Supporting Information for

Limonene-in-Water Pickering Emulsion and On-Demand Separation Using Thermo-Responsive Biodegradable Nanoparticles

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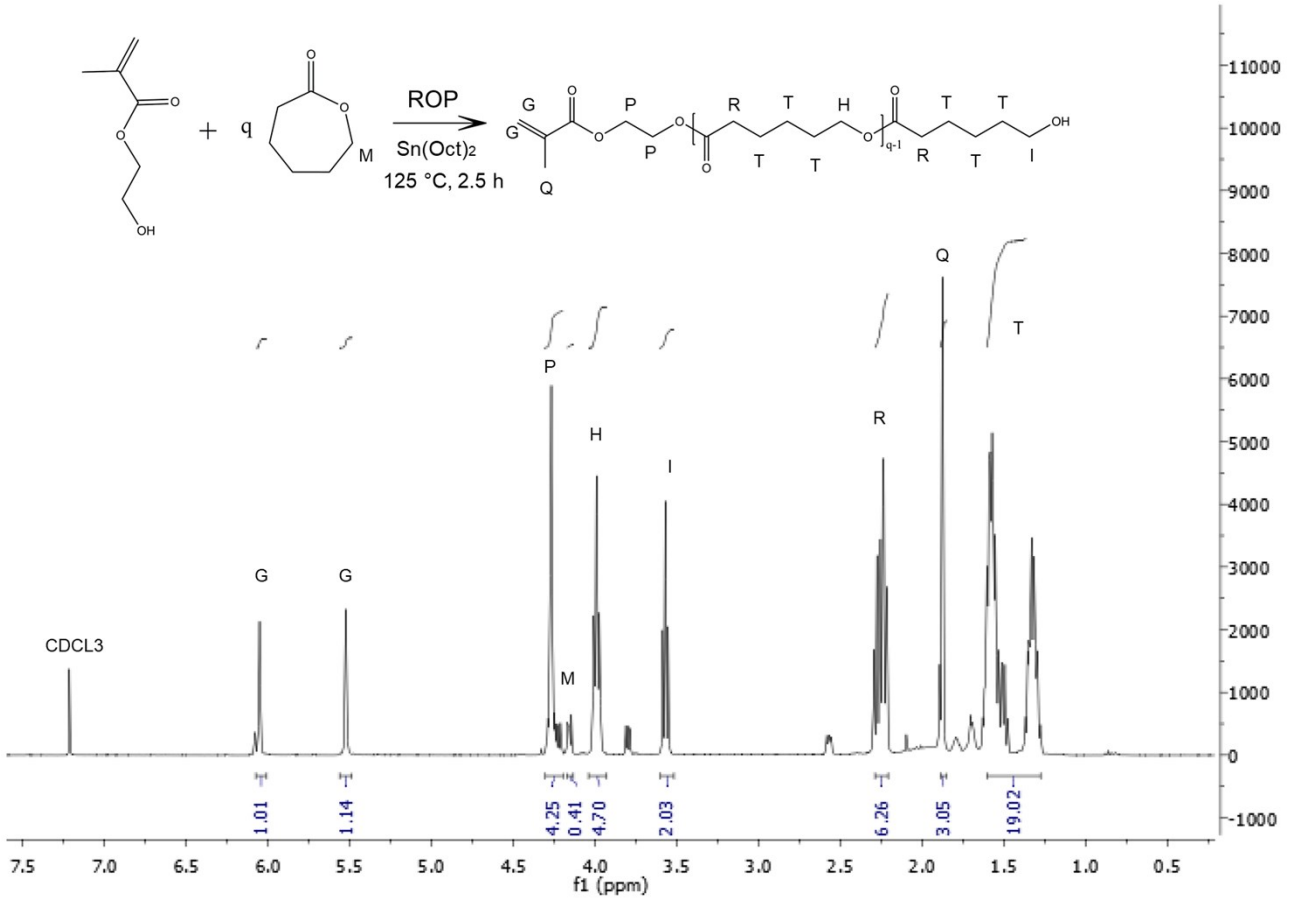

Figure S1: *[1]H-NMR characterization and proton assignment for HEMACL3 (q=3). The analysis was performed on a Bruker Ultrashield 400 MHz spectrometer using deuterated chloroform ($CDCl_3$) as solvent.*

The monomer conversion (X_{CL}) was calculated according to **eq. S1**:

$$X_{CL} = \left(\frac{H + I}{H + I + M}\right) * 100 \quad \text{(S1)}$$

Where M represents the area under the signal of the two hydrogens adjacent to the ester group in the CL monomer, H indicates the peaks equivalent to the two hydrogen atoms adjacent to the ester group and I corresponds to hydrogens of the carbon near the chain-end hydroxyl group.

The degree of polymerization (q) was obtained using the area of the same signals according to **eq. S2**:

$$q = \frac{H}{I} + 1 \quad \text{(S2)}$$

Table S1: *Properties of the oligoesters synthesized. The ε-caprolactone conversion (X_{CL}) and average macromonomer chain length (q) were determined via NMR according to eqs. S1 and S2. The number-average molecular weight (Mn) and dispersity (Đ) were obtained via GPC.*

Sample	X_{CL} **[%]**	***q*** **[-]**	**Mn [Da]**	**Đ [-]**
HEMACL3	94.25	3.31	577	1.25
HEMACL5	98.91	5.24	858	1.22

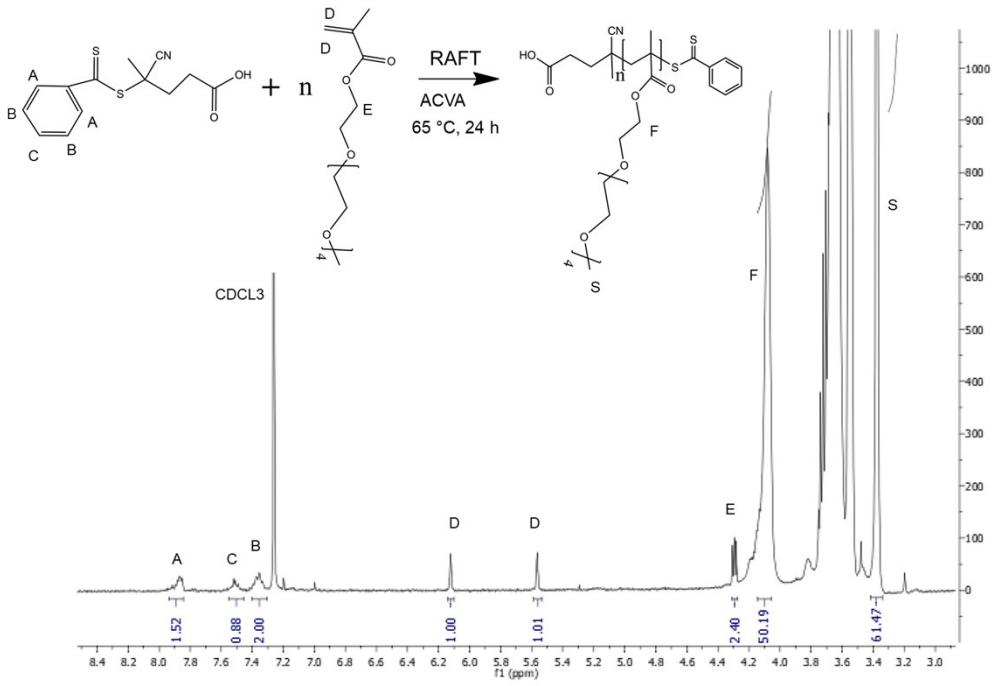

Figure S2: *^{1}H-NMR characterization and proton assignment for 20EG$_4$ (n=20). The analysis was performed on a Bruker Ultrashield 400 MHz spectrometer using deuterated chloroform ($CDCl_3$) as solvent.*

The monomer conversion (X_{EG_4}) was calculated according to **eq. S3**:

$$X_{EG_4} = \left(\frac{F}{E+F}\right) * 100 \tag{S3}$$

Where E and F are the area of the peaks attributed to the two hydrogens close to the oxygen in the unreacted monomer and polymer, respectively.

The degree of polymerization (n) was calculated with **eq. S4:**

$$n = \frac{F}{B} \tag{S4}$$

Where B is associated to the two hydrogens of the aromatic ring in the chain transfer agent.

Table S2: *Properties of the macro CTAs synthesized. The monomer conversion (X_{EG4}) and average chain length (n) were determined via NMR according to eqs. S3 and S4. The number-average molecular weight (Mn) and dispersity (Đ) were obtained via GPC.*

Sample	X_{EG_4} [%]	*n* [-]	Mn [Da]	Đ [-]
$20EG_4$	95.43	25.09	8456	1.12
$40EG_4$	96.23	43.41	12013	1.07

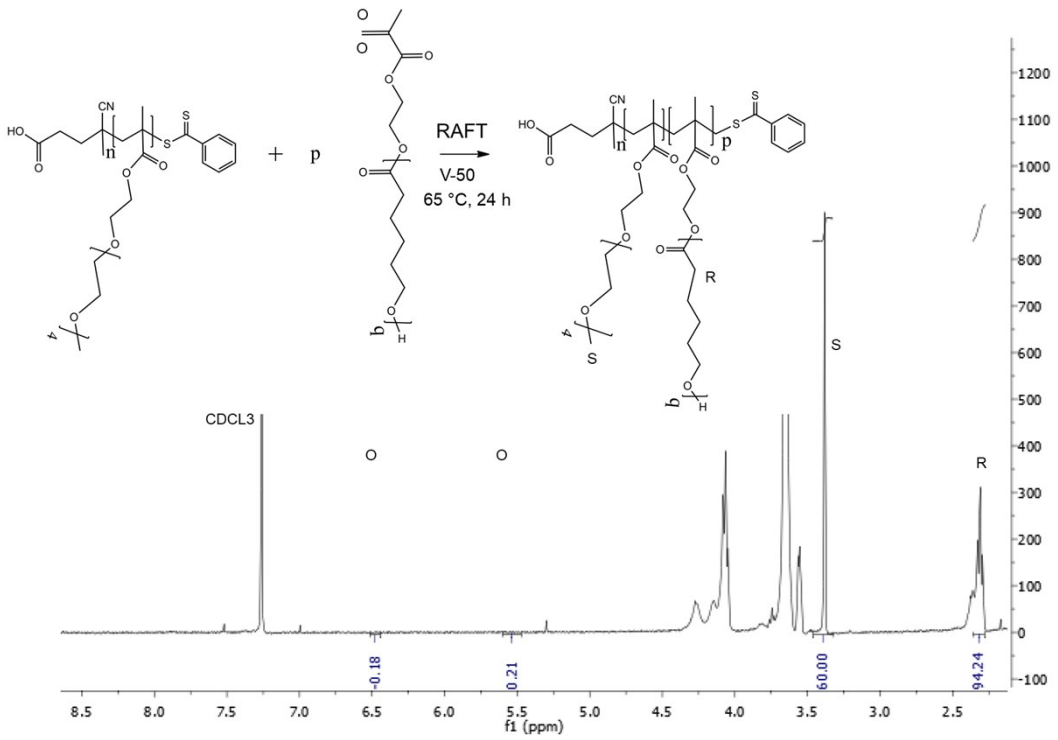

Figure S3: *[1]H-NMR characterization and proton assignment for $20EG_4$-15CL3 (p=15). The analysis was performed on a Bruker Ultrashield 400 MHz spectrometer using deuterated chloroform ($CDCl_3$) as solvent.*

The monomer conversion (X) according to **eq. S5**:

$$X = \left(1 - \frac{2qO}{R}\right) * 100 \tag{S5}$$

R is the area of the peak attributed to the two vinyl hydrogens in the unreacted monomer, O is the area of the peak associated to the hydrogens near the carbonyl group either in the monomer or in the polymer and q the average chain length of the macromonomer.

The degree of polymerization (p) was calculated according to **eq. S6:**

$$p = \frac{\frac{R}{2q}}{\frac{S}{3n}} = \frac{3nR}{2qS} \quad \text{(S6)}$$

Where R and S are the areas of the corresponding peaks shown in **Figure S3**, while q and n are the average chain lengths of the macromonomer and the macro CTA adopted using the synthesis and reported in **Table S1** and **Table S2**, respectively.

Table S3: *Properties of the synthesized NPs in terms of monomer conversion (X) and average degree of polymerization (p) determined from ^{1}H NMR and number-average molecular weight (Mn) and dispersity (Đ) measured via GPC.*

Sample	*X* [%]	***p*** [-]	**Mn** [Da]	**Đ** [-]
20EG$_4$-15CL3	98.90	15.42	23145	1.11
20EG$_4$-25CL3	98.65	23.27	26432	1.11
20EG$_4$-50CL3	98.90	52.59	42145	1.21
40EG$_4$-15CL3	98.21	17.30	28121	1.11
40EG$_4$-25CL3	99.62	24.80	29573	1.17
40EG$_4$-50CL3	99.16	53.32	52890	1.21
20EG$_4$-25CL5	98.72	25.17	32113	1.26
40EG$_4$-15CL5	99.52	13.51	31065	1.19
40EG$_4$-25CL5	99.26	27.43	43125	1.21
40EG$_4$-50CL5	97.94	48.15	56859	1.12
20EG$_4$-25CL3_Rh	99.33	26.78	28819	1.32

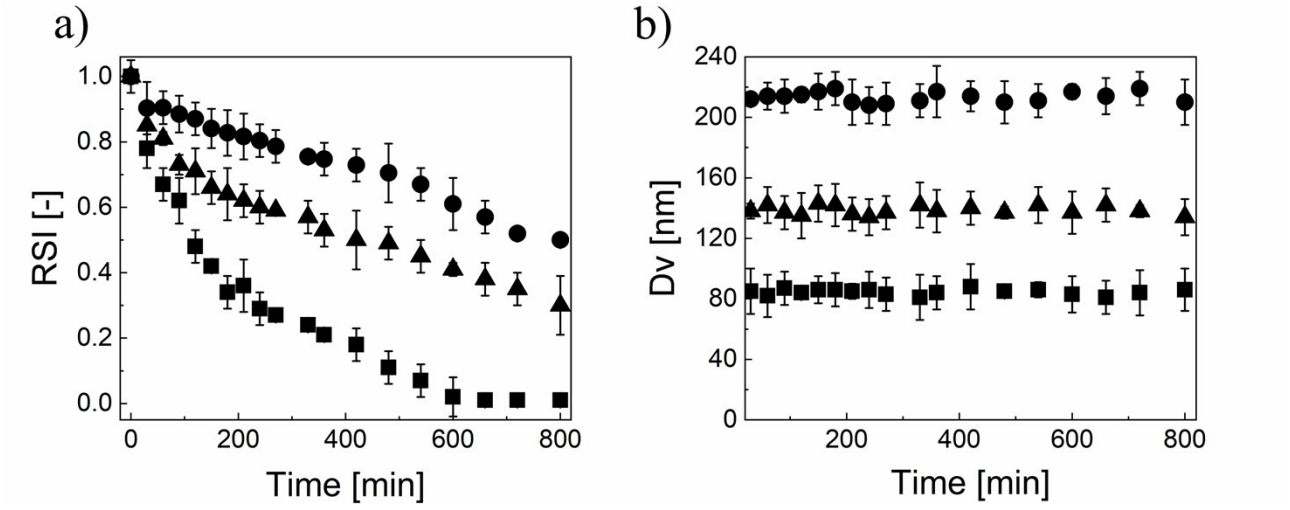

Figure S4: *(a) Relative scattering intensity (RSI) as a function of time in the case of 40EG$_4$-15CL5 (■) 40EG$_4$-25CL5 (▲) and 40EG4-50CL5 (●), when the samples are diluted to 0.5% w/w in a solution of NaOH 0.1 M. (b) NP size as function of time in the case of 40EG$_4$-15CL5 (■) 40EG4-25CL5 (▲) and 40EG4-50CL5 (●), when the samples are diluted to 0.5% w/w in a solution of NaOH 0.1 M.*

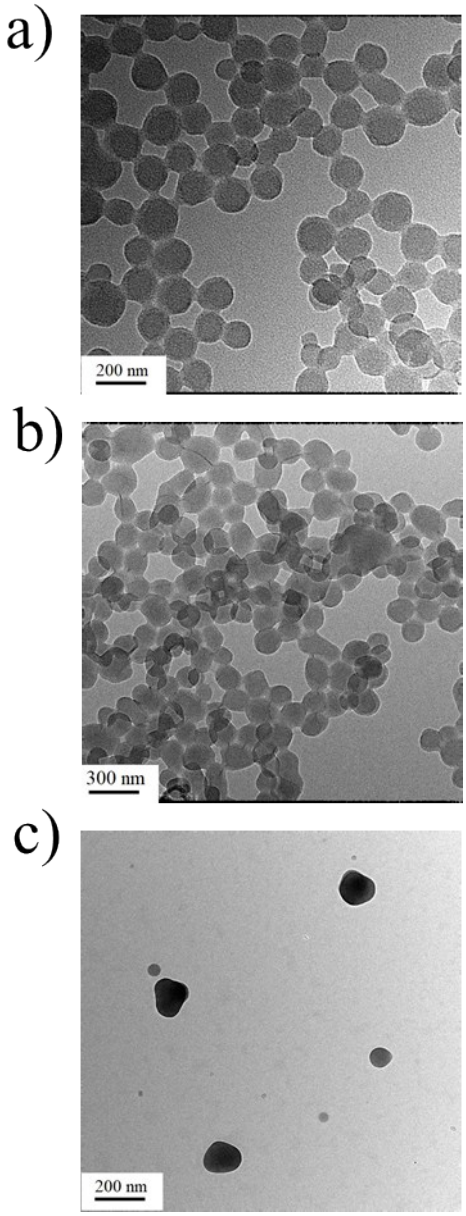

Figure S5: (a) TEM image of $40EG_4$-50CL5, scale bar = 200 nm. (b) TEM image of $20EG_4$-50CL3, scale bar = 300 nm. (c) TEM image of $20EG_4$-25CL3_Rh, scale bar = 200 nm