Microarray Nanotechnology perspectives are essentially determined by the methods and the materials available for device manufacturing on the nanoscale. In this scope, copolymers (CP) constitute fascinating building units due to their natural tendency to organize into arrays of domains with molecular dimensions. This assembly is thermodynamically driven and depends on a few system parameters[1]. The inherent tendency of CP to organize can be combined with means of external control, such as chemically patterned substrates, to create thin films of nanostructures with desired shape and spatial arrangement. This work refers to several questions arising when using this kind of molecular materials characterized by a thermodynamically preferred, “natural”, structure.

First, we discuss the robustness of the polymer morphologies to possible local imperfections of the chemical pattern guiding the assembly. This is of key importance for understanding[2] their interfacial roughness in scope of potential applications in semiconductor industry. When[3],[4] the pattern symmetry and the length scales match those of the CP natural structure, defect free ordering is achieved over arbitrarily large length scales. However, prospective technological applications require the replication on nanoscale of patterns with non-regular, isolated, device oriented features such as lines, bends, spots, jogs, e.t.c.. Generally, a pronounced mismatch between the pattern and the thermodynamically preferred, bulk, morphology will create structures neither resembling the natural structure nor the two-dimensional pattern. Nevertheless, adjusting material parameters such as composition, molecular architecture and film thickness can significantly expand the collection of patterns[5] that can be perfectly replicated by the assembly. This is demonstrated through an example of CP, assembled on substrates patterned with isolated stripes preferential to one block. Finally, we illustrate how a significant mismatch between the natural CP morphology and the pattern geometry can be exploited to create novel structures with unique properties. This will be demonstrated using the paradigm[6] of lamella-forming CP blends ordering on a square array of spots attracting one block. In this case, the surface reconstruction creates a three dimensional bicontinuous network.