*Supplementary material #2 for:*

**Tethered pyro-Electrohydrodynamic spinning for patterning well-ordered structures at micro- nano scale**

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Further experiments were conducted aimed at obtaining more intriguing patterns. Controlling the fluid relaxation and the elongation viscosity of the polymer (case 3) it is possible to print the capillary polymer break-up leading to the formation of knotted fibers. This kind of fibers could be useful for the incorporation of nanometer sized objects (drugs, dyes, enzymes) to produce functional fibers [**1**]. In others experiments, in order to fabricate more complex patterns the buckling phenomenon was induced on the tip of the liquid fibre in contact with the substrate (see supplementary movie #4) by a slight approaching of the lower substrate to the collector substrate. In this case, the polymer jet works in oscillating mode under the action of the pyroelectrodynamic field, as depicted in Figure 1(a). The experimental data presented in Figures 1(b-d) show the PLGA buckling patterns. The diameters of the jets in Figure 1(b) are about 1-5 μm. Sinusoidal coiling and overlapping script-like "e" are observed and compared with a continuous fibre. The buckled patterns obtained are due to the jet compression at impingement on the collector used as substrate and moved in the direction shown by the blue arrow in the figures. The profiles are very regular and similar to those obtained in case of ES jets **[2]** but the substrate is slower than those reported for conventional ES experiments (0.01 m/s), which is a significant experimental advantage. Increasing the distance ***d*** the frequency decreases, while at shorter distances it becomes higher. Balancing the frequency and the velocity ***v*** we can control the type of profiles produced. The results show that the buckling frequency and the wavelength varies as a function of experimental and rheological parameters. In particular different patterns with different wavelengths $\lambda$, ranging from 15 to 50 μm were realized after the impingement onto a microscope glass slide, Figure 1(d). A further experiment was performed in order to demonstrate the possibility of combining the use of the TPES to fabricate design more complex geometries Figures 1(e)-(f) and suspended fibers over a polymeric open channel, Figures 1(g-i). These results open the way to the fabrication of high-resolution three dimensional periodic microstructures with great potential and two different applications with TPES microstructures were demonstrated in biology and photonics fields, respectively.

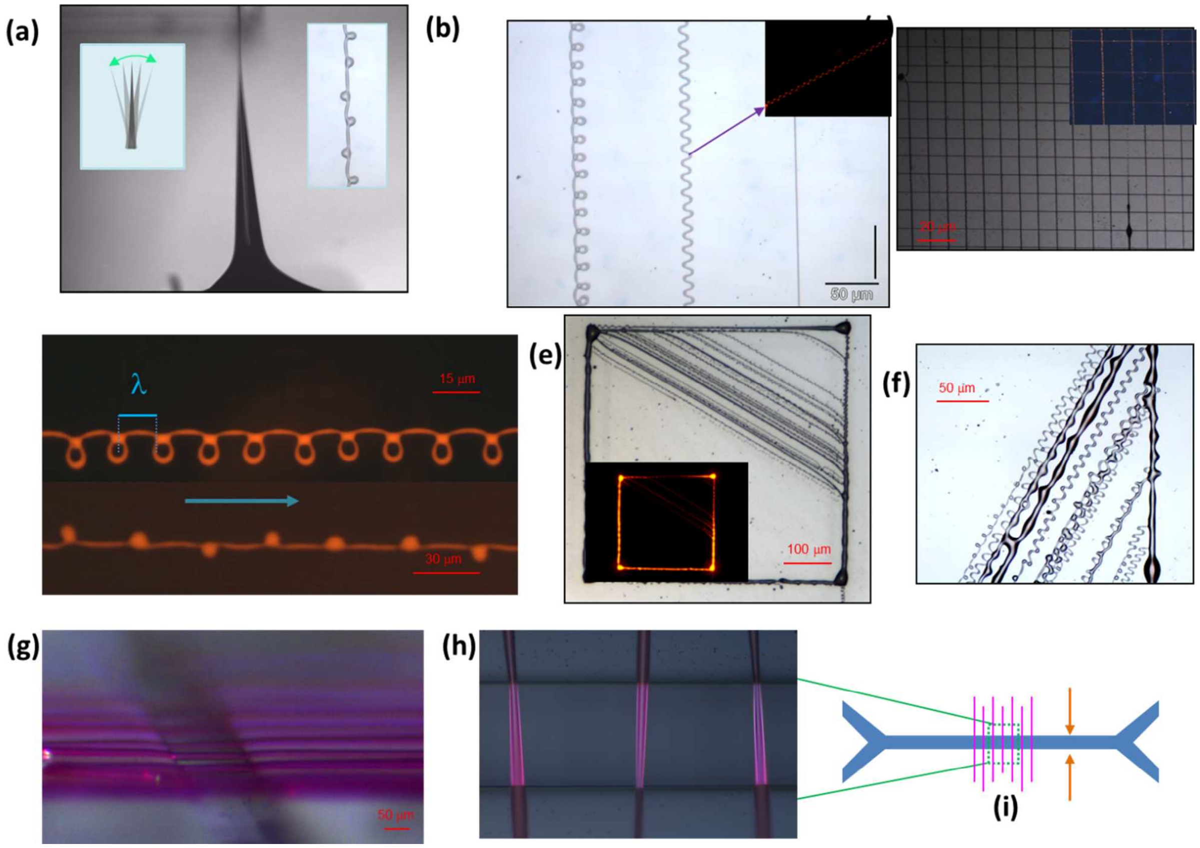


**Figure 1: Embroidery and buckilng patterns at the microscale.** (a) Polymer jet works under the pyroelectric pressure. (b) Controlling buckling patterns. (c) Ordered gird with a period of 10μm combining uniform lines (horizontals) with buckled lines (verticals). (d) Periodic (λ) buckling patterns. (e)-(f) Complex geometries at the micrometer scale. (g) Perspective view and top view (f) of suspended three dimensional fibers over a polymeric double y channel 150 μm width (i).

References:

[1] Zhao, P. C., Jiang, H. L., Pan, H., Zhu, K. J. & Chen, W. Biodegradable fibrous scaffolds composed of gelatin coated poly(epsilon-caprolactone) prepared by coaxial electrospinning. *J. Biomed. Mater. Res., Part A* **83**, 372-382 (2007).

[2] Yang, F., Xu, C. Y., Kotaki, M., Wang, S. & Ramakrishna, S. Characterization of neural stem cells on electrospun poly(L-lactic acid) nanofibrous scaffold. *J. Biomater. Sci., Polym. Ed.* **15**, 1483-1497 (2004).