

Supporting Information

The influence of composition on the physical properties of PLA-PEG-PLA-co-Boltorn based polyester hydrogels and their biological performances

David K. Wang,^{a,b} Srinivas Varanasi,^c David J.T. Hill,^d Firas Rasoul,^{*a,b} Anne L. Symons,^c and Andrew K. Whittaker^{a,b}

^aAustralian Institute for Bioengineering and Nanotechnology, University of Queensland, Brisbane Qld 4072, Australia.

^{*}f.rasoul@uq.edu.au; d.wang1@uq.edu.au and a.whittaker@uq.edu.au

^bCentre for Advanced Imaging, University of Queensland, Brisbane Qld 4072, Australia.

^cSchool of Dentistry, The University of Queensland, Brisbane, Queensland,

Australia. srinivas.varanasi@uqconnect.edu.au, a.symons@uq.edu.au

^dSchool of Chemistry and Molecular Biosciences, University of Queensland, Brisbane Qld 4072, Australia. d.hill@uq.edu.au

A typical synthesis of PLA₅PEG₂₀PLA₅ copolymer (1kL₅)

All reactants were dried overnight in a freeze-dryer to remove traces of solvent or moisture. In a two-neck round bottom flask equipped with magnetic stirrer, the dihydroxyl 1kPEG (10.0 g, 10.0 mmol) was dissolved in 100 mL of CH₂Cl₂ under Ar atmosphere followed by the addition of D,L-lactic acid (7.20 g, 50.0 mmol). After the complete dissolution of the PEG and D,L-lactic acid, 1 wt % of DBU (0.17 g, 1.13 mmol), diluted 100 fold using dry CH₂Cl₂, was added via a pressure-equalizing dropping funnel. The DBU solution was slowly added over 30 min and the reaction was further stirred for 4 h at room temperature under the argon atmosphere. Once the reaction was completed, the polymer solution was precipitated into an excess of diethyl ether, leading to a white, sticky product. A total of 15.8 g (9.19 mmol) of triblock copolymer was collected (91.9% yield) and dried under vacuum at 40 °C. ATR-FTIR (neat, cm⁻¹): 3550-3230 (O-H str), 3000-2850 (C-H str), 1754 (C=O str), 1382 (C-H sym def), 1100 (C-O-C asym str). ¹H NMR (d-CHCl₃, 500 MHz): δ 1.40-1.56 (m, CH₃CH, 30H), 3.55-3.68 (m, OCH₂CH₂O, 92H), 4.20-4.35 (m, CH₂CH₂O.COCHCH₃, 6H), 5.08-5.20 (m, COCHCH₃O.CO, 8H).

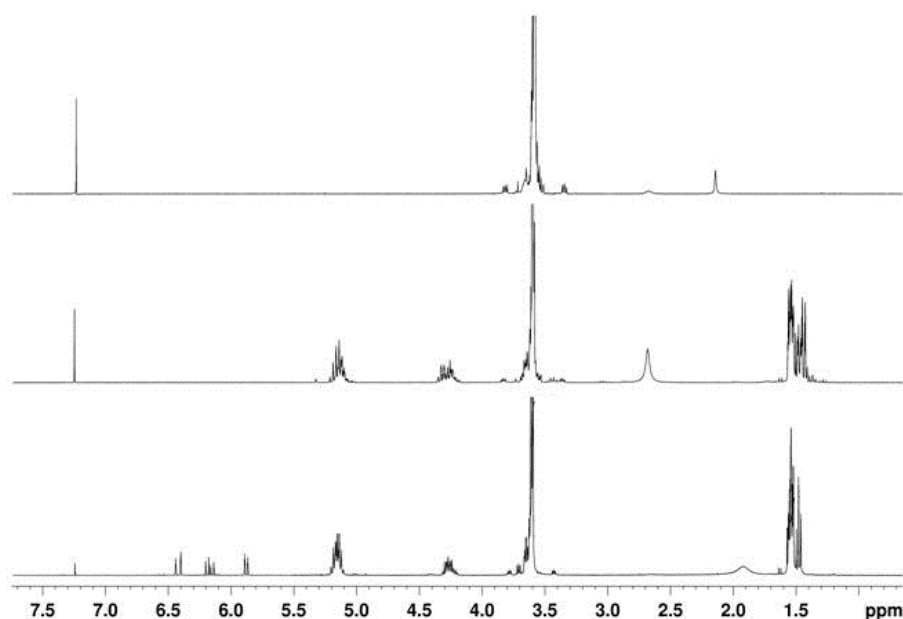
A typical synthesis of PLA₅PEG₂₀PLA₅ diacrylate (1kL₅DA)

To a solution of PLA₅PEG₂₀PLA₅ copolymer (15 g, 8.72 mmol) in 100 mL of dry CH₂Cl₂ in a two-neck round bottom flask at 0 °C, NEt₃ (2.45 g, 26.16 mmol) was added. ACC (3.16 g,

34.88 mmol) dissolved in 10 mL of dry CH_2Cl_2 was then slowly added to the polymer mixture over 1 h using a pressure-equalizing funnel and the solution stirred for a further 4 h at 0 °C under an argon atmosphere. The reaction mixture was then stirred at room temperature for another 36 h. 200 mL CH_2Cl_2 was added to the mixture and it was then washed with 1M HCl (3 x 40 mL), followed by saturated NaHCO_3 (aq) (3 x 40 mL), and brine (3 x 40 mL). The organic layer was then collected and partially dried under reduced pressure and then precipitated in an excess of diethyl ether. The product (12.59 g, 6.89 mmol, 79.0% yield) was dried under vacuum at 40 °C. ATR-FTIR (neat, cm^{-1}): 3000-2850 (C-H str), 1754 (C=O str), 1727 (C=O str), 1640-1620 (C=C str), 1410 (C-H def), 1382 (C-H sym def), 1100 (C-O-C asym str), 810 (CH_2 vinyl def). ^1H NMR ($d\text{-CHCl}_3$, 500 MHz): δ 1.40-1.56 (m, CH_3CH , 29H), 3.55-3.68 (m, $\text{OCH}_2\text{CH}_2\text{O}$, 92H), 4.20-4.35 (m, $\text{CH}_2\text{CH}_2\text{O.COCHCH}_3$, 4H), 5.08-5.20 (m, $\text{COCHCH}_3\text{O.CO}$, 9H), 5.85-5.88 (dd, $J' = 10.31$, $J'' = 1.40$ Hz, cis $\text{CH}_c=\text{CH}_a\text{H}_b$, 2H), 6.12-6.19 (td, $J' = 17.33$, $J'' = 10.31$ Hz, $\text{CH}_c=\text{CH}_a\text{H}_b$, 2H), 6.40-6.44 (dd, $J' = 17.33$, $J'' = 1.40$ Hz, trans $\text{CH}_c=\text{CH}_a\text{H}_b$, 2H).

^1H NMR spectra of the polymers

^1H NMR spectra were used to characterize and confirm the purity of the ≈ 1 k PEG starting polymer and the two reaction products synthesized as described above.



S1. ^1H NMR spectra of $\approx 1\text{kPEG}$ (top), 1kL_5 (middle) and $1\text{kL}_5\text{DA}$ (bottom) in CDCl_3

Flame atomic absorption spectrophotometry (AAS)

A Varian SpectrAA 220FS flame atomic absorption spectrophotometer, AAS, was used in conjunction with a copper hollow cathode lamp operated at 4 mA and an air-acetylene flame. The nebulizer free uptake rate was 5 ml min⁻¹ and the wavelength was set to 324.8 nm with a spectral slit width of 0.5 nm. A computer with SpectrAA software was connected to the spectrophotometer for data handling.

Ten standard samples of Cu(II) in ultrapure MilliQ Millipore water at a concentration ranging from 0 to 10 ppm were prepared from cupric nitrate standards. The absorbances were measured and a linear calibration curve was plotted and used for the determination of Cu content. For analysis of the crosslinked, insoluble BH20PEGA/PLA_aPEG_bPLA_aDA copolymers, the polymers were first digested in 10 mL of 30% nitric acid at 90 °C for 3 h, and then before analysis the solutions were diluted by mixing 1 part of the digested polymer solution with 9 parts of MilliQ Millipore water.