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## **Reactive nano-pattern in triple structured bio-inspired honeycomb film as a clickable platform**

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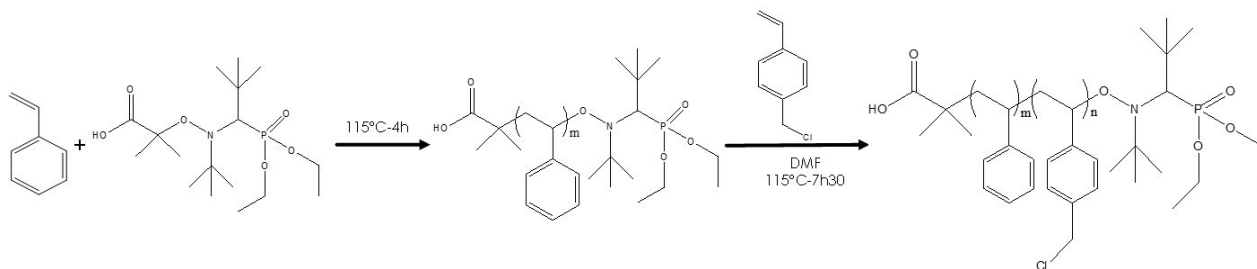
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### **Materials and methods**

*PS-*b*-PVBC synthesis:* The diblock copolymer was synthesized in two separate steps. Firstly, styrene (sigma Aldrich, 99%, S, 10.95 g, 105 mmol) and BlocBuilder (ARKEMA, 0.067 g, 0.17 mmol) were added to a round bottom flask. The mixture was degassed for 15 minutes with nitrogen and then immersed in an oil bath at 115 °C for 4 h. The resulting polystyrene (PS) was precipitated twice into ethanol, filtered, and dried at 40°C under vacuum. In the second step, the purified PS (0.679 g, 2.5 x 10<sup>-2</sup> mmol), 4-vinylbenzylchloride (sigma Aldrich, 90%, VBC, 0.588 g, 3.8 mmol), and dimethylformamide (DMF, 1.71 g) were mixed in a round bottom flask and degassed 15 minutes. The mixture was immersed in an oil bath at 115°C for 7.5h, and the resulting block copolymer was purified by two precipitation in ethanol, filtered, and dried at 40°C under vacuum. Final polymer was characterized by <sup>1</sup>H NMR and SEC in THF allowing to determine the copolymer composition which correspond to 270 units of styrene and 52 units of 4-vinyl benzyl chloride for a M<sub>n,SEC</sub> of 35 000 g.mol<sup>-1</sup> (vs PS standards) with a dispersity of 1.5, forming the so-called PS<sub>270</sub>-*b*-PVBC<sub>52</sub> mentioned in the text.

*Honeycomb film formation:* Honeycomb films were obtained by the static breath figure method. A polymer solution in dichloromethane (VWR, technical) was cast on a glass lamellae and placed on a hermetically closed chamber with controlled atmosphere according to solvent vapor equilibrium. Honeycomb films were firstly produced with a 10 g.L<sup>-1</sup> solution of PS<sub>270</sub>-*b*-PVBC<sub>52</sub> with a relative humidity (RH) of 65% at 20 °C for both 100% water and water/ethanol 50:50 (v/v) atmosphere. Ethanol was

purchased by VWR with a purity of 99.8%. The film was withdrawn two minutes later after total evaporation of solvent and water.



**Film functionalization:** film modification were performed by immersion of glass lamellae supporting the film in a typical centrifugation tube. Absolute ethanol was used at each step as a non-solvent of the honeycomb supported film and good solvent of reactives. A large excess of different reactives, *i.e.* compared to the low surface content of actives site, were introduced inside tube and the mixture was stirred using a magnetic stirrer.

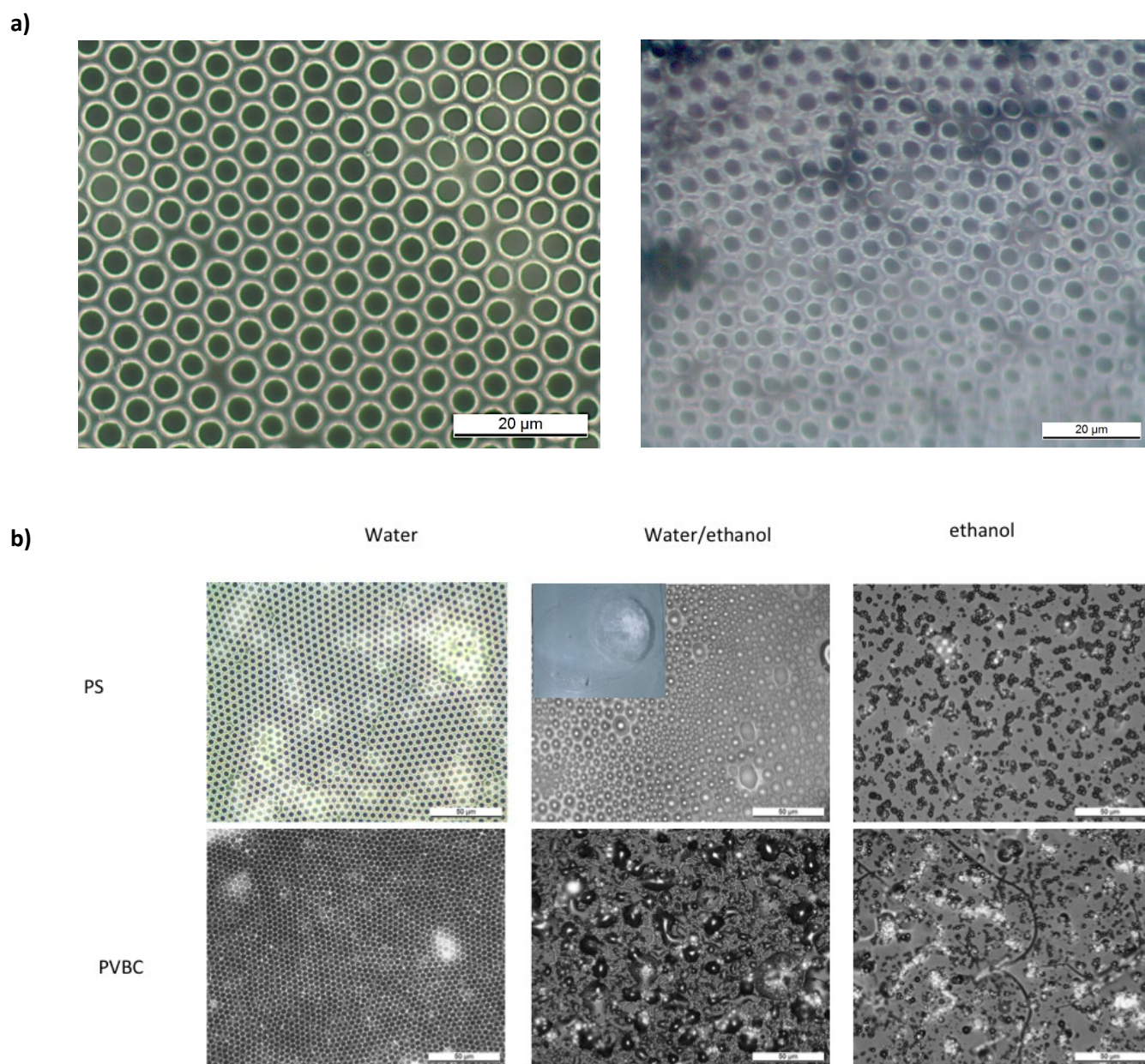
**Microscopy:** Optical microscopy pictures were taken using a DMLM microscope (LEICA©) equipped with DFC280 camera. Scanning electron microscopy (SEM) images were taken using a Hirox© SH-3000 device. Atomic force microscopic (AFM) images were obtained using MultiMode 8 Atomic Force Microscope (AFM) from Bruker in a PeakForce QNM (Quantitative NanoMechanics) mode.

**Nuclear magnetic resonance (NMR) spectroscopy:**  $^1\text{H}$  and diffusion order spectroscopy (DOSY) NMR experiments were carried out on a Bruker 400 MHz spectrometer at 25°C.

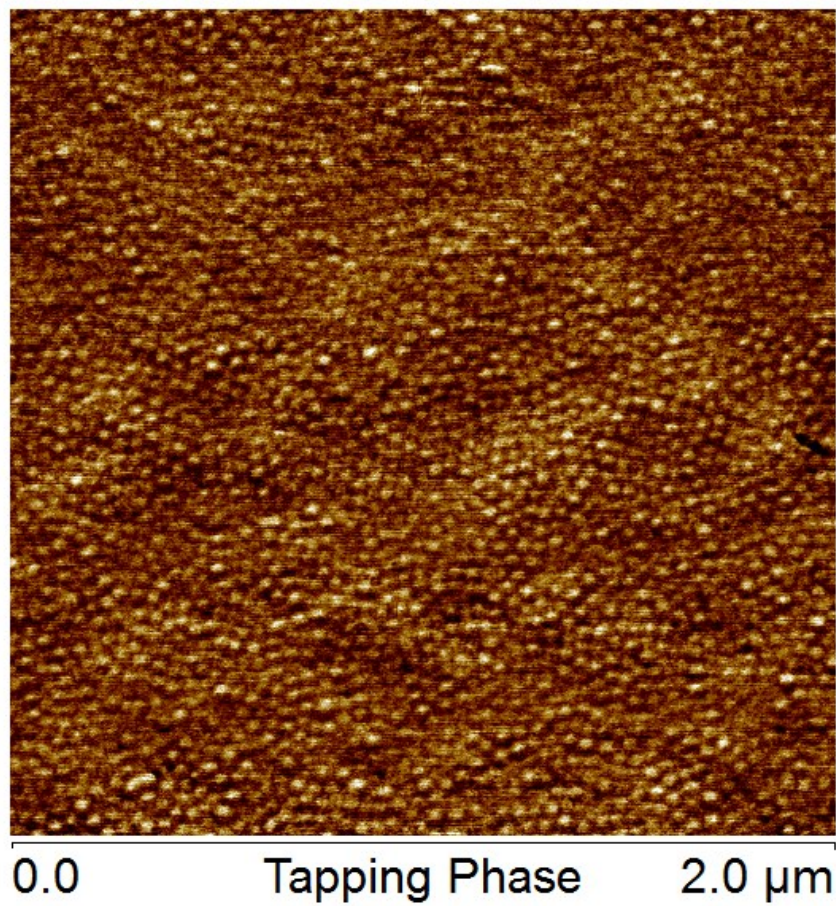
**Size exclusion chromatography:** the molar mass and molar mass distribution of all synthesized polymers were measured using size exclusion chromatography (SEC) with THF as eluent (flow rate  $1.0 \text{ mL min}^{-1}$ ) at 30 °C. The SEC is equipped with a Viscotek VE 5200 automatic injector, a precolumn and two columns (Styragels HR 5E and 4E (7.8 ft, 300 mm)) and 4 detectors: UV-visible spectrophotometer (Viscotek VE 3210), a Multiangle Light Scattering detector (Wyatt Heleos II), a viscosimeter (Wyatt Viscostar II) and a refractive index detector (Viscotek VE 3580). Polystyrene standards were used to determine the dispersity of the polymers. Polymer samples were prepared at  $5 \text{ g L}^{-1}$  and filtered through  $0.45 \mu\text{m}$  PTFE filters.

**Fourier transform infrared (FTIR) spectroscopy:** Spectra were recorded on a Nicolet iS50 at 25°C with Attenuated total reflectance (ATR) mode.

**X-Ray Photoelectron Spectrometry (XPS):** XPS measurements were performed on a Thermo K-alpha spectrometer equipped with a 120 mm mean radius Hemispherical Analyzer (HAS) and a microfocussed monochromated radiation (Al K $\alpha$ , 1486.6 eV, microspot continuously variable from 30 to 400  $\mu\text{m}$  diameter) operating under UHV conditions (residual pressure of  $1 \times 10^{-9}$  mbar). The Xray power was operating at 72 W (12 kV, 6 mA) for a typical 400  $\mu\text{m}$  beam diameter. The spectra were recorded in the constant Pass Energy (PE) mode CAE, both for wide high sensitivity survey spectra (PE = 200 eV) and high energy resolution analyses (PE = 20 eV) for quantitatively resolved chemical analyses. Charge effects were compensated by the use of a charge neutralisation system (low energy electrons) which had the unique ability to provide consistent charge compensation. All the neutraliser parameters remained constant during analysis and allowed one to find a 285.0 eV C1s binding energy for adventitious carbon. Spectra were mathematically fitted with Casa XPS software using a least squares algorithm and a non-linear baseline. The fitting peaks of the experimental curves were defined by a combination of Gaussian (70%) and Lorentzian (30%) distributions. Only core level spectra for the elements with highest photoionization cross section were recorded in order to extract more reliable information.

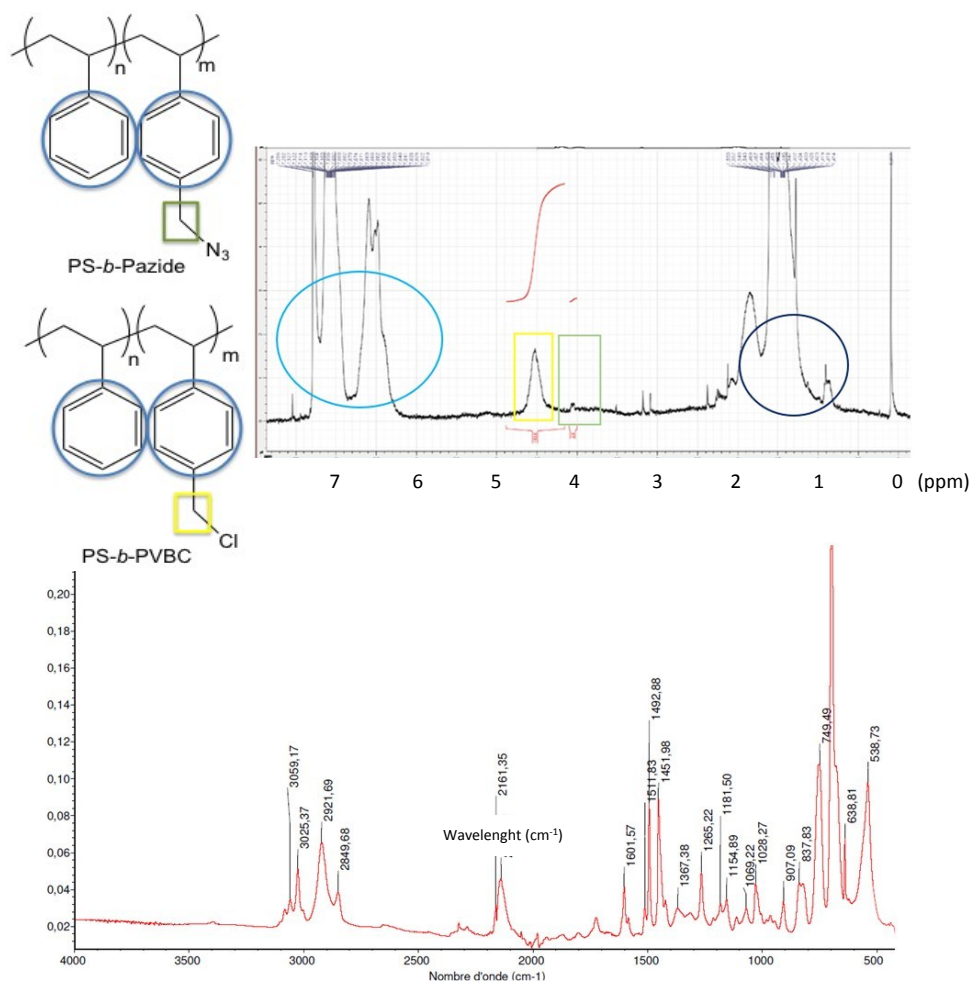


**Figure S1:** a) PS (Left) and PVBC (Right) homopolymers honeycomb films obtained by breath Figure method from dichloromethane solution under pure water atmosphere with a relative humidity of 65%RH @ 20°C and b) PS and PVBC homopolymers films obtained (scale bare = 20 microns) in different atmospheric conditions (water, water/ethanol and ethanol).

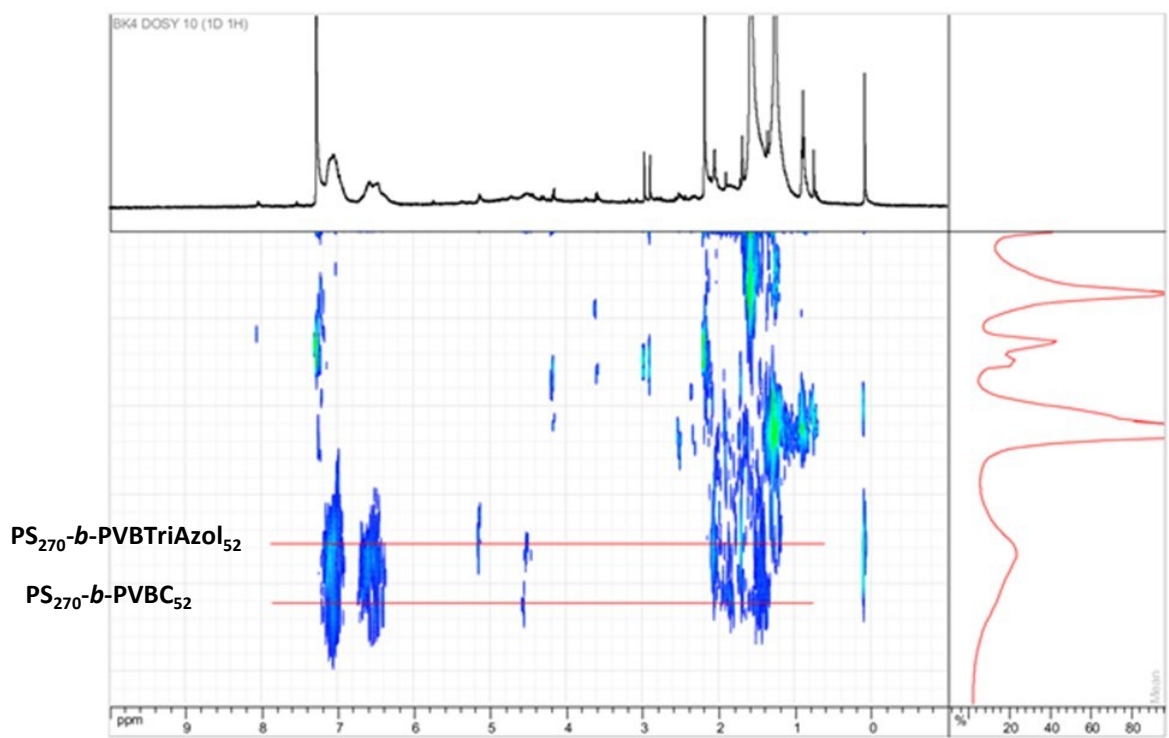
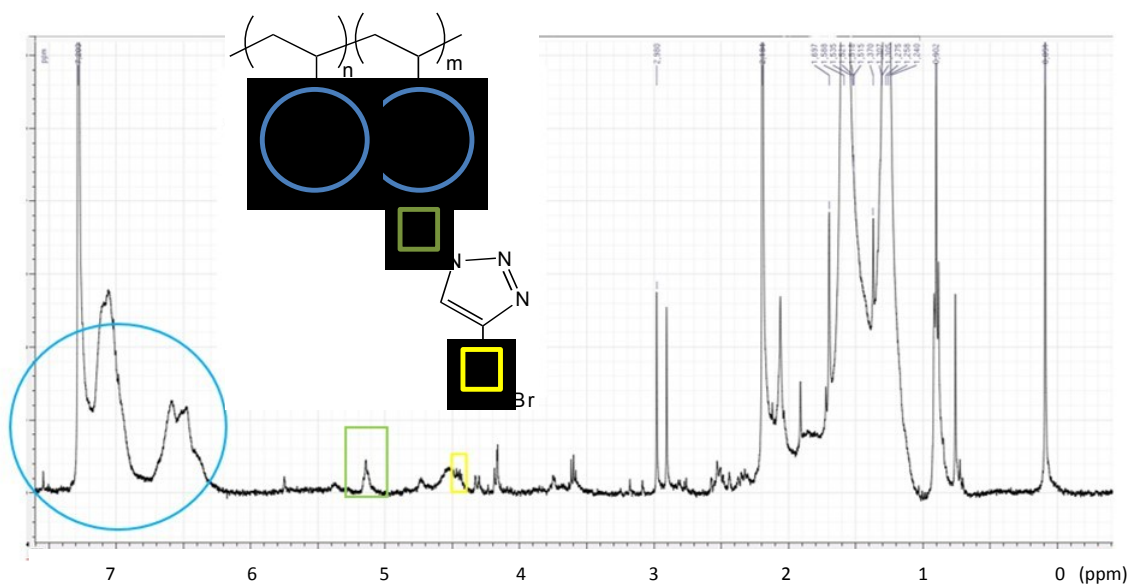


**Figure S2:** AFM tapping image of PS<sub>270</sub>-*b*-PVBC<sub>52</sub> spin coated on a glass lamellae at 2000rpm with a 10g.L<sup>-1</sup> solution in CS<sub>2</sub>.





**Figure S3:**  $^1\text{H}$  NMR spectra of solubilized film after azidation (top) and FTIR spectra of film top surface after azidation (bottom).



**Figure S4:**  $^1\text{H}$  NMR spectrum of solubilized film after CuAAC with propargyl bromide in  $\text{CDCl}_3$  (top) and NMR DOSY 2D spectrum (bottom).