functionalities and molecular sizes. Crude bio-oil is also thermally instable even at room temperature¹⁵, and often contains intrinsically stable free radicals¹⁶. Therefore, the polymer synthesis using crude bio-oils as the starting feedstocks is much more challenging than using homogenous monomers that have simple functionalities. For example, phenolic oligomers in the crude bio-oils have more than one hydroxyl group

in their molecules. When these oligomers are (meth)acrylated, multiple polymerizable sites in a molecule could result in over-crosslinking and gelation even with controlled radical polymerization technologies such as RAFT or ATRP. At the same time, free phenolic and quinonic moieties are exceptionally efficient at stabilizing free radicals, further narrowing the range of synthetic parameters where radical polymerization proceeds yet gelation is suppressed. To overcome these challenges, we have recently developed a hybrid two-step functionalization method to successfully synthesize thermoplastic polymers from a crude lignin bio-oil (LB)¹⁷. Specifically, hydroxyls in the LB were partially (meth)acrylated to limit the number of polymerizable sites and thus the crosslinking tendency. The remaining hydroxyls in the partly (meth)acrylated bio-oil was then acetylated to reduce radical inhibitory effects of the hydroxyls in the subsequent radical polymerization. As a result, a lightly branched linear thermoplastic polymer was obtained. While our study demonstrated a new concept to synthesize thermoplastic polymers from crude LBs, this technique has not yet been well-studied. For example, the range of obtainable molecular weights and yields in relationship to synthetic parameters such as the concentrations of free radical initiator, the degree of acrylation and the presence of chain transfer agent must be known to rationally design useful materials. Properties intrinsic to real crude bio-oil related to its molecular heterogeneity, thermal instability and the presence of free radicals, and their potential effects on the polymer synthesis process also have not been evaluated. To gain further understanding about this synthetic method, a series of acrylate polymers were prepared in this study using a crude LB derived from red oak lignin under various synthesis

conditions and the properties of the resulting polymers were investigated.

2. Experimental

2.1. Materials

The LB was provided by Biocentury Research Farm at Iowa State University and it was produced by fast pyrolyzing red oak in a fluidized bed reactor. The description of the pyrolysis reactor and bio-oil recovery method can be found in the literature¹⁸. Briefly, red oak was pyrolyzed at 500°C using nitrogen as the carrier gas at atmospheric pressure. Bio-oil recovered from first condenser was washed with cold water to remove carbohydrate-derived compounds and obtain the LB as a water-insoluble fraction. The chemicals including 2,2'-Azobis(2-methylpropionitrile) (AIBN), acryloyl chloride, triethylamine, dichloride methylene (DCM) and acetyl chloride were purchased from Sigma-Aldrich. As-received AIBN was recrystallized in methanol and then stored at -20°C. 2-cyanopropan-2-yl methyl carbonotrithioate (CYCART), a chain transfer agent (CTA), was synthesized according to established procedure¹⁹ and stored at -20 °C. Deuterated chloroform for NMR tests was purchased from Sigma-Aldrich and used as received.

2.2. LB functionalization

Prior to polymer synthesis, LB was subjected to two-step functionalization by combining partial acrylation and acetylation. The typical functionalization process is given as below: about 25g of LB was dissolved in DCM in a sealed flask with a ratio

of 1g LB to 20mL DCM. Triethylamine was added to the solvent mixture prior to adding an acryloyl chloride according to the desired degree of acrylation: 0.5, 1 or 1.5 moles per mole of LB as calculated through the Mw of the LB. Acrylation was conducted at room-temperature for 12 h with magnetic stirring. Acetylation of the partly acrylated LB was conducted by adding triethylamine and an excess amount of acetyl chloride (1 mol LB: 6mols acetyl chloride). The acetylation was also carried out for 12 h at room temperature with a constant stirring rate of 500 RPM. After the acetylation was completed, an excess amount of water was added to the beaker to remove water-insoluble solids. The liquid fraction was further washed with an excess amount of sodium bicarbonate solvent (8g sodium bicarbonate: 200mL water). The liquid product was then vacuum dried at 40 °C for overnight to remove residual DCM. In this study, the functionalized LBs were denoted as LBA-0.5, LBA-1 and LBA-1.5 depending on the degree of acrylation. For example, LBA-0.5 stands for the LB functionalized using 0.5 moles acryloyl chloride per mole of LB followed by acetylation. The yields of the functionalized LBs were calculated based on the initial mass of the LB.

2.3. Polymer synthesis

For polymerization, the LBAs were first dissolved in 1, 4-dioxane at the ratio of 1 g of LBA to 3ml of 1,4-Dioxane at room temperature, followed by adding 0.1-5 wt % of AIBN. CTA (CYCART) was also added to the solvent at a 35:1 molar ratio of LB:CTA. The polymerization was performed at 90°C for 4 hr under nitrogen and constant agitation of 500RPM. After the polymerization, the products were vacuum dried overnight to remove 1,4-Dioxane and the remaining solids were washed with methanol

for at least two times before they were again vacuum dried. The resulting polymers were denoted as LBAP-A-B, where “A” is the degree of acrylation and “B” indicates the concentration of AIBN added during the polymerization. For example, LBAP-1-0.5 stands for a polymer obtained after the LB was functionalized with 1 mole acryloyl chloride per mole LB (followed by acetylation), and then polymerized in the presence of 0.5wt% of AIBN and CTA. The LBA-1.5 was also polymerized with 5wt% of AIBN in the absence of CTA.

In addition to above, the LBA was only acetylated and then polymerized in the absence of AIBN, or presence of 1 or 5wt% of AIBN and CTA using the same method described above. The resulting polymers are denoted as LBAP-0-0, LBAP-0-1 and LABP-0-5.

2.4. Characterizations

A gel permeation chromatography (GPC) analysis was conducted using Dionex Ultimate 3000 series high performance liquid chromatography (HPLC) system to obtain molecule weight distribution. The HPLC was equipped with a Shodex Refractive Index (RI) and Diode Array Detectors (DAD), and a UV detector at 254 nm was used to detect the peaks. Two GPC columns (3 mm, 100 Å, 300 × 7.5 mm; PLgel, Agilent, p/n PL1110-6320) were calibrated with six monodisperse polystyrene standards ranging from 162 g/mol to 45120 g/mol. Tetrahydrofuran was both the eluent and the solvent.

A Bruker Biospin Advance 600 MHz was used to conduct ¹H NMR analysis. The samples were dissolved in CDCl₃, and 4-nitrobenzaldehyde was used as the internal

standard (IS). To analyze LB, it was first acetylated with an excessive amount of acetyl chloride at room temperature prior to the analysis. The OH content in the LB was calculated based on the peak area between 2-2.3ppm. For LBAs, their peak areas between 6-7 ppm were subtracted by the corresponding peak area of the LB to determine the C=C bond concentrations.

An Agilent 7890B gas chromatograph (GC) with Agilent 5977A mass-selective detector (MSD) and flame ionization detector (FID) was used to identify and quantify the monomers. The capillary column used in the GC was ZB-1701 (60 m \times 250 μ m \times 0.25mm). The flow rate of the front inlet was 156 ml/min with a split ratio 100:1, and the temperature at the GC inlet was 250°C. During the analysis, the oven temperature ramped from 40 °C to 280 °C with a 6 °C/min heating rate and hold for additional 3min. The compounds were identified by the MS based on NIST library database and quantified by the FID. The standard chemicals with five different concentrations were injected to the GC to create calibration curves.

Fourier Transform Infrared (FTIR) analysis was carried out using Thermo Scientific Nicolet iS10 equipped with a Smart iTR accessory. The wave numbers ranged from 750 cm^{-1} to 4000 cm^{-1} and each sample was scanned 32 times at a resolution of 4 cm^{-1} and interval of 1 cm^{-1} .

A Bruker ELEXYS E580 FT-EPR spectrometer at the X-band (9.5 GHz) microwave frequency with a magnetic field modulation of 100 kHz at room temperature was applied to conduct Electron Paramagnetic Resonant (EPR) analysis. The sample was dissolved in 1,4-dioxane with a ratio of 100mg:1mL. After the sample was fully

dissolved, the liquid was transferred to a quartz tube and kept in cool environment. The standard used in the EPR was DPPH (2,2-diphenyl-1-picrylhydrazyl). EPR parameters were given as following: center field of 3340 G, sweep width of 200 G, sweep time of 83.9 s and receiver gain of 30-50 dB and modulation amplitude of 2 G.

A TGA-DSC 1 STARe (Mettler Toledo) system was used to conduct thermal stability tests on polymers under both nitrogen and air environment. The flow rates of the gases were both 100 mL/min. During the tests, about 20 mg of sample was heated from room temperature up to 900 °C with the heating rate of 10 °C/min.

A differential scanning calorimeter (DSC, Q2000, TA instruments) was applied to detect the glass transition temperature (T_g) of polymers. The sample was first rapidly heated to 120°C, hold for 2 min and then cooled down to remove moisture. The sample was then reheated to 250°C with a heating rate of 20°C /min and then hold for 2 min. Nitrogen with a flow rate of 50 mL/min was used as the purge gas. The midpoint T_g of the precursor was determined using a TA software.

A Discovery Hybrid Rheometer (DHR-2, TA Instruments) with 25mm parallel-plate geometry was used to perform rheology tests. For isochronal temperature scan, the temperature increased from 90°C to 250°C at a heating rate of 10 °C/min. The angular frequency was fixed at 10 rad/s and the strain was 1.25%. The frequency sweep scan was conducted at 200 °C, and strain was fixed at 1.25%. The initial angular frequency was 100 rad/s, and decreased to 0.01 rad/s.

3. Results and Discussions

3.1. LB characterizations

The compositions of GC-MS detectable monomers in the LB are given in Table 1. There were only small amounts of monomers in the crude LB and their total yield was lower than 2%. The majority of the LB comprises phenolic oligomers with insufficient volatility for GC. In general, accurate molecular structures of the oligomers in crude LBs are difficult to determine. However, their molecular weight distribution can be obtained based on GPC analysis.

In Fig. 1 (a), a broad molecular distribution was observed, reflecting the complex composition of the LB. The number/weight average molecular weight (M_n/M_w) values are 388 g/mol and 653 g/mol ($\bar{D} = 1.68$). Three basic units constructing lignin are paracoumaryl alcohol (P unit), coniferyl alcohol (G unit) and sinapyl alcohol (S unit) and the molecular weights are 180, 190 and 210 g/mol, respectively. Therefore, the average degree of polymerization (DP) in the molecules in the LB is roughly 3-4. Based on the GPC result and ^1H -NMR result of the LB (Fig. 1 (b)), the mass average hydroxyl content is calculated to be 5.6 moles OH per mole of LB.

3.2. LB functionalization

Three LBAs with different degrees of acrylation were obtained depending on the amount of acryloyl chloride added. Based on the NMR analysis (Fig. 2), the concentrations of newly generated C=C bonds due to acrylation were 0.586, 0.944 and

1.625 mol/mol LB for LBA-0.5, LBA-1 and LBA-1.5. Since each mole of acryloyl chloride added to the LB is supposed to generate one mole of new vinyl C=C, the increased C=C concentrations in the LBAs were close to their theoretical values.

FTIR spectra of the LB and LBAs are compared in Fig. 3(a). The peak at 1510 cm^{-1} corresponds to the aromatic skeleton vibration and serves as a reference to compare different FTIR spectra. The broad peak at 3500 cm^{-1} for hydroxyl groups decreased in all LBAs, confirming the consumption of -OH through the acrylation/acetylation reactions. The peaks at 1670 cm^{-1} in all LBAs correspond to vinyl C=C stretching, further supporting the successful acrylation of the crude oil. As expected, the peak intensity corresponds to the degree of acrylation as $\text{LBA-0.5} < \text{LBA-1} < \text{LBA-1.5}$. The yields of LBA-0.5, LBA-1 and LBA-1.5 were 67.4%, 70.3% and 76.5%, respectively, increasing with the degree of acrylation.

3.3. Polymerization of LBAs

Gelation was not observed when the LBAs were polymerized in the presence of CTA regardless the AIBN concentration. As given in Table 2, higher AIBN concentration was beneficial in achieving higher polymer yield and molecular weight. Comparing the three polymers with same degree of acrylation, the yield of LBAP-1.5-0.1 (0.1% AIBN) was only 27.2%, increased to 46.1% for LBAP-1.5-1 (1% AIBN) and 63.2% for LBAP-1.5-3 (3% AIBN). Further increasing AIBN concentration to 5% only slightly improved the yield to 68.8% for LBAP-1.5-5. The same trend was also observed for LBAP-1-3 and LBAP-1-5. In the FTIR spectra of the polymers shown in

Fig. 3 (b), the peak at 1670 cm^{-1} standing for vinyl C=C bonds was absent at LBAP-1.5-3 and LBAP-1.5-5, whereas it was still visible in LBAP-1.5-0.1 and LBAP-1.5-1. In the RAFT polymerization process, AIBN serves as a persistent source of free radicals that ultimately become managed by the RAFT equilibrium mediated by the CTA. Ordinarily, only a fraction of the molar CTA concentration is needed to create the “persistent radical effect”. Higher AIBN dosing is required in systems that feature lower radical efficiency, such as systems containing radical sinks like inhibitor species. Clearly, the radical efficiency in LBs is quite low, with low polymer yield unless counteracted by relatively high AIBN dosing.

At fixed AIBN concentration, the LB functionalized with a lower degree of acrylation had a lower polymer yield. The yield of LBAP-0.5-5 was 46%, lower than 65.3% for LBAP-1-5 and 68.8% for LBAP-1.5-5. Since vinyl C=C bonds serve as radically polymerizable sites, increasing the degree of acrylation improves polymer yield. Nevertheless, there were no significant increases in the polymer yield when the degree of acrylation exceeds to above 1 mole/mole LB.

The molecular weight averages of the LBAPs are also presented in Table 2. Overall, the polymers with higher molecular weights were obtained with higher AIBN concentrations. This is consistent with the higher yield observations, since in pseudo-living polymerizations all chains are extended as propagation continues. The effect of AIBN concentration on increasing molecular weights of the polymers was significant up to 3% of AIBN. For instance, the M_w was 4260 g/mol with LBAP-1.5-0.1 and it increased to 6840 g/mol with LBAP-1.5-1 and 21395 g/mol with LBAP-1.5-3. In

comparison, the M_w of LBAP-1.5-5 was 22150 g/mol, only a slight increase from that with LBAP-1.5-3. As shown previously, increasing AIBN concentration to above 3% also did not increase the polymer yield noticeably. Higher degree of acrylation also promoted the polymers with higher molecular weights. Among the polymers synthesized using 5% AIBN, the M_w was 4641 g/mol with LBAP-0.5-5, increased to 11666 g/mol with LBAP-1-5 and 20320 g/mol with LBAP-1.5-5. This may be understood through three complementary effects. First, the fraction of inert LB species is reduced as the acrylic content increases. Second, the fraction of multiply acrylated species increases; the reactivity of these species will be higher. Finally, multiply acrylated species will participate in both intra- and inter-molecular crosslinking reactions, which will lead to branched chain architectures and higher molecular weights due to the combination of multiple polymer chains. During RAFT polymerization, the presence of CTA reduces the dispersity by mediating the radical polymerization process to allow the chains to grow homogeneously. In this study, the \bar{D} values of LBAPs range from 2.37 up to 4.83. These values are higher than the methacrylate LB polymers reported in previously, where $\bar{D} < 1.5$.¹⁷ In gelation-suppressed branching systems, high dispersity values are typical and increase with extent of reaction. To further confirm that the CTA is controlling the LBA polymerizations, LBA-1.5 was polymerized with 5% of AIBN in the absence of CTA. As a result, gelation was observed during the polymerization. Therefore, it was confirmed that a CTA is necessary in order to inhibit over-crosslinking reactions and prevent gelation.

It is also worth to note that in the present study, the RAFT polymerization had

also been conducted under reaction time longer than 4 hr (up to 24 hr), or different reaction temperatures (65 °C, 70°C, 80°C and 100°C), and higher sample concentration in the solvent (up to 1g LBA in 1.5ml 1,4-dioxane) for further optimizations. However, these factors had negligible impact on the molecular weight distribution or yield. As the monomer-to-solvent ratio increases, cross-linking and gelation occurs even in the presence of CTA. Therefore, the polymerization condition used above (i.e., 90 °C, 4 hr, 1g LBA: 3ml dioxane) was an optimal condition in the present study in terms of the polymer yields and their Mws. The results also suggested that LB as the feedstock is much different than other RAFT based polymer syntheses used simpler monomer feedstocks⁴.

3.4 Effect of intrinsic properties of LB on radical polymerization

3.4.1. Functionalization of multi-hydroxyl compounds

As described previously, the LBs produced from actual lignin conversions are very different from those bio-oil mimics or a few extracted monomers used in previous studies. Crude LBs have compositions and properties that cannot be duplicated by simply mixing a few strictly mono-vinyl functional monomers. The vinyl functionalization of -OH via (meth)acrylation will inevitably lead to crosslinker-like moieties with multiple polymerizable sites. Many constituents within LBs contain several -OH groups, with an average of 5.16 moles OH/mole LB in this study. Due to their heterogeneity, some of the molecules will have more than the average number of OHs, whereas others have lower than the average numbers of OHs. Unless special

techniques are employed, (meth)acrylation cannot be homogenous among different molecules. For example, suppose LB has 5 equally reactive -OH sites and that esterification proceeds via simple 2nd-order kinetics; the population balances are

$$\frac{d[LB]_{i+1}}{dt} = -k[LB]_{i+1}[A] + k[LB]_i[A],$$

$$\frac{d[A]}{dt} = -k[A] \sum_{i=0}^4 [LB]_i$$

where $[LB]_i$ denotes the concentration of LB with i acrylate substitutions, $[A]$ the acryloyl chloride concentration and k the rate constant. In the case of stoichiometric feed, 1 mole of acryloyl chloride per mole of LB, the initial condition is $[LB]_0 = [A]_0$; $[LB]_{i>0} = 0$. Under such conditions, on complete consumption of the acryloyl chloride, nearly 37 mol% of the LB remains unfunctionalized, 37 mol % is monofunctional, and the remaining 26 mol % of the LB is at least doubly substituted. To evaluate the actual acrylation process of the LB, the methanol solution remaining after a polymer (LBAP-1.5-5) was recovered was subjected to GC/MS analysis and the chromatogram is given in Fig. 4. The compounds remaining in the solution are the portion of the two-step functionalized LB (i.e., LBA-1.5) that could not be polymerized into the polymer chain. As shown, most of the monomer compounds detected in the GC/MS had ester groups but no vinyl C=C group, suggesting that the monomers could not be acrylated in the first step, but were acetylated in the subsequent step. Since vinyl C=C was absent, these acetylated monomers could not be polymerized. It was also observed that some phenolic monomers were neither acrylated nor acetylated. Although their concentration in the LBAs is very low, these compounds could act as radical inhibitors during polymerization due to their phenolic OHs. Despite the acrylation

among different molecules is not uniform, the total added C=C bonds in the LB were close to the stoichiometric numbers, as described above. Therefore, the results also imply that some phenolic molecules are more easily acrylated than others to gain higher than the stoichiometric numbers of vinyl C=C bonds, although it is difficult to determine which molecular structures prefer the acrylation in this study. Not only the location of the OH (e.g., either it is a phenolic OH, primary or secondary aliphatic OH), but other neighboring non-OH functionalities in the molecules may also influence the selectivity and rate of acrylation. Nevertheless, the molecules containing higher numbers of OH definitely have higher probability for acrylation than the monomers with single OH.

3.4.2. The effect of self-polymerization of LB

It is well known that LBs are usually thermally instable attributed by their complex compositions containing various functionalities¹⁵. Due to their high reactivity, LBs could self-polymerize in the absence of catalyst or additives, accelerated by increasing temperatures¹⁶. To investigate the effect of self-polymerization during the radical polymerizations, fully acetylated LB was thermally polymerized in the absence of AIBN and CTA and also with 5% of AIBN and CTA for comparison.

As shown in Table 3, the M_w of the acetylated LB (LBA-0) was 962 g/mol and it slightly increased to 1022 g/mol when it was thermally polymerized without AIBN and CTA (i.e., LBA-0-0), suggesting self-polymerization of the LB does not have significant effect on the result of the RAFT polymerization in this study. On the other hand, the M_w increased to 2246 g/mol when the non-acrylated LB was polymerized

with 5% AIBN and CTA (i.e., LBAP-0-5). The fact that M_w increased by adding AIBN suggests that there are intrinsic radically polymerizable sites present in the non-acrylated LB. For instance, the ether cleavages during lignin polymerization can generate vinyl phenols that are radically polymerizable²⁰. From the NMR result of the LB given in Fig. 3, some peaks were detectable in the range of 6-7ppm, which could stand for natural vinyl C=C bonds. However, the peak of C=C was not noticeable in the FTIR of the LB shown above in Fig. 1, suggesting its concentration could be very low. Also, the M_w of LBAP-0-5 was still significantly lower compared to other polymers produced from acrylated LBs using the same amount of AIBN. Thus, polymerizations mainly occurred at the newly added C=C sites in LBAPs.

3.4.3. The effect of intrinsic free radicals

In addition to the phenolic molecules, LBs can also contain stable free radical species. Free radical formation is known as an important pathway to depolymerize lignin²¹. Most of the free radicals derived during lignin decomposition are highly reactive and thus immediately stabilized through radical couplings or by hydrogen abstraction. However, studies also indicated that some less-reactive free radicals could remain in bio-oils during storage²². Our previous study showed that these intrinsically stable free radicals usually do not contribute to thermal polymerization of bio-oil¹⁶. However, their role during the radical polymerization is yet to be determined. One possibility is that these intrinsic free radicals could participate in radical polymerization, like the AIBN radical initiators when there are vinyl C=C bonds. Another possibility is that they cause radical quenching or radical terminations by coupling with the AIBN radical initiators

or other radicals. If the latter is true, the concentration of the intrinsic radicals would become lower when the LB is polymerized in the presence of AIBN. To verify this hypothesis, raw LB and the polymers synthesized from non-acrylated LB in the absence or presence of 1 and 5% AIBN (i. e., LBAP-0-0, LBAP-0-1 and LBAP-0-5) were subjected to EPR analysis, and the spectra are compared in Fig. 5. EPR spectroscopy has been widely used to identify and characterize free radicals in chemical systems. The intrinsic free radicals in the LB include carbon-centered (e.g., benzyl radicals) and oxygen-centered (e.g., phenoxy radicals) organic species because they are delocalized in a pi system. In Fig. 5, a single peak appeared at around 3508 G in all four samples. No clear peak splitting was observed, which may indicate that multiple types of free radicals exist simultaneously. However, it should be noted that this broader peak shape could also be a result of unresolved hyperfine interactions. Peak intensities and the corresponding G-values of the samples are listed in Table 4. The G-value is related to the location of free radicals. The oxygen-centered phenoxy radical, thought to be a major radical species produced during pyrolytic depolymerization of lignin, typically has G-values ranging from 2.0040 to 2.0053 or higher. The G value slightly changed from 2.00677 in the LB to 2.00692 in LBAP-0-0. The corresponding peak intensity also decreased slightly, possibly because the acetylation of the LB before the polymerization influenced the structure of the intrinsic free radicals. On the other hand, the G values were very similar at LBAP-0-0, LBAP-0-1 and LBAP-0-5 (2.00690-2.60092), suggesting that they contain same types of radicals. As hypothesized, the peak intensities decreased with increasing AIBN concentration during the polymerization,

from 0.764 with LBAP-0-0 to 0.703 with LBAP-0-1 and 0.529 with LBAP-0-5. Increasing amounts of the intrinsic free radicals were converted to non-radical species when AIBN concentration increased. Since there will be more AIBN radical initiators available to couple the LB radicals with higher AIBN concentrations, the intensity of the LB radicals decreased. In other words, the intrinsic free radicals are consumed by the AIBN radical initiators, which may explain why higher AIBN concentrations were required when the LB was radically polymerized in this study and our previous study¹⁷. In fact, the AIBN concentration higher than 3% was required in this study to achieve reasonably high polymer yields and molecular weights. When acrylated LB was polymerized, the intrinsic free radicals may also couple with chain propagation radicals to prematurely terminate the chain growth of LBAPs.

3.5. Characterizations of LBAPs

3.5.1. Thermal properties

In the present study, five acrylate polymers (LBAP-0.5-5, LBAP-1-3, LBAP-1.5-1, LBAP-1.5-3 and LBAP-1.5-5) were further characterized. LBAP-1.5-0.1 was excluded from the characterization since its yield and Mw were both the lowest. As given in Table 5, glass transition temperatures (T_g) were between 93.6 and 160.6 °C for different polymers. Overall, the polymers with higher degrees of acrylation or higher AIBN concentrations had higher T_g s. The M_{ns} of LBAPs and their T_g s could not be related using the Flory–Fox equation, suggesting the LBAPs cannot be described using same polymer system. However, when the T_g s of the LBAPs were plotted against their

corresponding M_{ns} in Fig. 6, a linear increasing trend was observed.

Thermal stability of LBAPs was evaluated using TGA and the results are given in Fig.

7. When the TGA was conducted under N_2 environment (Fig. 7 (a)), all five LBAPs showed similar mass loss trends, which was unexpected. The T_d (for 5% mass loss) was ~ 225 °C and T_{max} (for maximum mass loss rate) was ~ 350 °C. The polymers were relatively stable at temperatures above 450 °C. The solid residues remaining after pyrolysis to 900 °C were between 32.5% and 35.9%, with the lowest yield obtained with LBAP-0.5-5 and the highest yield observed with LBAP-1.5-5. It is expected that the LB-derived acrylate polymers have slightly crosslinked pendant structures made of the oligomers attached on acrylate backbones, and they are less likely decompose than pendants made of monomers. On the other hand, when the TGA was conducted using the air, distinctively different mass loss profiles among the polymers were observed in Fig. 7 (c). Both LBAP-1.5-3 and LBAP-1.5-5 had much lower thermal stability than the other polymers with lower degrees of acrylation. The LBAP-1-3 was most stable at lower temperature regions up to 380 °C, and LBAP-0.5-5 had the better thermal stability at higher temperature region above 380 °C. Higher degree of acrylation introduces more aliphatic bonds to molecules, causing the polymers to become more susceptible for oxidative degradation.

3.5.2. Rheological properties

The rheological properties of LBAPs are given in Fig. 8. During the isochronal temperature scan tests, the complex viscosity (η^*) of the polymers decreased with increasing temperatures before it reversed the trend (Fig. 8 (a)). The increase of η^* at

higher temperatures is associated with crosslinking during the polymer degradation. Overall, a higher degree of acrylation or higher AIBN concentration led to the formation of more rigid polymers that have both higher viscosity and T_r (i.e., the temperature where η^* reversed the trend). Among the polymers, LBAP-0.5-5 had the fastest viscosity drop along with increasing temperature. Its viscosity decreased to 22 Pa.s at 215°C before the viscosity started to increase at higher temperatures.

The $\tan(\delta)$ profiles versus increasing temperatures are plotted in Fig. 8 (b). The $\tan(\delta)$ of LBAP-1.5-5 was constantly lower than 1, indicating it behaves as an elastic material at the tested temperature range. This result corresponds to its high η^* values at Fig. 8 (a). In comparison, other polymers all had temperature ranges where $\tan(\delta)$ is higher than 1. As shown, the polymers become viscous materials at wider temperature ranges as the degree of acrylation or the AIBN concentration decreased. The melt-processable temperature range was from 145 °C to 200 °C for LBAP-1-3, and 130 °C to 230 °C for LBAP-0.5-5.

The frequency sweep of the polymers plot is shown in Fig. 8 (c). For all the polymers, η^* decreased with increasing frequency for shear thinning effect. The η^* of LBAP-0.5-5 was lowest, and it increased for other polymers with higher acrylation degrees. The η^* s of LBAP-1-3 and LBAP-1-5, or LBAP-1.5-3 and LBAP-1.5-5 showed similar trends, suggesting the effect of AIBN concentration was not significant.

4. Conclusions

In this study, RAFT polymerization of a red oak-derived crude LB based on partial

acrylation and subsequent acetylation was investigated. It has shown that increasing either acrylation degree or AIBN concentration enhances both the molecular weights and yields of the acrylate polymers. Even with controlled acrylation, a CTA was still required to suppress gelation especially for the polymer with a higher degree of acrylation. The effects of intrinsic properties of the LB on the polymer synthesis were also investigated. It was found that some of the LB compounds with single OH were not acrylated but acetylated, or neither acrylated nor acetylated, which suggest that the compounds with multi-OHs are preferentially acrylated to gain more than stoichiometry numbers of polymerizable sites during the partial acrylation. The LB was able to be polymerized in the presence of AIBN even without pre-acrylation, suggesting there are small amounts of radically polymerizable sites in the LB. It was also found that the intrinsic free radicals in the LB could combine AIBN radicals or chain propagation radicals during the radical polymerization to become non-radical species. The T_g s of the acrylate polymers obtained in the present study were between 93.7 and 160.6°C. A higher degree of acrylation and a higher AIBN concentration both resulted in a higher T_g of corresponding polymer. While the M_n s of the acrylate polymers and their T_g s could not be related using the Flory–Fox equation, there was a linear increasing trend between them. The thermal stability of all acrylate polymers was similar during pyrolysis, leaving about 32.5-35.9% of carbon residues at 900 °C. However, the polymers with lower degrees of acrylation were much more resistant to oxidative thermal degradation in the air. The polymers with lower degree of acrylation also had lower η^* s during rheology tests and could be melt-processed at wider temperature

ranges.

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