

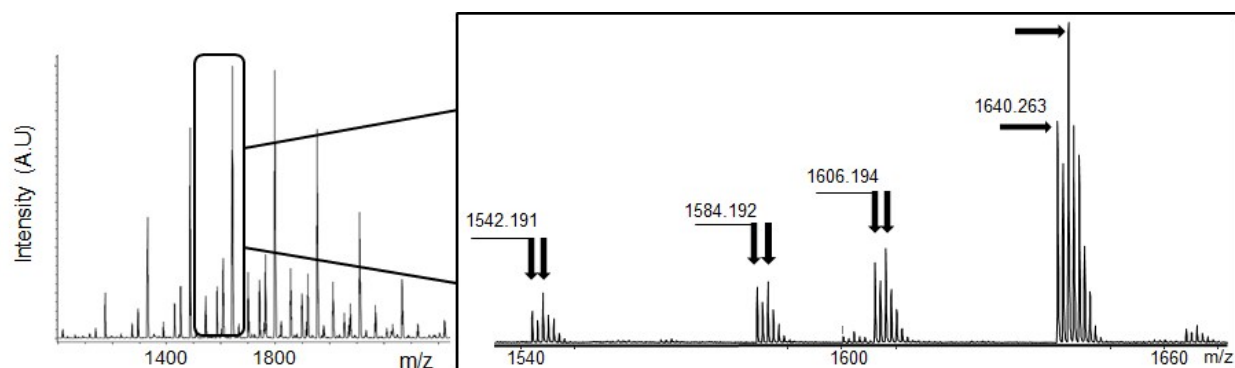
## Supporting Information

# Alternating Ring-Opening Copolymerization of Epoxides with Saturated and Unsaturated Cyclic Anhydrides: Reduced Viscosity Poly(Propylene Fumarate) Oligomers for use in cDLP 3D Printing

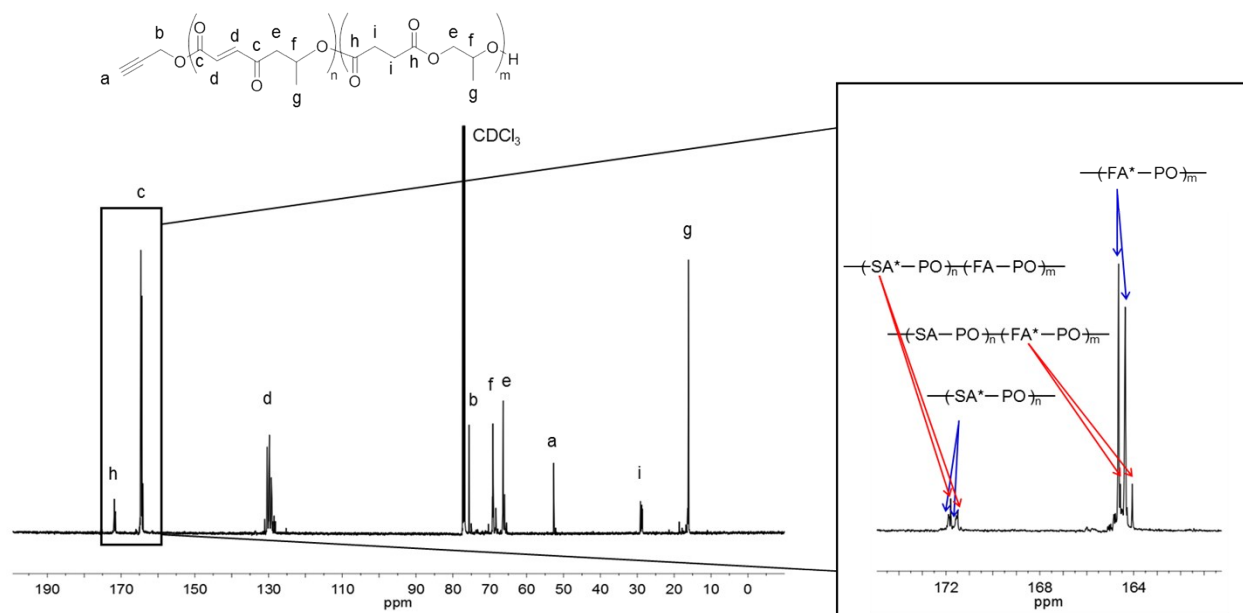
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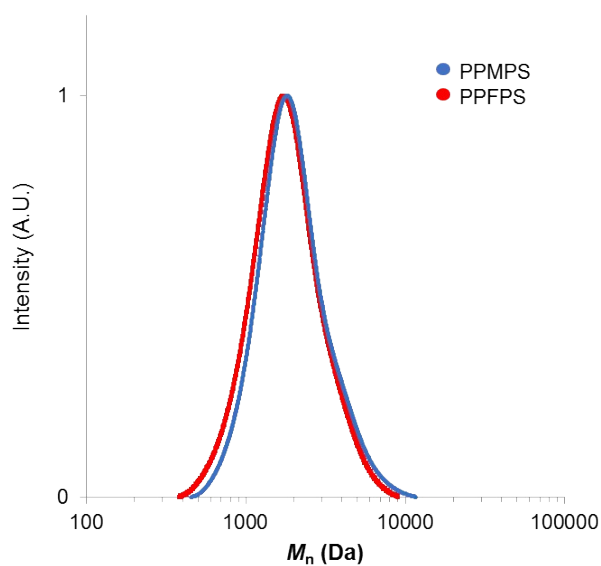
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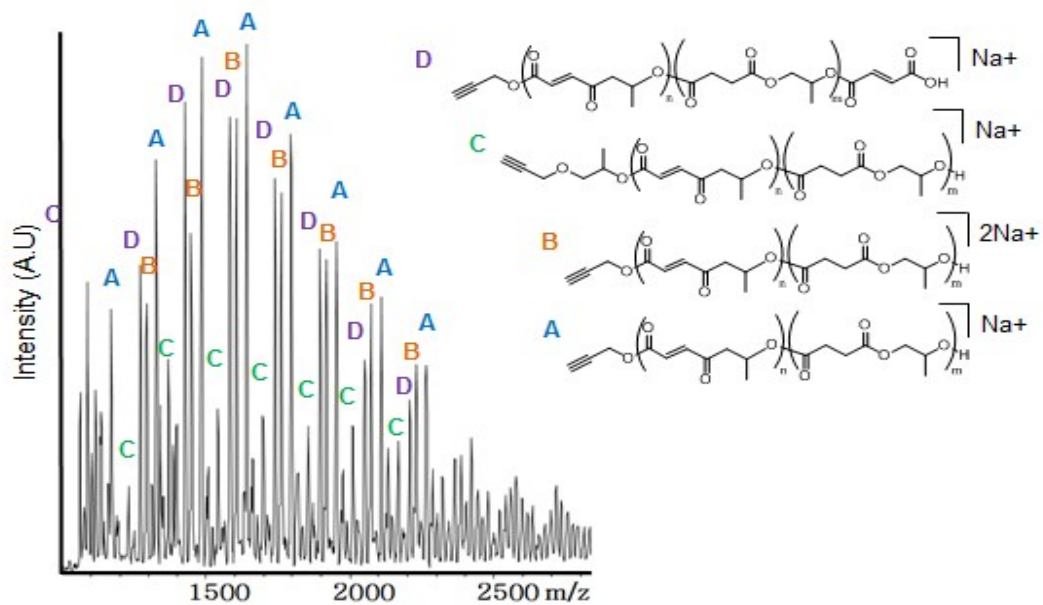
**Figure S1.** MALDI-TOF MS data of PPMS initiated with propargyl alcohol with 10 mol% succinic anhydride and DP of 10. Magnification of MALDI-ToF MS data shows in inset. The highest peak is the addition of 2 Da from the initial monoisotopic mass, confirming the presence of propylene succinate units in the polymer chain..



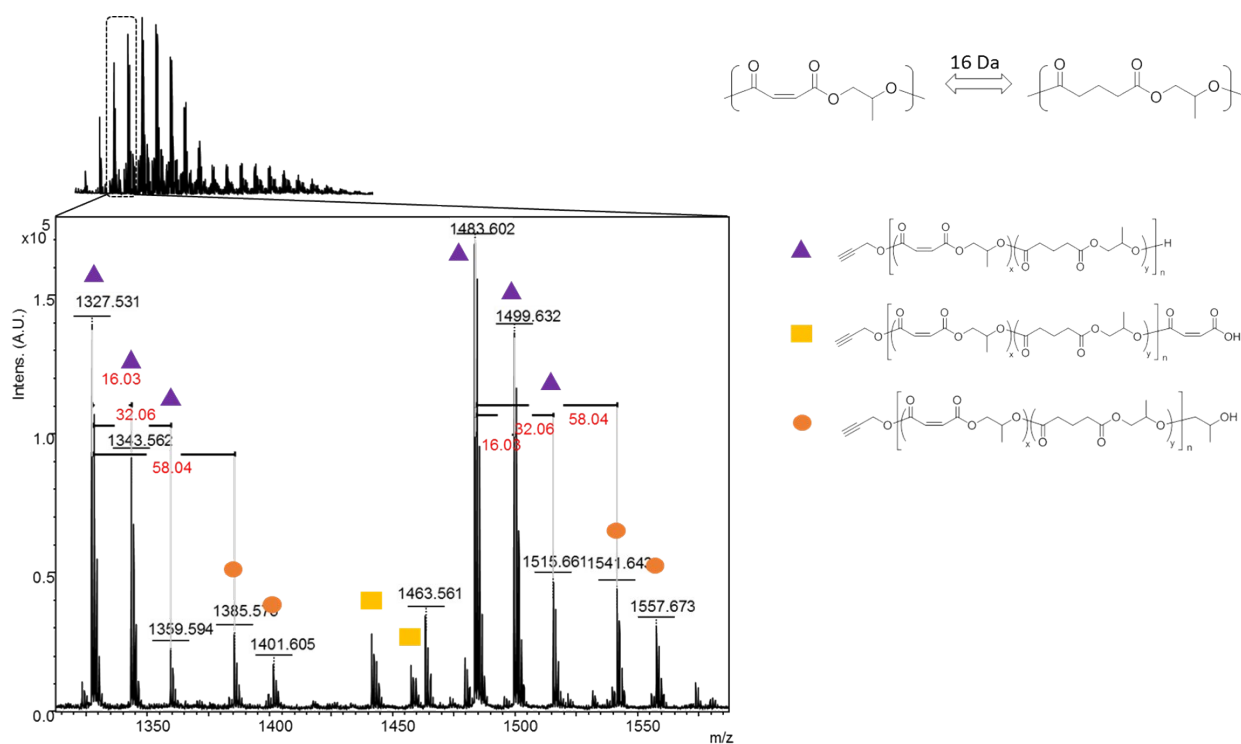
**Figure S2.** Quantitative  $^{13}\text{C}$  NMR of PPMPs initiated with 20 mol% succinic anhydride and DP of 10 (Table1, Entry 11) (500 MHz,  $\text{CDCl}_3$ , 303 K)



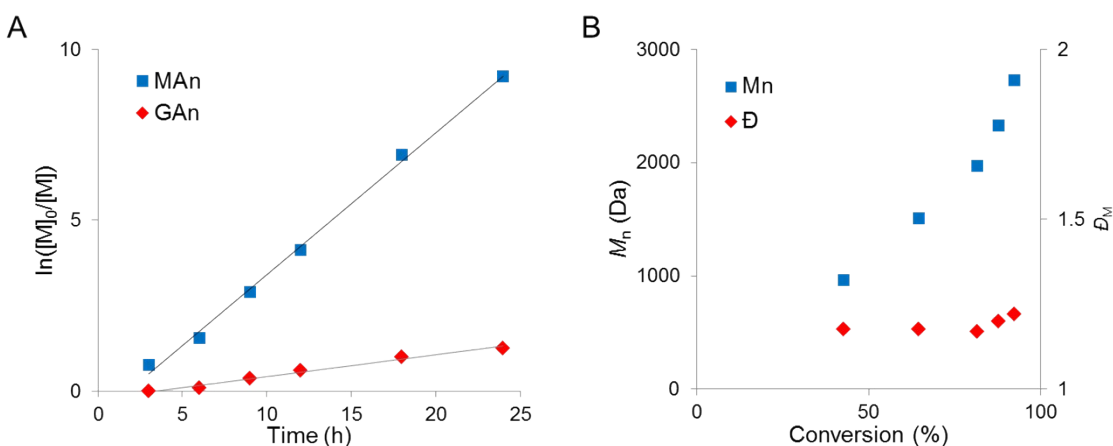
**Figure S3.** SEC chromatogram of PPMPs (blue) and PPFPS (red) with 20 mol% succinic anhydride and DP of 10 (Table1, Entry 11) determined against polystyrene standards.



**Figure S4.** MALDI-ToF mass spectrum of PPMPs initiated with propargyl alcohol with 20 mol% succinic anhydride and DP of 10.



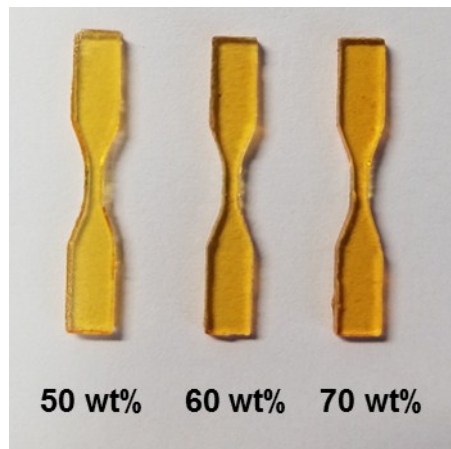
**Figure S5.** MALDI-ToF MS of of PPMPG initiated propargyl alcohol with 20 mol% glutaric anhydride and DP of 10 (Table 1, Entry 13).



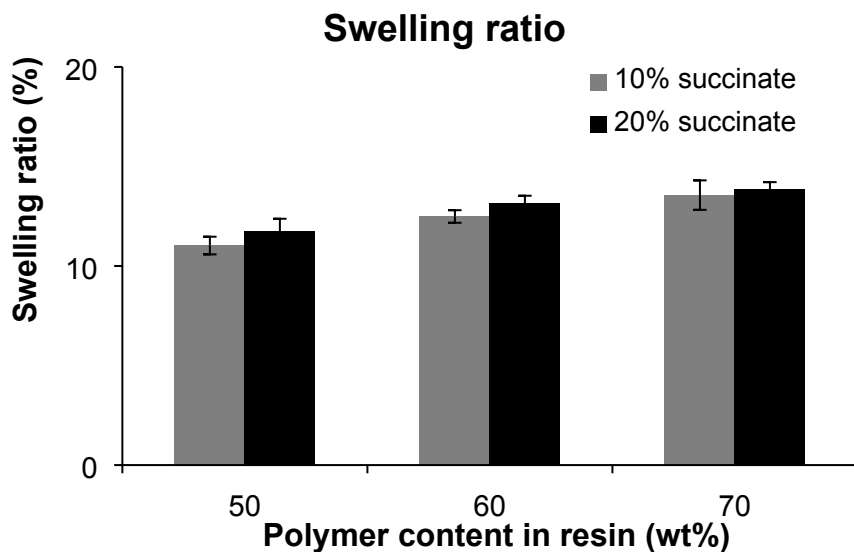
**Figure S6.** (A) Kinetic plot for the copolymerization of maleic anhydride, glutaric anhydride and propylene oxide, conducted at 80 °C in toluene with  $[MA]_0:[GA]_0:[PO]_0:[I]_0:[Cat]_0 = 80:20:100:10:1$ , total monomer concentration = 7 M. (B) Changes in number-average molecular mass ( $M_n$ ) and  $\bar{D}_M$  over increasing monomer conversion for the same copolymerization, determined by SEC against poly(styrene) standards.

**Table S1.** Kinetic study data for the copolymerization of MA, SA and PO, conducted at 80 °C in toluene with  $[MA]_0:[SA]_0:[PO]_0:[PrOH]_0:[Cat]_0 = 80:20:100:10:1$ , total monomer concentration = 7 M

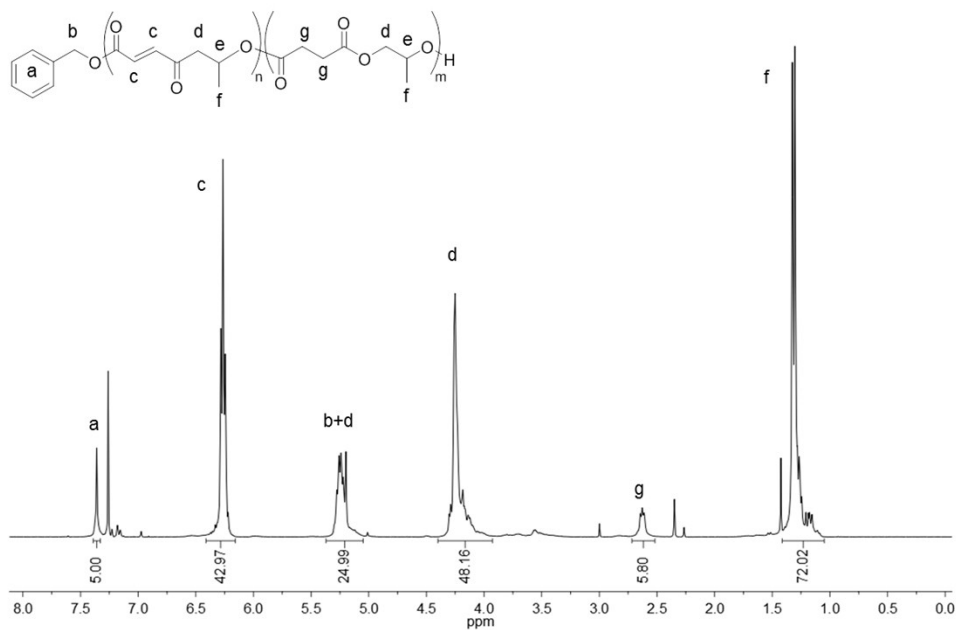
|                                | An | Time (h) |    |    |    |    |
|--------------------------------|----|----------|----|----|----|----|
|                                |    | 3        | 6  | 12 | 18 | 24 |
| Conversion (%)                 | MA | 34       | 63 | 79 | 96 | 97 |
|                                | SA | 7        | 19 | 28 | 50 | 72 |
| Mole fraction in copolymer (%) | MA | 95       | 94 | 92 | 91 | 89 |
|                                | SA | 5        | 6  | 8  | 9  | 11 |



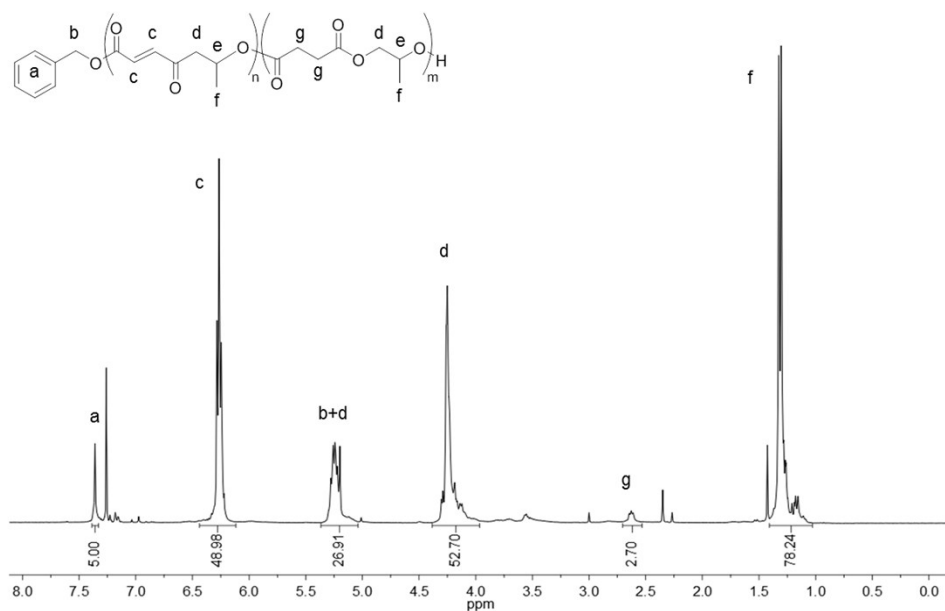
**Figure S7.** Tensile bars 3D printed from resins containing 50 , 60 and 70 wt% of 20 mol% succinate PPFS of DP 10



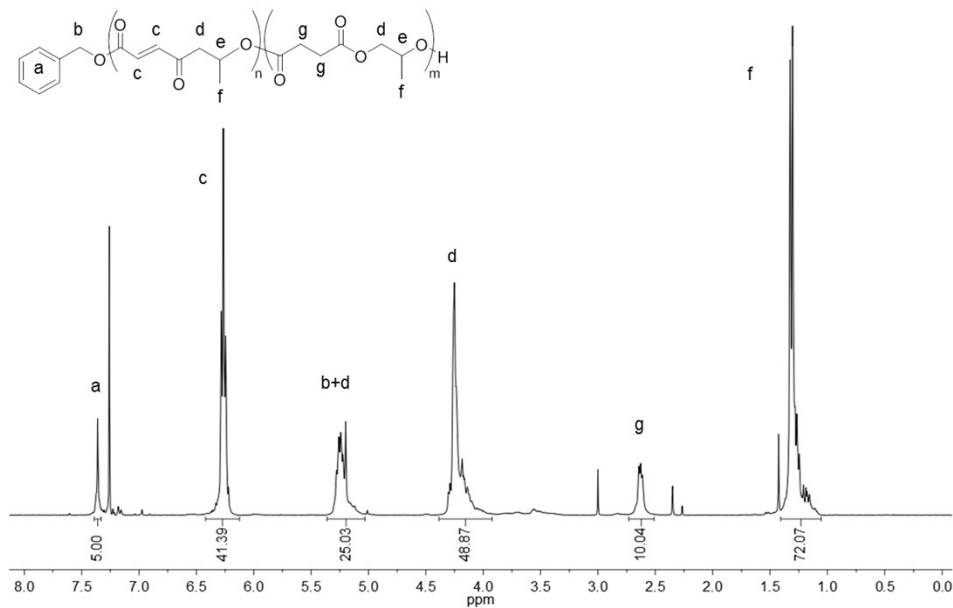
**Figure S8.** Swelling ratio of 3D-printed tensile bars at varying polymer loading resin formulation with 10 and 20 mol% succinate PPFPS of DP 10 using toluene solvent



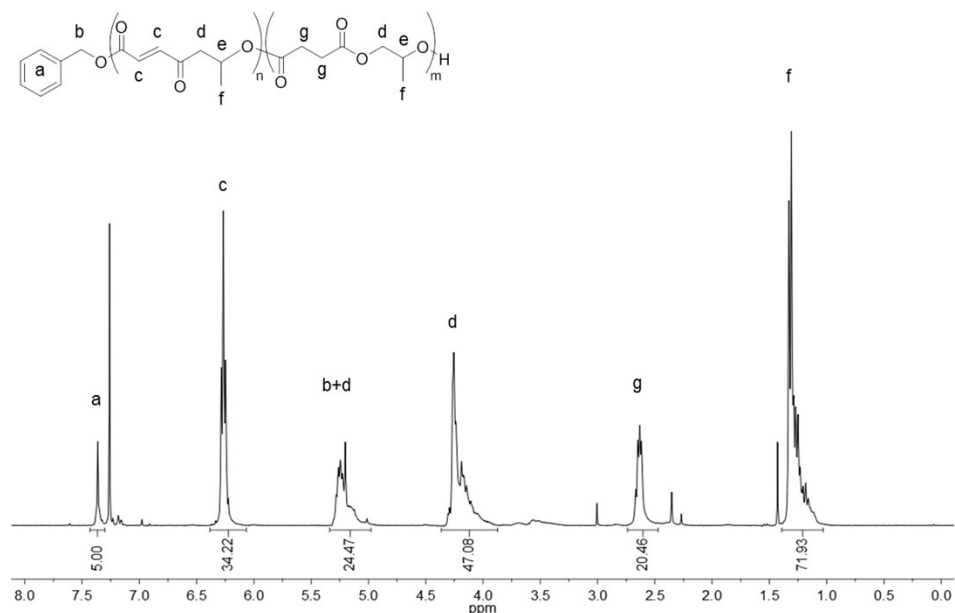
**Figure S9.** <sup>1</sup>H NMR spectra of PPMPs initiated with benzyl alcohol with 5 mol% succinic anhydride and DP of 20 (Table 1, Entry 2) (300 MHz, CDCl<sub>3</sub>, 303 K)



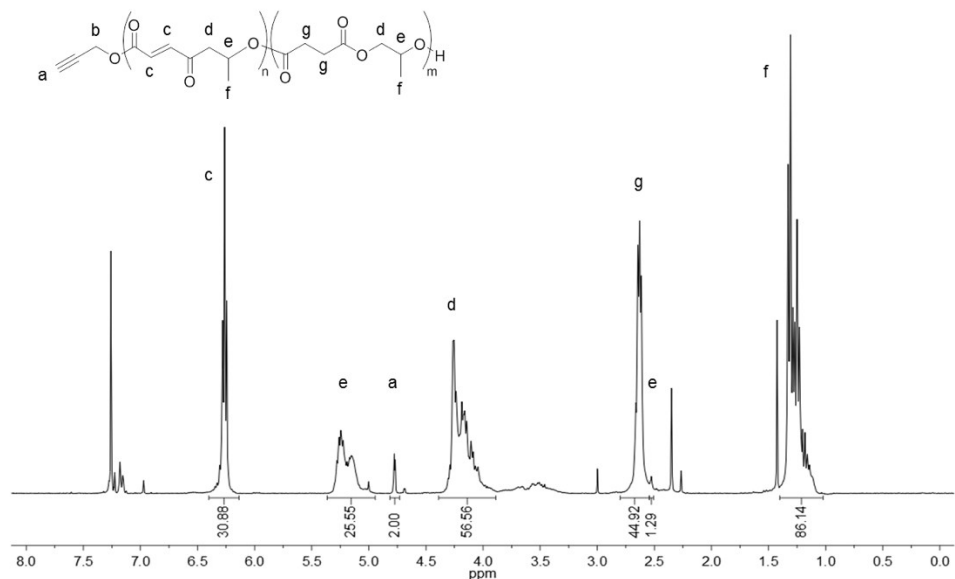
**Figure S10.**  $^1\text{H}$ NMR spectra of PPMS initiated with benzyl alcohol with 10 mol% succinic anhydride and DP of 20 (Table 1, Entry 3) (300 MHz,  $\text{CDCl}_3$ , 303 K)



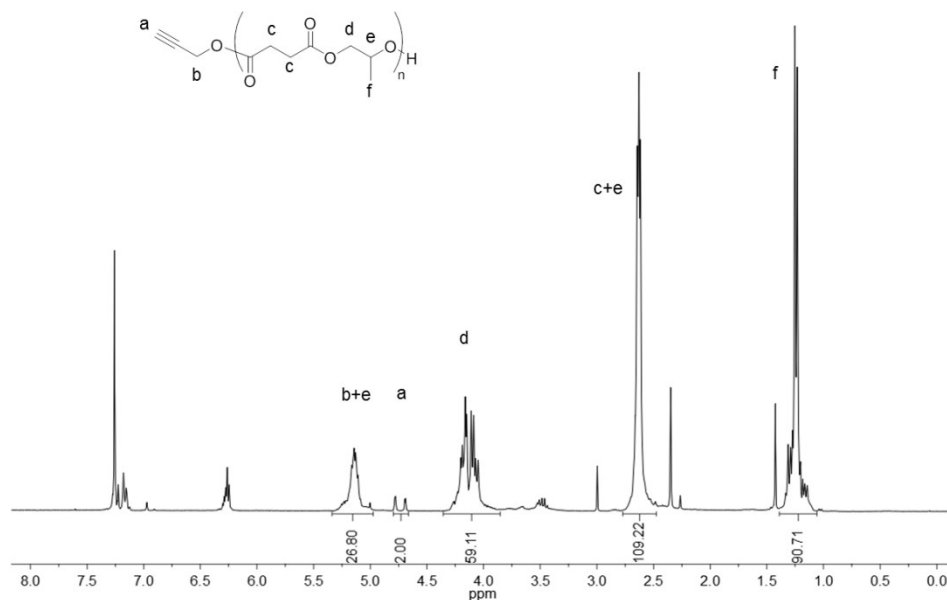
**Figure S11.**  $^1\text{H}$ NMR spectra of PPMS initiated with benzyl alcohol with 20 mol% succinic anhydride and DP of 20 (Table 1, Entry 4) (300 MHz,  $\text{CDCl}_3$ , 303 K)



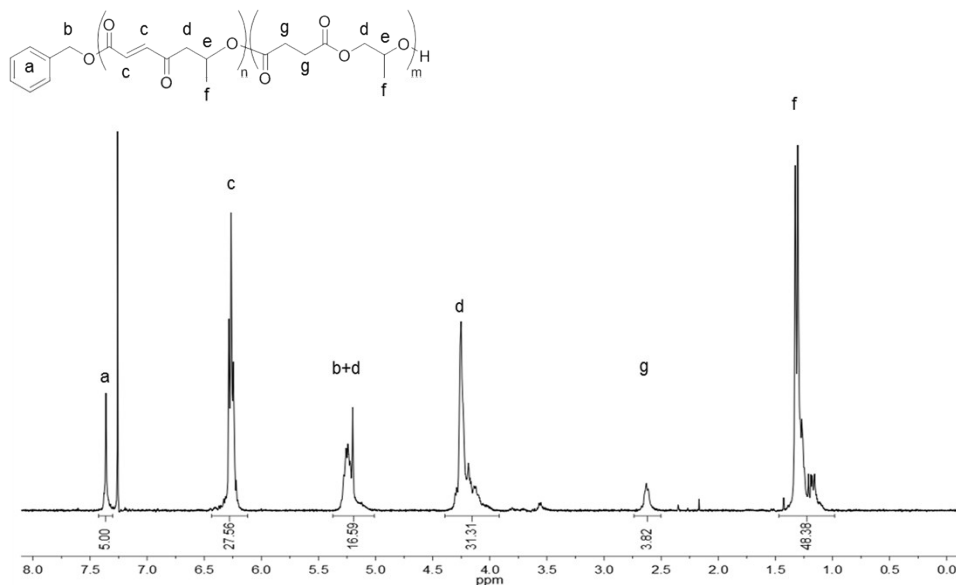
**Figure S12.**  $^1\text{H}$ NMR spectra of PPMS initiated with benzyl alcohol with 30 mol% succinic anhydride and DP of 20 (Table 1, Entry 5) (300 MHz,  $\text{CDCl}_3$ , 303 K)



**Figure S13.**  $^1\text{H}$ NMR spectra of PPMS initiated with propargyl alcohol with 50 mol% succinic anhydride and DP of 20 (Table 1, Entry 6) (300 MHz,  $\text{CDCl}_3$ , 303 K)

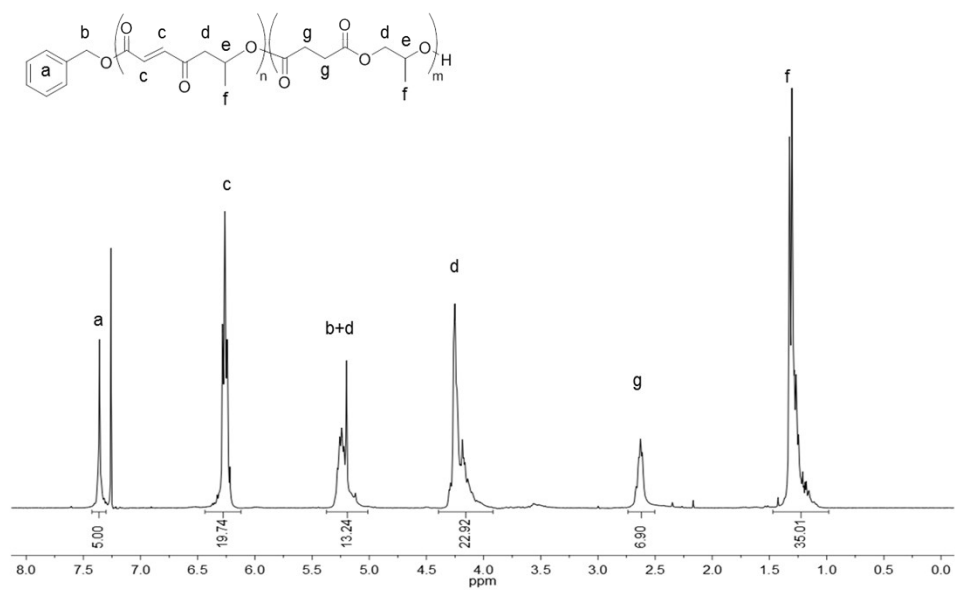


**Figure S14.** <sup>1</sup>H NMR spectra of poly(propylene succinate) (PPS) initiated with propargyl alcohol with DP of 20 for DP20 (Table 1, Entry 7) (300 MHz, CDCl<sub>3</sub>, 303 K)

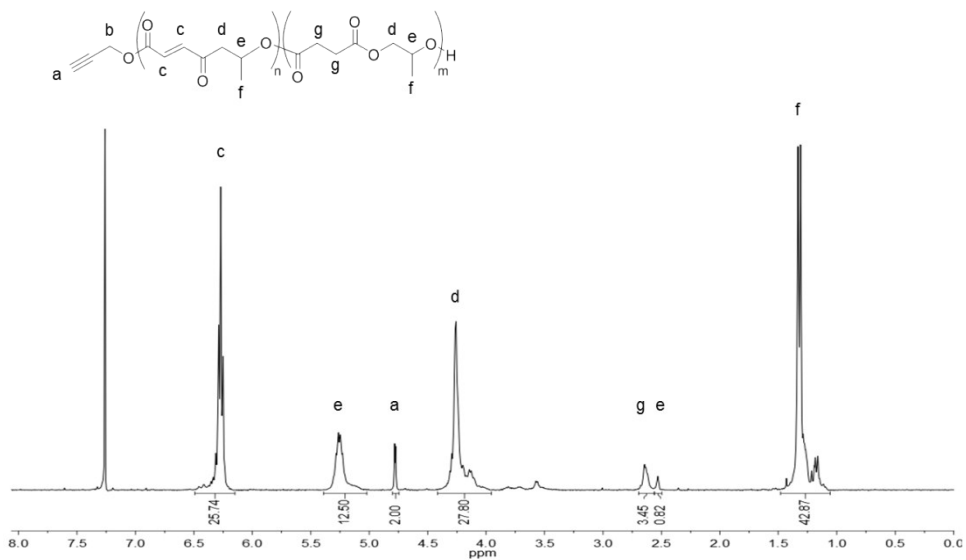


**Figure S15.** <sup>1</sup>H NMR spectra of PPMPs initiated with benzyl alcohol with 10 mol% succinic anhydride and DP of 10 (Table 1, Entry 8) (300 MHz, CDCl<sub>3</sub>, 303 K)

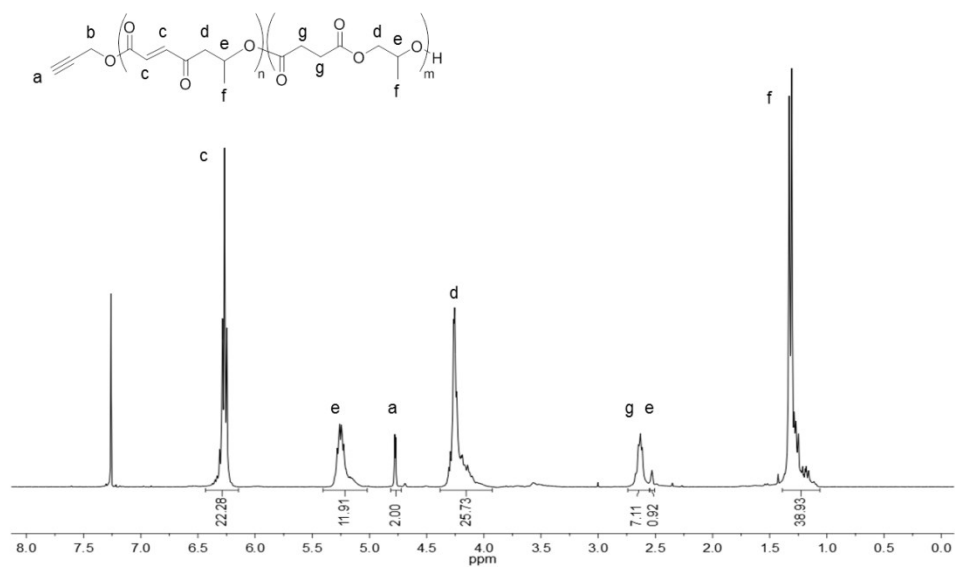




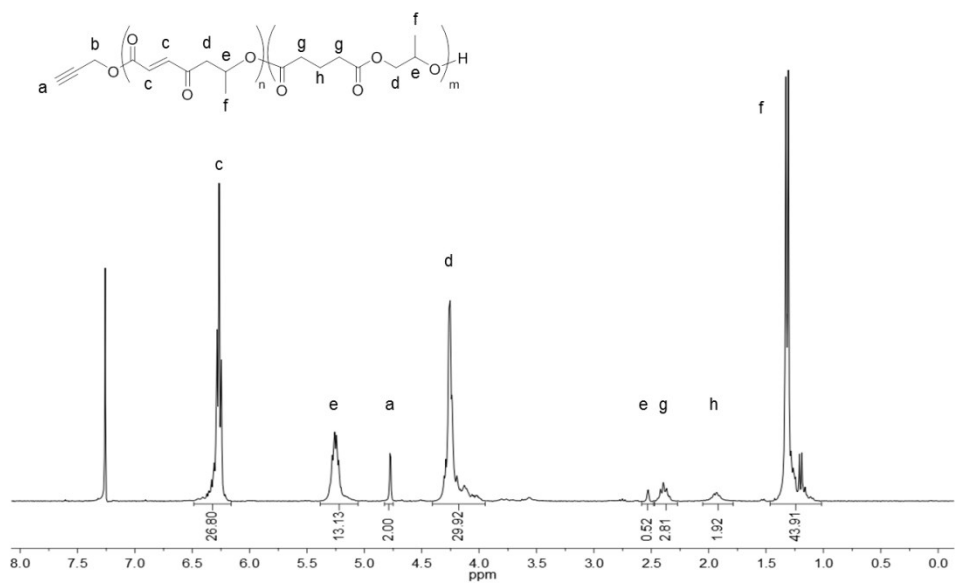
**Figure S16.**  $^1\text{H NMR}$  spectra of PPMS initiated with benzyl alcohol with 20 mol% succinic anhydride and DP of 10 (Table 1, Entry 9) (300 MHz,  $\text{CDCl}_3$ , 303 K)



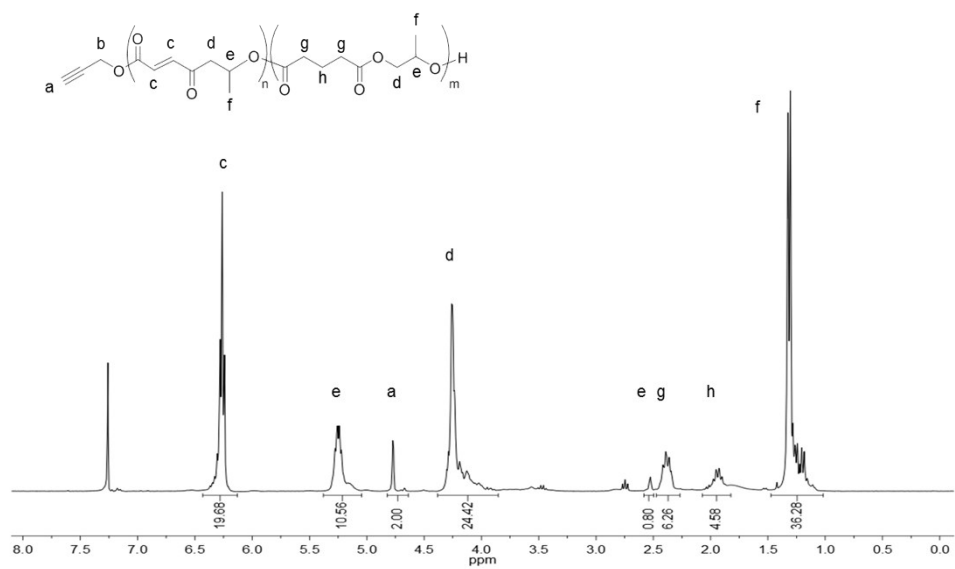
**Figure S17.**  $^1\text{H NMR}$  spectra of PPMS initiated with propargyl alcohol with 10 mol% succinic anhydride and DP of 10 (Table 1, Entry 10) (300 MHz,  $\text{CDCl}_3$ , 303 K)



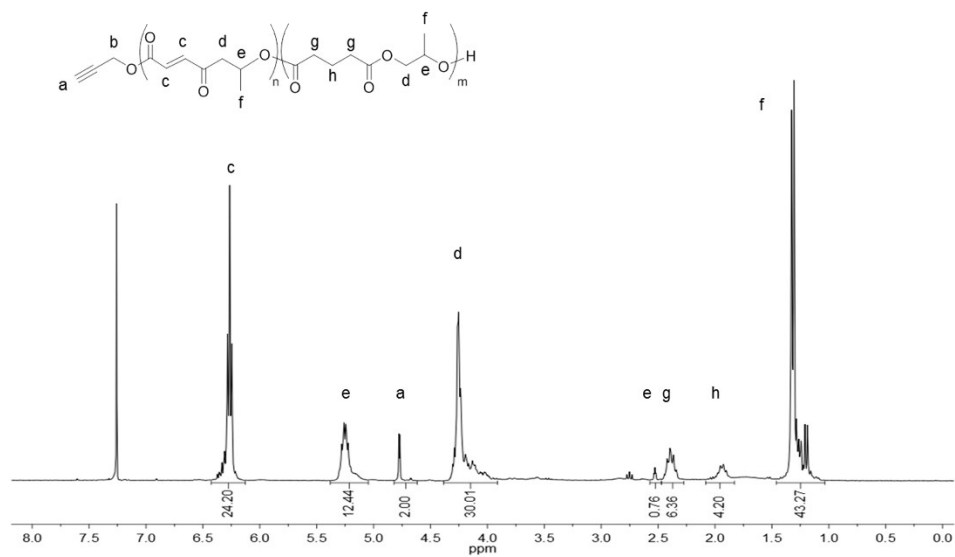
**Figure S18.** <sup>1</sup>H NMR spectra of PPMPs initiated with propargyl alcohol with 20 mol% succinic anhydride and DP of 10 (Table 1, Entry 11) (300 MHz, CDCl<sub>3</sub>, 303 K)



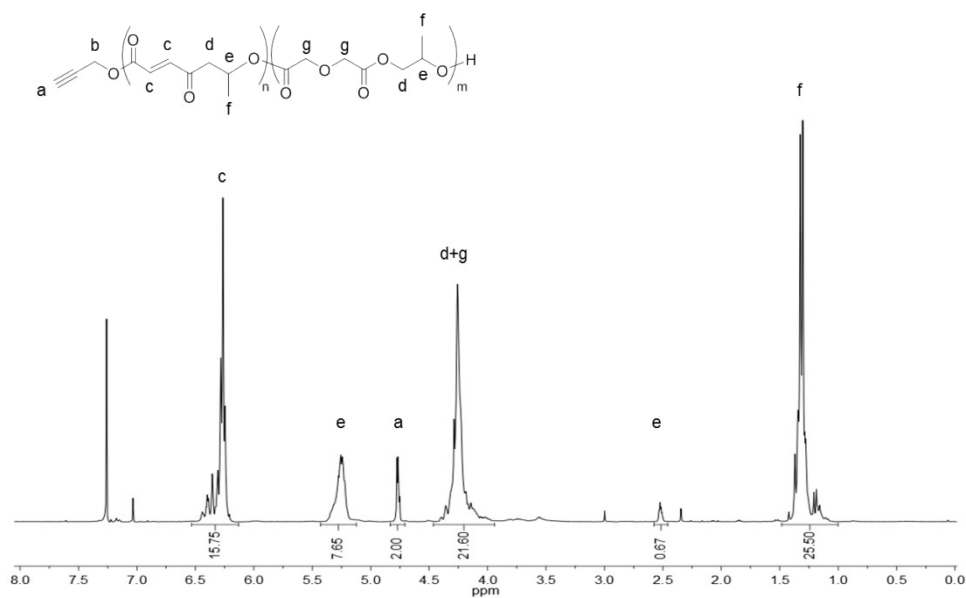
**Figure S19.** <sup>1</sup>H NMR spectra of PPMPG initiated with propargyl alcohol with 10 mol% glutaric anhydride and DP of 10 (Table 1, Entry 12) (300 MHz, CDCl<sub>3</sub>, 303 K)



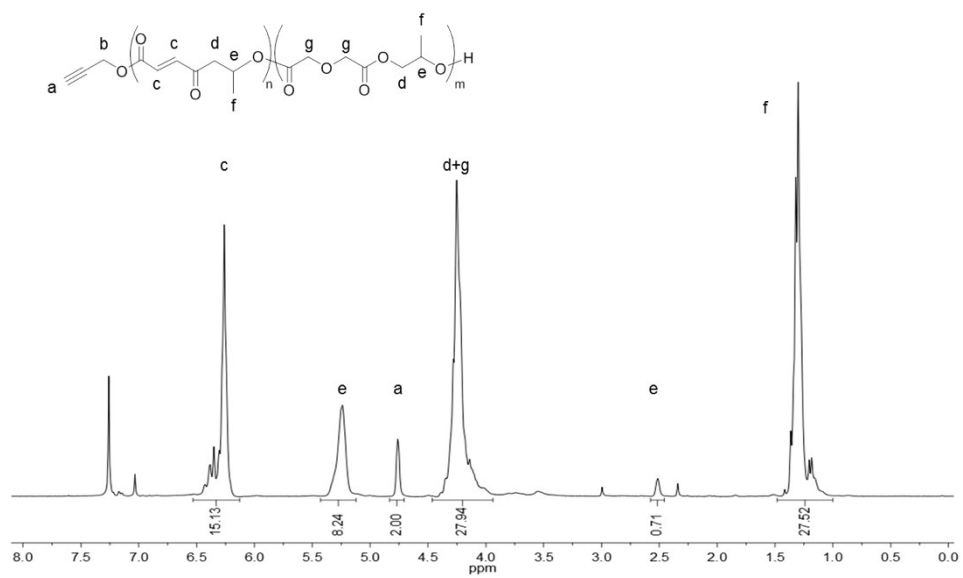
**Figure S20.** <sup>1</sup>H NMR spectra of PPMPG initiated with propargyl alcohol with 20 mol% glutaric anhydride and DP of 10 (Table 1, Entry 13) (300 MHz, CDCl<sub>3</sub>, 303 K)



**Figure S21.** <sup>1</sup>H NMR spectra of PPMPG initiated with propargyl alcohol with 20 mol% glutaric anhydride and DP of 20 (Table 1, Entry 14) (300 MHz, CDCl<sub>3</sub>, 303 K)



**Figure S22.** <sup>1</sup>H NMR spectra of PPMPDG initiated with propargyl alcohol with 10 mol% diglycolic anhydride and DP of 10 (Table 1, Entry 17) (300 MHz, CDCl<sub>3</sub>, 303 K)



**Figure S23.** <sup>1</sup>H NMR spectra of PPMPDG initiated with propargyl alcohol with 20 mol% diglycolic anhydride and DP of 10 (Table 1, Entry 18) (300 MHz, CDCl<sub>3</sub>, 303 K)