

Supporting Information for:

Production of Poly (Lactic Acid) Macromonomers in scCO₂ with Well-Defined Molecular Structure

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Macromonomer characterization

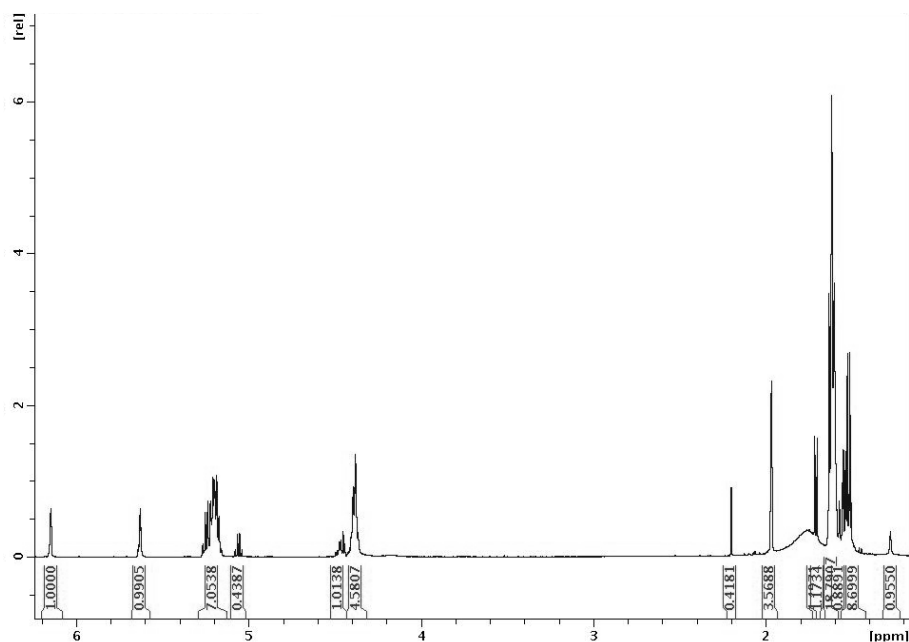


Figure S1. ¹H-NMR spectrum of Figure 2a with the peak integrals.

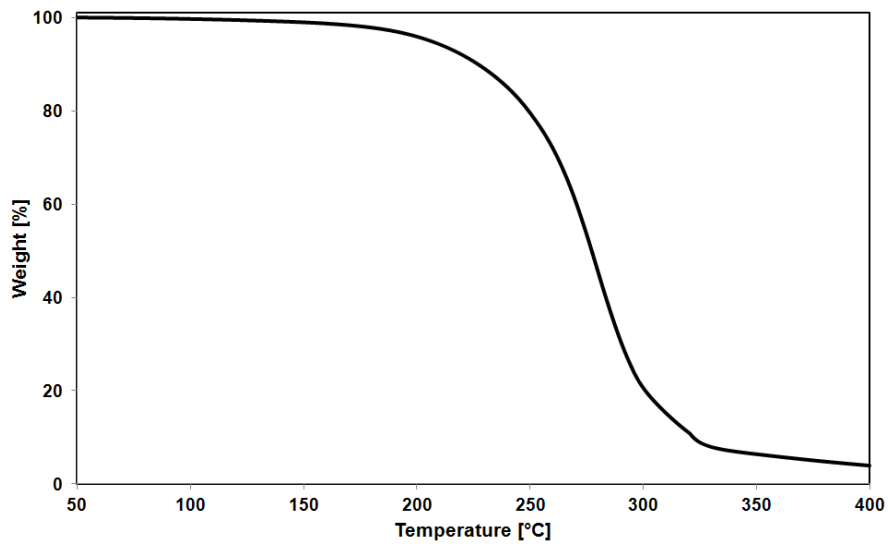


Figure S2. TGA thermogram of HEMA-LA₆ produced in scCO₂ at 90 °C for 4 days.

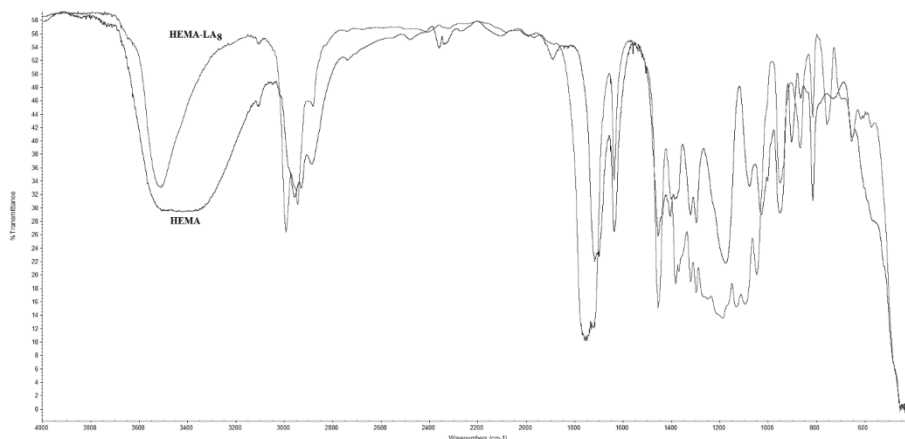
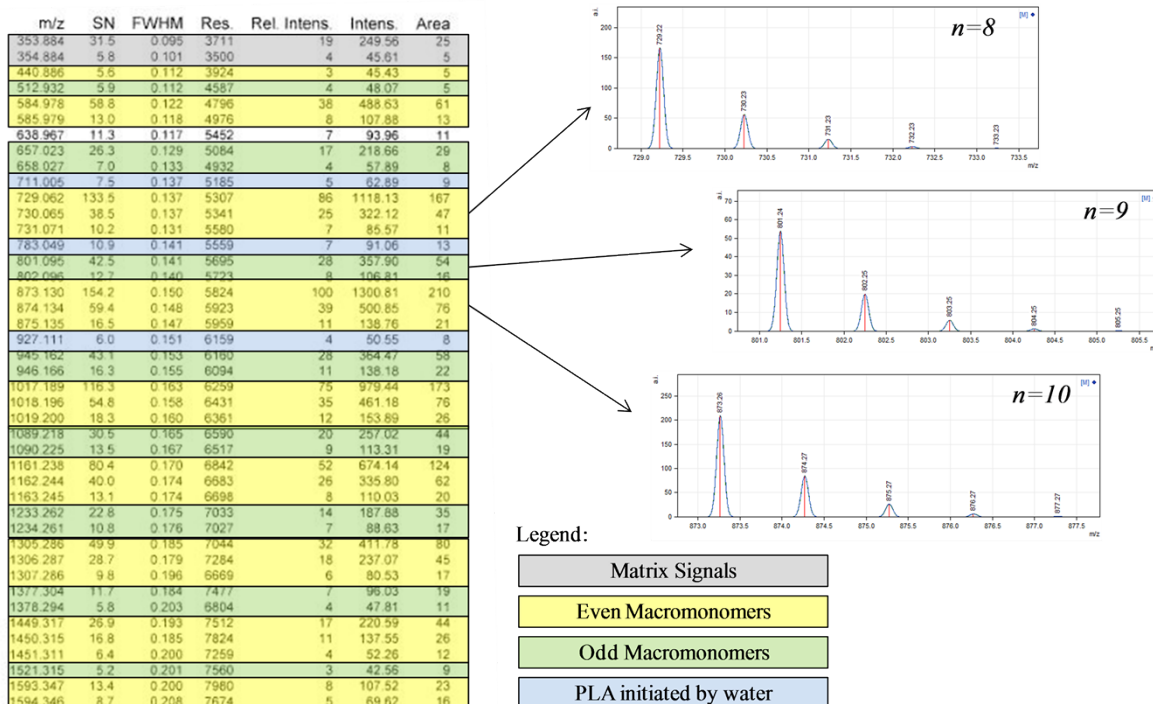


Figure S3. FT-IR spectra of HEMA and HEMA-LA₈ produced in scCO₂ at 90°C, 4 days.

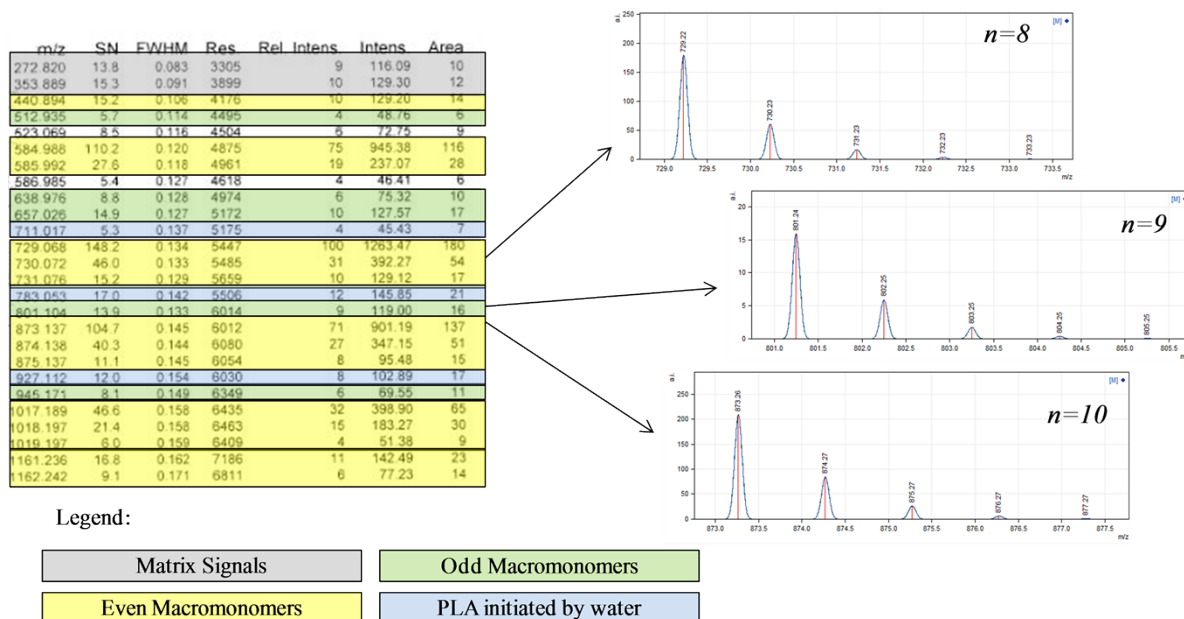
FT-IR analysis has been carried out in order to provide a further evidence of the macromonomer formation. A comparison between the spectra of HEMA and HEMA-LA₈ is shown in **Figure S3**. The increase of the signal in the region of 1700 cm⁻¹ is clearly visible, indicating a significant increase of the amount of ester bonds compared to HEMA, thus proving the addition of lactic acid units. Moreover, the region of the vinyl bond stretching does not show differences between the two compounds, proving the effective retaining of HEMA double bond after ROP reaction.

MALDI-TOF analyses

The main signals revealed from MALDI-TOF, and their comparison with the theoretical one are reported in **Table 2**, while the details of the spectra reported in **Figure 5** are listed here in **Figure S(4-5)**.



(a)



(b)

Figure S4. Mass list of MALDI-TOF for: (a) HEMA-LA₈ macromonomer produced at 130°C, 6h (**Figure 5a**), (b) HEMA-LA₈ macromonomer produced at 90°C, 72h (**Figure 5b**). Examples of isotopic distributions determined using the freeware mMass [Strohalm, M.; Kavan, D.; Novák, P.; Volný M.; Havlíček V.; *Analytical Chemistry* **2010**, 82, 4648-4651] of selected macromonomers are reported on the right side.

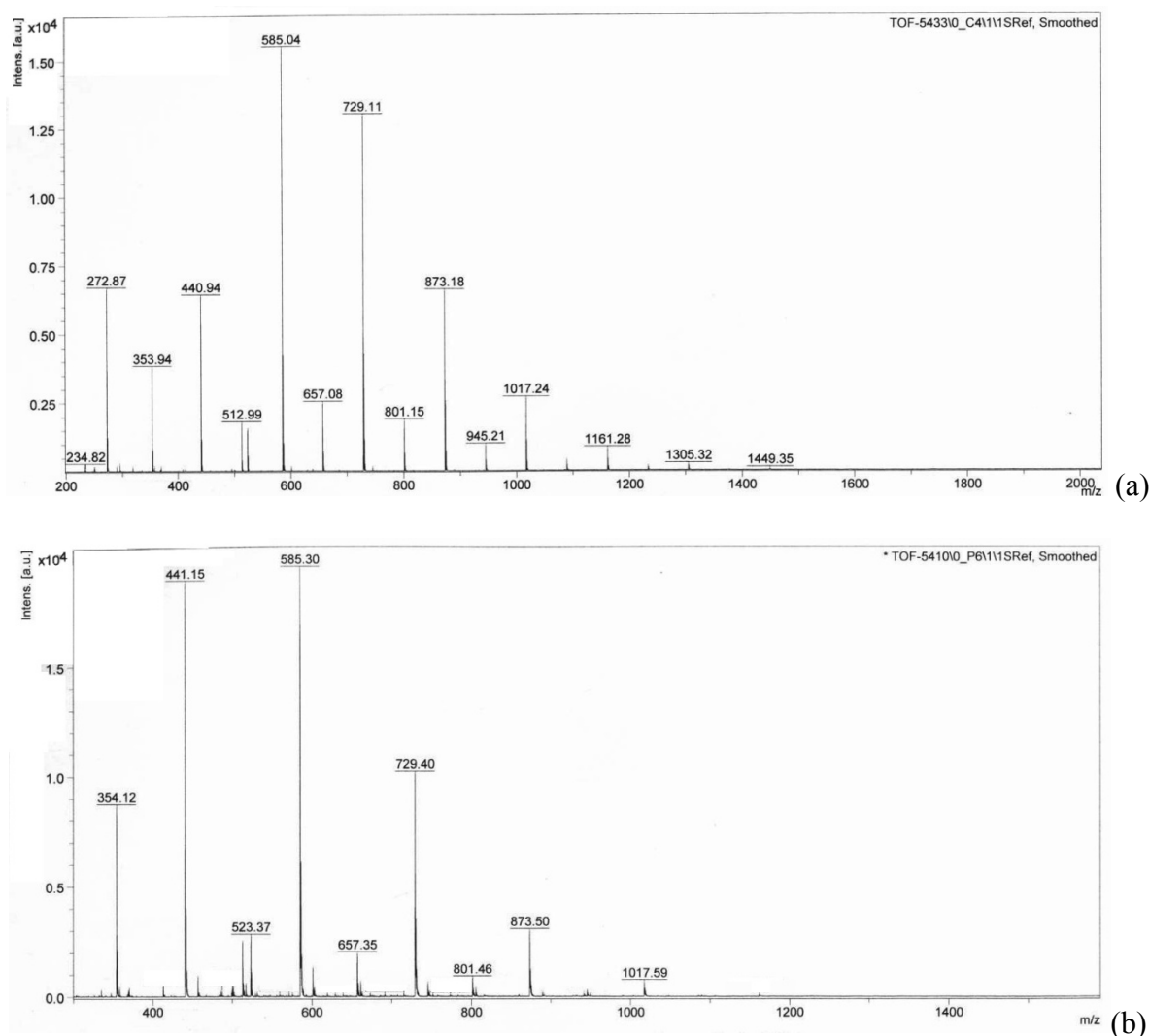
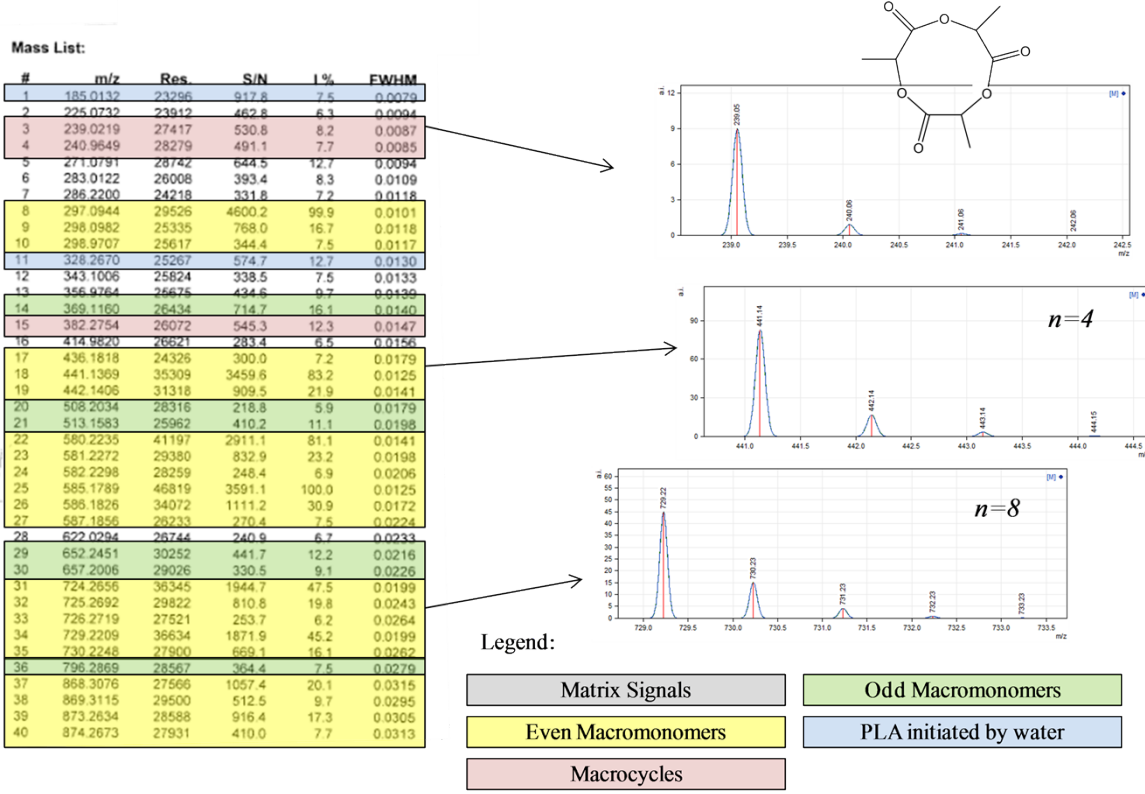
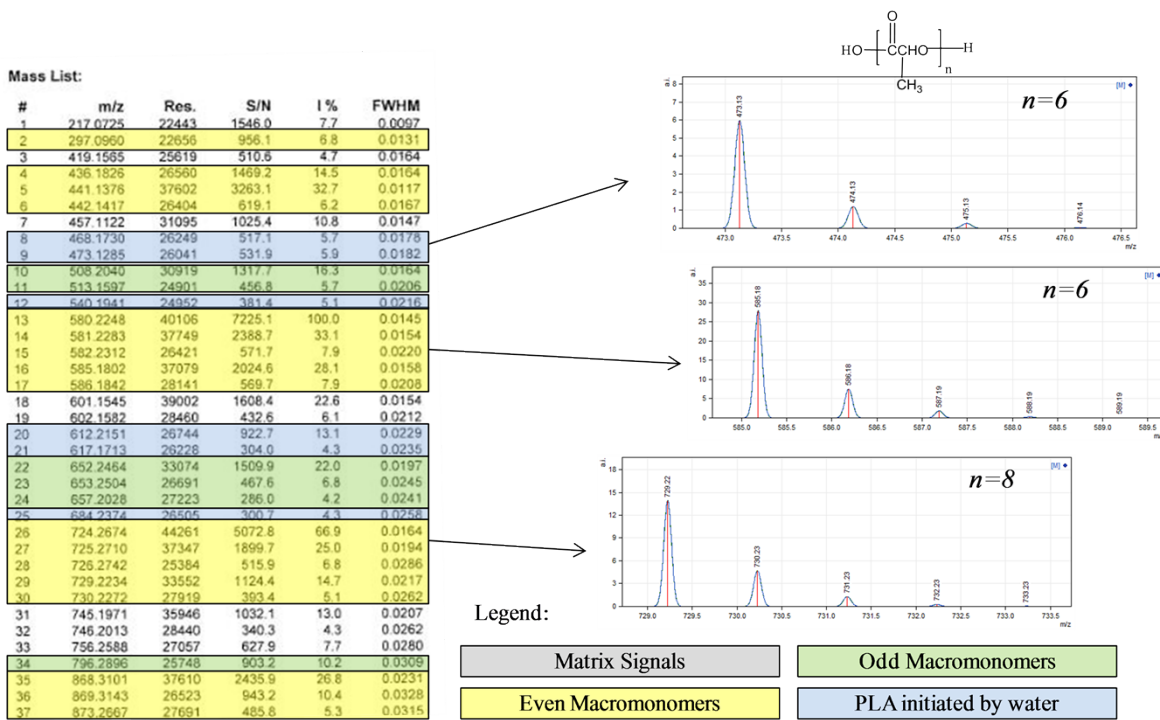


Figure S5. MALDI-TOF of HEMA-LA₆ macromonomer produced in scCO₂ at (a) 130 °C, 6h and (b) 90°C, 72h.

ESI analyses



(a)



(b)

Figure S6. Mass list of HEMA-LA₈ ESI for: (a) macromonomer produced at 130°C, 6h (**Figure 6a**), (b) macromonomer produced at 90°C, 72h (**Figure 6b**). Examples of isotopic distribution determined using the freeware mMass [Strohalm, M.; Kavan, D.; Novák, P.; Volný M.; Havlíček V.; *Analytical Chemistry* **2010**, *82*, 4648-4651] of selected macromonomers are reported on the right side; sodiated distribution are reported although species ionized with [NH₄]⁺ cation are also present.

Table S1. MALDI-TOF characterization of the macromonomers produced at the optimum reaction time.

macromonomer	Temp. [°C]	Time [h]	MALDI-TOF		
			M_n [Da]	M_w [Da]	M_w/M_n
HEMA-LA ₈	130	6	845	886	1.06
HEMA-LA ₈	110	18	844	903	1.07
HEMA-LA ₈	90	72	725	775	1.06
HEMA-LA ₆	130	6	697	728	1.05
HEMA-LA ₆	110	18	590	627	1.07
HEMA-LA ₆	90	72	581	614	1.05