Supporting Information

Hierarchically structured block copolymer films through "breath figure" templating and microwave annealing.

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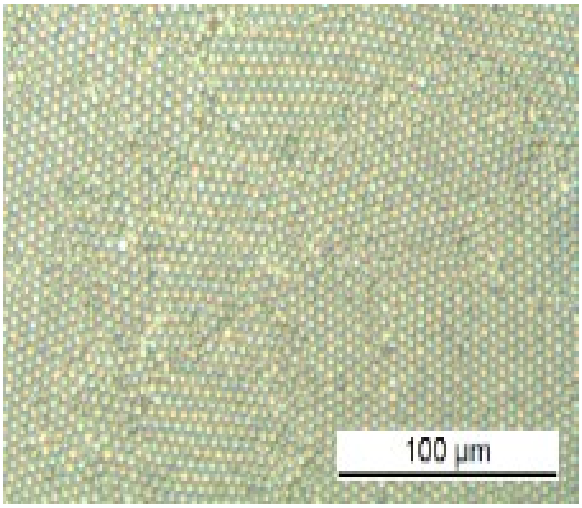

Figure S1. Optical microscopy of honeycomb structures made in static method at 60% of relative humidity. A solution of MBM20 in dichloromethane (5g/L) has been used for the drop casting.

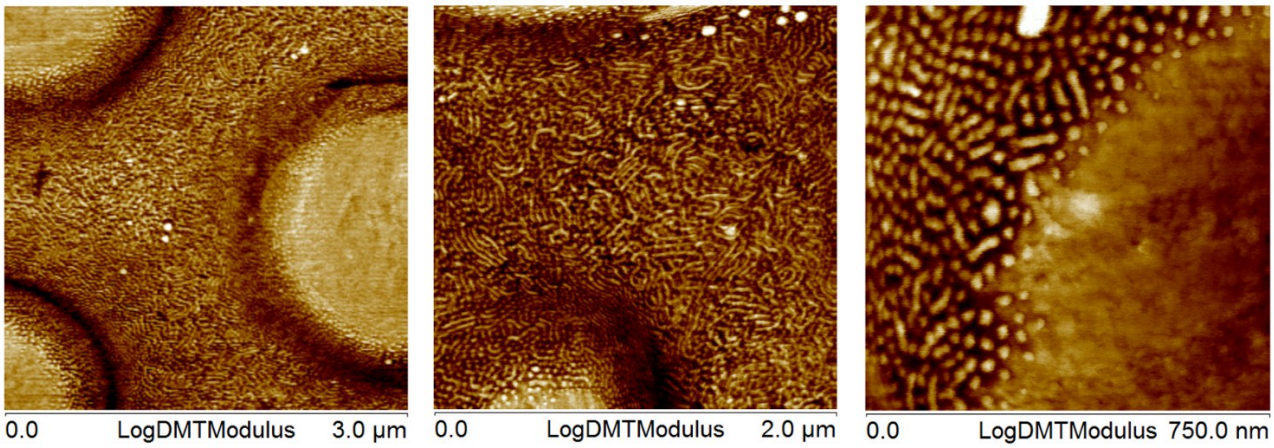

Figure S2. AFM images of honeycomb structures made in static method at 60% of relative humidity, with a solution of MBM20 in dichloromethane has been used for the drop casting. 5g/L. Zoom on the pillar zone (image in the middle) and on the side pore zone (image on the right).

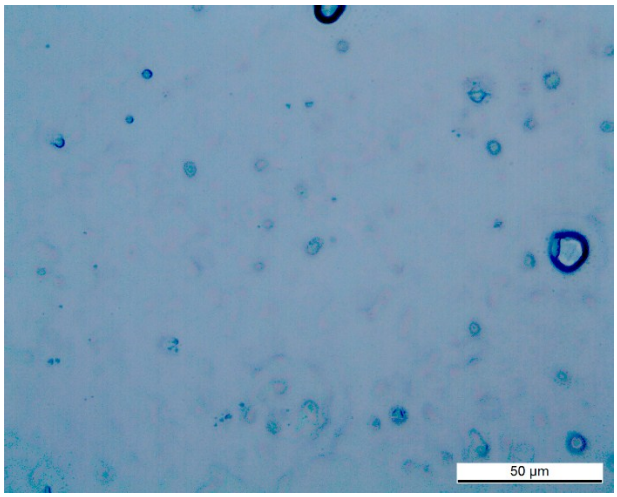

Figure S3. Optical microscopy of honeycomb structures after a thermal annealing at 160°C during 5 min. The film was made in static method at 60% of relative humidity, with a solution of MBM20 in dichloromethane has been used for the drop casting.

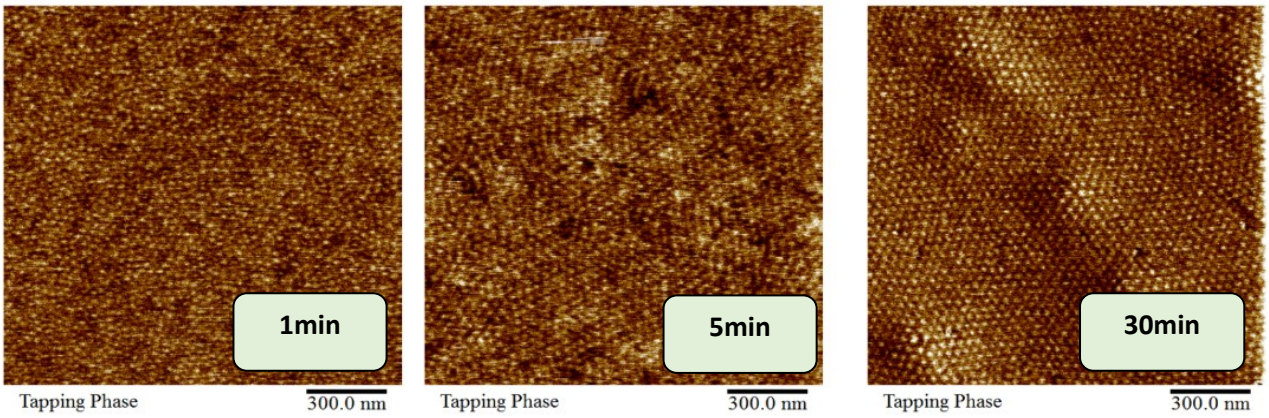

Figure S4. AFM pictures in tapping mode of MBM20 solutions at 1,5w% in DCM spin-coated at 3000rpm on a cut glass microscope slide, washed with acetone. The samples has been annealed in a CEM microwave at 200W annealed at 0,5cm from the bottom of the vial. The annealing time was 1 min, 5 min and 30 min.

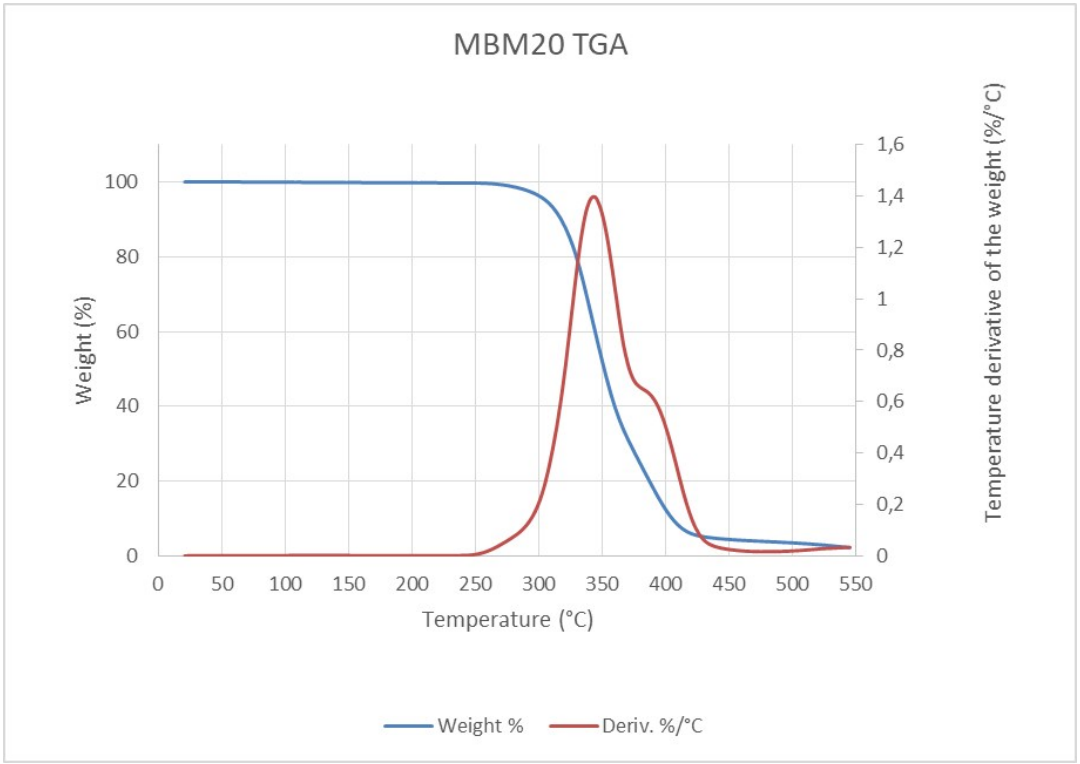

Figure S5. TGA curves of MBM20. The sample was heated from ambient temperature to 550 °C with a heating rate of 10°C/min under air. The graph shows the evolution of the weight (blue) and its temperature derivative (red), in function of the temperature.

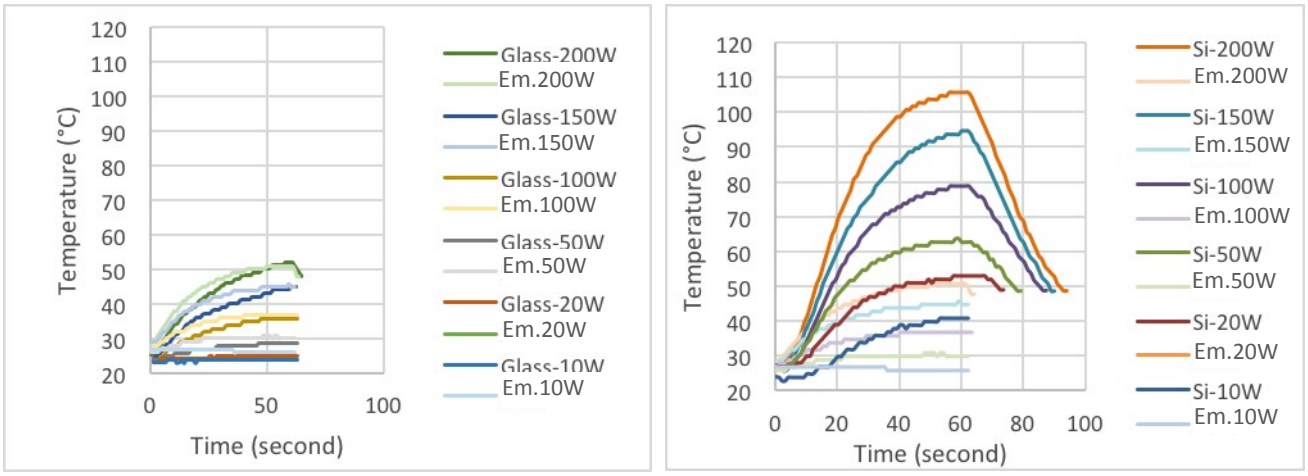

Figure S6. Evolution of measured temperatures at different powers in function of time with cooling of the vial during the microwave annealing. Results of vials with silicon shard (right) and with glass piece (left) are compared with empty vials (Em.) temperature measurements.

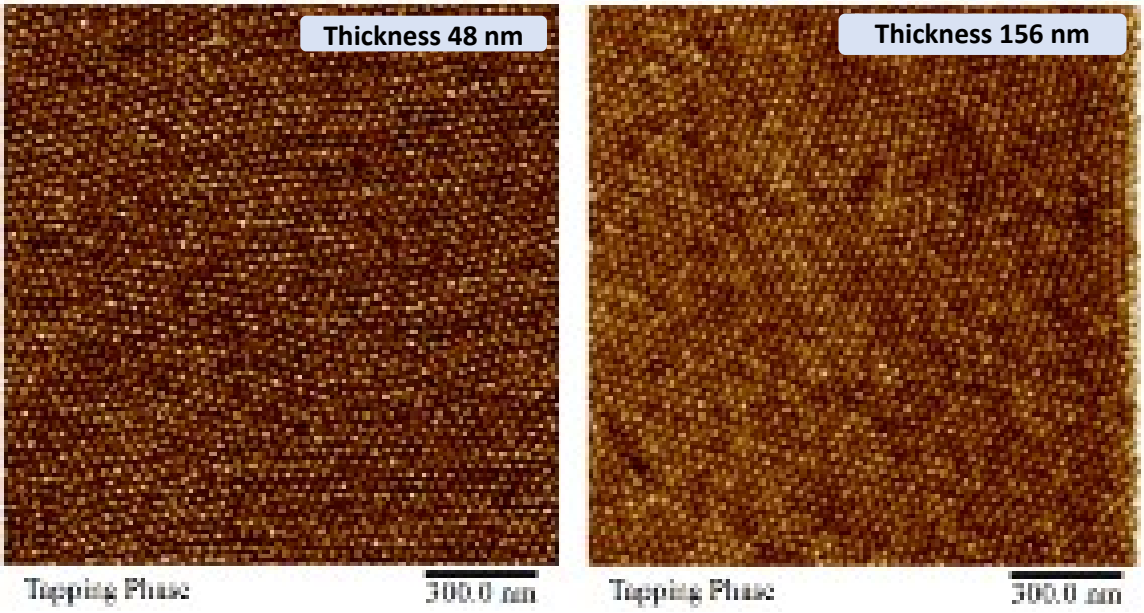

Figure S7. AFM pictures in tapping mode of MBM20 solutions at 8.7 g.L-1 (1 wt%) in toluene (left) and at 20,3 g.L-1 (1.5 wt%) in DCM spin-coated on a cleaned silicon wafer respectively at 2000 rpm and 3000 rpm. The samples has been annealed in a CEM microwave at 5 W for 1 minute at 0,5 cm from the bottom of the vial.

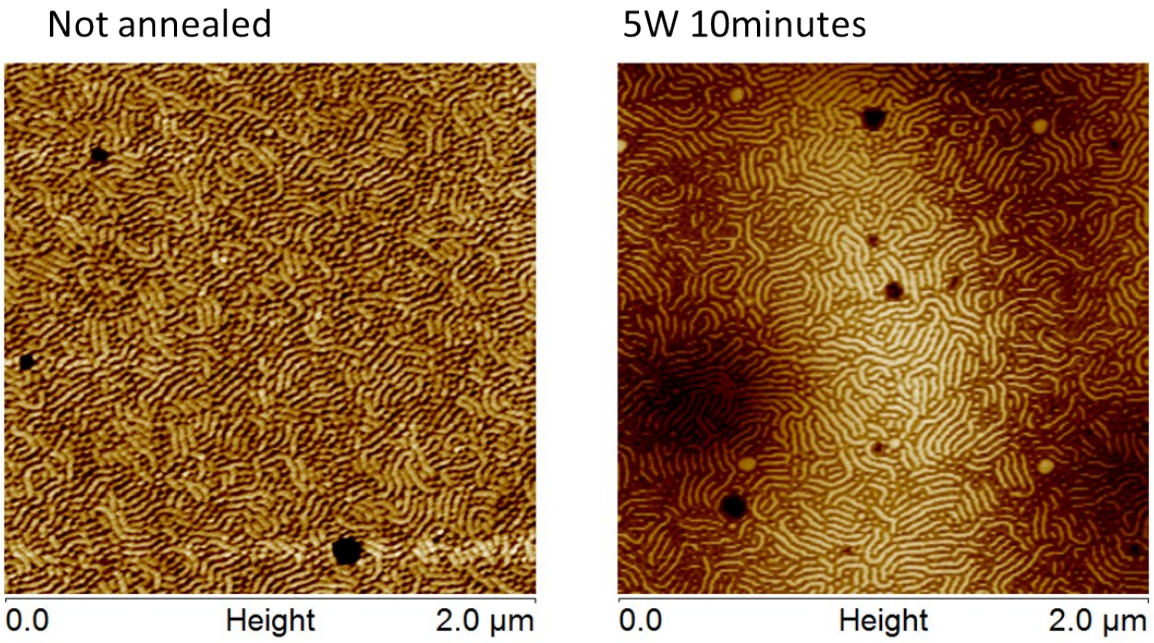

Figure S8. AFM images of MBM films made on silicon substrate from drop casted dichloromethane solution (5 g/L, **film thickness 1500 nm**). The left image shows the film without any annealing and the right one presents the film annealed at 5W during 10 minutes. We first tried an annealing for 1 minute at 5W but the structuration didn't change. Then we increased the irradiation time to 5 and even 10 minutes but we couldn't obtain perpendicular cylinders. These continuous films were produced to compare with porous honeycomb films.

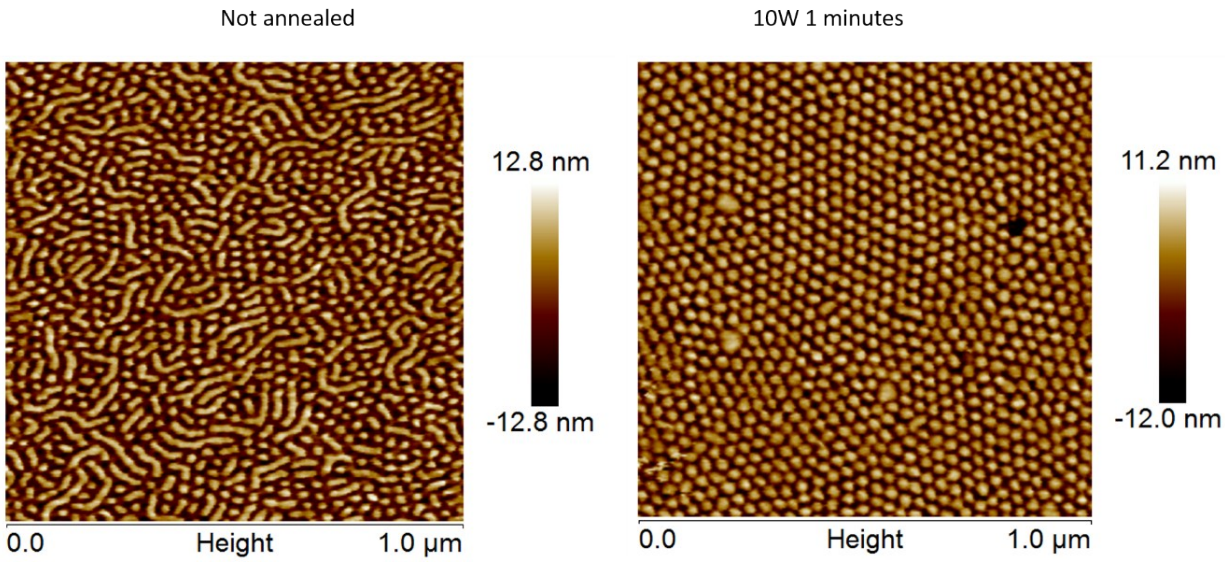

Figure S9. AFM images of continuous MBM films made on silicon substrate from drop casted dichloromethane solution (5 g/L, **film thickness 1500 nm**). These continuous films were produced to compare with porous honeycomb films.

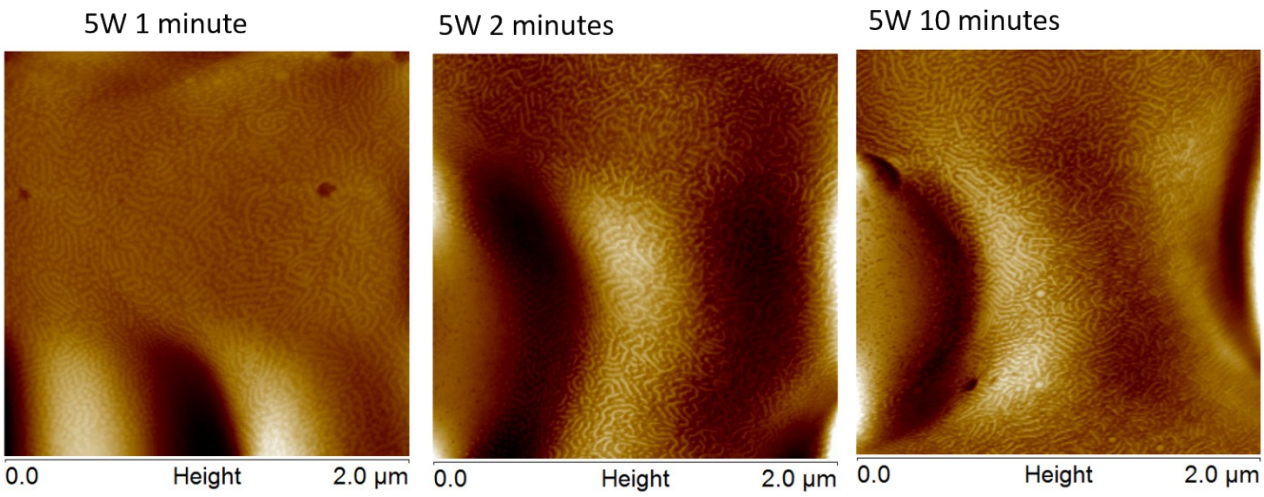

Figure S10. AFM images of honeycomb structures made in static method at 80% of relative humidity, with a solution of MBM20 in dichloromethane has been used for the drop casting. 5g/L. These films have been annealed with microwave irradiation at 5W during different times.

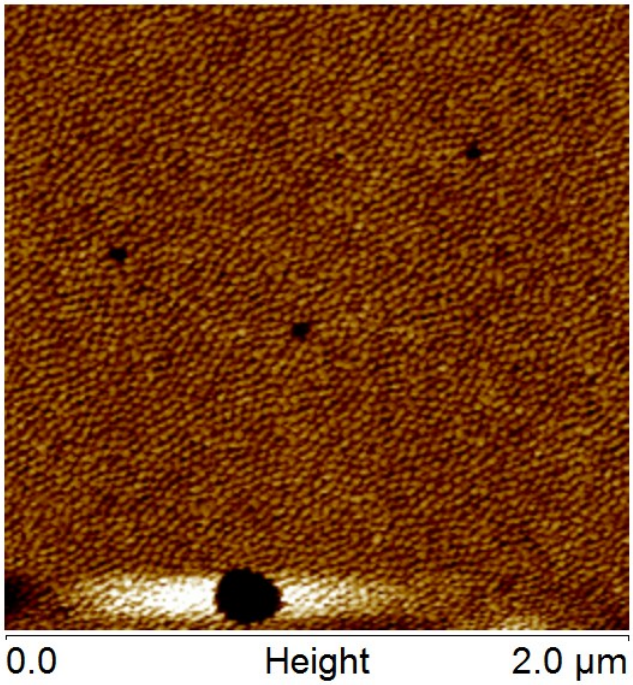

Figure S11. AFM image of honeycomb structures made in static method at 80% of relative humidity, a solution of MBM20 in dichloromethane has been used for the drop casting. 5g/L. This films has been annealed with microwave irradiation at 10W during 2 minutes

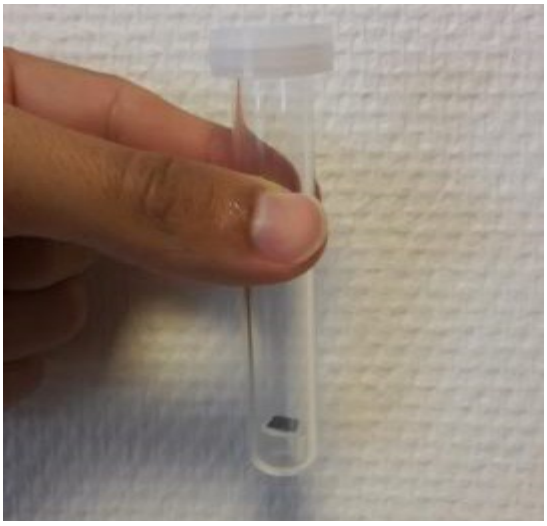

Figure S12. Picture of the set-up used to submit the wafers to the microwave irradiation.

The thickness of the continuous films were calculated through ellipsometry measurement. The ellipsometric values, Is and Ic were measured in a spectrum of 0.6 eV to 6 eV at an incidence angle of 70° in configuration II and configuration III, by an Uvisel® ellipsometer from Horiba©. According to the relations below, the ellipsometric parameters Δ and ψ are determined respectively with acquisition data from *configuration II* and *configuration III*.

Configuration II: $Is = \sin 2\Psi \sin\Delta$ $Ic = \sin 2\Psi \cos\Delta$

Configuration III: $Is = \sin 2\Psi \sin\Delta$ $Ic = \cos 2\Psi$

The model used to fit the parameters is composed of a classical Si <100> material as substrate, and a layer upon it with a variable thickness. This thickness is guessed in a range between 1 nm and 300 nm. The composition of the layer in PMMA and PnBua is fixed as the volume fraction of each block has been previously determined by NMR. The optical behavior of the PMMA is described with the new amorphous model found in the software. However, for the PnBuA, thin layers of PnBuA homopolymer spin-coated at 1500 and 2000 rpm on silicon. Finally the BCP model was composed with each modelled material, following the volume fraction of each block.

The PnBuA optical parameters are determined by using an absolute fitting process, in which each parameter is guessed between limits that keep a physical meaning, as it's described in the Table 1. The term n_∞ is at least greater than one and equal to the value of the refractive index when the incident beam energy tend to the infinite. The parameter ω_g is correlated to the energy band gap. It's the energy from which the absorption starts to be non-zero. In the same way, ω_1 is approximately the energy at which the extinction coefficient is maximum (peak of absorption). The f_1 and Γ_1 parameters are related respectively to the strength (amplitude) and the broadening of the extinction peak.

Table 1. Limits used for the absolute fitting process to determine the new amorphous parameters of the PnBuA block

$1 < n_\infty < 2$
$1{,}5\ eV < \omega_g < 10\ eV$
$0\ eV < f_1 < 1\ eV$
$1{,}5\ eV < \omega_1 < 10\ eV$
$0{,}2\ eV < \Gamma_1 < 8\ eV$

The optical parameters of the new amorphous model has been taken from a 3w% solution of PnBuA in toluene. This solution has been spin coated at 1500 rpm and 2000 rpm on a piece of silicon wafer. The average value of each parameter is used for the MBM20 model.

Table 2. New amorphous model parameter fitted from spin-coated

Rotation speed [rpm]	*1500*			*2000*			***Average***		
n_{∞}	1,513	±	0,005	1,533	±	0,013	**1,523**	**±**	**0,009**
ω_g [eV]	4,182	±	0,047	4,367	±	0,099	**4,274**	**±**	**0,073**
f_1 [eV]	0,032	±	0,004	0,039	±	0,006	**0,035**	**±**	**0,005**
ω_1 [eV]	4,066	±	0,13	4,119	±	0,439	**4,092**	**±**	**0,284**
Γ_1 [eV]	0,758	±	0,118	1,434	±	0,259	**1,096**	**±**	**0,189**

Quantitatively, the polymer film thickness h follows the empiric formula, where k and β are material specific constants, η_0 is the initial polymer solution viscosity, Ω is the spin-coating angular velocity and α is a constant for the system with certain dispersity in function of the studied system with a value in general around -0,5 for most polymers.

$$h = k\eta_0{}^{\beta}\Omega^{\alpha}$$

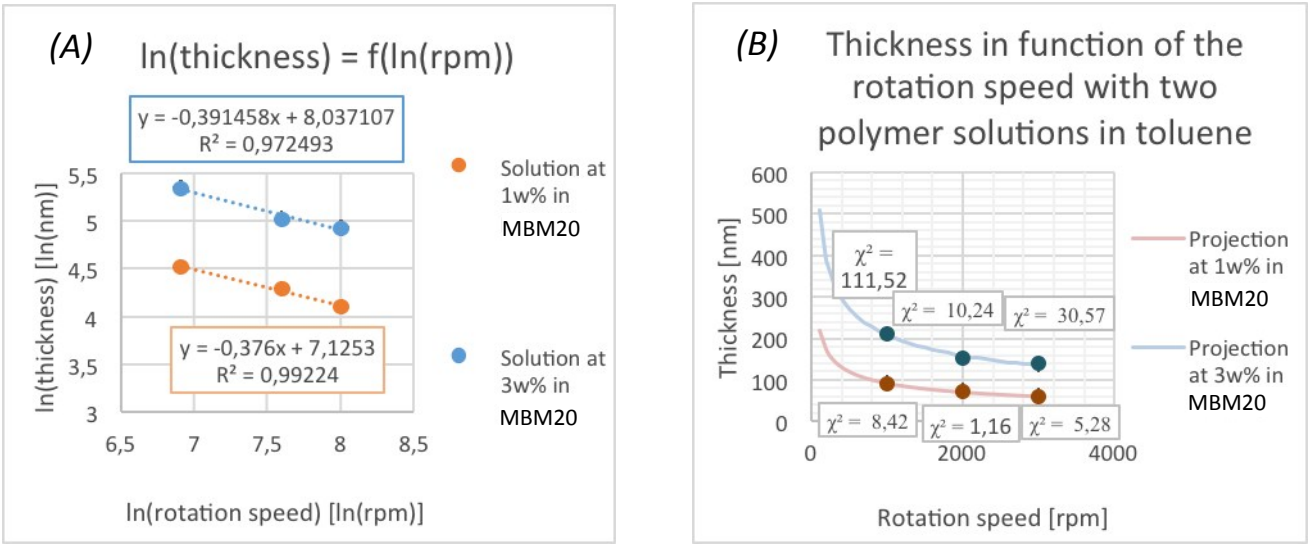

Figure S13. (A) Representation of the logarithm of the thickness taken in nanometers in function of the logarithm of the rotation speed taken in rpm. (B) Representation of the thickness in nanometer in function of the spin coating rotation speed in rpm. The red dots and blue dots line are respectively from a 8.7 g.L-1 (1 wt%) and a 26.8 g.L-1 (3 wt%) solution of MBM20 in Toluene. The projection is

According to this relation, we can verify the relative validity of the thickness measurement by tracing: $ln(h) = ln(k\eta_0^{\beta}) + \alpha \times ln(\Omega)$. As show the *Figure SI2*-(A), the coefficient α obtained by a linear regression is coherent with the empiric relation presented above. The linear regression coefficient for the two solution is quit satisfying, with a R^2 close to 1. Here χ^2 is correlated with the difference between the acquisition graph and the graph calculated from the model. As show the *Figure SI2*-(B), the 1w% solution show good χ^2 parameter inferior to 10. However the 3w% solution show a χ^2 value higher. As show the following chapter, this system demonstrate a strong phase separation without any annealing process.

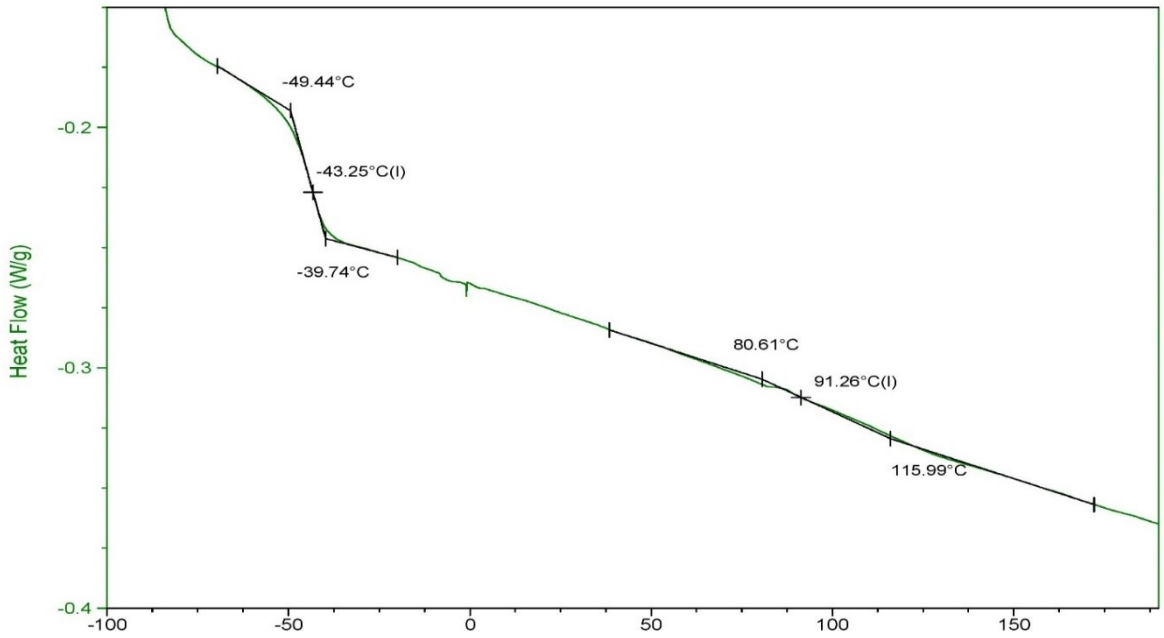

Figure S14. Differential Scanning calorimetry graph of MBM20. The PnBuA Tg and PMMA Tg are found respectively between -49°C and -40°C, at -43°C and between 80°C and 116°C, at 91°C.