

ELECTRONIC SUPPLEMENTARY INFORMATION

Electrospray loading and release of hydrophobic gramicidin in polyester microparticles

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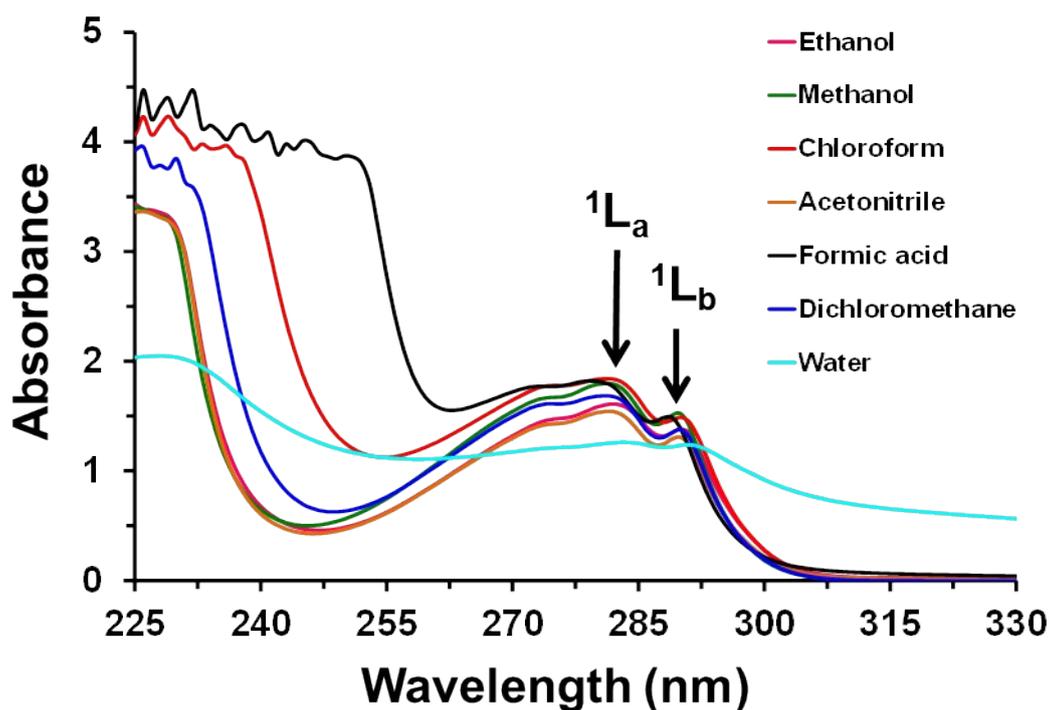


Figure S1. (Absorption (absorbance expressed with arbitrary units) spectra of GA determined in different solvents (dilute solution).

It is well-known that the UV-vis spectrum of GA is not characteristic of its entire structure, the uncharacteristic absorbance at 200-300 nm being due to the chromophoric units of the molecule (*i.e.* the aromatic residues) The UV-vis spectrum of dissolved in ethanol, which exhibit two peaks of similar intensity at 280 and 288 nm that correspond. These correspond to the 1L_a and 1L_b bands, respectively, of the $\pi \rightarrow \pi^*$ transitions in the four Trp residues of GA of type A, which is the most abundant in the purchased sample (see Methods section). Discussion of these bands, which is out of the scope of this work, has been widely reported in the literature.²⁸⁻³⁰ The spectrum of GA remains practically unaltered when the ethanol solvent is replaced by methanol, chloroform, acetonitrile, formic acid and dichloromethane while important changes occur in water. Thus, the clear absorption peaks at around 280 and 288 nm become a shoulder in water.

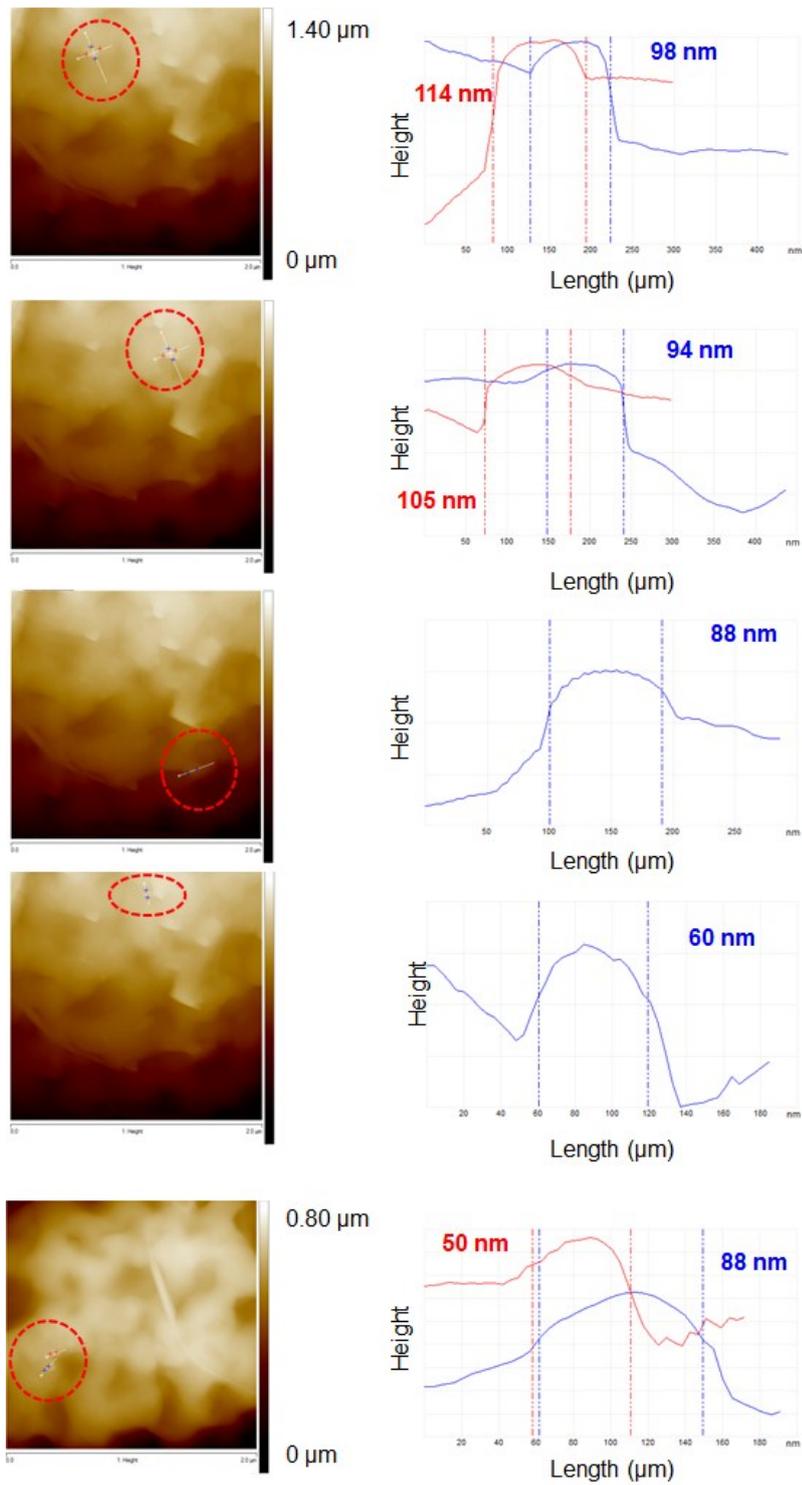


Figure S2. Cross-section profiles of GA particles located on the surface of PE44-GA electrospayed microspheres.

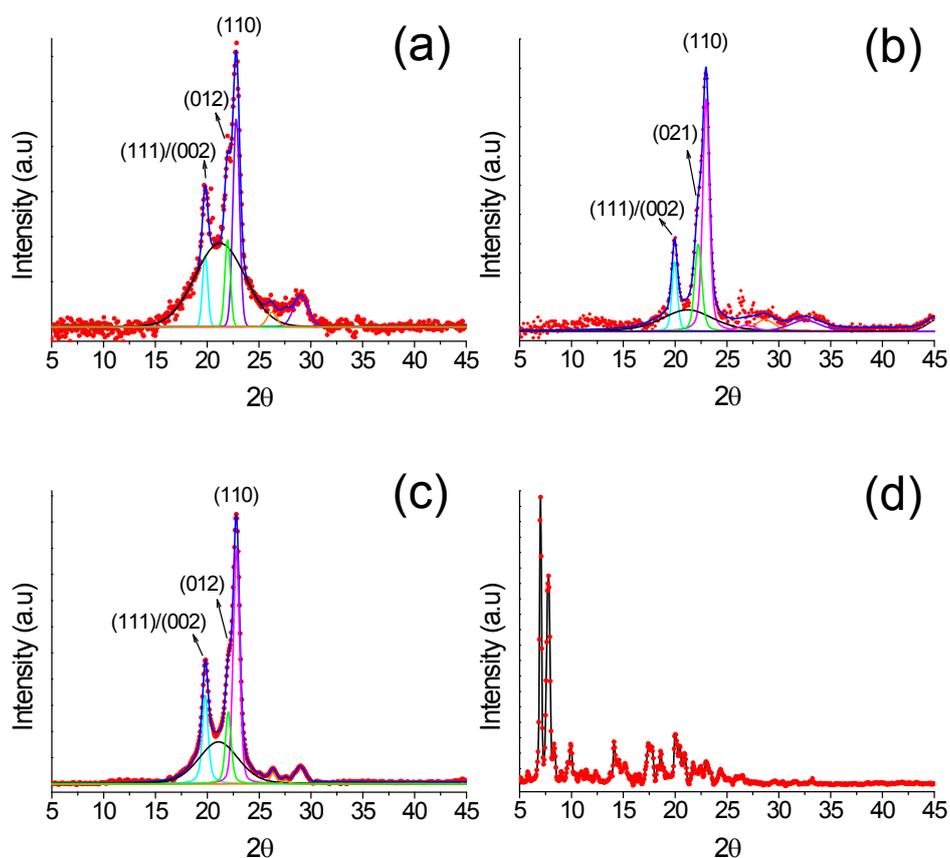


Figure S3. WAXD patterns of (a) U-PE44 and (b) PE44-GA electrospayed microspheres, (c) PE44 film prepared by solvent-casting (reference sample), and (d) gramicidine.

The X-ray diffraction peaks at $2\theta = 19.7^\circ$, 22.1° , 22.8° , 26.2° and 29.1° , which correspond to $(11\bar{1})/(002)$, (012) , (110) , $(12\bar{1})$ and (111) planes of PE44 monoclinic crystal lattice, respectively, are identified. Deconvolution of the X-ray diffraction patterns into the crystalline peaks and the amorphous halo reveals significant differences between electrospayed microspheres and the raw-materials. According to Eqn 2, variations in the $L_{(hkl)}$ values are consistent with changes in crystalline structure of the PE44. Thus, although $L_{(hkl)}$ in the (110) plane is similar for all samples, $L_{(hkl)}$ in the $(11\bar{1})/(002)$ plane direction is 12.4 nm in the reference PE44 film and of 13.4 nm in the U-PE44 microspheres. In the (012) plane, $L_{(hkl)}$ is 0.7 nm higher for U-PE44 than for the film. These results indicate that the electrospaying process affects the supramolecular structure of the polymer.

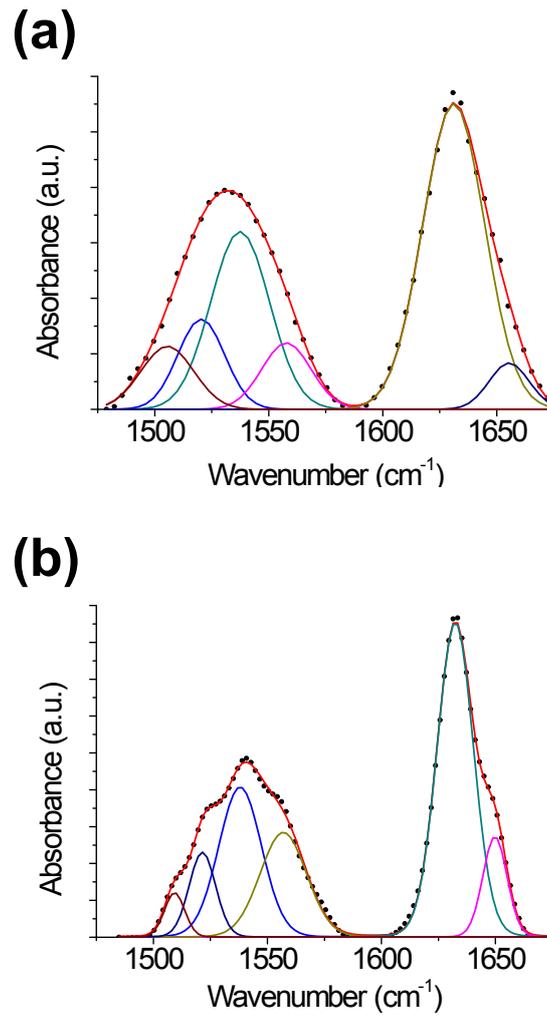


Figure S4. Deconvolution of the amide I and amide II absorption bands recorded by FTIR spectroscopy for (a) GA and (b) GA loaded into PE44 microspheres at room temperature.

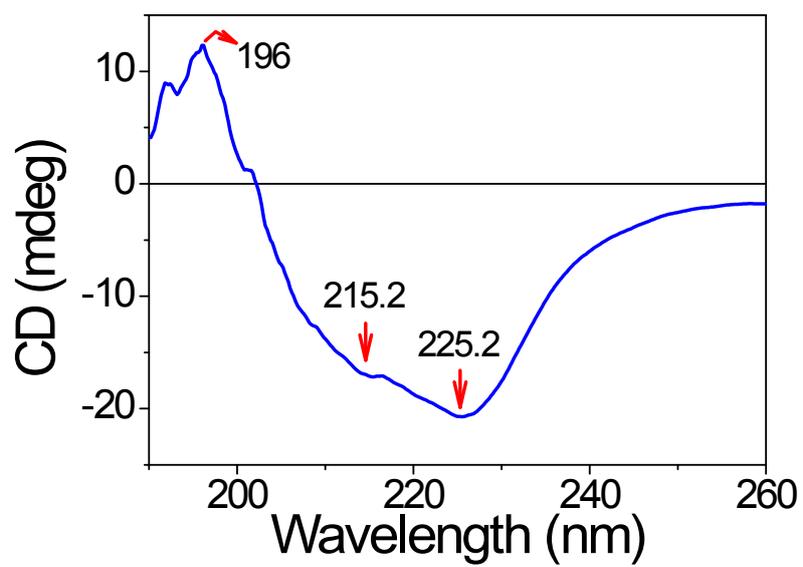


Figure S5. CD spectrum of GA dissolved in ethanol.

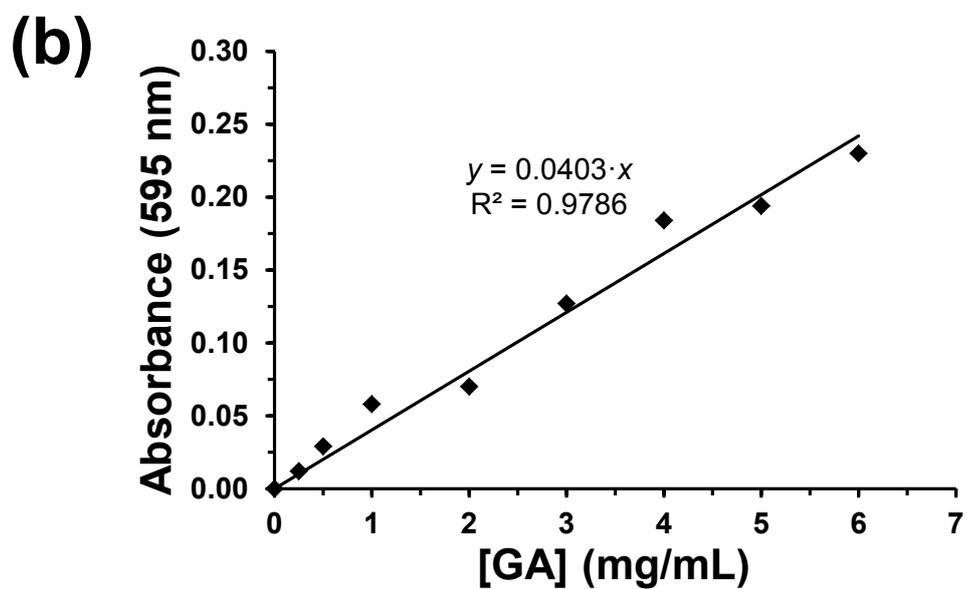
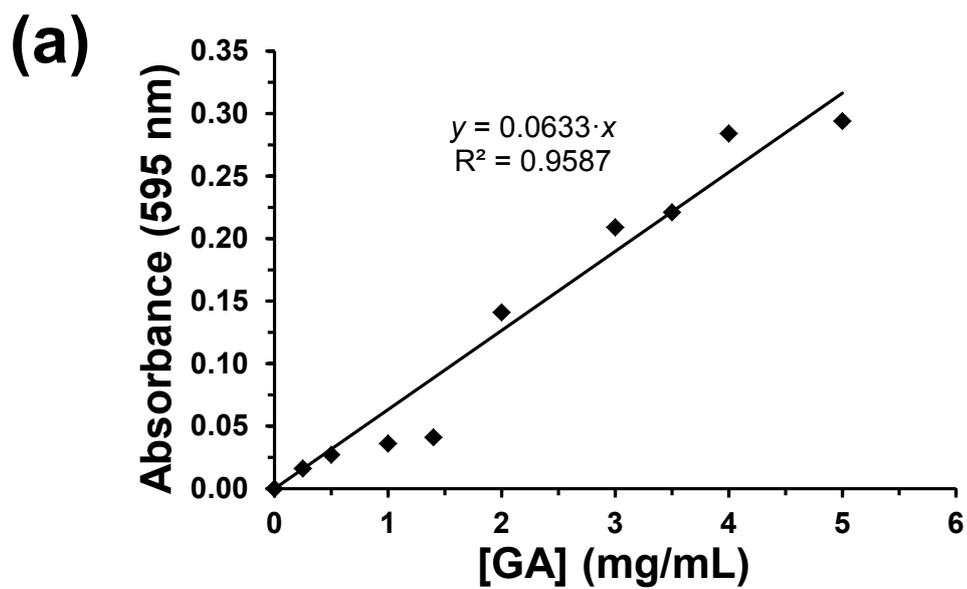


Figure S6. Calibration curves used to study the release of GA in (a) PBS and (b) PBS-EtOH.

Table S1. Degree of crystallinity (χ_c) and crystallite size ($L_{(hkl)}$) of PE44 films prepared by solvent casting (reference sample) and both U-PE44 and PE44-GA electrospayed microspheres.

Sample	χ_c	$L_{(11\bar{1})/(002)}$ (nm)	$L_{(012)}$ (nm)	$L_{(110)}$ (nm)
Reference (film)	0.63	12.4	12.2	11.0
U-PE44	0.42	13.4	12.9	10.7
PE44-GA	0.76	12.9	10.0	10.6