

Figure1SI. ^1H NMR (400 MHz, Acetone- d_6 ; δ , ppm): 5.31 (m, 1H), 5.10 (m, 1H), 4.90–3.50 (m, 6H), 2.39 (m, 4H), 2.07 (acetone- d_6), 1.66 (m, 4H). PGA synthesized at 70 °C.

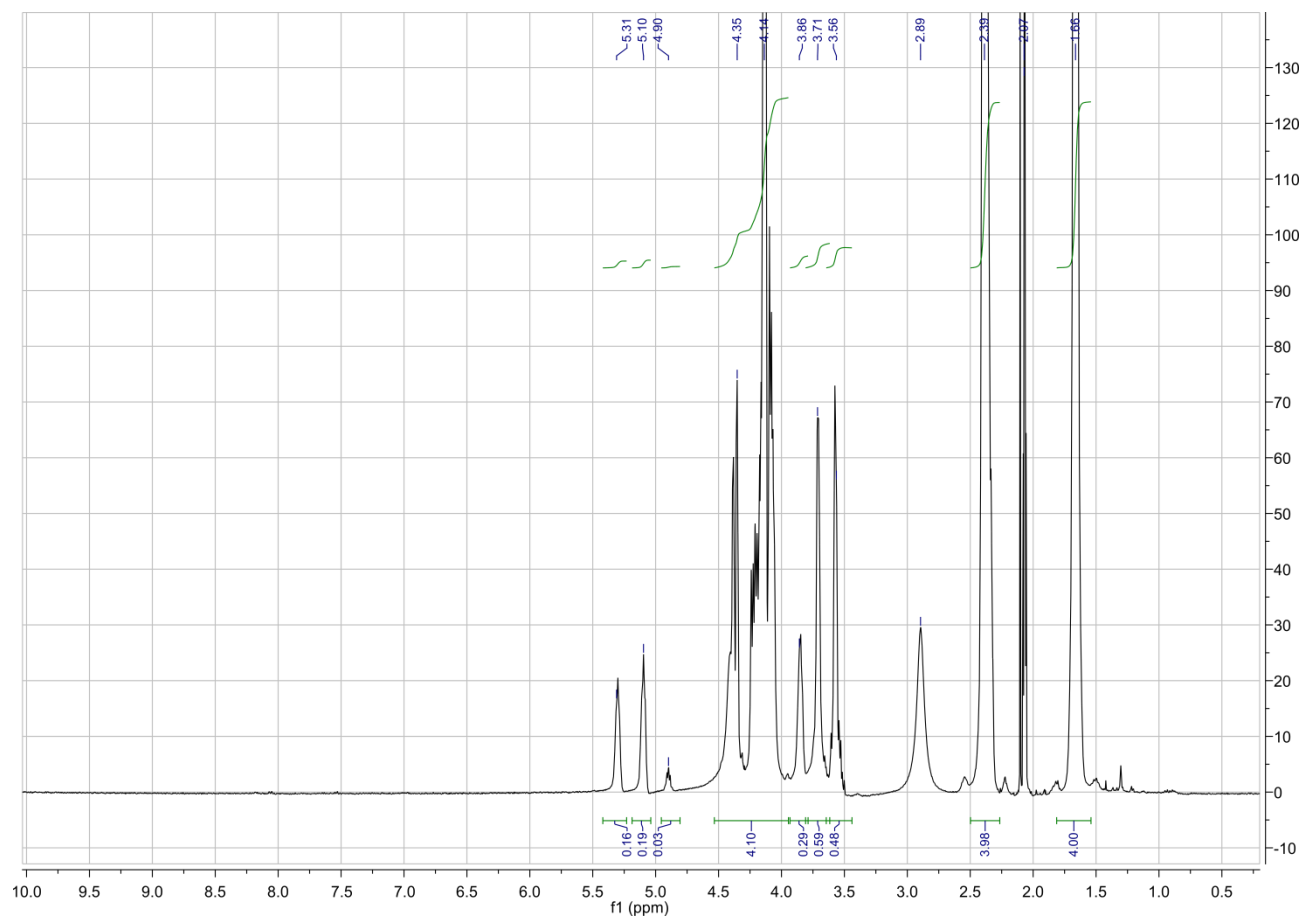
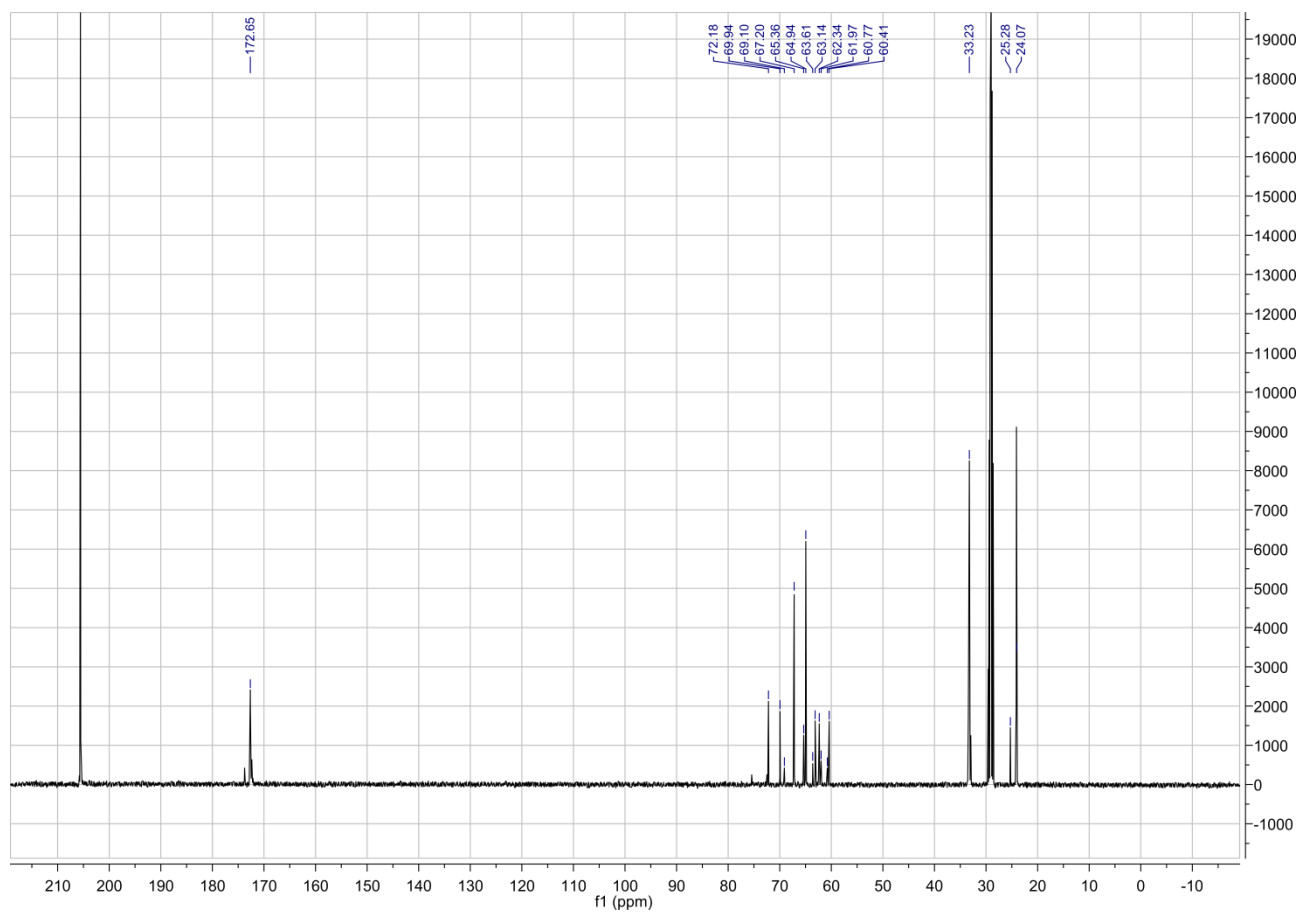


Figure2SI. ^{13}C NMR (400MHz Acetone- d_6 ; δ , ppm): δ 172.65, 72.18, 69.94, 69.10, 67.20, 65.36, 64.94, 63.61, 63.14, 62.34, 61.97, 60.77, 60.41, 33.23, 25.28, 24.07. PGA synthesized at 70 °C.



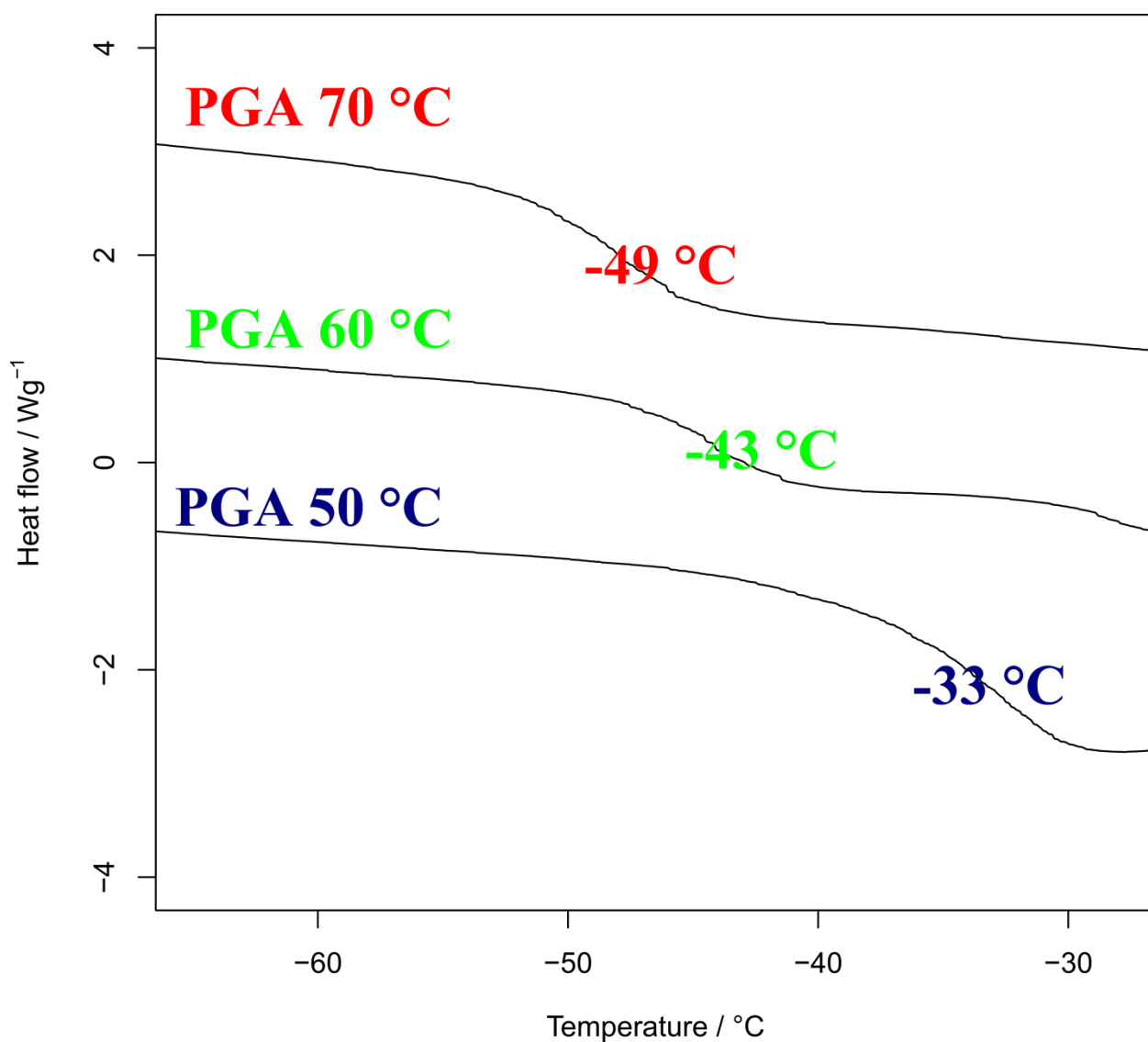


Figure 3SI. DSC thermograms of PGAs synthesized at different temperatures.

Table 2SI.

Polymers	M_n (SEC) kDa	\bar{D}	1,2,3- trisubstitution (from ^1H NMR)
1) PGA 50 °C	10.5	2.6	9%
2) PGA 50 °C	13.0	2.5	5%
3) PGA 40 °C	10.4	2.8	10%
4) PGA 40 °C	11.4	2.7	8%

Molecular Weights, Dispersities and 1,2,3- trisubstitution ¹HNMR % amount of polymers, from different batches, synthesized at the same temperature to evaluate synthesis reproducibility.

Table 3SI.

	Method 1	Method 2	Method 3
Mw of product	>32.5kDa	4.8kDa	3.7kDa
Synthesis temperature (°C)	40-50	60	60
Conversion	>98%	>98%	95%
catalyst	3.7%	3.0%	3.0%
Atom Efficiency	67%	73%	83%
Cost of monomer (per 100g)	£60	£25	£40

Method 1 [26]. Divinyl adipate in solvent (THF), normal pressure, 24h

Method 2. [23]. Dimethyl adipate in solvent (THF), under vacuum, molecular sieves 48h

Method 3 [22]. Adipic acid in bulk, under vacuum, 48h.