

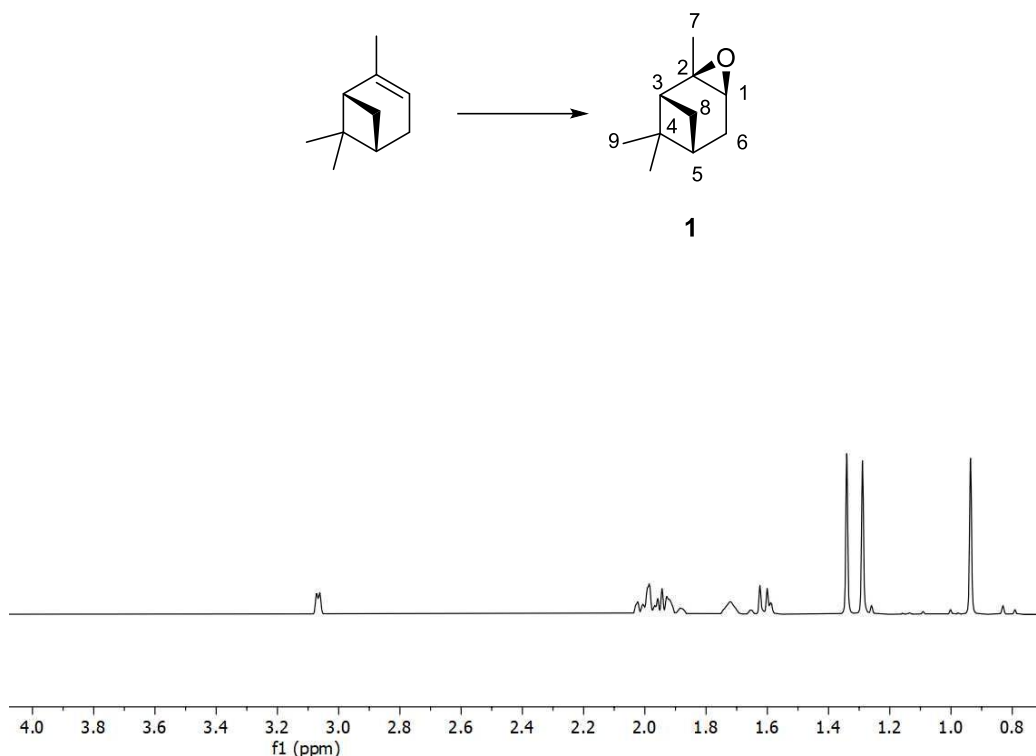
## Supplementary Material

### Comparative hydrodynamic characterisation of two hydroxylated polymers based on $\alpha$ -pinene- or oleic acid-derived monomers for potential use as archaeological consolidants

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## $\alpha$ -Pinene oxide (**1**)

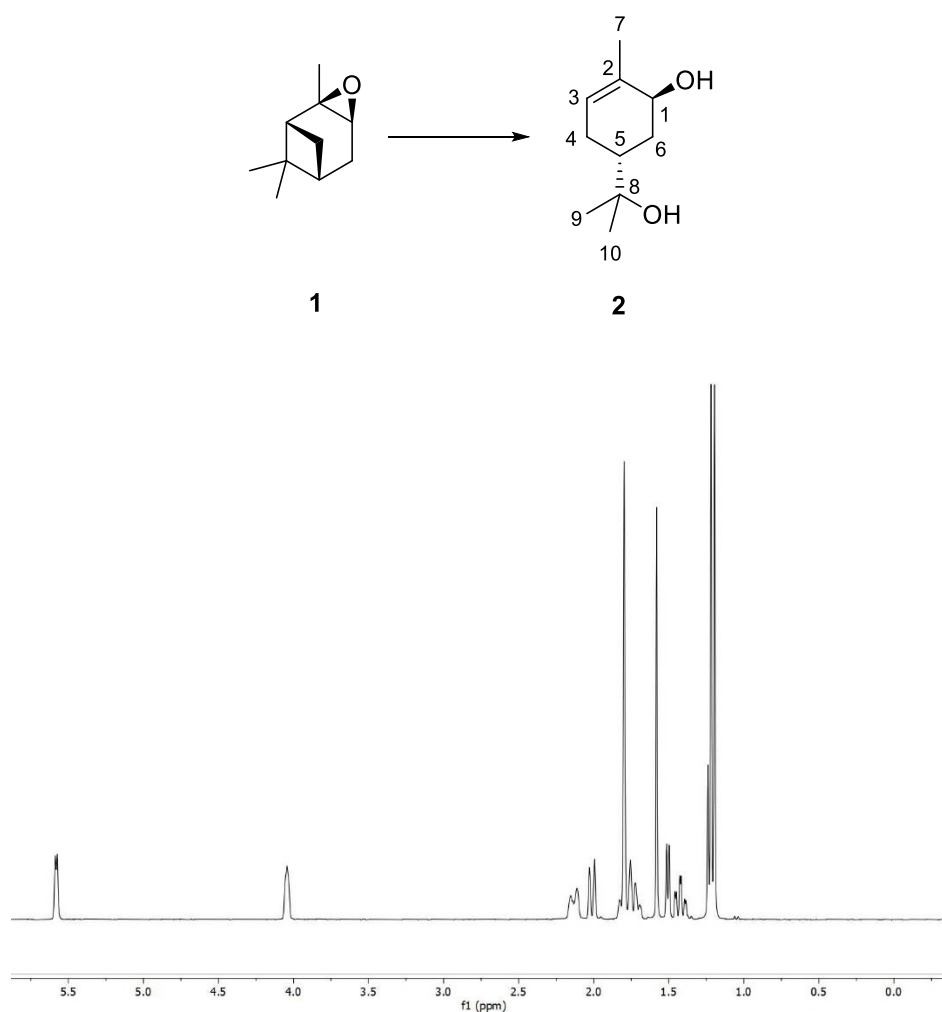


**Figure S1.**  $^1\text{H NMR}$  spectra for **1**

*Synthesis of  $\alpha$ -pinene oxide, 1<sup>1</sup>.* 1S-(-)- $\alpha$ -pinene (5.82 mL, 36.7 mmol) was added to a suspension of  $\text{NaHCO}_3$  (3.92 g, 46.6 mmol) in  $\text{CH}_2\text{Cl}_2$  (7.5 mL) and then cooled to 0 °C. *Meta*-chloroperbenzoic acid (*m*CPBA) (~70%, 9.22 g, 37.4 mmol) was gradually added to the solution. The reaction was stirred for 1 hour, after which saturated aqueous solution of  $\text{Na}_2\text{SO}_3$  (27 mL) was added to the reaction mixture. The reaction was allowed to settle to room temperature and stirred for a further 30 minutes. The reaction mixture was diluted with saturated aqueous solution of  $\text{NaHCO}_3$  (30 mL) and  $\text{CH}_2\text{Cl}_2$  (60 mL). The aqueous washings were extracted with  $\text{CH}_2\text{Cl}_2$  (75 mL). The organic phase was washed with saturated aqueous solution of  $\text{NaHCO}_3$  (100 mL x 3). The organic extracts were then combined, washed with brine (100 mL x 3), dried over  $\text{MgSO}_4$ , filtered and concentrated under reduced pressure to yield the title compound (**1**) (4.78 g, 31.4 mmol, 86% yield).

**FTIR** (ATR)  $\nu_{\max}/\text{cm}^{-1}$ : 2977, 2914, 2834, 1229, 1084, 943, 818;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  3.07 (d,  $J = 4.1$  Hz, 1H), 2.01 – 1.83 (m, 4H), 1.72 (s, 1H), 1.61 (d,  $J = 9.4$ , 1H), 1.34 (s, 3H), 1.29 (s, 3H), 0.94 (s, 3H);  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  60.3, 56.9, 45.1, 40.5, 39.7, 27.6, 26.7, 25.9, 22.4, 20.2.

### ***Trans-sobrerol* (2)**



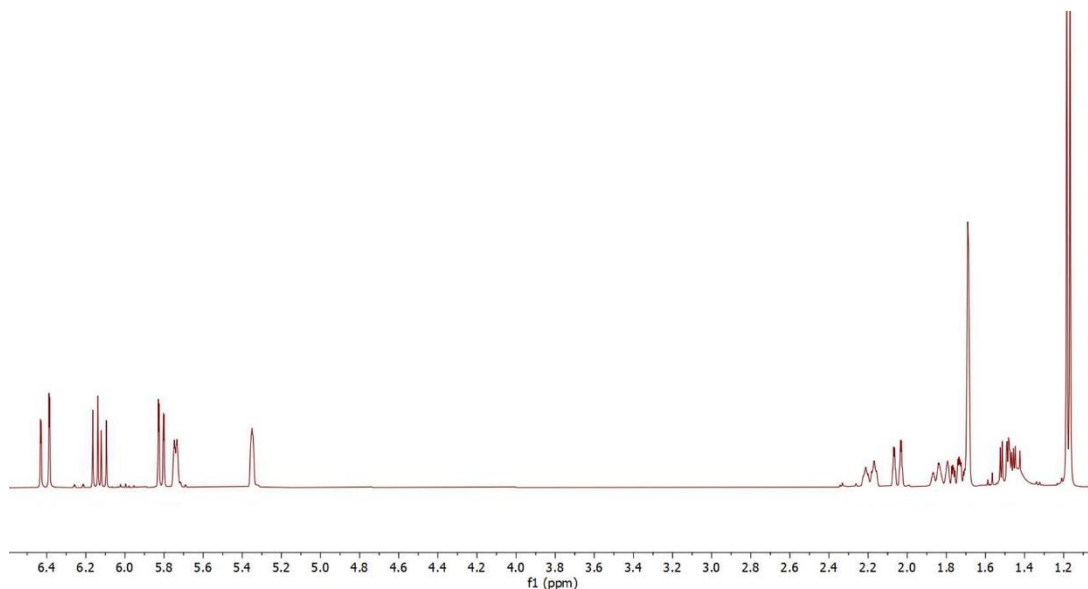
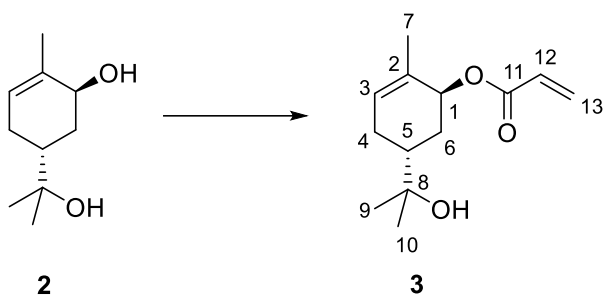
**Figure S2.**  $^1\text{H NMR}$  spectra for **2**

*Synthesis of trans-sobrerol, 2.*<sup>1</sup>  $\text{CO}_2$  was continuously passed through  $\text{H}_2\text{O}$  (52 mL) until the pH was approximately 4.5 – 5. **1** (4 g, 26.3 mmol) was then added and the mixture stirred at room temperature for 24 hours. The solution was concentrated under reduced pressure and

a white solid precipitated. The crude solid was washed with cold ethyl acetate (5 mL x 2) to give the title compound as a white, crystalline solid (**2**) (2.4 g, 14.4 mmol, 55% yield).

**FTIR** (ATR)  $\nu_{\max}/\text{cm}^{-1}$ : 3321, 2973, 2887, 1376, 1052, 919;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  5.58 (d,  $J = 5.4$  Hz, 1H), 4.04 (s, 1H), 2.17 – 2.08 (m, 1H), 2.05 – 1.97 (m, 1H), 1.84 – 1.67 (m, 5H), 1.42 (td,  $J = 13.1, 3.9$  Hz, 1H), 1.22 (s, 3H), 1.19 (s, 3H);  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  133.2, 126.6, 71.3, 68.8, 38.9, 33.8, 27.8, 27.3, 26.5, 21.0; **HRMS** (ESI)  $m/z$  calculated for  $[\text{C}_{10}\text{H}_{18}\text{NaO}_2]^+$  193.1204 found 193.1210 ( $\text{M}^+ \text{Na}^+$ ).

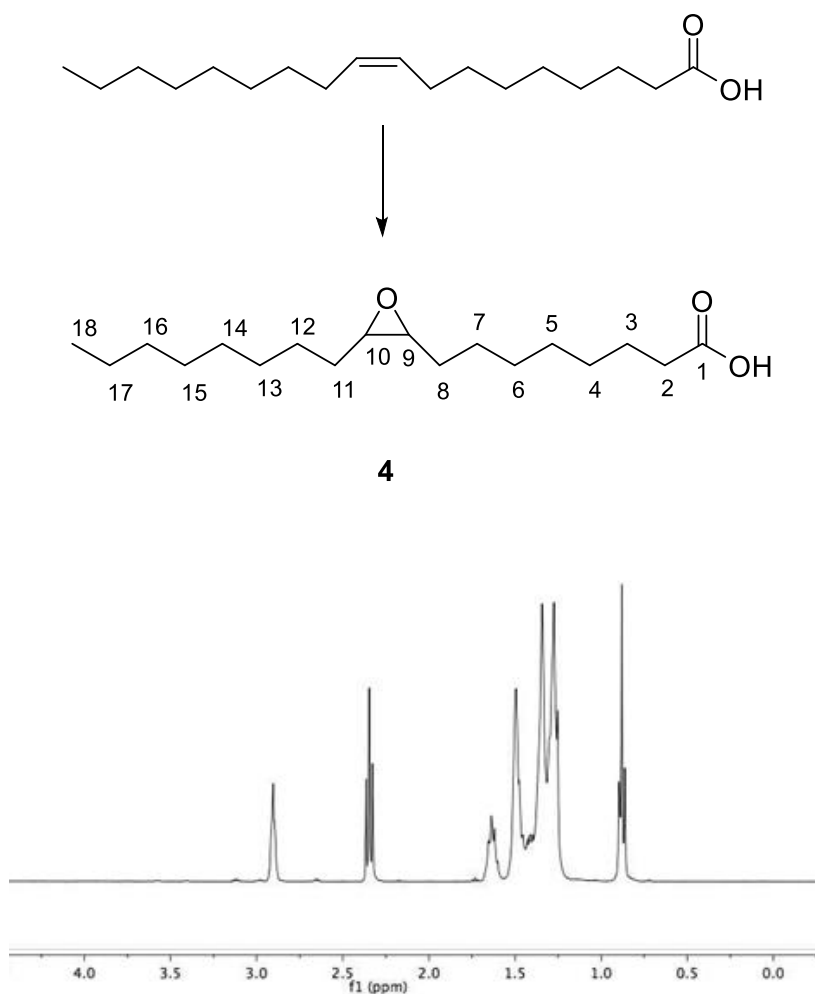
**(1S,5R)-5-(2-hydroxypropan-2-yl)-2-methylcyclohex-2-en-1-yl acrylate (**3**)**



**Figure S3.**  $^1\text{H NMR}$  spectra for **3**

**FTIR** (ATR)  $\nu_{\max}/\text{cm}^{-1}$ : 3421, 2969, 2935, 1717, 1704, 1404, 1294, 1267, 1192, 1162, 1038.  
 **$^1\text{H NMR}$**  (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta_{\text{H}}$  6.42 (dd,  $J = 17.3, 1.5, 1\text{H}$ ), 6.14 (dd,  $J = 17.3, 10.4, 1\text{H}$ , H-12), 5.82 (dd,  $J = 10.4, 1.5, 1\text{H}$ ), 5.75 (dt,  $J = 5.6, 1.8, 1\text{H}$ ), 5.36 (dt,  $J = 3.5, 1\text{H}$ ), 2.19 (dddt,  $J = 17.0, 5.7, 4.3, 1.6, 1\text{H}$ ), 2.05 (dq,  $J = 14.0, 2.2, 1\text{H}$ ), 1.90–1.82 (m, 1H), 1.74 (tdd,  $J = 2.4, 4.0, 12.5, 1\text{H}$ ), 1.71 (dt,  $J = 2.8, 1.5, 3\text{H}$ ), 1.49 (ddd,  $J = 14.1, 12.9, 4.0, 2\text{H}$ , H-6), 1.18 ( $J = 6.9, 6\text{H}$ );  **$^{13}\text{C NMR}$**  (101 MHz,  $\text{CD}_3\text{OD}$ )  $\delta_{\text{C}}$  166.1, 131.0, 130.6, 128.1, 125.3, 72.2, 71.0, 39.5, 30.0, 27.6, 27.4, 26.8, 20.9; **HRMS** (ESI): Calculated for  $[\text{C}_{13}\text{H}_{20}\text{NaO}_3]^+$  247.3000 obtained 247.1309 ( $\text{M}^+ \text{Na}^+$ ).

#### 8-(3-octyloxiran-2-yl)octanoic acid (**4**)

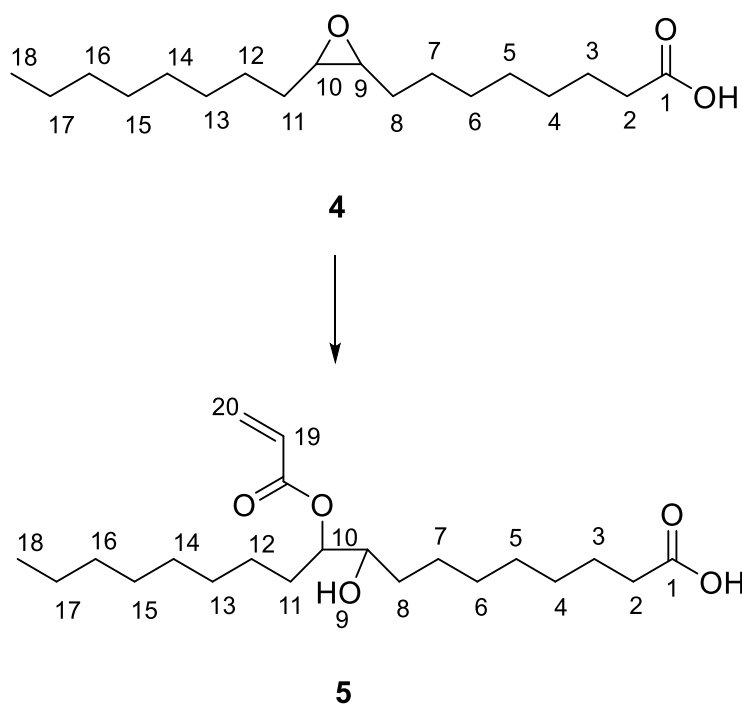


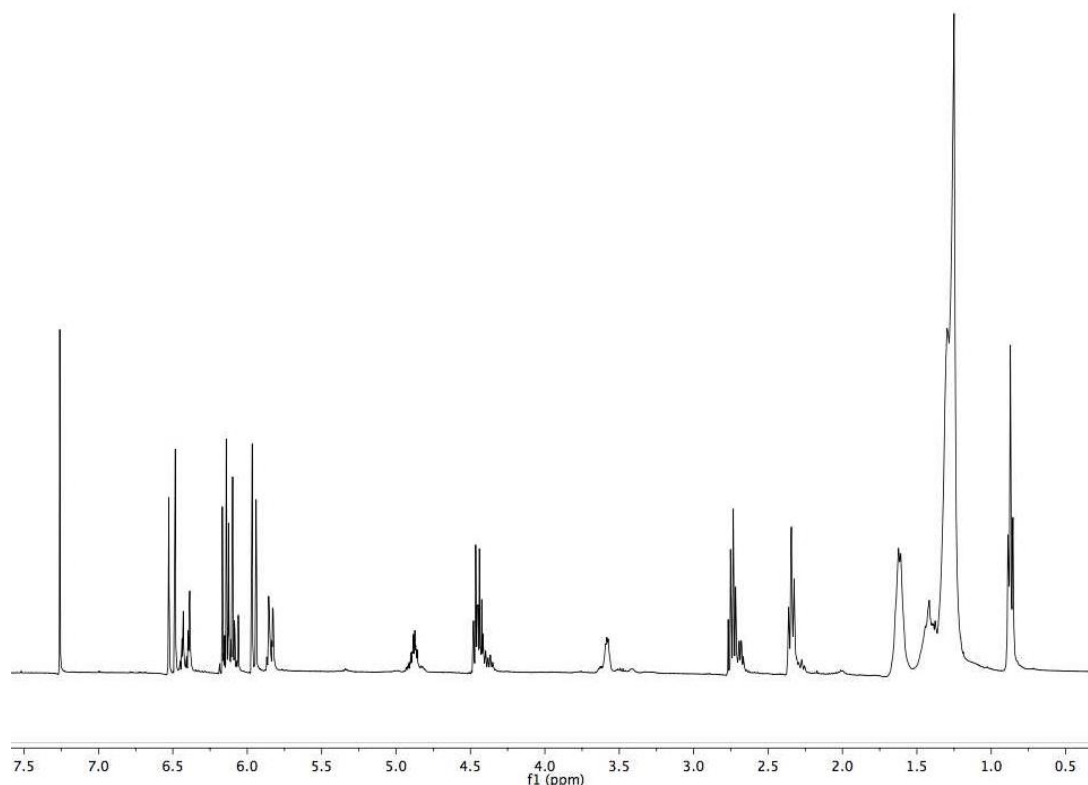
**Figure S4.**  $^1\text{H NMR}$  spectra for **4**

*Synthesis of epoxidized oleic acid, 4*. To oleic acid (33.8 mL, 106.4 mmol) in toluene (180 mL) was added formic acid (12.3 mL, 326.0 mmol). The solution was stirred under reflux at 30 °C. H<sub>2</sub>O<sub>2</sub> (72.1 mL, 2352.8 mmol) was added dropwise (over 1 hour) and the mixture left to stir for 24 hours. This was then transferred to a separation funnel and the organic phase was purified using NaHCO<sub>3</sub> (sat. aq., 50 mL x 3), DI water (50 mL x 3) and dried with MgSO<sub>4</sub> and filtered. The solution was then concentrated under reduced pressure to yield the product (**4**) as a white solid (26.5 g, 88.8 mmol, 84% yield).

**FTIR** (ATR)  $\nu_{\max}/\text{cm}^{-1}$ : 2958, 2849, 1696, 1473, 1431, 1276, 1031, 1012, 846. **<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>OD)  $\delta_{\text{H}}$  2.92 (m, 2H), 2.35 (t,  $J = 7.5$ , 2H), 1.65 (d,  $J = 6.9$ , 2H), 1.49 (dt,  $J = 6.9$ , 3.9, 4H), 1.35 (m, 10H), 1.29 – 1.27 (10H, m, 10H), 0.92 – 0.84 (m, 3H); **<sup>13</sup>C NMR** (101 MHz, CD<sub>3</sub>OD)  $\delta_{\text{C}}$  57.44, 57.39, 34.01, 32.00, 29.70, 29.68, 29.46, 29.32, 29.31, 29.09, 27.96, 27.92, 26.74, 26.70, 24.79, 22.81, 14.25; **HRMS** (ESI): Calculated for [C<sub>13</sub>H<sub>20</sub>NaO<sub>3</sub>]<sup>+</sup> 320.47 obtained 321.24 (M<sup>+</sup> Na<sup>+</sup>).

#### 10-(acryloyloxy)-9-hydroxyoctadecanoic acid (**5**)





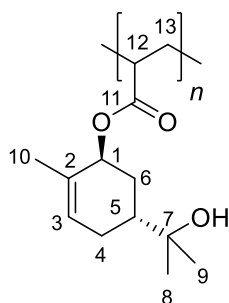
**Figure S5.**  $^1\text{H}$  NMR spectra for **5**

*Synthesis of acrylated oleic acid, 5<sup>2</sup>.* To a solution of **4** (40 g, 0.1 mmol) were added acrylic acid (acid with low  $\text{H}_2\text{O}$  content, 99.5% stab. with ca. 200 ppm methoxyphenol, 76.12 mL, 1109.2 mmol) and hydroquinone (24 mg, 0.2 mmol). The reaction mixture was maintained at a mass ratio 2 : 1 acrylic acid : epoxidized oleic acid and left to stir for 6 hours at 100 °C. The aqueous layer was separated with diethyl ether (100 mL x 3) and the organic layer was washed with  $\text{NaHCO}_3$  (sat. aq., 50 mL x 3). The reaction mixture was then dried with  $\text{MgSO}_4$ , filtered and concentrated to yield the title compound (**5**) as a whitish viscous liquid (48.2 g, 130.1 mmol, 97% yield).

**FTIR** (ATR)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3461, 2959, 2873, 1697, 1431, 1261, 1193, 771.  **$^1\text{H}$  NMR** (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta_{\text{H}}$  6.56 – 6.36 (m, 1H, H-20), 6.11 (ddd,  $J = 17.3, 15.2, 10.4$ , 1H, H-19), 5.96 (dd,  $J = 10.4, 1.4$ , 1H), 4.87 (m, 1H), 4.44 (tt,  $J 10.1, 6.3$ , 1H), 3.58 (m, 1H), 2.39 – 2.23 (m, 1H), 1.61 (m, 4H), 1.43 (m, 2H), 1.30 (m, 10H), 1.26 (m, 10H), 0.91 – 0.80 (m, 3H);  **$^{13}\text{C}$  NMR** (101

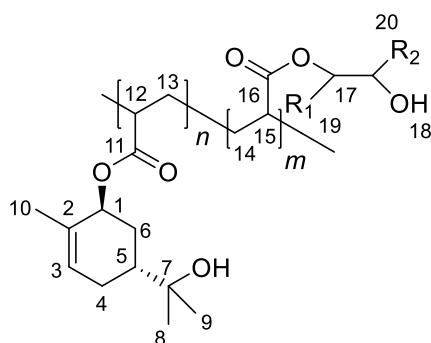
MHz, CD<sub>3</sub>OD)  $\delta_c$  171.10, 133.14, 131.53, 128.12, 128.07, 60.19, 34.08, 33.71, 31.99, 29.64, 29.39, 29.05, 25.50, 24.74, 22.80, 14.24; **HRMS** (ESI): Calculated for [C<sub>13</sub>H<sub>20</sub>NaO<sub>3</sub>]<sup>+</sup> 392.57 obtained 393.26 (M<sup>+</sup> Na<sup>+</sup>).

### Polymer TPA6



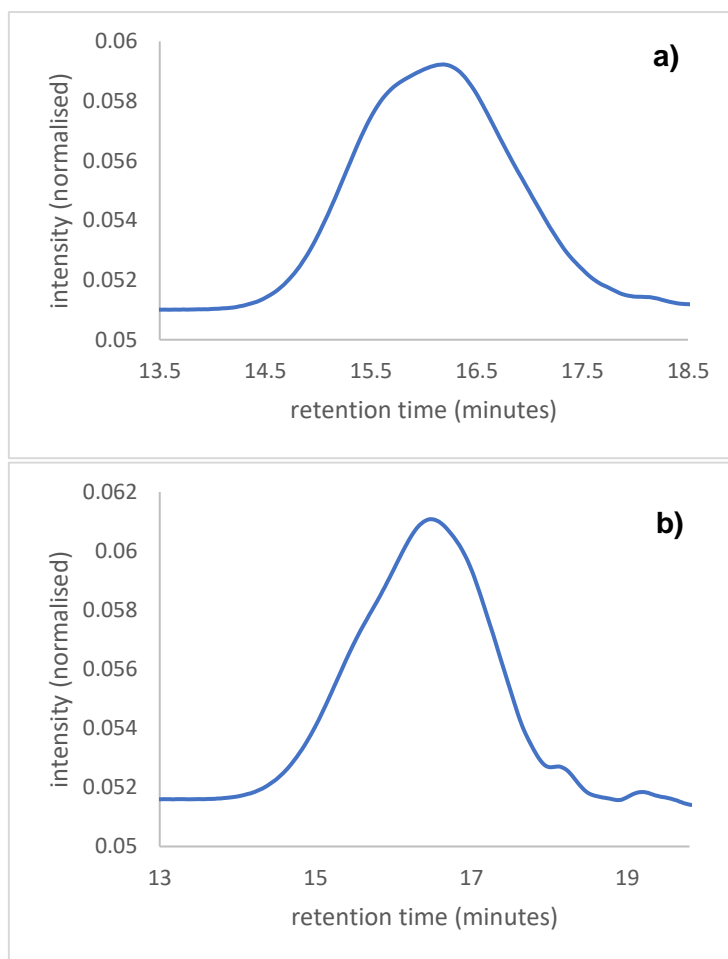
**FTIR** (ATR)  $\nu_{\max}/\text{cm}^{-1}$ : 3434 (-OH), 2931 (C-H), 1725 (C=O), 1448 (C-H), 1378 (-OH), 1245 (-OH), 1154 (C-O), 1025 (C-O), 943 (C=C), 914 (C=C), 840 (C=C), 814 (C=C); **<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>OD)  $\delta_H$  5.69 (br), 5.24 (br), 2.09 (br), 1.73 – 1.67 (br), 1.21 – 1.07 (br).

### Copolymer TPA7

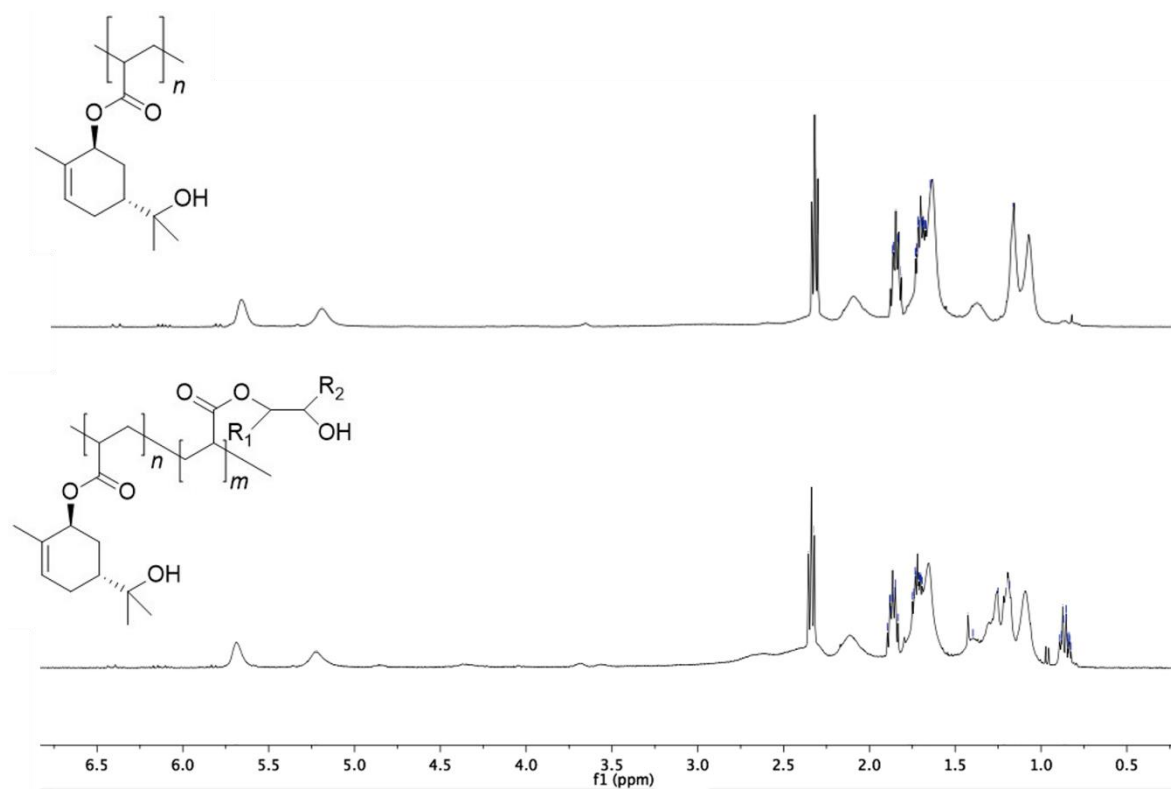




**FTIR** (ATR)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3434 (-OH), 2931 (C-H), 2856 (C-H), 1725 (C=O), 1448 (C-H), 1378 (-OH), 1245 (-OH), 1154 (C-O), 1025 (C-O), 943 (C=C), 914 (C=C), 840 (C=C), 814 (C=C);  **$^1\text{H}$  NMR** (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta_{\text{H}}$  5.69 (br), 5.24 (br), 4.85 (br), 3.56 (br), 2.09 (br), 1.87 (br), 1.73 – 1.67 (br), 1.34 – 1.25 (br), 1.21 – 1.07 (br).



**Figure S6.** The polymer peaks from the GPC analyses of a) TPA6 and b) TPA7



**Figure S7.** A comparison of the  $^1\text{H}$  NMR analyses of TPA6 and TPA7 after purification with hexane. The peaks at  $\delta = 6.42$  and  $5.75$  ppm representing the acrylate peaks no longer appeared, indicating that there were no residual monomer molecules left in the products.

**Table S1.** The  $M_{w,\text{app}}$  obtained from the sedimentation equilibrium experiment for all concentrations for TPA6.

Concentration (mg/mL)	$M_{w,\text{app}}$ ( $M^*$ ) (kDa)	$M_{w,\text{app}}$ (hinge point) (kDa)
0.5	3.3	-
0.75	3.8	-
1.0	4.1	3.6
1.5	3.0	3.2

**Table S2.** The  $M_{w,app}$  values obtained from the sedimentation equilibrium experiment for all concentrations for TPA7.

Concentration (mg/mL)	$M_{w,app}$ ( $M^*$ ) (kDa)	$M_{w,app}$ (hinge point) (kDa)
0.5	4.4	3.8
0.75	4.0	3.9
1.0	4.2	3.8
1.5	4.7	4.3
2.0	4.7	4.2
3.0	4.6	4.1
4.0	4.6	4.1

## References

1. Cutajar, M. *et al.* Terpene polyacrylate TPA5 shows favorable molecular hydrodynamic properties as a potential bioinspired archaeological wood consolidant. *Sci. Rep.* **11**, 7343 (2021).
2. Neto, W. S. *et al.* Superparamagnetic nanoparticles stabilized with free-radical polymerizable oleic acid-based coating. *J. Alloys Compd.* **739**, 1025–1036 (2017).