

Support Information

Poly (glycerol adipate) (PGA) Backbone Modifications with a Library of Functional Diols: Chemical and Physical Effects

Philippa L. Jacob,^a Laura A. Cantu Ruiz,^b Amanda K. Pearce,^c Yinfeng He,^b Joachim C. Lentz,^a Jonathan C. Moore,^a Fabricio Machado,^{a,d} Geoffrey Rivers,^b Edward Apebende,^a Maria Romero Fernandez,^a Iolanda Francolini,^e Ricky Wildman,^b Steven M. Howdle^a and Vincenzo Taresco^{a*}

- a. School of Chemistry, University of Nottingham, University Park, NG7 2RD, Nottingham, United Kingdom
- b. Faculty of Engineering, University of Nottingham, University Park, Nottingham, NG7 2RD UK
- c. School of Chemistry, University of Birmingham, Birmingham, B15 2TT United Kingdom
- d. Laboratory of Chemical Processes Development, University of Brasília, Chemistry Institute, Campus Universitário Darcy Ribeiro, 70910-900 Brasília, DF, Brazil
- e. Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro, 00185, Italy

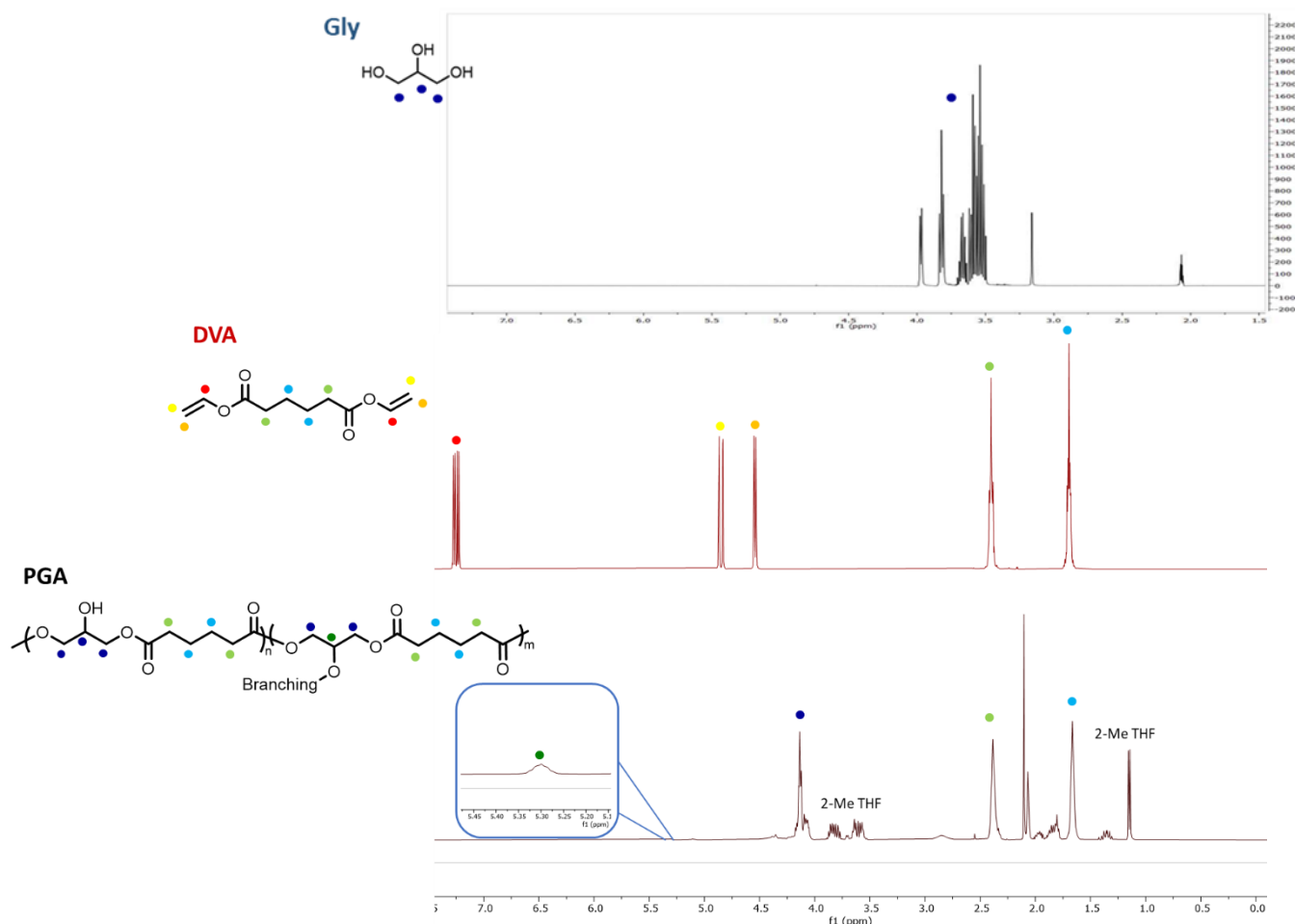


Figure S1. ¹H NMR of divinyl adipate, glycerol and poly (glycerol adipate) (PGA) produced after 3h of enzymatic reaction.

Glycerol: (400 MHz, CDCl₃; δ, ppm): 4.0-3.5 (m, 5H).

DVA: (400 MHz, CDCl₃; δ, ppm): 7.27 (q, 2H), 4.87 (dd, 2H), 4.53 (dd, 2H), 2.40 (q, 4H), 1.70 (q, 4H).

PGA, 50 °C, 3h: (400 MHz NMR, Acetone- d_6 ; δ , ppm): 5.30 (m, 1H), 5.10 (m, 1H), 4.94-3.98 (m, 5H), 2.39 (m, 4H), 2.07 (acetone- d_6), 1.66 (m, 4H).

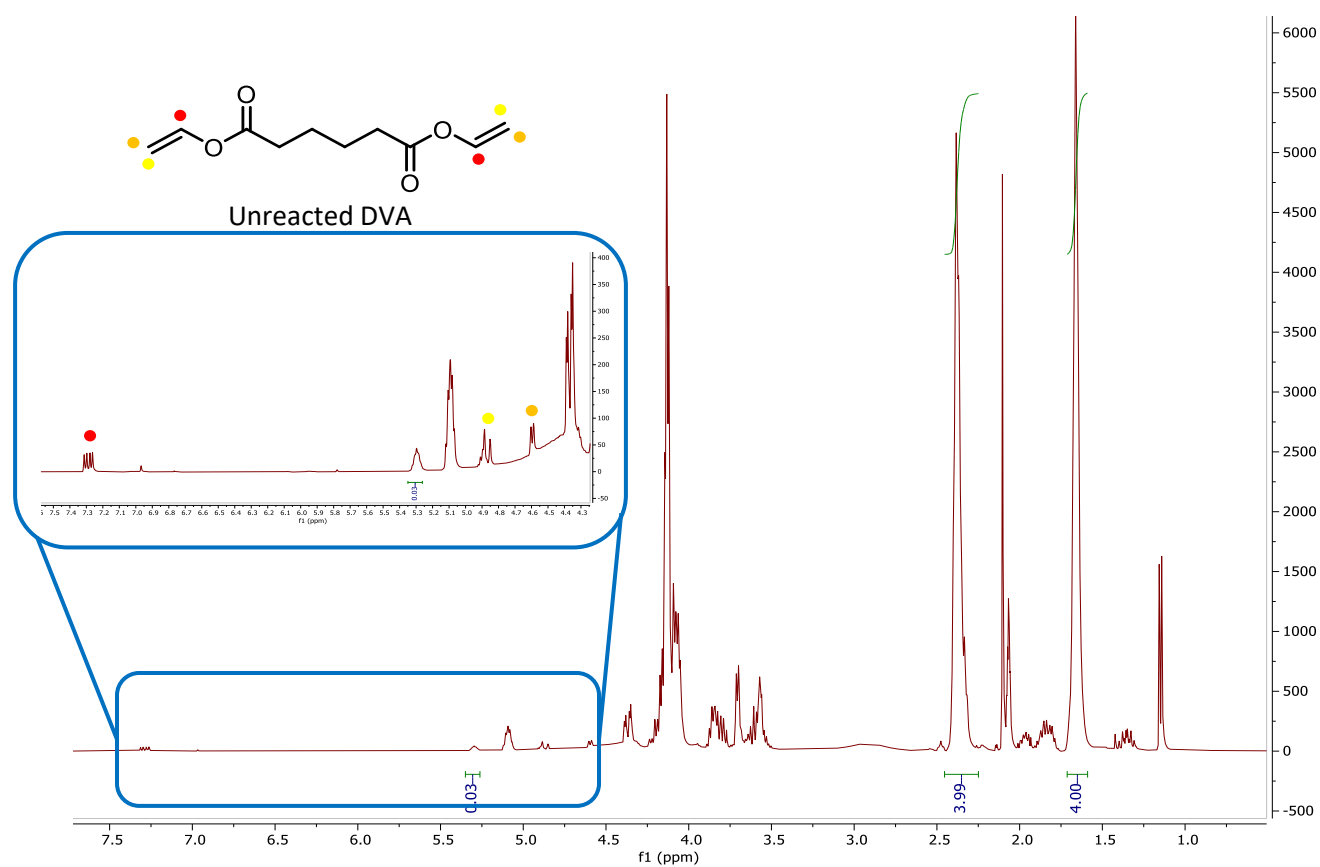


Figure S2. ^1H NMR of PGA, 1.5h, 50 °C. Unreacted vinyl protons visible at 7.28, 4.87 and 4.60 ppm.

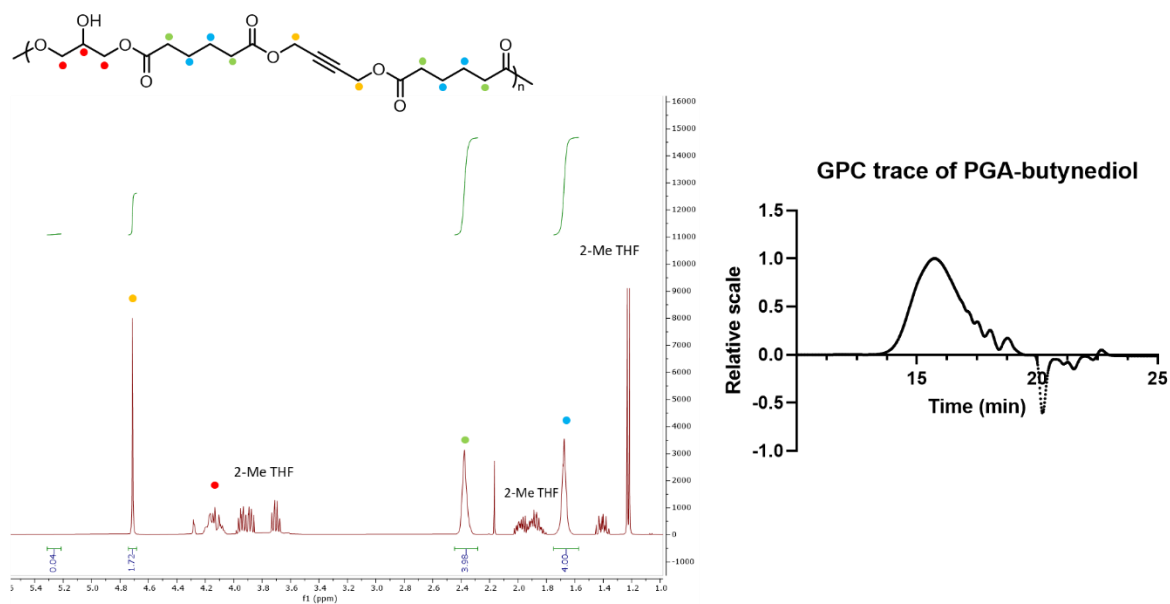


Figure S3. ¹H NMR of PGA + 1,4-butynediol. (400 MHz NMR, CDCl₃; δ , ppm): 5.30 (m, 1H), 4.71 (s, 1H), 4.38-4.01 (m, 5H), 2.39 (m, 4H), 2.07 (acetone-*d*₆), 1.66 (m, 4H). GPC trace of PGA-butynediol.

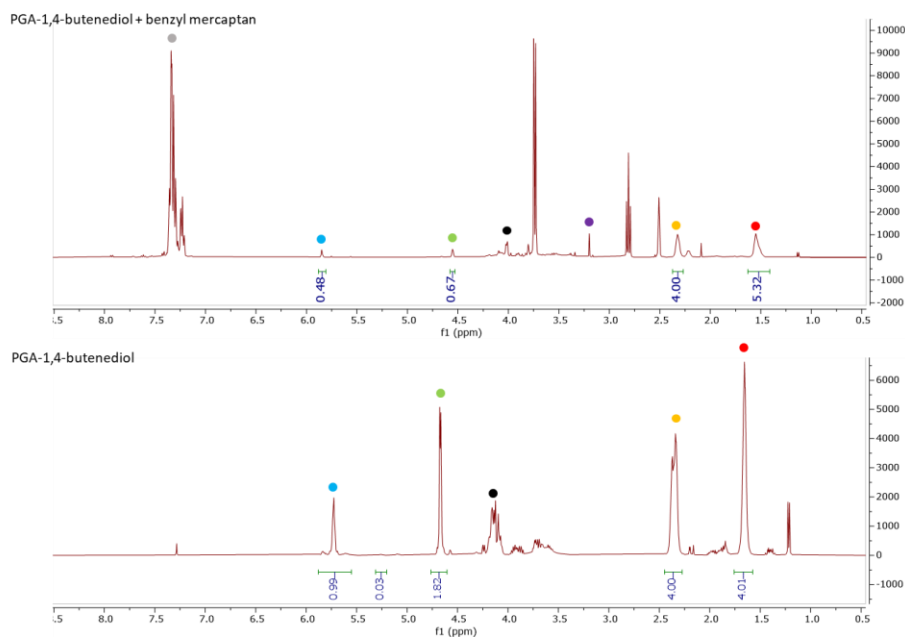
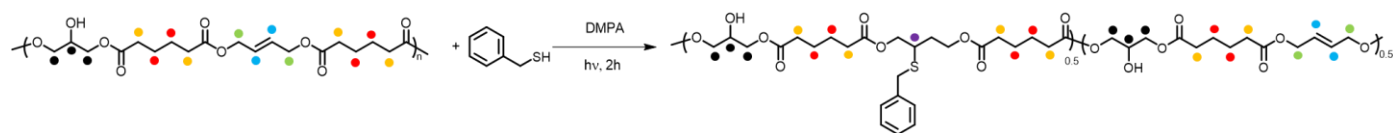
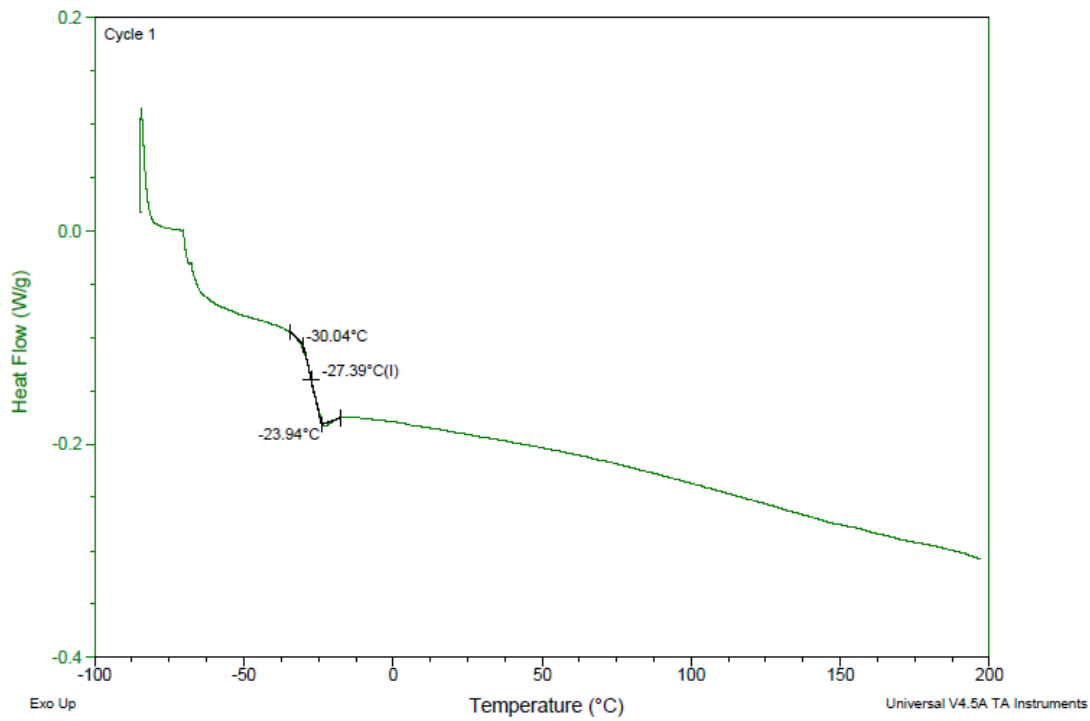


Figure S4. ^1H NMR of PGA + butane diol before and after thiol-ene reaction. Alkene protons at 5.71 ppm have reduced by $\sim 50\%$ following reaction.

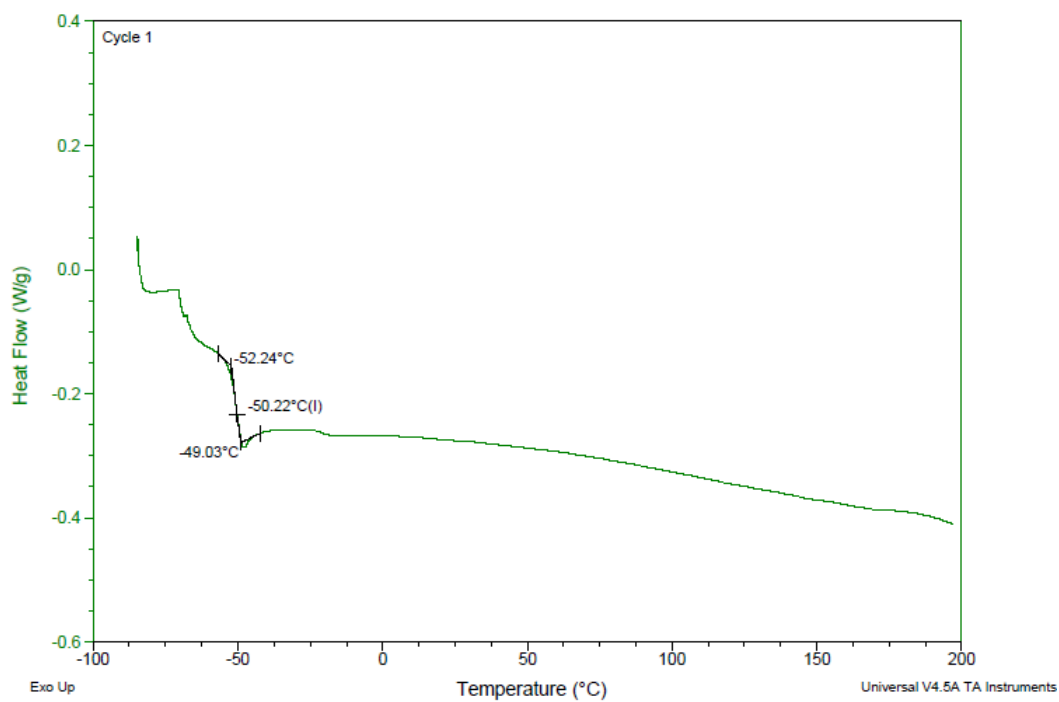
PGA + butenediol: (400 MHz NMR, CDCl_3 ; δ , ppm): 7.73 (m, 2H) 5.30 (m, 1H), 4.68 (m, 4H), 4.70-4.01 (m, 5H), 2.33 (m, 4H), 1.66 (m, 4H).

DSC analysis of polymers

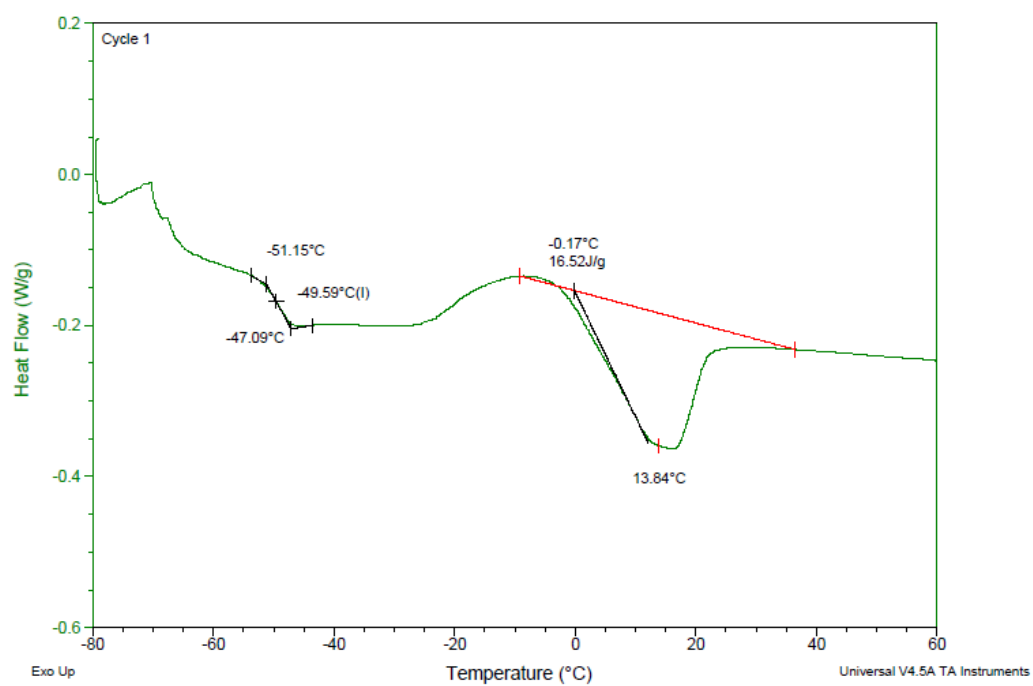
DSC analysis of PGA



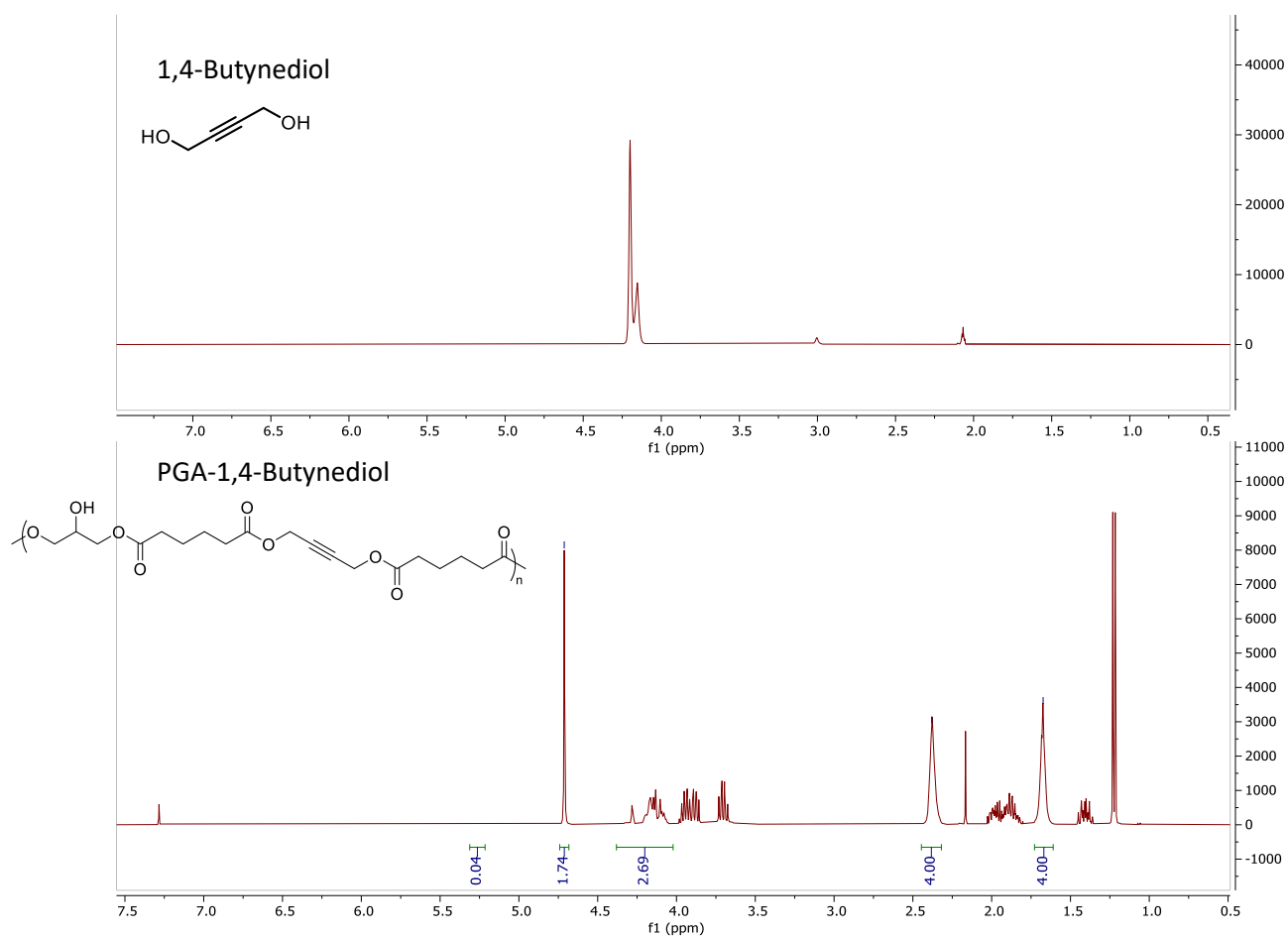
DSC analysis of PGA-PEG400.



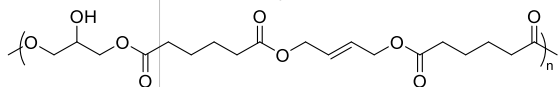
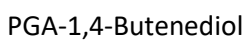
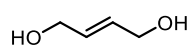
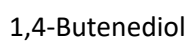
DSC of PGA-1,6-n-hexanediol



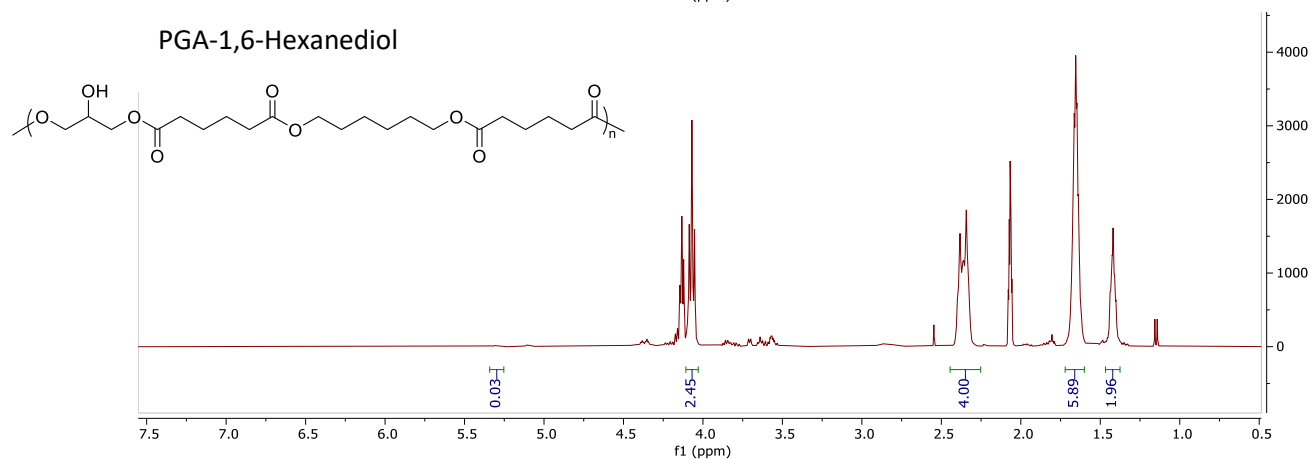
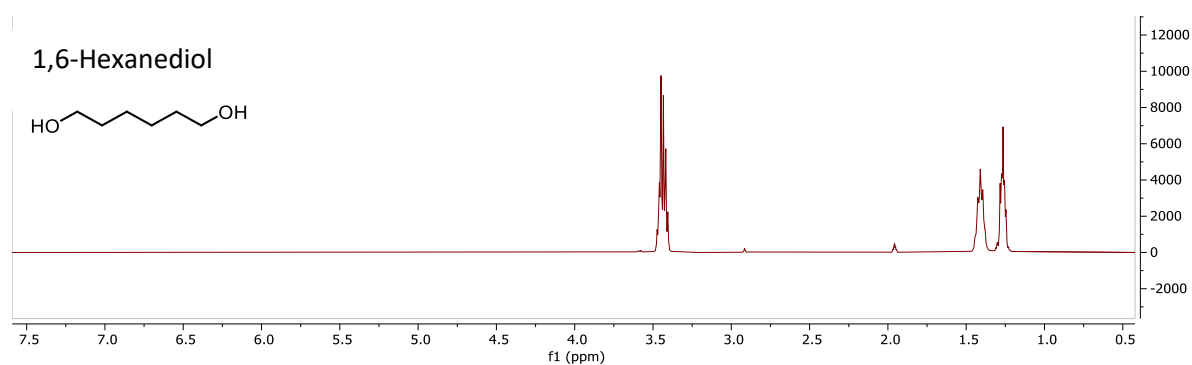
Appendix



PGA-1,4-butynediol: (400 MHz NMR, CDCl_3 ; δ , ppm): 5.30 (m, 1H), 4.71 (s, 4H), 4.38-4.02 (m, 5H), 2.33 (m, 4H), 1.66 (m, 4H).



PGA-1,4-butenediol: (400 MHz NMR, CDCl₃; δ , ppm): 5.73 (m, 2H), 5.30 (m, 1H), 4.68 (m, 4H), 4.38-4.02 (m, 5H), 2.33 (m, 4H), 1.66 (m, 4H).



PGA-1,6-hexanediol: (400 MHz NMR, acetone- d_6 ; δ , ppm): 5.30 (m, 1H), 4.38-4.02 (m, 9H), 2.33 (m, 4H), 1.66 (m, 6H), 1.43 (m, 2H).