Supporting Information

From Tree to Tape: Direct Synthesis of Pressure Sensitive Adhesives from Depolymerized Raw Lignocellulosic Biomass
Shu Wang,†,# Li Shuai,§,% Basudeb Saha,§ Dionisios G. Vlachos,†,§ and Thomas H. Epps, III†,‡,*

†Department of Chemical & Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States
§Center for Energy Innovation, University of Delaware, Newark, DE 19716, United States
‡Department of Materials Science & Engineering, University of Delaware, Newark, DE 19716, United States

*Corresponding Author. Email: thepps@udel.edu

Present Address
#(S.W.) Bridgestone Americas, 10 E Firestone Blvd., Akron, OH 44317, United States
%(L.S.) Department of Sustainable Biomaterials, Virginia Tech, 230B Cheatham Hall, Blacksburg, VA 24060, United States
Materials and Experimental Methods

Synthesis and characterization of 4-propylsyringyl acrylate, 4-propylguaiacyl acrylate, 4-propylsyringyl methacrylate, and 4-propylguaiacyl methacrylate.

The aromatic monomer mixture was acrylated following a procedure adapted from the literature. The aromatic monomers and triethylamine (1.2 mol eq, Fisher Scientific, 99%) were dissolved in dichloromethane (DCM, anhydrous, Fisher Scientific) in a three-neck round bottom flask. The mixture was sparged with argon for 15 min while the flask was immersed in an ice-water bath. A solution of acryloyl chloride (1.2 mol eq, Sigma Aldrich, 97%) in DCM was added drop wise using a constant pressure dropper. The reaction was left to proceed overnight, after which, a white precipitant was filtered by vacuum filtration and discarded. The DCM permeate phase was washed consecutively with solutions of saturated sodium bicarbonate, 1.0 M NaOH (twice), 1.0 M HCl, and deionized water. DCM was removed by rotary evaporation, and the monomers were further purified by flash chromatography using silica gel (Standard Grade, 230 × 400 mesh, 60 Å) with ethyl acetate/hexanes mixture as an eluent (ethyl acetate volume fraction gradually increased from 0% to 10%). Two pure products, 4-propylsyringyl acrylate (4pSA) and 4-propylguaiacyl acrylate (4pGA), were obtained. $^1$H NMR (CDCl$_3$, 600 MHz, δ) for 4pSA: 6.62 (1H, d), 6.44 (2H, aromatic, s), 6.40 (1H, q), 6.00 (1H, d), 3.80 (6H, s), 2.56 (2H, t), 1.65 (2H, m), 0.97 (3H, t); 4pGA: 6.96 (1H, d), 6.79 (1H, d), 6.76 (1H, d), 6.60 (1H, d), 6.35 (1H, q), 5.99 (1H, d), 3.81 (3H, s), 2.58 (2H, t), 1.65 (2H, m), 0.96 (3H, t). Aromatic monomers (4pS and 4pG) also were methacrylated using the same procedure, except substituting methacryloyl chloride (1.2 mol eq, Alfa Aesar, 97%) for acryloyl chloride. Two products, 4-propylsyringyl methacrylate (4pSMA) and 4-propylguaiacyl methacrylate (4pGMA) were collected. $^1$H NMR (CDCl$_3$, 600 MHz, δ) for 4pSMA: 6.45 (2H, s), 6.40 (1H, s), 5.76 (1H, t), 3.82 (6H, s), 2.58 (2H,
t), 2.10 (3H, s), 1.65 (2H, m), 0.97 (3H, t); 4pGMA: 6.95 (1H, d), 6.78 (1H, d), 6.76 (1H, d), 6.34 (1H, s), 5.72 (1H, t), 3.81 (3H, s), 2.57 (2H, t), 2.06 (3H, s), 1.65 (2H, m), 0.96 (3H, t).

Additional details for the synthesis of poly(4pSA), poly(4pGA), poly(4pSMA), poly(4pGMA), and poly(4pSMA-co-4pGMA).

The polymerization solvent, anisole (Sigma-Aldrich, ≥99.7%) with 5 wt% N,N-dimethylformamide (DMF, Sigma-Aldrich, ≥99.9%), was prepared and stored on molecular sieves to minimize water content. The monomer, BTCBA (or CPB; see Main Text), and AIBN were dissolved in the polymerization solvent and transferred to a pressure vessel. The reaction mixture was degassed by three freeze-pump-thaw cycles, backfilled with argon to a pressure of 3 psi, sealed with a stopcock, and immersed in an oil bath (70 °C) with vigorous stirring. The reaction was quenched at a predetermined time (typical reaction time was 6-7 h) by immersing the pressure vessel in liquid nitrogen. Tetrahydrofuran (THF, Fisher Scientific, certified) was added to the mixture, and the polymer was purified by precipitating into excess hexanes at least two times to ensure no monomer remained (confirmed by $^1$H NMR spectroscopy).

Characterization of polymers.

Glass transition temperatures ($T_g$s) of all polymers were determined using a differential scanning calorimeter (DSC, Discovery Series, TA Instruments). The DSC was calibrated using an indium standard. Polymer sample (2-5 mg) was loaded into an aluminum pan and hermetically sealed in air. A heating-cooling-heating cycle was carried out at a rate of 5 °C min$^{-1}$ under continuous N$_2$ flow (50 mL min$^{-1}$). For SaBSa, the sample was first heated from 35 °C to 120 °C, held at 120 °C for 2 min, cooled down to -90 °C, held at -90 °C for 2 min, and ramped to 120 °C. The procedure for poly(methyl methacrylate-b-butyl acrylate-b-methyl methacrylate) (MBM,
Kurarity LA2140e, Kuraray Co. Ltd.) was the same except that the experimental temperature window was -90 °C to 150 °C. The $T_g$ was determined as the midpoint of the inflection in the second heating.

The thermal degradation behavior of SaBSa was characterized using thermogravimetric analysis (TGA, Discovery Series, TA Instruments). 9-11 mg of SaBSa polymer was loaded into a 100 µL platinum pan and heated under continuous airflow (50 mL min$^{-1}$ sample purge, 20 mL min$^{-1}$ balance purge). The sample was heated at 20 °C min$^{-1}$ to 110 °C, annealed at 110 °C for 15 min to remove possible residual water, cooled at 10 °C min$^{-1}$ to 50 °C, held at 50 °C for 1 min, and heated at 10 °C min$^{-1}$ to 600 °C.

Dog-bone-shaped testing bars (following ASTM D638, bar type 5, 5.3 mm gauge width, 0.8 mm thickness) were prepared by compression molding into a Teflon PTFE sheet (McMaster Carr) on a PHI Hotpress at 200 °C, with an applied load of 9000 lb. Tensile testing was performed with a RSA-G2 Solids Analyzer (TA Instruments) in tension mode. The lower grip was stationary, and the upper grip was raised at a speed of 10 mm min$^{-1}$ to obtain tensile strength and elongation at break of SaBSa at room temperature. The measurement was repeated with four test specimens. Tensile testing on MBM also was performed for comparison, except that the testing specimens were prepared with an aluminum mold, and the pressing temperature was 220 °C.

The micro-phase separation characteristics of SaBSa and MBM were probed by small-angle X-ray scattering (SAXS) (Rigaku SAXS instrument at the University of Delaware). The wavelength of the beam was 0.154 nm, and the sample to detector distance was 2 m. The 2D
scattering patterns were azimuthally integrated to a 1D profile of intensity \( I(q) \) vs. scattering vector \( q, q = 4\pi \sin(\theta/2)/\lambda \) (\( \theta \) is the scattering angle, \( \lambda \) is the wavelength).
Figure S1. $^1$H NMR spectra of 4pSA (a) and 4pGA (b) in chloroform-d (with TMS as an internal standard). Residue water was from the chloroform-d bottle.
Figure S2. $^1$H NMR spectra of 4pSMA (a) and 4pGMA (b) in chloroform-d (with TMS as an internal standard). In b), peaks labeled with * are from residue un-reacted 4pG (not separated from 4pGMA by flash column chromatography). The existence of 4pG did not affect the polymerization of 4pGMA, thus no attempt was made to remove it until the washes following polymerization.
Figure S3. $^1$H NMR spectra of P4pSA (a) and P4pGA (b) in chloroform-d (with TMS as an internal standard). Residue water was from the chloroform-d bottle.
Figure S4. $^1$H NMR spectrum of SaBSa in chloroform-d (with TMS as an internal standard). The weight percentage of the 4pSA block was calculated as:

$$\frac{\text{area}(a) \times MW(4pSA)}{\text{area}(a) \times MW(4pSA) + \text{area}(A) \times MW(n - BA)} \times 100\% = \frac{2 \times 250.29}{2 \times 250.29 + 13.94 \times 128.17} \times 100\%$$

$$= 22\%$$
Figure S5. DSC traces of the second heating (exotherm up, heating rate = 5 °C min⁻¹ under continuous N₂ flow at 50 mL min⁻¹) for SaBSa (blue solid line, $M_n = 66.4$ kg mol⁻¹, 22 wt% P4pSA) and MBM [black dashed line, $M_n = 66.9$ kg mol⁻¹, 23 wt% poly(methyl methacrylate) (PMMA)].
Figure S6. a) 2D SAXS pattern and b) Azimuthally-integrated 1D SAXS data for SaBSa [principal scattering peak, $q^*$, at 0.030 Å$^{-1}$ (arrow), corresponding to a domain spacing ($d^* = 2\pi/q^*$) of ~21 nm]; c) 2D SAXS pattern and d) Azimuthally-integrated 1D SAXS data for MBM [$q^* = 0.031$ Å$^{-1}$ (arrow), corresponding to a domain spacing of ~20 nm].
**Figure S7.** Mass remaining (solid line) and the first derivative of mass change (dashed line) vs. temperature for SaBSa (blue, $M_n = 66.4$ kg mol$^{-1}$, 22 wt% P4pSA) and MBM (black, $M_n = 66.9$ kg mol$^{-1}$, 23 wt% PMMA). The heating rate was 10 °C min$^{-1}$ under air flow.
Figure S8. 180° peel force of a) SaBSa ($M_n = 66.4$ kg mol$^{-1}$, 22 wt% P4pSA), b) Scotch® Magic™ Tape, c) Fisherbrand™ Labeling Tape, and d) MBM ($M_n = 66.9$ kg mol$^{-1}$, 23 wt% PMMA).
Figure S9. Loop tack force of a) SaBSa ($M_n = 66.4$ kg mol$^{-1}$, 22 wt% P4pSA), b) Scotch® Magic™ Tape, and c) Fisherbrand™ Labeling Tape.
Figure S10. Stress-strain curves for SaBSa (blue solid lines, $M_n = 66.4$ kg mol$^{-1}$, 22 wt% P4pSA) and MBM (black dashed lines, $M_n = 66.9$ kg mol$^{-1}$, 23 wt% PMMA).
Figure S11. Photo of tensile testing experiment.
References

(1) Wang, S.; Bassett, A. W.; Wieber, G. V.; Stanzione, J. F., III; Epps, T. H., III. Effect of methoxy substituent position on thermal properties and solvent resistance of lignin-inspired poly(dimethoxyphenyl methacrylate)s. *ACS Macro Letters* **2017**, *6* (8), 802-807.