

## Supporting Information

# Retinol initiated poly(lactide)s: Stability upon polymerization and nanoparticle preparation

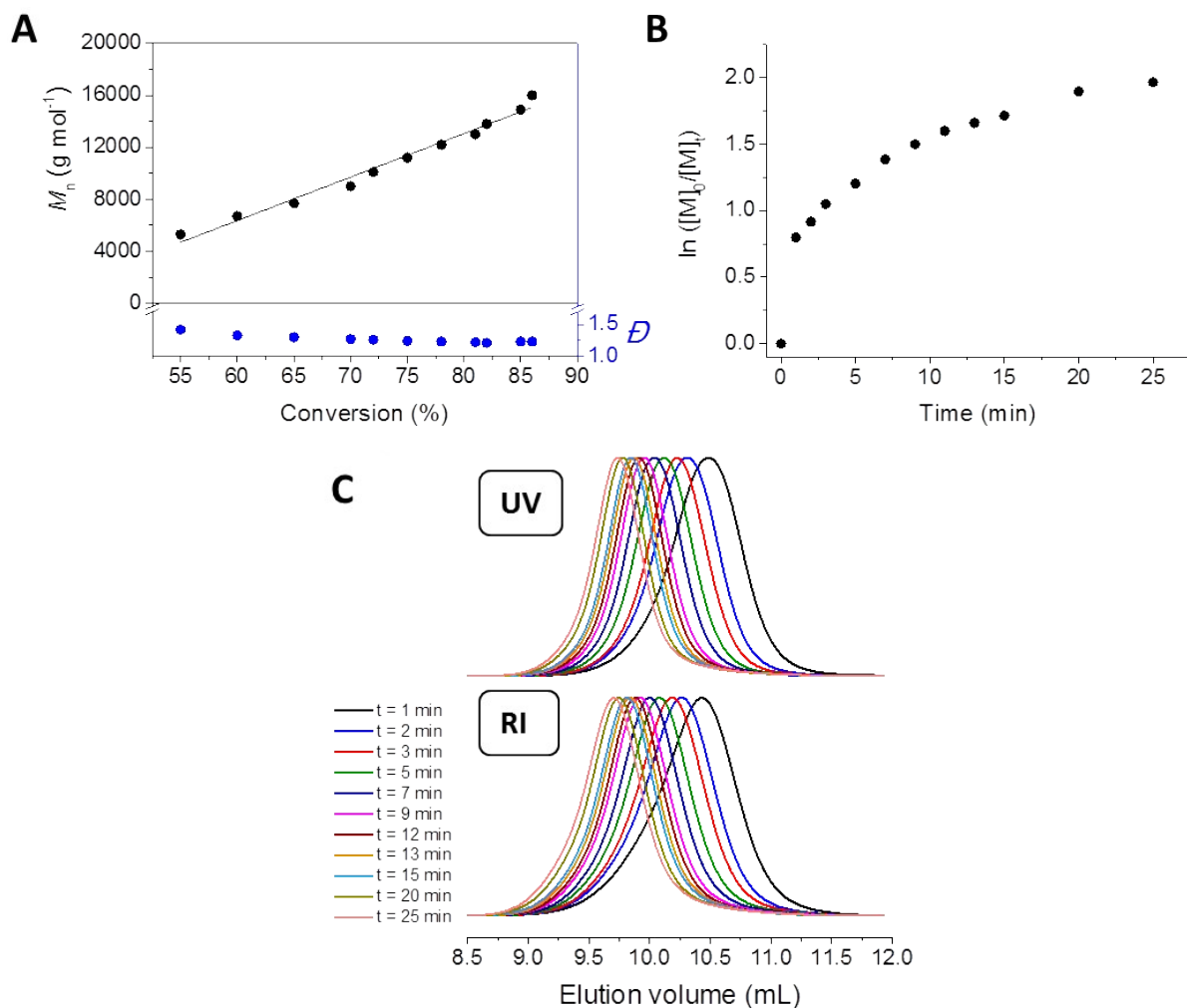
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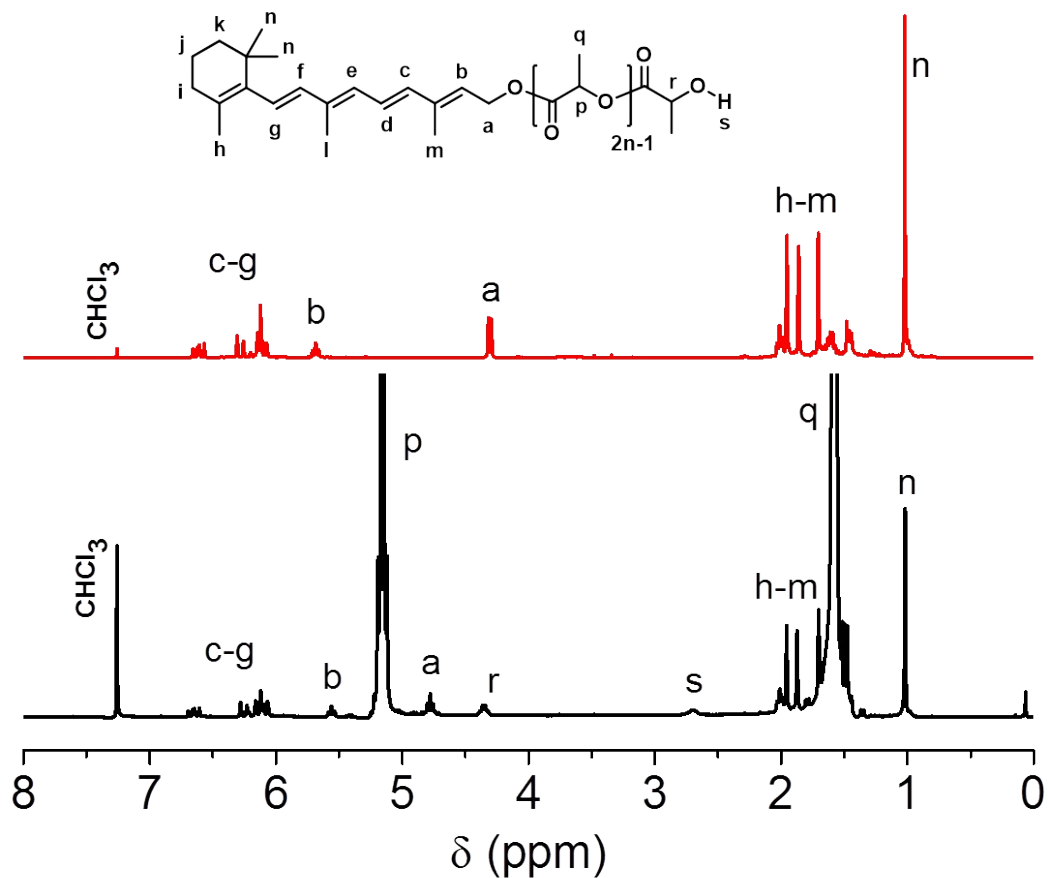
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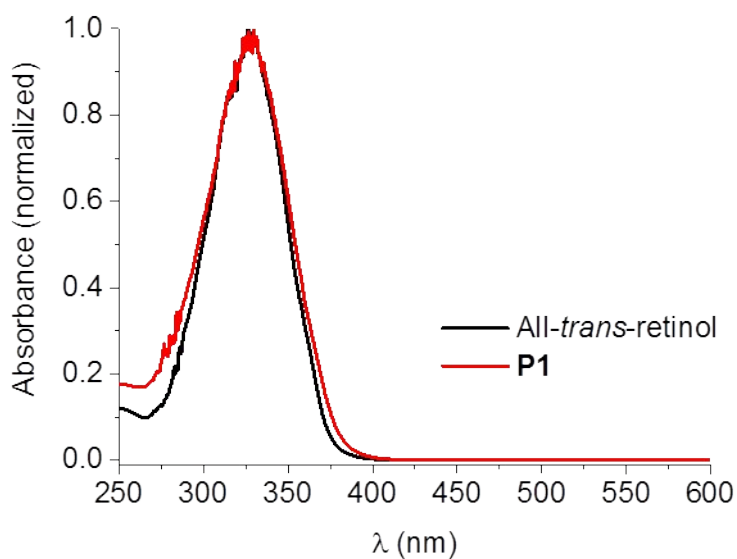
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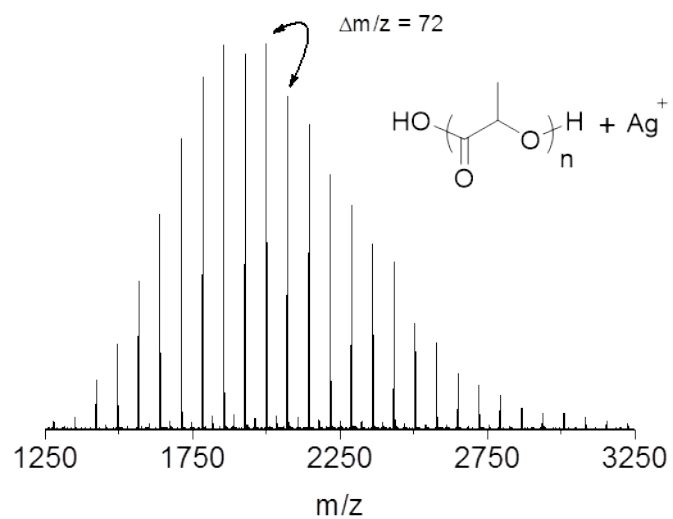
**Figure S1.** Kinetic study of retinol initiated ROP of L-lactide performed at room temperature in THF with a total monomer concentration of 1 mol L<sup>-1</sup>. [M]/[Retinol]/[Ca]= 100/1/0.5. **(A)** Dependence of  $M_{n,SEC}$  and  $\bar{D}$  of the obtained PLA on the conversion of L-lactide. **(B)** Semilogarithmic kinetic plot. **(C)** Overlay of the SEC elugrams recorded with RI and UV ( $\lambda = 340$  nm) detection.



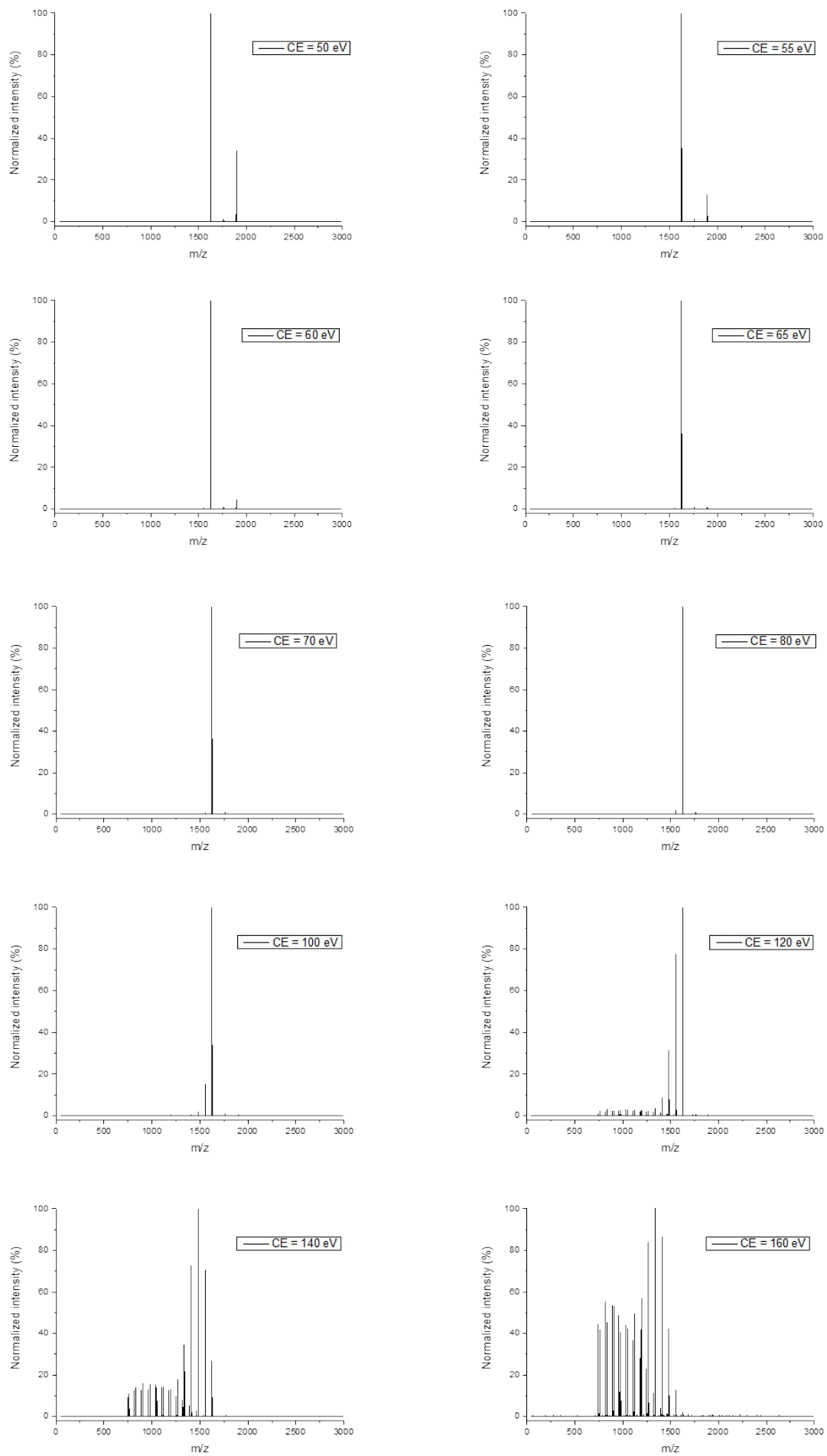
**Figure S2.** Overlay of  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3$ ) of retinol and retinol initiated PLA (**P1**) together with the assignment of the observed peaks.



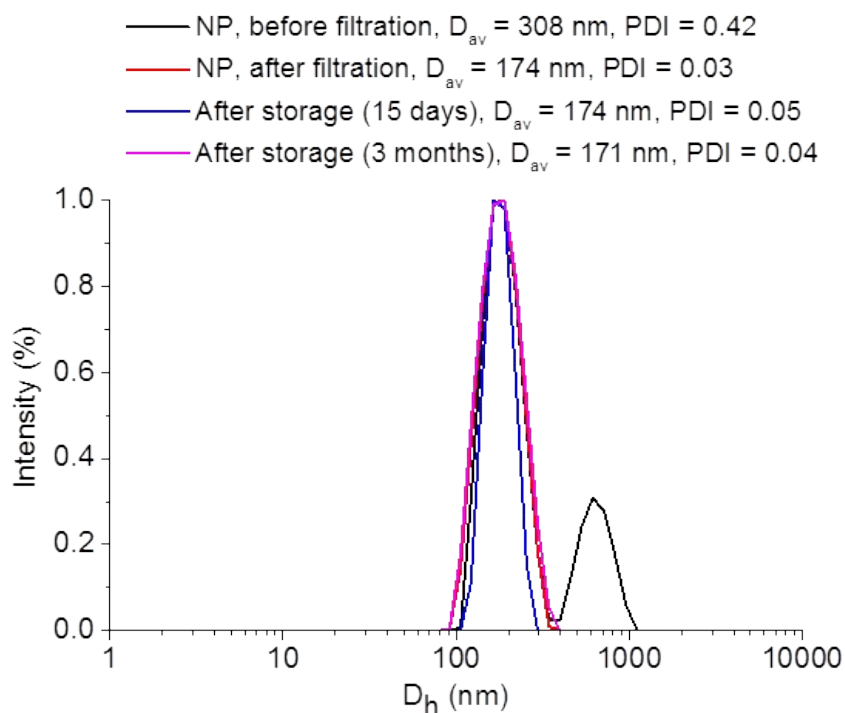
**Figure S3.** Overlay of UV/vis spectra of all-*trans*-retinol ( $c = 0.015 \text{ mg mL}^{-1}$ ) and **P1** ( $0.185 \text{ mg mL}^{-1}$ ) recorded in THF.



**Figure S4.** MALDI-ToF mass spectrum of **P1** (AgTFA, DCTB).



**Figure S5.** ESI-Q-ToF MS/MS spectra of sodiated **P1** at  $m/z = 1893.7$  recorded at different collision energy values (50 to 160 eV).

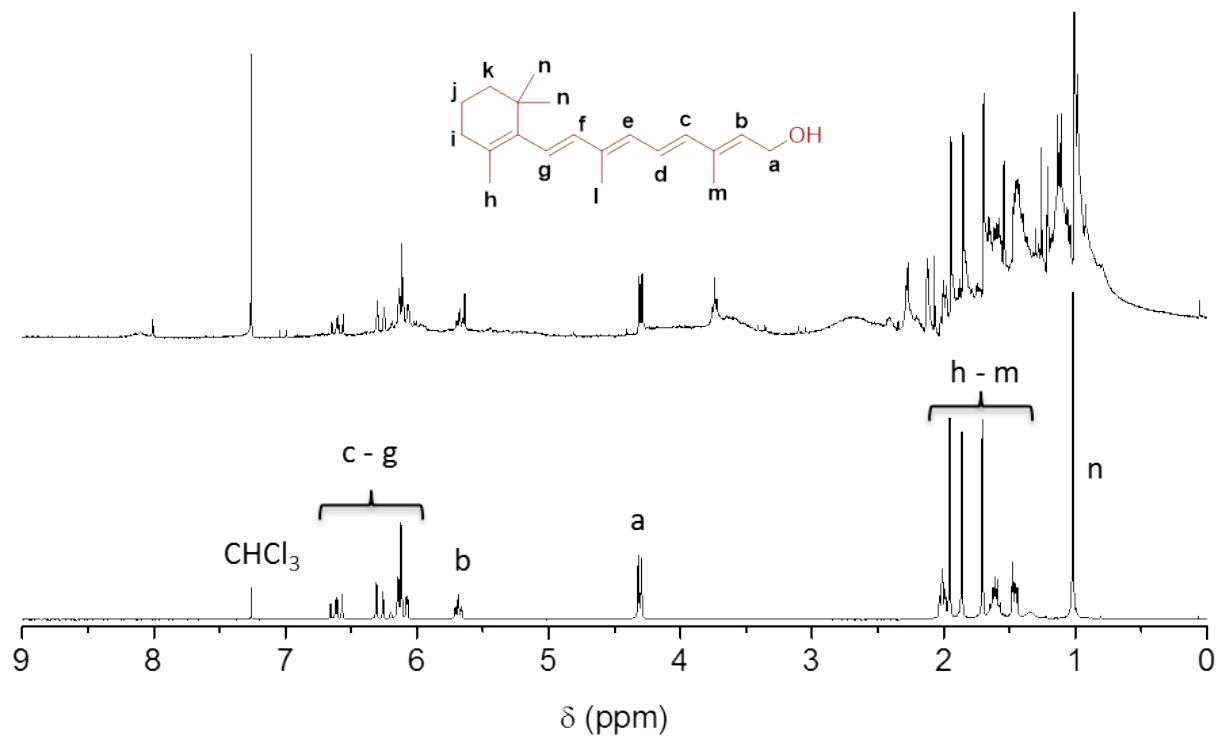


**Figure S6.** Normalized intensity size distributions of **P1** nanoparticles in water.

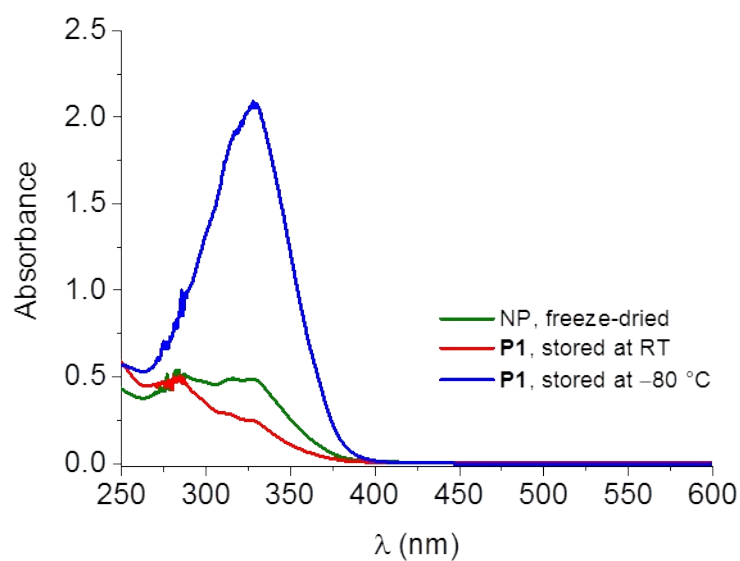
**Table S1.** Zeta potential values of the nanoparticles in aqueous suspension.

Entry	Method <sup>a</sup>	Zeta potential <sup>b</sup> [mV]
<b>P1</b>	AW	$-53 \pm 2$
	WA	$-40 \pm 1$
<b>P2</b>	AW	$-52 \pm 2$
	WA	$-49 \pm 2$
<b>P3</b>	AW	$-48 \pm 2$
	WA	$-32 \pm 1$
<b>P4</b>	AW	$-30 \pm 1$
	WA	$-50 \pm 2$

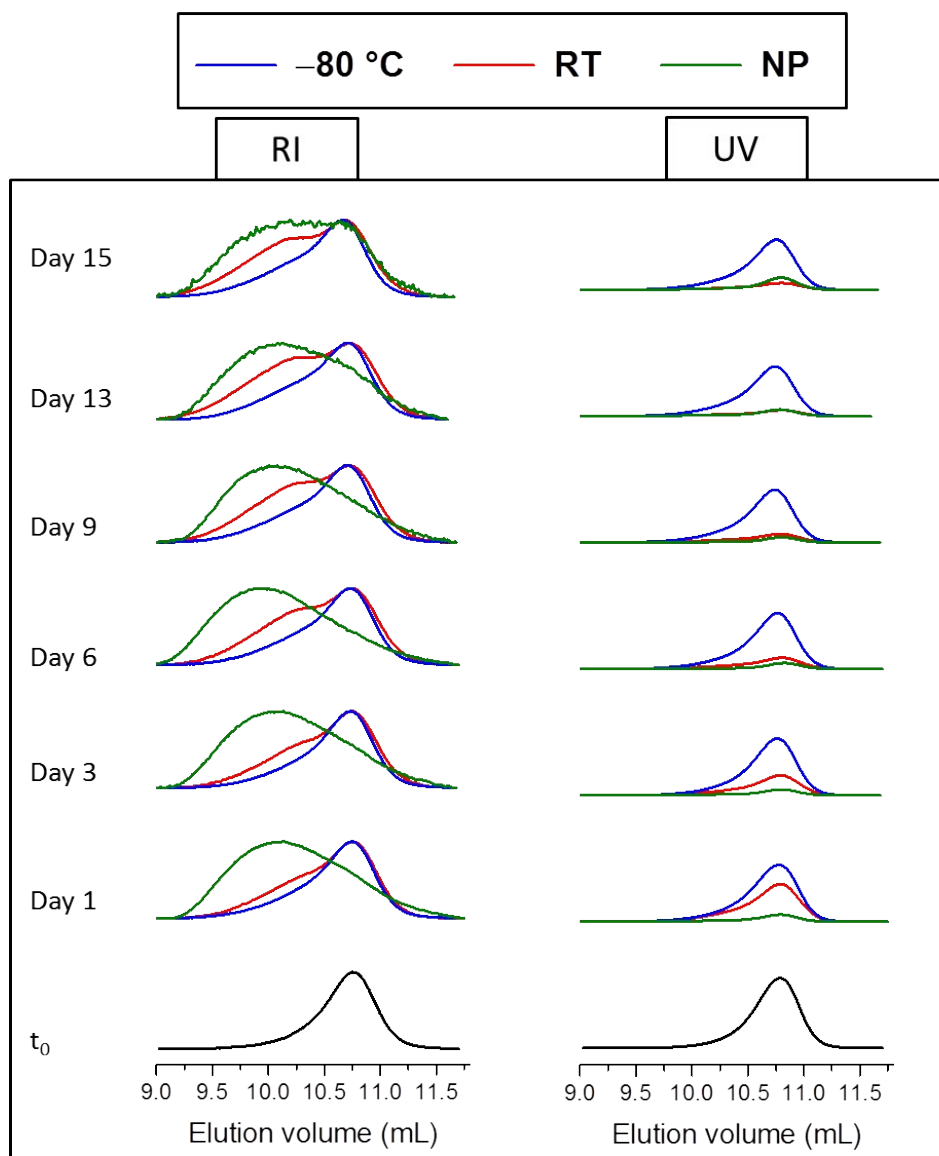
<sup>a</sup>AW, dropping acetone to water; WA, dropping water to acetone. <sup>b</sup>Average values of three zeta potential measurements.



**Figure S7.** Overlay of  $^1\text{H}$  NMR spectra of fresh retinol (bottom) and retinol after storage for 15 days at room temperature under daylight (top).

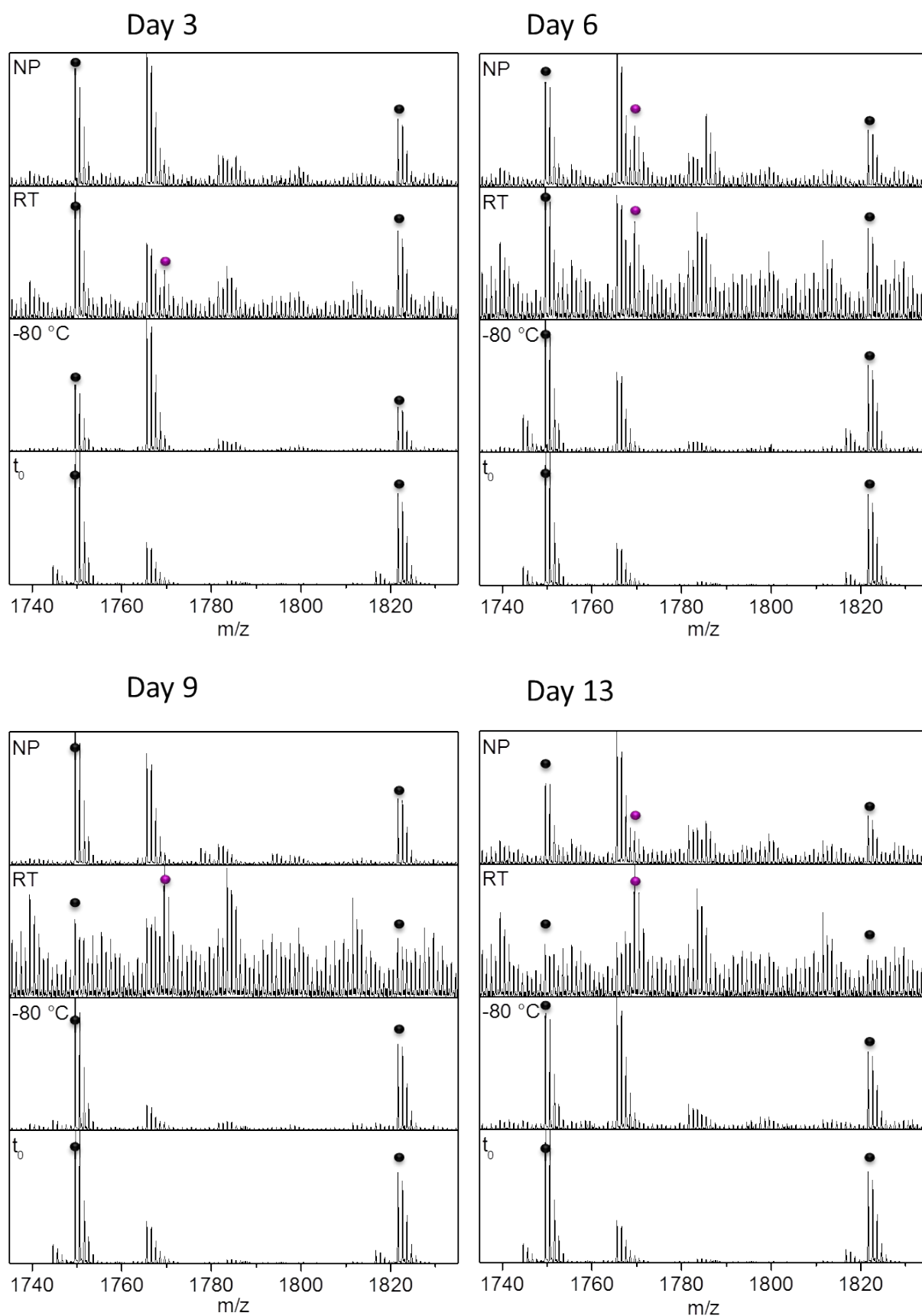


**Figure S8.** Overlay of UV/vis spectra of the freeze-dried NP with P1 stored at RT and  $-80\text{ }^\circ\text{C}$  for 15 days.

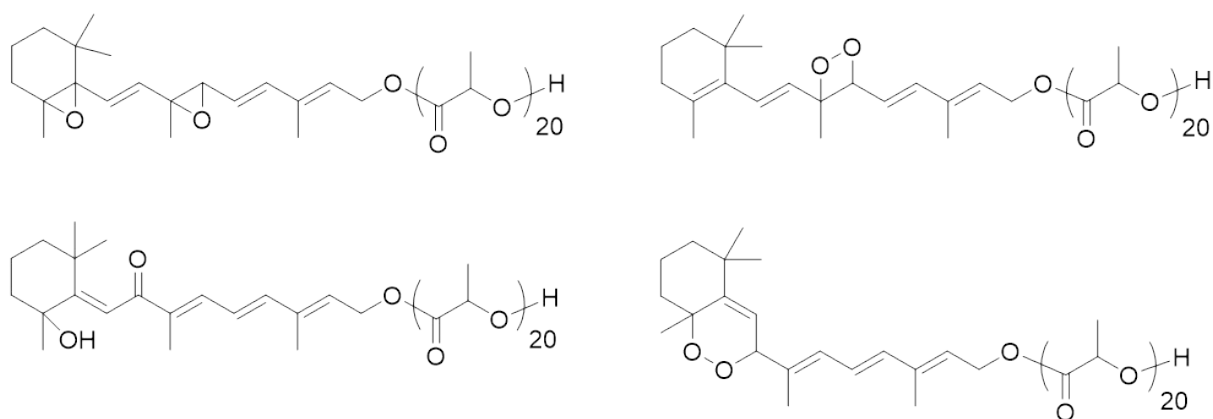
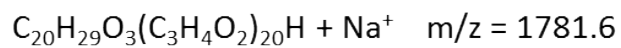


**Figure S9.** Overlay of normalized SEC elugrams recorded with RI and UV ( $\lambda = 340$  nm) detection during stability tests of **P1** ( $t_0$ , and different storage conditions; RT and  $-80$  °C) and the corresponding NP. SEC curves recorded with UV detection were normalized according to corresponding RI signals.

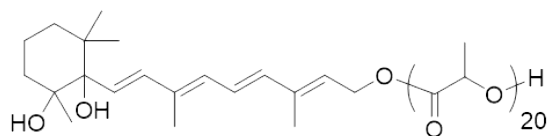
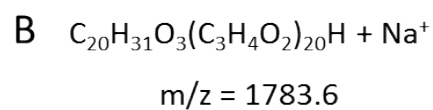
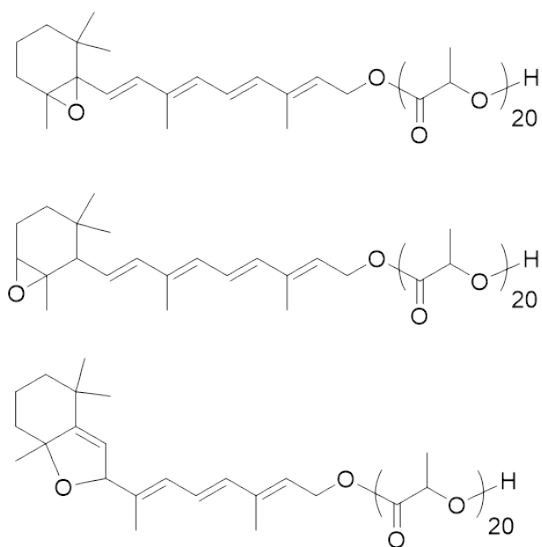
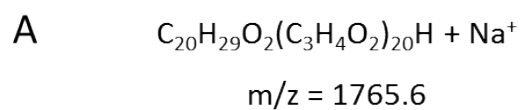




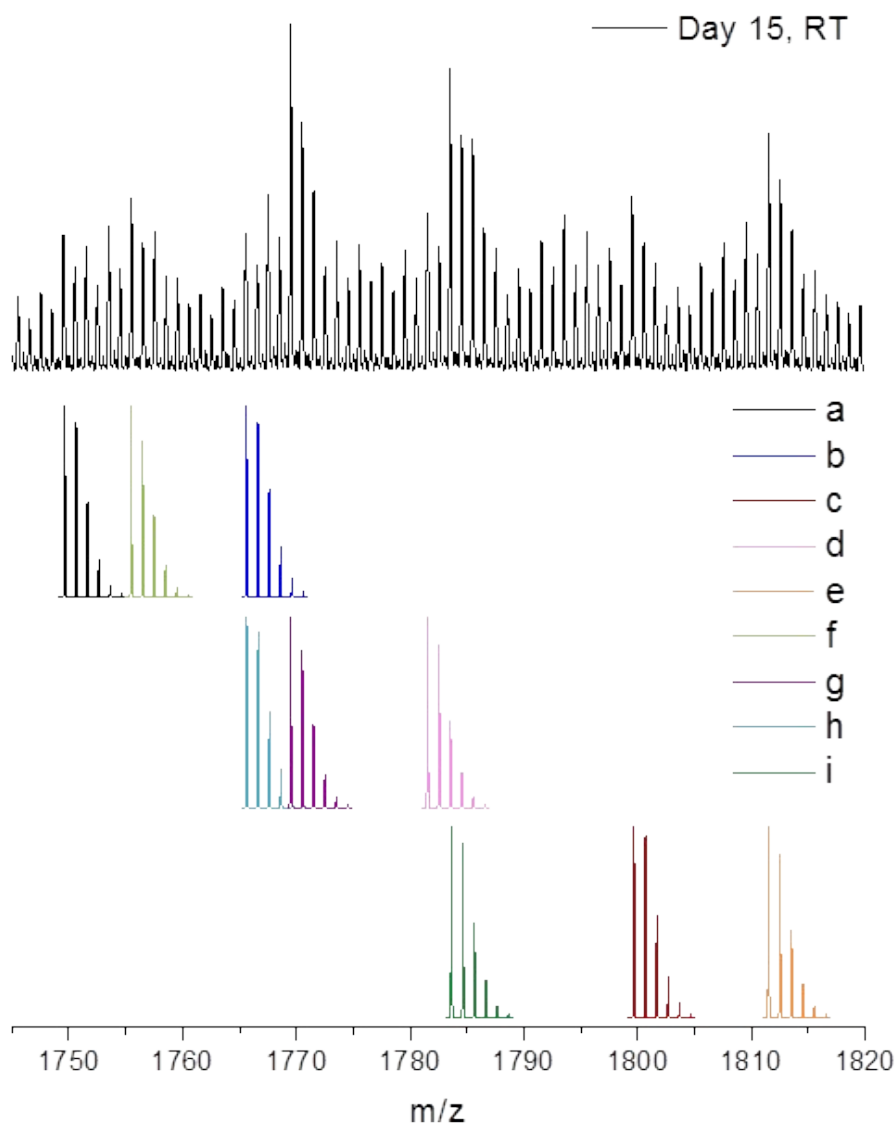
**Figure S10.** Overlay of ESI-Q-ToF mass spectra of **P1** ( $t_0$  and different storage conditions; RT and -80 °C) and of the corresponding NP. The black and purple dots are added for clarity to indicate the presence of species “a” and “g” (See **Figure 8**).



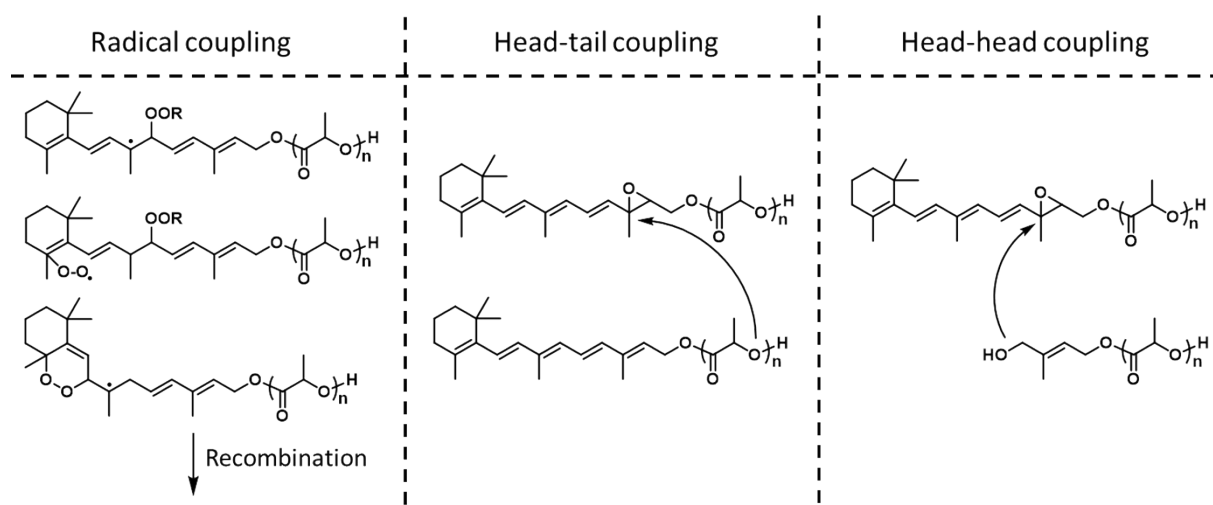
**Figure S11.** Examples for possible isomers of species "d" in **Figure 8**.



**Figure S12.** Examples for possible isomers of species "h" (**A**) and species "i" (**B**) in **Figure 8**.



**Figure S13.** Overlay of the ESI-Q-ToF mass spectrum of **P1** recorded after 15 days of storage at room temperature and under daylight with the calculated isotopic patterns of likely degradation products (compare **Figure 8**).



**Figure S14.** Examples for possible coupling pathways.