

## MALDI-LID-ToF/ToF Analysis of Statistical and Diblock Polyacrylate Copolymers- Supplementary Information

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### Materials

All materials were purchased from Sigma Aldrich and used as received unless otherwise stated. Tris[2-(dimethylamino)ethyl]-amine (Me<sub>6</sub>Tren) was synthesized according to the literature (Ciampolini, M.; Nardi, N., *Inorg. Chem.* 1966, 5 (1), 41-44) and stored under nitrogen and refrigerated prior to use. Methyl acrylate and ethyl acrylate were passed through a plug of basic alumina prior to polymerization in order to remove inhibitor.

### Instrumentation and Analysis

NMR spectra were recorded on Bruker AV-300 and DPX-400 spectrometers using deuterated solvent (CDCl<sub>3</sub>) purchased from Sigma-Aldrich. Monomer conversion was calculated by comparison of vinyl protons with methyl ether protons (methyl acrylate) and ethyl ether protons (ethyl acrylate).

SEC analysis was performed on an Agilent 390-LC MDS instrument with differential refractive index (DRI) and dual wavelength UV detectors. The system was equipped with 2 x PLgel Mixed C columns (300 x 7.5 mm) and a PLgel 5 μm guard column. The eluent was THF with 2% TEA (triethylamine) and 0.01% BHT (butylated hydroxytoluene) additives run at 1 ml/min at 30°C. Poly(methyl methacrylate) (Agilent Poly(methyl methacrylate) EasiVials between 550 and 1.5 million Da) and polystyrene standards (Agilent Polystyrene Medium EasiVials between 162 and 364,000 Da) were used for calibration and fitted with a second order polynomial. Analyte samples were filtered through a GVHP membrane with 0.22 μm pore size before injection.

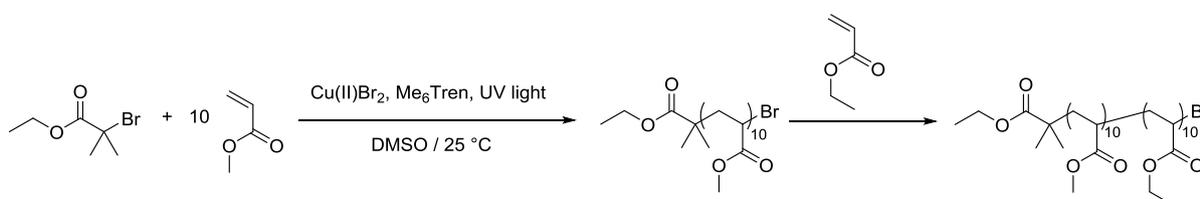
The UV source used for all polymerizations was a UV nail gel curing lamp ( $\lambda_{\text{max}} \sim 365 \text{ nm}$ ) with four 9 Watt bulbs (figure S1).



**Figure S1:** UV curing lamp used for polymerizations.

## Synthesis

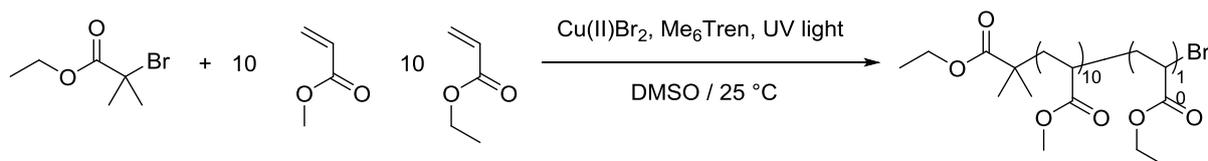
### *Synthesis of poly(methyl acrylate)<sub>10</sub>-block-poly(ethyl acrylate)<sub>10</sub> by photo ATRP*



**Scheme S1:** Scheme of block copolymer synthesis by photo ATRP.

A 20 mL vial was charged with a magnetic stirrer bar and Cu(II)Br<sub>2</sub> (9.9 mg, 0.044 mmol, 0.2 eq.). 2 mL of DMSO was added and the Cu(II)Br<sub>2</sub> was dissolved by sonication. Me<sub>6</sub>Tren (7.1 μL, 0.27 mmol, 0.12 eq.) was added by microliter syringe, followed by methyl acrylate (2 mL, 22 mmol, 10 eq.). The vial was fitted with a rubber septum and the solution was deoxygenated by sparging with nitrogen gas. After 15 minutes deoxygenated ethyl bromoisobutyrate (326 μL, 2.2 mmol, 1 eq.) was added *via* a deoxygenated syringe. The reaction was placed on a stirring plate in a UV nail gel curing lamp (4 x 9W bulbs). After 3 hours the reaction was sampled via degassed syringe and monomer conversion was determined to be >99% by NMR analysis. Block copolymer synthesis was achieved by *in-situ* chain extension through addition of a solution of ethyl acrylate (2.4 mL, 22 mmol, 10 eq.) in 2.4 mL of DMSO *via* deoxygenated syringe, and the reaction was once again placed in the UV curing lamp. After 8 hours the reaction was sampled and monomer conversion was found to be ~98%. The reaction mixture was diluted in THF, passed through alumina to remove copper salts, precipitated in 50/50 water/methanol and dried in a vacuum oven to yield a highly viscous material.

### *Synthesis of poly(methyl acrylate)<sub>10</sub>-stat-poly(ethyl acrylate)<sub>10</sub> by photo ATRP*

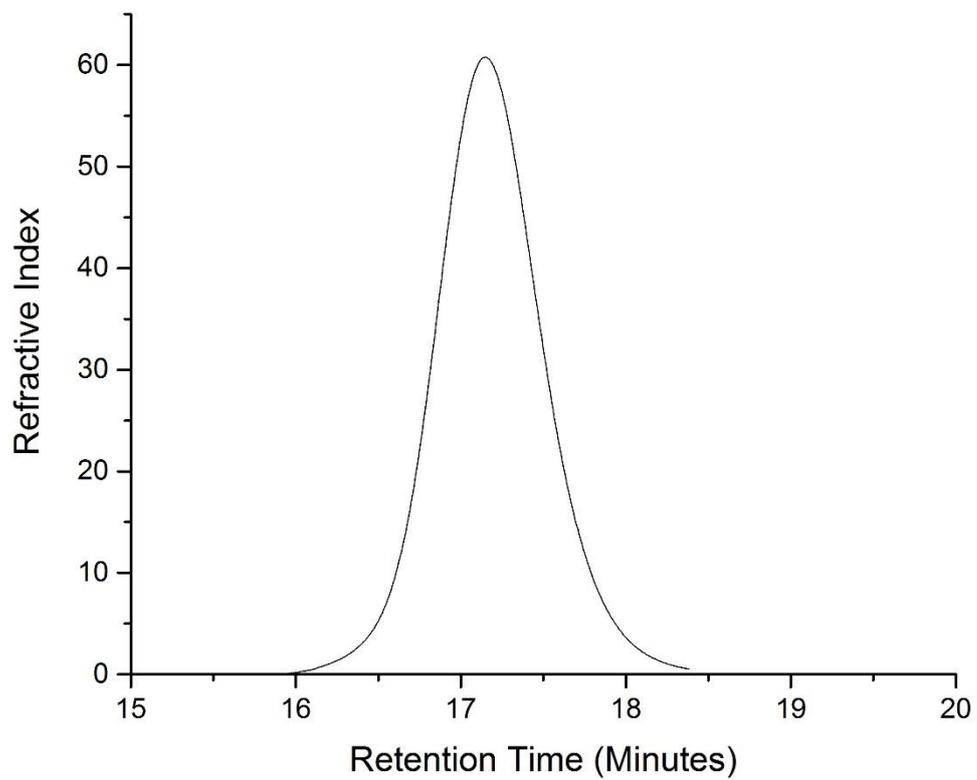


**Scheme S2:** Scheme of statistical copolymer synthesis by photo ATRP.

A 20 mL vial was charged with a magnetic stirrer bar and Cu(II)Br<sub>2</sub> (9.9 mg, 0.044 mmol, 0.2 eq.). 4.4 mL of DMSO was added and the Cu(II)Br<sub>2</sub> was dissolved by sonication. Me<sub>6</sub>Tren (7.1 μL, 0.27 mmol, 0.12 eq.) was added by microliter syringe, followed by methyl acrylate (2 mL, 22 mmol, 10 eq.) and ethyl acrylate (2.4 mL, 22 mmol, 10 eq.). The vial was fitted with a rubber septum and the solution was deoxygenated by sparging with nitrogen gas. After 15 minutes deoxygenated ethyl bromoisobutyrate (326 μL, 2.2 mmol, 1 eq.) was added *via* a deoxygenated syringe. The reaction was placed on a stirring plate in a UV nail gel curing lamp (4 x 9W bulbs). After 12 hours the reaction was sampled and monomer conversion was found to be ~97%. The reaction mixture was diluted in THF, passed through alumina to remove copper salts, precipitated in 50/50 water/methanol and dried in a vacuum oven to yield a highly viscous material.

### GPCs

Gel permeation chromatography (GPC) was performed on the two copolymers, using an Agilent Infinity II running in THF at 1 ml/min with Agilent PLgel mixed C columns. A refractive index detector was used to calculate Mn, Mw and polydispersity index, the results are shown below.



*Figure 1: Poly (methyl acrylate - b - ethyl acrylate) GPC results  $M_n=1994$ ,  $M_w=2231$  and  $PDI=1.19$ .*

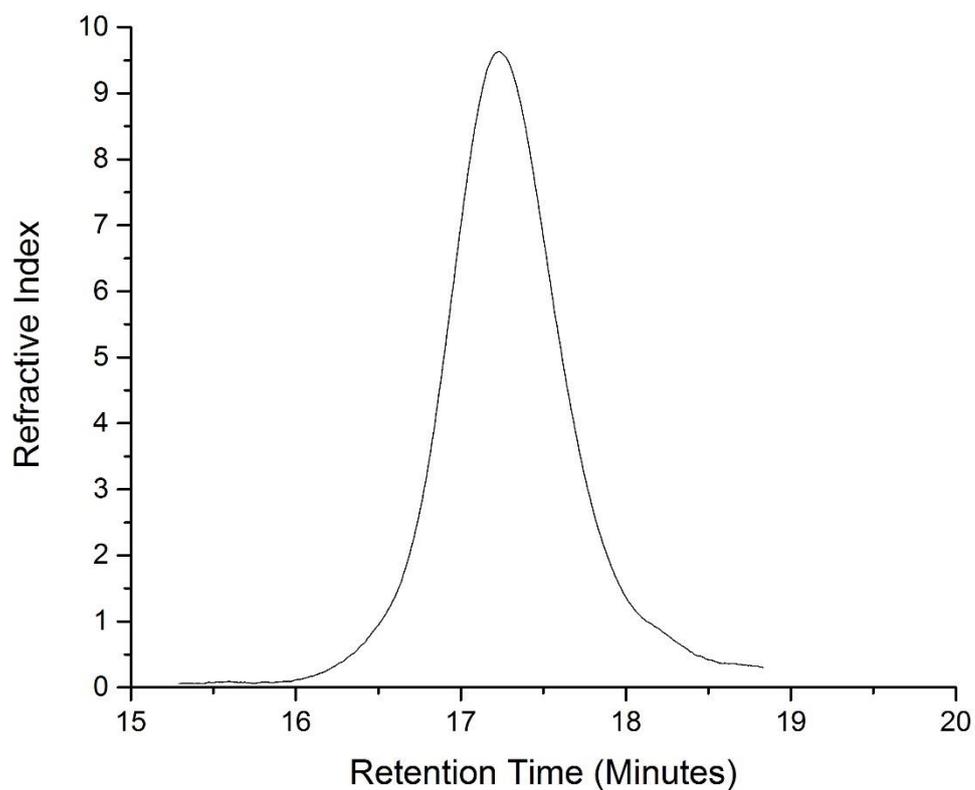


Figure 2: Poly (methyl acrylate - n - ethyl acrylate) GPC results,  $M_n=1694$ ,  $M_w=2085$ ,  $PDI=1.13$

#### **Additional MALDI-LID-ToF/ToF Results**

Other peaks were isolated and examined by MALDI-LID-ToF/ToF to ensure the results were valid and the same fragmentation pattern was examined for different polymer chains.

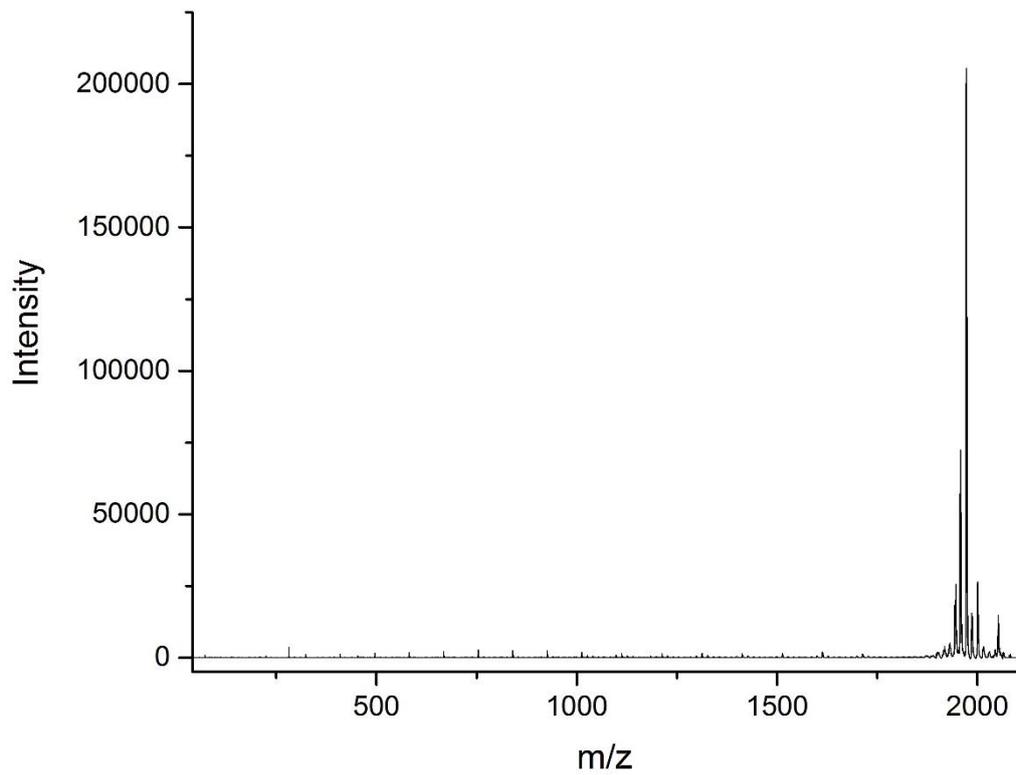


Figure 3: PMA-EA diblock copolymer MALDI-LID-ToF/ToF results for the 2077 m/z peak.

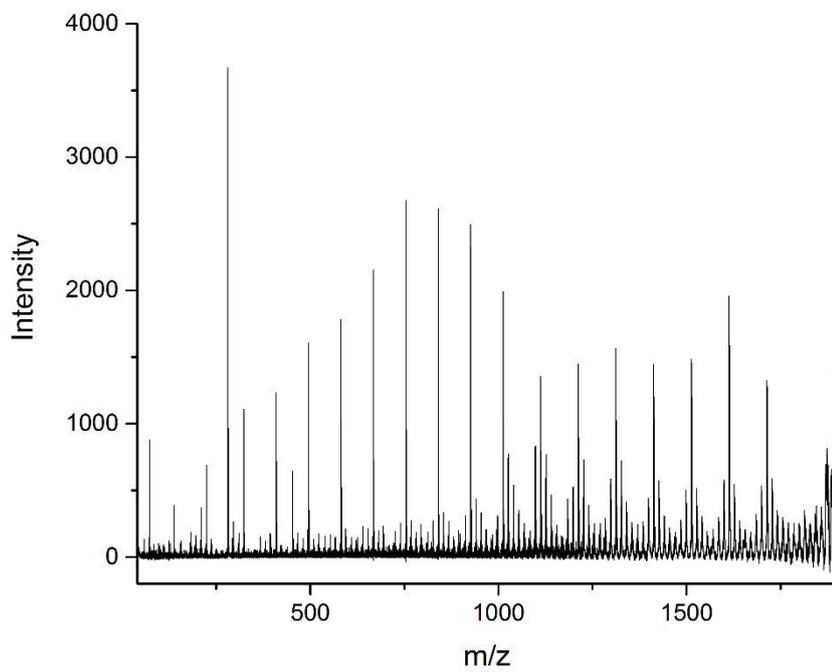


Figure 4: Zoom of the PMA-EA Diblock MALDI-LID-ToF/ToF results for the 2077 peak.

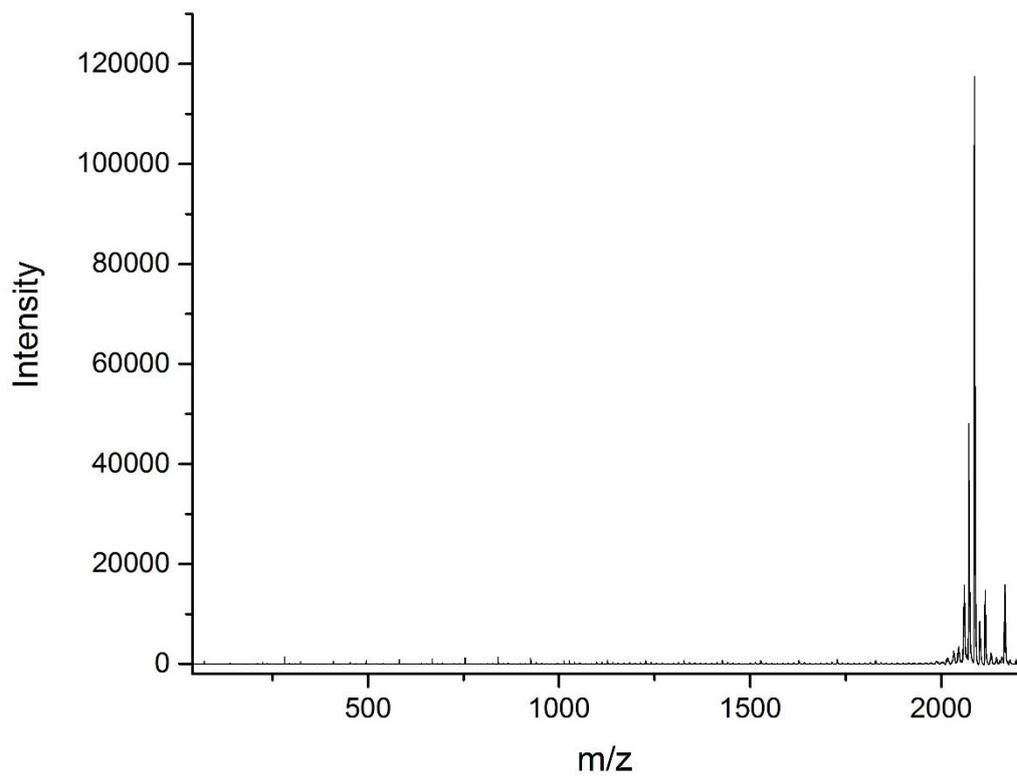


Figure 5: PMA-EA diblock copolymer MALDI-LID-ToF/ToF results for the 2178 m/z peak.

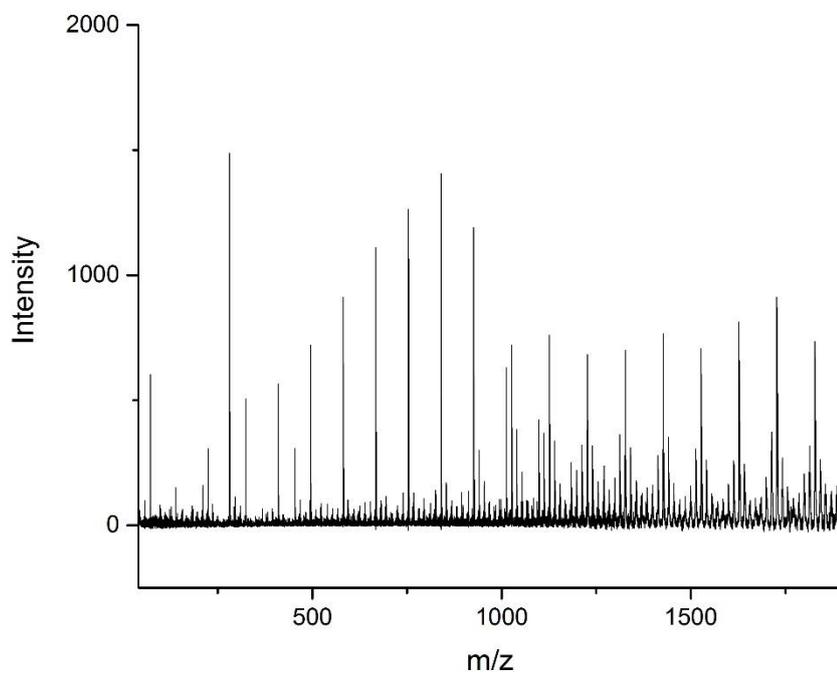


Figure 6: PMA-EA Diblock MALDI-LID-ToF/ToF results for 2178 m/z peak, zoom.

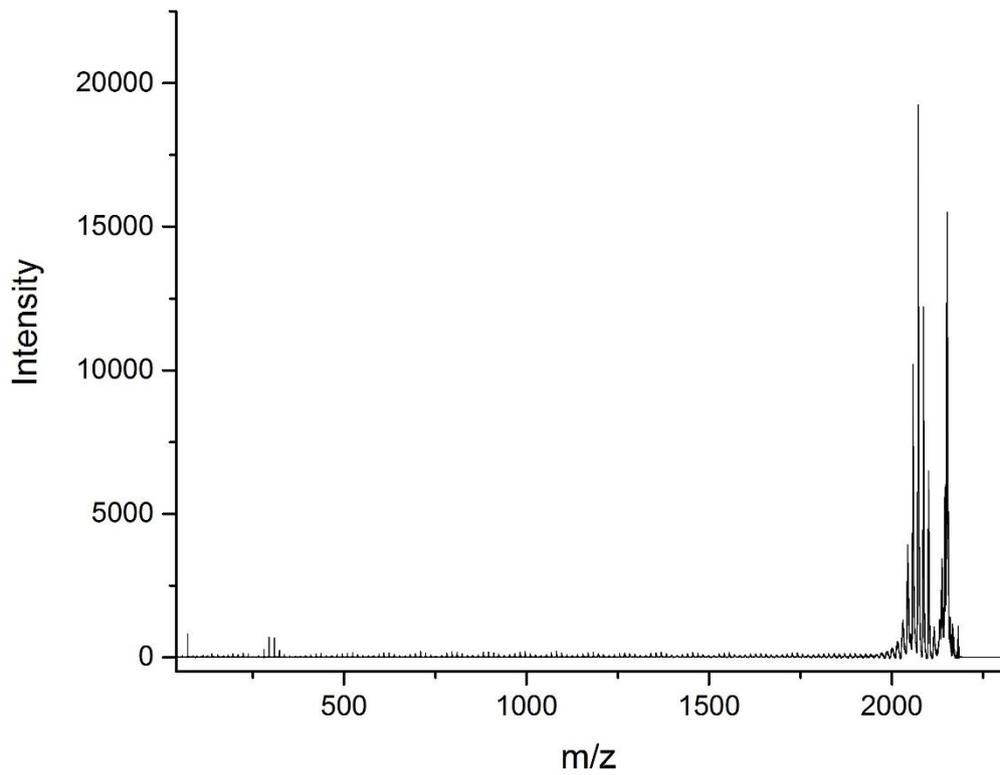


Figure 7: PMA-EA Statistical Copolymer MALDI-LID-ToF/ToF results for the 2178 m/z peak.

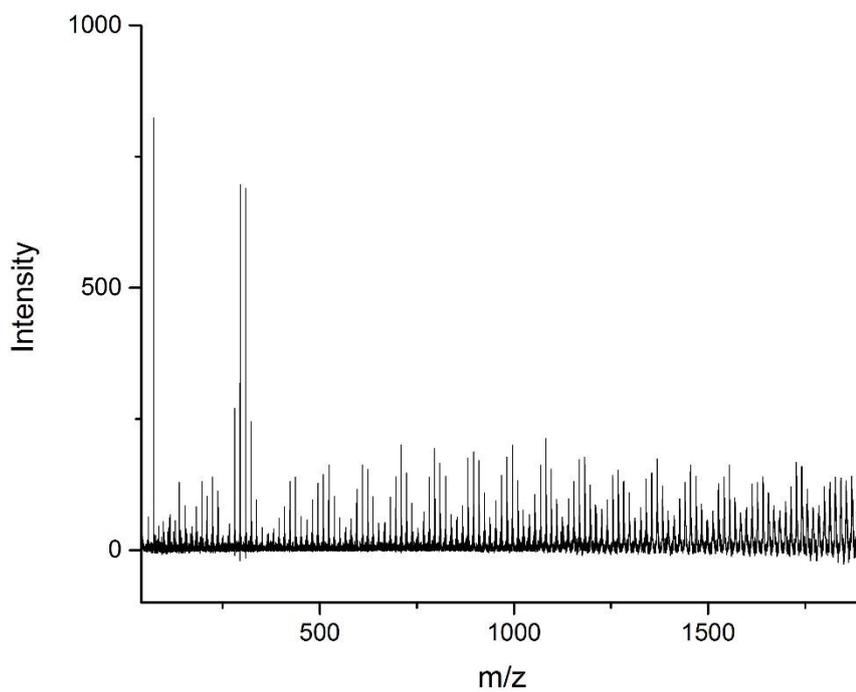


Figure 8: PMA-EA Statistical copolymer MALDI-LID-ToF/ToF results 2178 m/z zoom.

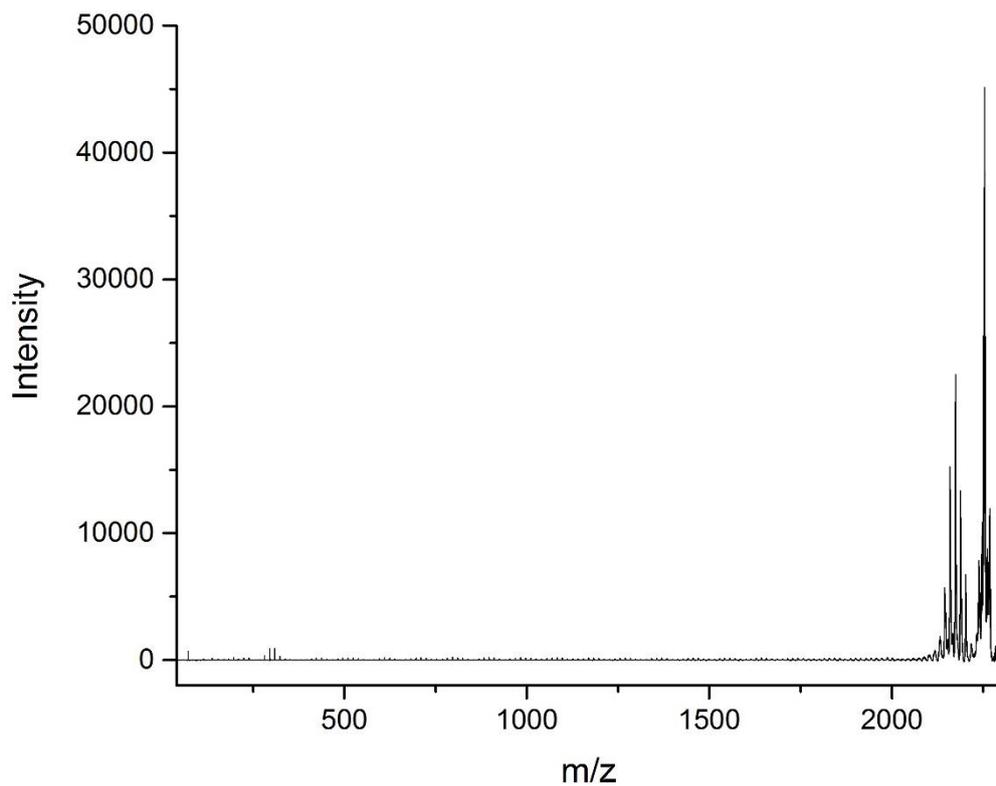


Figure 9: PMA-EA Statistical Copolymer MALDI-LID-ToF/ToF results for the 2279 m/z.

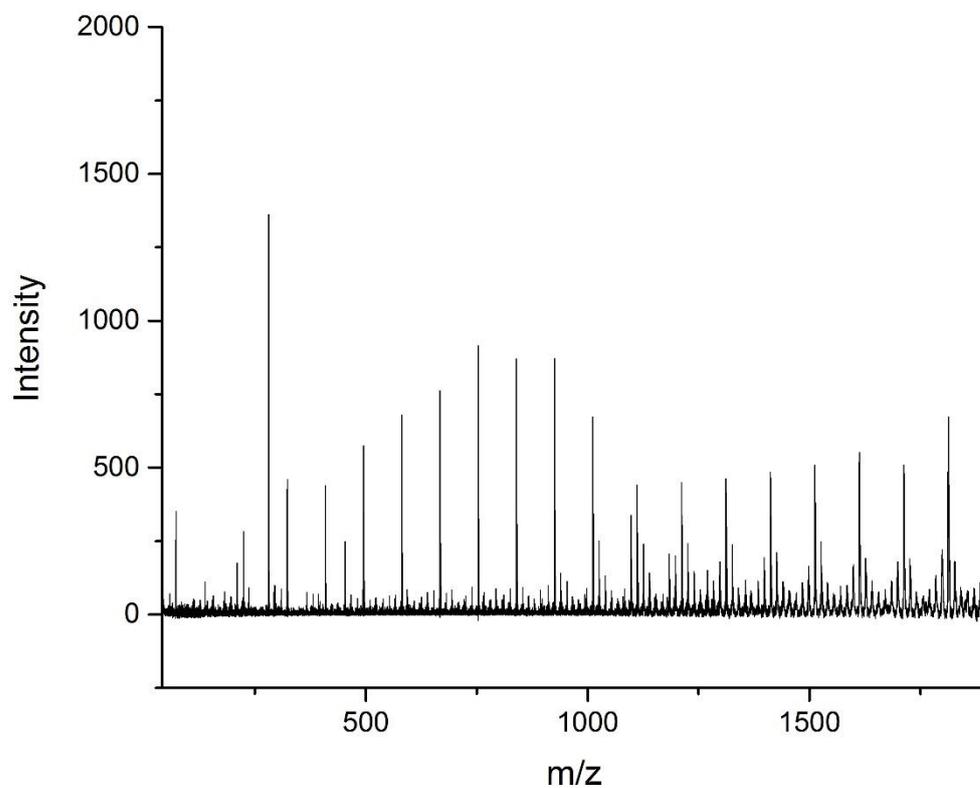


Figure 10: PMA-EA Statistical MALDI-LID-ToF/TOF results for 2278m/z zoom

