A study of the application of graphite MALDI to the analysis of short-chain polyethylene glycols

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Supplementary information

Table S1: Parameter values for the Gaussian modelling using equation 1.

Figure S1: ESI-MS analysis of (a) PEG200, (b) PEG400, (c) PEG600 and (d) PEGMIX.

Figure S2: The GC-MS analysis of PEG200 (a),and PEG400 (b).

Figure S3: MALDI imaging of PEG400 with various matrices.

Figure S4: MALDI imaging of PEG600 with various matrices.

Figure S5: MALDI imaging of PEG200, PEG400 and PEG600 equimolar mix with various matrices.

ESI-MS conditions:

ESI-MS analyses was performed on a 7 Tesla Apex IV Fourier-transform ion cyclotron resonance instrument (Bruker Daltonics, Billerica, MA, USA) using an Apollo off-axis ESI source. The PEG polymer solutions were made up to 0.1 mg/mL in methanol:water (2:1, v/v) and introduced directly into the ESI source from a syringe pump at 100 µL/min. The acquisition parameters were: capillary voltage, 4500 V; end plate voltage, 3500 V; capillary exit potential, 200 V and drying gas temperature, 200 °C. Spectra were obtained by summing eighty 0.5 s scans. The same stock solutions were used for ESI analysis as were used with the MALDI analysis only diluted to 1 in 50 in MeOH/Water (50/50) prior to analysis.

GC-MS conditions:

GC-MS analyses were performed on a GC QExactive (Orbitrap) fitted with a Trace 1310 GC system (Thermo Scientific, Hemel Hempstead, UK). The Orbitrap was run in EI mode and acquired spectra from *m/z* 50 to 800 at 160,000 resolution. The electron energy was12eV to minimise fragmentation. The source temperature was 200 ºC, MS transfer line was 250 ºC and the transfer capillary was 200 ºC. The column was a TraceGOLD low polarity silarylene column (TG-5SILMS, Thermo Scientific, Hemel Hempstead, UK) with the following dimensions: 30m x 0.25 mm with 0.25um film thickness. The column oven temperature was ramped from 50 to 300 ºC over 30 minutes with the inlet set to 200 ºC. The filament delay was set to 2 minutes. Stock solutions of PEG200 and PEG400 were dissolved to 1mg/mL in DCM and then diluted to 1 in 20 for PEG200 and 1 in 40 for PEG 400 prior to analysis.

Gaussian modelling:

The Gaussian model used the following equation for the curve fitting in figures 2 and 3:

$$y = \frac{A}{\omega\sqrt{\pi/2}} exp\left[-2\left(\frac{x - x_c}{\omega}\right)^2\right] + y_0$$

Table S1: Parameter values for the Gaussian modelling above.

Parameter	Value	Standard Error
Reduced χ^2	1.56842x10^7	
Adjusted R Squared	0.97869	
y_o	-590.40659	1092.56816
x_c	9.36094	0.07417
ω	4.08577	0.16752
A	415144.22146	17641.04104
σ (ω/2)	2.04288	0.08376
FWHM	4.81063	0.19724
Height	81070.93444	2663.54797

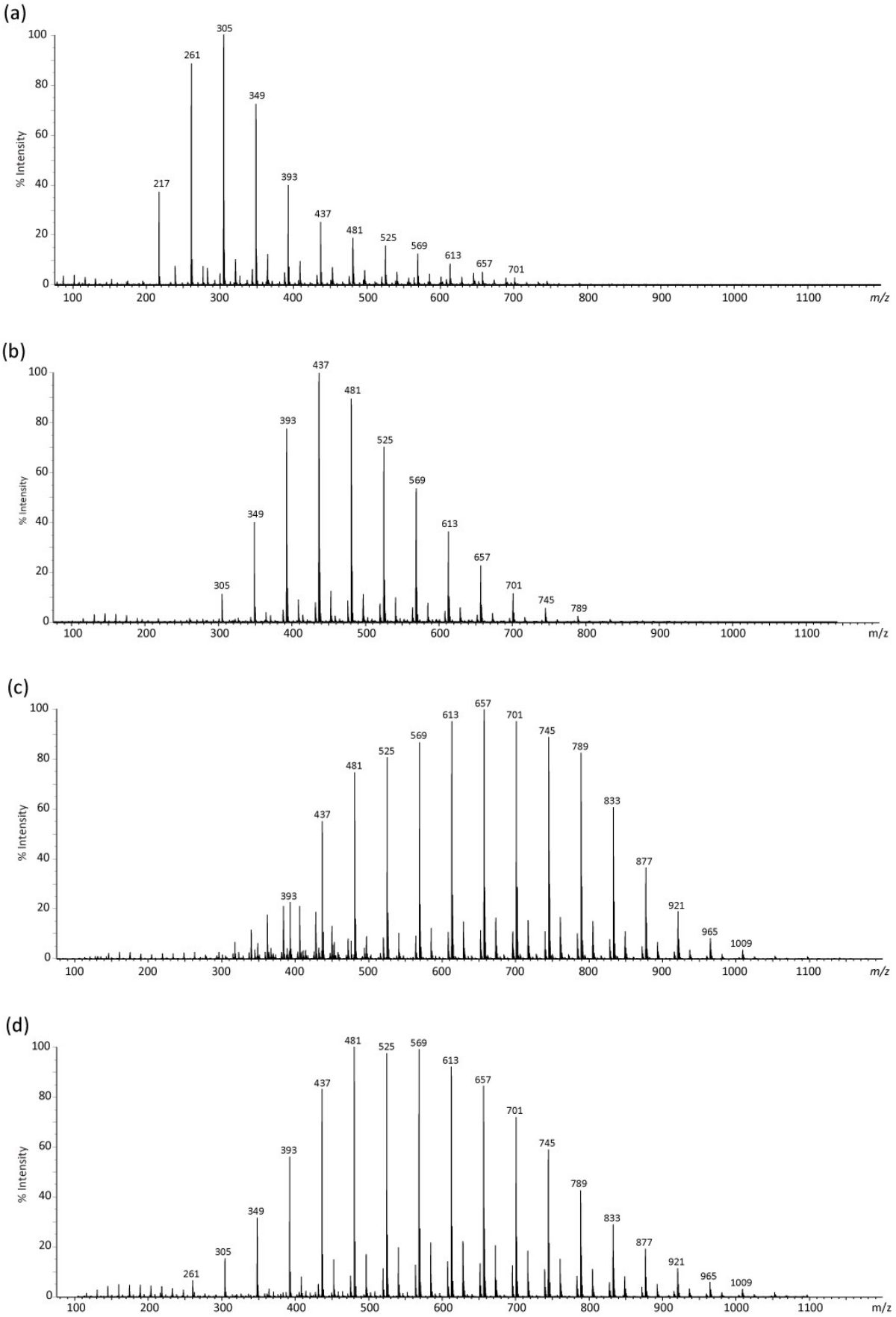
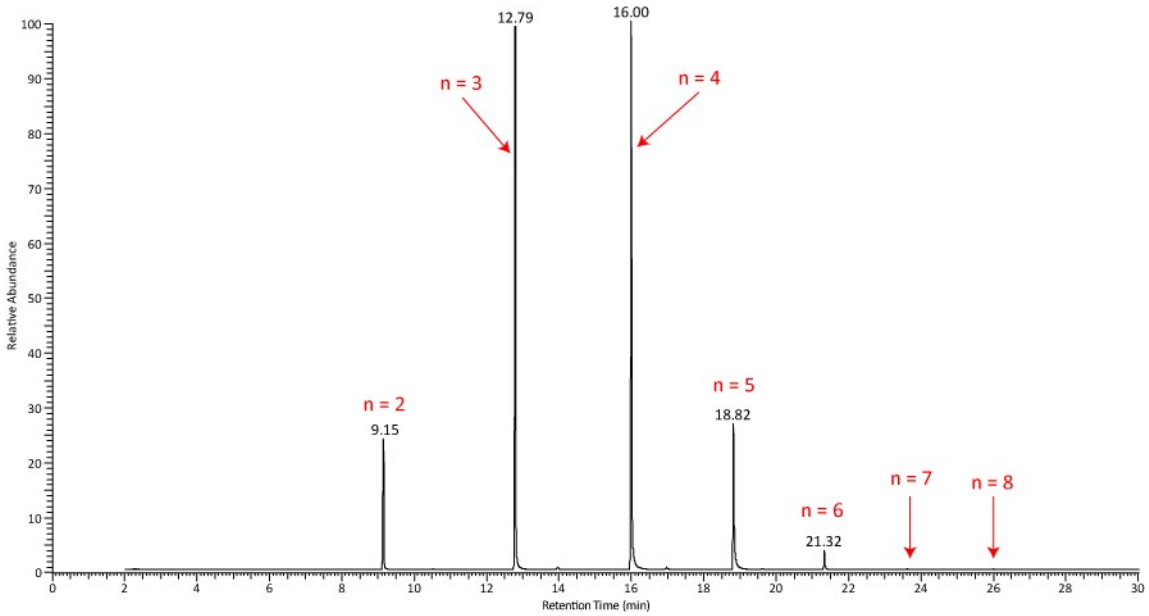


Figure S1: The ESI-MS analysis of PEG200 (a), PEG400 (b), PEG600 (c) and PEGMIX (d).

(a)



(b)

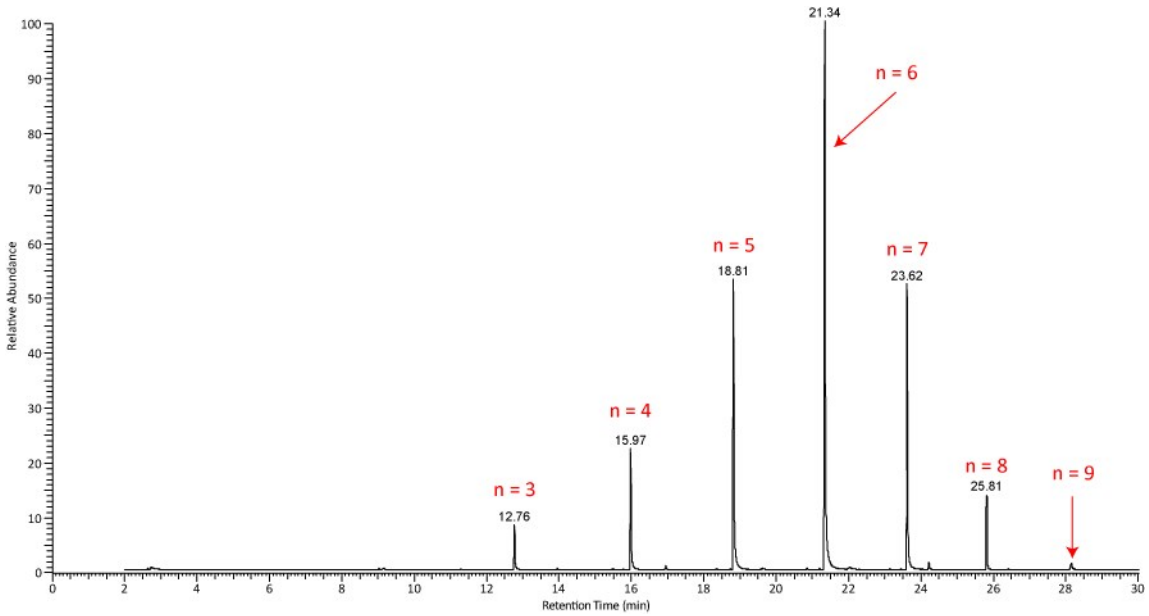


Figure S2: The GC-MS analysis of PEG200 (a),and PEG400 (b). The degree of polymerisation is labelled in red.

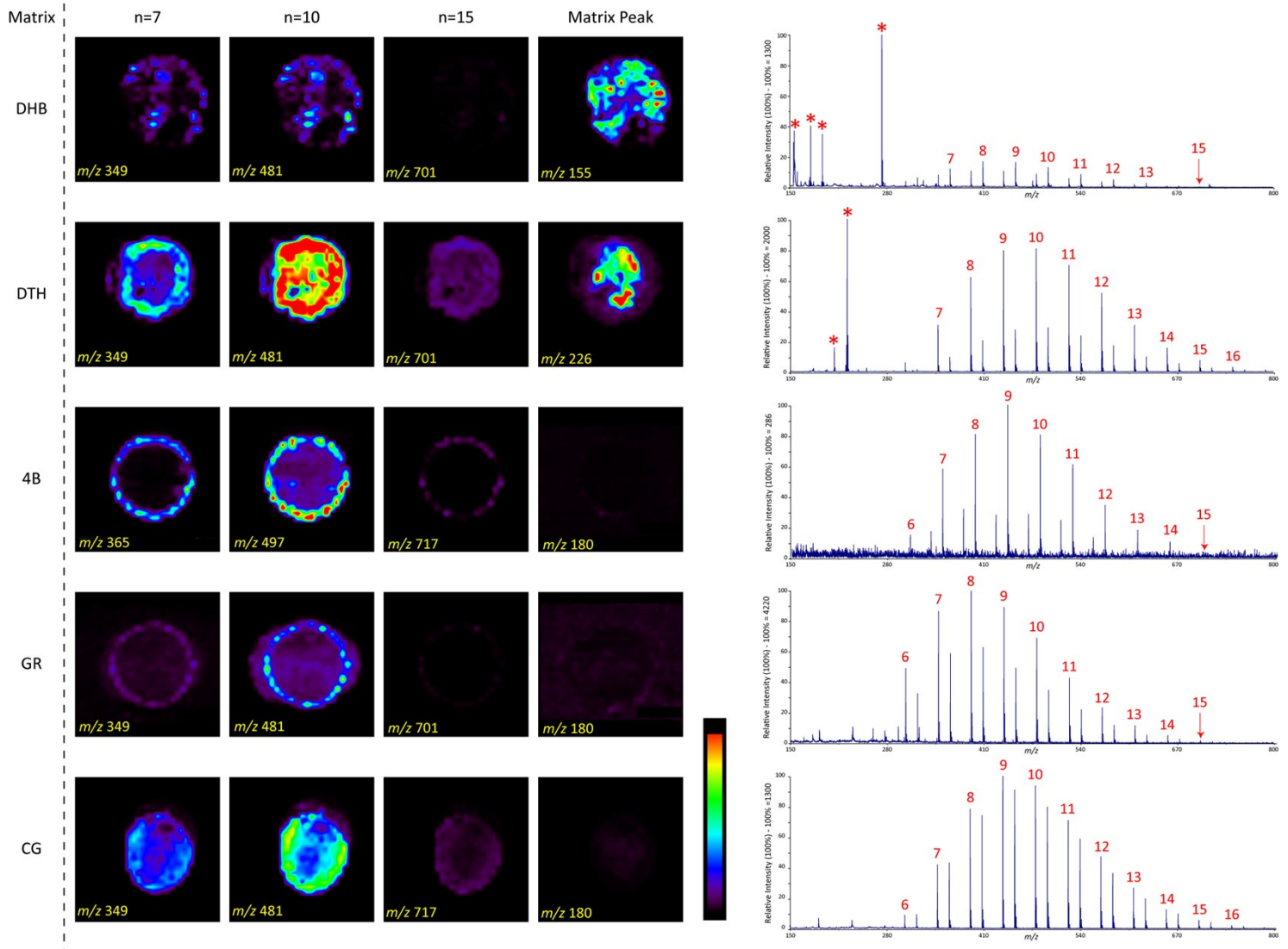


Figure S3: MALDI imaging of PEG400 with various matrices. The 5 matrices (DHB, DTH, 4B, GR and CG) are all imaged at fixed oligomer masses for the PEG400 (n = 7, 10 and 15) and a monitoring mass for the matrix (*m/z* 155 for DHB, *m/z* 226 for DTH and *m/z* 180 for 4B, GR an CG). A linear colour scale is also provided from red (high intensity) to purple/black (low intensity). The mass spectrum of the same spot is provided on the right-hand side. Matrix peaks for DHB and DTH are indicted by a red star and PEG peaks with the corresponding chain length in red.

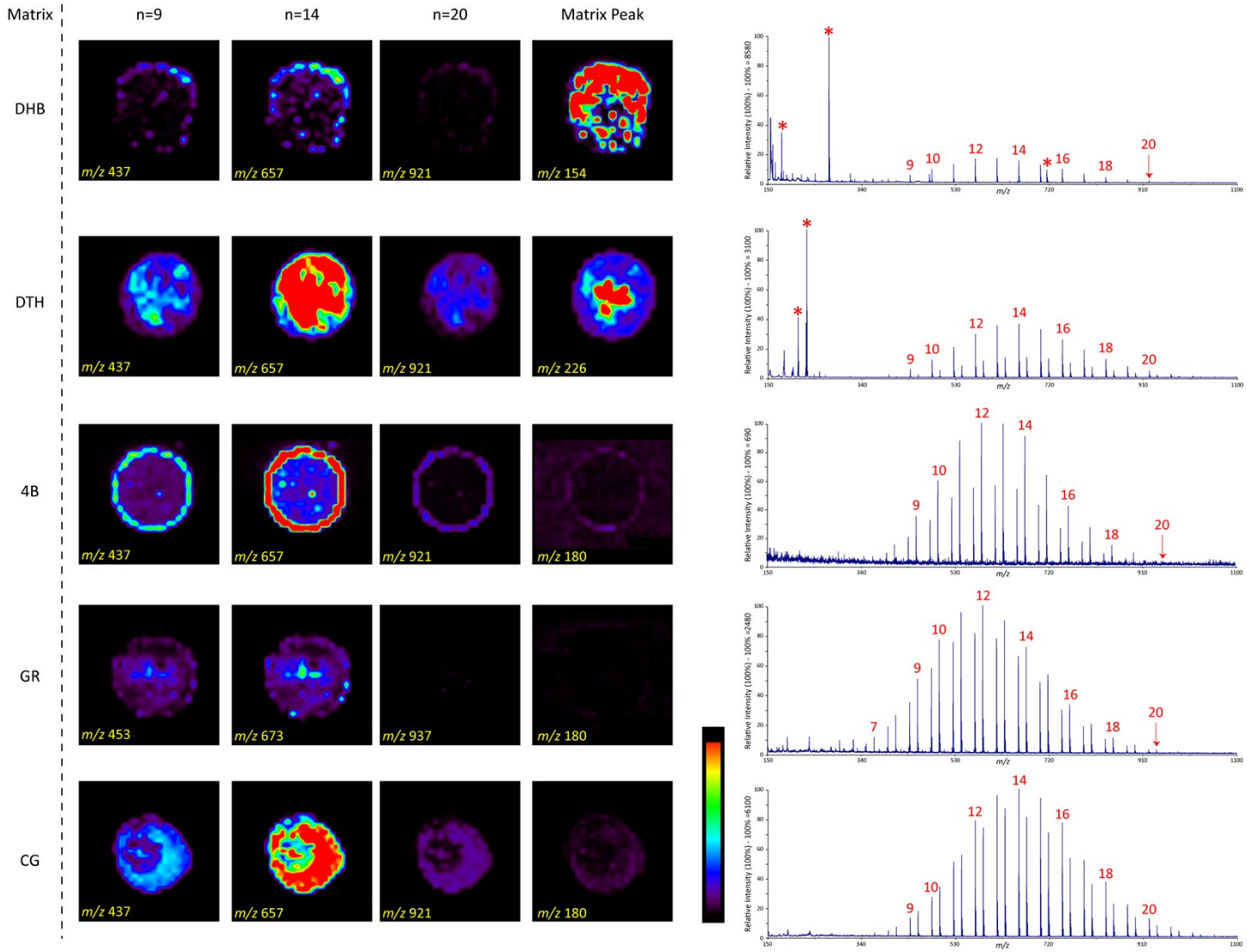


Figure S4: MALDI imaging of PEG600 with various matrices. The 5 matrices (DHB, DTH, 4B, GR and CG) are all imaged at fixed oligomer masses for the PEG400 (n = 9, 14 and 20) and a monitoring mass for the matrix (*m/z* 155 for DHB, *m/z* 226 for DTH and *m/z* 180 for 4B, GR an CG). A linear colour

scale is also provided from red (high intensity) to purple/black (low intensity). The mass spectrum of the same spot is provided on the right-hand side. Matrix peaks for DHB and DTH are indicted by a red star and PEG peaks with the corresponding chain length in red.

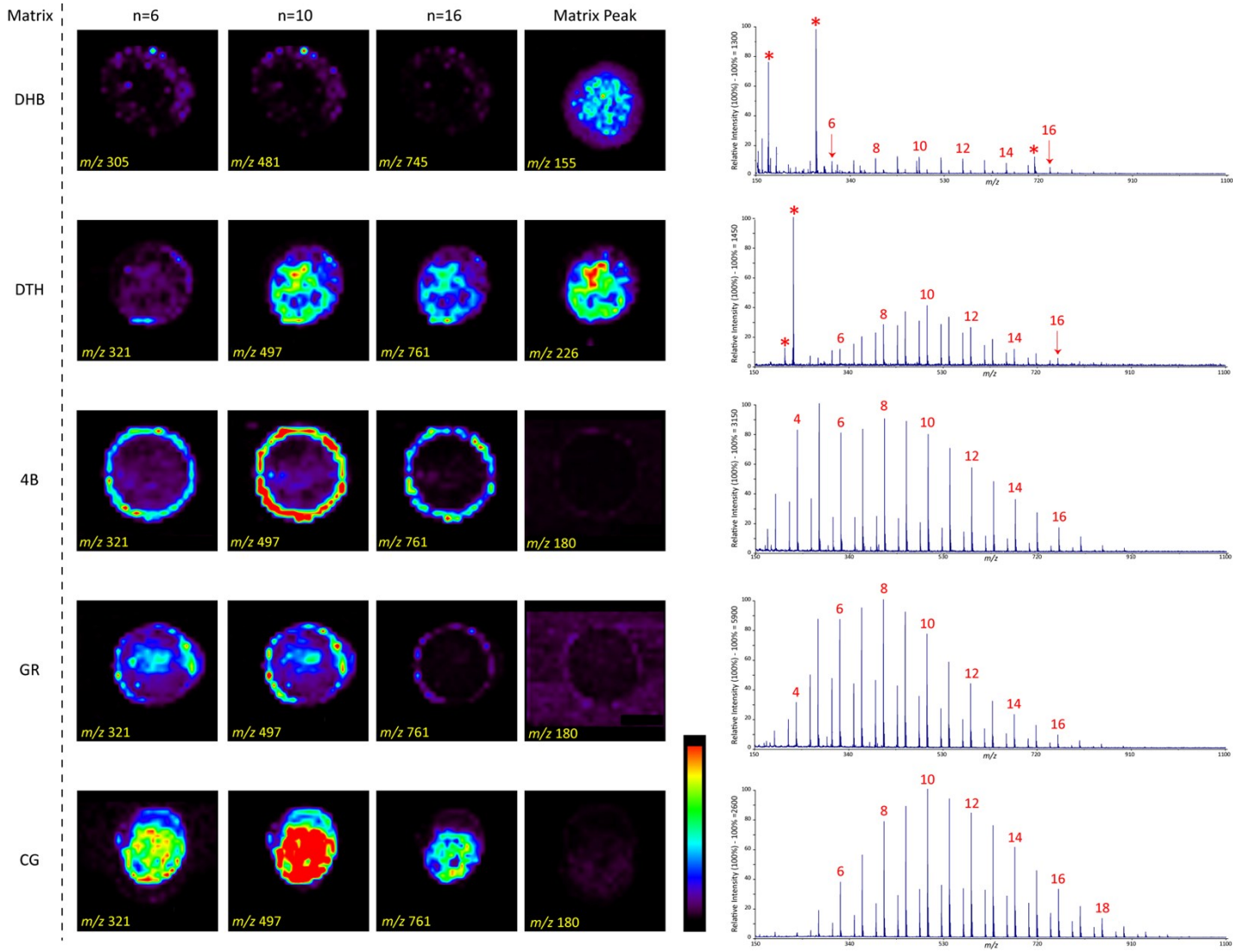


Figure S5: MALDI imaging of a equimolar mix of PEG200, PEG400, PEG600 with various matrices. The 5 matrices (DHB, DTH, 4B, GR and CG) are all imaged at fixed oligomer masses for the PEG400 (n = 6, 10 and 16) and a monitoring mass for the matrix (*m/z* 155 for DHB, *m/z* 226 for DTH and *m/z* 180 for 4B, GR an CG). A linear colour scale is also provided from red (high intensity) to purple/black (low intensity). The mass spectrum of the same

spot is provided on the right-hand side. Matrix peaks for DHB and DTH are indicted by a red star and PEG peaks with the corresponding chain length in red.