

Supporting Information

Sustainable valorization of Lignin with levulinic acid and its application in polyimine thermosets

Kaifeng Huang,^{a,b} Songqi Ma,^{*b} Sheng Wang,^{b,c} Qiong Li,^{b,c} Zhijun Wu,^a Jingcheng Liu,^{*a} Ren Liu,^a Jin Zhu^b

^a International Research Center for Photoresponsive Molecules and Materials, The Key Laboratory of Synthestic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi, Jiangsu 214122, P. R. China

^b Key laboratory of bio-based polymeric materials technology and application of Zhejiang province, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, P. R. China.

^c University of Chinese Academy of Sciences, Beijing 100049, P. R. China

*Corresponding authors: (Songqi Ma) E-mail: masongqi@nimte.ac.cn, Tel: 86-0574-87619806; (Jingcheng Liu) E-mail: liujingcheng@jiangnan.edu.cn

Experimental Section

Materials

The enzymatic hydrolysis lignin (EHL) extraction from corncob was supplied by Shandong LongLi Biotechnology Co., Ltd, China. Before use, it was dried in a vacuum oven at 70 °C for 24 h. Levulinic acid (LA), N, N'-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), hexamethylenediamine (HMD), 1,12-

diaminododecane (DAD), ethyl levulinate, acetyl bromide, dimethyl sulfoxide (DMSO), pentafluorobenzaldehyde and cyclohexanol were purchased from Aladdin-Reagent Co., China. N, N-dimethylformamide (DMF, anhydrous grade), acetone, tetrahydrofuran (THF), methanol (MeOH), trichloromethane, dichloromethane (DCM), acetonitrile (MeCN), 1,4-dioxane (Diox), ethanol (EtOH) were provided by Sinopharm Chemical Reagent Co., Ltd., China. 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP, 95%) was obtained from Sigma-Aldrich. All materials were used as received unless stated otherwise.

Synthesis of levulinate enzymatic hydrolysis lignin (LEHL)

Enzymatic hydrolysis lignin (EHL) (220 g, 0.920 mol hydroxyl groups), 4-dimethylaminopyridine (11.22 g, 0.092 mol) and LA (160 g, 1.38 mol) were dissolved in 1300 mL DMF in a flask. After that, solution of DCC (208.8 g, 1.012 mol) in 300 mL of DMF was added slowly to the previous reaction mixture. Then the mixture was stirred magnetically at room temperature for 48 h. After reaction, the mixture was vacuum filtered to remove by-product N, N'-dicyclohexylurea, and the collected black solution was condensed by rotary evaporator and precipitated in component solvent of deionized water and methanol (1/1, v/v) under vigorously stirring. After vacuum-assisted filtration, the obtained solid was washed three times with deionized water followed by vacuum drying at 60 °C for 48 h. Ultimately, 210 g resulting product presented light brown powder and the yield was 64.3%. Moreover, DMSO was used as a green alternative to toxic DMF in the synthesis of LEHL with the same molar feed ratio and the yield was 68.2%. The ¹H NMR of LEHL using DMSO as the

solvent during the modification was presented in Fig. S2.

Schiff base reaction of model compounds

A reaction flask equipped with a magnetic stirring was charged with CH₃OH (5 mL), DAD (2 g, 0.01 mol), ethyl levulinate (2.6 g, 0.02 mol) was added. After being heated at 70 °C for 5 h, the reaction mixture was evaporated to remove CH₃OH under reduced pressure. The obtained light yellow liquid was used for ¹³C NMR analysis.

Preparation of polyimine thermosets

LEHL (10g, 35 mmol ketone groups) and trichloromethane (150 mL) were placed in a one-neck round-bottom flask equipped with a magnetic stirring bar. The mixture was stirred for 20 min. Then hexamethylenediamine (2.033 g, 17.5 mmol) in 5 mL methanol was added dropwise into the preceding solution while stirring. After stirring for about 30 min, the mixture solution was poured into a 20 cm × 20 cm × 1cm teflon mold and put in a fume hood overnight to evaporate the solvent followed by further reaction in a blow oven at 70 °C for 4 h. In order to ensure complete polymerization, the pre-cured polymer was hot pressed at 160 °C for 30 min and post-cured at 180 °C for 2 h in a vacuum oven to obtain LEHL-H. The preparation of LEHL-D followed the same method. Similarly, LEHL-D was prepared using MeCN as the green alternative to trichloromethane (Fig. S6), and the glass transition temperature (T_g) (Fig. 8S) is similar to that of LEHL-D using trichloromethane as the solvent (Fig. 4a).

Calculation of molecular weight of EHL

The acetobromination of EHL is shown in Scheme S1. According to the integration of ^{31}P NMR spectrum, the total content of aromatic and aliphatic hydroxyl groups is 4.18 mmol g^{-1} . Considering the high reactivity of acetyl bromide, it can be assumed that all hydroxyl groups have been replaced. Suppose the number average molecular weight of EHL is M_{EHL} , and the number average molecular weights of AEHL (M_{AEHL}) and acetyl group are 1418 g mol^{-1} and 42 g mol^{-1} . M_{EHL} can be calculated as follow equation.

$$M_{\text{AEHL}} = 1418 \text{ g mol}^{-1} = M_{\text{EHL}} + 0.00418 \times M_{\text{EHL}} \times 42$$

$$M_{\text{EHL}} = 1216 \text{ g mol}^{-1}$$

Characterizations

^1H NMR, ^{13}C NMR, ^{31}P NMR and 2D heteronuclear single quantum coherence (2D-HSQC) spectra were recorded at room temperature on a Bruker Avance III 400 MHz instrument with tetramethylsilane (TMS) as an internal reference. DMSO- d_6 and CDCl_3 were used as deuterated solvents for dissolving the samples. The content of levulinyl groups was calculated by ^1H NMR using pentafluorobenzaldehyde as the internal standard. ^{31}P NMR spectra were obtained according to the method of Granata¹ and the amounts of different types of hydroxyl groups were calculated by integrating the peak area using cyclohexanol as the internal standard.

Fourier Transform Infrared (FT-IR) measurements were performed on a Thermo

Scientific Nicolet 6700 FT-IR Spectrometer using the KBr pellet method. All spectra were recorded in the range of 400 to 4000 cm^{-1} with 32 scans with a resolution of 4.0 cm^{-1} at room temperature. For better contrast, the spectra were normalized based on the internal standard peak at approximately 1514 cm^{-1} which belongs to the benzene skeleton.

The molecular weight and polydispersity index of samples were determined by EcoSEC HLC-8320GPC Tosoh with a refractive index detector and an Auto-injector. Tetrahydrofuran (THF) was used as eluent with a constant flow rate of 0.5 mL min^{-1} . To ensure the complete solubility of samples in THF, enzymatic hydrolysis lignin was modified by acetyl bromide according to the previous report and the modified lignin was named acetylated enzymatic hydrolysis lignin (AEHL).²

Dissolution tests of EHL and LEHL were operated in a 10 mL capped glass vial. About 7.5 mg sample and 7.5 mL solvent were loaded into glass vials and shaken for several minutes at room temperature.

The gel content of cross-linked polyimine thermosets was performed by the following procedure. The samples (around 0.4 g) were extracted with acetone by using a Soxhlet extractor at 70 °C. Then the extracted samples were dried at 80 °C under vacuum for 24 h. m_0 and m_1 are initial mass and final mass after extraction, respectively. The gel content was calculated as $100\% \times m_1/m_0$. Three replicates were performed.

The chemical stability of polyimine thermosets was tested in 0.1 M HCl solution (organic solvent/water=8/2, v/v). Taking LEHL-D as an example, a specimen around 40 mg was placed in 6 mL of a solution with different organic solvents and water (8/2, v/v) in a 10 mL vial at 25 °C for 48 h. The samples were dried at 100 °C for 24 h under reduced pressure after experiments and the changes of all specimen were recorded before and after measurement. Test method for LEHL-H was the same with LEHL-D.

Dynamic mechanical properties were performed on a TA Instruments DMA Q800 in tension mode. Samples with dimensions of 21 mm (length) × 5 mm (width) × 0.3 mm (thickness) were measured at a constant frequency of 1 Hz, a amplitude of 2 μm, temperature range from -50 to 250 °C, and a heating rate of 5 °C min⁻¹. LEHL-D prepared with MeCN was also measured (Fig. S8).

The thermal stability of the polyimine thermosets was probed by a Mettler-Toledo TGA/DSC1 Thermogravimetric Analyzer. A sample (around 5 mg) was put into a ceramic crucible and heated from 30 to 800 °C at 10 °C min⁻¹ with nitrogen as purge gas at a flow rate of 50 mL min⁻¹.

The tensile tests were performed using an Instron 5567 Electric Universal Testing Machine with at a cross-head speed of 2 mm min⁻¹. Seven repeated specimens with dimensions of around 50 mm (length) × 5 mm (width) × 0.7 mm (thickness) were

used for the evaluation.

UV-vis transmittance curves of films were determined by a Lambda 950 UV-vis Spectrophotometer equipped with an integrating sphere. The films were approximately 200 μm in thickness and were vacuum dried at 60 $^{\circ}\text{C}$ for 12 h before testing.

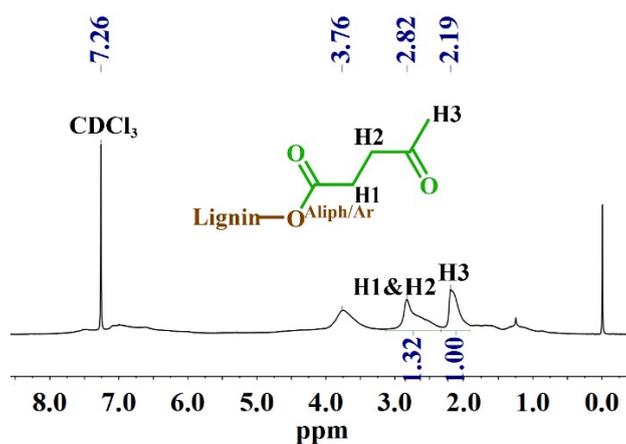


Fig. S1 ^1H NMR spectrum of LEHL in CDCl_3 .

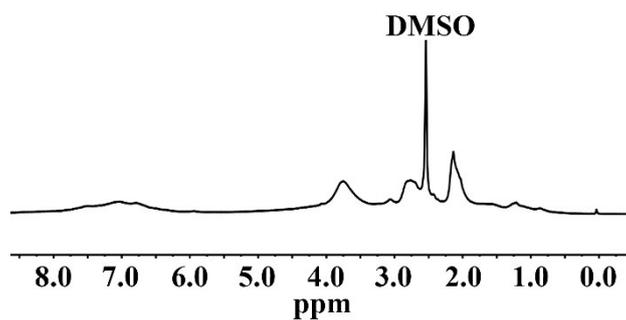


Fig. S2 ^1H NMR spectrum of LEHL using DMSO as the solvent during the modification instead of DMF.

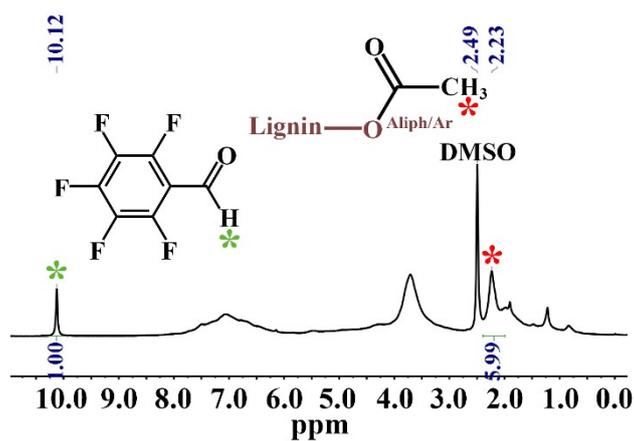
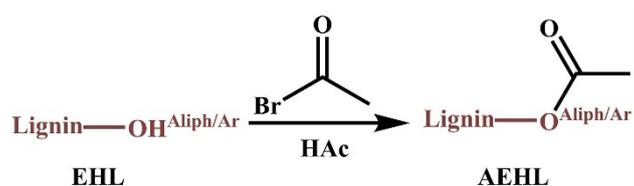


Fig. S3 ^1H NMR spectrum of AEHL in DMSO using pentafluorobenzaldehyde as the internal standard.



Scheme S1 Acetobromination of EHL.

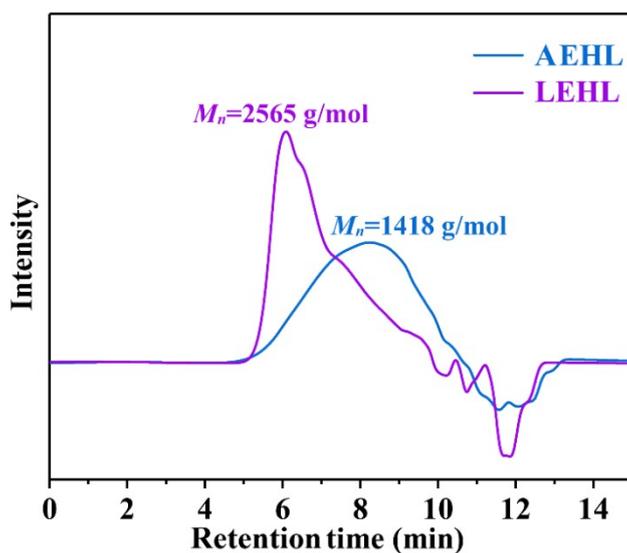


Fig. S4 GPC curves of AEHL and LEHL.

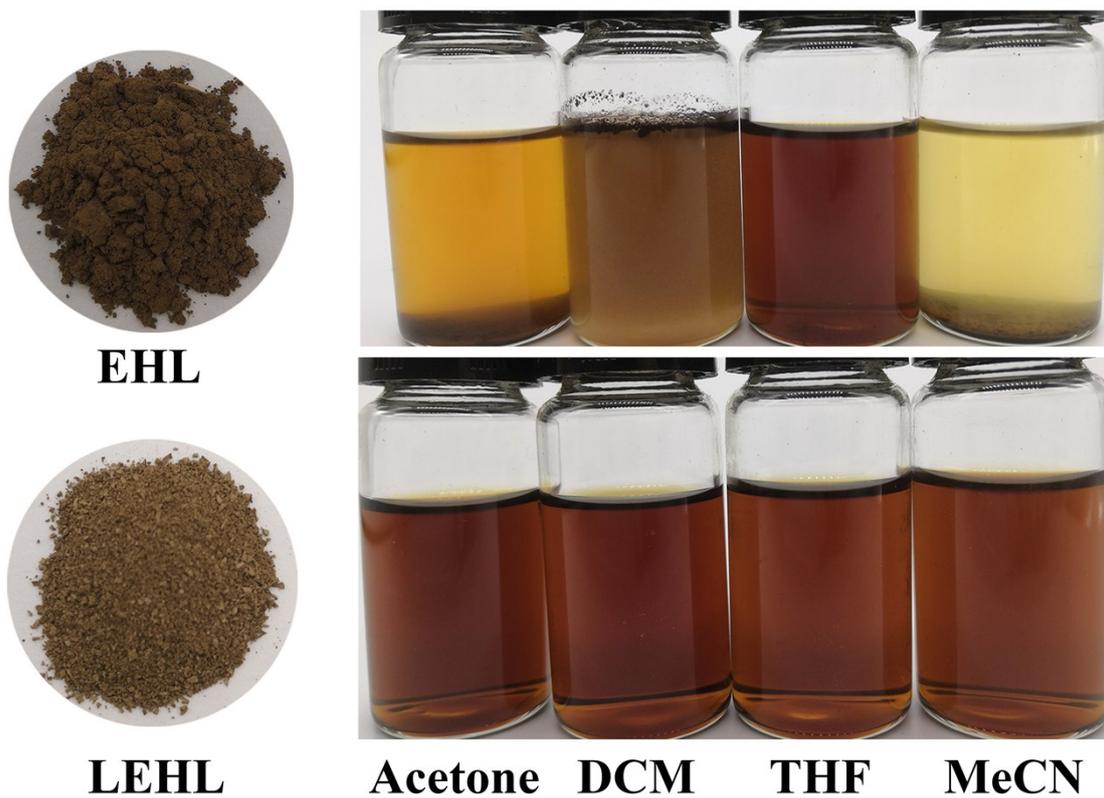


Fig. S5 Digital photos of EHL, LEHL and their dissolution behaviors in acetone, DCM, THF and MeCN (concentration = 1 mg mL⁻¹).

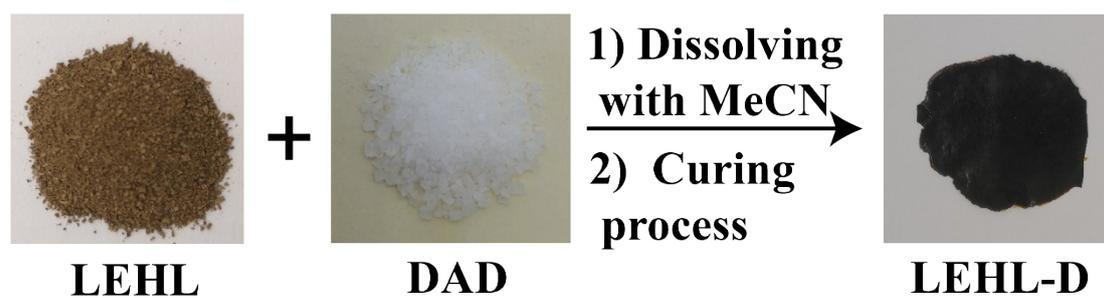


Fig. S6 Schematic diagram of the preparation of LEHL-D using MeCN as the solvent.

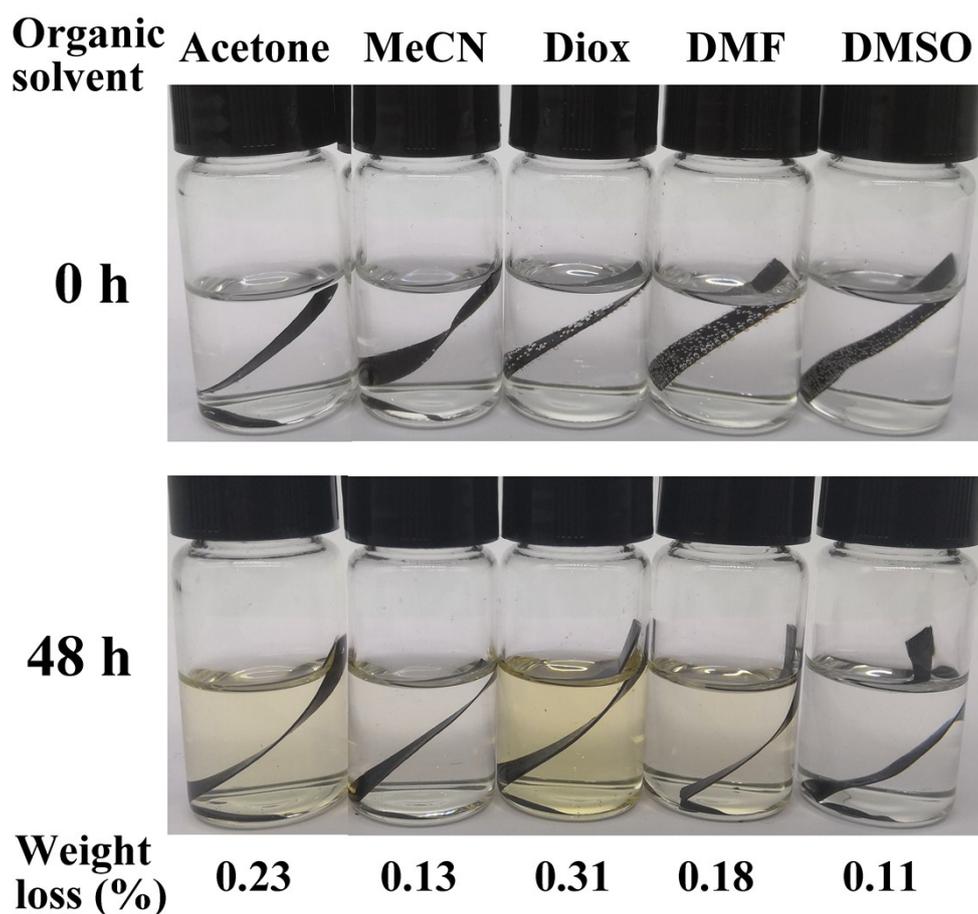


Fig. S7 Digital photos of LEHL-D samples in 0.1 M HCl solution (organic solvent/water=8/2, v/v) at 0 h and 48 h and the weight loss of all samples.

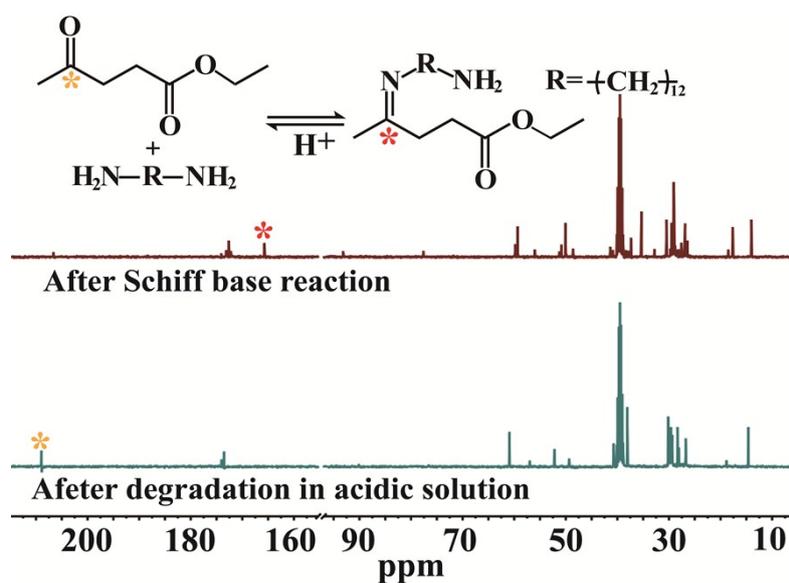


Fig. S8 Synthesis and degradation of model Schiff base compound from ethyl levulinate and 1,12-diaminododecane (DAD) monitored by ^{13}C NMR spectra.

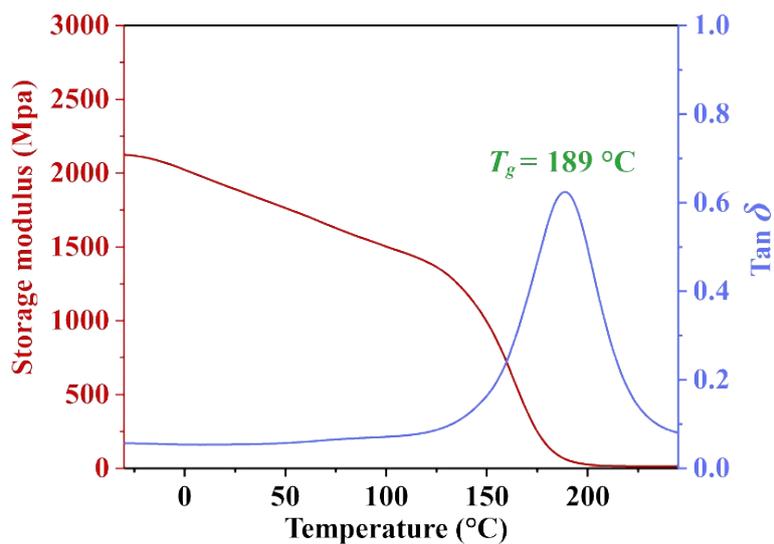


Fig. S9 Storage modulus (E') and $\tan \delta$ versus temperature of LEHL-D prepared by MeCN instead of trichloromethane.



Fig. S10 Photographs of films with the thickness of 100 μm .

Reference

- 1 A. Granata and D. S. Argyropoulos, *J. Agric. Food Chem.*, 1995, **43**, 1538-1544.
- 2 J. Asikkala, T. Tamminen and D. S. Argyropoulos, *J. Agric. Food Chem.*, 2012, **60**, 8968-8973.