Supporting information

Imidazolium end-functionalized poly(L-lactide) for Efficient Carbon Nanotube Dispersion.

Franck Meyer,[a] Jean-Marie Raquez,[a] Olivier Coulembier,[a] Julien De Winter,[b] Pascal Gerbaux,[b] and Philippe Dubois*[a]

a Laboratory of Polymeric and Composite Materials, Center of Innovation and Research in Materials and Polymers (CIRMAP), University of Mons UMONS, Place du Parc 20, 7000 Mons (Belgium)

b Mass Spectrometry Research Group, Centre Interdisciplinaire de Spectrométrie de Masse (CISMa), University of Mons, 20 Place du Parc, 7000 Mons (Belgium)

Experimental Section

Materials. Multi wall carbon nanotubes (MWCNTs) are Grade 7000 from Nanocyl (Belgium): (average diameter: 9.5nm; average length: 1.5µm; carbon purity: 90%; metal oxide: 10%). 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was purchased from Aldrich. DBU and dried on a 4A molecular sieves. Chloroform ($CHCl_3$, Labscan, 99%) was dried using an MBraun solvent purification system under N_2. L-lactide was gratefully gifted by Purac. 1-pyrenemethanol (98%), 9-anthracenemethanol (97%), 1-methylimidazole (99%) and 11-Bromoundecanol (98%) were purchased from Aldrich.

Instrumental. Size exclusion chromatography (SEC) was performed in THF/NEt_3 (2wt%) at 35°C using a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (flow rate = 1 mL/min), a Marathon autosampler (loop volume = 200 µL, solution conc. = 1 mg/mL), a PLDRI refractive index detector and three columns: a PL gel 10 µm guard column and two PL gel Mixed-B 10 µm columns. Centrifugations were made with a HETTICH Universal 16 Centrifuge. ^{1}H NMR spectra were recorded at ambient temperature with Bruker AV500 spectrometer. Thermal gravimetric analyses (TGA) were recorded on a TA Instrument Q500 under helium. Transmission electron microscopy (TEM) was performed with a Philips CM200 with an acceleration voltage of 200 kV. MALDI mass spectra were recorded using our Waters QToF Premier mass spectrometer equipped with a nitrogen laser, operating at 337 nm with a maximum output of 500 J/m^2 delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight mass

analysis were performed in the reflectron mode at a resolution of about 10 000. The matrix, trans-2-[3-(4-t-Butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), was prepared as 20 mg/mL solution in chloroform. The matrix solution (1 µL) was applied to a stainless steel target and air dried. Polymer samples were dissolved in Chloroform to obtain 1mg/mL solutions. 1µL aliquots of these solutions were applied onto the target area already bearing the matrix crystals, and then air dried.

Typical synthesis of PyPLLA 1, AntPLLA 2 and ImPLLA 3

L-lactide (5.8 g, 40.3 mmol) and ionic liquid **4** (192 mg, 0.57 mmol) are stirred in 20 mL of chloroform. DBU (21 µl, 0.15 mmol) is added and the solution is stirred at room temperature for 5 mn. Then, three drops of acetic acid are added and PLLA is precipitated in hexane. After filtration, the white powder is dried at 70°C under vacuum overnight. Yield = 95%.

PyPLLA 1: M_n determined by SEC (universal calibration) = 9400 g mol^{-1}, PDI = 1.10, ^{1}H NMR ($CDCl_3$): δ 8.15 (m, CH Arom.), 5.94 (d, J = 12.6, C<u>H</u>H), 5.83 (d, J = 12.6, CH<u>H</u>Ph) 5.15 (q, J = 7.1 Hz, CH), 1.57 (d, J = 7.1 Hz, CH_3).

AntPLLA 2: M_n determined by SEC (universal calibration) = 10100 g mol^{-1}, PDI = 1.13, ^{1}H NMR ($CDCl_3$): δ 8.53 (s, CH Arom.), 8.25 (d, J = 8.6 Hz, CH Arom.), 8.04 (d, J = 8.6 Hz, CH Arom.), 7.57 (t, J = 7.2 Hz, CH Arom.), 7.50 (t, J = 7.2 Hz, CH Arom.), 6.25 (d, J = 12.6, C<u>H</u>H), 6.13 (d, J = 12.6, CH<u>H</u>Ph) 5.15 (q, J = 7.1 Hz, CH), 1.57 (d, J = 7.1 Hz, CH_3).

ImPLLA 3: M_n determined by SEC (universal calibration) = 8500 g mol^{-1}, PDI = 1.18, M_n determined by MALDIToF = 9500 g mol^{-1}, ^{1}H NMR ($CDCl_3$): δ 10.60 (s, CH), 7.18 (s, CH=CH), 7.16 (s, CH=CH), 5.15 (q, J = 7.1 Hz, CH), 4.28 (t, J = 7.4 Hz, OCH_2), 4.09 (s, NCH_3), 1.62 (m, CH_2), 1.57 (d, J = 7.1 Hz, CH_3), 1.30 (m, CH_2).

Synthesis of 1-(11-hydroxy-undecyl)-3-methylimidazolium bromide 4: Methyl imidazole (2.3 mL, 29 mmol) and bromoundecanol (8 g, 31.8 mmol) are stirred in 4 mL of refluxing chloroform overnight. Then, the oily residue is washed 3 times with ether to give the ionic liquid **4** in 95% yield. ^{1}H NMR ($CDCl_3$): δ 9.83 (1H, s, CH), 7.42 (1H, s, CH=CH), 7.37 (1H, s, CH=CH), 4.06 (2H, t, J = 7.4 Hz, OCH_2), 3.83 (3H, s, NCH_3), 3.28 (2H, t, J = 6.3 Hz, NCH_2), 2.93 (1H, br s, OH), 1.64 (2H, m, CH_2), 1.24 (2H, m, CH_2), 0.96 (14H, m, CH_2).

Typical procedure for the preparation of MWCNTs dispersion with PyPLLA 1, AntPLLA 2 and ImPLLA 3 in chloroform: 100 mg of PLLA derivative and 5 mg of MWCNTs are stirred in 10mL of chloroform overnight. Then, the mixture was centrifugated at 4000 rpm for 10 mn.

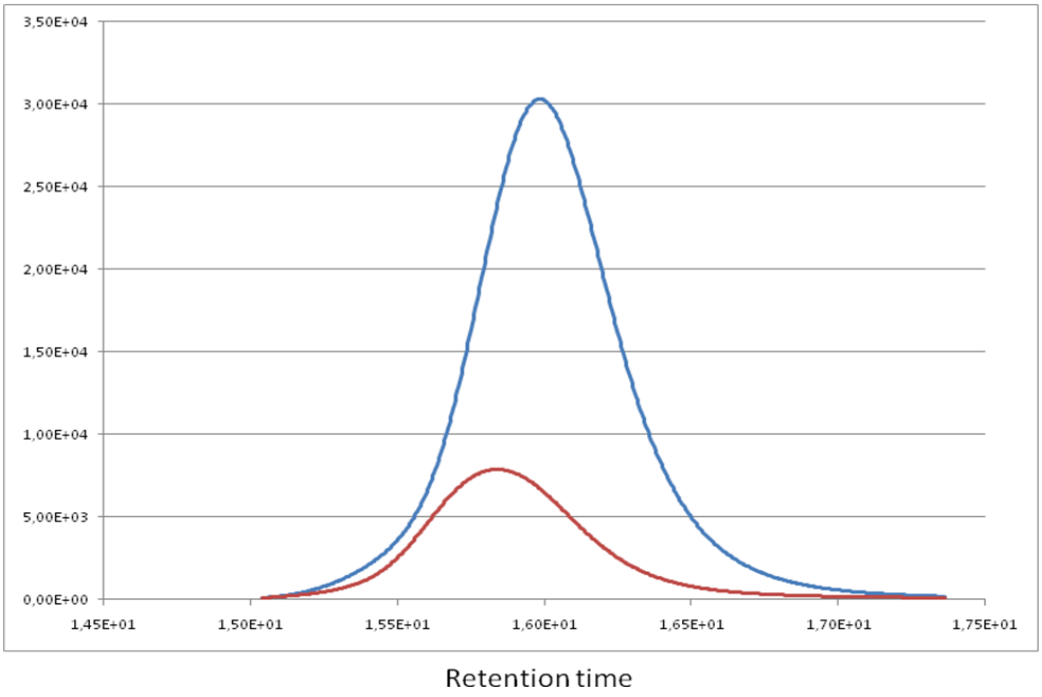

Figure S1. SEC traces of PyPLLA **1** showing the correlation between the molecular weight (blue) and the signal at 260 nm (red)

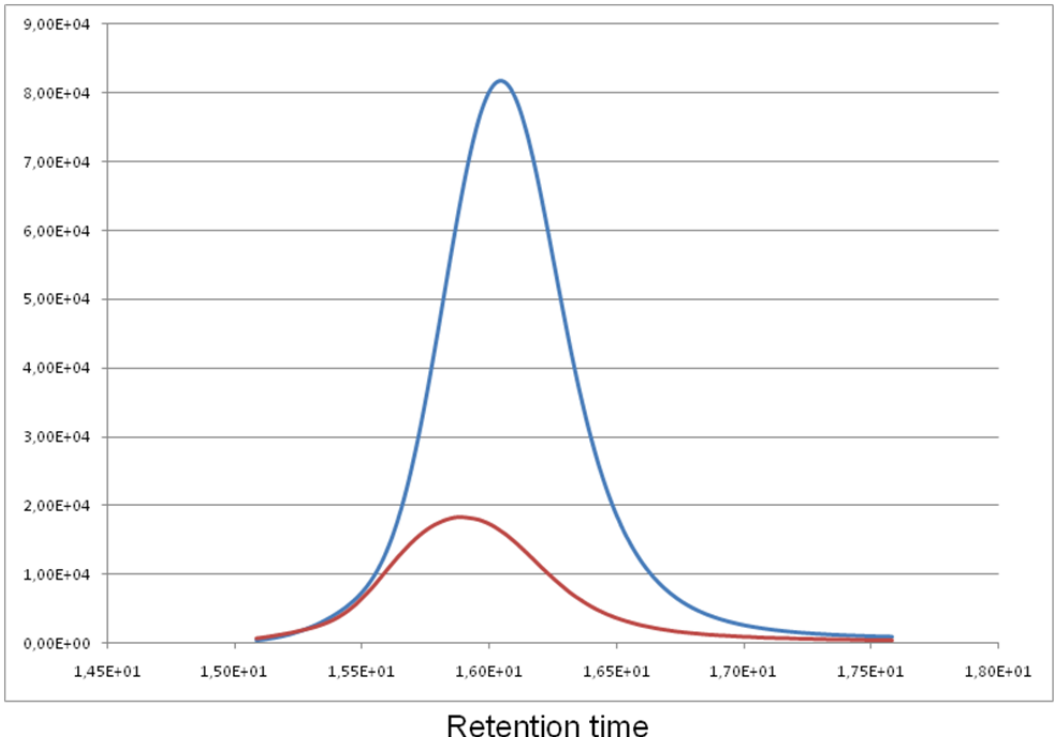

Figure S2. SEC traces of AntPLLA **2** showing the correlation between the molecular weight (blue) and the signal at 260 nm (red)

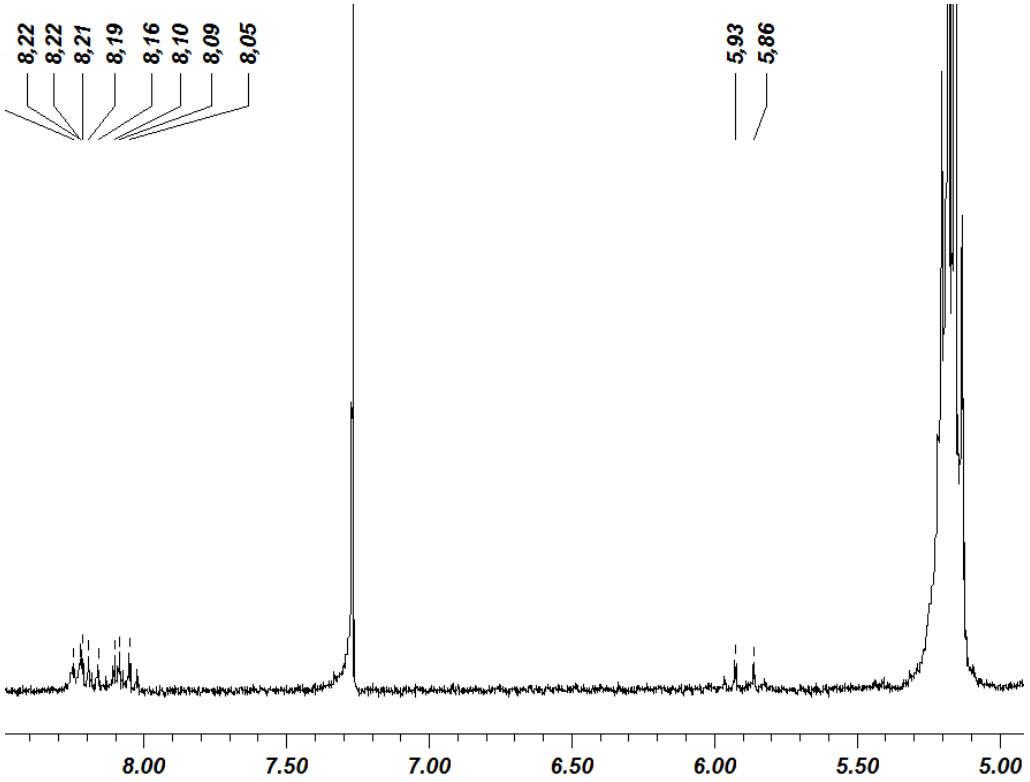

Figure S3. ^{1}H NMR spectrum of PyPLLA **1** in the 5.00-8.50 ppm region revealing the presence of pyrene aromatic group

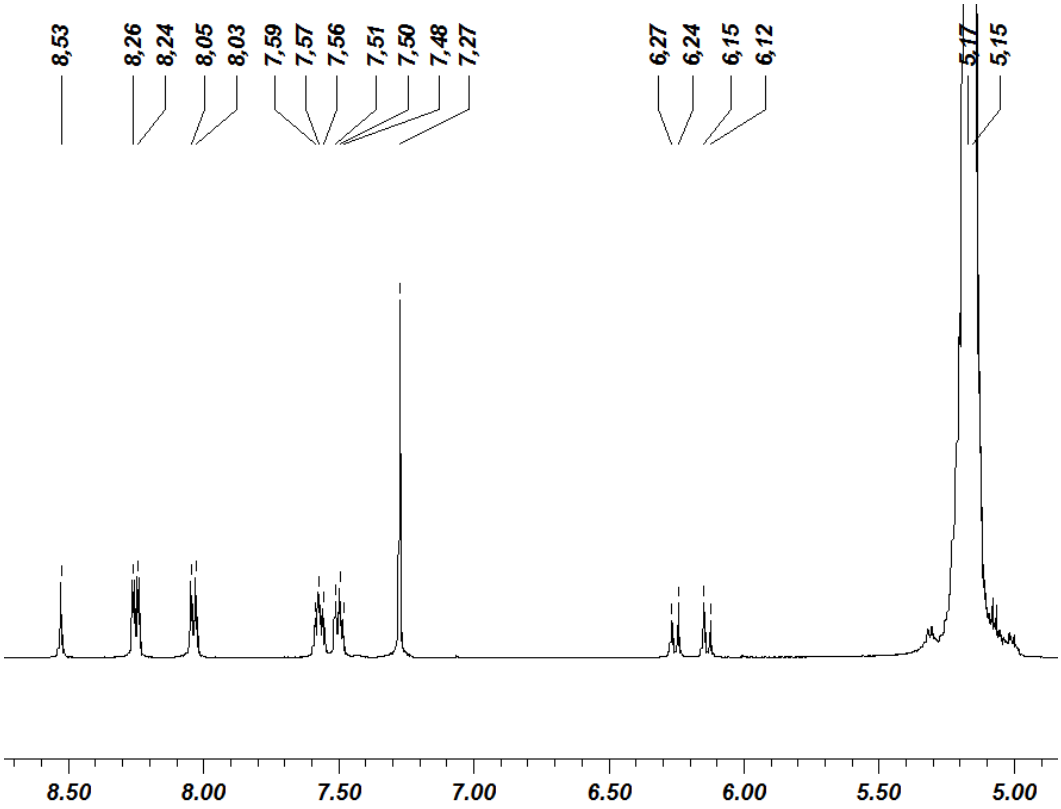

Figure S4. ^{1}H NMR spectrum of AntPLLA **2** in the 4.90-8.60 ppm region revealing the presence of anthracene aromatic group

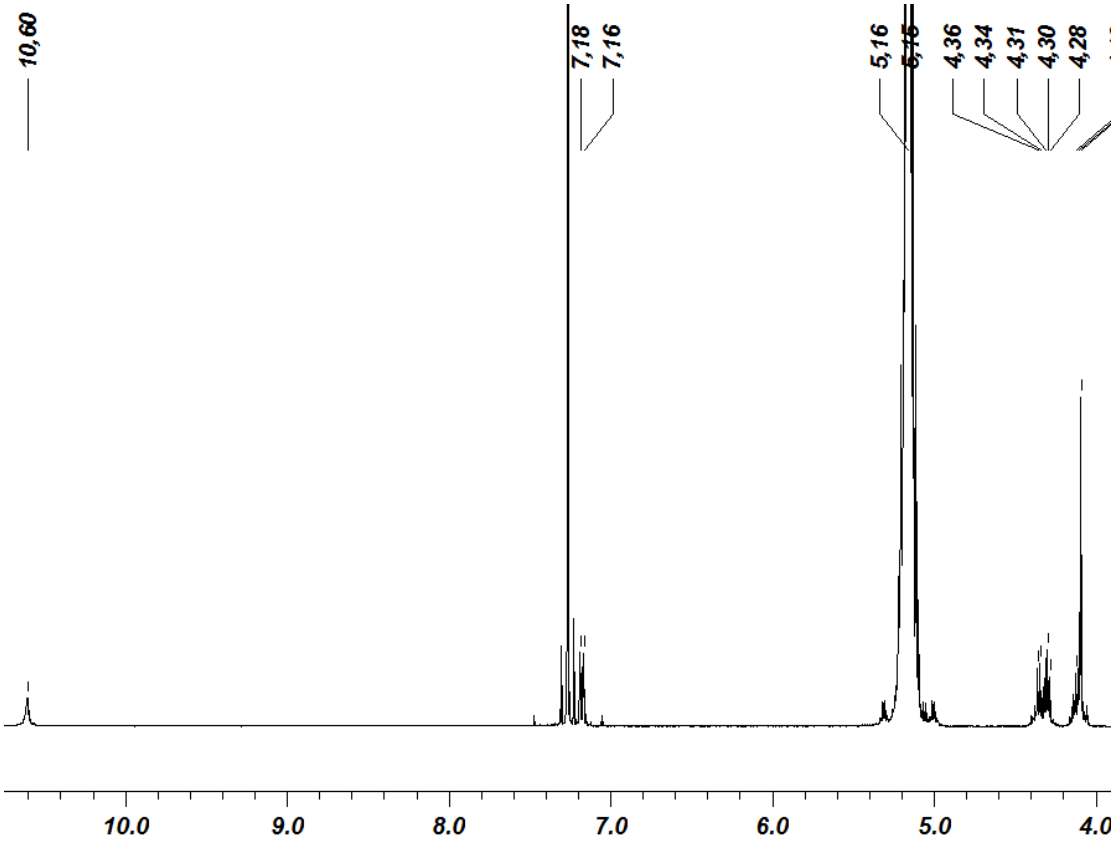

Figure S5. ^{1}H NMR spectrum of ImPLLA **3** in the 4.00-10.60 ppm region attesting for the presence of the imidazolium ring

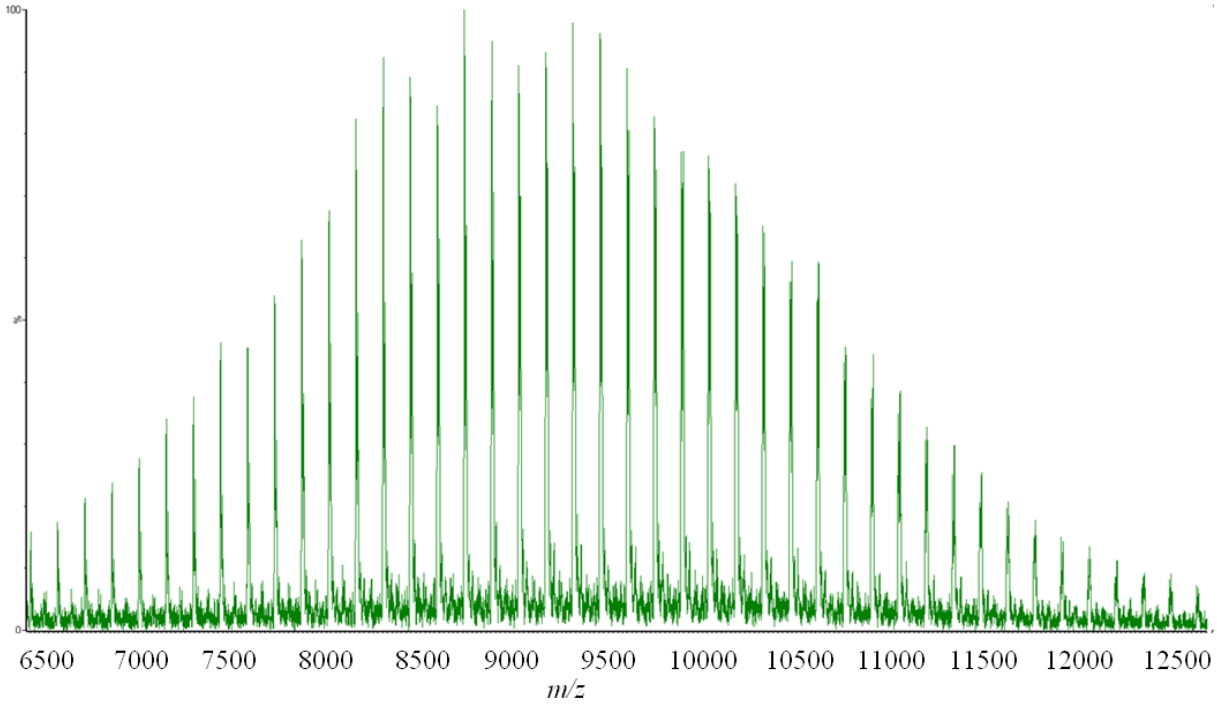

Figure S6. MALDI ToF spectrum of PyPLLA **1** after 30 mn

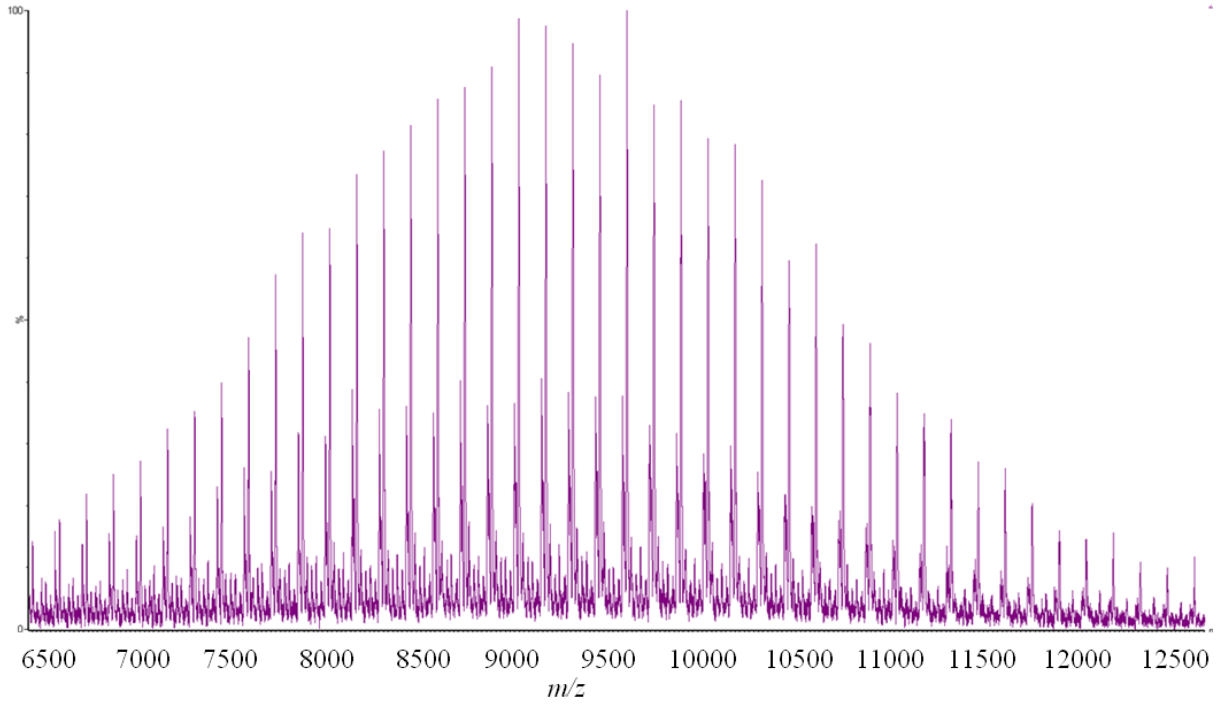

Figure S7. MALDI ToF spectrum of AntPLLA **2** after 30 mn

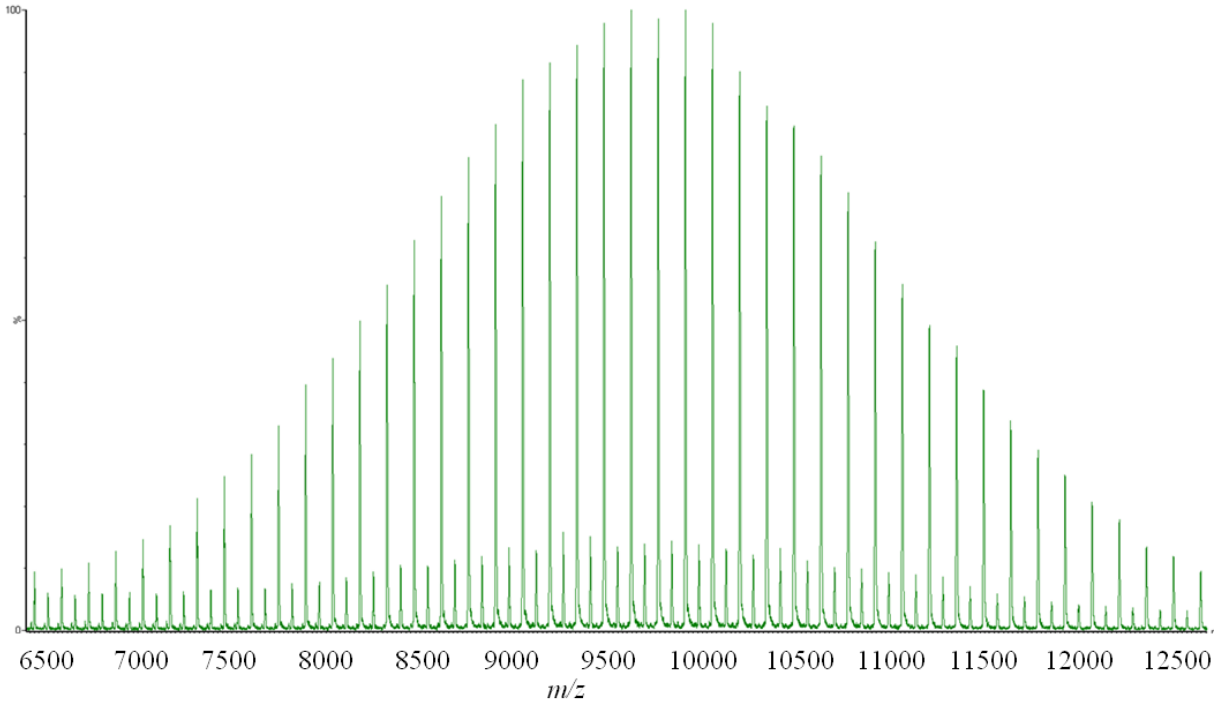

Figure S8. MALDI ToF spectrum of ImPLLA **3** after 10 mn

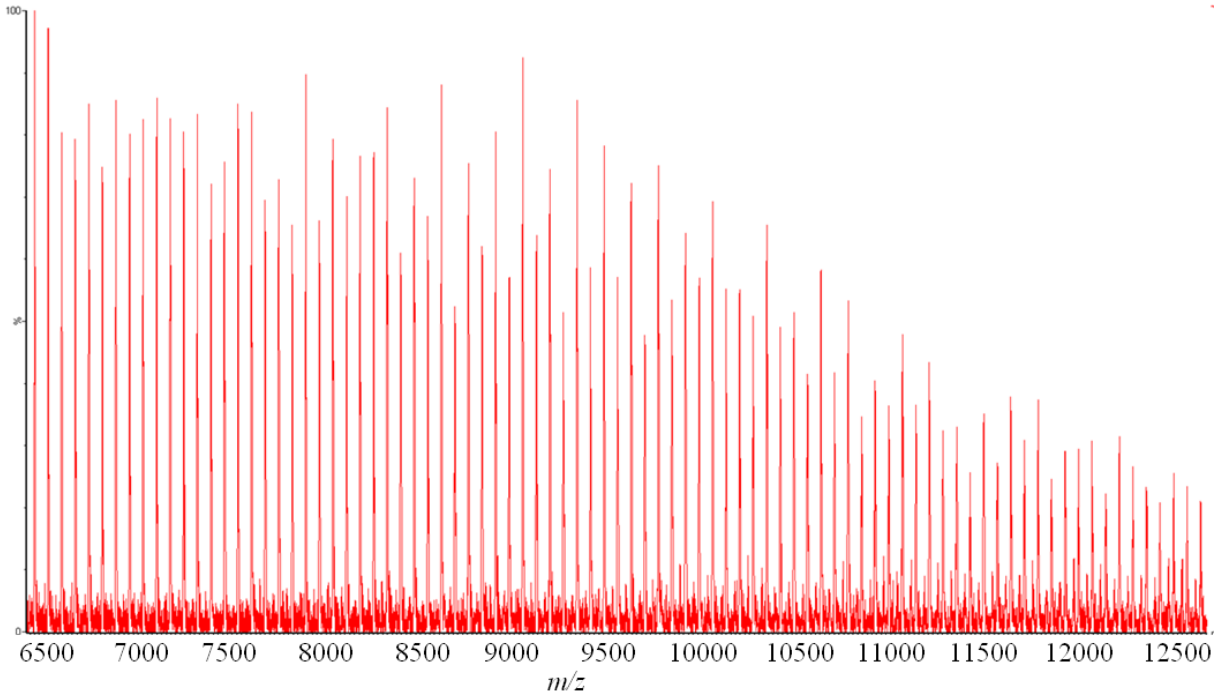

Figure S9. MALDI ToF spectrum of ImPLLA **3** after 20 mn