Hydrolytic degradation of ROMP thermosetting materials catalysed by bio-derived acids and enzyme: from network to linear materials

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$^1$H and $^{13}$C NMR of Monomer 1

$^1$H NMR, CDCl$_3$, 500 MHz, $\delta$ (ppm): 7.41 (5H, m, Ar-H, H$_M$), 6.33 (2H, s, CH, H$_A$), 3.39 (2H, d, N-CH$_2$, H$_F$), 3.32 (2H, d, CH, H$_B$), 2.84 (2H, s, CH, H$_C$), 1.60 (1H, m, CH$_2$, H$_D$), 1.48 (1H, d, $J_{HH}$ = 10.8 Hz, CH$_2$, H$_E$), 1.32 (6H, m, CH$_2$, H$_{G,K,L}$).

$^{13}$C NMR, CDCl$_3$, 126 MHz, $\delta$ (ppm): 177.5 (C$_5$), 151.9 (C$_{10,11}$), 138.2 (C$_1$), 126.5 (C$_9$), 48.1 (C$_3$), 46.1 (C$_2$), 43.2 (C$_4$), 35.0 (C$_6$), 28.2 (C$_7$), 22.8 (C$_8$).

$^1$H and $^{13}$C NMR of Monomer 2

$^1$H NMR, CDCl$_3$, 500 MHz, $\delta$ (ppm): 6.12 (2H, s, CH, H$_A$), 3.17 (2H, d, N-CH$_2$, H$_F$), 3.09 (2H, s, CH, H$_B$), 2.51 (2H, s, CH, H$_C$), 1.52 (1H, m, CH$_2$, H$_D$), 1.32 (1H, d, $J_{HH}$ = 10.9 Hz CH$_2$, H$_E$), 1.09 (9H, m, CH$_2$ and CH, H$_{G,I,K,L,M}$), 0.71 (6H, t, CH$_3$, H$_{J,N}$)

$^{13}$C NMR, CDCl$_3$, 126 MHz, $\delta$ (ppm): 178.0 (C$_5$), 137.6 (C$_1$), 47.6 (C$_3$), 45.0 (C$_2$), 42.6 (C$_4$), 42.2 (C$_7$), 37.6 (C$_6$), 30.3 (C$_8$), 28.2 (C$_{10}$), 23.7 (C$_{11}$), 22.8 (C$_{12}$), 13.9 (C$_{13}$), 10.2 (C$_9$)
Synthesis and characterisation of di-functional norbornene dicarboximide monomer 3

1,4 butanediol divinyl ether (0.71 g, 5 mmol), and 4-methoxyphenol (0.016 g, 0.13 mmol) (inhibitor) were added to a dry two necked round bottom flask (250 mL), fitted with a reflux condenser and kept under nitrogen. The reaction mixture was heated to 90°C and compound 2 (3.0 5 g, 11 mmol) was added in several portions over a period of 1 hr, upon which the colourless mixture turned orange. The mixture was left to stir for further 10 hr at 90°C and was then allowed to reach ambient temperature. Amberlyst A21 ion exchange resin (4.76 g) and toluene (dry, 19 mL) were added and the mixture was stirred for an additional 2 hours. The Amberlyst A21 was removed by filtration, and toluene was removed under reduced pressure. The product was then dried under reduced pressure at ambient temperature. The product 3 was obtained as a highly viscous orange-brown liquid in a 50% yield (1.741 g, 2.50 mmol).

IR (neat) ν/cm⁻¹: 2942 (C-H), 1693(C=O), 1133 (acetal C-O). Found: C, 65.26; H, 7.56; N, 3.96; O, 23.22 %. \( \text{C}_{38}\text{H}_{52}\text{O}_{10}\text{N}_{2} \) requires C, 65.50; H, 7.52; N, 4.02; O, 22.96%.

NMR: 6H (500 MHz; CDCl₃): 6.22 (4H, t, J_{HAHB} = 1.59, H₄), 5.87 (2H, q, J_{HLHM} = 5.24, H₃), 3.62-3.48 (4H, m, H₉), 3.42 (4H, t, J_{HFHG} = 7.44, H₅), 3.21 (4H, m, H₇), 2.64 (4H, d, J_{HBHC} = 0.98, H₁), 2.32 (4H, t, J_{HHH} = 7.32, H₆), 1.61 (4H, m, H₁), 1.60 (4H, m, H₈), 1.57 (4H, m, H₇), 1.48 (2H, d, J_{HDHE} = 9.76, H₂), 1.36 (6H, d, J_{HLHM} = 5.24, H₆), 1.32 (4H, m, H₂), 1.19 (2H, d, J_{HDHE} = 9.76, H₂)

\(^{13}\text{C}\) NMR, CDCl₃, 126 MHz, δ (ppm): 178.3 (C₄), 173.3 (C₁₁), 138.0 (C₁), 96.4 (C₁₂), 69.0 (C₁₄), 48.0 (C₃), 45.4 (C₂), 42.9 (C₅), 38.7 (C₆), 34.5 (C₁₀), 27.7 (C₇), 26.7 (C₈), 26.4 (C₁₅), 24.6 (C₉), 21.0 (C₁₃).
Figure S1. 500.0 MHz $^1$H NMR spectrum of monomer 3, in CDCl$_3$

Figure S2. 126 MHz $^{13}$C NMR spectrum of monomer 3, in CDCl$_3$
Figure S3: % Mass loss of cross-linked polymer 11-13 and 14 after acid-catalysed hydrolysis using citric, acetic and hydrochloric acid.

Figure S4. Schematic structure of copolymer obtained from the hydrolysis of cross-linked polymers 6-13.
In Figure S6, we plot the phase angle, tan(δ), defined as the ratio of G''/G'. This property is typically used (e.g. Ref. 18) to find the glass transition temperature T_g, indicated by a peak in tan(δ) when plotted as a function of temperature. We show temperature sweeps performed with a similar protocol to the linear rheology at a heating rate of 2°C/min for samples 5, 11, and both 11 and 12 after acid hydrolysis in HCl. All three samples show a similar T_g of around 83°C±2°C.