Supporting Information

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

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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\(^{-1}\). [M]/[Retinol]/[Ca]= 100/1/0.5. (A) Dependence of \(M_n,SEC\) and \(D\) 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 $^1$H NMR spectra (400 MHz, 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 mg mL$^{-1}$) and P1 (0.185 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.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Method&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Zeta potential&lt;sup&gt;b&lt;/sup&gt; [mV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>AW</td>
<td>-53 ± 2</td>
</tr>
<tr>
<td></td>
<td>WA</td>
<td>-40 ± 1</td>
</tr>
<tr>
<td>P2</td>
<td>AW</td>
<td>-52 ± 2</td>
</tr>
<tr>
<td></td>
<td>WA</td>
<td>-49 ± 2</td>
</tr>
<tr>
<td>P3</td>
<td>AW</td>
<td>-48 ± 2</td>
</tr>
<tr>
<td></td>
<td>WA</td>
<td>-32 ± 1</td>
</tr>
<tr>
<td>P4</td>
<td>AW</td>
<td>-30 ± 1</td>
</tr>
<tr>
<td></td>
<td>WA</td>
<td>-50 ± 2</td>
</tr>
</tbody>
</table>

<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 $^1$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 °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 (t₀ 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.

$$C_{20}H_{29}O_3(C_3H_4O_2)_{20}H + Na^+ \quad m/z = 1781.6$$

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

A  \hspace{1cm} C_{20}H_{29}O_3(C_3H_4O_2)_{20}H + Na^+ \hspace{1cm} B  \hspace{1cm} C_{20}H_{31}O_3(C_3H_4O_2)_{20}H + Na^+
 m/z = 1765.6 \hspace{1cm} m/z = 1783.6
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.