

## Supplementary Data

### **Poly(lactic acid) nanoplastics through laser ablation: Establishing a reference model for mimicking biobased nanoplastics in aquatic environments.**

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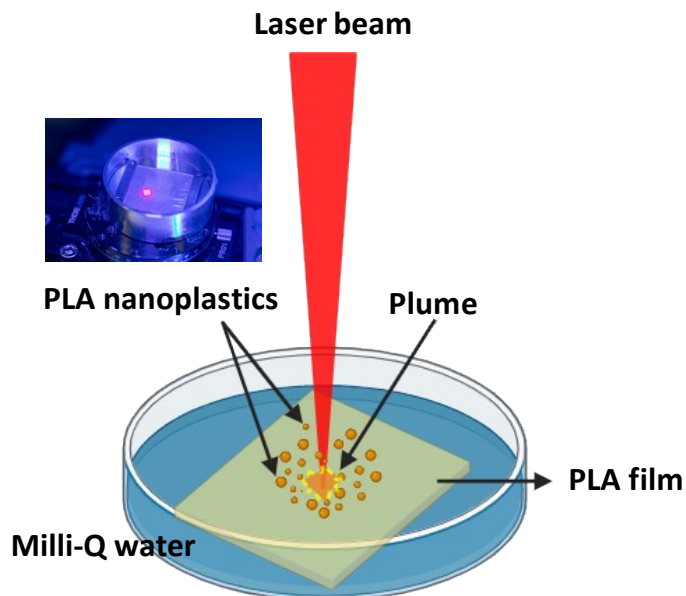
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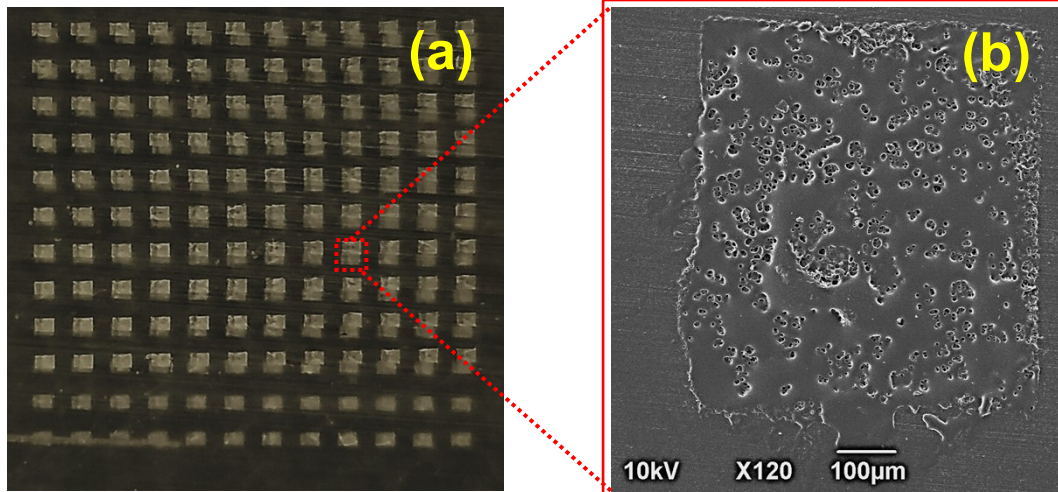
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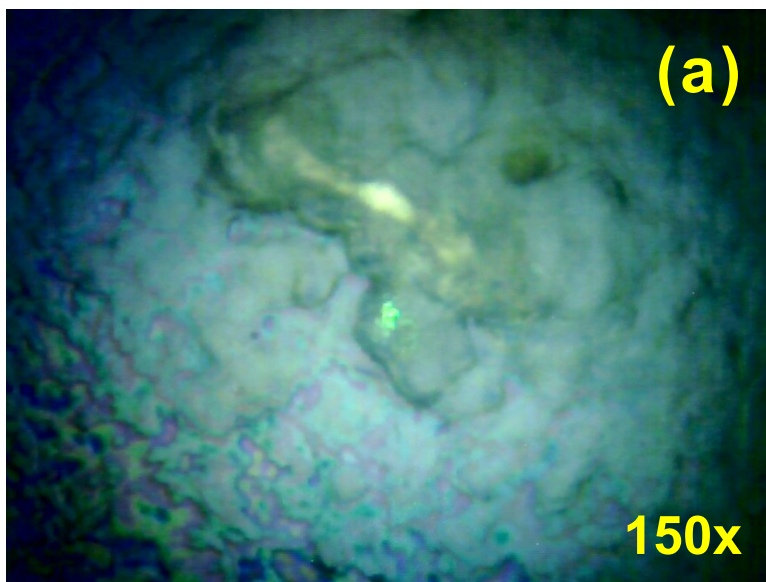
**Figure S1.** Schematic representation of the setup for the laser ablation process.

Upon irradiation with a KrF excimer laser at a wavelength of 248 nm, the PLA film undergoes ablation, generating PLA NPs that are dispersed within the surrounding aqueous medium.

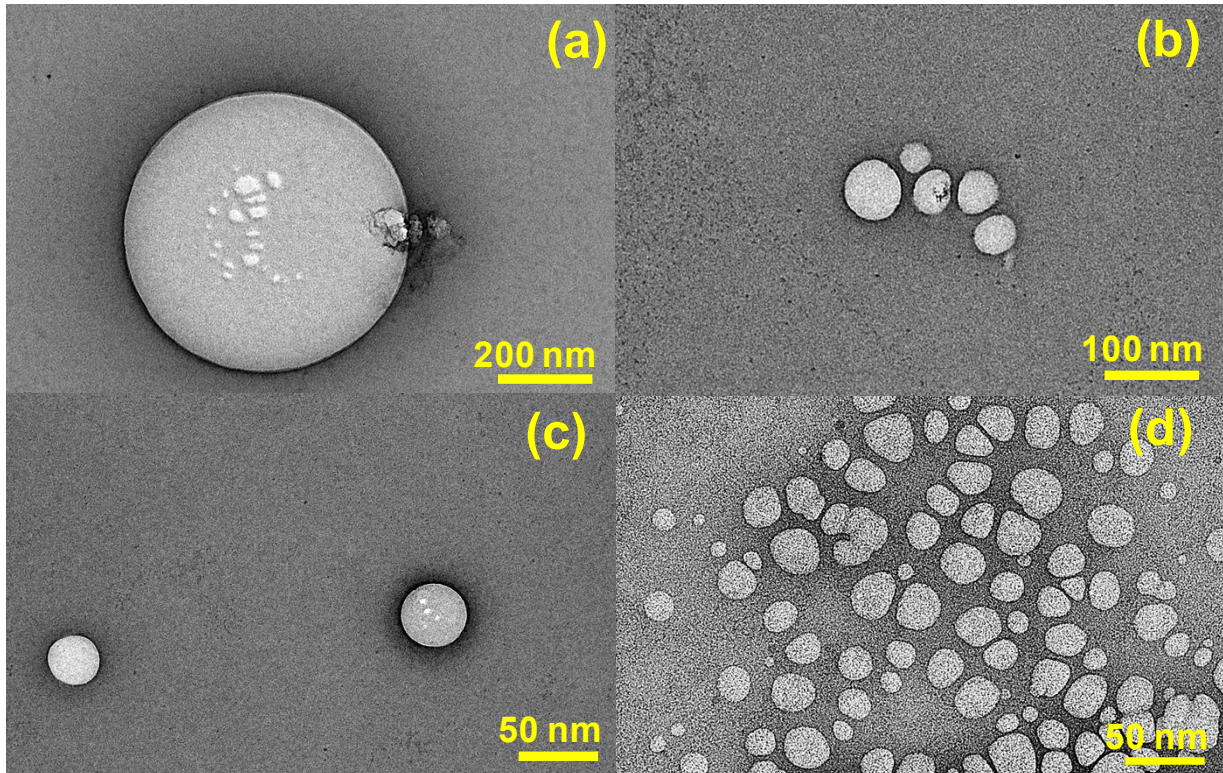


**Figure S2.** (a) The formation of a  $12 \times 12$  grid on the PLA surface after laser ablation in water to complete one ablation cycle. (b). SEM micrograph of the ablation spot, showing the material removal from the treated region.

In Figure S2, it can be observed that the laser-treated area of PLA film appears rougher than the surrounding untreated area. The laser ablation of the film has resulted in the formation of micropore-like surface structures, where the material removal has occurred.



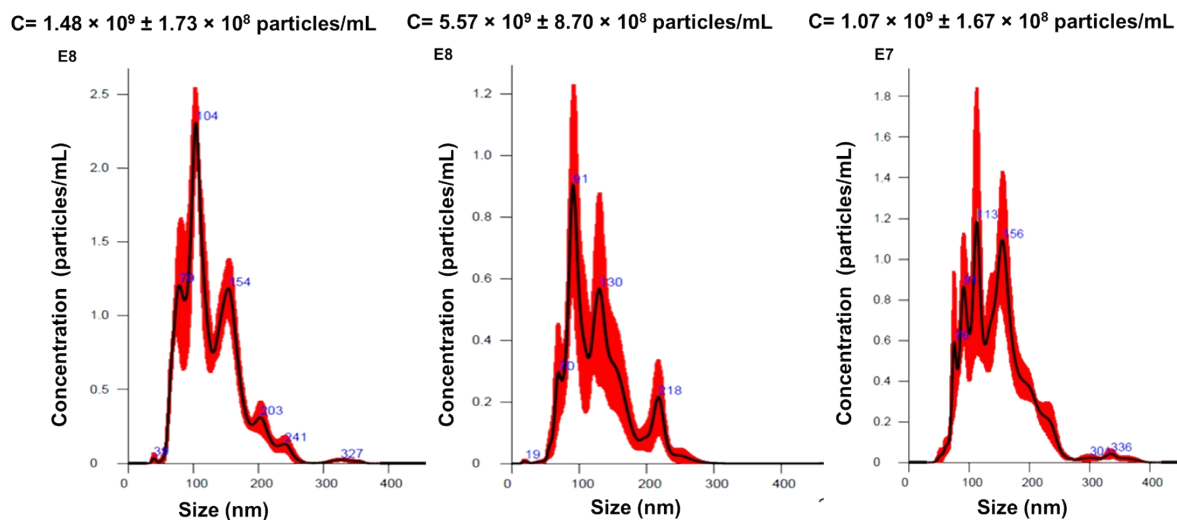
**Figure S3.** Optical microscopy images of PLA NPs drop-casted on Si substrate, prepared for collecting the Raman spectra.



**Figure S4.** The TEM micrographs of the formed PLA NPs.

**Table S1.** NTA analysis of generated PLA NPs from different ablation cycles.

<b>Sample</b>	<b>Concentration (Particles/mL)</b>	<b>Mean size (nm)</b>	<b>Standard deviation (nm)</b>
<b>1</b>	$1.48 \times 10^9 \pm 1.73 \times 10^8$	127.3	45.1
<b>2</b>	$5.57 \times 10^9 \pm 8.70 \times 10^8$	124.0	41.7
<b>3</b>	$1.07 \times 10^9 \pm 1.67 \times 10^8$	147.2	53.4
<b>4</b>	$1.29 \times 10^9 \pm 6.46 \times 10^7$	127.0	43.3



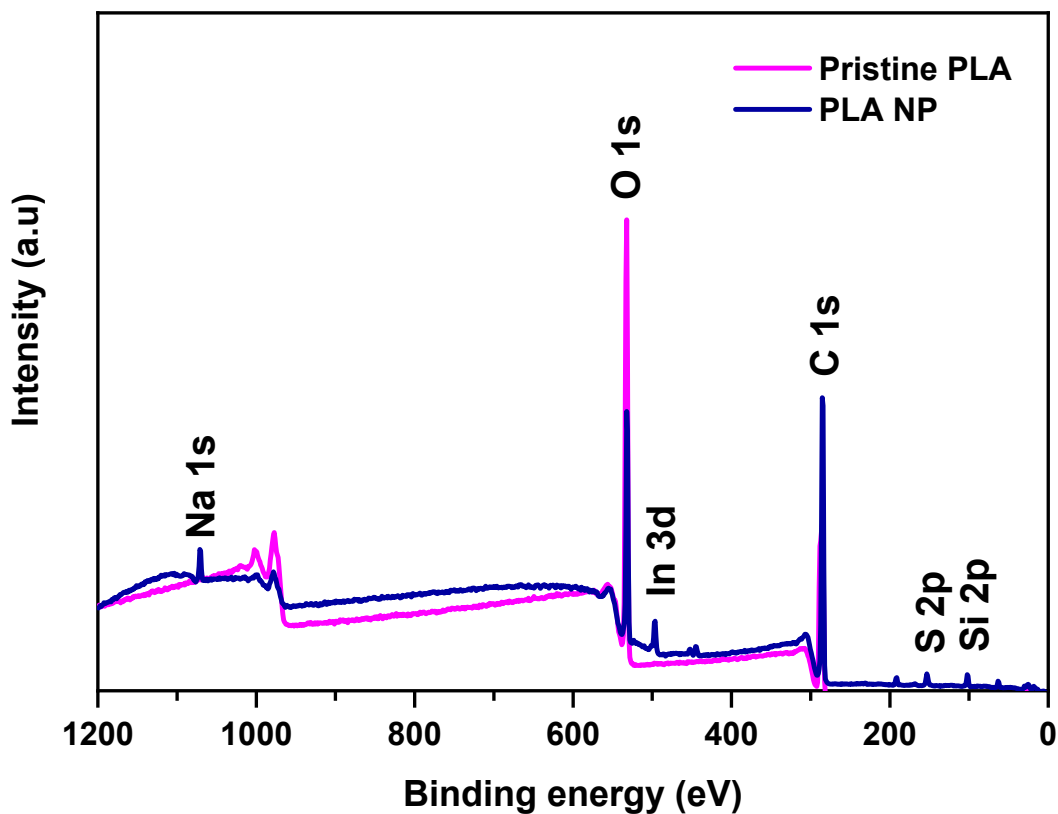
**Figure S5.** The concentration and size distribution of PLA NPs produced from different ablation cycles.

**Table S2.** XPS data analysis of C 1s peak.

	Relative area of different chemical bonds (At%)				
	<u>C</u> -C; <u>C</u> -H	<u>C</u> -O-C=O	O- <u>C</u> =O	<u>C</u> -OH	<u>COOH</u>
PLA film	39	30	30	0	0
PLA NP	56	19	4	17	1

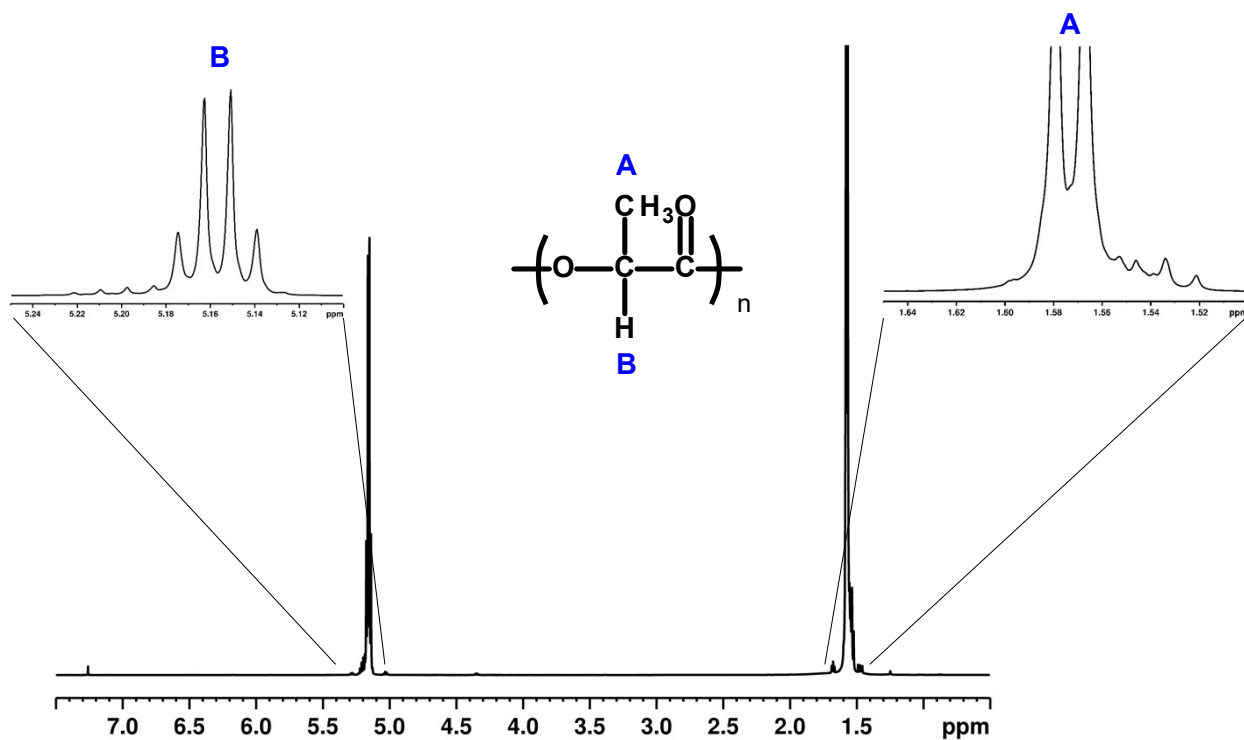
**Table S3.** XPS data analysis of O 1s peak.

	Relative area of different chemical bonds (At%)			
	<u>O</u> =C-O	C- <u>O</u> -C	SiO	InOx
PLA film	40	52	0	0
PLA NP	50	42	1.32	0.50



**Figure S6.** Comparative survey XPS spectra of PLA film and PLA NPs.

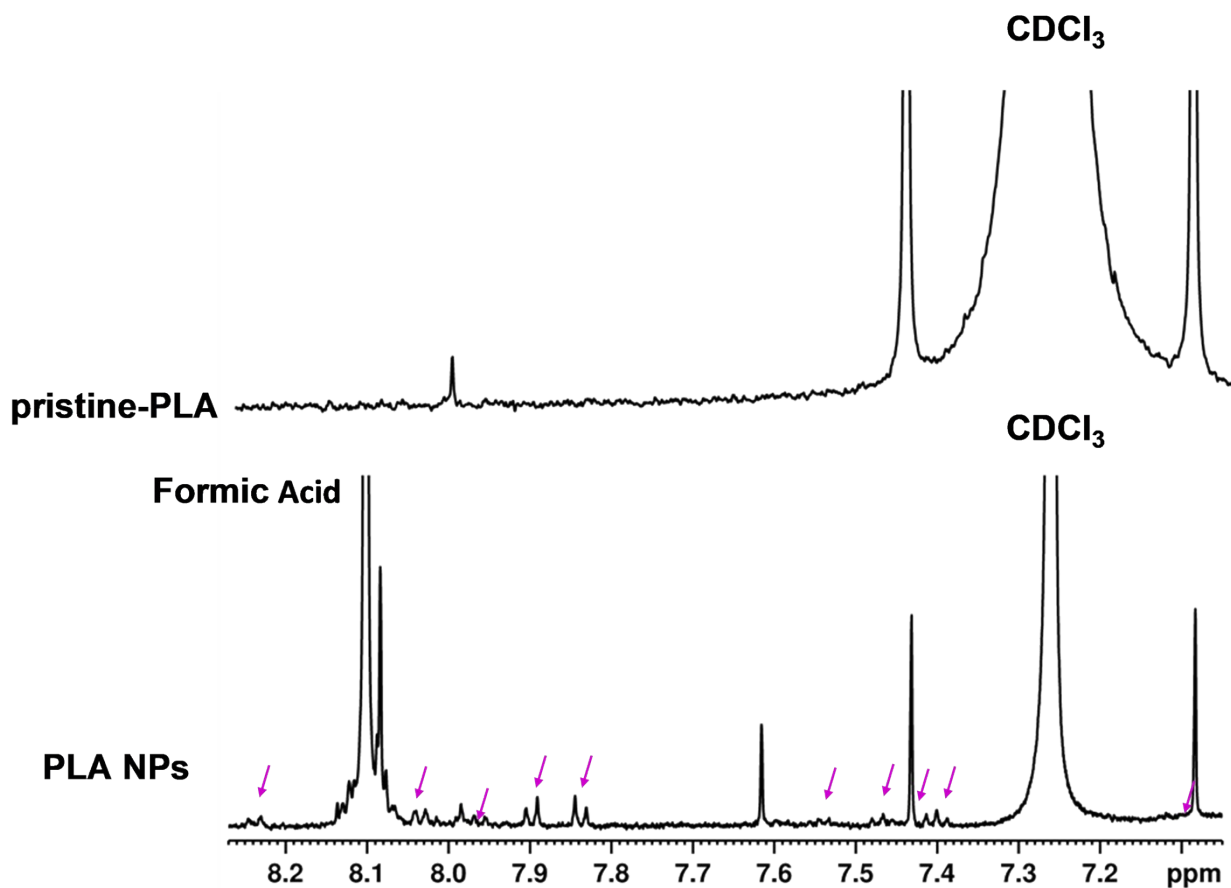
In the survey spectra, some additional elements can be observed. The presence of Indium (In) is due to the substrate on which the sample was drop-cast, and the other contaminants are in minute presence and could originate from the PLA pellets from which the films are prepared for the experiment. However, due to their minimal presence and the larger surface-to-volume ratio, they might not be detected in PLA films as readily as in the NPs.



**Figure S7.**  $^1\text{H}$  NMR of PLA film in  $\text{CDCl}_3$

The analysis is in agreement with previously reported results (1). The presence of minor signals can be observed in the zoomed-in regions, possibly attributed to the presence of different forms of PLA, i.e., poly(L-PLA), poly(rac-PLA), isotactic PLA, or syndiotactic PLA. (1).

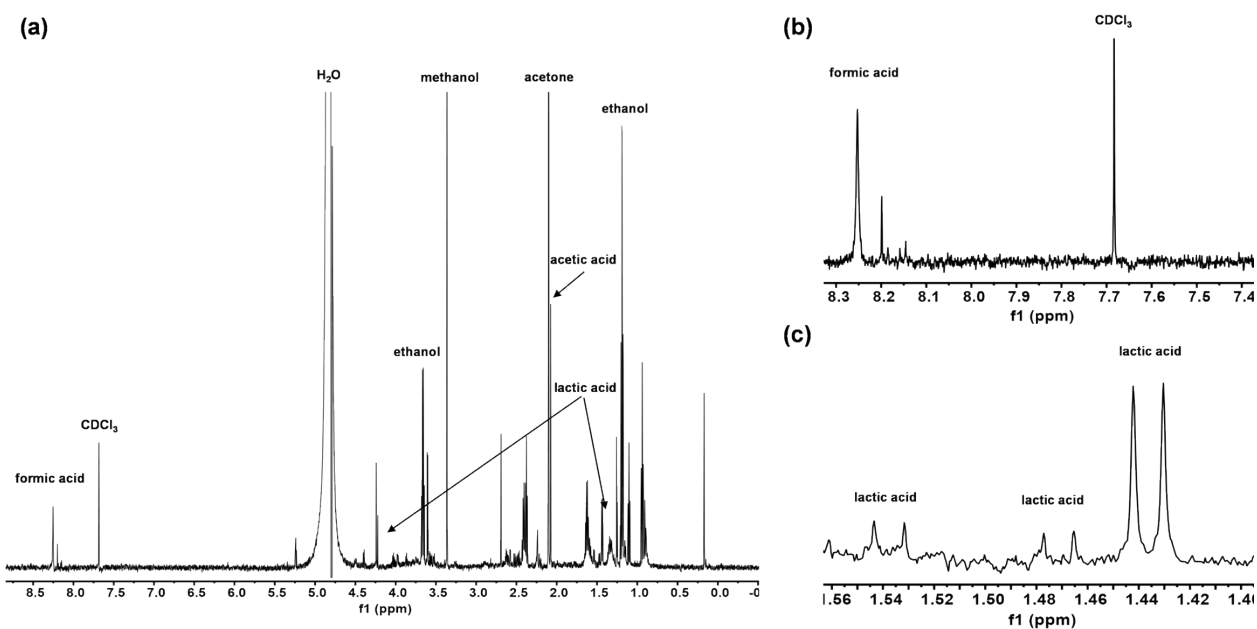




**Figure S8.**  $^1\text{H}$  NMR spectra of the aromatic region of the pristine PLA film (top) and PLA NPs (bottom) in  $\text{CDCl}_3$ . The purple arrows indicate signals of aromatic molecules visible only in the PLA NPs spectrum.

In the aromatic regions, it is possible to observe some unexpected and unassigned NMR signals, some of which could be ascribed to a phenyl ring (7.6-7.4 ppm) or a bi-substituted phenyl group (7.95-7.80 ppm). At 8.1 ppm, the  $^1\text{H}$  NMR signal of formic acid was assigned, and a small amount of formic acid was also spotted in the same NMR tube (data not shown). These unexpected signals, observed in PLA NPs, could be the result of the chemical degradation of PLA upon laser irradiation. It has been reported that the chemical degradation of PLA under elevated temperatures can cause intramolecular

transesterification, which gives rise to cyclic oligomers (2, 3). It was also noted that if the thermal degradation started in non-activated C-H bonds, the degradation could produce acidic groups with benzene rings (like O-phthalic acid) (2).



**Figure S9.** (a).  $^1\text{H}$  NMR spectra of the PLA NPs in  $\text{D}_2\text{O}$  showing the presence of lactic acid and different solvents. (b). Zoom-in of the aromatic region, showing the signals of  $\text{CDCl}_3$  and formic acid. (c). Zoom-in of lactic acid methyl groups, showing the presence of different methyl doublets, which can be due to different forms of lactic acid (monomer, dimer, etc.)

## References

1. Pérez JM, Ruiz C, Fernández I. Synthesis of a Biodegradable PLA: NMR Signal Deconvolution and End-Group Analysis. *Journal of Chemical Education*. 2021;99(2):1000-7.
2. Kopinke F-D, Remmler M, Mackenzie K, Möder M, Wachsen O. Thermal decomposition of biodegradable polyesters—II. Poly (lactic acid). *polymer Degradation and Stability*. 1996;53(3):329-42.
3. Kopinke F-D, Mackenzie K. Mechanistic aspects of the thermal degradation of poly (lactic acid) and poly ( $\beta$ -hydroxybutyric acid). *Journal of Analytical and Applied Pyrolysis*. 1997;40:43-53.