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► **To cite this version:**

Aynur Guliyeva, Marylène Vayer, Fabienne Warmont, Anne-Marie Faugère, Pascal Andreatza, et al.. Thin Films with Perpendicular Tetragonally Packed Rectangular Rods Obtained from Blends of Linear ABC Block Terpolymers. *ACS Macro Letters*, 2018, 7 (7), pp.789 - 794. 10.1021/acsmacrolett.8b00272 . hal-01885762

**HAL Id: hal-01885762**

**<https://hal.science/hal-01885762>**

Submitted on 24 Jan 2022

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# Thin Films with Perpendicular Tetragonally-Packed Rectangular Rods Obtained from Blends of Linear ABC Block Terpolymers.

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**KEYWORDS:** Nanolithography, Block Copolymer, Thin Films, Square array, **Non CMC interfaces**

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**ABSTRACT:** A binary blend of poly(isoprene-block-styrene-block-(2-vinylpyridine)) (ISP) triblock terpolymers, having the same chain length but different compositions, was used to achieve an ordered lattice with 4-fold symmetry of rectangular-shaped rods of poly(isoprene) (I) and poly(2-vinylpyridine) (P). In given conditions, the I and P domains were oriented perpendicularly to the substrate, providing **new** appealing type of templates for nanopatterning. Thin films were prepared by spin coating, exposed to solvent vapor (providing morphological reorganization) and then characterized by Atomic Force Microscopy, Transmission Electron Microscopy and Grazing-Incidence Small-Angle X-Ray scattering. Selective I and P identifications were carried out by AFM and TEM on a model ISP, as well as development of a technique of electronic contrast enhancement to better assign the self-assembly structure in GISAXS

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In the latest development of block copolymer lithography, there is a great need to generate advanced morphology to widen the possibility of surface patterning, beyond the now well established lamellar and cylindrical geometries.[1-5] For that purpose, it is already well known that ABC block terpolymer possesses a larger morphological diversity and complexity in comparison to their diblock counterparts. If the phase behavior is still primarily governed by the Flory Huggins parameters ( $\chi$ ), the overall degree of polymerization (N) and the volume fraction of each blocks, the addition of a third block increases the possible placement of the blocks, allowing for a larger variety of morphologies. [6,7] This diversity of morphology can be also enhanced if one considers blends such as homopolymer/block copolymer [8] or block copolymer/block copolymer,[9,10] where new morphologies that are rarely (if not) found for the neat system can be formed. It has been recently reported that blends of linear poly(isoprene-block-styrene-block-(2-vinylpyridine)) (ISP) triblock terpolymers having the same total chain lengths but different compositions could exhibit an ordered array of rectangular-shaped rods with 4-fold symmetry in bulk [11]. This **unusual morphology rectangular form of the interface** (for linear block copolymer) arises from the presence of blocks with a pronounced difference in length that leads to a peculiar spatial location of the chains, inducing a non-constant mean curvature (non-CMC) interface. If prepared in the form of thin films, these rectangular features arranged in 4-fold symmetry would provide a very appealing template for applications in lithography since it is more compatible with the device layout design rules of the microelectronic industry.[12-14] However, it is quite well known that bulk block

copolymer morphology is not always easily reproduced in the form of thin film due to confinement effect.[15] Moreover, orientation of features (perpendicular vs parallel) is highly dependent with the conditions of preparation and post-treatment of the films.[16] **Formation of thin films with perpendicular ordered arrays of rectangular-shaped domains as described in bulk by Asai et al [11] is then quite challenging since comparable morphologies have only been reported with star polymers [17] producing Archimedean tiling pattern with sharp interfaces [18] (which are generally more difficult to synthesize than linear block copolymers), or complex multi-step processes [19]. It has to be noted that if block copolymer self-assembly in 4-fold symmetry is quite well known in bulk and thin films [20-22], it only leads to cylindrical features in case of linear architectures.**

In this work, our goal was to study the effect of confinement (limited amount of matter) and surface interaction on the process of self-assembly of a blend of linear ISP triblock terpolymers that normally exhibits an ordered array of rectangular-shaped rods with 4-fold symmetry in bulk. For this purpose, we considered in this work the same ISP blend as treated in ref [11], namely a blend of two ISP block polymers having a total molar mass of 122 (ISP<sub>1</sub>) and 124 (ISP<sub>2</sub>) kg.mol<sup>-1</sup> with a volume fraction of I, S and P of (0.06, 0.62, 0.32) and (0.39, 0.56, 0.05) for ISP<sub>1</sub> and ISP<sub>2</sub> respectively (**see table Si** in supporting information for detailed description). The behavior of a neat ISP block polymer (ISP<sub>0</sub>) having a total molar mass of 90 kg.mol<sup>-1</sup> with a fraction of I, S and P of (0.12, 0.76, 0.12) was also investigated. ISP<sub>0</sub>, that exhibits ordered tetragonal packing of two kinds of cylinders (I and

P) in bulk [23] was used as a model system to optimize the preparation and the structuration of the films (particularly regarding to the ordering and orientation of the domains).

Fig. 1 shows the AFM images of the neat ISPo thin films after spin coating (Fig. 1a), tetrahydrofuran (THF) vapor exposure (Fig. 1b) and post treatments for selective identifications of the domains (Fig. 1c, 1d). Ordered nanostructures were not observed after spin coating but required THF vapors exposure at room temperature. After 8 hours exposure (Fig. 1b), AFM height image displays tetragonally-packed features but a clear observation of the three phases (I, S and P) is not straightforward. For that purpose, we performed ozonolysis (UVO) for a selective elimination of I on one hand (forming depression on the surface as showed in Fig. 1c) and selective swelling of P in ethanol on the other hand (forming protuberance on the surface as shown in Fig. 1d).

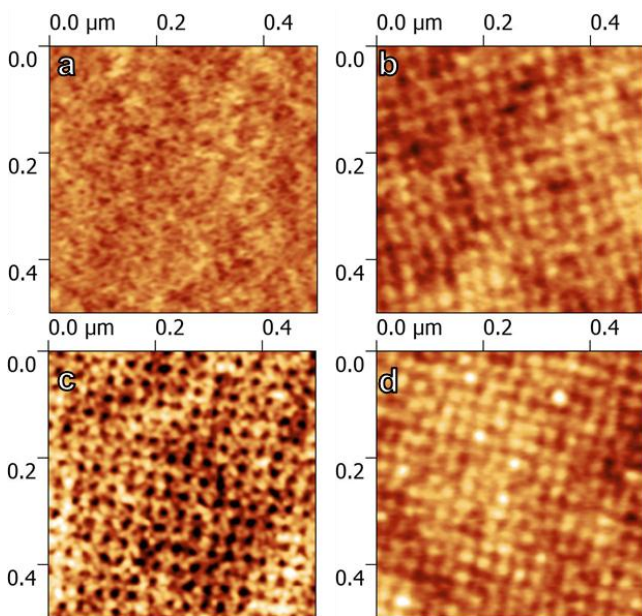


Figure 1. Height AFM of ISPo thin films after: a) spin coating b) solvent annealing c) solvent annealing and UVO d) solvent annealing and swelling in ethanol. z scale: 3nm

After ozonolysis, a distinct tetragonally-packed pattern of holes was observed, suggesting that the parent I domains (estimated diameter 20 nm from the image) occupied the exact same locations. Optimal conditions for the selective elimination of I was studied on homopolymer thin films of I, S and P (see Fig. S1). From the image analysis of extracted samples, a center-to-center distance of 33 nm between the I features was determined, in good agreement with the data obtained in the bulk for such composition [23]. In a similar way, the exposure to ethanol vapors resulted in the selective swelling of the P domains highlighting their tetragonal arrangement (center-to-center distance 33 nm). The presence at the surface of the film of a double and imbricated pattern of tetragonally-packed features of I and P strongly suggests that the bulk morphology (tetragonal packing of I and P cylinders [23]) is preserved, with I and P domains being oriented perpendicularly to the surface. These results also sug-

gest that despite different surface energy levels of the I, S and P phase ( $\gamma_I$ : 32 mJ/m<sup>2</sup>;  $\gamma_S$ : 40,7 mJ/m<sup>2</sup>;  $\gamma_P$ : 47 mJ/m<sup>2</sup> [24,25]) no wetting layer is formed at this stage. This can be explained by a mediation of the surface energies in the swollen state, which contributes to stabilize a perpendicular orientation.[26-28] For longer solvent exposure time (24h) the nanostructuration displayed elongated features (Fig. S3) suggesting a parallel orientation of the cylinders to the surface. The interfacial effect, as well as the role of the thickness in the orientation is discussed in the blends results section.

In order to confirm this structuration and to better characterize the geometry of the I and P domains, we carried out TEM observation (perpendicularly to the surface of the film) on floated films. Fig. 2 compares the TEM images after selective staining of I by OsO<sub>4</sub>, P by I<sub>2</sub> and fine staining of I and P altogether by OsO<sub>4</sub> and I<sub>2</sub>. This leaves the S matrix mostly unstained (white) while the I and P domains appear darker (a difference of grey level between I and P domains can be obtained by optimizing the staining duration). This staining sequence allowed us to selectively reveal the I pattern (Fig. 2a, OsO<sub>4</sub> exposure) and the P pattern (Fig. 2b, I<sub>2</sub> exposure), with a clear observation of a tetragonal packing for both polymers. In the two cases, the minority domains appear as circular domains, confirming that I and P domains form cylinders oriented perpendicularly to the surface of the film. The successive staining (Fig. 2c and 2d) confirms that ISPo triblock terpolymer self-assembles in tetragonal packing with two kinds of cylinders. From the TEM images we measured a center-to-center distance for the I and P domains of 34 nm, which was in good agreement with the distance previously found in AFM.

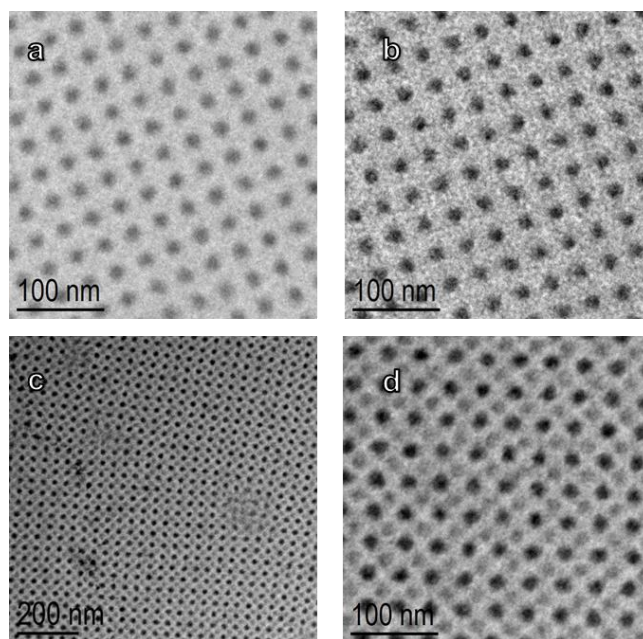


Figure 2. TEM images of ISPo solvent annealed thin films after: a) selective staining by OsO<sub>4</sub> b) selective staining by I<sub>2</sub> c) and d) selective staining by OsO<sub>4</sub> and I<sub>2</sub>. Black, white and gray domains represent I, S and P block respectively.

Samples were also analyzed by GISAXS in order to gain more insight into the internal structure of the films. Fig. 3a and 3b show a typical GISAXS profile obtained for a nanostructured thin film after solvent vapor exposure. Two diffraction peaks were observed at  $q_0 = 0.185 \text{ nm}^{-1}$ ,  $q_1 = 0.414 \text{ nm}^{-1}$ . Peaks of higher order were not observed due to the weak electronic contrast between the different polymers ( $\rho_{eI}$ :  $0.512 \text{ mol electron.cm}^{-3}$ ;  $\rho_{eS}$ :  $0.565 \text{ mol electron.cm}^{-3}$ ;  $\rho_{eP}$ :  $0.608 \text{ mol electron.cm}^{-3}$ ). The ratio of the position of these two experimental diffraction peaks  $q_1/q_0 = 2.24 (\sqrt{5})$  is in good agreement with a tetragonal packing for two kinds of cylinders where the electronic density contrasts between I and S on one hand and P and S on the other hand are approximately opposite. This peculiar feature leads to a strong attenuation of the diffraction peaks corresponding to the planes having a sum of their (h,k) Miller indices equal to an even number.[29] As a consequence, one can assign the two peaks observed in GISAXS to the diffraction of the (10) and (21) planes. From the  $q_0$  value, we calculate a center-to-center distance spacing of 34 nm which agrees quite well with the AFM and TEM results. In order to confirm the structure, P selective staining was carried out to increase the electronic density contrast between the domains. After this treatment, a new diffraction peak appeared at  $q_1 = 0.262 \text{ nm}^{-1}$  ( $q_0$  at  $0.185 \text{ nm}^{-1}$  being unchanged) as shown in Fig. 3d. The ratio of the positions of the two first peaks is now  $q_1/q_0 = 1.42 (\sqrt{2})$  which is consistent with a tetragonal packing with only one type of cylinder. This is due to the considerable increase of electron density between P and S (due to the  $I_2$  fixation on the P domains) making the difference of electron density between S and I now negligible. Sample is seen by X-rays as in Fig. 2b, i.e a simple tetragonal packing of stained P cylinders in a homogenous continuous phase where all reflections are now possible. Fig. 3d shows the positions expected for the higher order diffraction peaks (i.e. (11), (20), (21)) calculated from  $q_0$

=  $0.185 \text{ nm}^{-1}$  that fits quite well with the experimental positions of the maxima. This method which leads to an enhanced electronic contrast between the scattering domains have never been reported to our knowledge for the small angle X-ray scattering study of block polymers. This could be very useful for the structural characterization of block copolymer composed of segments with similar electronic density.

Taken together, these results confirm that ISPO gives in thin films an ordered tetragonal packing of two kinds of cylinders (I and P), oriented perpendicularly to the surface after THF solvent vapors annealing of 8 hours. We have shown here that the morphology was not subjected to any confinement and/or surface effect since the thin film morphology was strictly identical to the bulk morphology as described in ref [21]. Radlauer et al. have recently shown a different kind of behavior for poly(styrene)-block-poly(isoprene)-block-poly(lactide) (PS-b-PI-b-PLA, SIL) that exhibited a profound modification of the morphology in thin films compared to the bulk [30]. They attributed this behavior to the frustrated configuration of the polymer that displays a pronounced incompatibility between the adjacent I and L block. This type of behavior was not observed here, suggesting that block sequence plays a significant role in the destabilization of the bulk morphology in thin film.

Using the experimental conditions allowing to reach this well ordered self-assembled lattice of I and P cylinders (with CMC interface) oriented perpendicularly to the surface, we examined the behavior of a blend of two ISP linear triblock terpolymers namely (ISP1 and ISP2) which have similar total and midblock (S) molecular weights, but differ in the molecular weights of their I and P end-blocks (different chain lengths). As previously recalled, this blend showed a rectangular-shaped rods with 4-fold symmetry in bulk.[11]

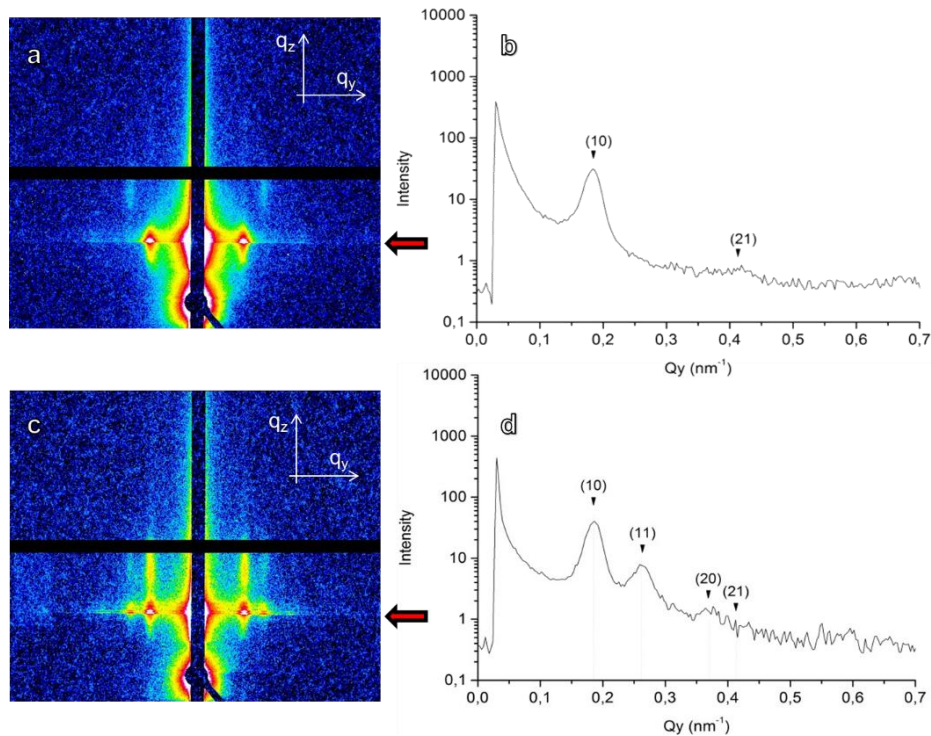


Figure 3. GISAXS pattern and corresponding in plane profile of ordered ISPO thin film a) and b) after solvent annealing c) and d) after solvent annealing and selective staining by I<sub>2</sub>. Profile position is marked by an arrow on the pattern.

Fig. 4 shows the AFM images of a blend of ISP<sub>1</sub> and ISP<sub>2</sub>, after spin coating, solvent vapor exposure and post-treatments for identification of domains. Topographical features organized in a tetragonal lattice were observed after 8h of THF exposure (Fig. 4b). Selective elimination of I by ozonolysis (Fig. 4c) and selective swelling of P by EtOH (Fig. 4d) allowed us to confirm the presence of the two minor phases (I and P) at the surface of the film, forming an imbricated lattice of two tetragonal arrangements of I and P domains. Similarly to ISPO, no wetting layer could be observed at that stage which is in favor of a mediation of the surface energies in the swollen state. The choice of solvent is critical in this regard (see Fig. S4 for annealing in other solvents). Annealing in THF vapor constitutes a favorable situation by being a good solvent for the three blocks. This was experimentally confirmed by swelling the three homopolymers in THF vapor (Fig. S5). This differs from the thermal annealing situation where the difference in surface energy cannot be overcome,<sup>[31]</sup> rapidly leading to the formation of a wetting layer (presumably I), preventing from the detection of the nanostructuration by AFM (Fig. S6).

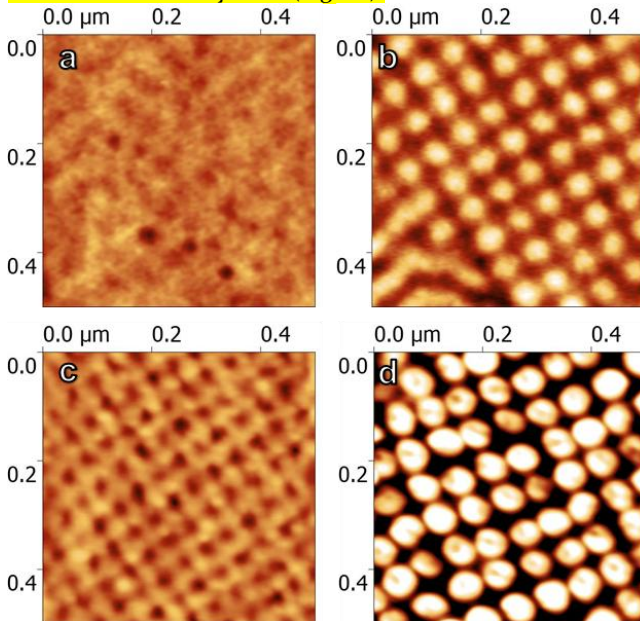


Figure 4. AFM topographic view of blend of ISP<sub>1</sub> and ISP<sub>2</sub> (60/40) thin films: a) after spin coating b) after solvent annealing c) after solvent annealing and UVO d) after solvent annealing and swelling in ethanol. z scale: 6nm

For longer solvent exposure time (24h) a parallel orientation of the rods was observed (not shown, similar to ISPO). We<sup>[32]</sup> and other<sup>[33]</sup> have already observed the transition from perpendicular to parallel orientation for cylindrical forming block copolymer upon annealing. This is driven by the tendency of blocks to progressively wet the interfaces (even in the situation of a surface energy mediation by solvent, a perfect non-selectivity towards the interface cannot be obtained). The parallel orientation constitutes the thermodynamically stable state but requires the thickness of the film to be commensurate with the natural period of the self-

assembly. Consequently, a perpendicular orientation is obtained for moderate annealing time (metastable) and progressively evolves towards a parallel orientation thanks to a self-adaptation of the thickness film (by polymer diffusion). Intermediate solvent vapor exposure durations showed mixed orientations with a typical morphology consisting of islands and holes (Fig. S7) with parallel orientation only on the islands (where the thickness is commensurate with the natural period of the self-assembly). This indirectly highlights the importance of the initial film thickness on the morphology control of the film.

From these images, we measured a center-to-center distance of 65 nm (except in Fig. 4c where the center-to-center distance decrease to 50 nm presumably due to a global shrinkage of the lattice during the UVO treatment – see TEM results for confirmation of the center-to-center distance). At that stage, the rectangular shape of those features cannot be confirmed, due to tip convolution effect.

In Fig. 5, TEM observations are compared after selective staining I by OsO<sub>4</sub> (Fig. 5a), P by I<sub>2</sub> (Fig. 5b) and staining both I and P (Fig. 5c). It confirms the presence of tetragonal-packed structures of two different kind of domains (I and P) and clearly demonstrates the rectangular shape (non-CMC) of the domains, oriented perpendicularly to the surface of the film. From these images, we measured a center-to-center distance of 70 nm for the I and P domains. As proposed by Asai et al. <sup>[11]</sup> this very singular interface curvature could result from the systematic localization of component polymer chains along the domain interfaces, creating non-CMC rectangular-shaped domains. This can be only obtained if the two components of the blends display different compositions of their I and P blocks (but the same chain length), introducing a molecular weight distribution in the I and P domains and favoring a non-uniform placement of the chains. This was of course not observed with ISPO, where the narrow distribution in the I and P domains can only produces round interfaces.

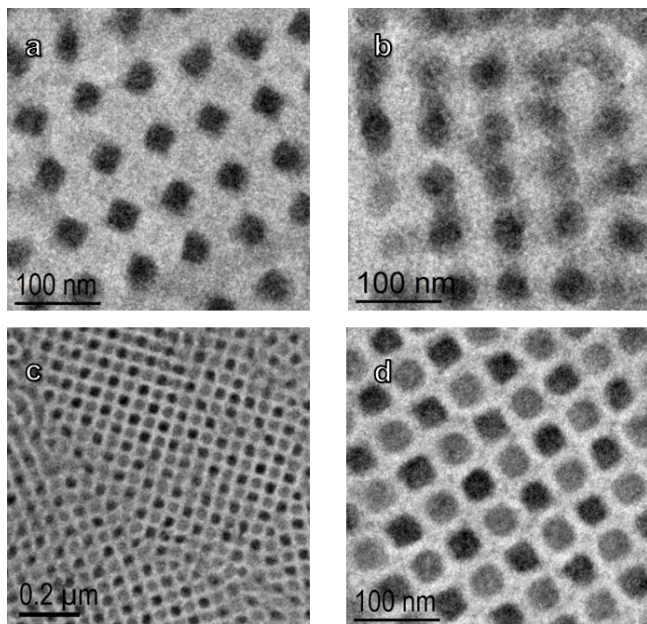


Figure 5. TEM images of blend of ISP<sub>1</sub> and ISP<sub>2</sub> (60/40) solvent annealed thin films: a) after selective staining by OsO<sub>4</sub> b) after selective staining by I<sub>2</sub> c) and d) after selective staining by OsO<sub>4</sub> and I<sub>2</sub>. Black, white and gray domains represent I, S and P block respectively.

Fig. 6 shows the GISAXS profile of the ISP<sub>1</sub> and ISP<sub>2</sub> blend after solvent vapor exposure, a strong diffraction peak is observed at  $q_0 = 0.0975 \text{ nm}^{-1}$ , with a weak shoulder at  $0.203 \text{ nm}^{-1}$ . For the reasons given earlier (the electronic density level of the three component S, P, I leads to specific extinction rules), these two peaks can be attributed to the reflection of the (10) and (21) plane of a tetragonal packing of I and P rods. This allows to calculate the center-to-center distance

( $2\pi/q_0 = 65 \text{ nm}$ ) which is again in good agreement with the AFM and TEM results. Using the same enhanced electronic contrast approach we used earlier by staining the P domains, we performed this time a more conventional selective removal of the I phase. In a very similar way, this led (Fig. 6) to the observation of additional peaks due to increased difference of electron density between I and S, making in this case the difference of electron density between S and P negligible in comparison. The lattice can be then considered as a simple tetragonal packing of pores (resulting from the I elimination) in a homogenous continuous phase where all reflections are now possible. Fig. 6b shows the positions expected for the higher order diffraction peaks calculated from  $q_0 = 0.0975 \text{ nm}^{-1}$  that fits quite well with the experimental positions of the maxima.

In summary, using ISP triblock terpolymer in thin films, we have demonstrated the possibility to achieve the formation of lattices of tetragonally-packed domains of I and P domains, oriented perpendicularly to the surface of the film. The structures were fully characterized by means of a complementary set of characterization tools in order to address the morphology at the surface of the film but also in the film. Interfaces with CMC (cylinders) and non-CMC (rectangular-shaped rods) were isolated from the neat ISP and the ISP blend respectively. For these two different systems, the morphologies observed in thin films are similar to the one obtained in bulk, which suggests that the confinement of the chains does not, in this case, influences their organization. The non-CMC case, which is observed for the first time in thin films for linear block terpolymer, offers exciting potential for nanopatterning where the need for rectangular shape features in a square symmetry is high.

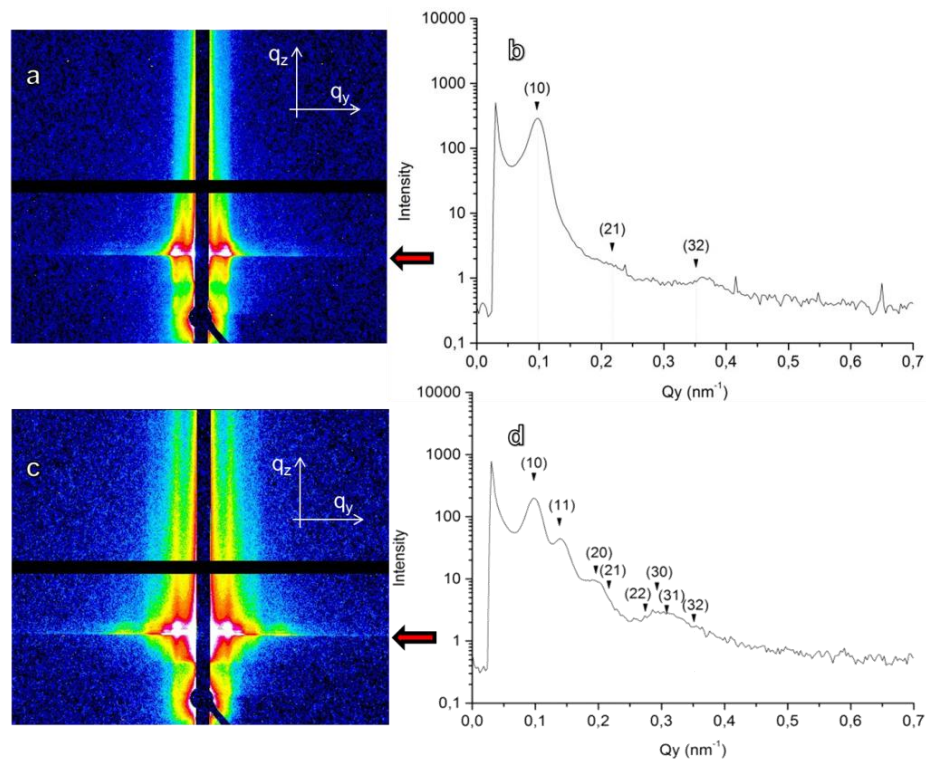


Figure 6. GISAXS pattern and corresponding in plane profile of blend of ISP1 and ISP2 (60/40) thin films in which tetragonal-packed structures of two different kind of domains were observed by AFM and TEM: a) and b) after solvent annealing c) and d) after solvent annealing and UVO. Profile position is marked by an arrow on the pattern.

## ASSOCIATED CONTENT

### Supporting Information.

Materials and methods, thickness variation upon UVO treatment, AFM image analysis using Power Spectral Density, AFM image of a parallel orientation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## ACKNOWLEDGMENT

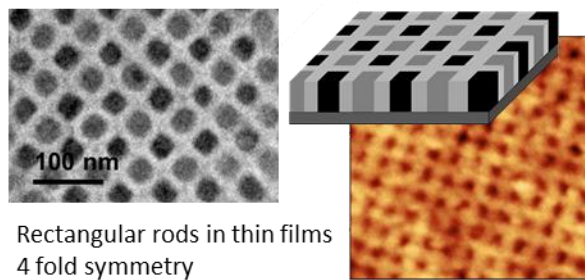
Alain Pineau is acknowledged for fruitful discussions. Siham Ahoud, Lilian Marié, Julie Mercié and Sarah Serrano, from the PIA-IDEFI-EDIFICE project (ANR-11-IDFI-0015) are thanked for their help in the optimization of the selective degradation of PI. We gratefully acknowledge the financial support provided to the PIVOTS project by the Région Centre – Val de Loire (ARD 2020 program and CPER 2015 -2020) and the French Ministry of Higher Education and Research (CPER 2015 -2020 and public service subsidy to CNRS and Université d'Orléans).

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Rectangular rods in thin films  
4 fold symmetry

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