Supplementary Information (SI) for Environmental Science: Nano.

Extensive HPLC-tandem mass spectrometry characterization of soluble degradation products of biodegradable nanoplastics under environmentally relevant temperature and irradiation conditions

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Electronic Supplementary Information

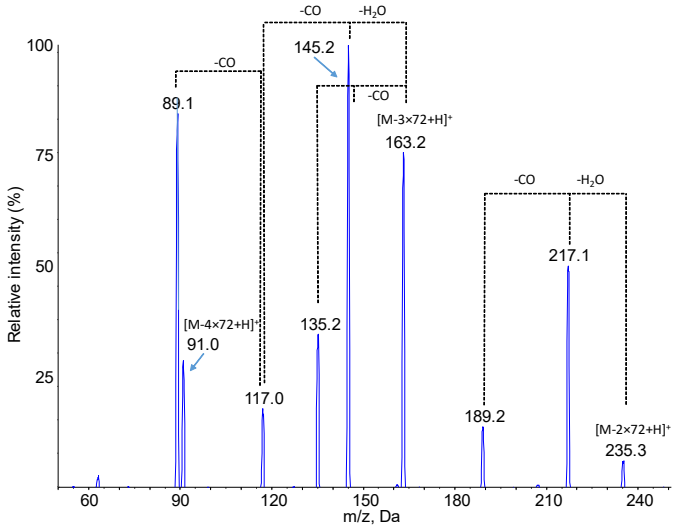

Figure S1: *Positive electrospray ionization fragmentation mass spectra of the $[M+NH_4]^+$ pseudo-pseudo molecular ion of compound PLA2, namely the PLA pentamer. The pseudo-molecular ion was at m/z=396. The first product ion was observed at m/z=235, which corresponds to loss of NH3, and two lactic acid monomers. Subsequent fragmentations involve loss of water and CO. A fragment corresponding to the loss of 3 lactic acid units is also observed, which also undergoes loss of water and CO. A final product ion correspond to the loss of 4 lactic acid units.*

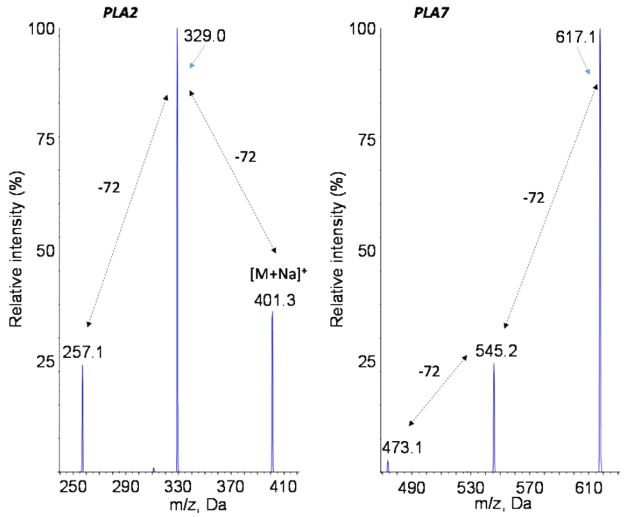

Figure S2: *Positive electrospray ionization fragmentation mass spectra of the $[M+Na]^+$ pseudo-pseudo molecular ion of compounds a) PLA2 and b) PLA7, namely the PLA pentamer and decamer.*

Table S1: *Summary of the precursor ions scan and neutral loss data obtained during analyses of aged PLA performed with positive and negative electrospray ionization.*

Compound #	PLA1	PLA2	PLA3	PLA4	PLA5	PLA6	PLA7
retention time (min)	15.0	17.3	18.5	19.4	19.9	20.3	20.7
m.w.	306	378	450	522	594	666	738
Number of PLA units	4	5	6	7	8	9	10
positive ionization							
$[M+Na]^+$ MS1	329	401	473	545	617	n.d.	n.d.
precusor of ions	257	257 329	329 401	401 473	473 545	n.d.	n.d.
$[M+Na]^+$ with NL72	n.d.	401	473	545	617	689	761
negative ionization							
$[M-H]^-$ MS1	n.d.	377	449	521	593	665	737
precusor of ions	n.d.	n.d.	n.d.	449	449 521	449 521 593	521
$[M-H]^-$ with NL 72	n.d.	377	449	521	593	665	n.d.

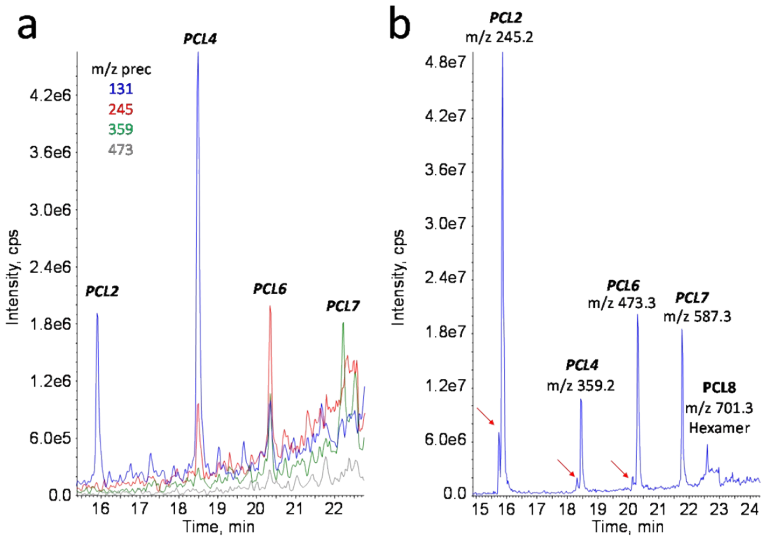

Figure S3: *a) Precursor ion scan analysis of aged PCL with negative electrospray ionization. The targeted ions were those identified by MS2 analyses and are listed on the figure; b) Neutral loss analysis of aged PCL with negative electrospray ionization. The monitored loss was -72. The value of the determined pseudo-molecular ion is shown on top of each peak. The red arrows show the peaks corresponding to methylated PCL oligomers.*

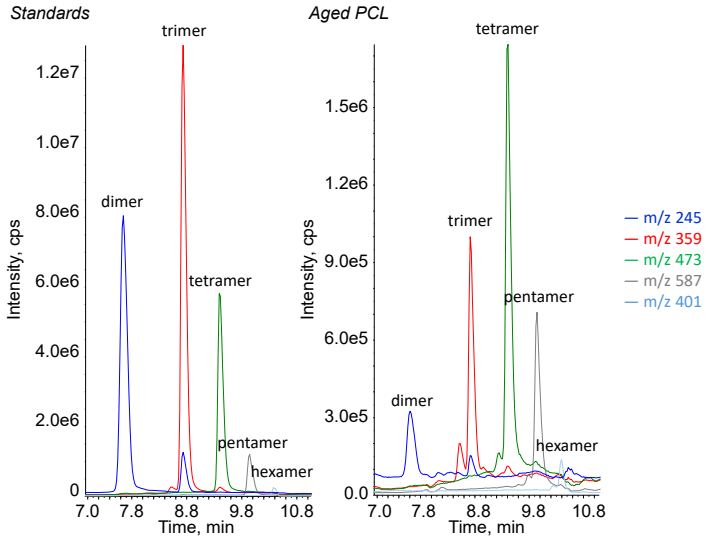

Figure S4: *Comparison of the HPLC-MS detection of synthetic standards of PCL oligomers (100 ng total) and products detected after 60 h of aging of PCL particles in water. The reported chromatograms corresponded to the pseudo-molecular ions of the oligomers of PCL (m/z 245, 359, 473, 587 and 701 for the dimer, trimer, tetramer, pentamer and hexamer, respectively).*

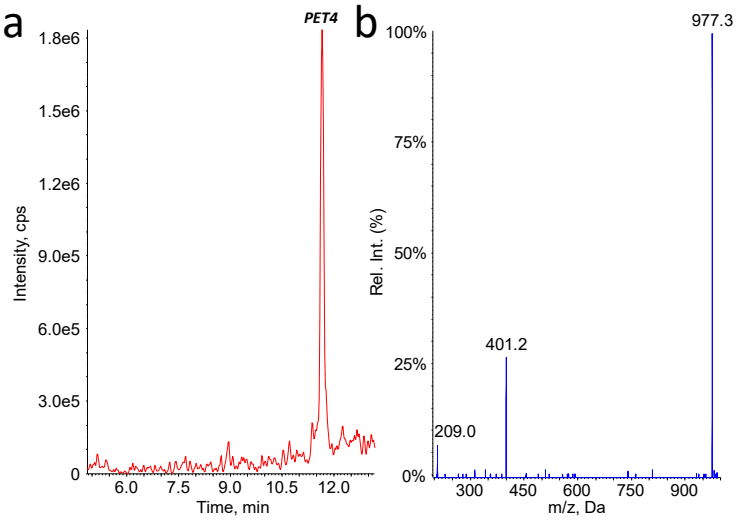

Figure S5: *Product ion scan characterization of PET4, the PET pentamer. The pseudo-molecular ion was set at 977. a) Chromatogram representing the total ion current in the 200-1000 mass range; b) fragmentation mass spectra of the product eluting at 11.6 min, the PET pentamer.*