Well-defined Renewable Polymers Derived from Gum Rosin

Yijun Zheng¹, Kejian Yao¹, Sangmin Lee¹, David Chandler¹,
Jifu Wang², Chunpeng Wang², Fuxiang Chu², Chuanbing Tang¹*

¹University of South Carolina, Department of Chemistry and Biochemistry,
631 Sumter Street, Columbia, South Carolina 29208
²Chinese Academy of Forestry, Beijing, China 100086
Email: tang.c@chem.sc.edu

Supporting Information

Materials.
Dehydroabietic acid (DHAA, ~90%) was obtained from Wuzhou Chemicals, China and used as received. Tetrahydrofuran (THF, Aldrich) and anisole (Aldrich) were refluxed with sodium and distilled just before use under nitrogen atmosphere. Tris(2-(dimethylamino)ethyl)amine (Me₆Tren) was prepared according to the literature.¹ 2-Hydroxyethyl acrylate (2-HEA) (stabilized, 97%, Aldrich), 2-hydroxyethyl methacrylate (2-HEMA) (stabilized, 97%, Aldrich) and 4-hydroxybutyl acrylate (4-HBA) (stabilized, 97%, Aldrich) were passed through basic alumina column. Oxalyl chloride, triethylamine, sodium borohydride (NaBH₄), acryloyl chloride, ethyl-2-bromoisobutyrate (EBiB) and copper(I) bromide (99.999%) were used as received (Aldrich).

Characterization.
Gas Chromatography-Mass Spectrometry (GC/MS) analysis of DHAA raw materials was carried out on Agilent 6890N Network GC system and Agilent 5973 mass selective detector. Prior to GC/MS analysis, DHAA was transformed into methyl DHAA by using TMAH (tetramethyl ammonium hydroxide) in the solution of methanol because DHAA was not gasified due to the presence of the carboxylic acid group. GC was performed on Agilent HP-5
capillary column (30m×0.25mm×0.25μm) with an oven temperature of 250 °C. Carrier gas was He at a flow-rate of 1.0 mL/min. The temperature of injection port was 250 °C. 0.2 μL of sample was injected into the GC system. The mass spectrometer was operated in electron ionization mode. The temperature of ion source was 230 °C.

\(^1\)H NMR and \(^{13}\)C NMR spectra were recorded on Bruker ARX 300 and ARX 400 spectrometers. The chemical shifts were recorded in ppm (δ) relative to tetramethylsilane. Mass spectra were measured on a VG S70 mass spectrometer. Gel permeation chromatography (GPC) was performed at room temperature on a Varian system equipped with a Varian 356-LC refractive index detector and a Prostar 210 pump. The columns were STYRAGEL HR1, HR2 (300×7.5 mm) from Varian. HPLC grade THF was used as eluent at a flow rate of 1 ml/min. THF and samples were filtered over microfilters with pore size of 0.2μm (Nylon, Millex-HN 13 mm Syringes Filters, Millipore, USA). The columns were calibrated using polystyrene standards. The thermal transitions of the copolymers were recorded using differential scanning calorimetry (DSC) on a TA Q200 calorimeter in a temperature range from 0 to 180 °C at a heating rate of 10 °C min\(^{-1}\) under a continuous nitrogen flow. All the data were collected during the second heating process after cooling at 2 °C min\(^{-1}\) from 180 °C. The average sample mass was about 5 mg, and the nitrogen flow rate was 50 mL min\(^{-1}\). Thermogravimetric analysis (TGA) data were collected on TA SDT Q600 using a heating rate of 5 °C/min from 25 to 600°C under helium.

**Synthesis.**

**Dehydroabietic ethyl acrylate (DAEA):** dehydroabietic acid (10 g, 33 mmol) was dissolved in dichloromethane (60 mL). Oxalyl chloride (5.66 g, 36.3 mmol) was added slowly. After the solution was stirred at 0°C for 3 h, excessive oxalyl chloride was removed by distillation. Triethylamine (5.0 g, 57 mmol) and 2-HEA (4.39 g, 37 mmol) were subsequently added. The reaction mixture was stirred at 0°C overnight and then washed with 5% NaCO\(_3\) solution followed by drying over anhydrous Na\(_2\)SO\(_4\) and evaporated to dryness. The product was further purified by silica gel chromatography (ethyl acetate /hexane: 1/9 (v/v)) to afford white powder (5.0 g) in 45% yield. \(^1\)H NMR (300 MHz, CDC\(_13\), δ, ppm): 7.26-7.14 (d, J = 8.21 Hz,
1H; Ar), 7.01-6.99 (d, J = 8.51 Hz, 1H; Ar), 6.91-6.87(s, 1H; Ar), 6.43-6.38 (d, J = 17.14 Hz, 1H; vinyl), 6.16-6.06(dd, J = 10.52, 10.41 Hz, 1H; vinyl), 5.85-5.82 (d, J = 10.00 Hz, 1H; vinyl), 4.36-4.27 (m, 4H; OCH2), 2.93-2.80(m, 3H), 2.34-1.21 (m, 21H). 13C NMR (400 MHz, CDCl3, ppm):16.49, 18.59, 21.76, 24.00, 25.19, 30.12, 33.48, 36.55, 36.95, 37.96, 44.77, 47.71, 62.01, 62.16, 123.96, 124.21, 126.91, 128.00, 131.34, 134.66, 145.76, 146.86, 165.86, 178.32. MS (ESI, m/z) for C25H34O4: 398 (M⁺).

**Dehydroabietic ethyl methacrylate (DAEMA):** The synthesis was similar to DAEA synthesis, using 2-HEMA instead of 2-HEA. 1H NMR (300 MHz, CDCl3, δ, ppm): 7.17-7.15 (d, J = 8.16 Hz, 1H; Ar), 7.00-6.98 (d, J = 7.79 Hz, 1H; Ar), 6.87-6.85(s, 1H; Ar), 6.17-6.09 (s, 1H; vinyl), 5.58-5.55 (s, 1H; vinyl), 4.38-4.26 (m, 4H; OCH2), 2.84-2.77(m, 3H), 1.91-1.16 (m, 23H). 13C NMR (400 MHz, CDCl3, δ, ppm):16.49, 18.26, 18.58, 21.74, 23.99, 24.02, 25.15, 30.06, 33.48, 36.57, 36.95, 37.97, 44.77, 62.22, 62.51, 123.95, 124.17, 126.03, 126.90, 134.64, 135.94, 145.75, 146.85, 167.09, 178.31. MS (ESI, m/z) for C26H36O4: 412 (M⁺).

**Dehydroabietic ethyl methacrylate (DABA):** The synthesis was similar to DAEA synthesis, using 4-HBA instead of 2-HEA. 1H NMR (300 MHz, CDCl3, δ, ppm): 7.12-7.09 (d, J = 7.83 Hz, 1H; Ar), 6.95-6.92 (d, J = 7.42 Hz, 1H; Ar), 6.83-6.81(s, 1H; Ar), 6.35-6.30 (d, J = 16.49 Hz, 1H; vinyl), 6.08-5.99 (dd, J = 10.31, 10.80 Hz, 1H; vinyl), 5.76-5.73 (d, J = 10.26 Hz, 1H; vinyl), 4.13-3.98 (m, 4H; OCH2), 2.82-2.71(m, 3H), 1.80-1.14 (m, 25H). 13C NMR (400 MHz, CDCl3, δ, ppm):14.00, 16.81, 19.30, 22.35, 23.82, 25.30, 25.45, 26.93, 30.16, 31.62, 33.31, 36.10, 37.47, 37.97, 45.00, 47.86, 64.65, 123.66, 124.00, 124.22, 126.64, 126.95, 127.94, 145.75, 146.85, 167.09, 178.31. MS (ESI, m/z) for C27H38O4: 426 (M⁺).

**Dehydroabietic acrylate (DAA):** Dehydroabietic acid (6.6 g, 22 mmol) was dissolved in diethyl ether (100 mL). NaBH₄ (4.54 g, 0.120 mol) in 40 mL diethyl ether were added in 30 min. After the solution was stirred at room temperature overnight, excessive NaBH₄ was destroyed by adding 120 mL methanol slowly. The reaction mixture was washed with 5% H₂SO₄ and the organic layer was collected and washed with 5% NaHCO₃ solution followed by drying over anhydrous Na₂SO₄ and evaporated to dryness, yielding dehydroabietic alcohol,
which was used immediately for next step reactions. Triethylamine (26 mL) and acrylory chloride (4 g, 44 mmol) were added slowly to the above dehydroabietic alcohol in dichloromethane (150 mL). The reaction mixture was stirred at 0°C overnight and the solution was washed with 5% NaCO₃ solution followed by drying over anhydrous Na₂SO₄ and evaporated to dryness. The product was further purified by silica gel chromatography (ethyl acetate /hexane: 1/9 (v/v)) to afford white powder (3.29g) in 46% yield. ¹H NMR (300 MHz, CDC1₃, δ, ppm): 7.20-7.17 (d, J = 8.78 Hz, 1H; Ar), 7.01-6.99 (d, J = 8.78 Hz, 1H; Ar), 6.90-6.87(s, 1H; Ar), 6.41-6.35 (d, J = 17.39 Hz, 1H; vinyl), 6.14-6.05 (dd, J = 10.30, 10.44 Hz, 1H; vinyl), 5.82-5.78 (d, J = 9.57 Hz, 1H; vinyl), 4.09-3.78 (dd, 2H; OCH₂), 2.93-2.74(m, 3H), 1.83-1.17 (m, 21H). ¹³C NMR (400 MHz, CDC1₃, ḋ, ppm):17.54, 18.58, 19.03, 24.02, 25.45, 30.30, 33.44, 35.60, 36.97, 37.49, 37.75, 44.32, 68.00, 72.47, 123.91, 124.22, 126.91, 128.54, 130.70, 134.79, 145.62, 147.12, 166.40. MS (ESI, m/z) for C₂₃H₃₂O₂: 340 (M⁺).

ATRP: use PDAEA synthesis as an example. A mixture of monomer DAEA (0.5 g, 1.2 mmol), Me₆Tren (2.76mg, 0.012 mmol), EBiB (1.84 μl, 0.012 mmol) and THF (3 mL) was introduced into a polymerization tube. After three freeze-pump-thaw cycles, CuBr (1.8 mg, 0.012 mmol) was added to the flask while the contents were at a solid state and deoxygenated by vacuum followed by back-filling with nitrogen three times. The tube was heated at 90 °C for 16 hours. The polymerization was stopped by diluting the reaction mixture with THF. The products were precipitated in methanol three times and dried to constant weight, yielding white powder. The conversion of monomers was 29% as determined from ¹H NMR analysis. Mₙ (PDAEA) = 11500 g/mol, PDI (PDAEA) = 1.20. ¹H NMR (300 MHz, CDCl₃, δ): 6.7-7.2 (broad, aromatic); 3.9-4.4 (d, OCH₂CH₂O); 2.6-2.8 (protons next to aromatic ring); 1-2.5 (broad, -CH₂CH- and all other protons from hydrophenanthrene ring).
Figure S1. GC traces of DHAA.

Figure S2. Mass spectrum of DHAA at 6.72 min.
**Figure S3.** Mass spectrum of DHAA at 6.93 min.

**Figure S4.** Mass spectrum of DHAA at 7.22 min.
Figure S5. $^1$H NMR 2D-COSY spectra of vinyl monomer DAEMA.
Figure S6. $^1$H NMR 2D-COSY spectra of vinyl monomer DABA.
Figure S7. GPC trace of PDAA prepared by ATRP (Run 1 from Table 1).

Figure S8. TGA traces of PDAEA, PDABA and PDAEMA polymers prepared by ATRP (Runs 2, 3 and 5 from Table 1).

References: