Electronic supplementary materials *Mendeleev Commun.*, 2019, **29**, 178–180

Synthesis of polyester from renewable feedstock: a comparison between microwave and conventional heating

Kuldeep K. Bansal, Prabhat K. Upadhyay, Deepak Kakde, Jessica M. Rosenholm and Ari Rosling

Materials and Methods

1.1 Synthesis of oligomer G0-Glycerol

G0-Glycerol was obtained via reaction of alcohol (1 equiv.) with DDSA (2 equiv.).

Conventional method: DDSA (9.83 g, 37.4 mmol) and glycerol (1.7 g, 18.7 mmol) were transferred into a flask under an inert nitrogen atmosphere. This mixture was then heated at 120 °C under stirring and nitrogen atmosphere for 7 h. The temperature probe was in direct contact with the reaction mixture. After 7 h, the reaction mixture was cooled down in order to terminate the reaction. A yellow viscous liquid was obtained, which was characterised by ^{1}H NMR and MALDI-TOF mass-spectrometry for conversion.

Microwave method: DDSA (9.83 g, 37.4 mmol) and glycerol (1.7 g, 18.7 mmol) were transferred into a flask and sealed with a modified stopper to allow a fibre optic temperature probe to be inserted into the bulk in a glass sleeve. The temperature was then increased to 80 °C under stirring and nitrogen atmosphere. This temperature was maintained for 2 h by supplying the forward power of 50 W (Sairem miniflow 200SS). After 2 h, the reaction mixture was cooled down in order to terminate the reaction. A yellow viscous liquid was obtained which was characterised by ^{1}H NMR and MALDI-TOF mass-spectrometry for conversion.

^{1}H NMR (400 MHz, Acetone-d_6), δ: 5.57 (m, $C\underline{H}$=CH, 2H), 5.48–5.34 (m, CH=$C\underline{H}$, 2H), 5.28 (m, $C\underline{H}$-O-COO-CH, 0.35H), 5.08 (m, $C\underline{H}$-O-COO-CH, 0.22H), 4.52–3.97 (m, CH_2-CH-

CH_2 of glycerol, 5H), 3.83–3.65 (m, CH-OH, CH_2-OH, 0.52H), 2.86 (m, CH_2-O-COO-$C\underline{H}_2$, 2H), 2.80–2.61 (m, CH_2-O-COO-$C\underline{H}_2$, 2H), 2.61–2.22 (m, $C\underline{H}_2$-C$\underline{H}$-COOH, 6H), 2.16–1.92 (m, CH=CH-$C\underline{H}_2$, 5H), 1.31 (m, $(CH_2)_7$, 30H), 0.90 (t, CH_3, 6H).

MS, *m/z*: calculated for $C_{35}H_{60}O_{09}$ 624.42 $[M]^+$; found 647.3 [M+Na].

1.2 Synthesis of oligomer G1-Glycerol

G0-Glycerol (4 g, 6.4 mmol) and glycerol (1.30 g, 14.8 mmol) were transferred to a flask. This mixture was then heated at 120 °C and stirred for 20 min to form a homogeneous mixture. Phosphoric acid (0.0062 g, 0.064 mmol) was then added to the above mixture using a syringe. The reaction mixture was then stirred for 17 h at 120 °C under a slow stream of nitrogen. After 17 h, the reaction mixture was cooled down and dissolved in DCM. The solution was then centrifuged for 10 min at 5000 rpm in order to remove excess of glycerol. DCM layer was collected and the solvent was evaporated *in vacuo* to yield the product. A light yellowish viscous liquid was obtained, which was characterised by ^{1}H NMR and MALDI-TOF mass-spectrometry.

Similar quantity was used to synthesise the G1-Glycerol using the microwave generator. The setting of microwave generator was kept exactly same that was used to synthesise G0-Glycerol. However, the reflection of approximately 90% of supplied microwave energy was observed.

^{1}H NMR (400 MHz, Acetone-d_6), δ: 5.67–5.48 (m, C$\underline{H}$=CH, 2H), 5.41 (m, CH=C$\underline{H}$, 2H), 5.31 (m, C$\underline{H}$-O-COO-CH, 0.1H), 5.08 (m, C$\underline{H}$-O-COO-CH, 0.3H), 4.55–3.99 (m, CH_2-CH-CH_2 of glycerol, 11H), 3.78–3.63 (m, CH-OH, 2H), 3.62–3.45 (m, CH_2-OH, 5H), 2.89 (m, CH_2-O-COO-$C\underline{H}_2$, 2H), 2.80–2.62 (m, CH_2-O-COO-$C\underline{H}_2$, 2H), 2.61–2.23 (m, $C\underline{H}_2$-C$\underline{H}$-COOH, 6H), 2.15–1.94 (m, CH=CH-$C\underline{H}_2$, 5H), 1.30 (m, $(CH_2)_7$, 30H), 0.89 (t, CH_3, 6H).

MS, *m/z*: calculated for $C_{41}H_{72}O_{13}$ 773 $[M]^+$; found: 796.40 $[M+Na]^+$.

1.3 Measurement of dielectric properties of glycerol and oligomer G0-Glycerol.

To understand the reason of reflection of microwave energy during the synthesis of G1-Glycerol from G0-Glycerol and glycerol, the dielectric properties of both materials were measured.[S1] These properties include the dielectric constant (ε') and dielectric loss (ε"). ε' is defined as the ability of a material to store electromagnetic energy whereas ε" is the ability of a material to convert stored electromagnetic energy into heat.[S2] From the dielectric properties, loss tangent (tan δ) can be calculated, which is the ratio of dielectric loss to the dielectric constant. The value of tan δ suggests the magnitude to which a material can absorb the microwave energy.[S2]

The reported cavity perturbation method[S3,S4] was used to measure the dielectric properties of oligomer G0-Glycerol and glycerol. The equipment contains a furnace with temperature control on the power input and a cavity. The sample was loaded into a quartz sampling tube up to the height of 20 mm. Sampling tube was then mounted vertically on an automated motor, which moves the sample in and out from the furnace situated just above the cavity. The dielectric properties were measured at the pre-set temperature between 20 and 160 °C. The sample was heated in the furnace until it has reached the target temperature and then was moved into the cavity. When the sample was lowered into the cavity from the furnace, any perturbations in the resonant frequency created by the presence of the sample were measured using a network analyser. The resonant frequency of the cavity containing the empty tube was also measured as the reference.[S3,S4]

1.4 Synthesis of oligomer G2-Glycerol

G1-Glycerol (4 g, 5.17 mmol) and DDSA (2.75 g, 10.34 mmol) were transferred in a flask. This mixture was then heated at 120 °C under stirring and retaining the nitrogen atmosphere for 11 h. After 11 h, the reaction mixture was cooled down in order to terminate the reaction.

A yellow viscous liquid was obtained which was characterised by ^{1}H NMR and MALDI-TOF mass-spectrometry and used in the next step without any purification.

^{1}H NMR (400 MHz, acetone-d$_6$), δ: 5.54 (m, C$\underline{H}$=CH, 4H), 5.42 (m, CH=C$\underline{H}$, 4H), 5.30 (C$\underline{H}$-O-COO-CH, 0.5H), 5.09 (m, C$\underline{H}$-O-COO-CH, 0.5H), 4.52–3.98 (m, CH$_2$-CH-CH$_2$ of glycerol, 14H), 3.69 (m, CH-OH, 1H), 3.64–3.49 (m, CH$_2$-OH, 0.7H), 2.92 (m, CH$_2$-O-COO-C$\underline{H}_2$, 4H), 2.83–2.62 (m, CH$_2$-O-COO-C$\underline{H}_2$, 4H), 2.62–2.23 (m, C$\underline{H}_2$-C$\underline{H}$-COOH, 12H), 2.17–1.93 (m, CH=CH-C$\underline{H}_2$, 10H), 1.32 (m, (CH$_2$)$_7$, 60H), 0.91 (t, CH$_3$, 13H).

MS, *m/z*: calculated for $C_{73}H_{124}O_{19}$ 1305.75 [M]$^+$; found: 1327.9 [M+Na]$^+$.

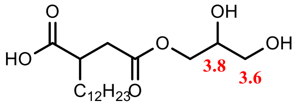
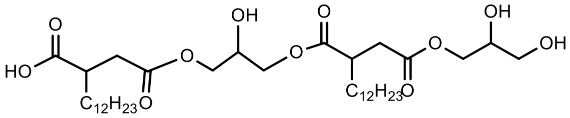
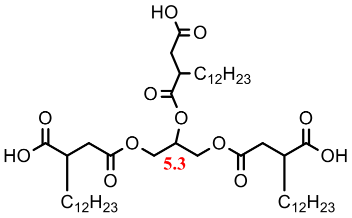
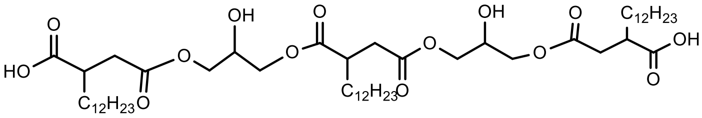
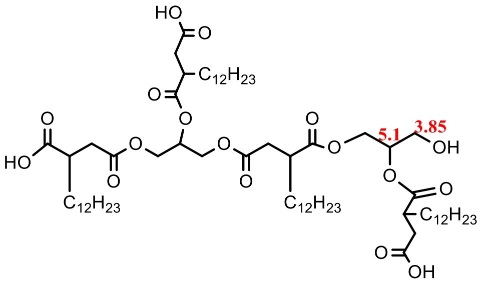
1.5 Synthesis of oligomer G3-Glycerol

The oligomer G2-Glycerol (2 g, 1.53 mmol), glycerol (0.3 g, 3.21 mmol) and phosphoric acid (0.0007 g, 0.0075 mmol) were used in the synthesis of G3-Glycerol. The identical procedure was followed, which was used to prepare G1-Glycerol *via* polycondensation reaction. A light yellowish viscous liquid was obtained, which was characterised by ^{1}H NMR and MALDI-TOF mass-spectrometry.

^{1}H NMR (400 MHz, acetone-d$_6$), δ: 5.67–5.48 (m, C$\underline{H}$=CH, 4H), 5.41 (m, CH=C$\underline{H}$, 4H), 5.31 (m, C$\underline{H}$-O-COO-CH, 0.5H), 5.08 (m, C$\underline{H}$-O-COO-CH, 0.5H), 4.55–3.99 (m, CH$_2$-CH-CH$_2$ of glycerol, 18H), 3.78–3.63 (m, CH-OH, 2H), 3.62–3.45 (m, CH$_2$-OH, 6H), 2.89 (m, CH$_2$-O-COO-C$\underline{H}_2$, 4H), 2.80–2.62 (m, CH$_2$-O-COO-C$\underline{H}_2$, 4H), 2.61–2.23 (m, C$\underline{H}_2$-C$\underline{H}$-COOH, 12H), 2.15–1.94 (m, CH=CH-C$\underline{H}_2$, 10H), 1.30 (m, (CH$_2$)$_7$, 60H), 0.89 (t, CH$_3$, 13H).

MS, *m/z*: calculated for $C_{79}H_{136}O_{23}$ 1453.91 [M]$^+$; found: 1476.0 [M+Na]$^+$.

Table S1 Possible impurities formed in the synthesis of G0-Glycerol (the desired product).

No.	Structures of the possible impurities[a]	Molecular weight (Calculated)
1		358.47
2		698.92
3		891.22
4		965.30
5		1231.38

[a] The numbers at atoms indicate peak positions (in ppm) in ^{1}H-NMR spectra.

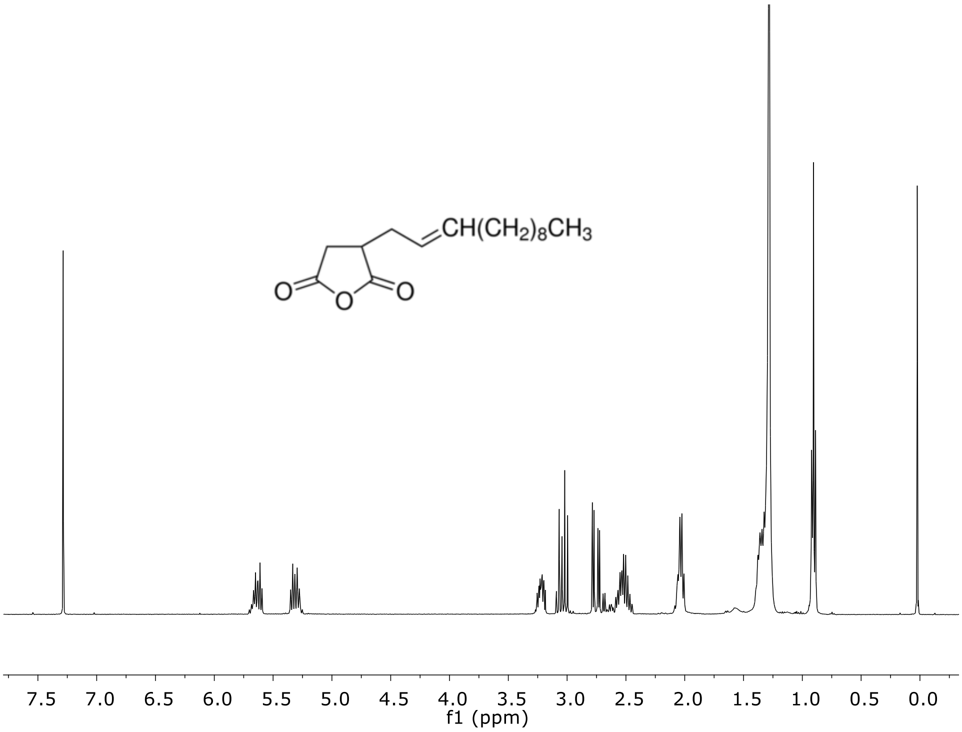


Figure S1 ^{1}H NMR spectra of DDSA.

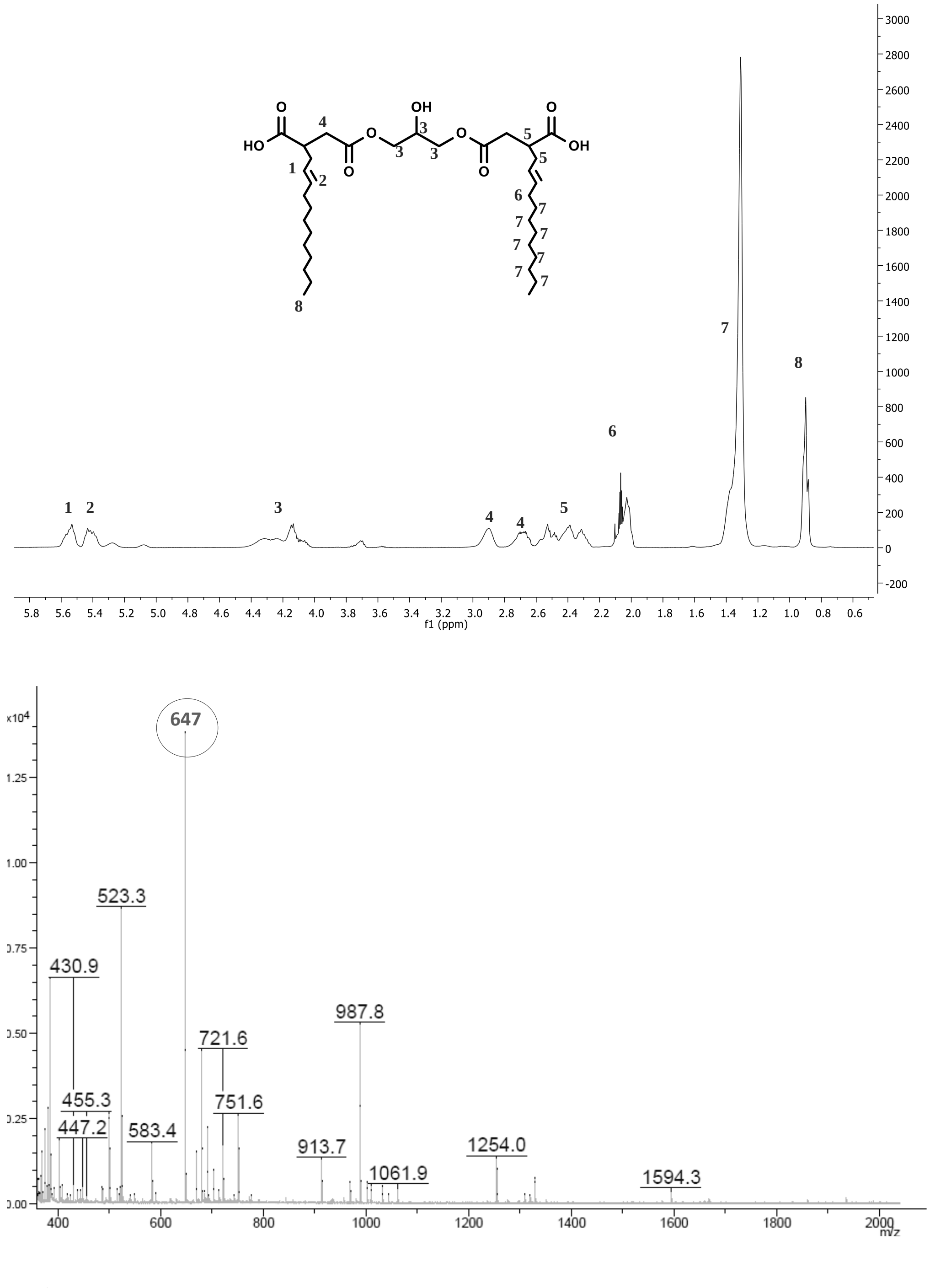


Figure S2 ^{1}H-NMR and MS (MALDI-TOF) of G0-Glycerol.

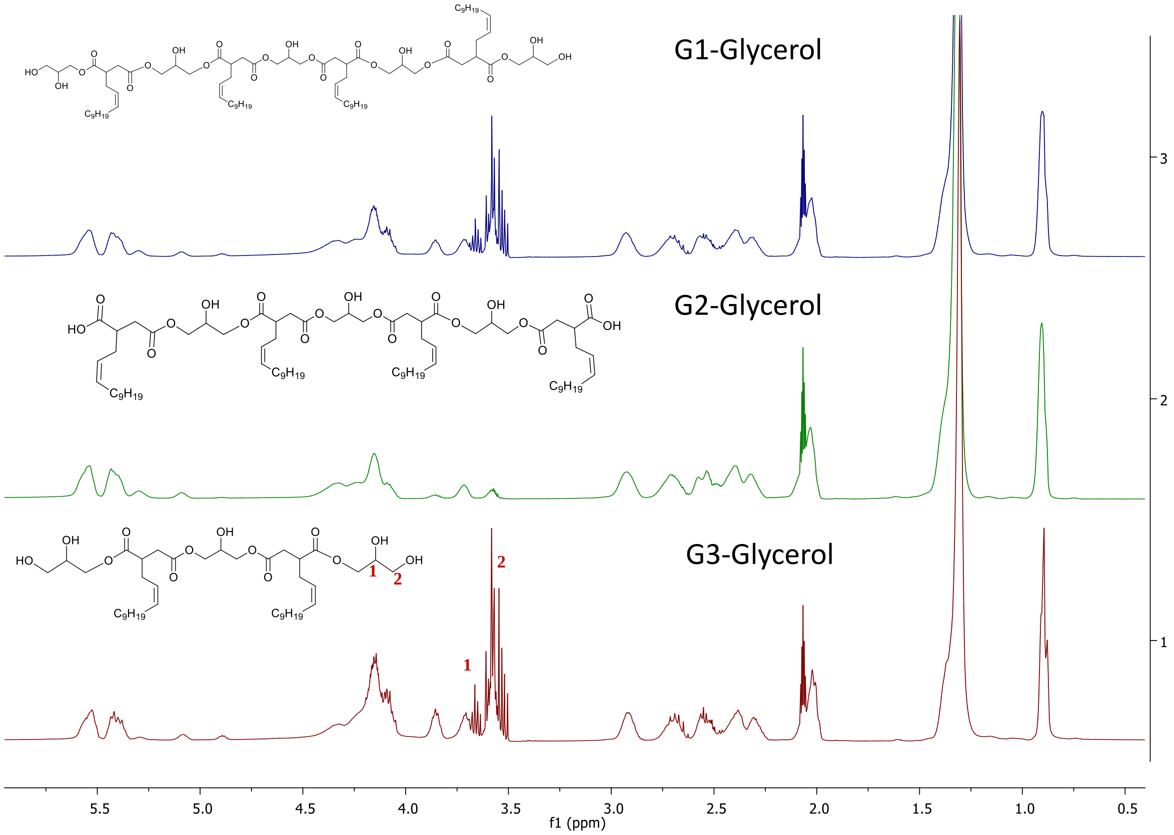


Figure S3 ^{1}H-NMR spectra of G1-Glycerol, G2-Glycerol, and G3-Glycerol.

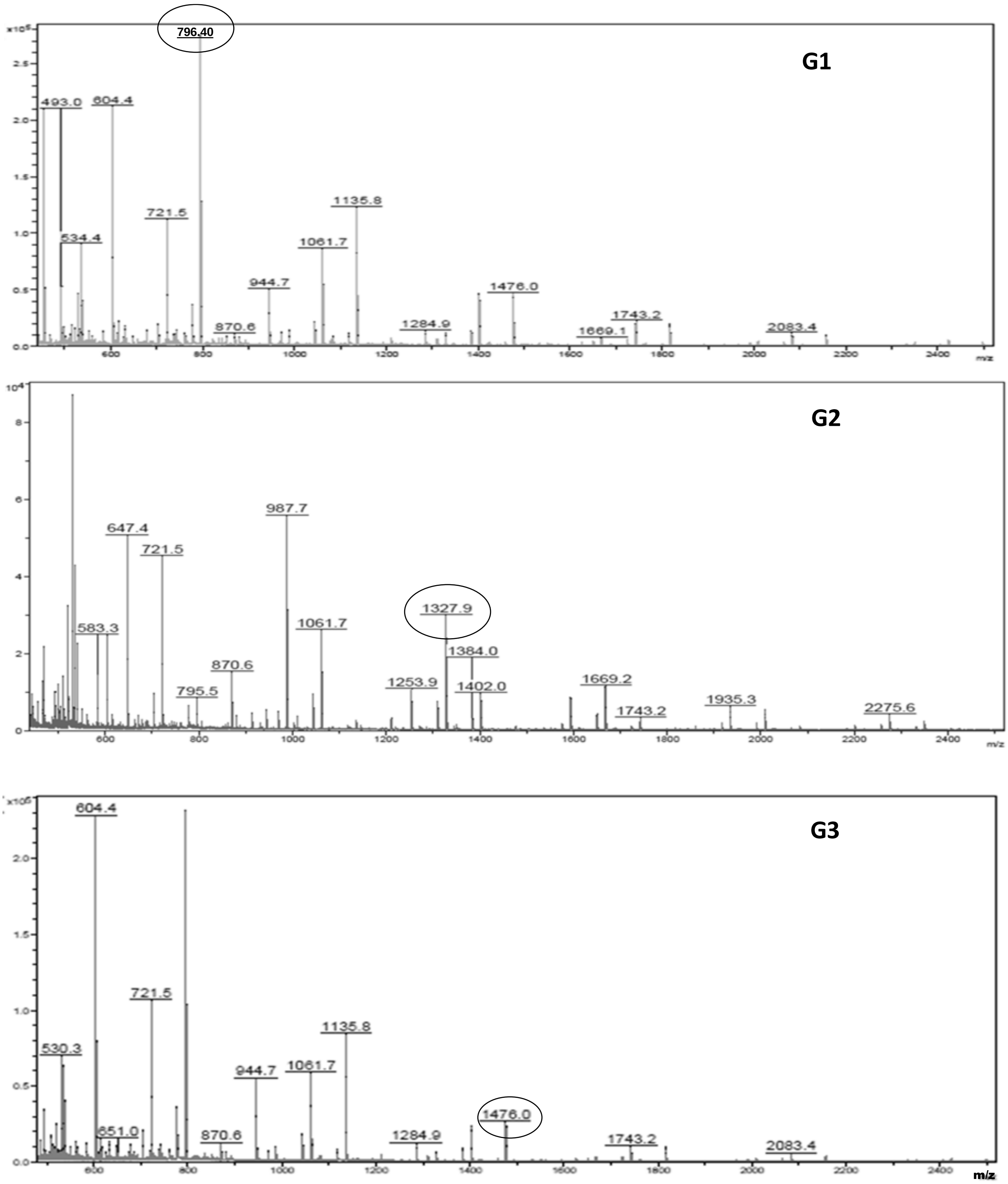


Figure S4 MS (MALDI-TOF) of G1-Glycerol, G2-Glycerol and G3-Glycerol.

References

S1 M. J. Kamaruddin, J. El Harfi, G. Dimitrakis, N. T. Nguyen, S. W. Kingman, E. Lester, J. P. Robinson and D. J. Irvine, *Green Chem.*, 2011, **13**, 1147.

S2 A. D. Smith, E. H. Lester, K. J. Thurecht, S. W. Kingman, J. El Harfi, G. Dimitrakis, J. P. Robinson and D. J. Irvine, *Ind. Eng. Chem. Res.*, 2010, **49**, 3011.

S3 N. T. Nguyen, E. Greenhalgh, M. J. Kamaruddin, J. El Harfi, K. Carmichael, G. Dimitrakis, S. W. Kingman, J. P. Robinson and D. J. Irvine, *Tetrahedron*, 2014, **70**, 996.

S4 A. D. Smith, E. Lester, K. J. Thurecht, J. El Harfi, G. Dimitrakis, S. W. Kingman, J. P. Robinson and D. J. Irvine, *Ind. Eng. Chem. Res.*, 2010, **49**, 1703.