

## Supplementary Material

### Injectable supramolecular hydrogels based on custom-made poly(ether urethane)s and $\alpha$ -cyclodextrins as efficient delivery vehicles of curcumin

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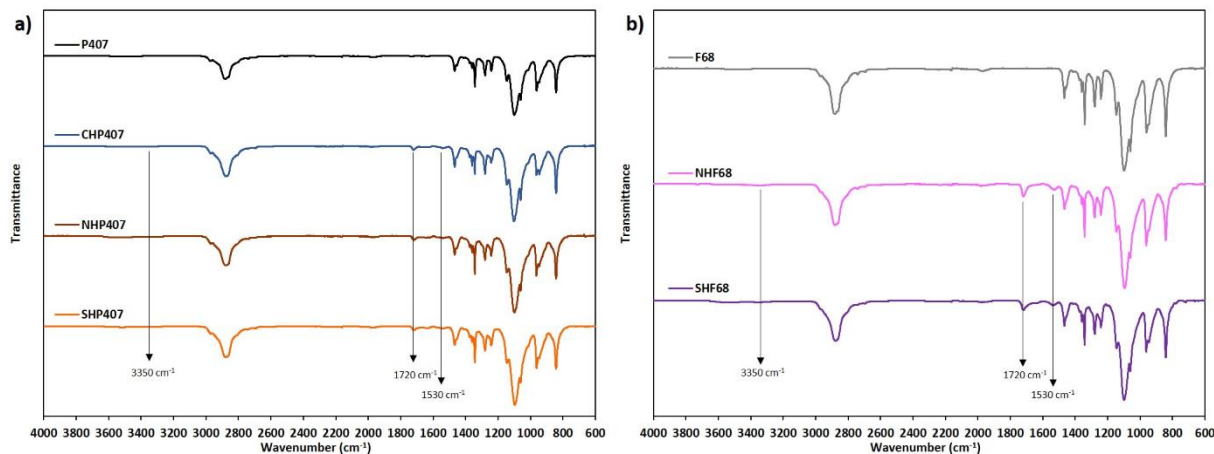
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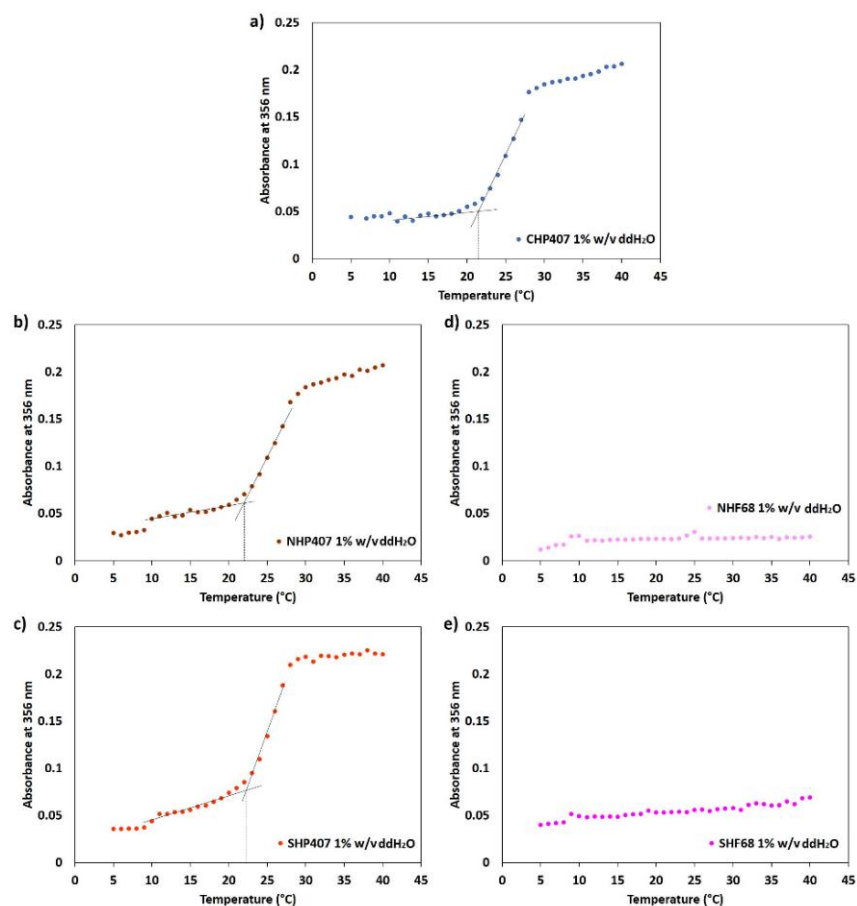
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# These authors contributed equally to the supervision of the first author

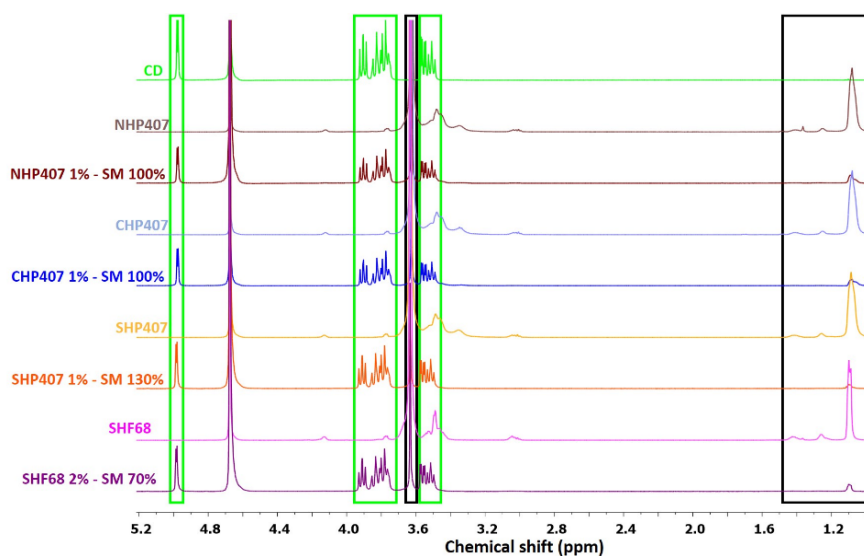
\* Corresponding author



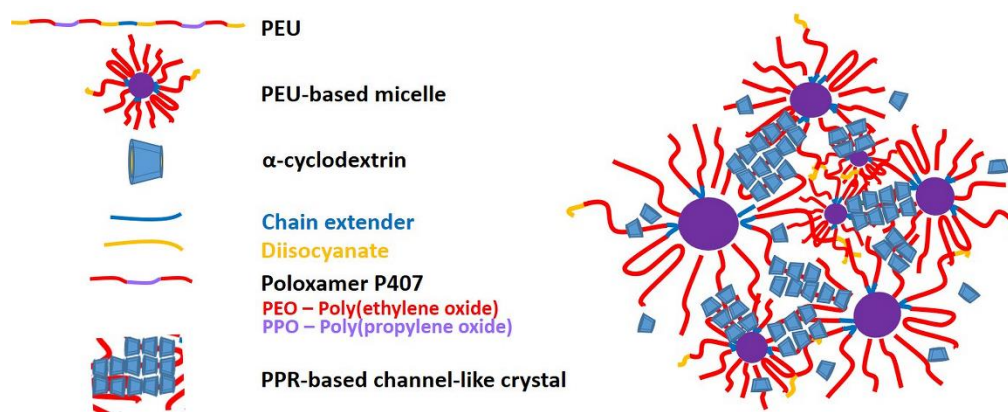
**Figure S1:** ATR-FTIR spectra of a) P407-based PEUs (i.e., CHP407 (blue), NHP407 (brown) and SHP407 (orange)) and P407 as such (black), and b) F68-based PEUs (i.e., NHF68 (pink) and SHF68 (purple)) and F68 as such (grey). Black arrows highlight specific urethane vibrations at 3350, 1720 and 1530  $\text{cm}^{-1}$  with respect to the native Poloxamer/Pluronic.



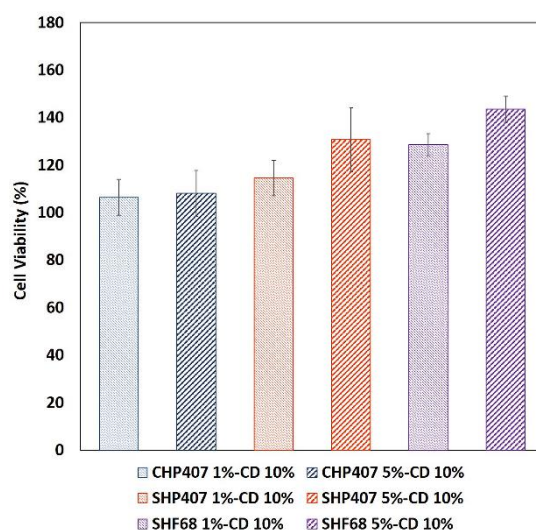
**Figure S2:** Absorbance measured at 356 nm as a function of temperature for a) CHP407 (blue), b) NHP407 (brown), c) SHP407 (orange), d) NHF68 (pink), and e) SHF68 (purple) solutions (1% w/v) in pure water (ddH<sub>2</sub>O).



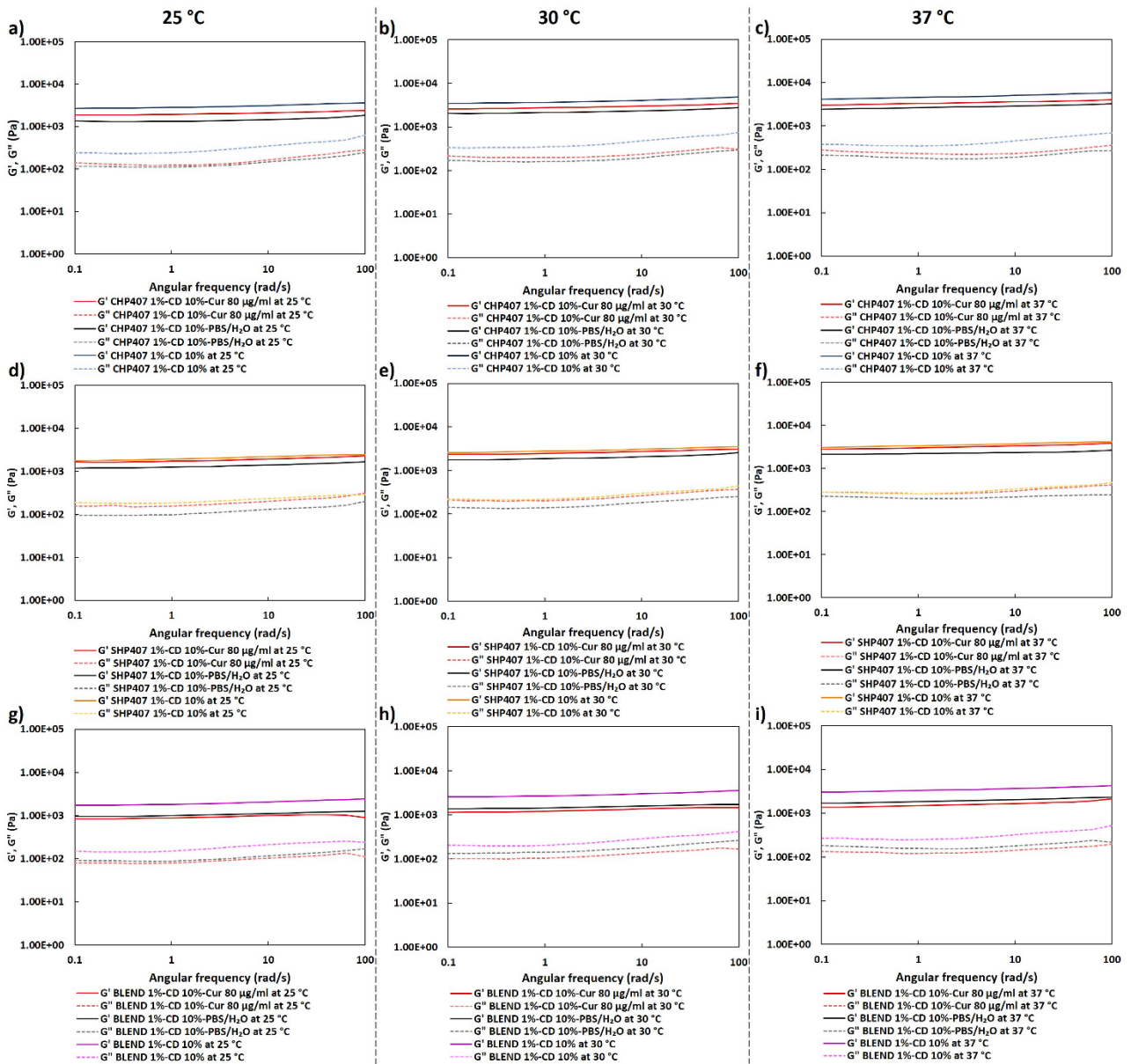
**Figure S3:** <sup>1</sup>H NMR spectra of CDs (green), NHP407 (light brown), NHP407 1% - SM 100% (brown), CHP407 (light blue), CHP407 1% - SM 100% (blue), SHP407 (light orange), SHP407 1% - SM 130% (orange), SHF68 (pink), and SHF68 1% - SM 70% (purple) samples solubilized in D<sub>2</sub>O. CD and PEU typical chemical shifts are embedded in green and black squares, respectively.



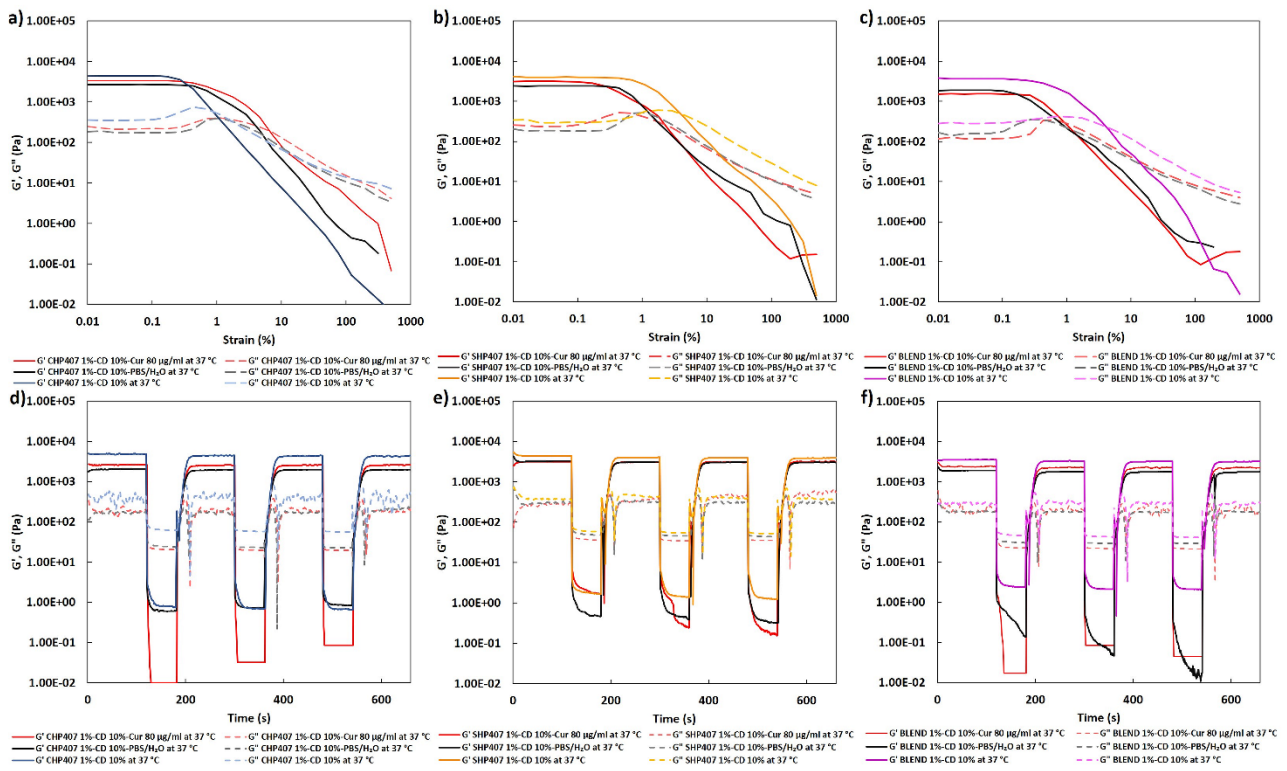
**Figure S4:** Qualitative and simplified representation of the hierarchical arrangement of PEU chains and CDs as constituent units of supramolecular hydrogels based on micelles and PPRs.



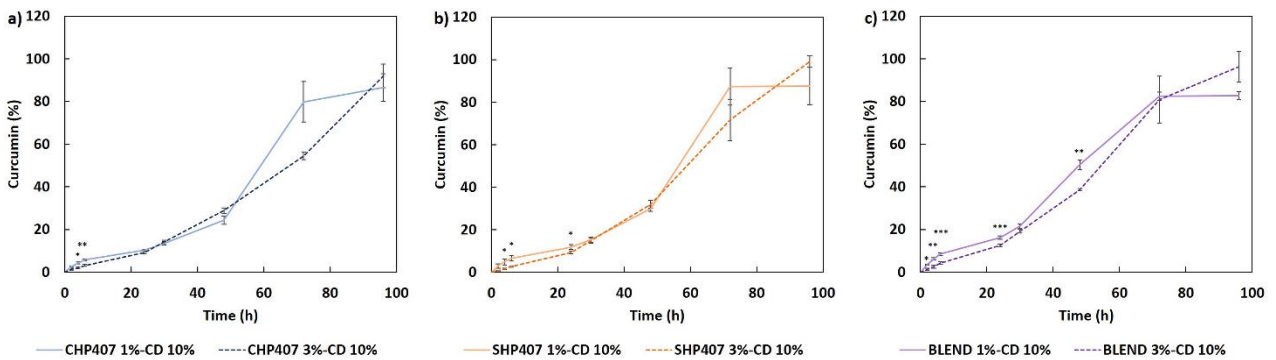
**Figure S5:** Cytotoxicity test results for CHP407-, SHP407- and SHF68-based hydrogels containing PEUs at 1 and 5% w/v concentration. No cytotoxic results were obtained, while the slight but not significant increase in the viability of cells in contact with gel eluates compared to the control (cells cultured in cell culture medium as such) could be correlated with the presence of a relevant amount of CDs in the extracts, as accurately documented by Roka *et al.* (Molecules 2015, 20(11), 20269-20285; <https://doi.org/10.3390/molecules201119694>) and Szente *et al.* (Molecules 2018, 23(5), 1228; <https://doi.org/10.3390/molecules23051228>).



**Figure S6:** Frequency sweep tests of PEU-based hydrogels at 25, 30 and 37 °C and formulated in different environments: PBS/H<sub>2</sub>O (65/35 % v/v, dark continuous line (G') and grey dashed line (G'')), Cur 80 µg ml<sup>-1</sup> (in PBS/H<sub>2</sub>O, red continuous line (G') and light red dashed line (G'')) and pure PBS (CHP407 (a, b, c) in blue, SHP407 (d, e, f) in orange and BLEND (g, h, i) in purple lines).



**Figure S7:** Strain sweep (a, b, c) and self-healing (d, e, f) tests of PEU-based hydrogels at 37 °C and formulated in different environments: PBS/H<sub>2</sub>O (65/35 % v/v, dark continuous line (G') and grey dashed line (G'')), Cur 80 µg ml<sup>-1</sup> (in PBS/H<sub>2</sub>O, red continuous line (G') and light red dashed line (G'')) and pure PBS (CHP407 (a, d) in blue, SHP407 (b, e) in orange and BLEND (c, f) in purple lines).



**Figure S8:** Curcumin release profiles expressed as percentages with respect to the theoretical payload (80 µg ml<sup>-1</sup>, 100%) for CHP407 (a, blue), SHP407 (b, orange) and BLEND (c, purple) hydrogels. In each graph, 1% (continuous lines) and 3% (dashed lines) w/w PEU concentrations are compared.