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Nanostructuration of poly(isoprene-b-styrene-b-2-vinylpyridine) linear triblock terpolymers in thin film

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*If you can't fly, then run.
If you can't run, then walk.
If you can't walk, then crawl,
But by all means, keep moving!*

Martin Luther King Jr.

To my Father, Mother, Brother and Zakir
Without you I would not be the person I am today...

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Titre et résumé en français :

Nanostructuration de terpolymères triblocs linéaires poly(isoprène-b-styrène-b-2-vinylpyridine) en films minces.

L'auto-organisation de copolymères à blocs (CPB) permet de former des motifs nanostructurés avec différentes morphologies qui ont attiré une attention considérable en tant qu'une solution alternative aux approches classiques de lithographie optique. Ils pourraient constituer une solution industrielle en raison de leur compatibilité avec la technologie au silicium déjà utilisée pour les matériaux en microélectronique.

Dans la littérature, l'auto-assemblage de copolymères diblocs est assez bien décrit et de nombreux travaux montrent toutes les nanostructures possibles en volume et en films minces. Pour aller plus loin, l'utilisation de CPB de type triblocs pour la nanostructuration a attiré l'attention des chercheurs. L'incompatibilité entre chaque bloc de terpolymères ABC et la position du bloc dans la chaîne permettent d'obtenir des morphologies plus complexes. Malgré une chimie très basique et une architecture simple, le poly(isoprène-b-styrène-b-2-vinylpyridine) (ISP) a récemment été utilisé pour développer une large gamme de nanostructures originales en utilisant des mélanges.

Dans cette thèse, nous nous sommes attachés à préparer des films minces nanostructurés à partir de CPB de type ISP et de les caractériser par différentes techniques (AFM, MET et GISAXS). Le but de la recherche est de réaliser des nanostructurations originales en films minces afin de prendre en compte l'effet de confinement (quantité de matière limitée, interaction avec la surface ...) et de comprendre les phénomènes se produisant au cours de la structuration d'ISP dans des films minces. Les travaux comportent une partie mise en œuvre des films minces, une partie réorganisation et une partie caractérisation des structures obtenues. Des triblocs seuls et des mélanges de triblocs ont été étudiés et caractérisés à l'aide de différentes méthodes de caractérisation. Les films déposés par spin coating sur le substrat de silicium doivent être réorganisés grâce à une exposition aux vapeurs de solvant pour obtenir des structures ordonnées à longue distance sur la surface et dans le volume du film mince.

Le premier chapitre de la thèse introduit le concept d'auto-assemblage des CPB. Pour des CPB de type AB, ce phénomène est assez bien décrit dans la littérature et des travaux montrent toutes les nanostructures possibles du copolymère diblocs en volume et en films minces tels que les sphères, les cylindres, la gyroïde et les lamelles. Pour divers types d'application de nanotechnologie de surface (telles que la lithographie, les capteurs, l'optique...), il est intéressant de générer des morphologies plus complexes. (Tallegas et al. 2013; C. M. Bates et al. 2014; Luo et Epps 2013; C. M. Bates et Bates 2017; Gu et al. 2012; Morris 2015). Comme cela a été mentionné précédemment, les CPB de type ABC sont des bons candidats qui présentent une diversité et une complexité de morphologies plus grandes par rapport au polymère diblocs en raison de l'addition d'un troisième bloc (F.S. Bates et al. 2012; Liu et al. 2012). De nouvelles morphologies peuvent également être développées en mélangeant des homopolymères ou d'autres CPB avec des triblocs, comme

le montre en volume Ahn et Izumi (Ahn et al. 2017; Izumi et al. 2015). Les travaux de Matsushita montrent que le mélange de triblocs linéaires simples permet de générer une grande variété de motifs inhabituels avec des interfaces planes. Il convient de noter que les polymères en étoile permettent de produire un pavage archimédien avec des interfaces planes ou d'autres morphologies complexes en couches minces en raison de l'architecture de la chaîne (Aissou, Choi et al. 2013; Aissou, Nunns et al. 2013; Aissou et al. 2016). Cependant, il est généralement plus difficile de synthétiser ce type d'architectures et c'est pour cette raison que cette approche est très attrayante. La production de domaines, avec des interfaces planes (non CMC), disposées en symétrie quadratique en couches minces (comme le montrent Asai et al. (Asai, Takano et Matsushita 2015b)) pourrait constituer un modèle très attrayant, plus compatible avec la forme des interfaces utilisées dans l'industrie de la microélectronique (Ruiz, Dobisz et Albrecht 2011; Chang et al. 2014; Tang et al. 2008). Nous concluons la fin du chapitre 1 par l'intérêt de cette étude, qui est donc d'obtenir des morphologies complexes originales avec des triblocs «simples», à savoir un terpolymère linéaire non frustré (seul ou en mélange) possédant une chimie «basique» basée sur les blocs bien connus PI, PS et P2VP. Notre objectif est de comparer la morphologie du système en volume et en couche mince et de comprendre le mécanisme de nanostructuration dans une couche mince. En raison des effets de confinement, il est en effet possible d'obtenir différentes structures en volume et en film mince. Il faut ensuite une étude précise pour comprendre la morphologie et l'orientation des structures en cas de film mince.

Dans le deuxième chapitre, les détails expérimentaux et les travaux préliminaires sont présentés. Avant d'approfondir l'étude du comportement des systèmes triblocs ISP, nous avons en particulier effectué plusieurs études préliminaires sur les polymères PI, PS et P2VP afin de caractériser les propriétés de chaque bloc. Cela nous a permis de comprendre l'interaction de chaque polymère pris séparément avec le solvant et le substrat, afin de mieux contrôler le processus d'auto-assemblage du CPB. Cette étape permet de prévoir le choix du solvant pour les étapes cruciales de la nanostructuration: élaboration de films (solution de solvant), réorganisation sous vapeurs de solvant (solvant vapor annealing : SVA), identification de blocs (gonflement sélectif d'un bloc dans le système ABC). Grâce à ces résultats, le DCE a été choisi comme un solvant de solution, l'éthanol comme solvant de révélation du PVP, le THF et le toluène comme solvant de SVA. Nous avons aussi développé des méthodes de caractérisation adaptées à ce polymère en film mince, associant le MET et une technique originale de GISAXS reposant sur le marquage sélectif des blocs par des éléments lourds (iode, osmium) afin d'augmenter le contraste de densité électronique entre différents domaines. A notre connaissance, cette méthode n'a jamais été rapportée pour l'étude de la diffusion de rayons X aux petits angles pour des CPB. Ceci nous a permis de confirmer la structure interne et la forme exacte de l'interface (rayon de courbure) des domaines minoritaires et d'observer les transitions originales entre des morphologies et des orientations. La présence de couches de mouillage aux deux interfaces du film (film/air et film/substrat) était une caractéristique commune à tous les systèmes.

Le troisième chapitre traite des résultats et de la discussion. **Il est divisé en deux parties.**

Dans la partie I, la nanostructuration de triblocs linéaires seuls, formant une morphologie cylindrique et gyroïde en volume, est étudiée en film mince. Ces deux polymères sont choisis pour leur position dans le diagramme de phases (se trouvant à la limite des différentes morphologies sur le diagramme de phase : cylindrique/sphérique d'une part gyroïde/cylindrique d'autre part) afin de favoriser les transitions de phase dans la configuration en couche mince.

Le CPB ISP19 a une masse molaire moyenne en nombre de 90 kg/mol avec la même fraction volumique pour les blocs PI et P2VP (0,12/0,76/0,12). Selon des travaux réalisés à l'Université de Nagoya, ISP19 présente en volume un arrangement tétragonal de deux types de cylindres (PI et P2VP dans une matrice PS, voir le Figure 1a). (Mogi et al. 1994). Il est intéressant de noter que Ahn et al. (Ahn et al. 2017) ont montré qu'un tribloc ISP avec une fraction volumique de 0,12/0,75/0,13 (presque la même composition ISP19 avec une masse molaire similaire de 84 kg/mol) présente à la place une morphologie avec coexistence de sphères (SPH) de PI et de cylindres (CYL) de P2VP (Figure 1b). Ce résultat n'est pas surprenant puisque ce CPB présente une composition à la frontière entre les domaines SPH et la structure CYL. (Mogi, Kotsuji et al. 1992; Matsushita 2000).

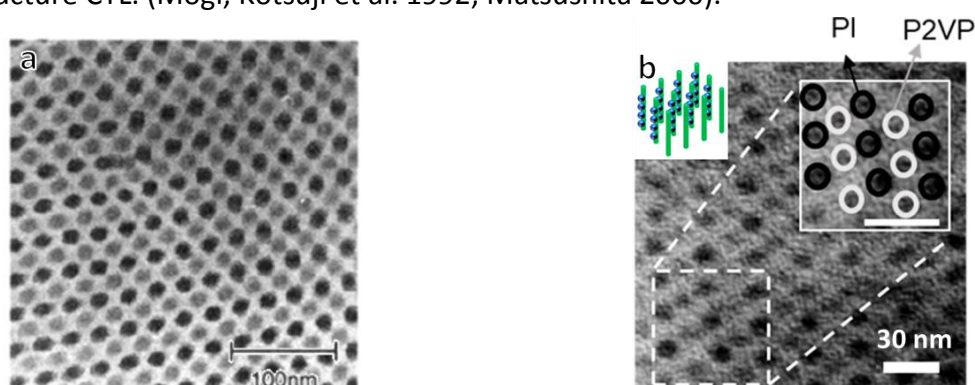


Figure 1. Les images de MET de (a) ISP19 en volume par Mogi et (b) ISP tribloc en volume par Ahn

En film mince, la nanostructuration ordonnée a été obtenue après SVA dans les vapeurs de THF. La difficulté de la nanostructuration dans le cas du toluène peut être expliquée par le taux de gonflement plus faible des polymères dans ce solvant ($P_{\text{toluène}} < P_{\text{THF}}$). De plus, le toluène est un solvant sélectif pour les blocs PI et PS, comme cela a été démontré dans la partie des études préliminaires, et il peut influencer sur la structuration (formation directe d'une couche de mouillage).

La nanostructuration d'ISP19 en couche mince est plus complexe que la morphologie simple décrite par Mogi pour l'organisation en masse. Après un temps de SVA modéré dans le THF (8h), les domaines sphériques dans un arrangement carré ont été observés sur les images d'AFM et MET « top-view ». Pour des temps d'exposition plus longs (24h), des domaines allongés ont été observés à la surface. Le couplage de différentes méthodes de caractérisation, à savoir AFM, MET et GISAXS, permet d'étudier la surface et la structure interne d'un film mince. En particulier, les résultats d'analyse de coupes par MET ont mis en

évidence la présence de sphères à l'intérieur du film après une durée modérée de SVA et de cylindres après une SVA plus longue dans le THF. Les images en coupe MET montrent également la présence de couches de mouillage de PI à l'interface film/air et de P2VP à l'interface film/substrat. Les résultats de GISAXS sont en bon accord avec les autres résultats et ils ont confirmé la morphologie carrée pour un traitement SVA plus court. De plus, le GISAXS montrait des signes de la présence d'une structure périodique à l'intérieur du film (direction q_z) suggérant la présence d'une morphologie sphérique. Donc, la nanostructuration obtenue en film mince n'est pas similaire à la morphologie en masse développée par Mogi et la transition CYL-SPH a été observée sous l'effet d'un film mince. Cette transition peut être facilitée par la position de ISP19 sur le diagramme de phases.

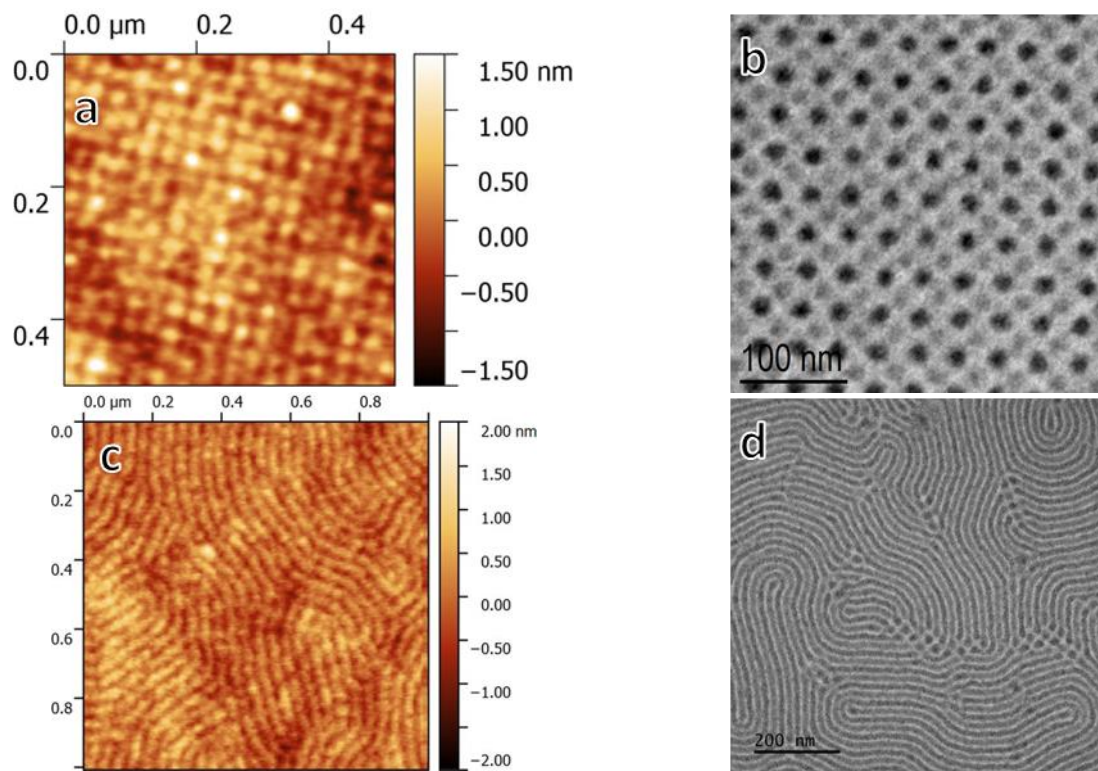


Figure 2. Les images d'AFM (a, c) et MET (b, d) d'ISP19 après une SVA modérée (8h, a et b) et une SVA longue (24h, c et d)

Le CPB ISP23 est un tribloc asymétrique ayant une masse molaire moyenne en nombre de 91 kg/mol avec une fraction de PI, PS et P2VP de (0,20/0,66/0,14) qui donne une structure gyroïde en volume (Mogi, Mori, et al., 1992; Suzuki, Seki et Matsushita, 2000). On sait qu'en fonction de la position dans le diagramme de phase ternaire, deux types de gyroïde peuvent être observés. La première correspond au même groupe d'espace Q_{230} que pour les diblocs (Hajduk et al. 1994) et présente deux réseaux imbriqués de cylindres cœur-coquille avec connecteurs triples. Ceci a généralement été observé pour des compositions asymétriques telles que 0,40/0,41/0,19 pour PI-b-PS-b-PDMS (Shelfelbine et al. 1999) où la matrice est PI et où l'arrangement cœur-coquille est constitué de PDMS comme cœur et de PS comme coque. Pour des compositions plus symétriques, la gyroïde alternée (GA) avec le groupe d'espace Q_{214} est généralement formée avec deux réseaux interpénétrés formés par chaque bloc terminal dans une matrice de bloc central.

Pour le ISP sélectionné dans ce travail (ISP23), il convient de noter que la fraction volumique du polystyrène à blocs centraux (0,66) est élevée. Une teneur légèrement plus élevée en PS conduirait à un arrangement tétragonal de cylindres. De la même manière qu'ISP19 qui se trouvait à la limite des cylindres et des sphères dans le diagramme de phases, ISP23 peut présenter le même type de transition ordre/ordre (gyroïde à cylindres) amplifié par une configuration en film mince. Cela a motivé le choix d'ISP23 pour cette étude sur les couches minces.

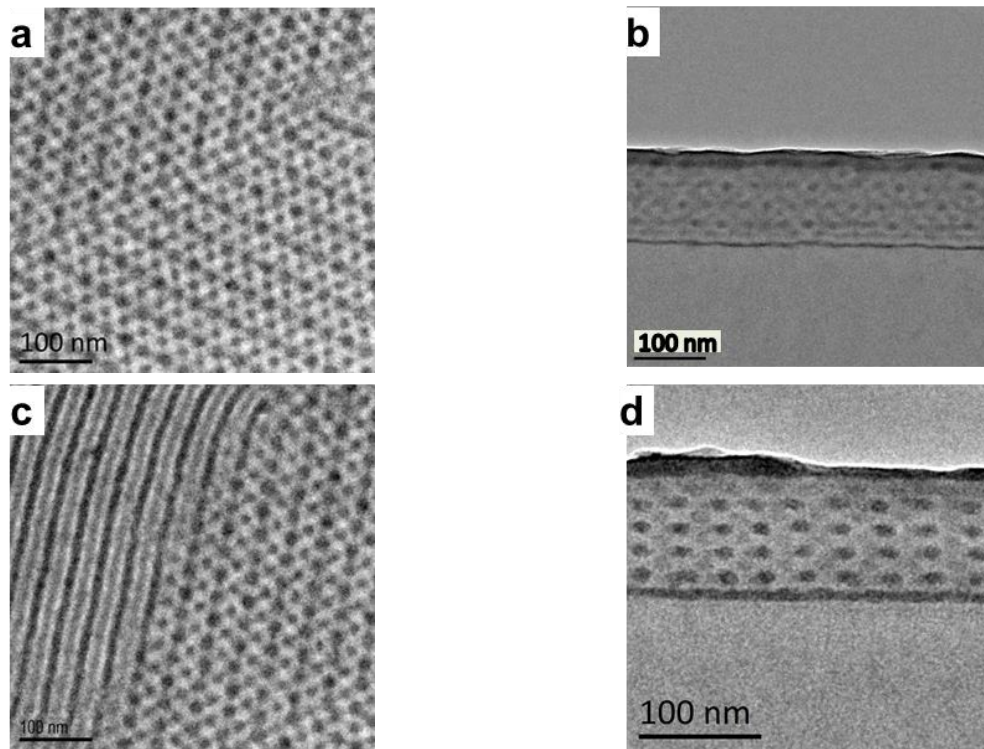


Figure 3. Les images de MET d'ISP23: (a et b) structure gyroïde (c et d) structure cylindrique

Les films minces d'ISP23 nanostructurés ont été obtenus uniquement après SVA dans les vapeurs de THF. Comme pour ISP19, la durée de SVA a un impact sur la morphologie formée (Figure 3). Pour des temps modérés, les films minces présentent une morphologie de type gyroïde alterné (G_A), identique à celle en volume. Cependant, nous avons constaté que cette configuration de film mince conduit à certaines caractéristiques telles qu'une orientation préférentielle de la structure G_A (avec le plan (011) parallèle à la surface), accompagnée d'une contraction du réseau dans la direction [011] en raison de dégonflement qui s'est produit pendant le séchage et la formation d'une couche de mouillage de P2VP à l'interface film/substrat et d'une couche de mouillage de PI à l'interface air/film. Un long temps de recuit au solvant a conduit à une transition de cette structure vers une structure de P2mm avec une alternance de cylindres de PI et de P2VP. Les plans {0-11} du gyroïde deviennent les plans {010} de la structure tétragonale et les cylindres sont développés dans la direction $\langle 010 \rangle$ parallèlement au substrat. Cette transition, qui n'a à notre connaissance jamais été observée, est représentée schématiquement à la figure 4. Elle constitue une des éléments marquant de ces travaux.

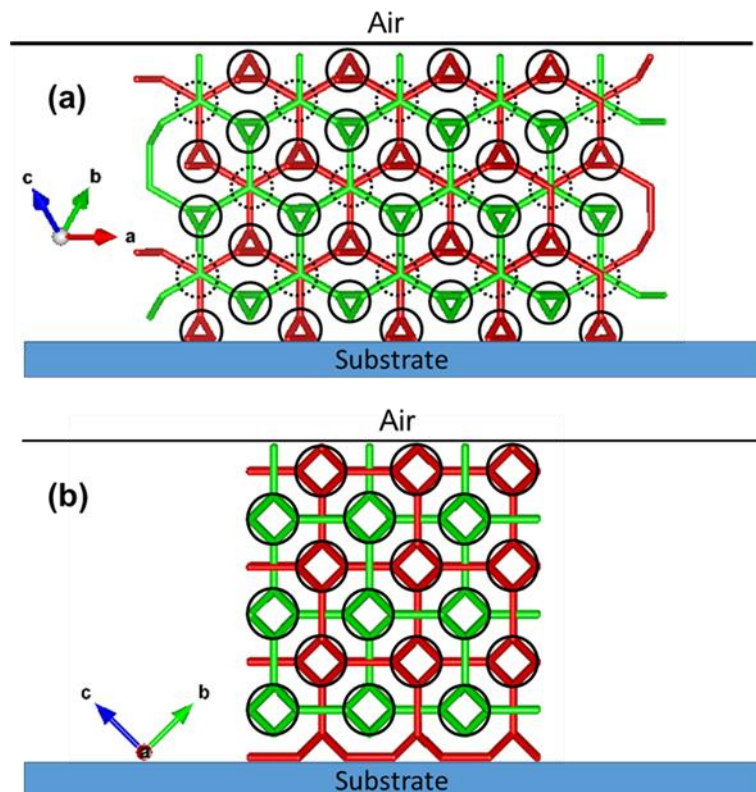


Figure 4. Schéma représentant la transition entre deux morphologies différentes: (a) G_D à HEX et (b) G_A à P2mm (PI en vert et P2VP en rouge). Les cercles pleins représentent la position des cylindres résultant de la réorganisation d'un type de réseau, tandis que les cercles en pointillés représentent la position des cylindres résultant de la fusion de deux types de réseaux. Pour la clarté de la représentation, les cellules unitaires de G_A et P2mm ne sont pas déformées. La voie (a) est impossible à réaliser pour un terpolymère triblocs.

En conclusion de la partie I, l'auto-assemblage des triblocs seuls ISP19 et ISP23 se trouvant à la frontière de domaines sur le diagramme de phase (sphères/cylindres pour ISP19 et cylindres/gyroïde pour ISP23) a été réalisé en couche mince. Nous avons montré que dans certaines conditions, les morphologies en couches minces d'ISP19 et ISP23 ne sont pas similaires aux structures en volume en raison de l'effet de confinement. La transition entre différentes structures (sphères/cylindres ou cylindres/gyroïde) a été observée en raison de l'effet de film mince et les résultats ont été confirmés par différentes méthodes de caractérisation.

Dans la partie II, des nanostructures plus complexes basées sur des mélanges de différents triblocs sont présentées. Le but de cette partie est d'étudier la possibilité de reproduire la morphologie observée en volume dans une configuration en film mince, où le confinement et l'effet de surface peuvent jouer un rôle important.

Les CPB $ISP\alpha$ et $ISP\beta$ ont une masse molaire moyenne en nombre de 122 kg/mol et 124 kg/mol, respectivement. Selon des travaux réalisés en volume par Asai (Asai, Takano et Matsushita 2015), $ISP\alpha$ possédant un très court segment de PI (0,06/0,62/0,32) présente des cylindres dans des lamelles (le composant mineur PI reste dans des cylindres isolés au centre des lamelles de PS, en raison de la composition très asymétrique). Le tribloc $ISP\beta$ avec une chaîne courte de P2VP (0,39/0,56/0,05) forme des sphères dans une structure gyroïde, où les composants mineurs de P2VP restent dans des sphères isolées au centre de la matrice de PS.

Des mélanges binaires d' $ISP\alpha$ et $ISP\beta$ avec des compositions différentes ont été réalisés par Asai (Asai et al. 2015) en volume (tableau 1). Ces mélanges présentent de nouveaux motifs à interfaces non CMC, constitués de piliers rectangulaires avec une symétrie quadratique ou bien des motifs cylindriques disposés en triangles et en pentagones.

Échantillon	Proportion de mélange	$\varphi_{PI}/\varphi_{PS}/\varphi_{P2VP}$
$ISP\alpha/ISP\beta$	60/40	0.20/0.60/0.20
	48/52	0.24/0.59/0.17
	40/60	0.26/0.58/0.16

Table 1. Caractéristique de mélanges de CPB: φ (fraction volumique).

L'étude de ces mélanges sous forme de film mince a attiré notre attention afin de développer une nanostructuration similaire (avec une interface non circulaire) et de comprendre l'auto-assemblage du mélange tribloc ISP sous effet de confinement.

Tout d'abord, nous nous concentrons sur un mélange 60/40 de CPB $ISP\alpha$ et $ISP\beta$ qui donne une composition finale avec la même fraction volumique pour les domaines minoritaires PI et P2VP (0,20). En utilisant ce mélange de triblocs dans des films minces, nous avons démontré la possibilité d'obtenir des domaines minoritaires de PI et P2VP présentant des interfaces rectangulaires, arrangés avec une symétrie tétragonale, orientés perpendiculairement à la surface du film (Figure 5). Mis à part la création de couches de mouillages au niveau des interfaces, nous n'avons pas observé de déviation de la

morphologie par rapport au volume de ce mélange. Cela suggère que la morphologie en volume est très stable et n'est pas perturbée par la configuration du film mince. Ces interfaces de forme rectangulaire, obtenues à partir de mélanges de triblocs linéaires dans des films minces constituent une autre innovation majeure de ce travail. L'origine de cette interface est due à la localisation spécifique des chaînes polymères de tailles différentes (mélange de chaînes courtes et longues des blocs terminaux), pendant la formation des domaines ordonnés. Comme mentionné précédemment, cette morphologie offre un potentiel excitant en nanotechnologie car il y a un grand besoin d'une symétrie carrée avec les domaines rectangulaires (Tang et al. 2008; Chang et al. 2014; Ruiz et al. 2011).

Après un recuit plus long, le mélange d'ISP α et ISP β avec la proportion 60/40 en films minces donne des piliers rectangulaires de PI et P2VP, avec une symétrie quadratique, orientés parallèlement à la surface du film. La formation de couches de mouillage aux interfaces a été observée sur les images de MET (sur les coupes). Aucun changement de morphologie (transition d'ordre à ordre) n'a été observé, mais en raison de l'effet de film mince, le changement d'orientation de la structure (perpendiculaire à parallèle) s'est produit pour ce mélange.

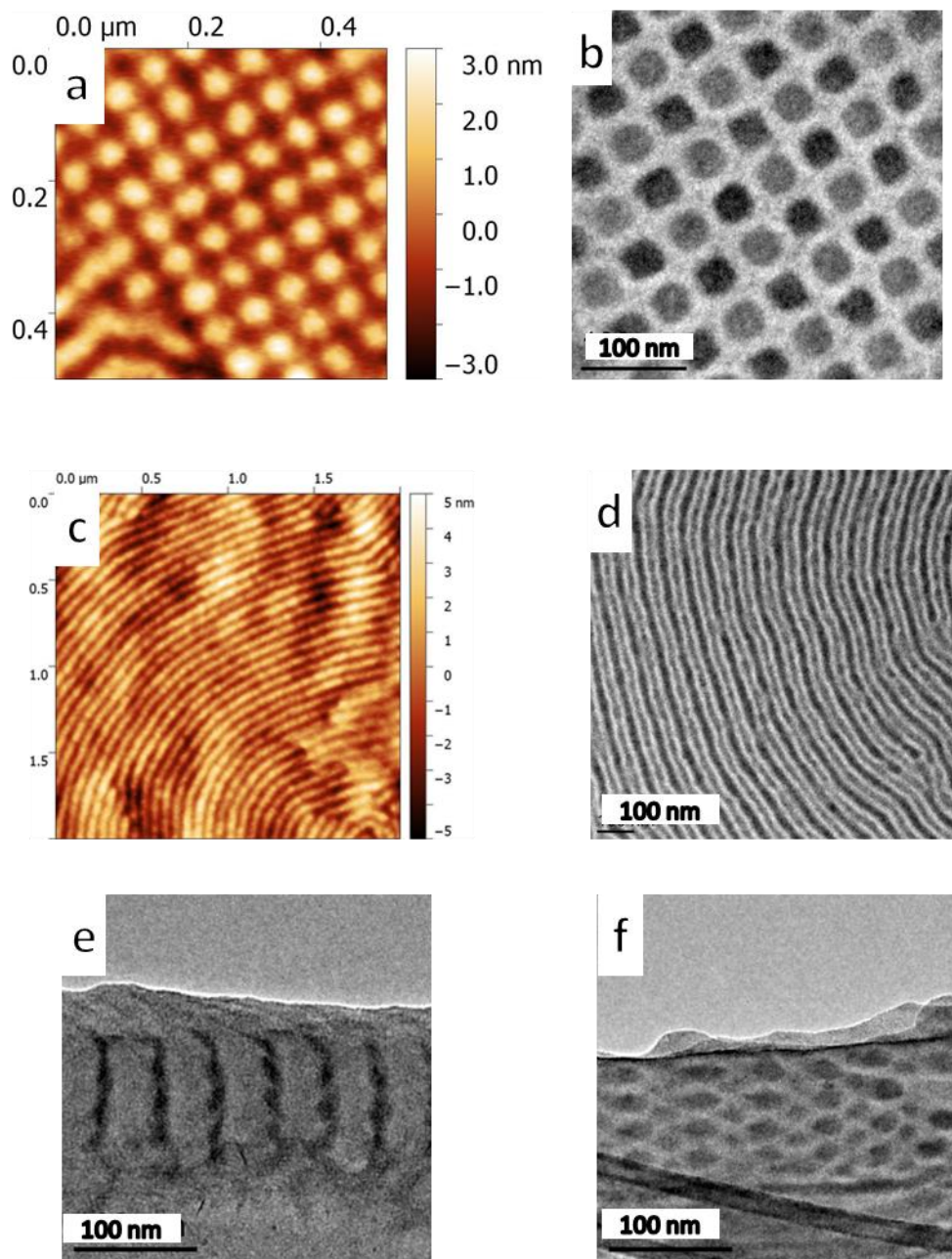


Figure 5. Les images d'AFM (a et c) et de MET (b, d, e et f) de mélange de ISP α et ISP β (60/40) en film mince : (a, b et e) après une SVA modérée et (c, d et f) après une SVA longue.

Les films minces de mélanges ISP α / β de 35/65 à 80/20 (7 compositions au total) ont aussi été étudiés. Nous nous sommes concentrés sur 2 mélanges typiques (48/52 et 40/60) qui ont été déjà étudiés en volume. Asai et al. ont montré que ces deux mélanges pouvaient donner des morphologies originales avec les motifs en triangles et en pentagones (Asai et al. 2015). Contrairement aux mélanges (60/40), cette morphologie a été déstabilisée par la configuration en couche mince (énergie de surface, ainsi que des couches de mouillages qui peuvent modifier artificiellement la fraction volumique des domaines minoritaires) et n'a pas pu être observée en film mince.

Finalement, nous nous sommes concentrés sur les mélanges d'ISP X et ISP Y , qui ont un poids moléculaire plus important que les autres systèmes ISP. Asai a étudié les

morphologies obtenues à partir de mélanges binaires de terpolymères triblocs ISPX et ISPY en volume. (Asai et al. 2016) Les piliers rectangulaires, arrangés de façon tétragonale ont été observés en volume pour des mélanges du 60/40 au 90/10. Dans ce travail, nous avons étudié deux proportions de mélange (85/15 et 60/40) en film mince et pour chaque système, deux types d'exposition aux vapeurs des solvants (toluène et THF) ont été effectués. Une transition d'ordre à ordre a été observée pour les mélanges ISPX / ISPY (85/15) et (60/40) en films minces et la présence de motifs carrés et hexagonaux est confirmée par différentes méthodes de caractérisation après SVA dans le THF et dans les vapeurs de toluène (voir la Figure 6). Nous avons observé une réorientation de la structure (cylindres perpendiculaires à parallèles) ainsi qu'une transition d'ordre à ordre.

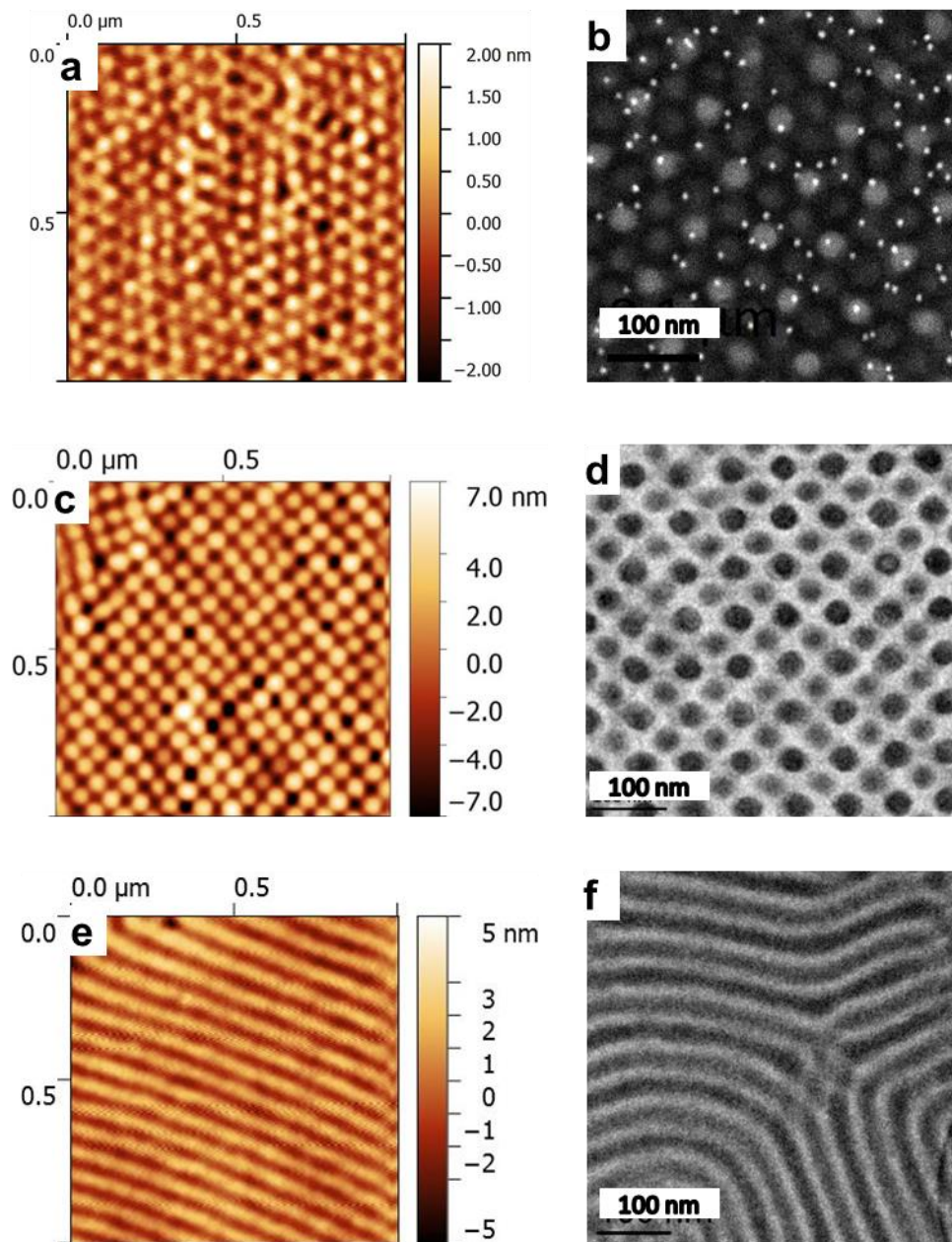


Figure 6. Images d'AFM (a, c et e) et MET (b, d et f) pour le mélange de ISPX/Y 85/15

La compréhension des phénomènes à l'origine de ce comportement n'est toujours pas atteinte et nécessiterait des expériences supplémentaires. Un scénario possible peut toutefois être proposé, en faisant notamment intervenir le taux de gonflement des polymères dans différents solvants. Avec la pression élevée et le taux de gonflement plus important dans le THF, les polymères n'ont pas le temps de se réorganiser pour s'adapter à toutes les morphologies possibles et l'orientation la plus thermodynamiquement stable a été obtenue rapidement dans les vapeurs de THF. Dans le cas du toluène, la transition de structure différente est observée en raison de la pression de vapeur de solvant et du taux de gonflement des polymères inférieurs à ceux du THF. Il est logique d'obtenir le motif hexagonal en tant que structure «finale» (avant les cylindres orientés parallèles) pour un mélange 60/40 avec une fraction volumique totale de (0,26 / 0,62 / 0,12) asymétrique (correspondance avec la structuration hexagonale sur le diagramme de phases). Les résultats expérimentaux confirment la même hypothèse pour un mélange 85/15 avec une fraction volumique finale de (0,17 / 0,65 / 0,18). La séquence de la morphologie et la transition de structure ont été expliquées par la formation de couches de mouillages sous l'effet d'un film mince. Nous avons besoin de plus de temps pour comprendre pleinement cette évolution morphologique. En bref, une transition d'ordre à ordre a été observée pour les mélanges ISPX / ISPY en couches minces.

En conclusion, dans cette thèse, l'effet de confinement dans les films minces a été étudié sur la nanostructuration de divers systèmes de terpolymères triblocs linéaires ABC (seuls ou en mélange). Pour des copolymères seuls (ISP19 et 23) des transitions de phases inédites ont été observées. Pour les mélanges binaires (ISP α / ISP β et ISPX / ISPY), plusieurs morphologies atypiques ont été obtenues qui n'ont jamais été observées expérimentalement en films minces.

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GENERAL INTRODUCTION

Self-organization of block copolymer (BCP) allows forming nanopatterns which have attracted considerable attention as an alternative approach to overcome the characteristic size limitation of the conventional lithography processes. They could be an excellent industrial alternative due to their compatibility with the silicon technology already used for microelectronic materials.

According to the literature review, self-assembly of diblock copolymer is quite well developed, and many works show all possible nanostructures of diblock copolymer in bulk and thin films. In order to go further, the utilization of the triblock type BCP for nanostructuration has attracted the attention of researchers. The incompatibility between each block of ABC terpolymers and the position of the block in chain gives the possibility to obtain different complex structures. Despite very basic chemistry, simple architecture and a non-frustrated situation ISP (Isoprene-*b*-Styrene-*b*-2vinylpyridine) linear triblock was recently used to develop a wide range of original nanostructures by using blends.

The purpose of this thesis is to study and understand ISP BCPs self-assembly phenomena in thin films. For this purpose, neat triblocks and blends of triblocks were analyzed and characterized using different characterization methods. The challenge of this work is to obtain ordered nanostructures despite all thin film effects and to control structuration kinetic.

The first chapter provides an overview of BCP self-assembly. Firstly, BCP and self-assembly of the diblock system are described. Then, the need for studying triblock systems has been shown to create more original morphologies. Adding another chemically different block leads to the formation of various morphologies based on ABC triblock terpolymer. The chapter ends with the context of the thesis.

In the second chapter, the experimental details and preliminary works are presented. We start to perform experiences on homopolymers (polyisoprene (PI), polystyrene (PS), and poly2vinylpyridine (P2VP)) to study our system carefully. This step allows us to predict the solvent choice according to the three types of blocks and to characterize selectively PI and P2VP lately in the triblock system.

The third chapter deals with results and discussion. It is divided into two parts.

In part I the nanostructuration of neat linear triblock, forming cylindrical and gyroid morphology in bulk are studied in thin film. These two polymers are selected for their position in the phase diagram (located on the boundary of cylindrical structure with spherical and gyroid morphologies) to favor order-order transitions in the thin film configuration.

In part II more complex nanostructures based on blends of different triblocks are presented. When linear triblocks are used in combination with other block polymers or homopolymers, they can lead in certain conditions to a particular organization, as demonstrated by Matsushita's group. A new structure of tetragonally packed rods with non-

constant mean-curvature (non-CMC) could be fascinating for nanopatterning applications. This section aims to study the ability to generate this morphology in thin film configuration, where confinement and surface effect may play a significant role. Firstly, four-fold symmetry based on blends of $\text{ISP}\alpha$ and $\text{ISP}\beta$ is presented which have already been tested in bulk and give non-CMC interfaces. Then, we focus on other combinations of ISP triblock in thin film that can provide original morphology such as a blend of ISPX and ISPY with different proportions.

The last chapter gives a conclusion and a perspective to go through in this domain.

LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
BCP	Block copolymer
CMC	Constant Mean-Curvature
CPS	Closely packed spheres
CSG	Core shell gyroid
C or CYL	Cylindrical
DCE	1, 2-dichloroethane
EtOH	Ethanol
G _A	Alternative gyroid
DG or G _D	Double gyroid
G or GYR	Gyroid
GISAXS	Grazing-incidence Small-Angle X-ray Scattering
HEX	Hexagonal
ISP	Poly (Isoprene- <i>b</i> -Styrene- <i>b</i> -2vinylpyridine)
L	Lamellar
ODT	Order-disorder transition
OM	Optical microscopy
PL	Perforated Lamellar
PI	Polyisoprene
PS	Polystyrene
RT	Room temperature
P2VP	Poly2vinylpyridine
S or SPH	Spherical structure
SR	Swelling ratio
SVA	Solvent vapor annealing
T _g	Glass transition temperature
TEM	Transmission Electron Microscopy
THF	Tetrahydrofuran
UVO	Ultra-violet Ozone
VR	Visible Reflectometry
SSL	Strong segregation limit
SCMF	Self-consistent mean-field
WSL	Weak segregation limit
IMDS	Intermaterial dividing surface

1. BIBLIOGRAPHIC STUDY

CHAPTER 1 briefly presents the state of art of the nanostructuration of triblock terpolymers. In this part, several points will be developed:

- General presentation of BCP: different types of copolymers, introduction to self-assembly of BCP.
 - Diblock copolymer self-assembly: phase diagram with typical morphologies of neat diblock and blend of diblock in bulk.
 - Triblock copolymer self-assembly: phase diagram with typical morphologies in bulk, presentation of different kinds of triblock (non-frustrated case and frustrated case), originality, and interest for working with triblock and triblock blends.
 - Thin film configuration: Difference between nanostructuration of BCP in bulk and thin film, challenge to reproduce unusual triblock morphology under confinement effect and potential application of films.
 - Context of thesis: presentation of the motivation of work
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I. BLOCK COPOLYMER

Polymers are macromolecules composed of many repeating units (monomers), linked by covalent bonds. Polymers can be divided into two classes based on the type of monomer: homopolymers consisting of only a single type of repeating unit, and copolymers comprising more than one chemically distinct monomer. Monomer units can be distributed in a variety of ways within the copolymer chain. The arrangement can generate: alternating copolymers with regular alternating A and B units (A-B-A-B-...), statistical copolymers in which the sequence of monomers follows a statistical rule (A-B-B-A-B-A-A-...), and BCP in which two or more distinct homopolymers are linked end to end through covalent bonds. The number of distinct segments determines the molecular architecture of BCP; diblock, triblock, or higher multiblock copolymers are possible. The simplest example is an AB diblock copolymer, with two covalently linked homopolymers. An essential property of BCPs is their ability to self-assemble into periodic nanostructures. Diblock copolymers have been studied the most extensively for a variety of possible nanostructures. The mixture of two thermodynamically incompatible homopolymers (A and B) tends to demix, such as the blend of water and oil, and the minimization of unfavorable interfaces drives to macrophase separation. When these individual homopolymers are covalently bonded to form a A-B diblock copolymer, the covalent linkages between these different blocks prevent macroscopic phase separation.

The phase behavior of diblock copolymers has been studied from experimental and theoretical perspectives (Leibler 1980; Semenov 1985; Ohta and Kawasaki 1986; Helfand 1975; Hashimoto et al. 1980). To my knowledge, the microphase separation of BCP was presented firstly by Matsuo et al. (Matsuo, Sagae, and Asai 1969) in literature. They gave the morphologies of poly (styrene-*b*-butadiene) (SB) diblock copolymer with different volume fractions. The morphological phase diagram of the model AB diblock system has been demonstrated by Leibler (Leibler 1980). The microphase separation of diblock copolymers is driven by three parameters (Leibler 1980; Bates and Fredrickson 1999): the volume fractions of the A and B blocks (ϕ_A and ϕ_B , with $\phi_A + \phi_B = 1$), the total degree of polymerization ($N = N_A + N_B$), and the Flory–Huggins parameter, χ_{AB} . The χ -parameter (Flory Huggins parameter) specifies the degree of incompatibility between the A and B blocks and is defined as:

$$\chi = (Z/k_B T) \left(\epsilon_{AB} - \frac{\epsilon_{AA} + \epsilon_{BB}}{2} \right)$$

which describes the free-energy cost per monomer (in units of the thermal energy $k_B T$) of contacts between A and B monomers. According to this definition, Z is the number of the nearest-neighbor monomers to a copolymer configuration cell, and ϵ_{ij} is the interaction energy (Bates and Fredrickson 1999).

In practice, χ has temperature dependence,

$$\chi = \alpha / T + \beta$$

χN controls the order/disorder state of BCPs and the microphase separation can occur when this value exceeds the critical value for order/disorder transition. An order-disorder transition can be observed, for example, by increasing temperature or decreasing χN (for example, at very low molecular weight).

II. DIBLOCK COPOLYMER SELF-ASSEMBLY

The phase behavior of BCPs in bulk is well understood both theoretically and experimentally on a model diblock copolymer. Poly(styrene-*b*-isoprene) (PS-*b*-PI) is a good example (Matsen and Bates 1997; Matsen 1997; Bates and Fredrickson 1999). Theoretically, different studies have been developed to understand the phase behavior of diblock copolymers in bulk (Leibler 1980; Matsen and Schick 1994; Matsen and Bates 1996). To determine ODT transition by χN value for each system, the self-consistent mean-field (SCMF) theory was developed (Matsen and Bates 1996; Matsen and Schick 1994). In terms of χN , the weak segregation limit (WSL) ($\chi N < 10$) and the strong segregation limit (SSL) ($\chi N \gg 10$) were introduced in the bibliography.

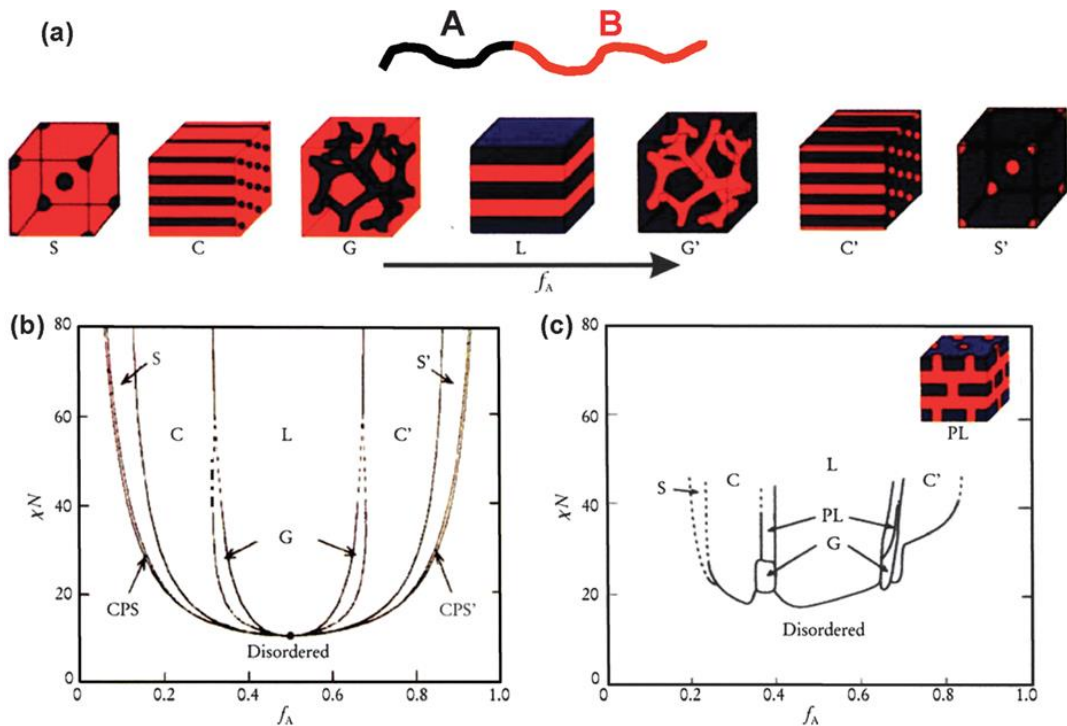


Figure 1-1. (a) Equilibrium morphologies of AB diblock copolymers in bulk: S and S' = body-centered-cubic spheres, C and C' = hexagonally packed cylinders, G and G' = bicontinuous gyroids, and L = lamellae. (b) Theoretical phase diagram of AB diblock predicted by the SCMF theory, depending on volume fraction (f) of the blocks and the segregation parameter, χN ; CPS and CPS' = closely packed spheres. (c) Experimental phase portrait of PS-*b*-PI, in which f_A represents the volume fraction of PI; PL = perforated lamellae. (Bates and Fredrickson 1999).

Figure 1-1b displays the phase diagram for diblock copolymers predicted by the SCMF theory. For a symmetric diblock copolymer system ($\phi_A = 0.5$), the order-disorder transition (ODT) is calculated theoretically at $\chi N_{ODT} = 10.5$, as shown in Figure 1-1b. Figure 1-1c shows an experimental phase diagram of PI-*b*-PS copolymers reported by Bates and co-workers (Bates and Fredrickson 1999; Khandpur et al. 1995). Different morphologies are obtained by changing the volume fraction of one block, as is illustrated by Figure 1-1a (S = Spherical structure; C = Cylindrical; G = Gyroid; L = Lamellar; CPS = Closely packed spheres (which

separates the disordered state and S phase) and PL = Perforated Lamellar) and the similarity between the theoretical and experimental diagram is remarkable.

Nowadays, self-assembly of AB-type BCP is quite well developed in the literature and most of the works show all possible nanostructure of diblock copolymer in bulk and in thin films such as the spheres, cylinders, gyroid, and lamellar. After the well-developed self-assembly of neat diblock in bulk, **blending has attracted** their attention.

II.1. DIBLOCK BLENDINGS

Firstly, the simplest blend system, **the binary blends of AB diblock copolymer and its constituent A (or B) homopolymers**, have been studied. Many experimental (Tanaka, Hasegawa, and Hashimoto 1991; Winey, Thomas, and Fetters 1991; Mayes et al. 1992; Dai, Kramer, and Shull 1992) and theoretical (Matsen 1995b; Semenov 1993; Matsen 1995a) studies have led to a comprehensive understanding on the phase behavior of these blend systems. Winey et al. have studied the influence of homopolymer molecular weight and homopolymer concentration on highly ordered morphologies (Winey, Thomas, and Fetters 1991). They have confirmed that the overall A composition of a blend, containing AB diblock copolymer and A homopolymers, generally determines the ordered morphology when the homopolymers molecular weight is comparable to or smaller than the molecular weight of the matching block of the copolymer. For the same overall composition, it is possible to observe lamellar or cylindrical morphology, respectively, with a higher (30k) or lower (2.6k) homopolymers molecular weight. Tanaka et al. have described qualitative predictions on the solubilization of homopolymers in this type of blends (Tanaka, Hasegawa, and Hashimoto 1991). Mayes et al. have also studied the influence of the molecular weight of homopolymers in blends of diblock and homopolymers and shown that for low molecular weights (low or comparable to the block molecular weight), the homopolymer is distributed almost uniformly in blend and is confined to the corresponding copolymer domain (Mayes et al. 1992). However, for high molecular weight homopolymers (more important than the BCP molecular weight), the homopolymer segregates to relatively small domains distributed throughout the film. In 1995, Matsen showed that a limited amount of homopolymers could be accommodated in the minority component region of a BCP microstructure before macrophase separation occurs (Matsen 1995b).

Blending BCP has also been examined. Binary diblock blends have been studied theoretically and experimentally by many researchers (Birshtein, Lyatskaya, and Zhulina 1992; Hashimoto et al. 1993; Matsushita 2007). Hashimoto studied the miscibility of two diblock copolymers (binary mixtures of poly(styrene-*b*-isoprene) (SI)) and the influence of their molecular weight ratio to form single morphology. A new, but unidentified bicontinuous ordered domain structure was also observed for a miscible pair. In order to go further, **utilization of BCPs** with more than two blocks, e.g., ABC, ABCA, ABCD, and nonlinear molecular architecture such as ABC star-shaped polymers for nanostructuration, has attracted the attention of researchers. The architecture of triblock chains may be linear or star miktoarm type by adding C block and it has an effect on structures obtained based ABC triblock.

III. LINEAR TRIBLOCK COPOLYMER SELF-ASSEMBLY

Triblock copolymers consist of three distinct polymers, A, B, and C, that are covalently bonded together. The microphase separation of ABC triblock copolymers is much more complicated compared to their diblock counterparts. The addition of the third component C to AB diblock copolymer increases significantly the number of morphological parameters that must be taken into account namely, three different interaction parameters (χ_{AB} , χ_{AC} and χ_{BC}), which describe the interactions of blocks within copolymer, degrees of polymerization (N_A , N_B and N_C), and block volume fractions (ϕ_A , ϕ_B and ϕ_C). Zheng and Wang showed a theoretical calculation of the morphological phase diagram for the bulk of ABC triblock copolymers in SSL, as shown in Figure 1-2.

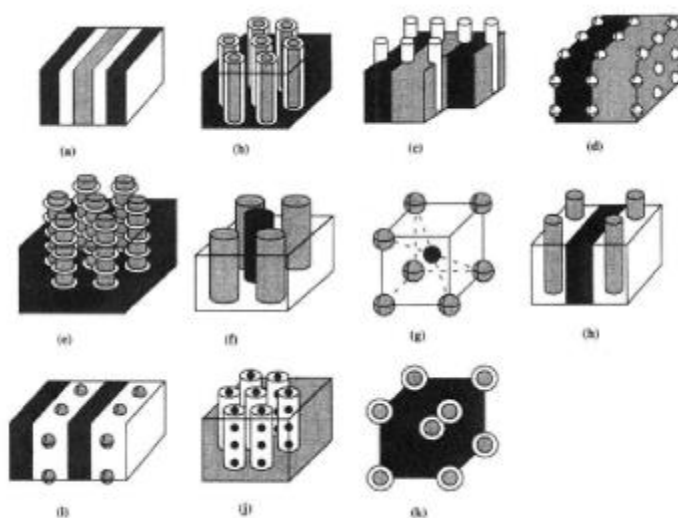


Figure 1-2. Schematic representation of the phases of ABC triblock copolymers (in the SSL) in bulk. A, B, and C blocks are respectively represented by dark, white, and gray colors. (a) Lamellar phase; (b) coaxial cylinder phase; (c) lamella—cylinder phase; (d) lamella-sphere phase; (e) cylinder—ring phase; (f) cylindrical domains in a square lattice structure; (g) spherical domains in the CsCl type structure; (h) lamella—cylinder—II; (i) lamella-sphere- II; (j) cylinder-sphere; (k) cocentric spherical domain in the bcc structure. (Zheng and Wang 1995).

By adding a third block, a large number of new ordered structures is created experimentally, such as tricontinuous network structures (Mogi, Mori, et al. 1992; Matsushita, Suzuki, and Seki 1998; Bailey et al. 2002; Epps et al. 2004; Tyler and Morse 2005) or two-dimensional "knitting" (Breiner, Krappe, and Stadler 1996) morphology which allow for patterning many different pattern geometries.

In the triblock case, the sequence of blocks in the chain and the relative strength of interaction parameters play an essential role in nanostructuration (Zheng and Wang 1995). For example, with volume ratio 1:1:1, poly(styrene-*b*-isoprene-*b*-2-vinylpyridine) (PS-*b*-PI-*b*-P2VP) (SIP) forms P2VP core and PI shell cylinders in a PS matrix (Gido et al. 1993) as shown in Figure 1-2b. On the other hand, with the same volume ratio, poly(isoprene-*b*-styrene-*b*-2-vinylpyridine) (PI-*b*-PS-*b*-P2VP) (ISP) forms lamellae (Mogi, Kotsuji, et al. 1992) as illustrated in Figure 1-2a.

The first interesting point is the difference in morphologies due to the sequence of blocks. The formation of PI/P2VP interface (in this case, PI and P2VP blocks linked by covalent bonding) is not favorable due to the strong incompatibility between two blocks and for that reason, in second case (study of Mogi), as PI and P2VP are located at the end of copolymer chain, a stable lamellar structure is obtained.

Secondly, the interface of hexagonally packed cylinders (non-CMC interface) should be highlighted. Mean curvature is defined as the arithmetic average of the two principal curvatures at any point on the intermaterial dividing surface (IMDS), and CMC surfaces represent local interfacial area minima under fixed volume constraints (Gido et al. 1993). By minimization of free energy of the system, various structures (with different types of shapes) are obtained from BCPs. Driving forces of morphology formation with different kinds of interfaces are generally incompatibility between blocks, interfacial energy, and conformational energy of the polymer chains (they are stretched or compressed). The competition between chain packing and interfacial shape leads to form original morphologies. In this case, Gido et al. have created a non-CMC morphology at the PS/PI interface and a CMC shaped domain at the PI/P2VP interface due to the incompatibility between three blocks and chain architecture. Indeed, as the middle block PI is obliged to link PS and P2VP, and due to PI-P2VP incompatibility, it is more favorable to create the non-CMC shape at the PI/PS interface.

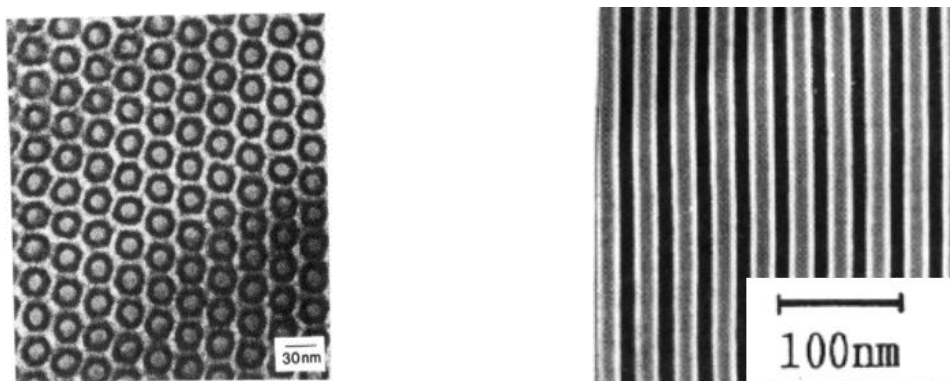


Figure 1-3. TEM images of (a) hexagonally-packed structural units based SIP; (b) lamellae morphology based ISP triblock. The darkest regions correspond to the OsO_4 -stained PI domains, while the gray regions are CH_3I -stained P2VP domains. The non-CMC interface between this PI microdomain and the PS matrix phase has a hexagonal shape with corners. (Gido et al. 1993; Mogi, Kotsuji, et al. 1992).

To understand the general phase behavior of ABC triblock copolymers in bulk, several theoretical and experimental works (Bates and Fredrickson 1999) have been presented in the bibliography and triblock systems have been classified in terms of the relative strength of χ parameters: χ_{AC}/χ_{AB} and χ_{BC}/χ_{AB} which is shown in following part.

III.1.FRUSTRATION IN BCP

Considering a linear triblock ABC, according to the interactions between different blocks (χ_{AC} , χ_{AB} , χ_{BC}), three frustration types have been described by Bailey (Bailey, Pham, and Bates

2001) depending on the interaction parameters. When the interaction parameters between A and C blocks (χ_{AC}) are larger than the two other interaction parameters ($\chi_{AC} > \chi_{AB} \approx \chi_{BC}$) (A and C blocks are more incompatible than A and B or B and C blocks), the linear ABC triblock is a **non-frustrated terpolymer**, with A/C interface limited as possible. In contrast, if $\chi_{BC} > \chi_{AB} \approx \chi_{AC}$, it is a **type I frustration** with B/C interface limited, while if χ_{AC} has the smallest value, it is a **type II frustration** ($\chi_{AB} \approx \chi_{BC} > \chi_{AC}$) where A/C interface is energetically favorable. Figure 1-2 illustrates a panel of possible morphologies observed for triblock composed of A, B, C.

Type I frustration ($\chi_{BC} > \chi_{AB} \approx \chi_{AC}$) polymer exhibits morphologies with a minimization of the B/C interface. As mentioned previously, Gido and co-workers studied the nanostructuration of SIP triblock composed of PS, PI, and P2VP blocks with the same volume proportion ($\phi_A \approx \phi_B \approx \phi_C \approx 1/3$). This is an example for self-assembly of a frustrated system (type I), SIP triblock gives a PS matrix perforated by hexagonally arrayed coaxial domains of P2VP (core) and PI (shell) as shown in Figure 1-3 with a non-CMC in PI/PS interface. As another example, we can show self-assembly of poly(styrene)-*b*-poly(isoprene)-*b*-poly-(lactide) (SIL) triblock polymer with equal volume fractions of each block in bulk and in thin film developed by Radlauer et al. (Radlauer et al. 2017). A core-shell cylindrical morphology with a non-CMC has been reported in bulk, however, in thin films, the structure can be assigned as spheres-on-cylinders due to the confinement effect.

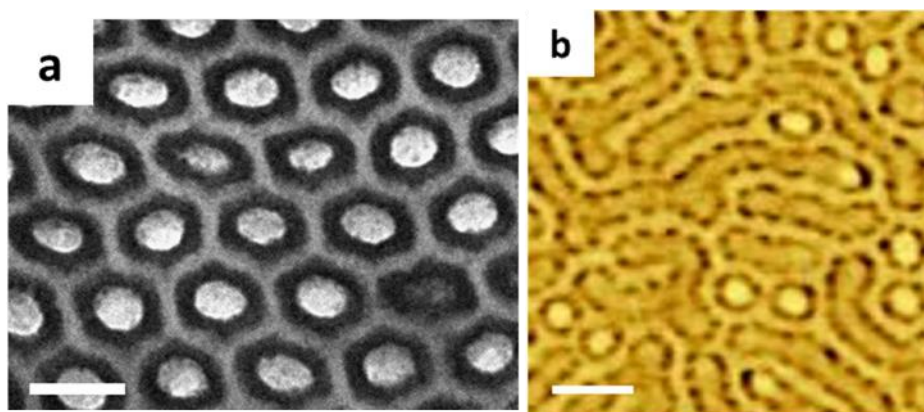


Figure 1-4. (a) TEM image of $S_{0.33}I_{0.34}L_{0.33}$ -49 bulk morphology (a core-shell cylindrical) after staining with OsO_4 . The PI domains are black, the PS domains are gray, and the PLA domains are white. (b) AFM image of thin film morphology of the same system. (Radlauer et al. 2017).

The frustration effect (type I) has also been observed in SBP (poly(styrene-*b*-butadiene-*b*-2-vinylpyridine)) systems (Hückstädt, Göpfert, and Abetz 2000; Hanno Hückstädt et al. 2000). They observed a core-shell double gyroid structure with a P2VP core domain (the smallest block) surrounded by a PB shell domain (the more significant repulsion between B and P blocks) in a PS matrix, whereas triblock with BSP chain configuration (non-frustrated state) give only lamellar pattern (core-shell double gyroid structure was not observed).

Type II frustrated ($\chi_{AC} < \chi_{AB} \approx \chi_{BC}$) systems show even more pronounced frustration than type I, because of the favorability to create A/C interfaces. Favorable A/C interface and the high incompatibility between covalently-connected A-B and B-C blocks lead to more

complex morphological behaviors than those of the corresponding non-frustrated systems. Experimentally, several triblock copolymers have been extensively investigated namely, poly(styrene-*b*-butadiene-*b*-methyl methacrylate) (PS-*b*-PB-*b*-PMMA) (Krappe, Stadler, and Voigt-Martin 1995) and poly(styrene-*b*-ethylene-*co*-butylene-*b*-methyl methacrylate) (PS-*b*-PEB-*b*-PMMA) by (Auschra and Stadler 1993; Stadler et al. 1995; Breiner, Krappe, and Stadler 1996; Breiner et al. 1998) with complex structures as helices around cylinders or knitting patterns. They have shown that obtained morphologies are governed by the relatively weak incompatibility of the end blocks PS and PMMA rather than the strong incompatibility of the PB or PEB midblock. Figure 1-5 presents TEM images of SEBM17 (48/17/35) and SEBM6 (45/6/49) systems. The left column of Figure 1-5 shows TEM images of SEBM17, where EB cylinders appear as spherical domains between PS and PMMA lamellae. The right column of Figure 1-5 shows TEM images of SEBM6, where the EB fraction is much reduced, and it forms rings encircling PS cylinders that are dispersed in the PMMA matrix. Self-assembly of the frustrated systems was also investigated by theoretical simulations (Zheng and Wang 1995; Liu et al. 2012) to understand the self-assembling mechanism of the complex phases and to guide experimental studies to create new structures.

When the A/C interface is the most energetically unfavorable ($\chi_{AC} > \chi_{AB} \approx \chi_{BC}$), the triblock copolymer will show **no frustration**. As A and C blocks position at the end of the covalently linked ABC triblock chain, the incompatibility for A and C units lead A and C units to avoid each other, and this is nicely supported by the chain sequence, and so, A/C interfaces are naturally not formed in these systems. Such self-assemblies have been found for example by Matsushita for ISP triblock copolymers (poly(isoprene-*b*-styrene-*b*-2-vinylpyridine)) where ($\chi_{IP} > \chi_{IS} \approx \chi_{SP}$) (Mogi, Mori, et al. 1992) or by Bates for ISO BCPs (poly(isoprene-*b*-styrene-*b*-ethylene oxide)) (Bailey et al. 2002).

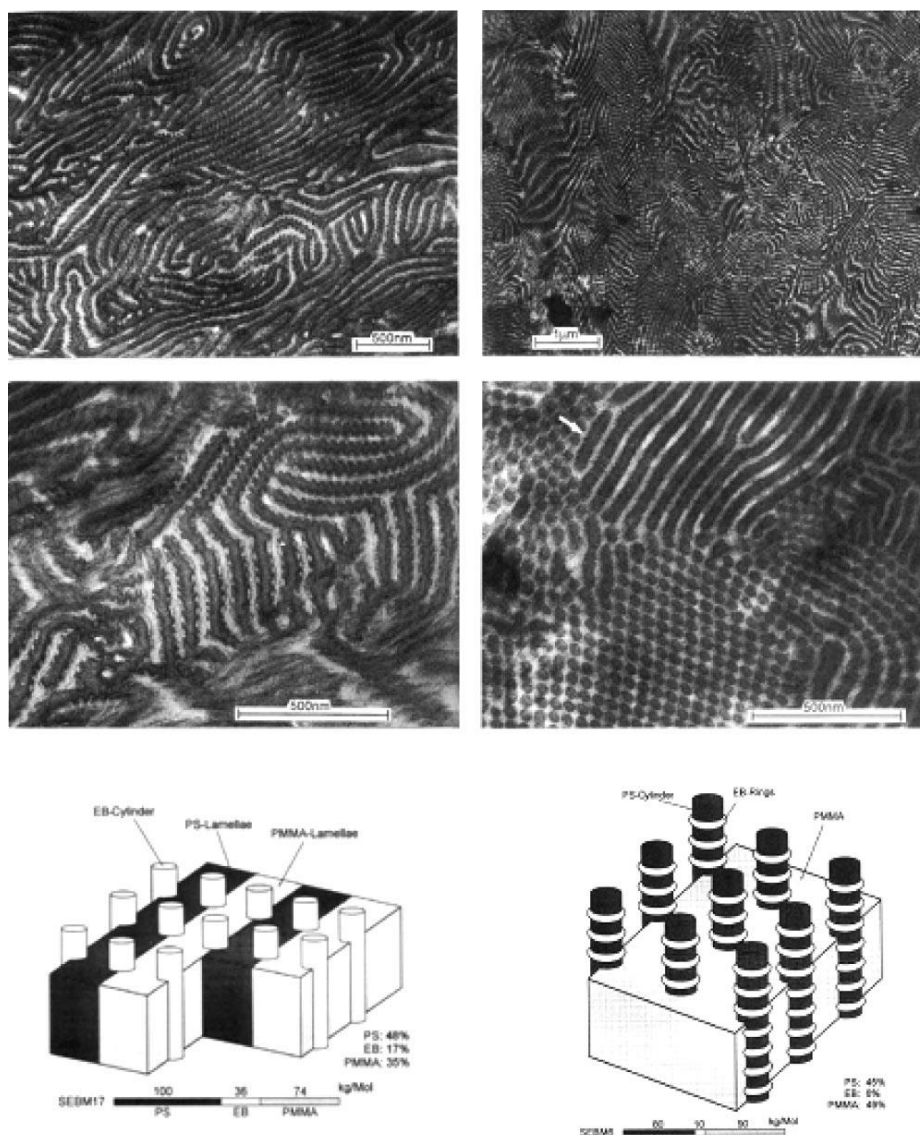


Figure 1-5. TEM views (at the top of the left side) of SEBM17 and (at the top of the right side) of SEBM6 with a schematic representation of morphologies at the bottom of figure: dark, PS lamellae; bright, PMMA lamellae. (Auschra and Stadler 1993).

As we will explain later, this work will focus on the study of **non-frustrated triblock** ($\chi_{AC} > \chi_{AB} \approx \chi_{BC}$). The following parts detail the behavior of such polymers.

Theoretical calculations were performed for non-frustrated ABC triblock terpolymers (Matsen 1998; Tyler et al. 2007; Sun et al. 2008; Zheng and Wang 1995). Analogous to this type of system, the phase behavior of poly(butadiene-*b*-styrene-*b*-2 vinylpyridine) (**PB-PS-P2VP**) and poly(methyl methacrylate-*b*-styrene-*b*-butadiene) (**PMMA-PS-PB**) by Abetz and coworkers (Hückstädt et al. 2000b; Abetz and Goldacker 2000) and poly(isoprene-*b*-styrene-*b*-ethylene oxide) (**PI-PS-PEO**) by Epps and coworkers (Bailey et al. 2002; Epps et al. 2004) were studied. Self-assembly of non-frustrated terpolymer often results in classical structures, like triple lamellae, tricontinuous structure, alternating spheres, and alternating cylinders morphology, as illustrated by experimental phase diagram shown in Figure 1-6 (Tureau et al. 2010). Tureau et al. have demonstrated on a ternary diagram the localization of neat ISM triblock copolymers and ISM triblock/homopolymer blends in the weak-to-

intermediate segregation regime near the styrene-rich network phase window. On the phase diagram, symbols with black outlines indicate neat ISM materials, whereas remaining symbols correspond to ISM blended specimens. Phase boundaries are estimated from experimental results and also guided by theoretical predictions for ABC phase diagram by Tyler et al. (Tyler et al. 2007) and AB diblock phase diagram by Matsen et al. (Matsen and Bates 1997). The experimental phase diagram exhibited similar trends to those found in the theoretical ABC triblock copolymer phase diagram.

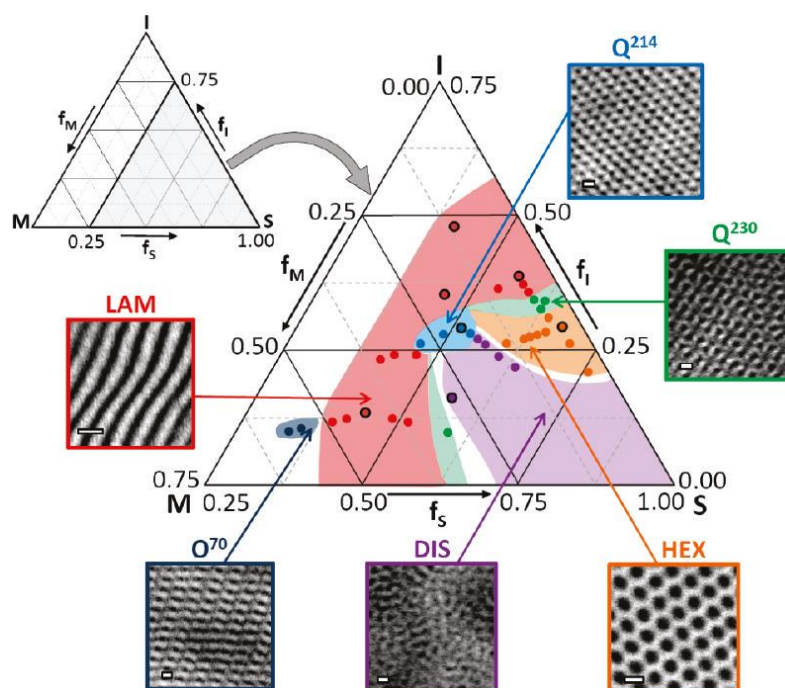


Figure 1-6. Experimentally determined ternary phase diagram determined for non-frustrated poly(isoprene-*b*-styrene-*b*-methyl methacrylate) (ISM) triblock terpolymers by Tureau et al. (Tureau et al. 2010).

ISP terpolymer is an excellent example of “simple non-frustrated” ($\chi_{IP} > \chi_{IS} \approx \chi_{SP}$) linear triblock ($\chi_{IP} \approx 0.2$; $\chi_{IS} \approx 0.06$; $\chi_{PS} \approx 0.1$) (Ahn et al. 2017; Kwak et al. 2015; Zhang, Sides, and Bates 2012). Matsushita and coworkers have synthesized ISP triblock terpolymers with different PS volume fractions ϕ_S (corresponding to the majority block, i.e., matrix), keeping the volume fraction of end block equal ($\phi_I = \phi_P$). They have shown that ISP triblock terpolymer in bulk develops three phase lamellae, double gyroid (DG), tetragonal packed rods, and CsCl type spheres with PI and P2VP minority blocks in PS matrix (Matsushita 2000; Mogi, Kotsuji, et al. 1992). They have shown that cylinder arrangement which is interesting for potential application is obtained for symmetric molecular design ($\phi_A \approx \phi_C$). In an ABC triblock terpolymer case the tetragonal packing of alternating A and C cylinders is more favorable than a hexagonal one. The tetragonal packing does not fill space as efficiently as the hexagonal (Matsen 1998). In reality, the system chooses this arrangement to guarantee domain symmetry, but it causes significant packing frustration. As a result, the cylinder region is substantially reduced in the phase map, and this, in turn, enlarges the complex phase (tricontinuous (TC)) region, as shown in Figure 1-7.

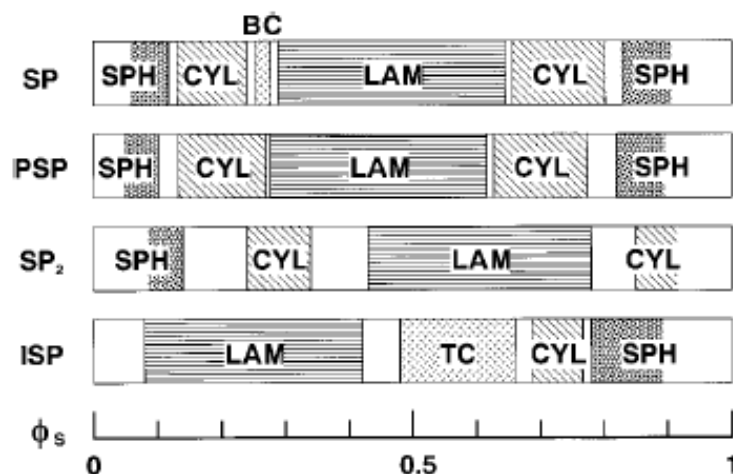


Figure 1-7. Composition dependence of equilibrium microphase-separated structures for four copolymers. The horizontal axis denotes the volume fraction of the polystyrene phase. SPH, CYL, LAM, BC, and TC indicate spherical, cylindrical, lamellar, bicontinuous, and tricontinuous structures. (Matsushita 2000).

Although there are a lot of studies on ISP in bulk, a global phase diagram has not yet been published. In order to get a more comprehensive picture, we have summarized in a ternary phase diagram (Figure 1-8a) all the data given in literature on ISP systems (neat ISP triblock and blend of ISP polymer) (Mogi, Kotsuji, et al. 1992; Mogi, Mori, et al. 1992; Mogi et al. 1994; Asai et al. 2014; Asai, Takano, and Matsushita 2015a, 2016a). Marks which represent the blend of polymers are not fully filled with color. Violet, green, pink, and blue colors represent the lamellar, gyroid, cylinders, and spheres phases, respectively. Other morphologies have also been reported, such as cylinders in lamellae, spheres in gyroid, or spheres in lamellae. With the data reported from the literature, it was only possible to fill the phase diagram partially. However, it can be compared to the theoretical phase diagram for the non-frustrated triblock proposed by Tyler (Tyler et al. 2007) (Figure 1-8b). This map represents a calculated phase diagram of an idealized ABC triblock copolymer, A and C being the most incompatible blocks (just like in the ISP system). In this theoretical diagram, most of the phases are also known to be stable in diblock copolymers (i.e., D (disordered melt), S (spheres), C (hexagonally packed cylinders), G (double-gyroid network), and L (lamellar)). G^A (alternating gyroid network), S^A (alternating spheres/CsCl structure), and O^{70} (noncubic (10,3)-c networks) have been additionally observed in this case. Figure 1-8c shows the superposition of two diagrams. Experimental and theoretical values match quite well for lamellar, cylinders, and alternating gyroid phase (coded respectively by violet, pink, and green color). The difference for the sphere can be due to the different N values of each block in the ISP case.

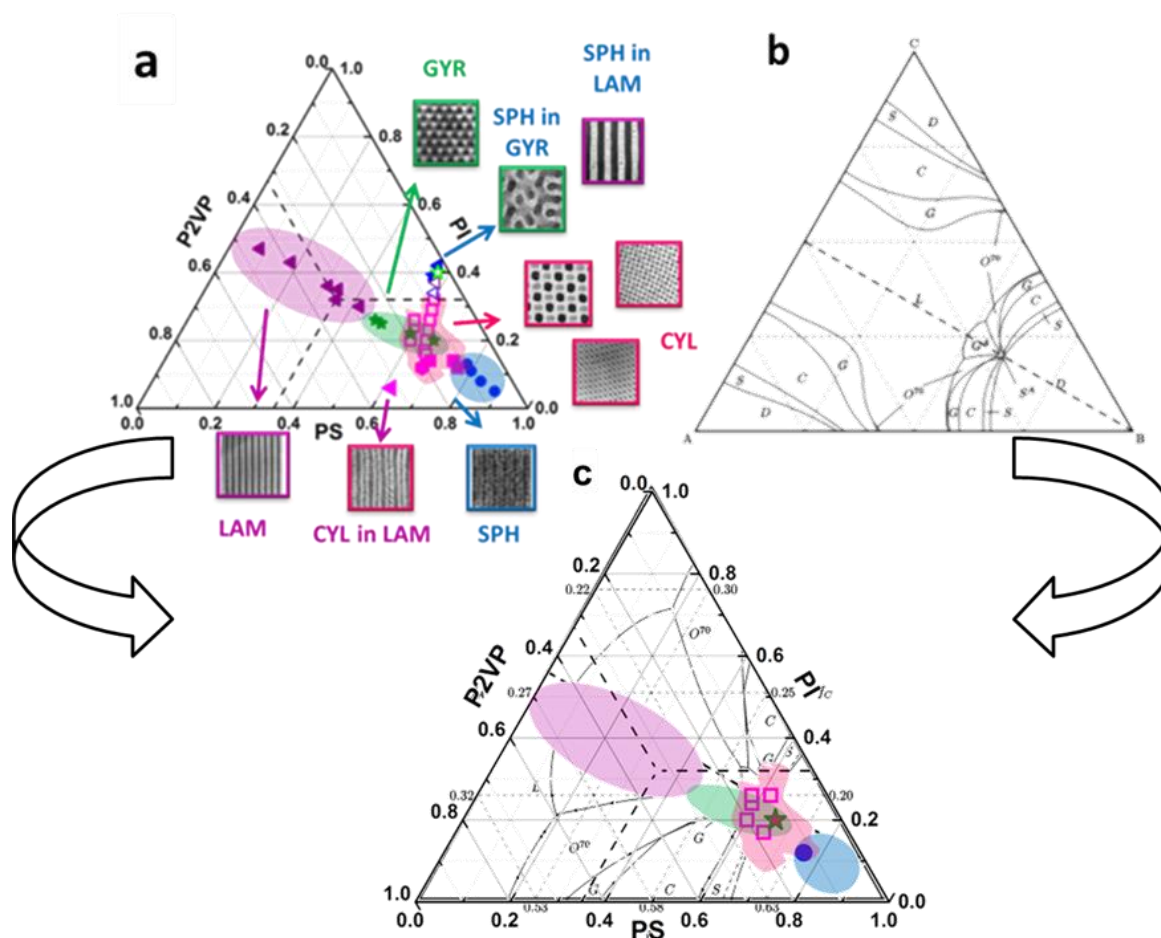


Figure 1-8. (a) Experimentally phase diagram of ISP triblock nanostructuration in bulk (the results of neat ISP triblock with the results of the blend of ISP triblocks); (b) SCFT phase behavior of an idealized triblock copolymer with equal statistical segment lengths for each block ((Tyler et al. 2007); (c) superposition of two phase diagram.

In conclusion, non-frustrated triblock terpolymer gives simple morphology in comparison to frustrated ones. However, we will see in the following part that blending BCPs is an efficient way to expand the variety of morphology that can be formed, even in the case of non-frustrated polymers.

III.2. TRIBLOCK BLENDEINGS

Even more complicated systems have been investigated. These are blends of triblock with diblock, blends of triblocks, blends of copolymer with different structures such as star polymer with linear polymer such as blends of ABC/AB, ABC/BC, ABC/AC blends ((Abetz, Stadler, and Leibler 1996; Abetz and Goldacker 2000; Goldacker et al. 1999; Hanno Hückstädt et al. 2000b; Tatiana M. Birshtein, Polotsky, and Amoskov 1999; Abetz and Simon 2005), ABC/ABC (BCA) blends (Matsushita et al. 2010; Asai et al. 2014; Asai, Takano, and Matsushita 2016b, 2015b; Abetz and Goldacker 2000), ABC star/AB blend (Abetz and Jiang 2004), BABCB/ABC blend (Liu et al. 2015) which give very complex morphologies never predicted theoretically.

Ahn et al. 2017 investigated core-shell gyroid (CSG) structure at highly asymmetric volume fractions obtained by blending a ISP triblock terpolymer and a IS diblock copolymer. Neat ISP with $\phi_I=0.12$ $\phi_S=0.75$ and $\phi_P=0.13$ has shown a new morphology with tetragonal packing of spheres and cylinders while neat IS with $\phi_I=0.11$ and $\phi_S=0.89$ shows conventional body-centered cubic spherical microdomains (Figure 1-9). Interestingly, a binary blend of ISP and IS with the overall volume fraction of $\phi_I=0.12$ $\phi_S=0.79$ and $\phi_P=0.09$ exhibits CSG at these volume fractions where P2VP having the smallest volume becomes a thin matrix (Ahn et al. 2017).

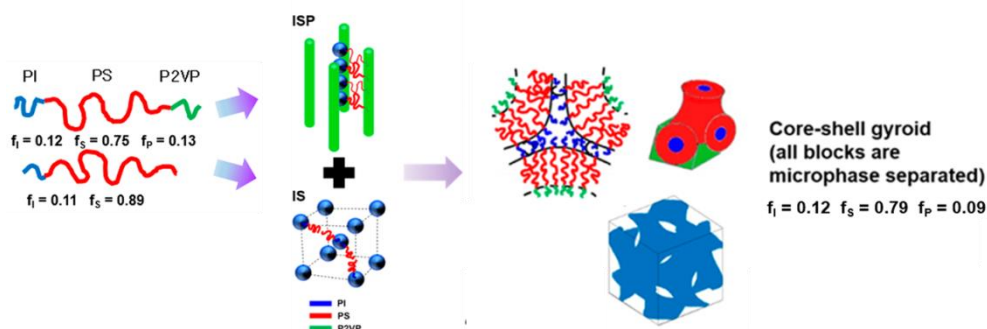


Figure 1-9. Schematic representation of morphologies of neat ISP and IS (left panel) and the formation of core-shell gyroid where all three constituted blocks are microphase separated) (right side). Blue, red, and green colors represent PI, PS, and P2VP domains, respectively. (Ahn et al. 2017).

Self-assemblies of ISP systems with blends of triblock have been very well developed in bulk, especially by Matsushita's group. For example, a mixture of three monodisperse ISP triblock terpolymers with same volume fractions (ϕ_I , ϕ_S and $\phi_P \approx 0.33$), but different molecular weights (2.6k, 9.6k, 15k) was studied by Matsushita et al. 2010. These terpolymers exhibit the same four-layer lamellar structure with a flat surface. Blending these three terpolymers (molar fractions of the shortest and the longest triblock are equal) introduces a distribution of the molecular weight of each block in the blend which has an effect on the formation of periodic structures. When the resulting dispersity index exceeds a certain value, flat interfaces PI/PS and PS/P2VP are transformed periodically into undulated ones, and an undulated lamellae structure is observed (Figure 1-10). Matsushita and coworkers have concluded that this new structure is formed due to periodic and "weak" localization of three chains along domain interfaces which produces regular surfaces with non-CMC. (Matsushita et al. 2010)

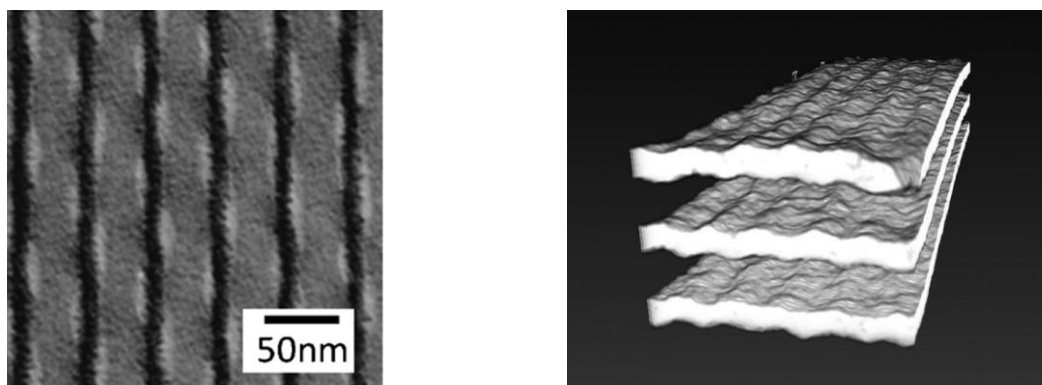


Figure 1-10. (a) Bright field TEM images of the blend sample with molecular weight distribution; PDI= 1.38; (b) 3D-TEM image reconstructed from 181 TEM images. The example is “blend 1.38” whose volume fractions of PI, PS, and P2VP components are 0.374, 0.312, and 0.315, respectively (Matsushita et al. 2010)).

Asai et al. (Asai et al. 2014) studied the blending of five ISP triblock terpolymers with constant molecular weights (c.a.130K) and similar center-block fraction around 0.55. ISP-I with the smallest PI volume fraction (0.08) and ISP-V with the smallest P2VP volume fraction (0.05) are sphere-in-lamella structures, in which the minor component PI or P2VP stay as isolated spheres at center of lamellae formed by PS. ISP-II, ISP-III, and ISP-IV, with more symmetric composition, exhibit tricontinuous gyroid structure. These five triblocks were blended within different proportions and composition heterogeneity was quantified using composition distribution indices of PI (similar as polydispersity index for homopolymers). It has been found that the tricontinuous gyroid structures gradually transform into a tetragonally packed structure of rods if composition distribution increases. The equimolar mixture of two highly asymmetric triblocks with similar molecular weights was also investigated (Figure 1-11). This blend has a symmetric composition and exhibits a tetragonally packed pattern of rods with a non-CMC interface due to polydispersity of PI and P2VP blocks in the blend (short and long chains of PI and P2VP blocks) favoring a non-uniform placement of chains around the interface. This is a very unusual result. As proposed by Asai et Al. (Asai et al. 2014), this unique interface curvature could result from systematic localization of polymer chains along the domain interfaces which lead to the formation of non-CMC rectangular-shaped domains.

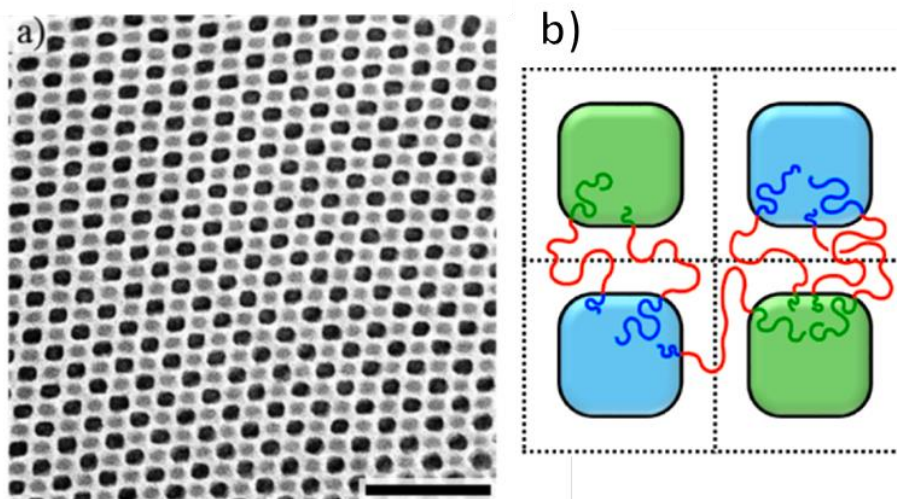


Figure 1-11. (a) Typical TEM image over a wide range of the binary blend from ISP-V and ISP-VI. Scale bar represents 200 nm and (b) Compare schematic illustrations of possible arrangements to form tetragonally packed rectangular-shaped rods. (Asai et al. 2014).

Asai et al. (Asai, Takano, and Matsushita 2015b) have studied binary blends of two asymmetric ISP triblock terpolymers coded as $\text{ISP}\alpha$ (0.06/0.62/0.32) and $\text{ISP}\beta$ (0.39/0.56/0.05) with the same molecular weight (c.a.122K). They investigated three blends compositions (proportion of two triblocks), specifically, 60/40, 48/52, 40/60, leading to following global composition 0.2/0.6/0.2, 0.24/0.59/0.17, and 0.27/0.58/0.15 respectively. For the 60/40 blend, the composition is symmetric and a tetragonally packed pattern of non-CMC rods has been observed, whereas for the two other asymmetric compositions, domains have non-constant sizes and shapes, and new tiling patterns consisting of triangles and pentagons have been found as shown in Figure 1-12.

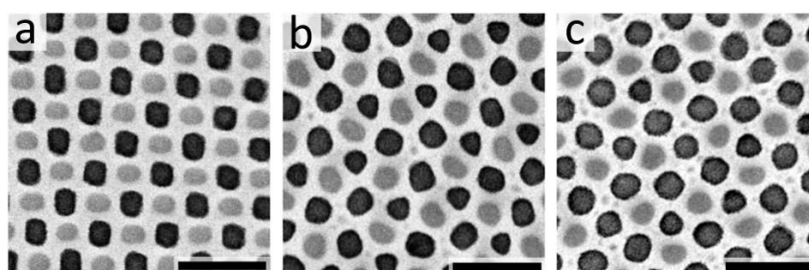


Figure 1-12. Comparison of TEM images of cross-sections of cylindrical morphology for the blend samples: (a) Blend(60/40), (b) Blend(48/52), and (c) Blend(40/60). Scale bars all represent 100 nm. (Asai, Takano, and Matsushita 2015b).

Asai, Takano, and Matsushita 2016 also developed a specific phase structure based on a binary blend of two ISP triblock terpolymers with asymmetric chain lengths of two end-blocks (ISPX (0.12/0.67/0.21) and ISPY (0.42/0.56/0.02)). The binary mixture has been prepared with the different molar ratios of $\text{ISPX} / \text{ISPY}$ from (9/1) to (1/9).

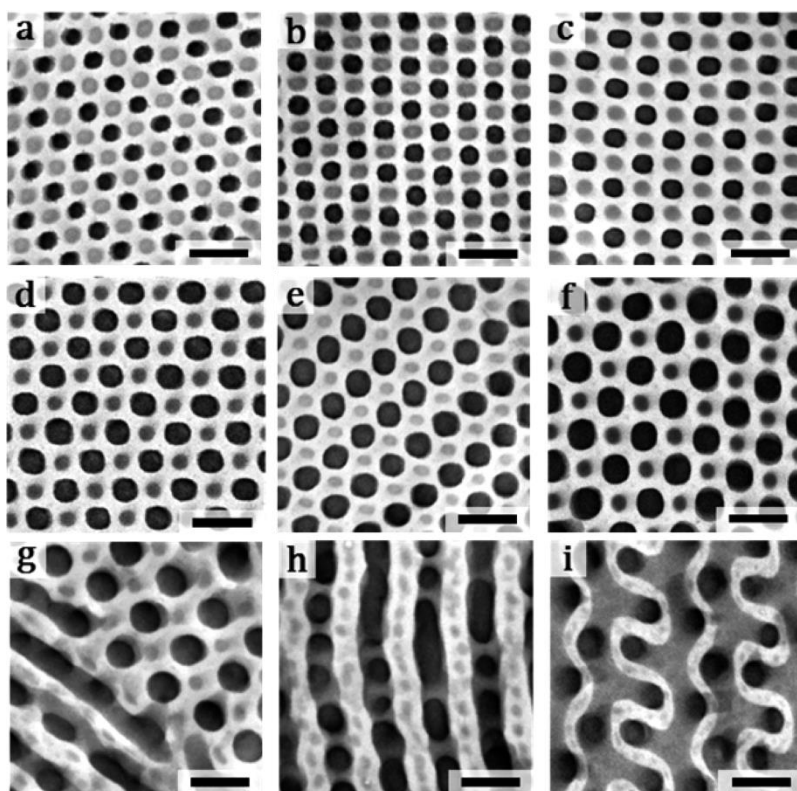


Figure 1-13. TEM images of blend samples at high magnification: (a) Blend(9/1), (b) Blend(8/2), (c) Blend(7/3), (d) Blend(6/4), (e) Blend(5/5), (f) Blend(4/6), (g) Blend(3/7), (h) Blend(2/1) and (i) Blend(1/9). All scale bars represent 50 nm. (Copy from (Asai, Takano, and Matsushita 2016b)).

TEM images of bulk morphology of the blends are shown in Figure 1-13. From blend (9/1) to blend (4/6), tetragonally packed cylinders have been observed in which cylindrical PI and P2VP domains are coarrayed tetragonally. Moreover, PI domains have non-CMC. At Blend (3/7), a transition of cylinders to perforated lamella-like morphology has been observed. The blends (2/8) and (1/9) show a perforated lamella-like morphology and a double gyroid structure respectively. Such morphologies of binary blends have never been found for monodisperse ABC triblock terpolymer.

III.3. THIN FILM

In thin film configuration, surface/interface energy becomes very important as film thickness decreases (Epps et al. 2007; Han et al. 2008; Fasolka and Mayes 2001) and nanodomains tend to be formed with a particular orientation to the substrate surface. For example, in the simplest case of an AB diblock copolymer on a solid substrate, one of the blocks which has a preferential interaction with the substrate will segregate at the film/substrate interface and it leads another block to locate at free surface (film/air). In this case, the connectivity of blocks can change the orientation of morphology (parallel to the substrate or free surface) for the cylindrical or lamellar pattern. Thin film morphology of BCPs can differ from bulk morphology under confinement and film thickness effects (Albert and Epps 2010; Russell and Chai 2017).

Self-assembly of linear triblock in bulk has been well investigated. In comparison, it has been less developed in thin films despite its interest for potential application in

nanolithography (van Zoelen and ten Brinke 2009; Segalman 2005; Segalman et al. 2009; Park, Yoon, and Thomas 2003; Stoykovich and Nealey 2006; Tallegas et al. 2013). We are now describing interesting examples of triblock self-assembly in thin films.

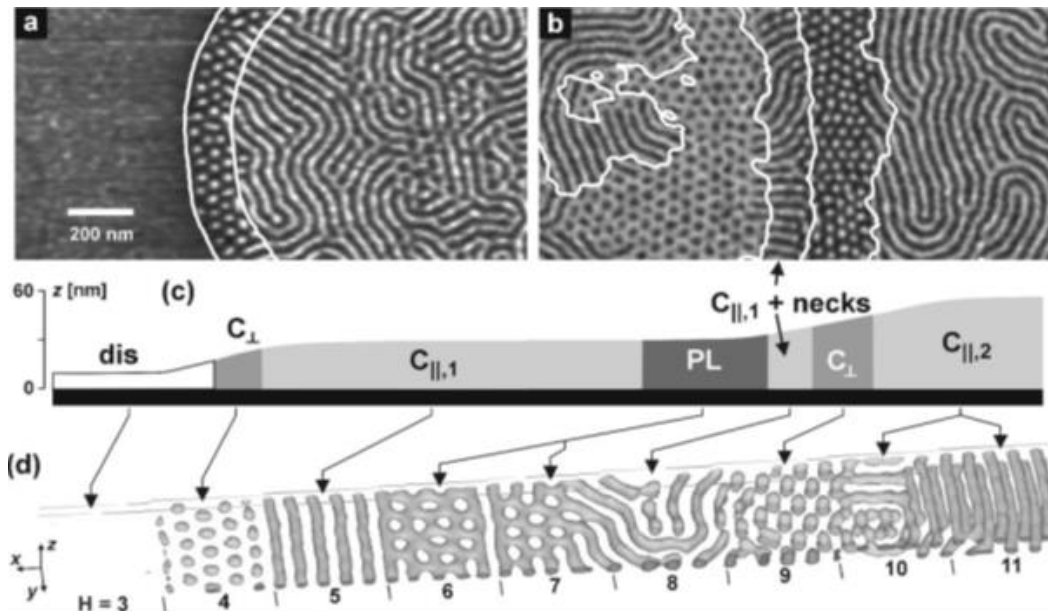


Figure 1-14. (a) and (b) TappingMode™ scanning force microscopy phase images of thin SBS (poly(styrene-*b*-butadiene-*b*-styrene) films on silicon substrates after annealing in chloroform vapor (with PB layer on the surface). Bright (dark) corresponds to PS (PB) microdomains below this top PB layer. Contour lines calculated from the corresponding height images are superimposed. (c) Schematic height profile of the phase images shown in (a) and (b). (d) Simulation of an $A_3B_{12}A_3$ BCP film in one large simulation box with from left to right increasing film thickness $H(x)$, $\epsilon_{AB} = 6.5$, and $\epsilon_M=6.0$. The isodensity surface $\rho_A=0.5$ is shown. (A. Knoll et al. 2002).

Knoll et al. have presented a detailed experimental phase diagram of a thin film based poly(styrene)-*b*-poly(butadiene)-*b*-poly(styrene) (SBS) triblock copolymer which give hexagonally packed poly(styrene) cylinders in a matrix of poly(butadiene) in bulk and very complex phase behavior in thin film (A. Knoll et al. 2002; Armin Knoll, Magerle, and Krausch 2004). Computer simulations of a corresponding $A_3B_{12}A_3$ triblock copolymer film match with experimental results (A. Knoll et al. 2002; Horvat et al. 2004). With increasing film thickness, they firstly observed a disordered phase for the smallest film thickness (dis), followed by very short upright standing cylinders ($C_{\perp}$), then cylinders oriented parallel to the film plane ($C_{||,1}$), later a perforated lamella (PL), afterwards parallel oriented cylinders with an elongated cross-section and necks and finally perpendicular oriented cylinders and finally two layers of parallel oriented cylinders ($C_{||,2}$) (Figure 1-14). Stability regions of the different phases are modulated by the film thickness via interference and confinement effects. As a result, deviation of bulk morphology and different orientations of the bulk structure were observed in the presence of an interface.

Elbs et al. and Fukunaga et al. have presented phase behavior in thin films of poly(styrene-*b*-2-vinylpyridine-*b*-tert-butyl methacrylate) (PS-*b*-P2VP-*b*-PtBMA) triblock terpolymers (Elbs et al. 1999, 2001, 2002; Fukunaga et al. 2002, 2003, 2000). They obtained

interesting morphologies like core-shell cylinders, spheres-in-cylinders, helices around cylinders, core-shell double gyroid. In all cases, PtBMA forms the matrix while P2VP forms the shell (cylinders), and PS the core. Depending on solvent vapor annealing (SVA) post-treatment and film thickness morphologies differ. They have also investigated the effect of substrate and solvent removal speed on structuration.

The behavior of ISP asymmetric copolymer in thin film was investigated by Huang et al. systematically with various control parameters, including solvent for polymer solution and annealing conditions. ISP triblock polymer was dissolved in toluene and spin-coated on silicon substrates. Various microphase-separated nanopatterns, such as ordered cylindrical and parallel nanostripe pattern have been obtained with specified treatment duration in toluene vapors at an appropriate temperature. Furthermore, fingerprint nanopattern has also been acquired by solvent annealing in tetrahydrofuran (THF) vapor. Order-order transition has been observed between various nanopatterns and it has been explained by incompatibilities of three blocks of PI-b-PS-b-P2VP under various solvent annealing conditions and different selectivity of solvents with three blocks. (Huang et al. 2017).

Other good examples of self-assembly in tri-block can be found in the following references (Tang et al. 2008; Aissou et al. 2017, 2015; Guo et al. 2006; Bang et al. 2006).

In summary, the existing literature on triblock thin films shows that the control of orientation and morphology is even more complicated than their diblock counterparts. However, when all parameters are controlled, well-oriented complex morphologies can be formed, allowing for exciting potential in surface nanopatterning.

IV. CONTEXT OF THESIS

For various kinds of surface nanopatterning applications (such as lithography, sensors, optics etc...), there is a great need to generate advanced morphologies based on BCP self-assembly. (Tallegas et al. 2013; C. M. Bates et al. 2014; Luo and Epps 2013; C. M. Bates and Bates 2017; Gu et al. 2012; Morris 2015). For that purpose, as previously mentioned, ABC BCP is the right candidate who has a more considerable morphological diversity and complexity in comparison to diblock polymer due to the addition of a third block (F. S. Bates et al. 2012; Liu et al. 2012). New morphologies can also be developed by blending homopolymers or other BCP with neat triblock as shown in bulk by Ahn and Izumi (Ahn et al. 2017; Izumi et al. 2015). Particularly, relevant is the work of Matsushita, showing that blending simple linear triblocks allows generating a great variety of unusual patterns with flat interfaces. It has to be noted that star polymers allow to produce Archimedean tiling with sharp interfaces or other complex morphologies in thin films due to the chain architecture (Aissou, Choi, et al. 2013; Aissou, Nunns, et al. 2013; Aissou et al. 2016). However, it is generally more difficult to synthesize such kind of architecture, and for that reason, the “blending” approach is desirable. Production of domains with flat (non-CMC) interfaces arranged in 4-fold symmetry in thin films (as shown by Asai et al. (Asai, Takano, and Matsushita 2015b)) could provide a very appealing template for potential applications due to compatibility of interface shape with microelectronic industry (Ruiz, Dobisz, and Albrecht 2011; Chang et al. 2014; Tang et al. 2008).

The challenge of this study is to obtain original complex morphologies with “simple” triblocks systems, namely, a linear non-frustrated terpolymer (neat or blend) having “basic” chemistry based on the well-known PI, PS, and P2VP blocks. Our goal is to compare the bulk and thin film morphology of the system and to understand the nanostructuration mechanism in thin film. Because of confinement effects, it is indeed possible to obtain different structures in bulk and thin film. It then requires an accurate study to understand the morphology and orientation of the structures in thin film case.

Seven compositions on the phase diagram shown in Figure 1-8 were chosen in this work to study their thin films’ behavior. Five of them are blends of linear ISP triblocks having the same total chain lengths but different compositions. These blends allow obtaining an ordered array of rectangular-shaped rods with 4-fold symmetry in bulk. (Asai et al. 2014; Asai, Takano, and Matsushita 2015b, 2016b). To better understand the behavior of ISP in thin films, two other compositions located on the boundary limit between CYL-SPH with $\phi_{PS} = 0.76$ and CYL-GYR with $\phi_{PS} = 0.66$, have attracted attention to observe the stability of bulk morphology in thin film and to study possible structure transition under confinement effect. Moreover, gyroid structures have attracted significant attention due to their co-continuous nature. Such architectures display multiple domains that continuously percolate across the specimen in three dimensions allowing for advanced mechanical (Pötschke and Paul 2003), optical properties (Hur et al. 2011; Dolan et al. 2015) and exciting applications as template for elaboration of metamaterials (Hur et al. 2011) or due to their high interfacial area per volume for filtration membranes and solar cells (Meuler, Hillmyer, and Bates 2009; Q. Zhang et al. 2018; Wang and Lodge 2002).

Before to go deeper into the study of the behavior of ISP triblock systems, we carried out several preliminary studies on PI, PS, and P2VP polymers to characterize the properties of each block. This allowed us to understand the interaction of each domain separately with the solvent and substrate, to better control the self-assembly process of the BCP.

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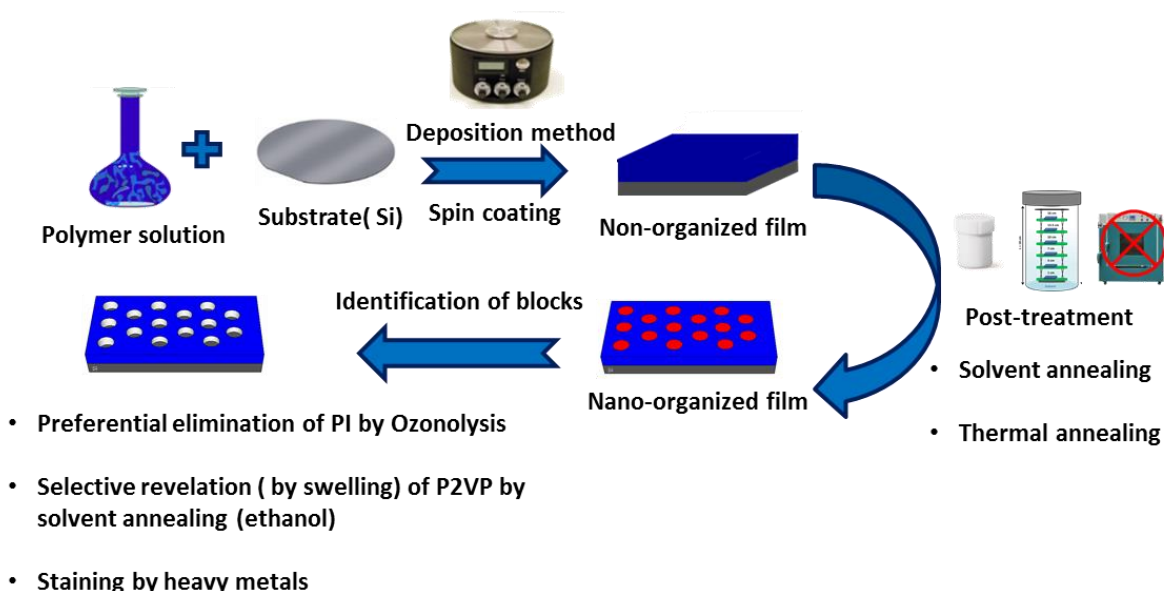
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2. MATERIALS, METHODS, OPTIMIZATION OF THE EXPERIMENTAL CONDITIONS AND PRELIMINARY STUDIES



CHAPTER 2 describes the materials and methods of this work. In this part, the optimization of experimental processes and methodological development are also presented. Some bibliographic studies are also added in several parts of the chapter when it is necessary. We will focus on:

- The presentation of used polymers
- The elaboration of thin film (deposition method)
- The nanostructuration of polymer film – post-treatment step (particularly Solvent Vapor Annealing (SVA) with several preliminary studies to optimize the experimental conditions and to observe the influence of different parameters on the swelling behavior of PI, PS, and P2VP)
- The characterization methods by Visible Reflectometry (VR), Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM), and Grazing-incidence Small-Angle X-ray Scattering (GISAXS) and development of specific revelation methods for PI, PS, and P2VP.

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I. PRESENTATION OF USED POLYMERS

I.1. HOMOPOLYMERS, DIBLOCKS AND TRIBLOCKS

Homopolymers PI (Polyisoprene), PS (Polystyrene) and P2VP (Poly2vinylpyridine) are presented in Table 2 with their number-average molar mass, molar-mass dispersity and origin.

Sample	$\overline{M}_n$ (kg/mol)	$\mathfrak{D}_M$	Origin
PS	10	1.05	Polymer Source
	64	1.04	Polymer Source
	132	1.06	Polymer Source
	170	2.06	Sigma Aldrich
	267	1.05	Polymer Source
PI	14	1.03	University of Nagoya
P2VP	16	1.02	University of Nagoya

Table 2. Characteristics of the used homopolymers: $\overline{M}_n$ (number-average molar mass); $\mathfrak{D}_M$ (molar-mass dispersity); origin (company or research team that provided it us).

All the block copolymers used were provided by the team of Prof. Matsushita at the University of Nagoya and were synthesized by anionic polymerization following a protocol described elsewhere (Mogi et al. 1992). Table 3 summarizes their molecular characteristics (total number-average molar mass ($\overline{M}_n$), the volume fraction of each block (ϕ), and nanostructure observed in bulk). The self-assembly of these triblock terpolymers has been already studied in bulk by Matsushita's team and the bulk morphology is presented in Table 3.

2. MATERIALS AND METHODS

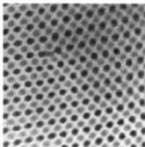
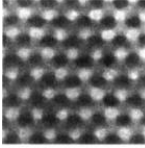
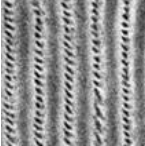
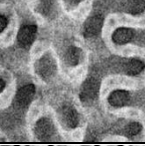
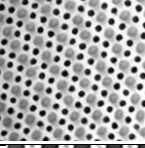
Sample	$\overline{M}_n$ (kg/mol)	$\phi_{PI}/\phi_{PS}/\phi_{P2VP}$	$\mathfrak{D}_M$	Bulk morphology	
IS	73	0.55/0.45/-	1.07	Lamellar	-
SP	89	-/0.48/0.52	1.09	Lamellar	-
IP	83	0.51/-/0.49	1.06	Lamellar	-
ISP-19	90	0.12/0.76/0.12	1.02	Tetragonally packed cylinders (Mogi et al. 1994)	
ISP-23	91	0.20/0.66/0.14	1.02	Gyroid (Seki et al. 2000; Mogi et al. 1994)	
ISP- α	122	0.06/0.62/0.32	1.02	Cylinders in Lamellae (Asai et al. 2015)	
ISP- β	124	0.39/0.56/0.05	1.05	Spheres in Gyroid (Asai et al. 2015)	
ISP-X	223	0.12/0.67/0.21	1.02	Hexagonally packed cylinders (Asai et al. 2016)	
ISP-Y	264	0.42/0.56/0.02	1.03	Spheres in Lamellae (Asai et al. 2016)	

Table 3. Characteristics of block copolymers used: $\overline{M}_n$ (number-average molar mass); ϕ (volume fraction); $\mathfrak{D}_M$ (molar-mass dispersity); bulk morphology.

I.2. BLEND OF TRIBLOCKS AND TRIBLOCKS/DIBLOCKS

The blends of triblock and triblock/diblock copolymers are presented in Table 4 with the final volume fraction of each block and the bulk morphology that were derived from the literature review (Table 4).

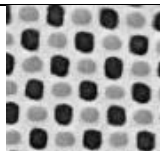
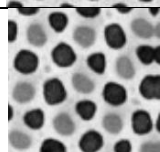
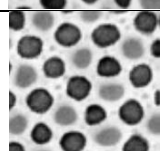
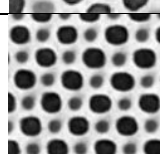
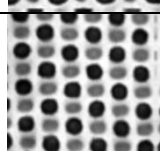
Sample	Blend proportion	$\phi_{PI}/\phi_{PS}/\phi_{P2VP}$	Bulk morphology	
ISP α /ISP β	60/40	0.20/0.60/0.20	Tetragonally packed rectangular rods (Asai et al. 2015)	
	48/52	0.24/0.59/0.17	Packed rods (Asai et al. 2015)	
	40/60	0.26/0.58/0.16		
ISPX/ISPY	60/40	0.26/0.62/0.12	Tetragonally packed rods (Asai et al. 2016)	
	85/15	0.17/0.65/0.18		
ISP α /IS	59/41	0.21/0.57/0.22	Not studied in bulk	

Table 4. Characteristics of blends of blocks copolymers: ϕ (volume fraction) and bulk morphology when already studied.

The volume fraction of each block in the blend was deduced from the mass fraction of the BCPs, the volume fraction of the block in each BCP and the density of the polymer. As an example, 11.9 mg of ISP α and 8.1 mg of ISP β were weighted and introduced in a vial with 1 mL of 1, 2-dichloroethane (DCE) (1.25 g). This results in a 20 mg/mL solution of polymer with a volume fraction of PI, PS and P2VP of respectively 0.20/0.60/0.20.

II. THIN FILM PREPARATION

DCE was used as a solvent for all polymer solutions (see 2.III.2.3 Choice of the solvent (in this chapter), for a detailed description of the polymer-solvent interactions). Typically, the solutions of polymers were prepared at 20 mg/ml and were left under stirring at room temperature (RT) for at least 2 h. The substrates were Si (100) wafer pieces of 10*10 mm² and were cleaned by sonication in tetrahydrofuran (THF), ethanol, and acetone for 10 minutes each.

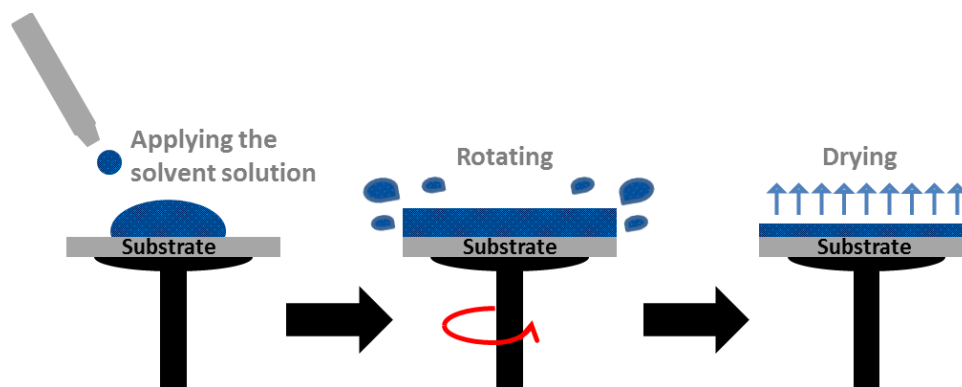


Figure 2-1. Elaboration of thin films by spin coating.

As a deposition method, the spin coating process was used. By this method, it is possible to obtain uniform thin films with only a few drops of the solution. The thickness of the film can be controlled by varying the rotation speed of spin coating or the polymer concentration in solution. A few drops of the solvent used for the polymer solution (DCE) were deposited on the substrate, then the substrate rotated at a constant rotation speed (2000-3000 rounds per minute (rpm)) for 10 seconds at RT and the solvent was evaporated (Figure 2-1). This step allows us to have a clean surface. The same process was repeated with the polymer solution in order to obtain thin films with 100-120 nm thickness on Si wafer.

III. POST TREATMENT

III.1. THERMAL ANNEALING

The self-assembly of BCP can be achieved by thermal annealing or solvent vapor annealing (SVA). The thermal annealing is a commonly used approach for bulk systems (Mogi et al. 1992, 1994; Asai et al. 2014; Welander et al. 2008; Bates et al. 2014; Han et al. 2009) because of easy operating and no presence of an organic solvent. It rapidly forms thermodynamically stable morphologies with controlled orientation, and alignments (on time scales compatible with industrial processes (Welander et al. 2008; Ferrarese Lupi et al. 2013)). The organization of BCP by thermal annealing is obtained by increasing the temperature above the glass transition temperature (T_g) of each domain to enhance the chain mobility and thus facilitate the nanostructuration.

We studied the possibility of using thermal annealing on polymer films to organize them. Thermal annealing was carried out at different temperatures (125 °C and 155 °C) higher than the glass transition temperature T_g of each block (PI (-65/-75 °C) (Burfield 1987; Widmaier and Meyer 1981), PS (+95/+105 °C) (Rieger 1996), P2VP (+90/+100 °C) (Papadopoulos et al. 2004)) and during different durations (2 and 5 days) in a vacuum oven. Whatever the condition, no ordered nanostructure was observed, as shown in Figure 2-2. We assume that this difficulty arises from the significant difference in T_g of the three components. Thermal annealing requires a temperature higher than T_g of more rigid polymers (i.e., PS and P2VP) which corresponds to a temperature where PI is in the liquid state. The difficulty of obtaining an ordered structure can also be explained by the large surface energy difference between PI, PS and P2VP (γ_{PI} : 32 mJ/m²; γ_{PS} : 40 mJ/m²; γ_{P2VP} : 47 mJ/m²) (Brandrup, Immergut, and Grulke 1999). According to these values, the presence of PI is more favorable than the PS and P2VP on the interface film/air and consequently, PI forms a layer on the surface. It is also expected that P2VP forms a layer on the substrate/film interface because of the similarity of the surface tensions of the polymer and the substrate used (γ_{Si} : 45.8 mJ/m²) determined using contact angles measurement of different liquids). In conclusion, the perpendicular orientation of nanostructures in thin films of polymer system (ISP) will be not favored by thermal annealing.

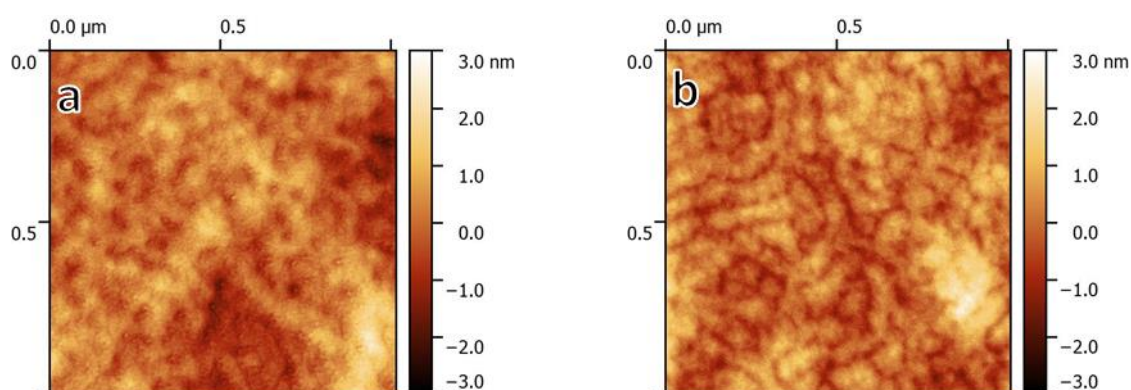


Figure 2-2. AFM height images (1 μm x 1 μm) after thermal annealing on ISPα/ISPβ 60/40 blend thin films (a) after 2 days at 125 °C (b) after 5 days at 155 °C.

III.2. SOLVENT VAPOR ANNEALING

Considering the results obtained with thermal annealing, SVA was used to achieve the structuration of ISP system. In this section, we will first provide a brief survey of the literature on the subject and secondly, we will describe a preliminary study on the influence of the experimental parameters on the swelling of the polymers (solvent nature, film thickness, molecular weight and composition of the polymer, the geometry of the experiment). This will enable the selection of the best conditions for SVA we will use in this work.

III.2.1. INTRODUCTION

When the film is exposed to a solvent atmosphere, solvent molecules are firstly adsorbed at the film surface and then diffuse in the film. This leads to a swollen state due to the increase of the solvent concentration in film. By absorption of the solvent molecules in the film volume the T_g of domains decreases and the chain mobility increases artificially. In theory, the film should swell until equilibration of the chemical potential of solvent in the vapor phase and film. However, the solvent uptake of the film is limited and often shows a plateau due to polymer entanglement in the film (resulting in a mechanical resistance), the initial thickness of the film, interaction with the substrate ... In this stage, the mechanical strength of the film against wettability is significant. It is known that a liquid film on a substrate is non-wetting if its spreading coefficient, $S = \gamma_S - \gamma_{SP} - \gamma_P$, is negative, where γ_S and γ_P are the surface free energies of the solid substrate and polymer, respectively and γ_{SP} is the interfacial free energy between the substrate and polymer (Wang et al. 2001; Qu et al. 1997). In literature, Reiter and Günter have shown that polymer film dewetting is generally driven by unfavorable enthalpic interactions between substrate and polymer. The progression of dewetting has been studied on heated polystyrene films above its glass transition temperature (T_g). He has shown that firstly, the film breaks up, thus creating randomly distributed holes. Secondly, the holes then grow and form rims ahead of them, which finally contact each other creating cellular structures. Third, the resulting ribbons are unstable and decay into droplets (Reiter Günter 1992). Studies have also focused on the dewetting of structured fluids such as BCPs (Fukunaga et al. 2002; Green 2003; Limary and Green 1999a, 1999b). The dewetting of BCPs induced by solvent vapor was studied by Peng in a more detailed way on PS-*b*-PMMA films deposited on silicon oxide (Peng et al. 2005). The anisotropy of the block polymer mobility results in the dewetting of the film. It can be assumed that a high swelling rate of the polymer can also create competition between swelling limit (mechanical resistance of film) and wetting on substrate and dewetting could occur due to instability of polymer (or difference of surface tension). Several parameters (molecular mass, temperature, film thickness, substrate interaction) influence the dewetting of thin polymer films. Lately, we will discuss the influence of each parameter on the dewetting process.

In the last step of a SVA, the deswelling of the polymer occurs (the solvent is removed) and this step represents a rapid and nonequilibrium process. In most cases, the fast evaporation of the solvent allows to freeze the BCP structuration (Sinturel et al. 2013).

One of the very first examples reporting an improvement in long-range order in block polymer films using solvents is Albalak et al. (Albalak et al. 1998). They studied the structural changes of poly(styrene-*b*-butadiene-*b*-styrene) (SBS) triblock copolymers after exposure to vapors of non-preferential (hexane and methylethylketone (MEK)) and preferential (toluene) solvents, using small-angle X-ray scattering. The cylindrical and lamellar morphologies are found to be similar in structure to thermal annealing and result in an improvement in the symmetry of the packing of microdomains. Kim and Liberia (Kim and Libera 1998) studied the influence of solvent evaporation rate on the final morphology of solvent cast (toluene)

SBS triblock in thin film (c.a. 100 nm) forming a cylindrical structure. They observed that after rapid solvent evaporation, microphase separated morphology with no long-range order is obtained, however slow evaporation rates lead instead to a highly ordered morphology of PS cylinders in a PB matrix with vertical (i.e., perpendicular to the surface plane) and/or in-plane (i.e., parallel) orientation. The cylinder orientation depends on solvent evaporation rate. It can be concluded that SVA parameter control is critical to be able to produce the desired morphology and for each polymer system, it is essential to realize preliminary studies to determine optimal experimental conditions.

According to the literature review, a great variety of experimental devices of SVA have been developed in order to tune process parameters. Generally, there are three different “typical” ways (Gu et al. 2016) to perform SVA experiment (Figure 2-3). The first approach is “jar annealing” depicted in Figure 2-3a, which consists of a closed sealed annealing chamber with BCP film and a solvent reservoir inside which is placed into a (like a beaker or desiccator) (Jung and Ross 2009). In this case, the vapor pressure of the solvent in the chamber depends on the solvent quantity in the reservoir, the surface area of the solvent, the volume of the chamber, temperature, humidity, and annealing time. In a second approach, a more controllable SVA technique is presented in Figure 2-3b where the solvent reservoir is located outside the annealing chamber (Gotrik et al. 2012). An inert carrier gas bubbles through a solvent reservoir and then into the annealing chamber. By this method, it is possible to control the partial vapor pressure inside the annealing chamber. Last one is “jar annealing” with inlet/outlet lines for inert gas flow (Di et al. 2012; Lee et al. 2019) where an inert gas flow can be used to modify the vapor pressure in chamber (Figure 2-3c) and solvent vapor flow via a carrier gas through inlet/outlet lines. There are other “controlled” SVA ((Lu et al. 2008), “advanced” SVA technique such as solvothermal annealing process (Zhang et al. 2010) and microfluidic device to perform SVA with different solvent vapor compositions in a single experiment (Albert et al. 2011).

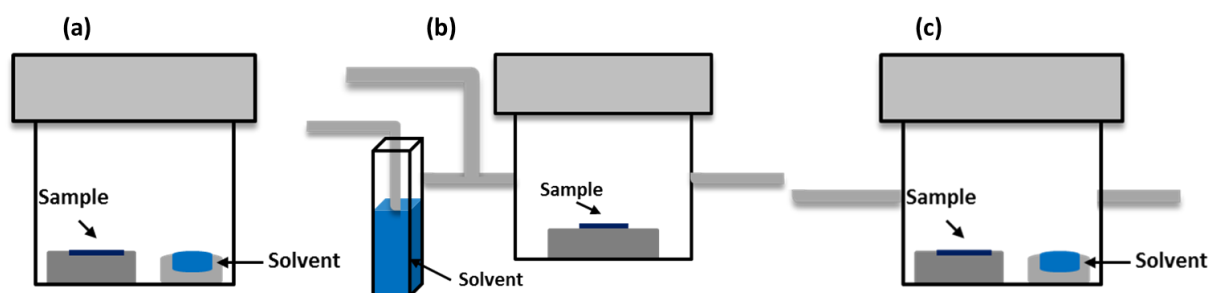


Figure 2-3. SVA methods; (a) annealing chamber with solvent reservoir inside (“jar annealing”) (b) Annealing chamber with an exterior solvent reservoir and solvent vapor flow via a carrier gas flow through inlet/outlet lines. (c) annealing chamber with a solvent reservoir inside a chamber and gas flow through inlet/outlet lines.

It can be seen that during the preparation of the nanostructured morphology of BCP by SVA, there are several important factors that influence the final state of the film especially, BCP composition, solvent selection, type of substrate, film deposition method,

SVA condition, etc. The following section describes how we selected the appropriate SVA conditions for our systems.

III.2.2. OPTIMIZATION OF THE SVA CONDITIONS

Figure 2-4 describes the parameters of the SVA we studied in order to find the optimal SVA condition. This was realized by the “jar annealing” system, as shown in Figure 2-3a, at various temperatures (25 °C and 30 °C) in different solvent vapors. Due to reproducibility issues, experimental conditions (volume of the jar, quantity of solvent, type of solvent, temperature, the pressure of solvent, etc.) must be fixed (Xuan et al. 2004). Several studies can be found in the literature on the control of the parameters that govern SVA process (Sinturel et al. 2013), especially we focused on solvent vapor pressure. It can be controlled in three ways: adding non-volatile organic molecule as squalane, changing the solvent quantity or changing the distance between film and solvent surface. We will focus on the third way. The calculation of solvent (THF and Toluene) quantity for each experimental chamber (Teflon box or glass jar) with different volumes and temperatures (25°C and 30°C) is presented in Annex 1.

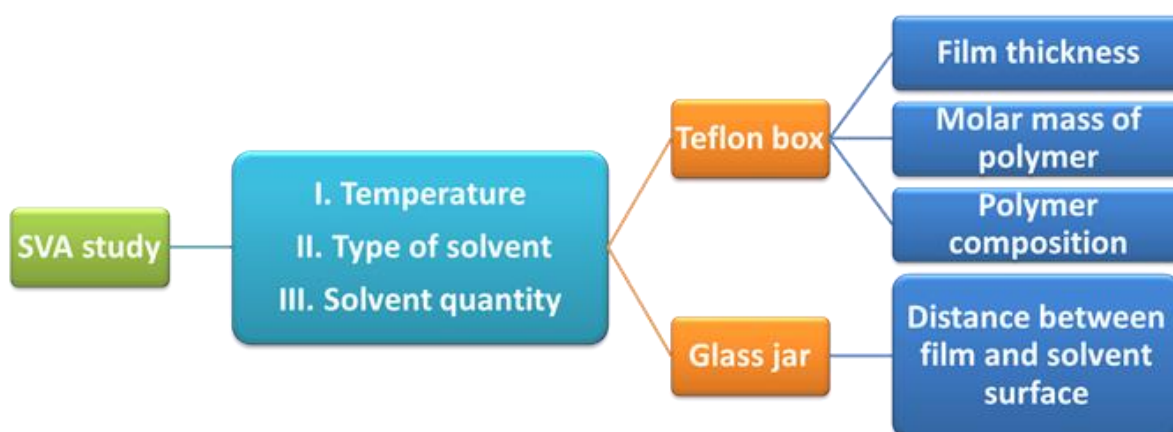


Figure 2-4. The SVA study to control several factors to obtain nanostructured morphology.

III.2.3. CHOICE OF THE SOLVENT

In BCP thin film field, choice of solvent is a crucial parameter because solvents are used for elaboration of thin films (such as spin coating or dip coating methods) where a polymer solution in a solvent is used (Miller-Chou et al. 2003; Huang et al. 2015; Ghosh et al. 2013; Müller-Buschbaum et al. 2001) and post-treatment step to drive the self-assembly of BCP such as SVA (Sinturel et al. 2013; Emerson et al. 2013; You et al. 2013). In the nanostructuration, the solvent selectivity is essential and leads to different ordered morphologies, different orientations of the structures and also transition between various organizations. For this reason, the estimation of the polymer-solvent affinity is of major importance. The most common solvent used for SVA of block polymers is one that is either neutral or only slightly selective for one block. Solvent uptake of each block is affected by solvent compatibility with the block and by the physical state of the block (e.g., glassy, rubbery or semicrystalline). These results in a differential swelling of the blocks and

consequently, an effective variation of the block volume fractions that can have a direct impact on the resultant ordered state symmetry (Sinturel et al. 2013). The affinity between polymers and solvent was firstly evaluated using theoretical parameters, then studied by several experimental tests and finally, the results are compared.

a. Theoretical results

The Hildebrand solubility parameters (δ) introduced in 1950 provides a numerical estimation of the degree of interaction between materials and can be a good indication of solubility, particularly for nonpolar materials such as many polymers (Hildebrand, J. and Scott, R. L. 1950). This solubility parameter δ of species (polymer or solvent) describes the attractive strength between the molecules of the same species and is defined as the square root of the cohesive energy density, the heat of vaporization divided by the molar volume. Hansen developed the Hildebrand method to estimate the relative miscibility of polar and hydrogen bonding systems (Hansen 2000). In Hansen's approach, the Hildebrand solubility parameter is divided into three components: the energies from polar (δ_p) force between molecules, dispersion (δ_d) force between molecules and hydrogen bonding (δ_h) between molecules.

Solvents/Polymers	Hildebrand Solubility Parameter (MPa ^{1/2})	PI/HSP difference	PS/HSP difference	P2VP/HSP difference
Polyisoprene (PI)	16.3			
Dichloroethane (DCE)	16.5	0.2	2	4.1
Cyclohexane	16.8	0.5	1.7	3.8
Toluene (Tol)	18.1	1.8	0.4	2.5
Polystyrene (PS)	18.5			
Tetrahydrofuran (THF)	19.5	3.2	1	1.1
1,4 dioxane	20.5	4.2	2	0.1
Poly(2-vinylpyridine) (P2VP)	20.6			
Ethanol	26.5	10.2	8	5.9

Table 5. Hildebrand solubility parameters and their differences for solvents and polymers (PI, PS and P2VP are depicted in orange, blue and green respectively). The compatibility between solvents and polymers are classified by color tone (color gradient from darker to lighter tone) according to the difference between polymer and solvent Hildebrand parameters.

An accurate prediction about polymer-solvent affinity can be obtained using the Hansen solubility parameters (HSP) by considering the contribution of all components of the HSP (equation in Annex 2). As a first approximation, the difference of Hildebrand solubility parameters of the species can be directly analyzed. Table 5 shows the Hildebrand solubility parameter values for solvents and polymers used in this study and polymer/solvent differences.

Similar solubility parameters between polymer and solvent (small difference in Table 5) result in solvation, miscibility or swelling. So, a solvent is considered as a good solvent for a given polymer when the difference between Hildebrand solubility parameters of the

solvent and the polymer is low (Table 5). The best solvent for PI is DCE or cyclohexane. In PS case, the solubility parameters of toluene and THF are close to the Hildebrand parameter of PS. P2VP is also miscible in 1,4 dioxane and THF. The consideration of polymer-solvent affinity estimated from the Hildebrand Solubility Parameter is a first approach that needs to be confirmed by experimental studies (Vayer, Vital, and Sinturel 2017). For that purpose, dissolution tests of thin film under a drop of solvent and thin film swelling in solvent vapors were performed.

b. Experimental results

Dissolution test

A dissolution test (Figure 2-5) is a simple and quick method to have a first idea about interaction between polymer and solvent. Thin films of homopolymers with thicknesses between 100 nm and 300 nm were deposited onto silicon substrate by spin coating. The films were scratched in order to differentiate polymer film and substrate. Samples were observed by optical microscopy (OM) and the thickness of the film was evaluated either by Visible reflectometry (VR) or Atomic Force microscopy (AFM). Then a drop of the tested solvent was added onto the film and blown after a few seconds by a jet of nitrogen. The resulting film was again observed by OM and thickness again evaluated. Film modification allows to evaluate compatibility between solvent and polymer: if the film is removed and bare silicon is observed, added solvent is a good solvent for the tested polymer as for PS and DCE in Figure 2-5. In contrast, if the film is still intact, polymer is not soluble in the added solvent as for PS and ethanol (non-solvent). If the film remains on substrate but its thickness decreases, this solvent is considered as a bad solvent.

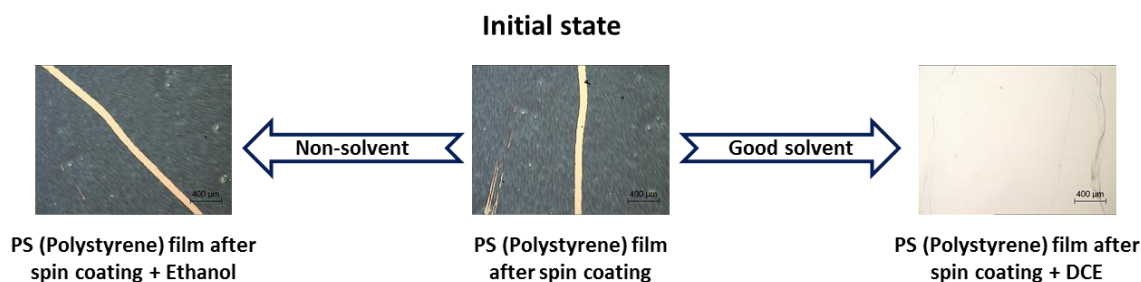


Figure 2-5. Optical Microscopy (OM) observation of polymer thin film before and after dissolution test.

Dissolution tests were performed for PS, PI and P2VP thin films with different solvents. The results are presented in Table 6. PI, PS and P2VP are depicted in orange, blue and green respectively (the same color code for theoretical and experimental results) and compatibility between solvents and polymers are classified by color gradient from darker (good solvent) to lighter tone (non-solvent) according to dissolution test results. DCE is a good solvent for all blocks. Ethanol is a selective solvent for P2VP as 1,4 dioxane for PS and cyclohexane for PI polymers. THF and toluene are good solvents for PI and PS.

Solvents/Polymers	PI	PS	P2VP
Cyclohexane	Good	Bad	Non-solvent
DCE	Good	Good	Good
1,4 dioxane	Non-solvent	Good	Non-solvent
Ethanol	Non-solvent	Non-solvent	Good
THF	Good	Good	Non-solvent
Toluene	Good	Good	Non-solvent

Table 6. Results of dissolution tests.

Swelling test in solvent vapor

This test allows the comparison of more quantitatively compatibility of polymers with solvents. The following procedure was used: samples (thin film onto silicon substrate) were laid into a teflon closed box (volume of the box= 60 mL) as seen in Figure 2-6 and then, a few drops of solvent (0.5 ml) was added on the bottom of the box. Box was closed with a glass cap (top) which allows to follow *in-situ* the film thickness in solvent vapor by visible reflectometry. Film thickness was recorded as a function of time during the solvent vapor exposition, swelling ratio (SR) was obtained by dividing the thickness by initial thickness. For example, SR equal 1 corresponds to a film that does not swell and SR equal 2 means that the swelled film has a double thickness. In these conditions, the entire set-up (Teflon box equipped with optical fiber) could not be fitted in an accurate temperature-controlled environment (like an oven). Experiments were therefore performed at RT (c.a. 21°C) where the temperature was only approximately controlled (+/- 1°C). In order to be able to compare the swelling of different polymers and avoid reproducibility issues (difference of temperature, humidity ...), several substrates were placed side by side together in the same experiment. The thicknesses of the films were measured sequentially during the SVA process, by moving visible reflectometer light spot from one sample to another.

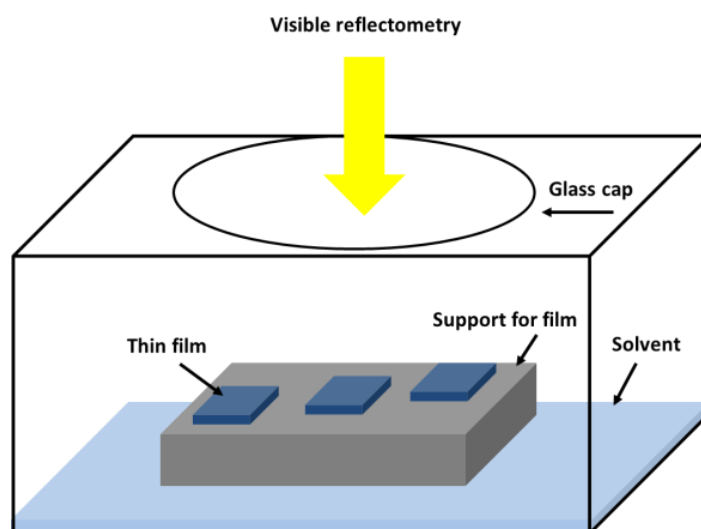


Figure 2-6. Swelling test in teflon box.

2. MATERIALS AND METHODS

The swelling ratio of polymers after 10 minutes of solvent exposure (for PS, PI and P2VP thin films with 100 nm thickness) in solvents were recorded at RT and presented in Table 7. Solubility results obtained from the dissolution test experiments are also indicated in the table (PI, PS and P2VP are depicted in orange, blue and green respectively and good, bad and non-solvent for each polymer are represented by color gradient from darker to lighter tone). Most of the swelling ratios measured with this technique are in good agreement with the dissolution test: high swelling ratios (>2) correspond to good solvents, moderate values (between 1.5 and 2) correspond to bad solvents and values close to unity correspond to non-solvents. However some discrepancies can be noted (1,4 dioxane for PI, THF for P2VP and toluene for PI). This kind of behavior has been already observed (Vayer et al. 2017; Lee et al. 2019) and related to the particular situation of polymer thin film. Moreover, the solvents have different vapor pressure which makes the comparison somehow difficult.

Solvent and Vapor Pressure at 20 °C/Polymers		PI	PS	P2VP
Cyclohexane	90 mmHg	2.7	1.8	1.1
DCE	60 mmHg	2.1	2.3	2.2
1,4 dioxane	29 mmHg	1.7	2.5	1.3
Ethanol	37.5 mmHg	1.1	1.1	4.1
THF	132 mmHg	2.5	2.5	1.5
Toluene	21 mmHg	1.5	2.9	1.1

Table 7. Swelling ratio of the homopolymers in various solvent for 10 minutes.

If we now compare the theoretical approach based on the solubility parameters and this experimental approach, we can see a pronounced deviation of the solvent polymer interaction in the case of P2VP, showing the limitation of a prediction only based on the solubility parameter. From these results we were able to select a common solvent for the preparation of the polymer solution (DCE is a good solvent as shown in dissolution and swelling tests). Also, with a view to doing SVA experiments, we considered the swelling ratios and select DCE as a non-selective solvent, cyclohexane as a selective solvent for PI, ethanol as a selective solvent for P2VP and toluene as a selective solvent for PS.

Preliminary SVA tests are shown on Figure 2-7. Non-selective solvent (DCE) vapors did not lead to ordered structuration of thin film. Other solvents such as, cyclohexane, 1,4dioxane, ethanol, THF and toluene, were also tested and ordered nanostructuration was obtained for THF and toluene vapors. In conclusion, THF and toluene were used as the SVA solvents regarding these experimental results.

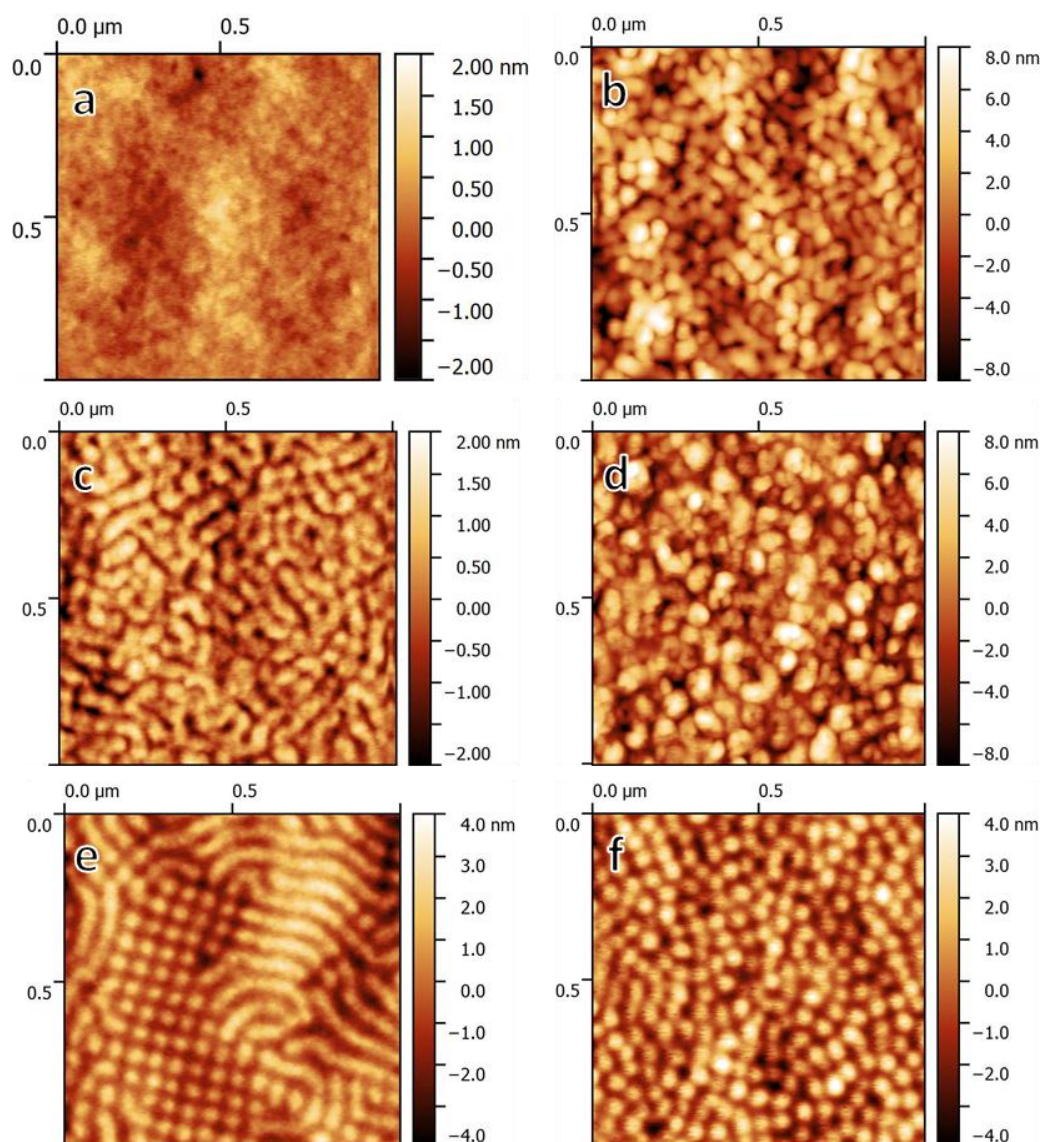


Figure 2-7. Nanostructuration of the ISP α /ISP β (60/40) blend thin films by SVA treatment in (a) DCE; (b) cyclohexane; (c) 1,4 dioxane; (d) ethanol; (e) THF and (f) toluene solvent vapors.

III.2.1. INFLUENCE OF DIFFERENT PARAMETERS ON SWELLING OF POLYMERS

In order to investigate in more detail the swelling behavior of polymers and BCP, swelling ratio as function of time was recorded and the influence of parameters such as film thickness, molar mass, temperature, type of polymers was investigated. All tests were performed in Teflon box (60 mL) in which thickness was measured continuously by VR, in the conditions previously described (i.e. with a gross control of temperature). Experiments were performed at RT (c.a. 20 °C). Higher temperature (c.a. 25 °C and 30 °C) were also obtained by local heating. A PS reference was used in order to be able to compare different swelling experiments. Equilibrium vapor pressure (P_0) is defined as the pressure exerted by a vapor in thermodynamic equilibrium with its condensed phases (solid or liquid). In our case, experiment was carried out at $P \geq P_0$ by adding an excess amount of solvent to compensate from possible leakage in the chamber (we verified that total quantity of solvent was not evaporated at the end of the experiment).

In the following paragraph, we will detail the influence of film thickness and molar mass on swelling of PS thin films used as a model sample. We will further develop the influence of polymer nature on swelling of PI, PS and P2VP polymers. Influence of composition of diblock and triblock on swelling of ISP system will be also studied. Lastly, we will present the influence of temperature (25 °C and 30 °C) on swelling of ISP system.

a. Influence of film thickness on swelling of PS films

Films of 70, 120 and 270 nm of PS 170K were deposited on substrate by spin coating. Exposures to toluene and THF at RT were performed and films thickness evolutions were recorded and displayed in Figure 2-8.

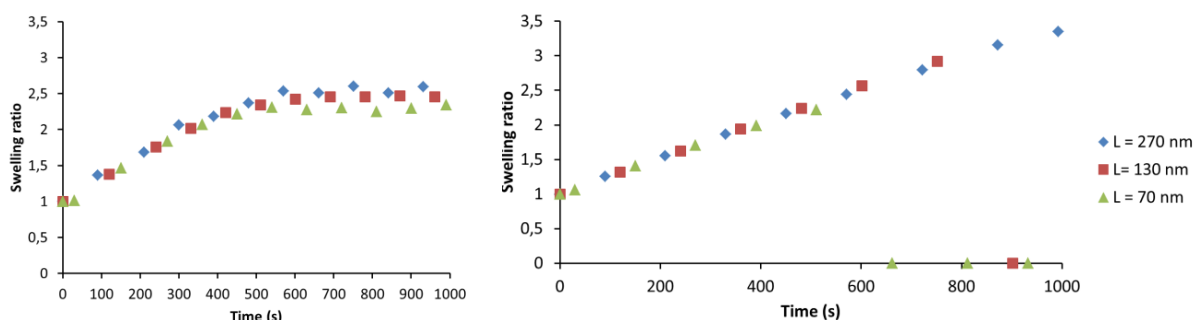


Figure 2-8. Swelling curves of PS films with different thicknesses in toluene and THF vapors at RT.

The graphs show the swelling rate of PS films with different thickness in THF and toluene vapors. For all thicknesses, the swelling ratio in toluene vapors increases progressively and starts to form a plateau after 500 seconds. During these experiments, some films dewetted (swelling ratio arbitrary is set to zero, thickness measurement is meaningless). The films thicknesses changed by the same manner for SVA treatment in THF, however the formation of plateau took more time and it was not observed after 600 seconds. The superposition of the swelling curves before dewetting shows that there was no visible effect of thickness of film on swelling of PS within the chosen range of thickness. Dewetting occurred mostly for thinner films due to film unstability arising from confinement effects (more important effect of surface energy). It also occurred faster in THF vapors than in toluene vapors, which could be explained by the higher swelling ratio obtained in THF for the same duration and difference in the interfacial tension of the swollen films. (Reiter et al. 2009).

b. Influence of molar mass on swelling of PS films

The effect of the polymer molar mass was also investigated. For that purpose, 100 nm thick films of PS with molar mass namely 10k, 64k, 132k, 170k and 267k were deposited on substrate by spin coating. Toluene and THF exposure were realized and thicknesses were measured during vapor exposure.

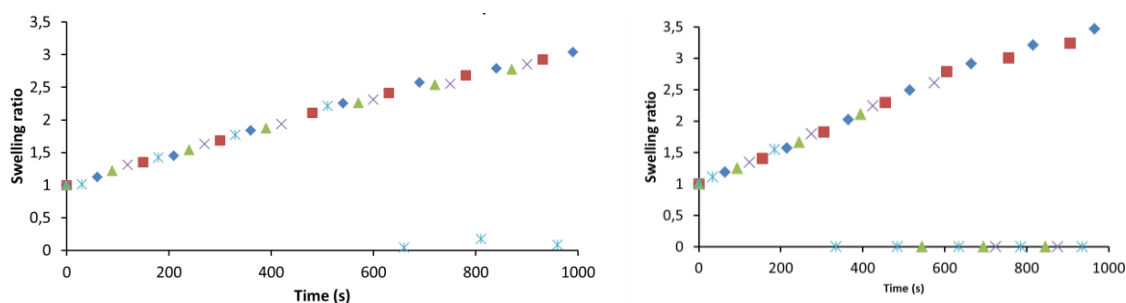


Figure 2-9. Swelling curves of different PS with different molar mass in toluene and THF at RT.

Again, superposition of the swelling curves shows that there is no visible effect of molecular weight of polymer film on swelling but affects dewetting within the chosen range of $\overline{M}_n$. It occurs mostly for low molecular mass which can be explained with the limited entanglement property of such polymer chains (Vilmin and Raphaël 2006). These entanglements between polymer chains give to polymer a transient elasticity, which is minimal for low molecular weight (Xu, Shi, and An 2008).

c. Influence of polymer nature on swelling

Swelling curves are displayed in Figure 2-10 and confirm the results shown in Table 7. In THF vapors, PI and PS thin films swell by the same manner but P2VP swelling ratio is slightly less important than others. In contrast, we observe important difference between P2VP and PI or PS swelling in toluene vapors. PI and PS swelling curves in toluene have the same form and increase linear, however P2VP polymer only swells after 3 minutes. Again, we observed some dewetting of the films due to the surface tension of polymers and solvents.

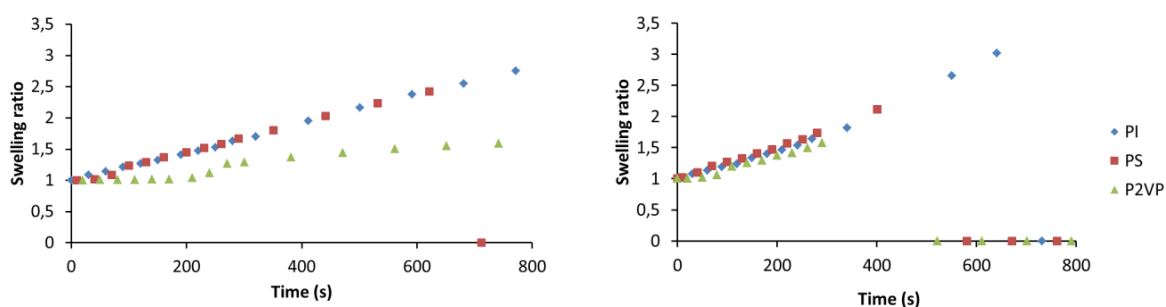


Figure 2-10. Swelling curves of PI, PS and P2VP in toluene and THF vapors at RT.

d. Influence of composition for diblock and triblock thin films*Diblock thin films*

Diblocks based on PI, PS and P2VP polymers, namely IS, SP and IP diblocks (with almost the same volume fraction for two blocks) were tested in THF and toluene vapors at RT. For reference, one PS film was added. For toluene, IS swelling curve increased faster than SP and IP due to the absence of P2VP block which has the lowest swelling ratio as shown on Figure 2-10. For THF, all diblock films swell by the same manner except IP which swell less. The results are in good agreement with the homopolymers tests.

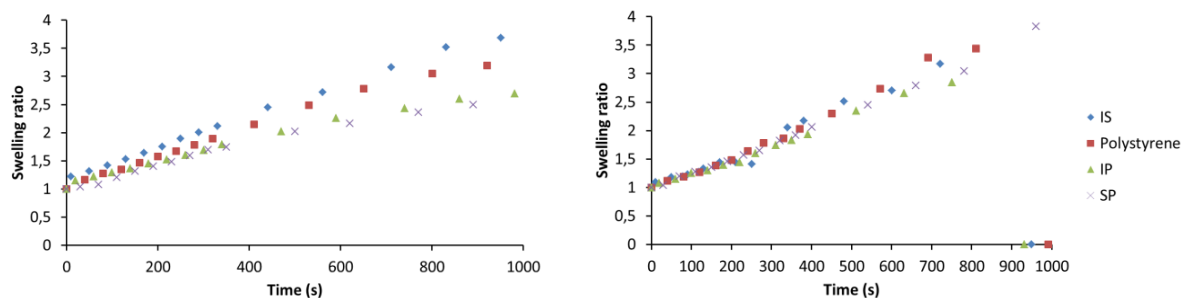


Figure 2-11. Swelling curves of diblock polymer in toluene and THF vapors.

Triblock thin films

After the study on homopolymers and diblocks, ISP triblocks were tested in THF and toluene vapors (Figure 2-12). For THF, swelling ratio of thin films of triblock evolved in the same manner except ISP α which has 32% of P2VP in triblock system. It shows that there is an influence of the composition of block polymer on the swelling behavior and for ISP systems, as P2VP has the lowest swelling ratio in THF, the swelling ratio of the triblocks depends on P2VP quantity in system. We assume that, for that reason, ISP α can behave as a diblock of SP and has the lowest swelling ratio for the same swelling duration.

For toluene, swelling ratio of thin films of triblock evolved in the same manner except ISP α which has 32% of P2VP in triblock system due to the same reason of THF case. In conclusion, the composition of BCP can affect the swelling ratio of polymer.

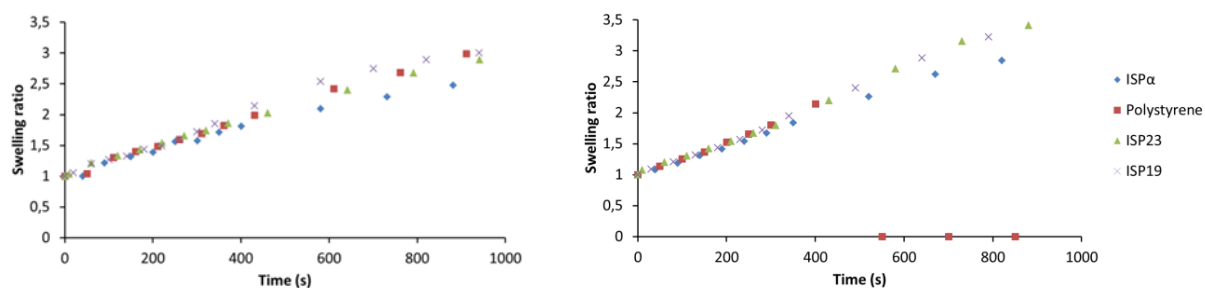


Figure 2-12. Swelling curves of ISP triblocks in toluene and THF vapors at RT.

e. Influence of temperature for diblock and triblock thin films

The increase of temperature modified the swelling behaviors of polymers but the curves confirm always the previous homopolymers swelling results. The results at 25°C and 30°C are represented in Figure 2-13 and Figure 2-14.

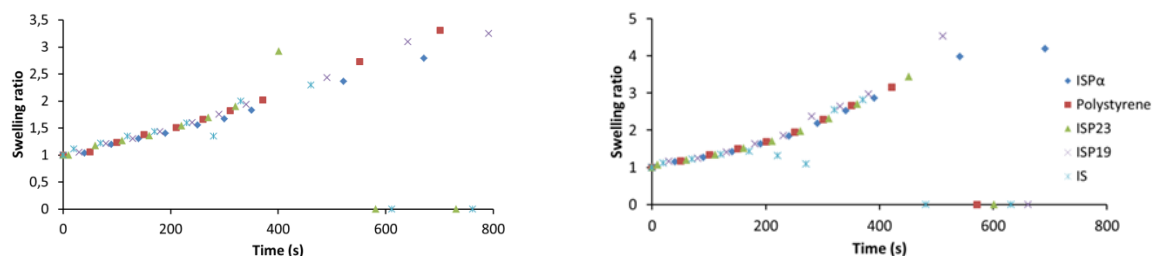


Figure 2-13. Swelling curves of ISP triblocks in toluene and THF vapors at 25°C.

At 25°C in THF, the swelling behaviors are the same at the beginning of experiments for all tested polymers. Swelling ratios increase by a factor 1.5 compared to RT. After 200 s, some films dewet. In toluene vapors, swelling ratio increases by a factor 1.2 compared to RT and there are a lot of “random” points due to important swelling ratio forming very rough surface and which makes VR measurement not possible.

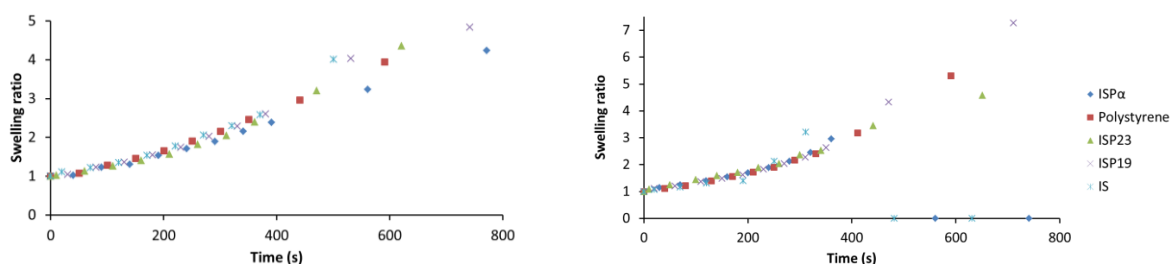


Figure 2-14. Swelling curves of ISP triblocks in Toluene and THF vapors at 30°C.

When the temperature is up to 30 °C, the phenomenon is amplified and the swelling degree increase comparing to 25 °C. The swelling ratio increases by a factor 2 compared to RT for THF and Toluene. After 400s, some films dewet. After 300s the swelling ratio reaches to approximatively 4. The results are in good agreement with the previous curves but the swelling ratio values are very important (c.a. 5 in Toluene and 7 in THF) and they are not interesting in order to obtain the ordered morphologies. Indeed, while the swelling ratio increases, order–disorder transition can occur (Flory–Huggins interaction parameters decrease). In literature, it has been shown that ordered nanostructures of BCP can be obtained with swelling ratio between 1.3 – 3 (Dolan et al. 2018; Gu et al. 2016; Gotrik et al. 2012).

After all these preliminary swelling test in Teflon box, it can be concluded that molar mass and thickness do not change the swelling of polymer but the temperature and the composition (nature of blocks) of polymers is important and could influence the structuration of BCP. When the temperature increases, swelling ratio (SR) of BCP reaches high values that

are not adapted to the structuration of the BCP film. Teflon box at RT, is well adapted to the structuration, however as the temperature was not accurately controlled in the setup, this led to reproducibility issues. One solution was to control the temperature in an oven, with a minimum temperature control of 25°C. In order to avoid undesirable excess of swelling ratio, we choose to increase the volume of the SVA chamber to decrease the diffusion rate of solvent molecules in polymers and therefore, reduce the swelling rate of polymer. The following paragraph describes the set-up we developed for that purpose.

f. Control of solvent vapor pressure by changing the distance between solvent surface and sample

A SVA chamber having a large volume (1 L) was developed in order to produce a moderate swelling ratio at $T > 25^{\circ}\text{C}$. To avoid multiple experiments, a system which allows to obtain different swelling ratio for the same duration was developed. In this set-up, various samples were placed at different distances from the solvent surface. This method was described in the literature as an efficient way to control the solvent pressure inside a chamber (Lu et al. 2008; Li et al. 2011). Inside the jar on each level (vapor pressure gradient), the pressure varied from the equilibrium vapor pressure (at the solvent level) to very low values (at the top of the system).

This system is presented in Figure 2-15. A calculated quantity of solvent is added to the bottom of jar and film is deposited on a ladder having variable distances between film and solvent surface (1 cm, 4 cm, 7 cm, 10 cm, 13.5 cm, 16 cm). We focus here on the results of the first level (1 cm), middle level (7 cm) and high level (13.5 cm).

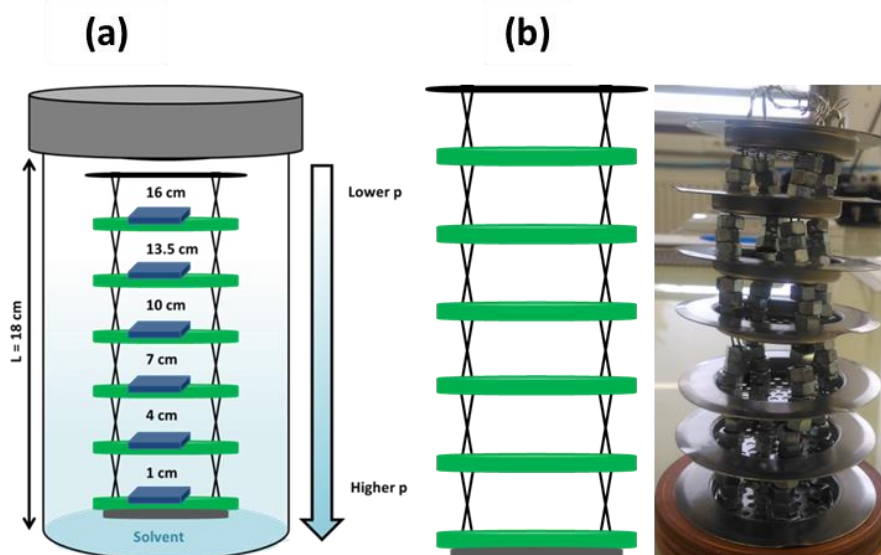


Figure 2-15. (a) SVA chamber having a volume of 1 L with the set-up where various samples were placed at different distances from the solvent surface; **(b)** Schematic image and photo of “ladder” type set-up having variable distances levels (1 cm, 4 cm, 7 cm, 10 cm, 13.5 cm, 16 cm) to realize SVA post treatment.

To confirm the effect of distance between solvent surface and film on swelling, tests were performed with PS homopolymer films on three levels –1, 7 and 13.5 cm of solvent

surface in THF and toluene vapors at RT (Figure 2-16). In both cases, the highest swelling ratio is obtained when the film is the closest to solvent surface but the vapor pressure gradient depends on the type of solvent as shown by the difference of swelling behavior of the films in the upper stages. This will be used in the study of the nanostructuration kinetics of the BCP films.

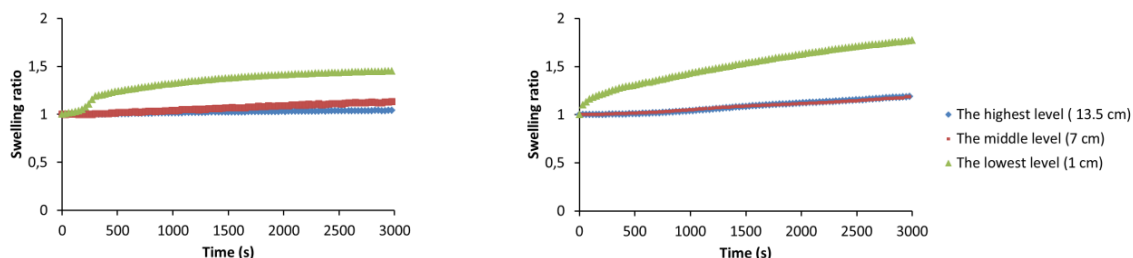


Figure 2-16. Swelling curve of PS films on different level in glass jar with THF and Toluene vapors at RT.

III.2.2. CONCLUSION

In conclusion, SVA annealing was performed in THF and toluene vapors in a annealing chamber (1 L) which allows to have different swelling ratios, in a accurately temperature controlled environment. The structuration kinetic of each system will be presented in Chapter 3.

IV. CHARACTERIZATION METHODS OF THIN FILM: VR, AFM, TEM AND GISAXS

IV.1. VISIBLE REFLECTOMETRY (VR)

The thicknesses of the films were measured by visible spectral reflectometry using F20 by Filmetrics. The advantage of this method is being able to measure the thickness rapidly. This gives the possibility to follow *in-situ* the thickness variations of films in different solvents.

The intensity of light reflected from the thin film (the total reflected light from the interface of film/substrate and film/air) is measured over a range of wavelengths (i.e., between 380 and 800 nm) and fitted with a calculated reflectance spectra based on the optical constants of the film (refractive index (n) and extinction coefficient (k)). Optical constants of refraction and extinction of PS (1.58 and 1.01 measured by ellipsometry at 632.8 nm previously) have been selected for all types of polymer tested since the values of optical constants for different types of polymers are very close.



Figure 2-17. *In situ* measure of film thickness by visible reflectometry (VR).

IV.2. AFM

The principle of the Atomic Force Microscopy (AFM) is based on the interactions between a tip, and a sample surface. A typical AFM consists of a cantilever with a small tip (probe) at free end, a laser, a 4-quadrant photodiode and a scanner (Figure 2-18). There are numerous modes of AFM (contact, tapping, non-contact, peak-force tapping, etc.) which give different types of information about the surface, not only 3D topography images, also information about physical property, adhesion, magnetic behavior etc.

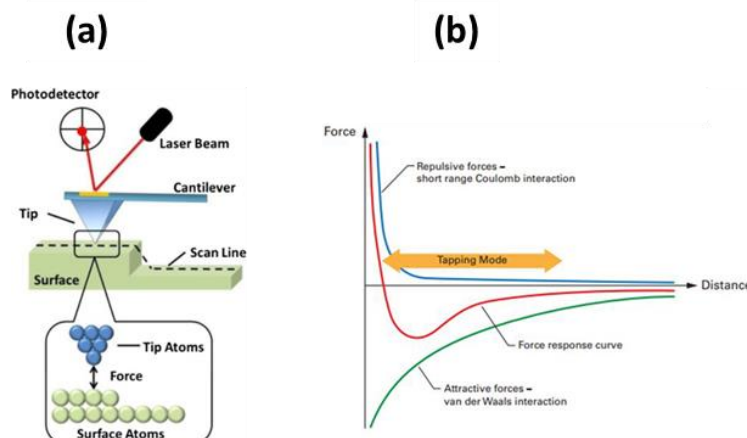


Figure 2-18. (a) Principle of AFM; (b) Force curves highlighting the motion of an oscillating cantilever in tapping mode.

AFM was carried out in the air with the AFM Dimension Icon model (Bruker ICON) to observe the morphology of polymer films surface. Silicon cantilevers RTESP300 from Bruker were used for characterization.

Different modes were tried in order to choose the most appropriate. Contact mode leads to a degradation of the surface and was consequently not selected for the observation of the surface. The QNM (Quantitative Nanoscale Mechanical) mode of AFM was also tested. This mode allows to determine the local mechanical property at the nanoscale. It can be very interesting for the morphological identification of BCP and especially for the determination of the placement of each domain on surface (i.e. PI, PS and P2VP) since the polymer may exhibit different mechanical properties (PI is in the rubbery state at RT whereas the others are glassy). However, we never succeeded to obtain valuable images with three different types of polymers on the surface by QNM. The characterizations of ISP thin films were performed in tapping mode(TM). This mode allows to observe the nanostructuration of the polymer even if a wetting layer is present at the surface. All displayed AFM images are handled by Gwyddion. The characteristic dimensions of patterns were determined by image analysis using power spectral density (PSD) or averaging 10 measures (± 2 nm).

At each step of the nanostructured film elaboration, samples were characterized by AFM since this technique does not modify the sample. However, if the method allows to observe the nanostructuration, it does not directly identify the type of polymers. To overcome these problems (recognition of the blocks in the structure), selective elimination of PI by UVO or selective swelling of P2VP in EtOH were proposed.

IV.2.1. SELECTIVE ELIMINATION OF PI BY UVO

In the literature, Chen et al. have described the selective degradation of PI in PI-*b*-PS diblocks films by ozone treatment in liquid (Chen et al. 2008). They showed that the effectiveness of ozone treatment (degradation percentage of PI block) depends on the contact surface between PI and ozone, total PI volume available in system and PI morphology of the film. They succeeded in degrading 90% of the PI from a lamellar morphology, 80% with a bi-continuous morphology, 70% with a cylindrical morphology and

50% with a spherical morphology. Mykhaylyk et al. (Mykhaylyk et al. , 2004) have studied the effect of time of ozone treatment on the surface morphology of films of PS-*b*-PI-*b*-PS polymers (82% of PI). The authors have shown that the degradation consists of two steps: firstly degradation of the PI without affecting the PS, and secondly, for longer times, PS crosslinking. For even longer treatment times, the porosity (holes) left by the degradation of the PI disappears, and the thickness of the film decreases. The PS layer becomes more compact and in the end, the authors have obtained a homogeneous monolayer of PS.

In order to find the optimal conditions for selective elimination of PI by UV Ozone treatment, the degradation of PI, PS, P2VP homopolymers films (between 100 and 200 nm of thickness) under UV Ozone treatment (UVO Cleaner, Model 18 by Jelight) was studied. The maximum possible distance between the UV lamp and sample is 5 cm. The thickness of film was measured by VR before UVO treatment. Then the films were exposed to ozone at RT. After UVO treatment, each film was washed by distilled water to remove polymer residue on surface and the thickness of each film was measured by VR. The influence of UVO duration and distance between UV lamp and film (0, 2.5, and 5 cm) were studied. The thickness ratio was determined by dividing the thickness of the film after UVO treatment by the initial value.

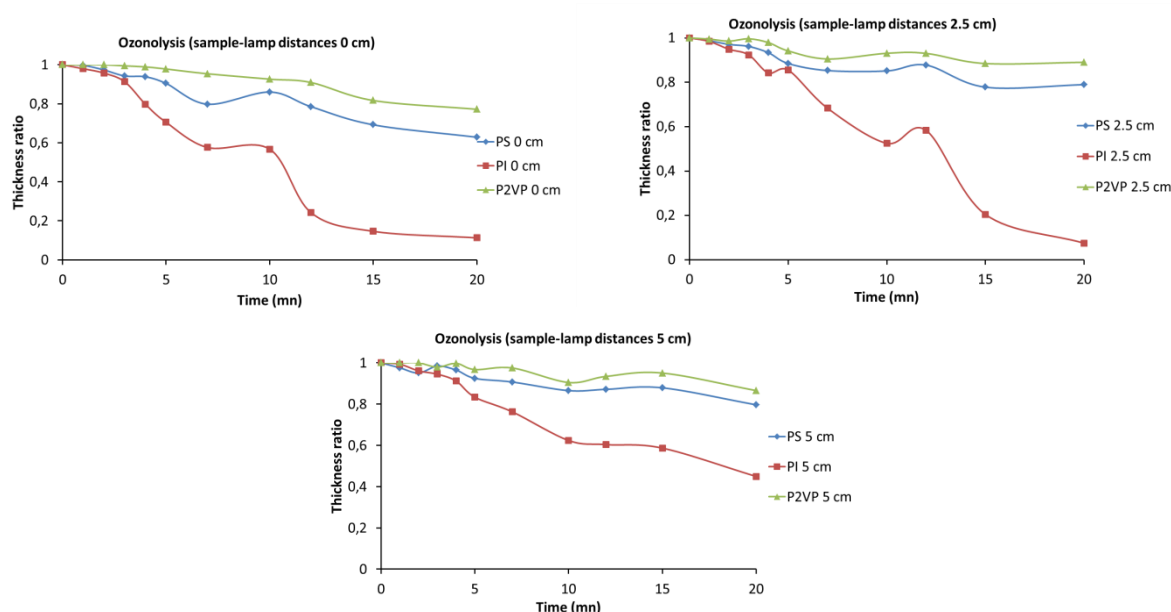


Figure 2-19. Influence of UVO duration and distance between the UV lamp and film (0, 2.5, and 5 cm) on the degradation of PI, PS and P2VP homopolymers.

As we show in Figure 2-19, UVO treatment with 0 cm distance between sample and UV lamp leads to elimination of 90% of PI after 20 minutes but removes almost 30% of PS and 20% of P2VP. Working at 5 cm distance eliminates only 10% of PS and P2VP and only 60% of PI after 20 minutes exposure. For a 2.5 cm distance, 90% of PI is removed with only 20% PS and P2VP after 20 minutes. 20 minutes exposure in one step (directly 20 minutes) at this last distance leads to PS crosslinking due to the heating of lamp. This was confirmed by the fact that it was not possible to eliminate PS film from substrate by a good solvent, such

as THF and toluene. To avoid crosslinking of PS, it was preferred to cool the sample for 30 minutes after each UVO treatment (5 minutes) and repeat several times the exposition to obtain 20 minutes in total.

IV.2.2. SELECTIVE SWELLING OF P2VP BY ETOH

As demonstrated by dissolution and swelling ratio tests, EtOH is a selective solvent of P2VP. Thus, it is an excellent solvent to reveal P2VP block in ISP system. For that purpose, the exposition of structured thin films in EtOH vapors was performed in the Teflon box for only 90 seconds at RT with a few drops of solvents. In Figure 2-20 AFM height image before and after revelation is presented. The z scale of the image shows the increase of surface roughness due to swelling of P2VP; thus the dots (clear zone of image) are P2VP domains.

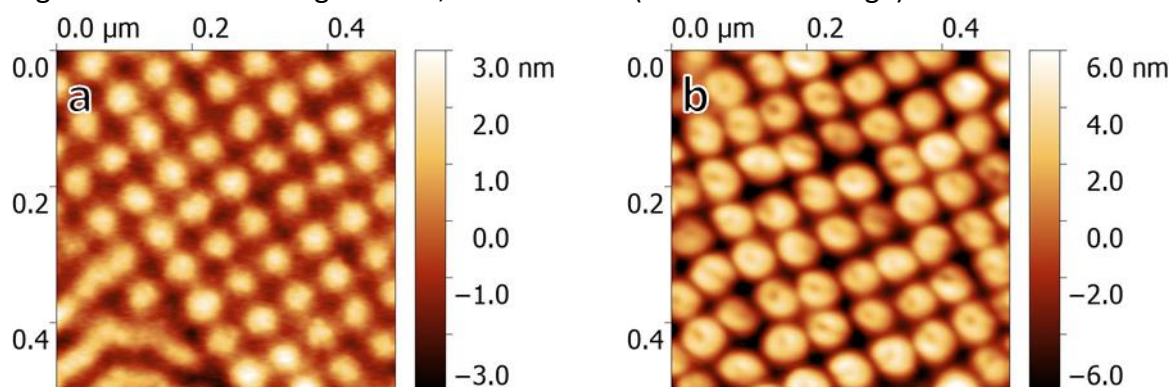


Figure 2-20. (a) Before and (b) after selective revelation of P2VP block by swelling in ethanol vapors after SVA in THF vapors of ISP α/β (60/40) blend thin films at RT.

IV.3. TEM

Transmission electron microscopy (TEM) was performed with a Philips CM20 operated at an accelerating voltage of 200 kV. Two kinds of TEM images were realized on films: top-view (perpendicular observation to the surface of the film) and section-view (side view). For that purpose, films were removed from Si/SiO₂ substrate by floatation at the surface of NaOH 1 M solution for more than 5 h. NaOH attacked the native silica layer and led to the detachment of film fragments from the substrate (Figure 2-21). The NaOH concentration in the media was then gradually reduced by the successive addition of distilled water and removal of the solution until neutralization of the media.

For top-view imaging, film fragments were then transferred onto a TEM grid and dried at RT for 1 day.

For section-view imaging, film fragments were transferred onto a plastic plate (1 x 0.5 x 0.1 cm) and dried at RT for 1 day. The plastic plate with the film fragment was covered by another plastic plate and cut by ultramicrotome. The obtained sections were transferred onto grids and further stained.

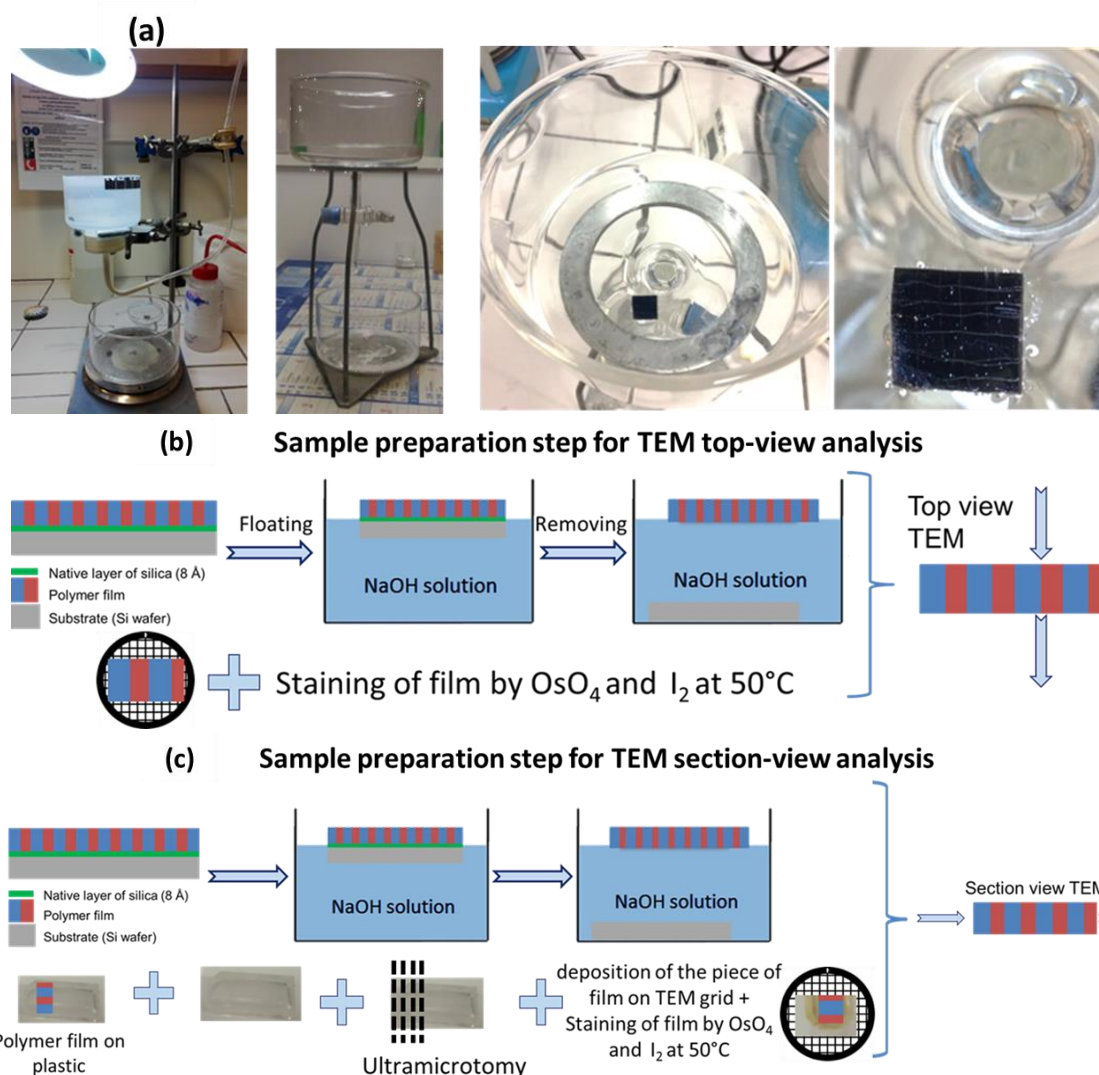


Figure 2-21. (a) Pictures of film removing set-up (profile and top-view of two types of removing chamber (in plastic and in glass)); (b) Schematic illustration of sample preparation step for TEM top-view analysis.

Characterization of the polymer by TEM is not simple because of the sensitivity of these materials to electron beam (polymers are particularly sensitive to electron beam irradiation due to their organic nature) and because of lack of contrast. The contrast between polymers is due to the difference of atomic number which is very low for polymers consisting of the same light elements (C, H, O, and others) that interact only weakly with the electron beam. So, it is important to artificially enhance the contrast of polymers by chemical staining methods (selective incorporation of heavy elements).

Two staining steps were performed on grids for selectively revealing domains and for ensuring the stability of film under electron beam: namely OsO_4 staining for PI and I_2 exposure for P2VP domains (Asai, Takano, and Matsushita 2016).

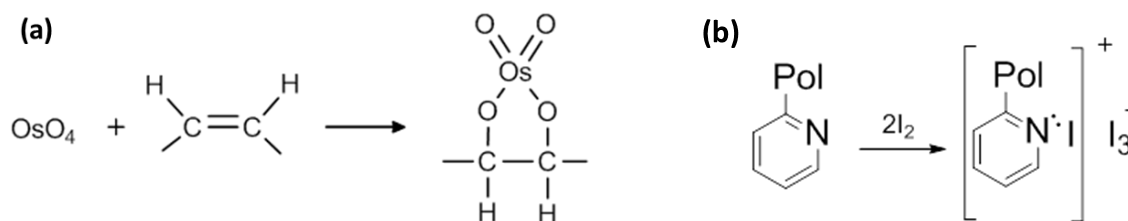


Figure 2-22. Reactions of selective staining (a) by OsO_4 and (b) by I_2 .

Staining and hardening of unsaturated synthetic rubber phases with OsO_4 has been introduced by Andrews and Stubbs (Andrews and Stubbs 1964), and then further developed by Kato (Kato 1966, 1967) to show the morphology of rubber-modified plastics and unsaturated latex particles, which flatten and aggregate upon drying. Os oxide is fixed on a double bond and stains the polymer.

Pyridinic polymers can bind chlorine, bromine, and iodine molecules, by a charge transfer complex (CTC) mechanism via the nitrogen atom of pyridine unit to form iodine polymer complex P2VP (Moulay 2013; Jandrey et al. 2007). Mechanisms of staining by OsO_4 and I_2 are depicted in Figure 2-22.

Osmium tetra oxide solution of 2% in water was provided in the ampulla (by EMS). The film was introduced in a glass jar (0.5 L) together with a small recipient containing osmium tetra oxide solution to produce the vapor of OsO_4 . Solid iodine balls were crushed to have small size in a mortar and 0.1 g of iodine was used for selective staining of P2VP. The film was put in the glass jar (0.5 L), and a small recipient with iodine was added in the same jar.

Most works describe staining in the vapor phase at RT for more than 24 hours for the bulk sample. To perform selective staining of blocks in optimal conditions, we optimized the protocol: different staining duration at various temperatures (from RT to 50 °C) was examined as a preliminary study. Finally, after observation of each step by TEM (see Annex3), OsO_4 staining during 1 h at 50 °C and I_2 staining only for 30 minutes at 50 °C were chosen as a final protocol of the staining. In Figure 2-23, the TEM images of triblock before and after staining are presented. These images confirm selective staining of the minority domain and observation of three contrasts after selective staining of PI and P2VP. However, it is important to note that there is a natural contrast for the neat ISP triblock due to the N atom of P2VP as seen in Figure 2-23.

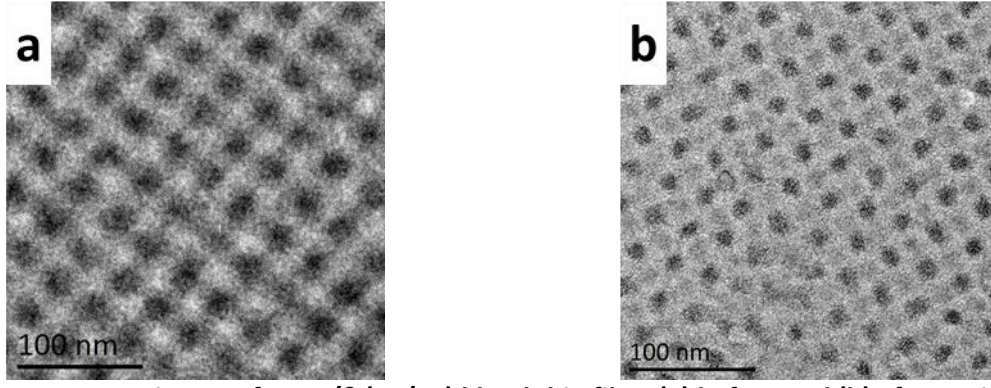


Figure 2-23. TEM image of ISP α/β (60/40) blend thin films (a) before and (b) after staining.

IV.4. GISAXS

Grazing-incidence small-angle X-ray scattering (GISAXS) is a surface-sensitive scattering technique used to study surfaces and thin layers. GISAXS analysis is very useful as a complementary method to AFM and TEM analyses since GISAXS gives information about large area (averaging over large area and information at different depth) and inner or surface information.

The geometry of the GISAXS experiment is illustrated in Figure 2-24. A monochromatic x-ray beam with the wave vector $\vec{k}_i$ is directed on a surface with a very small incident angle α_i with respect to the surface and scatters along the scattered wave vector $\vec{k}_f$. The scattered intensity, or cross section, in the direction $\vec{k}_f$ is governed by the diffusion vector (or moment transfer vector) $\vec{q} = \vec{k}_f - \vec{k}_i$, of modulus $|\vec{q}| = \frac{4\pi}{\lambda} \sin \theta$ where λ is the wavelength of incident beam and 2θ diffusion angle between $\vec{k}_i$ and $\vec{k}_f$. The z-axis is normal to the surface plane; the x-axis is the direction along the surface parallel to the beam and the y-axis perpendicular to it. The scattering wave vectors q for the three spatial directions are defined in Figure 2-24 (Renaud, Lazzari, and Leroy 2009).

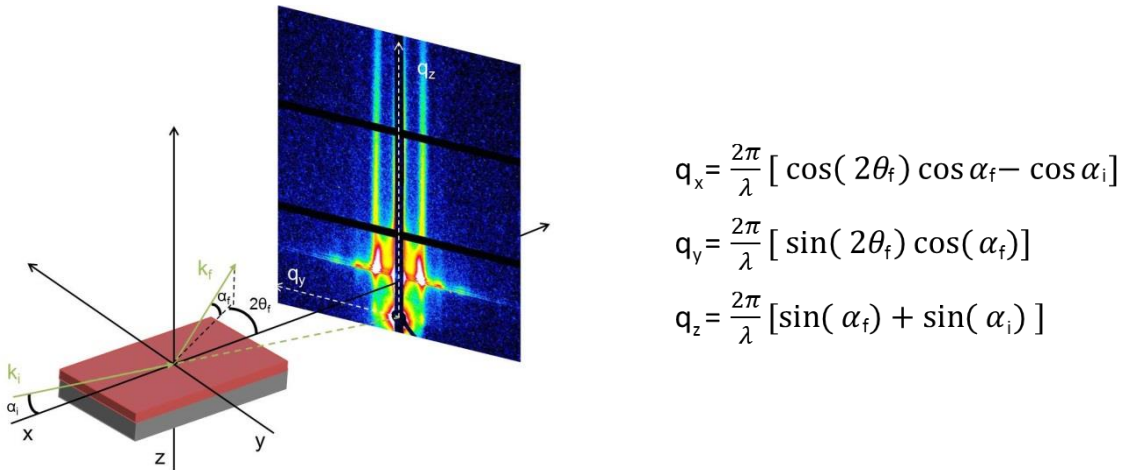


Figure 2-24. Configuration of the GISAXS experiment.

GISAXS experiments were performed on “Xeuss” Xenocs X-ray scattering setup. Two-dimensional GISAXS pattern was recorded using a high sensitivity low noise 2D detection (Pilatus 300K hybrid pixel) placed at a distance of 2329 mm from the sample, perpendicular

to the X-ray beam (parallel beam at 8042 eV) (Cummins et al. 2016). The incidence angle must be chosen between the critical angles of silicon SiO_2 (0.22°) and polymer ($\sim 0.15^\circ$). To choose this incidence angle, several tests were performed (Figure 2-25). The red arrows on image represented the cut place on q_y direction. The best contrast is obtained for 0.17° with clear observation of diffraction peaks.

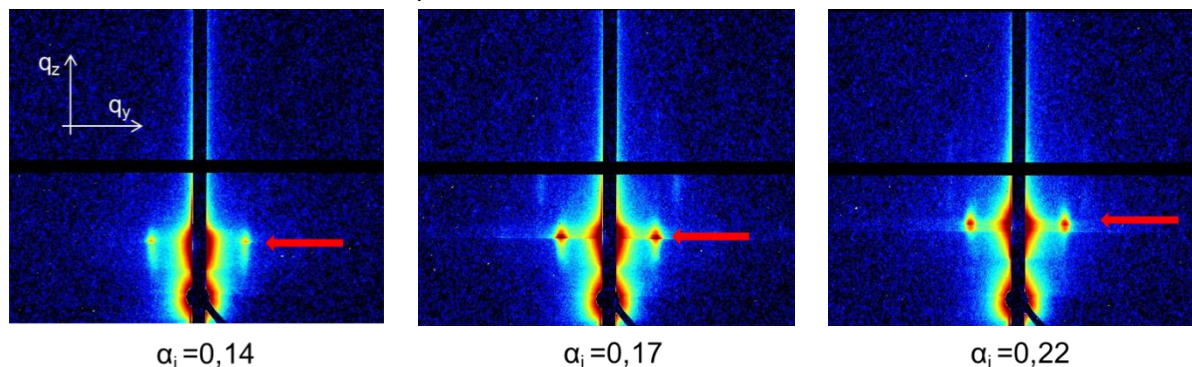


Figure 2-25. GISAXS preliminary test on polymer thin film to decide the grazing incidence angle

GISAXS is a technique based on scattering theory operated in reciprocal space. Unlike microscopy techniques, such as TEM or AFM, GISAXS could give results reflecting statistical averaged information on the sample. Thus, it is usually coupled with microscopy to provide information of the sample as we did. But we have the same contrast problem for GISAXS because of low electronic density difference between PI, PS, and P2VP (ρ_{ePI} : 0.512; ρ_{ePS} : 0.565; ρ_{eP2VP} : 0.608 mol.electron $\cdot\text{cm}^{-3}$). For this reason, GISAXS characterization performed on the UVO treated (PI selectively eliminated) or stained film (staining by I_2 for P2VP) to increase the electronic density contrast between different domains. This method, which leads to an enhanced electronic contrast between the scattering domains, has never been reported to our knowledge for the small-angle X-ray scattering study of block polymers. This could be very useful for structural characterization of BCP composed of segments with similar electronic densities.

Selective staining of P2VP by iodine was performed at 50°C for 30 minutes with 0.1g iodine. UVO treatment was performed on structured film with a 2.5 cm distance between sample and lamp for 10 minutes at RT. In Figure 2-26, GISAXS pattern of non-treated film and selectively stained film are presented. The contrast difference between the two pattern confirms the need for artificially increase of the electronic density.

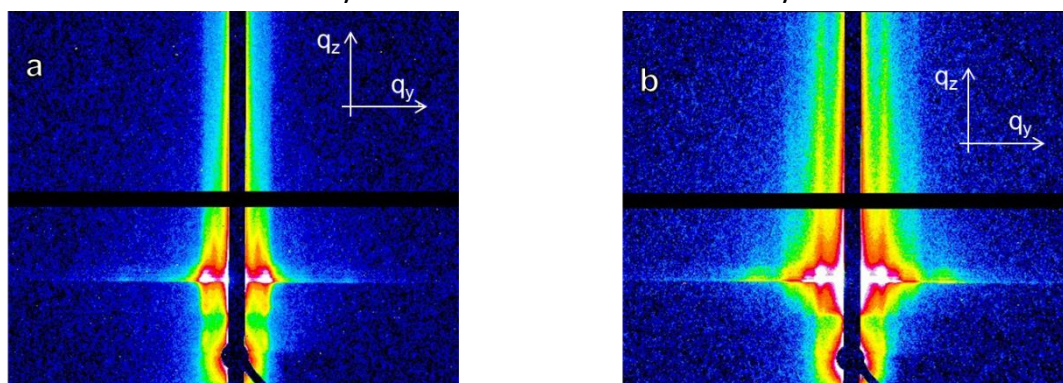


Figure 2-26. GISAXS pattern on (a) non-treated and (b) selectively stained film.

The diffraction pattern is analyzed using Fit2D for 2D morphology characterization and GIXSGUI (a Matlab-based tool for visualization and indexing of grazing incidence X-ray scattering data) for 3D structure characterization(Jiang 2015).

GISAXS pattern obtained for BCPs thin film gives the internal structure of the film. Müller-Buschbaum have showed schematic picture of 2D scattering pattern for different structures (Figure 2-27). For perpendicular pattern, only one type continuous mark must figured on GISAXS pattern in q_z direction. However, if we have some periodicity of structure in q_z direction such as parallel oriented cylinders or spheres, several marks have to appear in this direction on pattern as Figure 2-27a.

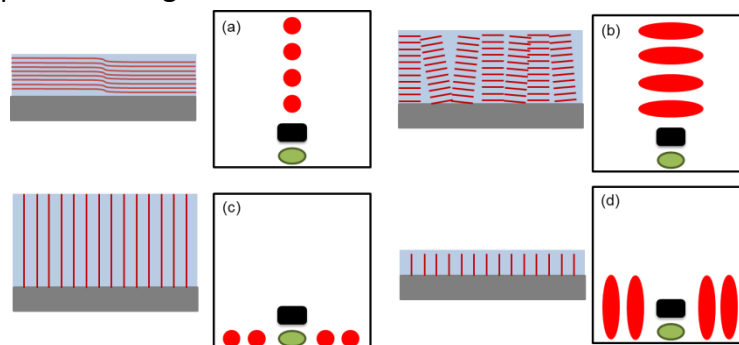


Figure 2-27. Schematic picture of the 2D scattering pattern arising from a characteristic micro-phase separation structure of a block copolymer with (a) parallel orientation, (b) perturbed parallel orientation, (c) perpendicular orientation and (d) monolayer with perpendicular orientation. On the detector the specular peak is shown with a black square, the Yoneda peak with a red circle and the characteristic scattering from the periodic nanostructure with the red features. (Müller-Buschbaum 2016)

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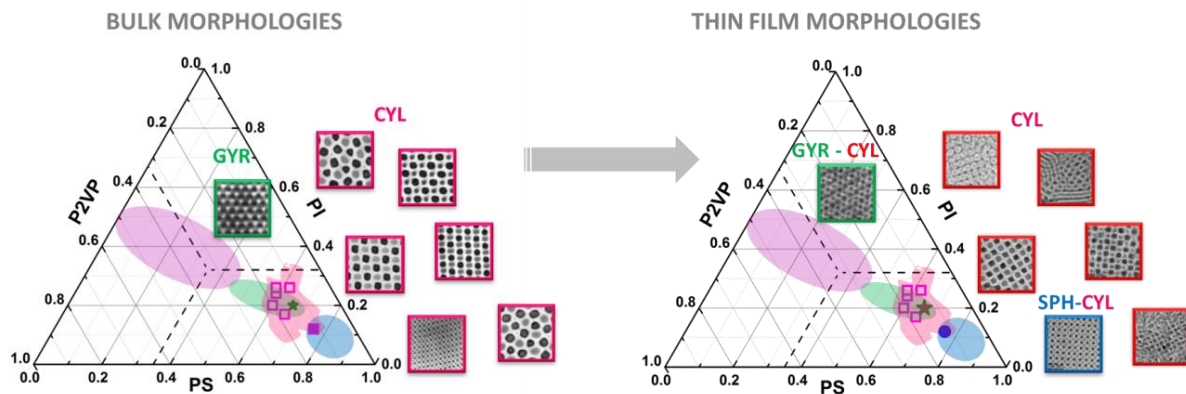
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3. RESULTS AND DISCUSSIONS



CHAPTER 3 describes main results and discussions on self-assembly of triblock copolymer. In this part, nanostructuration of thin films based on linear neat triblocks and blends of linear triblocks is presented with structuration kinetic. Each organization was characterized by AFM, TEM and GISAXS to investigate surface and internal morphology of film.

We will focus on:

PART 1: Nanostructurations of neat linear ISP triblocks (ISP19 and ISP23 which are located on boundaries on phase diagram of morphologies (Spheres - Cylinders for ISP19 and Cylinders – Continuous morphology for ISP23)) were investigated for thin film study. The goal is to compare the bulk and thin film morphology.

PART 2: Nanostructuration of blends of linear ISP triblocks (Blend of $ISP\alpha/ISP\beta$ and $ISPX/ISPY$) in thin film. Original tetragonal packing has been observed in bulk and it is interesting to compare again bulk and thin film morphology.

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I. NANOSTRUCTURATION OF NEAT LINEAR ISP TRIBLOCK IN THIN FILM

I.1. STRUCTURATION OF ISP19

ISP19 BCP has a number-average molar mass of 90 kg/mol with the same volume fraction for PI and P2VP (0.12/0.76/0.12). According to previous work performed at Nagoya University, ISP19 exhibits in bulk an ordered tetragonal packing of two kinds of cylinders (PI and P2VP within a PS matrix, see Figure 3-1a). (Mogi et al. 1994). It is interesting to note that Ahn et al. (Ahn et al. 2017) have shown that a ISP triblock with volume fraction 0.12/0.75/0.13 (almost the same composition ISP19 with similar molar mass of 84 kg/mol) exhibits instead a morphology with coexistence of spheres of PI and cylinders of P2VP (Figure 3-1b). This result is not surprising since this BCP presents a composition within transition between SPH and CYL structures. (Mogi, Kotsuji, et al. 1992; Matsushita 2000). The transition from cylinders to spheres can occur in the system.

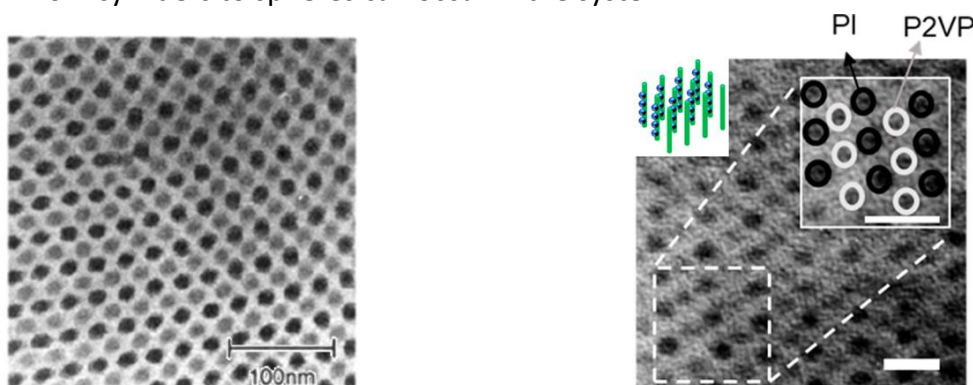


Figure 3-1. TEM image of ISP19 in bulk (a) by Mogi and (b) ISP triblock by Ahn.

I.1.1. STRUCTURATION KINETICS

Firstly we focus on SVA treatment results on ISP19 thin films in THF and toluene vapors. After spin-coating, non-organized film is obtained, as shown in Figure 3-2.

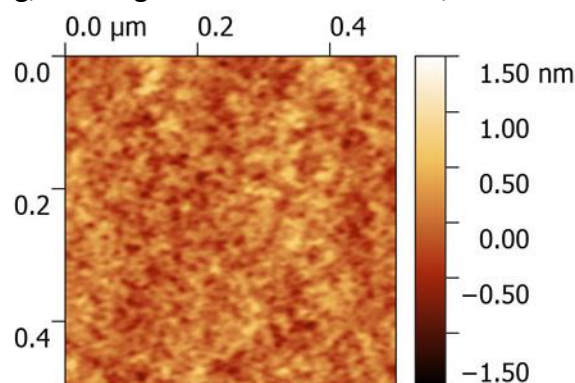


Figure 3-2. AFM height image of ISP19 thin film after spin-coating.

a. THF

SVA treatment was performed in THF vapors at 25 and 30°C. Figure 3-3 presents AFM images of ISP19 thin films after SVA treatment in THF vapors at 25°C as a function of SVA duration and distance between solvent surface and sample (1 cm, 7 cm and 13.5 cm). The films thicknesses are about 100 nm.

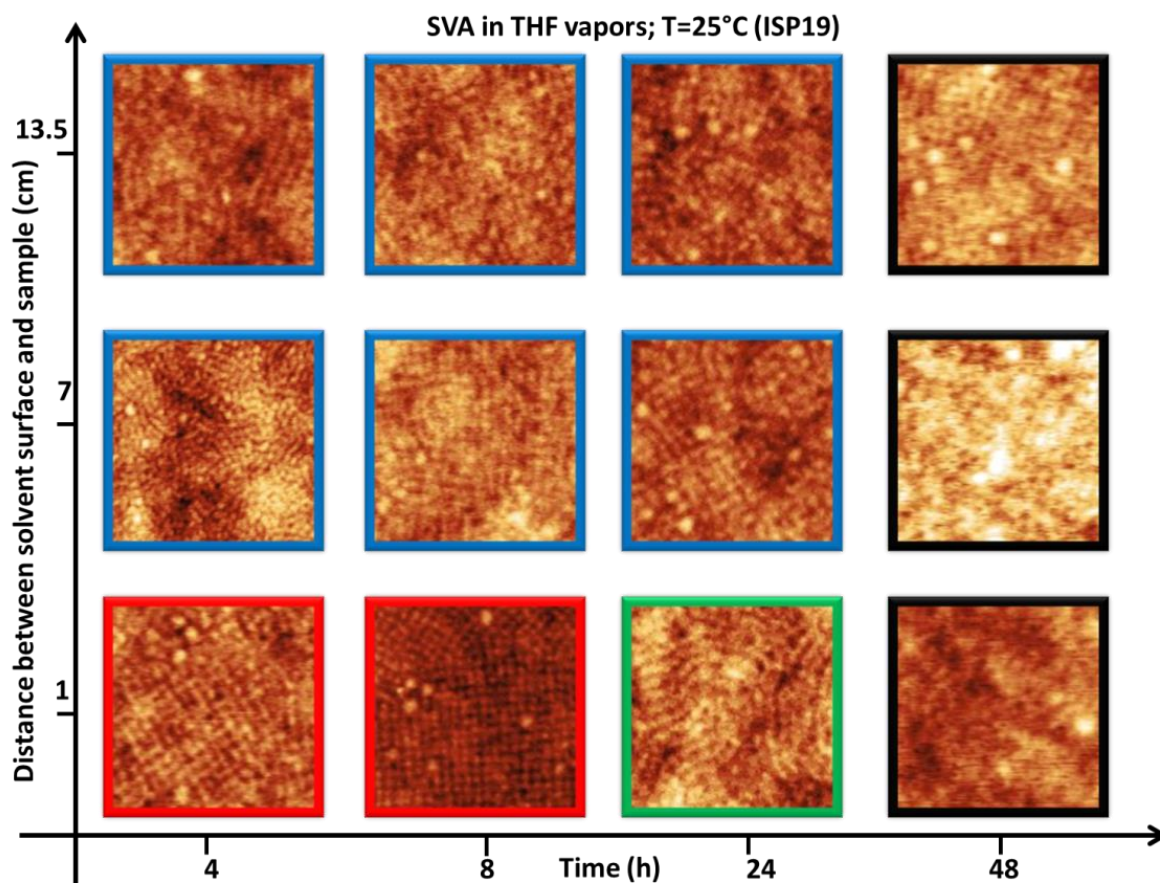


Figure 3-3. Structuration kinetics of ISP19 thin films in THF vapors at 25°C. Ordered dot pattern, line pattern, non-organized surface and dewetting are respectively represented by red, green, blue and black.

For the nearest sample (1 cm from the solvent surface), an ordered dot pattern was obtained after 4 and 8 h of annealing (in red), whereas a line pattern (green) was observed after 24 h. On the second and highest level of systems (7 and 13.5 cm), films were not fully organized after 4, 8 and 24 h SVA treatment due to the insufficient swelling ratio (blue). For all sample/solvent distances and longer annealing time (48 h) dewetting occurred (black). This graph depicts a structuration map where optimal annealing conditions are located in the bottom left, resulting from the best compromise, between swelling ratio and annealing time. Annealing in THF at 30°C was also studied but as THF is a very volatile solvent, with high vapor pressure, dewetting of films occurs (not shown here) after only a few hours for all conditions.

b. Toluene

SVA treatment in toluene vapors was performed at 25°C and 30°C on different levels in the annealing chamber. Films thicknesses were about 100 nm. No ordered structuration was observed during SVA in toluene at 25°C and after 12 h, the dewetting of the films occurred. SVA treatment was also studied at 30 °C, but in this case, the dewetting of the films was only observed after 3h for the first level due to the high swelling ratio. In contrast, on the second and highest level of systems, there was no dewetting phenomenon but the films were not organized.

c. Partial conclusion

In conclusion, ordered nanostructuration was obtained after SVA in THF vapors. The nanostructuration difficulty in toluene case can be explained by the lower swelling rate of polymers in this solvent ($P_{\text{toluene}} < P_{\text{THF}}$). Moreover, toluene is a selective solvent for PI and PS blocks, as shown in the preliminary studies part, and it may influence structuration (direct formation of the wetting layer). In the following section, the different observed structures of ISP19 will be investigated by AFM, GISAXS, and TEM.

I.1.2. MODERATE ANNEALING TIME

a. AFM characterization

After THF vapor exposure at 25 °C during 8 h on the first level of SVA chamber (the smallest solvent to sample distance (1 cm)), AFM height image displays square packed features with a characteristic center-to-center distance of 33 nm (Figure 3-4).

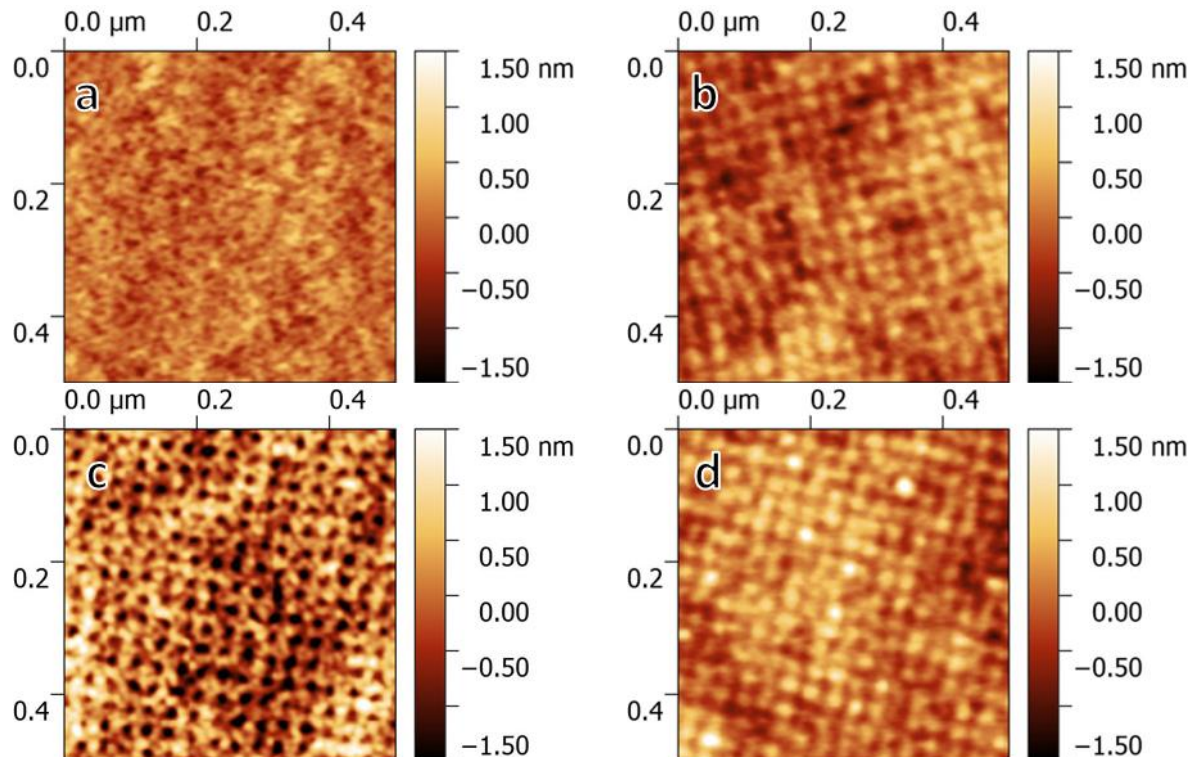


Figure 3-4. Height AFM of ISP19 thin films (film thickness is c.a. 100 nm) after: (a) spin-coating, (b) solvent annealing, (c) solvent annealing and UVO (d) solvent annealing and swelling in ethanol. z scale: 3 nm.

After UVO to selectively eliminate and identify the PI domains, a distinct square packed pattern of holes was observed, suggesting that the parent PI domains (diameter estimated to 20 nm) exhibited a square arrayed pattern. From AFM image analysis of samples after UVO, a center-to-center distance of 33 nm between the PI domains was determined. In a similar way, exposure to ethanol vapor resulted in selective swelling of P2VP domains, highlighting their square arrangement on the surface, as shown in Figure 3-4 (center-to-center distance is 33 nm). The presence at the film surface of square arrayed PI and P2VP patterns could result from tetragonally packed cylinders of PI and P2VP being oriented perpendicularly to the surface (as in the bulk structure of Mogi et al. 1994). However, this can also be a signature of a spherical structure similar to the morphology described by Ahn (Ahn et al. 2017).

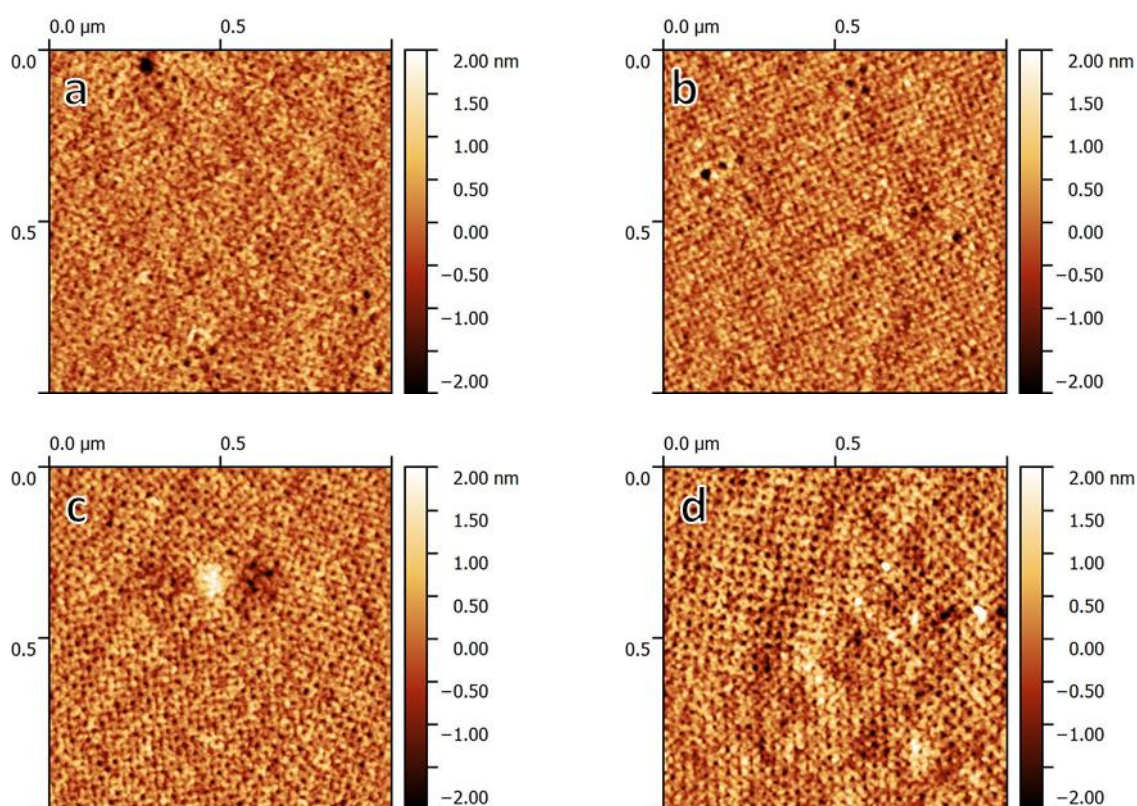


Figure 3-5. AFM height images of UVO treated ISP film (a) after 5 minutes (90 nm thickness); (b) 10 minutes (5*2) (70 nm); (c) 15 minutes (5*3) (60 nm); (d) 20 minutes (5*4) UVO treatment (45 nm) on the same sample.

Homogeneity of film nanostructuration was investigated in bulk (inside film) by exposing the same film to UVO treatment several times during 5 minutes and observing each time the resulting film surface. Each UVO treatment allowed to eliminate a layer with a thickness between 10 and 20 nm, which also means the elimination of 10-20 % of PS and P2VP domains (not only PI domain). After each exposition, AFM images displayed fourfold symmetry and confirmed that the ordered structuration continued from the surface to the bottom of the film (Figure 3-5).

b. TEM characterization

In order to get complementary information on ISP19 structuration in thin films, TEM top-view observation (perpendicularly to film surface) was firstly carried out. Figure 3-6 compares TEM images after staining of PI by OsO_4 , P2VP by I_2 , and staining of PI and P2VP altogether by OsO_4 and I_2 .

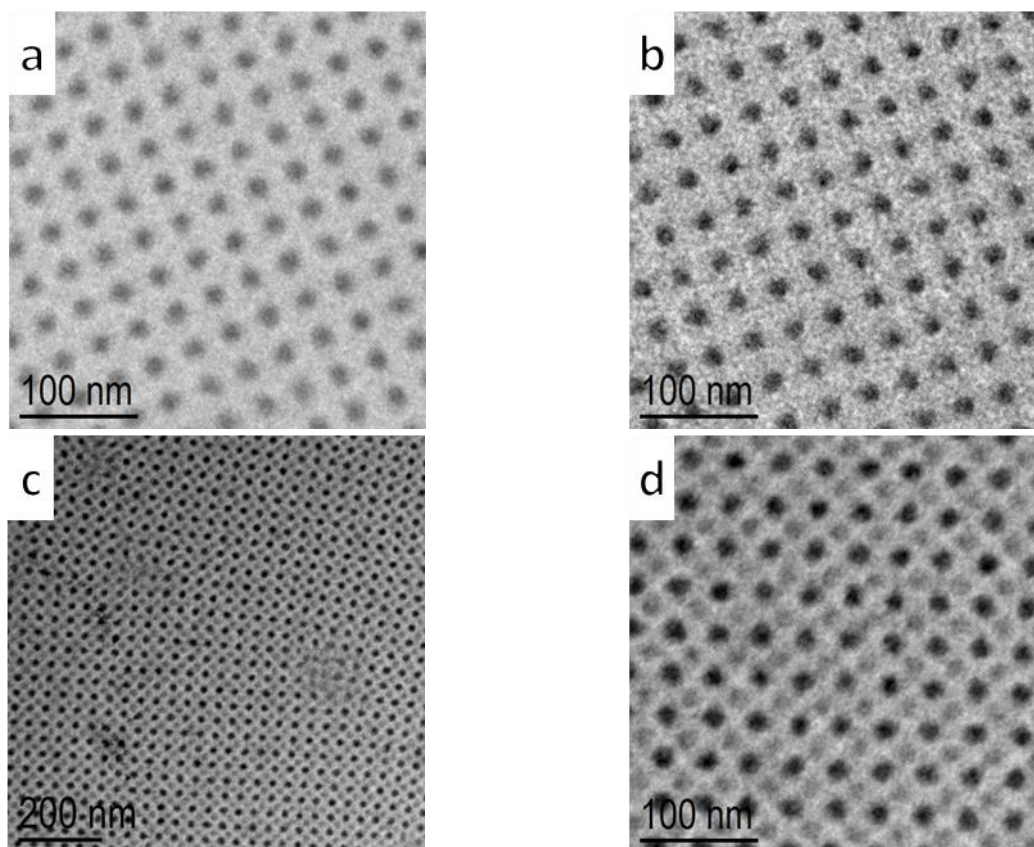


Figure 3-6. TEM images solvent annealed thin films of ISP19 after: (a) staining by OsO_4 , (b) staining by I_2 , and (c) and (d) staining by OsO_4 and I_2 . Black, white, and gray domains represent PI, PS, and P2VP block, respectively in (c) and (d).

After staining of PI, (Figure 3-6a), PI domains appear in the dark while P2VP and PS in light grey. PI domains formed square packed structure. After staining of P2VP, (Figure 3-6b), P2VP domains appear in the dark while P2VP and PS in light grey. P2VP domains are also arranged on a square lattice. After staining of PI and P2VP (Figure 3-6c and 6d), two kinds of dark dots (PI and P2VP) in the white unstained matrix (PS) are observed. A difference of gray level between PI and P2VP domains can be obtained by optimizing the staining duration. A square packing of both PI and P2VP domains was observed with one polymer domains in the center of the square constituted by the other polymer domains. These minority domains form circular domains. As the TEM image is formed by the projection of 3D morphology along the z-direction, these features could either result from spheres or cylinders oriented perpendicularly to the film surface (if cylinders are not oriented perpendicularly to substrate inside the film, TEM image should not give clear circular domains for PI or P2VP but

elongated domains). Successive staining confirmed that ISP19 triblock terpolymer self-assembled in a square packing with two kinds of domains with CMC interface. From the TEM images, a center-to-center distance of 34 nm was measured and for PI and P2VP domains, diameters was estimated to 20 nm, which was in good agreement with the distance previously found in AFM.

AFM and TEM top-view images cannot distinguish between perpendicular cylinders and spherical structures. Consequently, we performed TEM section-view imaging which can give more detailed information about internal morphology of film.

Figure 3-7 displays TEM section-view images. A dark layer on film/air interface was observed on the section-view image after PI staining indicating formation of PI wetting layer (5-10 nm thick). A wetting layer of P2VP was also found at film/substrate interface after I_2 staining. The presence of these wetting layers can be explained by difference of surface energy of PI, PS, and P2VP phases (γ_I : 32 mJ/m²; γ_S : 40 mJ/m²; γ_P : 47 mJ/m²) (Brandrup, Immergut, and Grulke 1999; Haryono and Binder 2006) favoring presence of PI, compared to PS and P2VP, at film/air interface. In contrast, P2VP is more selective than PS and PI to substrate (γ_{SI} : 45.8 mJ/m² determined using contact angles measurement of different liquids).

Section-view images indicate that a clear cylindrical morphology (as shown in bulk by Mogi (Mogi et al. 1994)), with a perpendicular orientation was not observed for thin film. Instead, a mixture of dots and lines was observed after PI and P2VP staining (see Figure 3-7a or c). For some samples, row of dark dots was clearly observed on images (like in Figure 3-7b after selective staining of P2VP domain). These section-views confirm that the internal morphology of ISP19 is more complex than the simple picture suggested by TEM top-view images. It is not easy to conclude on the actual morphology formed in this case unambiguously. However, these observations indicate that spheres are formed in the film, which is consistent with ISP19 position in the phase diagram, at the boundary between spheres and cylinders. Cylinders to spheres transition may be then facilitated by thin film configuration (limited amount of mater, strong interface effect). Depending on reorganization advancement, the system may be trapped in a more or less advanced stage between cylinders and spheres (including undulating cylinders that are known to be transition state (Chang Yeol Ryu et al. 1999)). It also resembles the type of morphology described by Ahn in bulk (Ahn et al. 2017) in which spheres of PI coexist with cylinders of P2VP. However, in our case, Figure 3-7b suggests the formation of P2VP spheres. These results show the limit of the characterization methods performed in this work. Electronic tomography analysis could be used to clarify the morphology and will be undertaken.

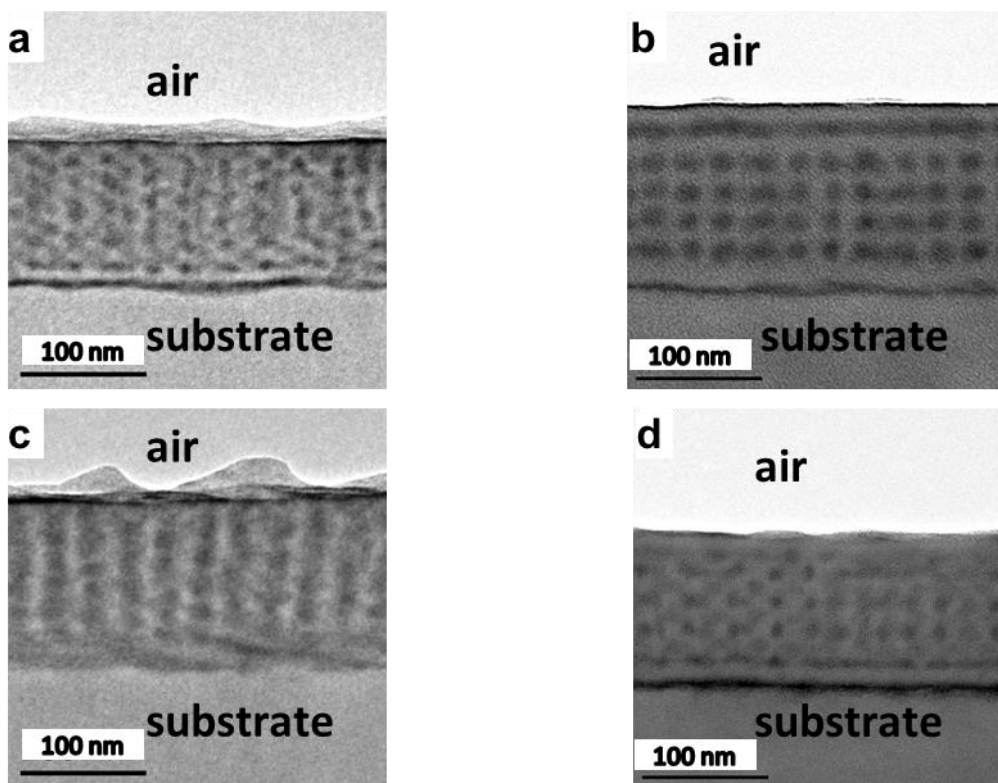


Figure 3-7. TEM Section-view images of dot pattern after: (a) staining by OsO_4 ; (b) staining by I_2 ; (c) and (d) staining by OsO_4 and I_2 .

c. GISAXS analysis

Figure 3-8 shows a typical GISAXS profile obtained for a nanostructured thin film and staining of P2VP. Three diffraction peaks are observed at $q_0 = 0.185 \text{ nm}^{-1}$, $q_1 = 0.262 \text{ nm}^{-1}$ and $q_2 = 0.368 \text{ nm}^{-1}$. Ratios of the position of these experimental diffraction peaks $q_1/q_0 = 1.41$ ($\sqrt{2}$) and $q_2/q_0 = 2$ ($\sqrt{4}$) are in good agreement with a square packing. From the q_0 value, we calculated a center-to-center distance spacing of 34 nm, which agrees quite well with AFM and TEM results. GISAXS pattern after staining showed the positions expected for (11), (20), diffraction peaks calculated from the position of (10) peak at $q_0 = 0.185 \text{ nm}^{-1}$. This fits quite well with the experimental positions. It could be highlighted that the analyzed thin film is only 100 nm thick, and for this reason, we are mostly interested in in-plane (q_y direction) peaks and especially, plane perpendicularly oriented to the surface. The red arrow shows cut place on the pattern.

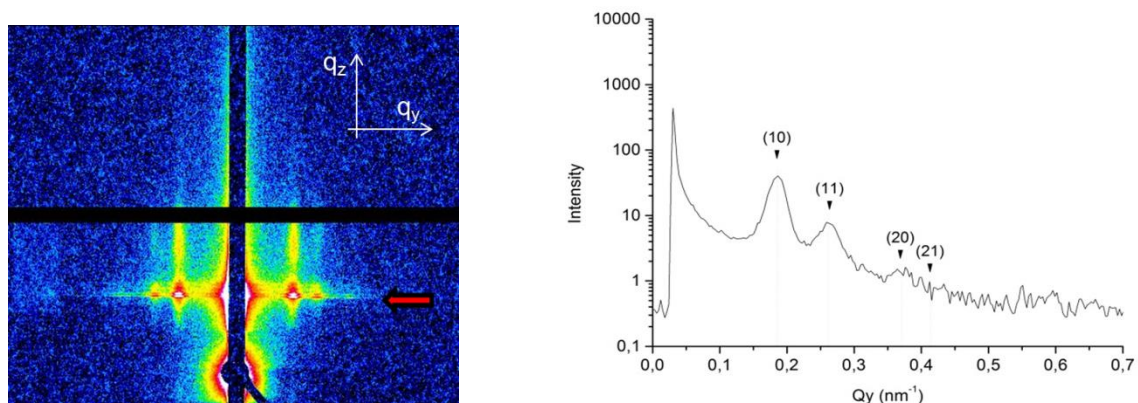


Figure 3-8. GISAXS pattern and corresponding in-plane profile of ordered ISP19 thin film after staining by I_2 . Profile position is marked by an arrow on the pattern.

As we mentioned in CHAPTER 2 (GISAXS part), GISAXS pattern also contains an indication of internal morphology. On this pattern, it should be noted that scattering marks show oscillation in the q_z direction and consist of two separate parts. Müller-Buschbaum has demonstrated that for the perpendicular pattern (perpendicular cylinders), only one type of continuous mark must be figured on GISAXS pattern in q_z direction (as we observed for other morphologies). Structures with some periodicity in q_z direction, such as parallel oriented cylinders or spheres can lead to marks in this direction on GISAXS pattern. In short, GISAXS results confirm a square packing morphology that is not homogenous inside the film (undulating cylinders and/or spheres).

d. Partial Conclusion

In summary, the nanostructuration obtained in thin film is not similar to the bulk morphology developed by Mogi and the CYL-SPH transition was observed under the thin film effect. This transition may be facilitated by the position of ISP19 on the phase diagram.

I.1.3. LONGER ANNEALING TIME

a. AFM Characterization

After 24h SVA in THF vapors at 25°C, AFM height image displays lines with a periodic distance of 25 nm, but a clear observation of three phases (PI, PS, and P2VP) was not straightforward (Figure 3-9). UVO treatment was performed on films for selective elimination of PI. Lines (with holes) were observed on the surface. From AFM image analysis of extracted samples, we could not conclude if this structure is cylindrical morphology or lamellar structure.

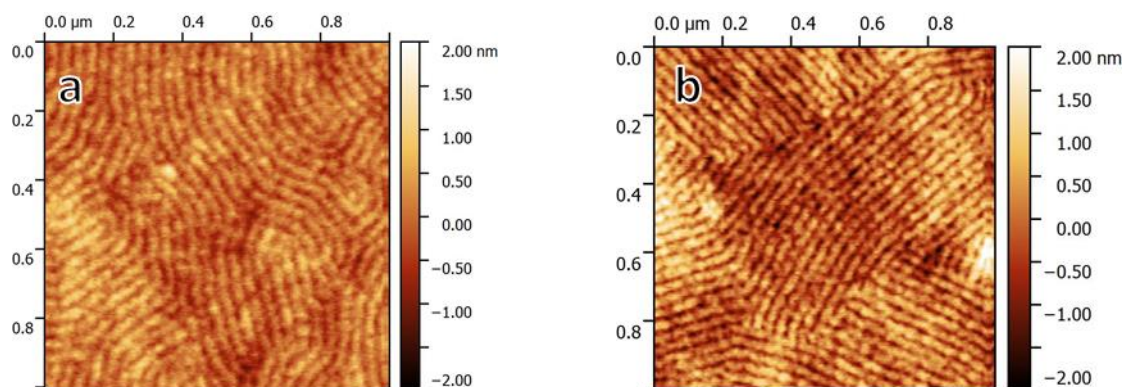


Figure 3-9. AFM height images of ISP19 thin films after (a) long SVA treatment in THF vapors and (b) UVO treatment.

Unlike bulk morphology, in thin films, the interactions between polymers and interfaces play an important role under confinement effect and as we mention, surface energy difference between the three blocks leads to reorganize the three domains towards more thermodynamically stable state (parallel orientation) after a long SVA in regards to preference with substrate surface or air.

b. TEM Characterization

Square packed cylinders oriented parallel to substrate (Figure 3-10) were confirmed by TEM top- and section-view images. Lines were observed on TEM top-view images. Selective staining of PI and P2VP domains confirms lines of minor domains.

TEM section-view images display square packed dots inside the film. After staining, dots of PI and P2VP domains were observed. It can be assumed that the line morphology was formed by the tetragonally packed of PI and P2VP cylinders oriented parallel to the substrate. In side-view, parallel cylinders are seen like dots structure inside film because of the parallel direction of the cylinder to the substrate. A wetting layer was observed on two interfaces.

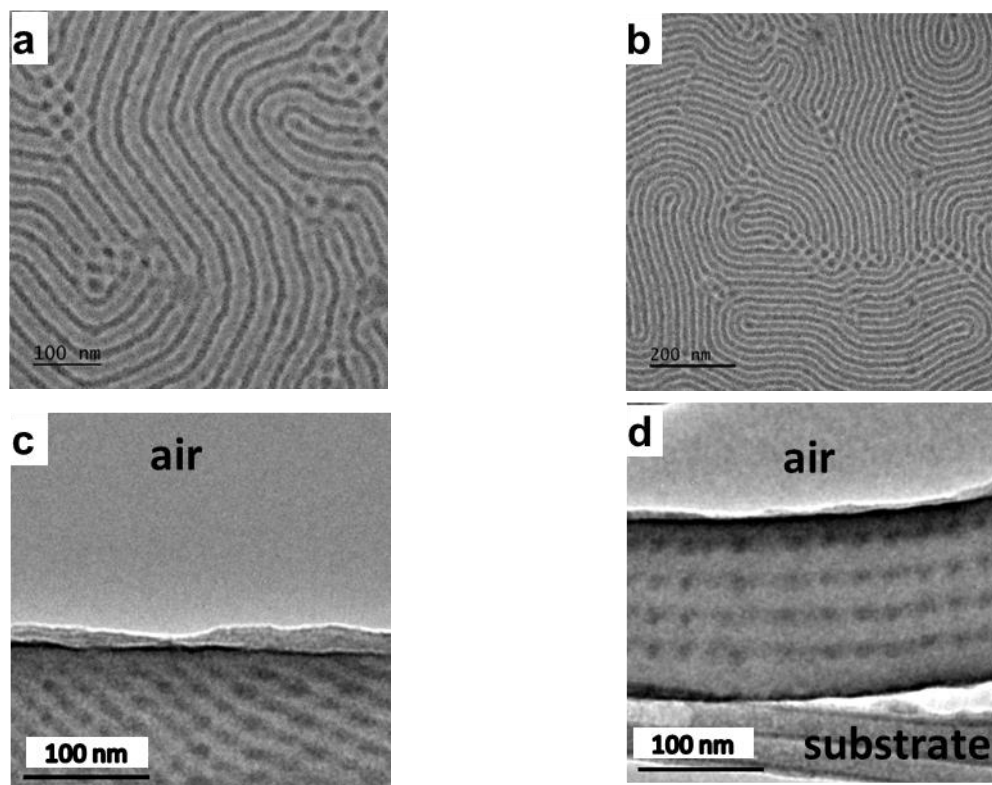


Figure 3-10. TEM top-view (a and b) and section view (c and d) images of parallel morphology.

1.1.4. CONCLUSION

Nanostructuration of ISP19 in thin film is more complex than the simple morphology described by Mogi for bulk organization. After a moderate SVA in THF, the square arrayed dots were observed on AFM height, and TEM top-view images and finger pattern morphology (elongated features) was depicted on the surface for longer SVA. Coupling of different characterization methods, namely AFM, TEM and GISAXS allows to study the surface and internal structure of the thin film. Especially, TEM section-view results highlighted the presence of the spheres inside the film after moderate SVA and of the cylinders after longer SVA in THF. TEM section-view images also highlighted the presence of wetting layers of PI at the interface of film/air and of P2VP at the interface of film/substrate. GISAXS results were in good agreement with other results, and it confirmed the square packed morphology for shorter SVA treatment. Moreover, GISAXS pattern showed marks of the presence of periodic structure inside the film (q_z direction), suggesting the presence of spherical morphology.

Taken together, all results confirm that ISP19 gives in thin films an ordered square packed PI and P2VP domains with CMC interface after short SVA in THF and tetragonal packed cylinders oriented parallel to the surface after long SVA in THF. This has never been observed in bulk.

I.2. STRUCTURATION OF ISP23

ISP23 block polymer is an asymmetric triblock having a number-average molar mass of 91 kg/mol with a fraction of PI, PS, and P2VP of (0.20/0.66/0.14) which gives Q_{214} gyroid structure in bulk (Mogi, Mori, et al. 1992; Suzuki, Seki, and Matsushita 2000). It is known that depending on position in the ternary phase diagram, two types of gyroid have been observed following composition for linear triblocks (Figure 3-11). The first corresponds to the same space group Q_{230} as for diblocks (Hajduk et al. 1994) and presents two interpenetrating networks of core-shell cylinders with 3-fold connectors. This has been typically observed for asymmetric compositions such as 0.40/0.41/0.19 for PI-*b*-PS-*b*-PDMS (Shelfelbine et al. 1999), where the matrix is PI and core-shell is constituted of PDMS as a core and PS as a shell. For more symmetric compositions, alternating gyroid (G_A) with space group $I4_132$ (also denoted Q_{214}) is generally formed with two different interpenetrating networks of each end block in a matrix of the middle block. Such morphology has been observed in bulk for PI-*b*-PS-*b*-PEO (Epps et al. 2004), PI-*b*-PS-*b*-P2VP (Suzuki, Seki, and Matsushita 2000) and for neat PI-*b*-PS-*b*-PMMA and blends of copolymer/ associated homopolymers (Tureau et al. 2010; Tureau and Epps 2009) and in thin films for PI-*b*-PS-*b*-PPC (Cowman et al. 2015).

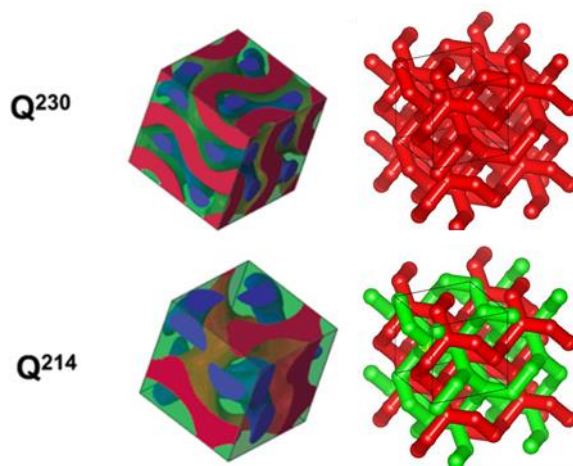


Figure 3-11. 3-D morphologies (Epps et al. 2004) and network lattice structures obtained by Vesta.

For the ISP selected in this work (ISP23), it should be noted that volume fraction of center block polystyrene (0.66) is the highest one for this ISP triblock series (equal fraction of end-block polymers) leading to tricontinuous morphology (G_A) (Mogi, Mori, et al. 1992; Matsushita 2000) (slightly higher PS content would lead to a tetragonal arrangement of cylinders). Similarly to ISP19, which was located on the boundary between cylinders and spheres in the phase diagram, ISP23 may exhibit the same type of order-to-order transition (gyroid to cylinders) amplified by thin film configuration. This motivated the selection of ISP23 for this thin film study.

I.2.1. STRUCTURATION KINETICS

As we showed for ISP19, thin film after spin coating exhibits nonperiodic topography (Figure 3-12). Now, we focus on the result of SVA treatment on ISP23 thin films in THF and toluene vapors.

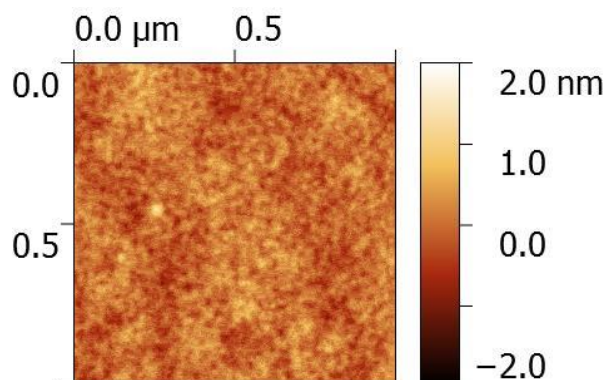


Figure 3-12. AFM height image of ISP23 thin film after spin coating.

a. THF

As we mention for ISP19, after SVA in THF at 30°C, film dewetting occurred directly, and nanostructure could not be obtained. SVA treatment was performed in THF vapors at 25°C in the annealing chamber with a variable sample/solvent distance (Figure 3-13). The films thicknesses are about 100 nm.

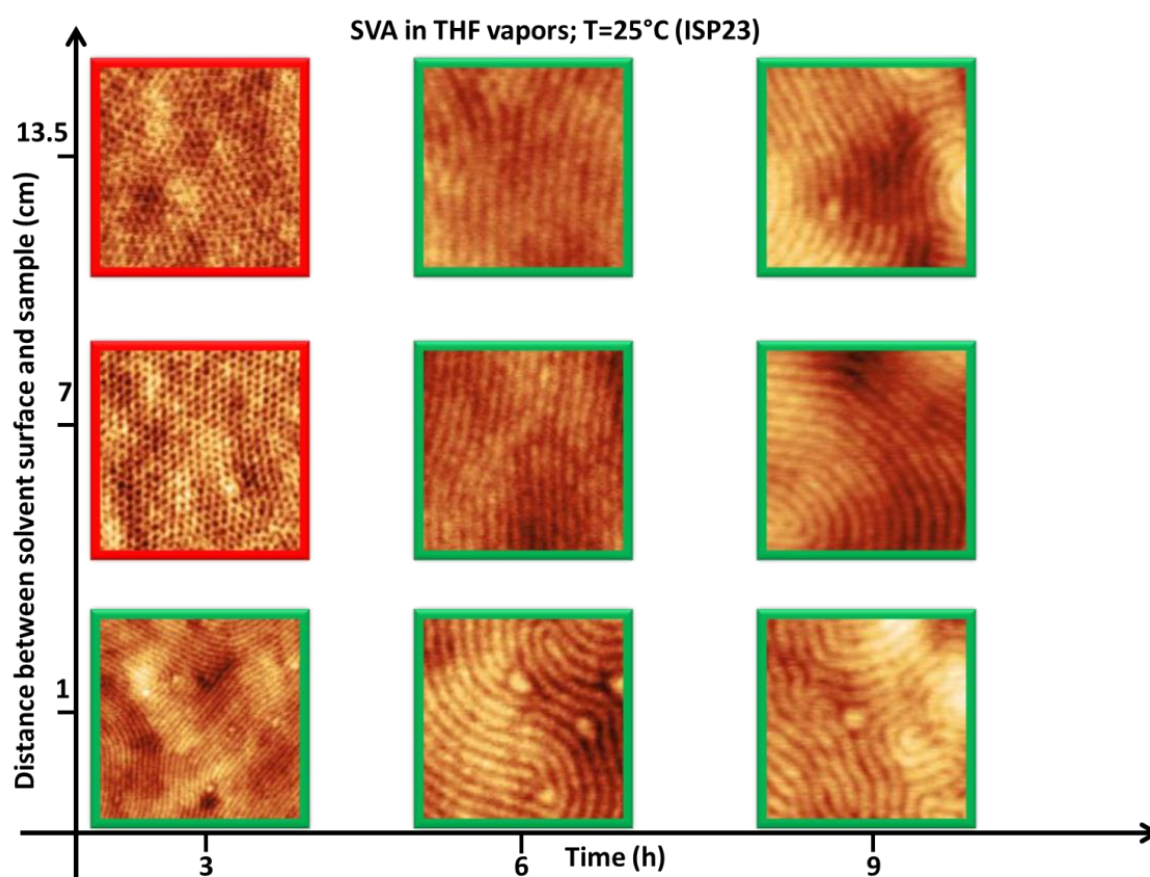


Figure 3-13. Structuration kinetics of ISP23 thin films in THF vapors at 25°C.

For the nearest sample (1 cm from the solvent surface) a line pattern was obtained after 3 h, 6 h and 9 h of SVA (green). On the second and highest level of system (7 and 13.5 cm), films were fully organized after 3 h (red), whereas a line structure (green) was observed after 6 h and 9 h SVA. For all sample/solvent distance, dewetting of films did not occur. Optimal annealing conditions are located in the top left resulting from the best compromise between the swelling ratios and annealing time. In conclusion, structuration of ISP23 in THF vapors was performed at 25°C for 3 h on the second and highest level of system (biggest solvent to sample distance).

b. TOLUENE

SVA treatment in toluene vapors was only tested at 25°C (SVA treatment at 30°C with toluene was not performed for ISP23 (ISP19 thin film with a similar molecular mass dewets at 30°C)). The thicknesses of the films were about 100 nm. Ordered structuration was not observed during SVA in toluene at 25 °C and there was no dewetting of films during 9 h.

In conclusion, nanostructured ISP23 thin films were obtained only after SVA in THF vapors. Characterization by AFM, GISAXS and TEM of the nanostructures will be presented in following part.

I.2.2. MODERATE ANNEALING TIME

a. TEM Characterization

TEM observation (top-view and cross-sectional view) was carried out after staining. After I₂ exposure (selective staining of P2VP domains), on top-view TEM image (Figure 3-14a) different gray tones were obtained. It can be interpreted as superposition of three-dimensional P2VP domains having different orientations inside the film. After osmium staining, the same type of TEM images were obtained as the I₂ staining, although the image was even more complex since a natural contrast is obtained for P2VP without staining (PI and P2VP are observed in the image). Successive staining led to a combination of the two previous images with rows of black dots alternating with rows of gray dots with a gray dot in the middle of the rectangle defined by 4 black dots.

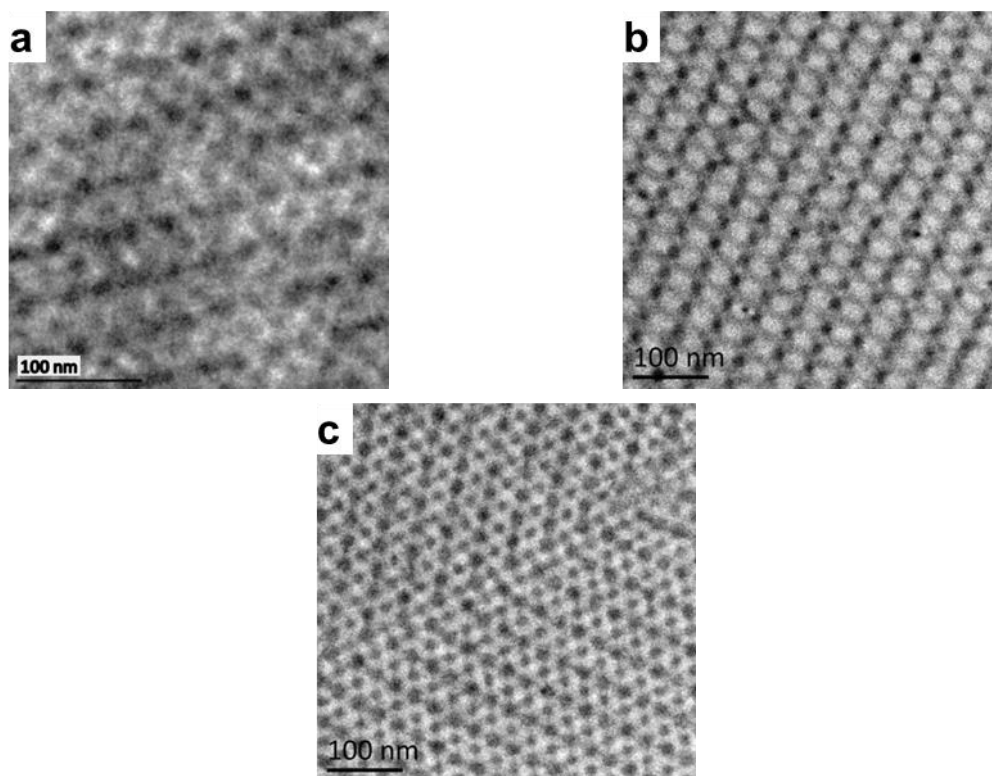


Figure 3-14. TEM top view images of ISP23 solvent annealed thin films after: (a) selective staining by OsO_4 , (b) selective staining by I_2 , and (c) selective staining by OsO_4 and I_2 .

Assuming a gyroid morphology (similar to the bulk) was formed in film, we found that an alternating gyroid G_A morphology consisting of two independent networks of PI and P2VP in matrix of PS, having a (011) plane parallel to the surface is in good agreement with the TEM top-view images.

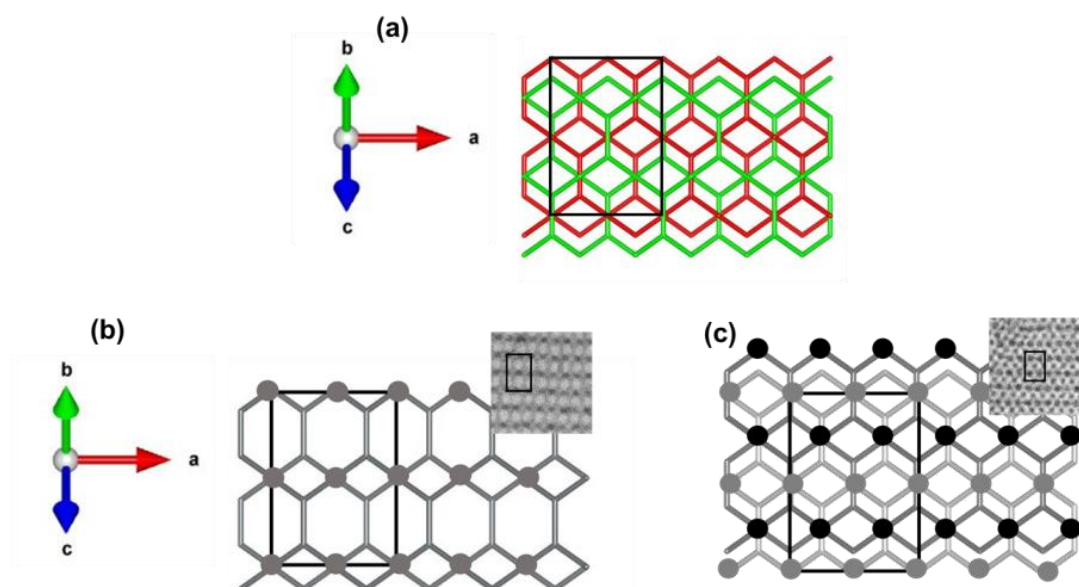


Figure 3-15. Skeletal model of an alternating gyroid G_A thin film with a (011) plane parallel to the surface: (a) top view (along the [011] direction) (PI in green and P2VP in red). Theoretical TEM top-view image deduced from the skeletal model: (b) considering a selective staining of the PI and (c) after successive staining of PI and P2VP.

Thin film with an alternating gyroid G_A structure exhibiting a (011) plane parallel to the surface is represented using Vesta software. Figure 3-15a displays the top view along the [011] direction. Figure 3-15b displays the theoretical picture of the top-view TEM image, in case of selective staining of one domain (e.g. P2VP). Vertical stained connectors will display darker dots whereas connectors in any other directions will form lighter lines. In addition, any non-stained domains will appear white (i.e. PI and PS if P2VP is selectively stained). It can be seen that this representation matches quite well with the top-view TEM images. The same considerations can be done for a successive staining of PI and P2VP domains where rows of black dots alternate with rows of gray dots (Figure 3-15c).

From distance measured on top-view TEM images (Figure 3-14), one can extract lattice parameter of the unit cell of the structure. As depicted in Figure 3-15b, the distance measured between 2 successive dots (31 nm) directly corresponds to half of lattice parameter (i.e. $a/2$) whereas the distance measured between two rows of dots (44 nm) corresponds to half of the diagonal distance of the cell (i.e. $(a\sqrt{2})/2$) assuming a cubic lattice where $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$.

Cross-section views stained by OsO_4 and by OsO_4 and I_2 are presented in Figure 3-16 and confirmed formation of a periodic structure having a 3D structure since a continuous 2D structure is also observed in direction perpendicular to surface. TEM section-view exhibited four rows of black marks as an indication of 4 stacks containing preferentially PI. Distances between these lines are between 25 and 30 nm.

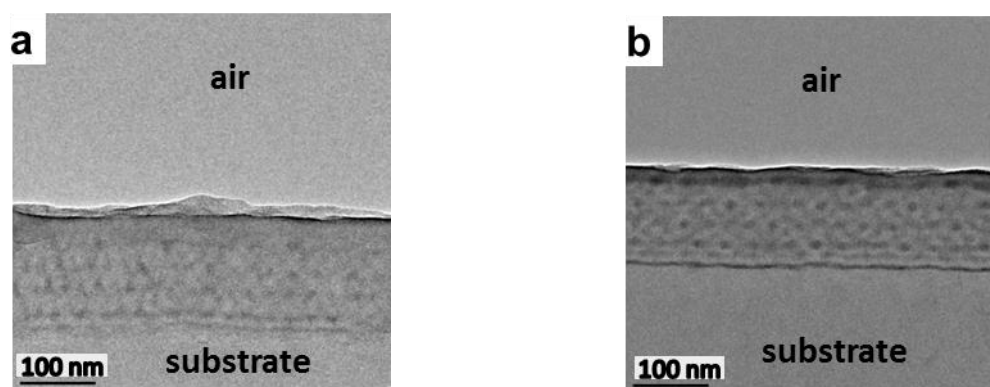


Figure 3-16. TEM section view images of ISP23 solvent annealed thin films after: (a) selective staining by OsO_4 , (b) selective staining by OsO_4 and I_2 .

This result was compared to the distance extracted from top-view TEM images. As the cut could be performed in any directions perpendicular to film surface, the corresponding section images can show any plane perpendicular to (011) plane (see Figure 3-17 for various examples). All these planes show stacks of layers containing mainly PI (or P2VP) in a matrix of PS that should be separated (according to geometry in cubic lattice) by a distance of $a\sqrt{2}/2$, i.e. 44 nm. Instead, we measured values ranging around 25 nm suggesting a contraction along the [011] direction (perpendicularly to the film substrate). Combining the characteristic average distances measured in top/cross-section view images and using simple geometric considerations, we found the following parameters of the unit cell; $a = 62$ nm, $b = c = 50$ nm $\alpha = 120^\circ$ $\beta = \gamma = 90^\circ$. This contraction of the lattice along the

direction perpendicular to the substrate (here [011] direction) can be explained by shrinkage occurring with film drying during solvent evaporation, which was directly associated with thin film configuration and observed by Dolan et al. 2018.

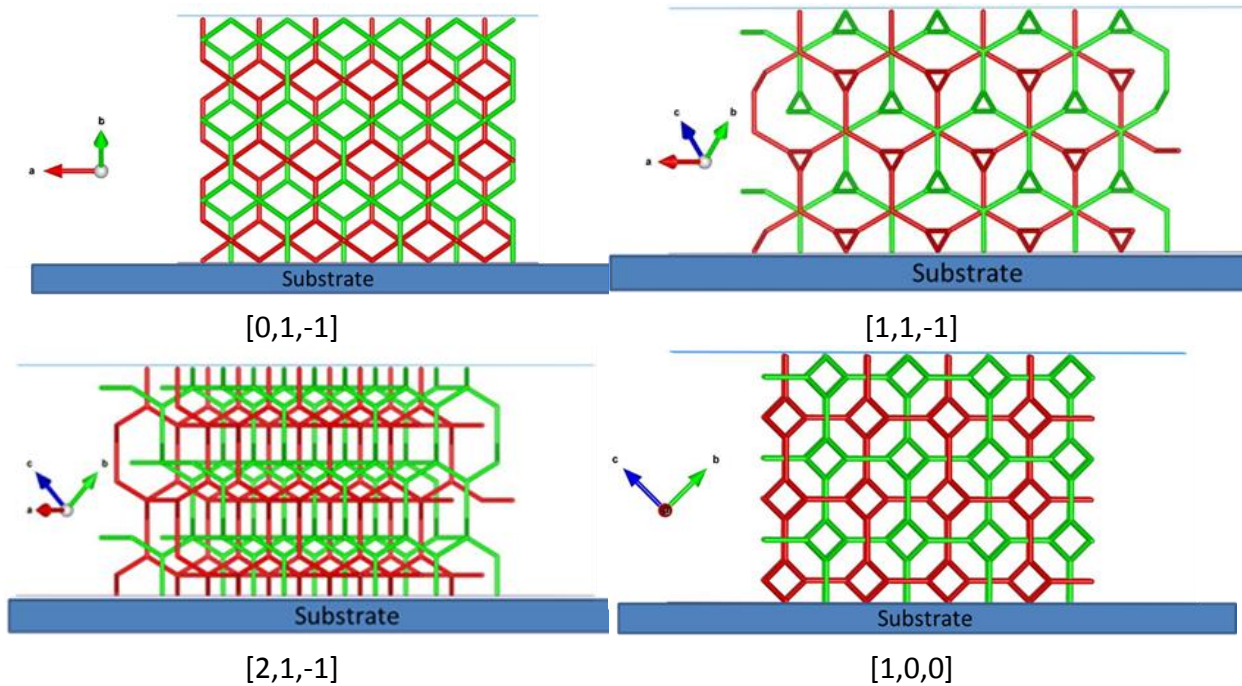


Figure 3-17. Side-view of different possible orientations of a G_A morphology having the (011) plane parallel to the surface (only 4 sections are shown, as examples), assuming a cubic lattice where $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$.

Moreover, observation of TEM cross-section images reveals the presence of wetting layers, which is also a specific behavior of thin films. TEM section view after only OsO_4 staining (PI domains) shows the absence of a stained layer at the interface with the substrate and the presence of a highly stained layer at the air/film interface which confirms the presence of PI wetting layer (around 5 nm) at this interface. For cut section stained by OsO_4 and I_2 , the presence of a stained layer at the interface with the substrate indicates the presence of a P2VP wetting layer between substrate and film. Formation of such wetting layers at both interfaces are in good agreement with the proposed (011) orientation. It is indeed well known that in gyroid morphology the fraction of each component in a crystallographic plan depends its family (100 or 110 etc.) and its distance from the origin. It has been particularly shown that (110) plane family exhibits the strongest modulation of fraction of each component within volume, in contrast to other crystallographic planes that exhibit a more constant composition. (Hashimoto, Nishikawa, and Tsutsumi 2007; Antoine et al. 2018) Such planes would thus lead to increased fraction of minor components for given position in volume, favoring formation of wetting layers (Figure 3-18).

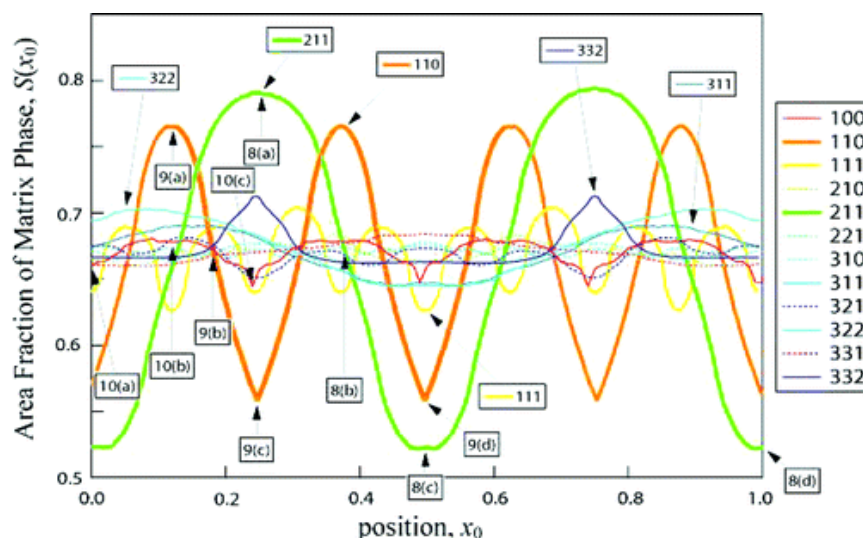


Figure 3-18. Calculated area fraction of the matrix phase $S(x_0)$ cut along the planes parallel to various crystallographic planes, as shown by three digits hkl in the legend, at various positions x_0 . (Hashimoto, Nishikawa, and Tsutsumi 2007)

b. GISAXS analysis

Figure 3-19a and 19b show experimental GISAXS patterns after staining of P2VP domains by I_2 and removing of PI by UVO treatment.

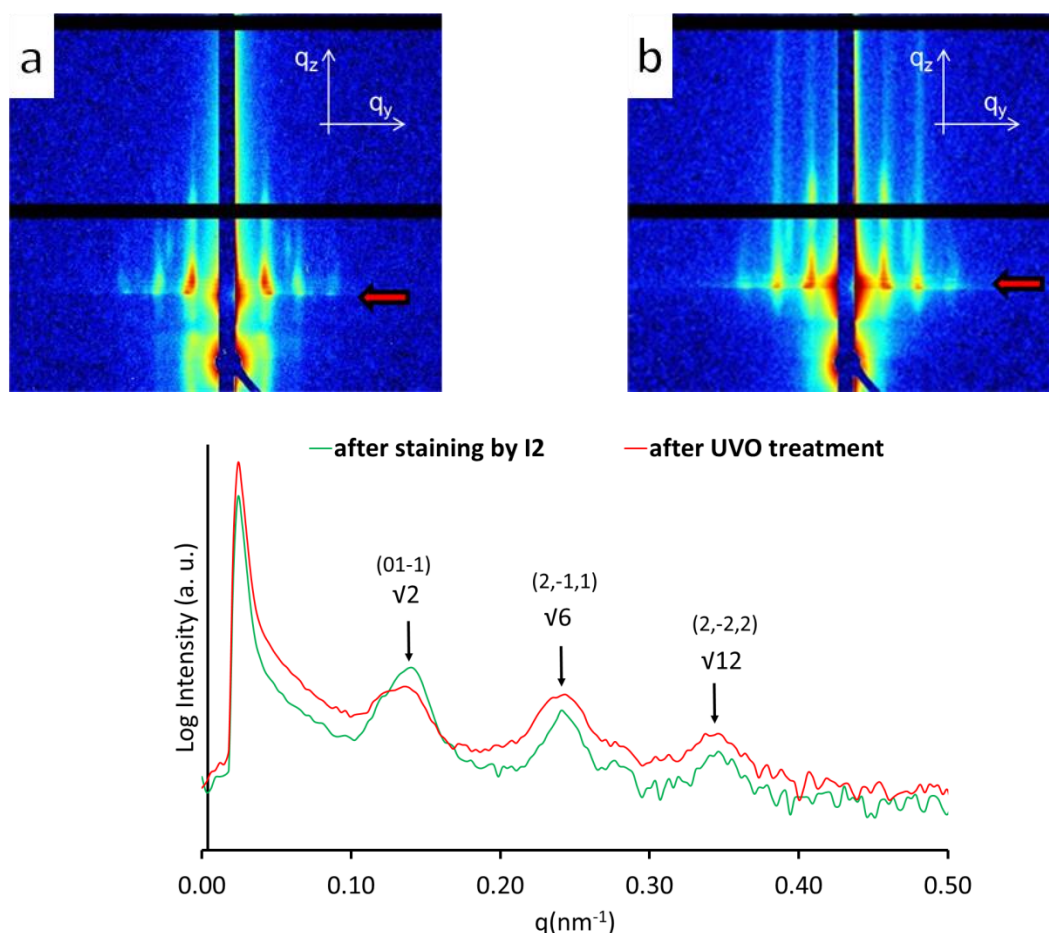


Figure 3-19. GISAXS pattern (after (a) selective staining by I_2 and (b) UVO treatment) and corresponding in-plane profile of solvent annealed (4 h) thin films.

On the pattern, there are several out of plane peaks, but as we mentioned, we are interested in this study of in-plane peaks on q_y direction and for this reason, linear cut is processed similarly in the center shown by red arrows on patterns. In both cases (after staining and UVO treatment), the main scattering peaks appeared at $q = 0.14, 0.24$ and 0.34 nm^{-1} . If we consider that the film has the (011) plane parallel to the surface, in-plane peaks correspond to scattering of planes perpendicular to the (011) film surface. Positions of these most intense peaks are in good agreement with a film having a Q_{214} space group and lattice parameter $a = 62 \text{ nm}$, the peaks being at $q/q_0 = \sqrt{2}, \sqrt{6}, \sqrt{12}$.

The formation of an alternating gyroid morphology (Q_{214}) consisting of two independent networks of PI and P2VP in matrix of PS, having a (011) plane parallel to the surface was then confirmed by GISAXS.

c. AFM characterization

Figure 3-20 shows AFM images of ISP23 thin films after SVA in tetrahydrofuran (THF) vapor and post treatments for selective identification of the domains. After 4 h annealing in THF vapors, AFM height image displays hexagonal packing of holes on surface, with two center-to-center distances: a short distance (52 nm) and a long distance (60 nm). After ozonolysis (UVO), hexagonal doughnut pattern of holes was observed which is typically observed for (011) plane of gyroid structure in bulk (Hashimoto, Nishikawa, and Tsutsumi 2007). From AFM image analysis of UVO treated sample, a center-to-center distance of 60 nm between PI domains was determined. In a similar way, exposure to ethanol vapor resulted in selective swelling of the P2VP domains with wavy lines being distant of 52 nm. To understand AFM images, it has to be kept in mind that in our case, AFM was performed in tapping mode and consequently probed an interfacial layer from surface to near surface layer. At room temperature, PI which is above glass transition temperature, behaves like a rubber and thus is not visible during AFM scanning (a wetting layer of PI exists probably on the surface as suggested by cross-section TEM images). The interfacial layer probed by AFM was modelized using Vesta and the top view of the network restricted to the layer near the surface is presented in Figure 3-20. The thickness of this interfacial layer (15 nm) was estimated from side view created by Vesta (Annex 4)). Top view shows a pseudo-hexagonal arrangement of P2VP connectors (represented by red connectors) within the center vertical connectors of PI (in green on the model). The pseudo-hexagonal center-to-center distances estimated by AFM (short 54 nm and long 62 nm) are in good agreement with the distances calculated using Vesta model based on TEM and GISAXS data (short distance is a and long distance is $\frac{1}{2}\sqrt{a^2+3b^2}$). Elimination of PI on the surface leads to holes in center of P2VP hexagons (represented by gray circles in Figure 3-20b) and swelling of P2VP leads to wavy lines (represented by wavy red thick lines in Figure 3-20c). This particular aspect is due to the fact that all the sides of the P2VP hexagons do not to swell equally because they are not at the same surface depth. All these hallmarks are in good agreement with the proposed G_A structure of the polymer having its (011) plane parallel to the surface.

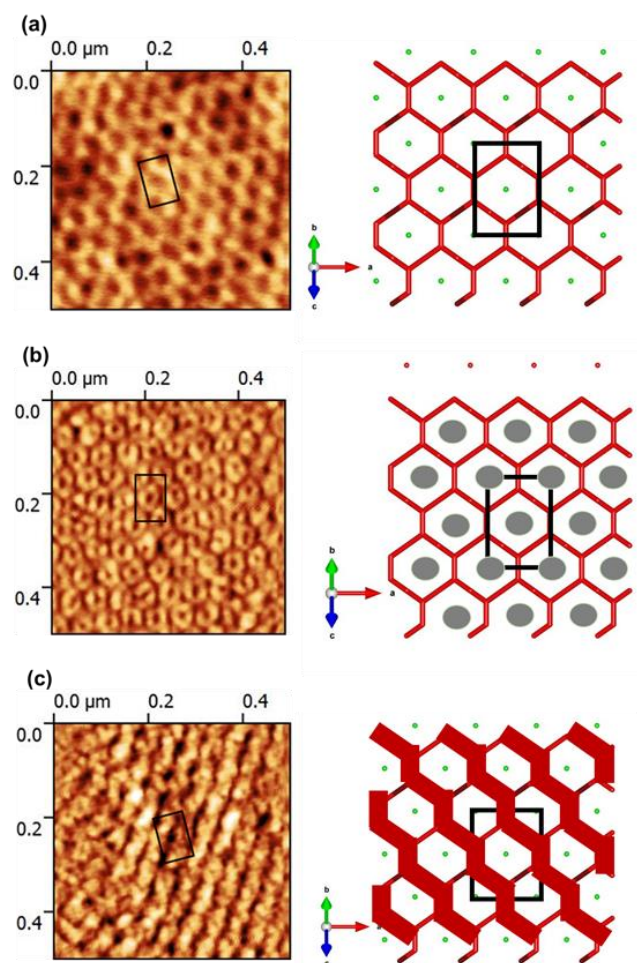


Figure 3-20. AFM topographic view (z scale is 3nm) of ISP thin films after solvent annealing (4 h), with models created by VESTA: (a) without treatment (b) After UVO treatment (c) after selective swelling of P2VP in ethanol.

Thin films with different thicknesses (between 45 nm and 250 nm) were also tested (in Figure 3-21) to investigate if there are other plane orientations of Q_{214} structure depending on film thickness. (Antoine et al. 2018) Film of 45 nm cannot be ordered, however the other films present the same sequence of two morphologies: alternating gyroid ($I4_132$) and fingerprint ($P2mm$) structure with cylinders oriented parallel to the surface (on surface, we observe always the same plane orientation of the Q_{214} for gyroid structure).

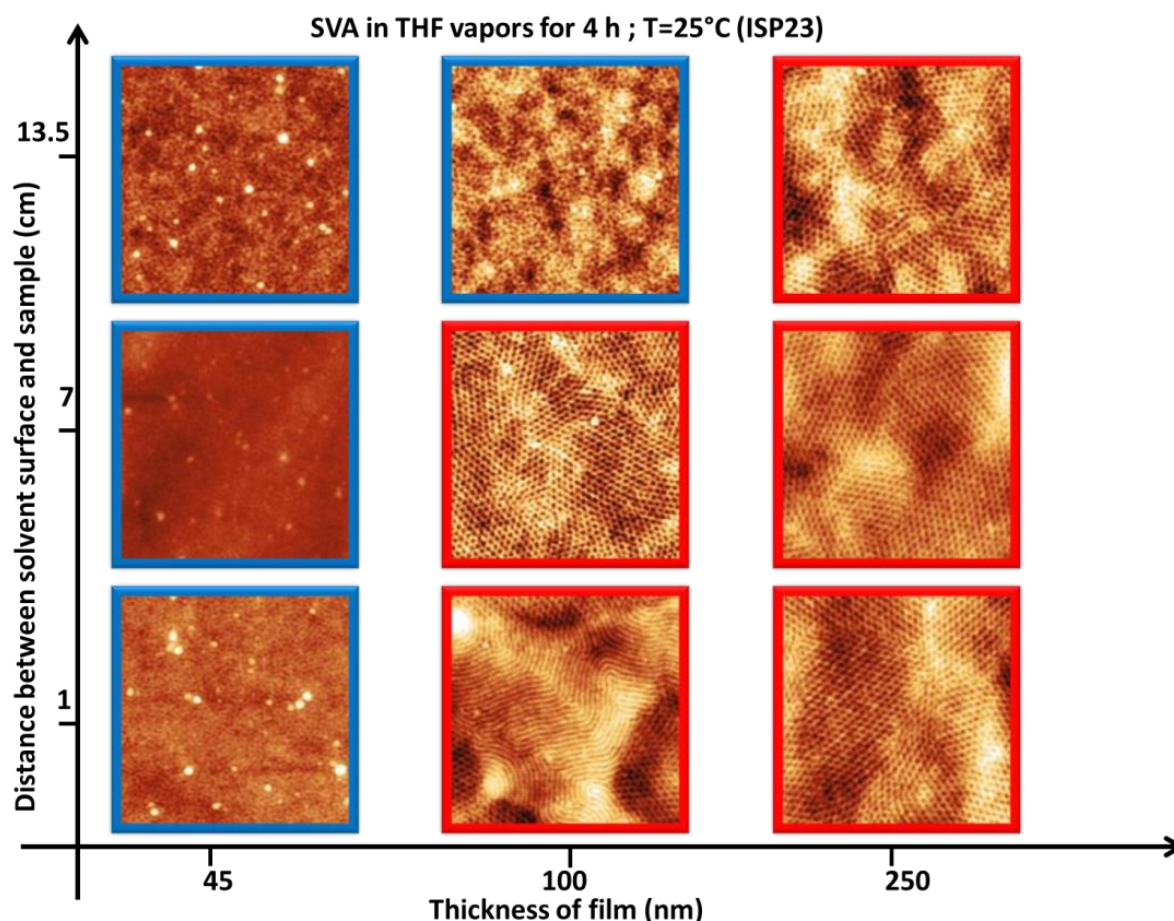


Figure 3-21. AFM height images of ISP23 thin films after solvent annealing in THF for 4h at 25°C as a function of thickness.

All organized films (the films of 100 and 250 nm) showed in optical microscopy a marbled aspect, indicating that film after solvent annealing has different thicknesses on the same sample (Figure 3-22). In order to respect structures of the gyroid or fingerprint, film in between the two wetting layers adopts thicknesses which are a whole or semi-whole number of unit cells and it leads various thicknesses on the same sample (holes and islands).

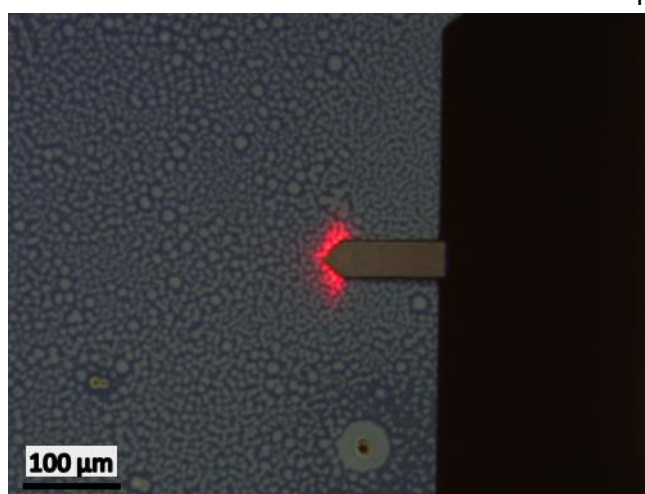


Figure 3-22. Optical image of a 120 nm thick thin film after 6 h solvent annealing.

d. Partial Conclusion

It can be concluded from this part that, for moderate annealing time, ISP 23 triblock copolymer forms a G_A morphology in thin film, similarly to what was observed in bulk. However, we found that this thin film configuration leads to some specific features that can be summarized as follow:

- a preferential orientation of G_A structure, with the (011) plane parallel to the surface
- a contraction of the lattice in the [011] direction (perpendicular direction to the surface)
- formation of a wetting layer of P2VP at the film/substrate interface and a wetting layer of PI at the air/film interface.

I.2.3. LONGER ANNEALING TIME

a. AFM and TEM characterizations

For longer solvent exposure time (24 h), a different kind of morphology was observed. Again, we combined AFM, TEM, and GISAXS analyses to identify the new structure (Figure 3-23). AFM presents lines with a periodic distance of 40 nm (Figure 3-23a and 23b). TEM top-view images show similar hallmarks in cases of selective staining of PI or P2VP, consisting of dark lines distant of 41 nm (Figure 3-23c and 23d, respectively). Staining PI and P2VP altogether leads to alternating black (PI), white (PS), and gray (P2VP) lines (Figure 3-23e). At this point, it cannot be unambiguously concluded on the morphology of the system since these top-view TEM images could result from the projection of parallel cylinders or perpendicular lamellae. The morphology was fully addressed by a cross-sectional TEM image as seen in Figure 3-23f, revealing cylinders of PI and P2VP parallel to the substrate. From the contrast of this image, it can be seen that all cylinders consisting of a given end component (PI or P2VP) are aligned along the vertical direction (i.e. perpendicularly to the surface), in good agreement with the top-view TEM images. The vertical distance between two cylinders of PI (or two cylinders of P2VP) was equal to ca. 20 nm. Such arrangement corresponds to a P2mm structure whose schematic view is shown in Figure 3-23e and 23f produced by Vesta. Again, as suggested in TEM cross-section images, wetting layers of PI at air/film interface and P2VP at substrate/film interface are present (see Figure 3-23f).

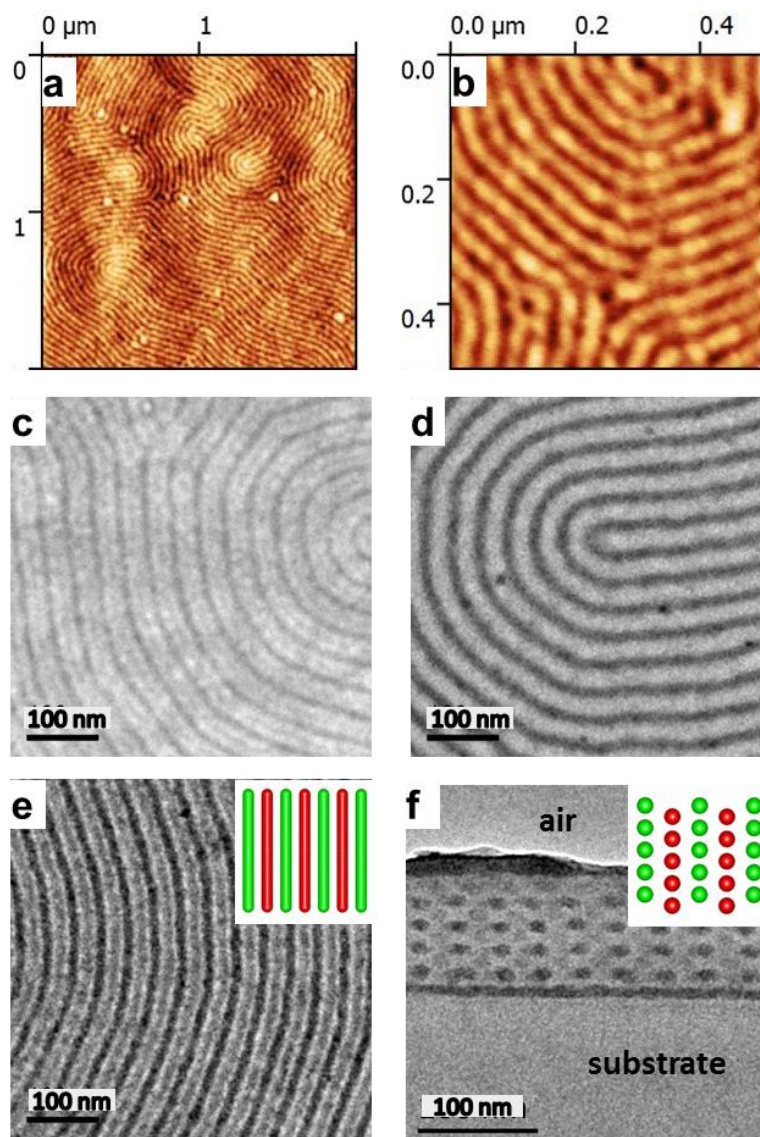


Figure 3-23. AFM and TEM (top and cross sections view) images of ISP thin films. AFM views after: (a) solvent annealing (24 h), (b) solvent annealing, and UVO. Z scale: 3 nm. TEM top (c, d, e) and cross sections (f) images of solvent annealed (24 h) thin films after: (c) selective staining by OsO_4 (d) selective staining by I_2 , (e,f) selective staining by OsO_4 and I_2 and vesta model of top and section view of P2mm. Black, white, and gray domains represent I, S, and P block, respectively.

b. GISAXS analysis

Again, the morphology was confirmed by GISAXS analysis. Figure 3-24a, 24b, and 24c show experimental GISAXS patterns obtained for a nanostructured thin film after UVO treatment and I_2 staining. GISAXS in-plane profile was extracted from these GISAXS patterns. Two main scattering peaks were observed for the film after I_2 staining at 0.16 and 0.32 nm^{-1} and correspond to scattering peaks of (100) and (200) planes perpendicular to (001) surface. The observed value is in agreement with the lattice parameter $a = 40 \text{ nm}$ of the square arrayed structure. An additional peak was observed after UVO treatment and corresponds to a sample where some areas with G_A structure remained. This additional peak was observed

like a bump near the first peak and it was not totally separated from the first peak which can be a good signification of heterogeneity (transition) of structure in the film.

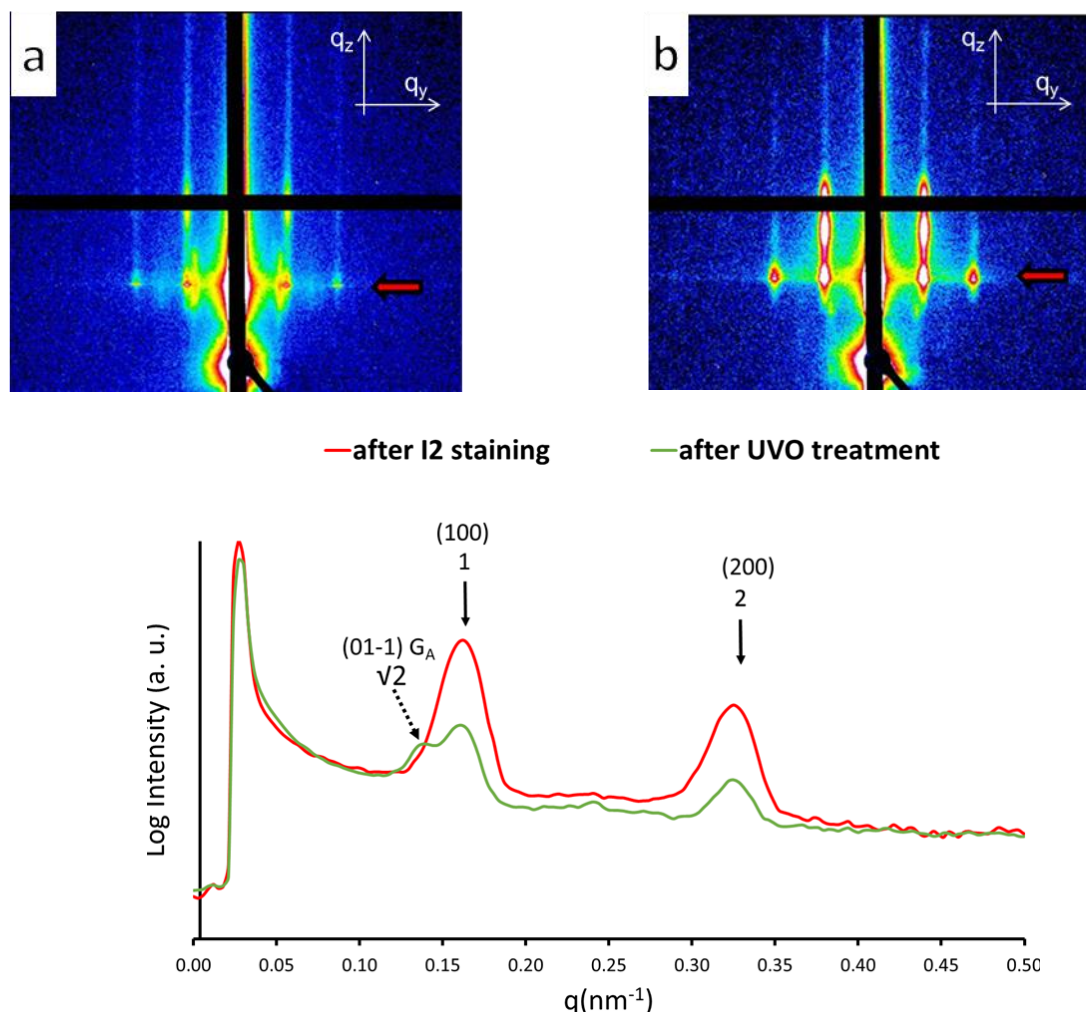


Figure 3-24. 2D GISAXS patterns of solvent annealed (24 h) thin films after (a) UVO treatment and (b) selective staining by I₂ and corresponding in-plane profile (profile position is marked by an arrow on the pattern).

As mentioned earlier (Matsushita 2000) in the introduction and according to previous work, the composition of this ISP BCP is close to boundary of cylindrical phase (obtained for higher PS volume fraction). Therefore, perturbation due to thin film configuration associated to solvent vapor annealing is sufficient to provoke a shift towards cylindrical phase. This is similar to what was previously observed (Suzuki et al. 2004) with morphological lamellar/G_A transition in a PI-b-PS-P2VP close to boundary of lamellar/G_A. We think that slightly selective swelling of domains could be partially responsible for such behavior (Sinturel et al. 2014), thanks to vicinity of the two morphologies in phase diagram. This is in good agreement with previous measurements of swelling of individual components, showing a preferential swelling of PS compared to PI, thus leading to an increased volume fraction of central block in swollen state. A rapid drying of swollen film freezes the new morphology. In addition, we postulate that formation of wetting layer which results from difference in surface energy of

the various components may also play an essential role in this transition. Whereas formation of PI and P2VP layers were observed in the two morphologies (see TEM cross-sections), we anticipate formation of a thicker layer in case of cylindrical morphology compared to G_A phase (respectively formed from a 2D and 3D arrangement of the minority domains). This needs to be confirmed by accurate determination of phenomenon occurring at both interfaces.

c. Discussion and Partial conclusion

Figure 3-25 presents TEM top-view images of transition zones between G_A and cylinders in a P2mm structure. These zones were observed for intermediate annealing time (typically 10 hours in THF). AFM and top-view TEM images reveal epitaxial relationship between (0-11) plane of G_A and (100) plane of the cylindrical structure, [100] direction of the G_A being parallel to cylinders' axe of the new structure.

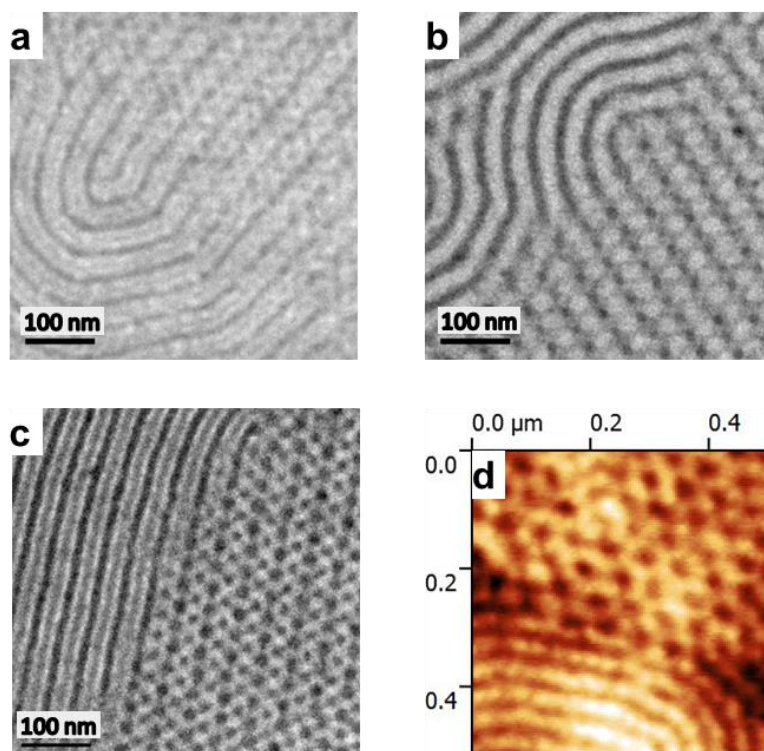


Figure 3-25. TEM top view and AFM height images of ISP solvent annealed (8h) thin films after: (a) selective staining by OsO_4 , (b) selective staining by I_2 , and (c) selective staining by OsO_4 and I_2 and (d) AFM height image of solvent annealed (8h) thin film. Black, white, gray domains represent I, S, and P block, respectively.

The transition pathway observed here is different from the various mechanisms that have been so far proposed to describe the transition G_D to HEX. This is because the mechanisms which have been proposed for G_D can simply not be applied to the G_A structure. This can be easily understood if one considers for example the well-known transition pathway implying the epitaxial relationship between the {121} planes of the G_D and the {100} planes of the HEX (cylinders are grown in the [111] direction of the G_D). For one third of the

newly formed cylinders, such mechanism implies fusion of the minor domains originating from different networks (Figure 3-26a). If this is possible for diblock polymers where the two interpenetrating networks have the same composition (red and green are equivalent in Figure 3-26a), this is no longer true for triblocks where the two terminal components (here, green is PI and P2VP is red) compose the two alternating networks. Such mechanism is therefore impossible in triblock terpolymer. For the same reasons, the other transition pathways can be discarded because they include a fusion of minor domains originating from different networks. If we now consider the [100] direction as the growth direction of the cylinders (Figure 3-26b), one can clearly see that each type of cylinders (PI and P2VP) will be formed from each network (PI and P2VP). The resulting arrangement of cylinders will display a P2mm symmetry, and not a typical HEX symmetry previously observed.

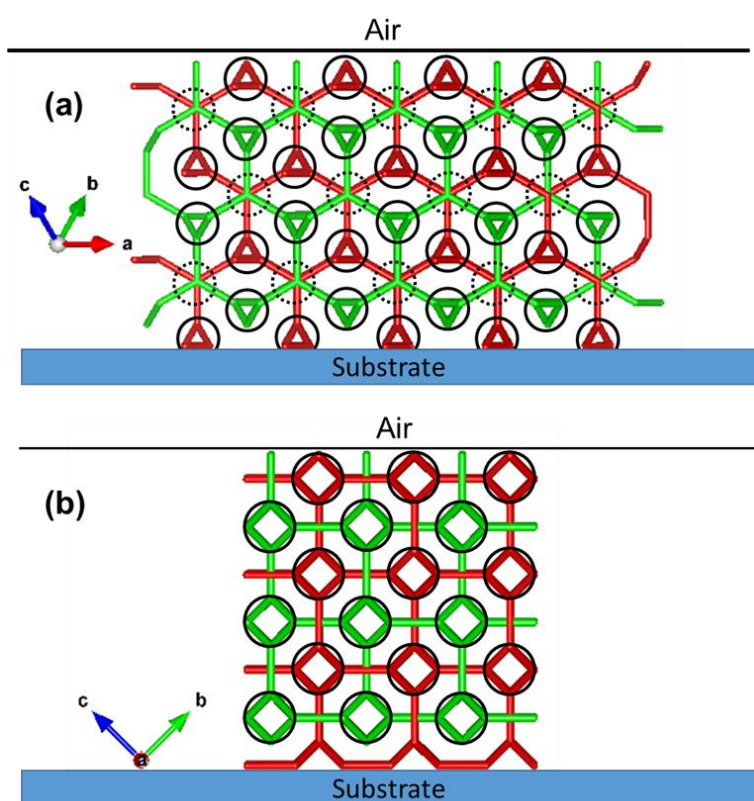


Figure 3-26. The transition pathway of two different morphologies: (a) G_D to HEX (red and green represent the same component) and (b) G_A to P2mm (PI in green and P2VP in red). Black circles represent the cylinders position resulting for the reorganisation of a given type on network whereas the dotted circles represent the cylinders position resulting for the fusion of two kind of networks. For clarity of the representation, the unit cell of G_A and P2mm are not deformed.

As a matter of characteristic distances, $b \cdot \sin(\alpha/2)$ of the gyroid unit cell (half of the long side of the projection of the unit cell) evaluated to be 44 nm has to be compared with the distance a of the P2mm unit cell (estimated to be 40 nm) and the $b \cdot \cos(\alpha/2)$ of the gyroid unit cell (distance between two stacks of PI or P2VP rich layers) evaluated to be 25 nm, has to be compared with the c distance of the P2mm unit cell (estimated to be 20 nm). The comparison of these values leads to the conclusion that the transition in the swollen

state between gyroid and P2mm went with shrinkage of the unit cell of the newly formed cylindrical structure which occurs probably during deswelling of the film. This can be understood since in the gyroid structure, PI and P2VP domains are interlaced in 3D directions whereas in the P2mm structure, PI and P2VP domains are oriented parallel to the surface and in one-dimensional direction. The deswelling of these two structures must not be the same.

In conclusion, thin films of a triblock terpolymer PI-b-PS-b-P2VP with a volume fraction of 0.20/ 0.66/ 0.14 exhibiting an alternating gyroid (G_A) could exhibit the same structure as in bulk. However, we found that this thin film configuration leads to some specific features such as a preferential orientation of the G_A structure (with the (011) plane parallel to the surface), accompanied by a contraction of the lattice in the [011] direction due to shrinkage which occurred during drying and formation of a wetting layer of P2VP at the film/substrate interface and a wetting layer of PI at the air/film interface. Long solvent annealing time led to a transition from this structure to a P2mm structure with alternating cylinders of PI and P2VP. The {0-11} planes of gyroid become the {010} planes of tetragonal structure and the cylinders are grown along the <010> direction parallel to the substrate. To our knowledge, this transition has never been observed.

I.3. CONCLUSION

In conclusion, the self-assembly of ISP19 and ISP23 neat triblocks which are located on the boundary between two different morphologies (spheres – cylinders for ISP19 and cylinders-gyroid for ISP23) was developed in thin film. Thin film morphologies of ISP19 and ISP23 are not similar to bulk structures due to confinement effect. The transition between different structures (spheres-cylinders or cylinders-gyroid) was observed due to thin film effect and results were confirmed by different characterization methods.

II. NANOSTRUCTURATION OF BLENDS OF TWO LINEAR TRIBLOCKS ISP IN THIN FILMS

II.1. ISP α /ISP β BLENDS

ISP α and ISP β triblock copolymers have a number-average molar mass of 122 kg/mol and 124 kg/mol respectively. According to previous work performed by Asai in bulk (Asai, Takano, and Matsushita 2015), ISP α with short PI chain (0.06/0.62/0.32) exhibits a cylinders in lamellae structure, in which the minor component PI remains in isolated cylinders at center of PS lamellae, due to highly asymmetric composition. ISP β neat triblock with short P2VP chain (0.39/0.56/0.05) forms sphere in gyroid structure where minor P2VP components remain in isolated spheres at center of PS matrix as shown in Figure 3-27.

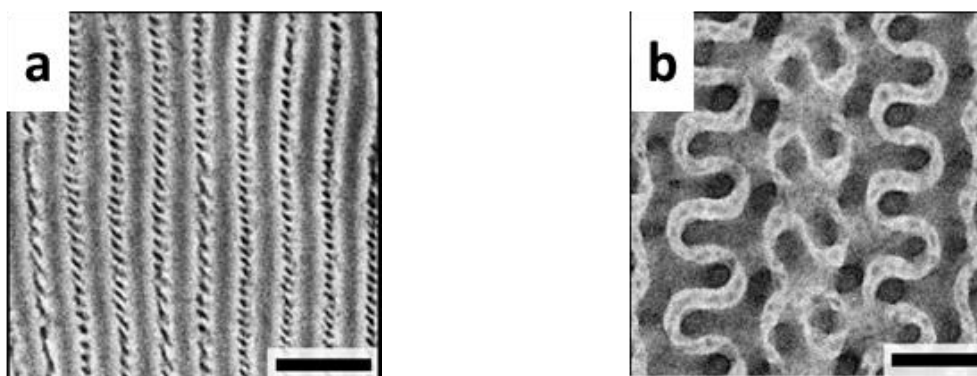


Figure 3-27. TEM images of the two triblocks ISP- α (a) and ISP- β (b) after selective staining of PI (by OsO₄) and P2VP (by I₂). The black, white, and gray domains represent PI, PS and P2VP phases respectively. Scale bars all represent 100 nm.

Binary blends of ISP α and ISP β with various compositions were developed by Asai (Asai et al. 2015) in bulk (**Table 8**). These blends exhibit new tiling patterns with non-CMC interface, consisting in rectangular-shaped rods with 4-fold symmetry or cylindrical pattern arranged in triangles and pentagons.

Sample	Blend proportion	$\phi_{PI}/\phi_{PS}/\phi_{P2VP}$
ISP α /ISP β	60/40	0.20/0.60/0.20
	48/52	0.24/0.59/0.17
	40/60	0.26/0.58/0.16

Table 8. Characteristics of blends of blocks copolymers: ϕ (volume fraction).

Study of these blends in form of thin film attracted our attention in order to develop similar nanostructuration (with non-CMC interface) and to understand self-assembly of ISP triblock blend under confinement effect.

II.1.1. 60/40 BLEND

Firstly, we focus on 60/40 blend of ISP α and ISP β triblock copolymers which give a final composition with the same volume fraction for PI and P2VP minority domain (0.20). According to previous work performed at Nagoya University, ISP α /ISP β (60/40) blend exhibited rectangular-shaped rods with 4-fold symmetry in bulk, as shown in **Figure 3-28** (Asai, et al. 2015).

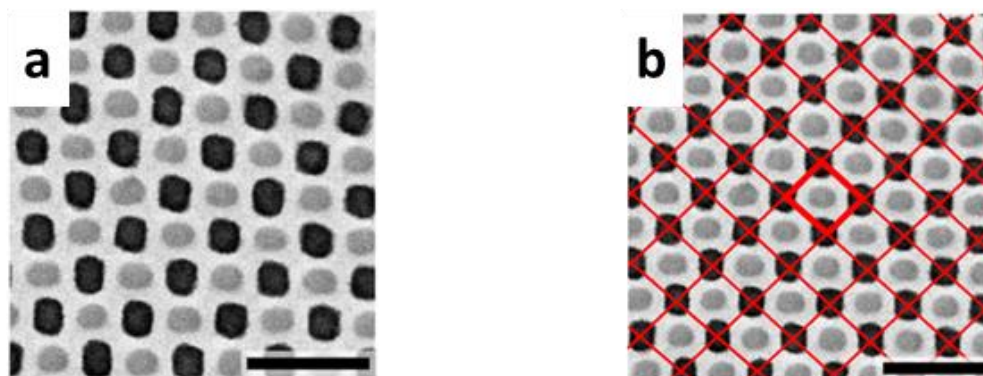


Figure 3-28. (a) TEM image of the nanostructure of ISP α /ISP β (60/40) blend in bulk. (b) Square tiling pattern. Scale bars all represent 100 nm.

a. Structuration kinetic

Firstly we focus on result of SVA on ISP α /ISP β (60/40) blend thin films in THF vapors. After spin coating, non-organized film is obtained as shown in Figure 3-29.

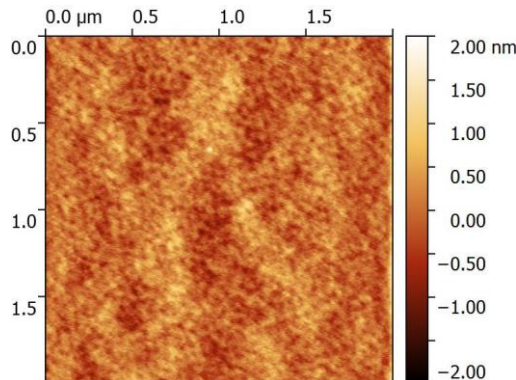


Figure 3-29. AFM height image of ISP α / β (60/40) thin film after spin coating.

The SVA was performed in THF vapors at 25°C and 30°C. In Figure 3-30, Films thicknesses are about 100 nm.

At 25°C, for the nearest sample (1 cm from the solvent surface), a “fingerprint” morphology (line pattern) was obtained after 4, 8 and 12 h of SVA (in green). On the second level (7 cm), mixture of dots and lines pattern (red) was observed after 4 and 8 h, whereas a line pattern (green) was again observed after 12 h SVA. On the highest level (13.5 cm) films show three different degree of structuration: no fully organized pattern after 4 h (blue) due to the insufficient swelling ratio, dots pattern after 8 h SVA (red) and finally line pattern (green) after 24 h SVA. For all sample/solvent distances, dewetting process was not observed. The top middle (center) part of graph represents optimal annealing conditions of

films. Annealing in THF at 30°C was also studied but dewetting of films occurs (not shown here) after only few hours for all conditions. In conclusion, structuration of ISP α /ISP β (60/40) blend thin films in THF vapors was performed at 25°C for 8 h on the second level of system. Despite a mixed morphology, this corresponds to the best annealing conditions in which areas with large perpendicular orientated grains were formed.

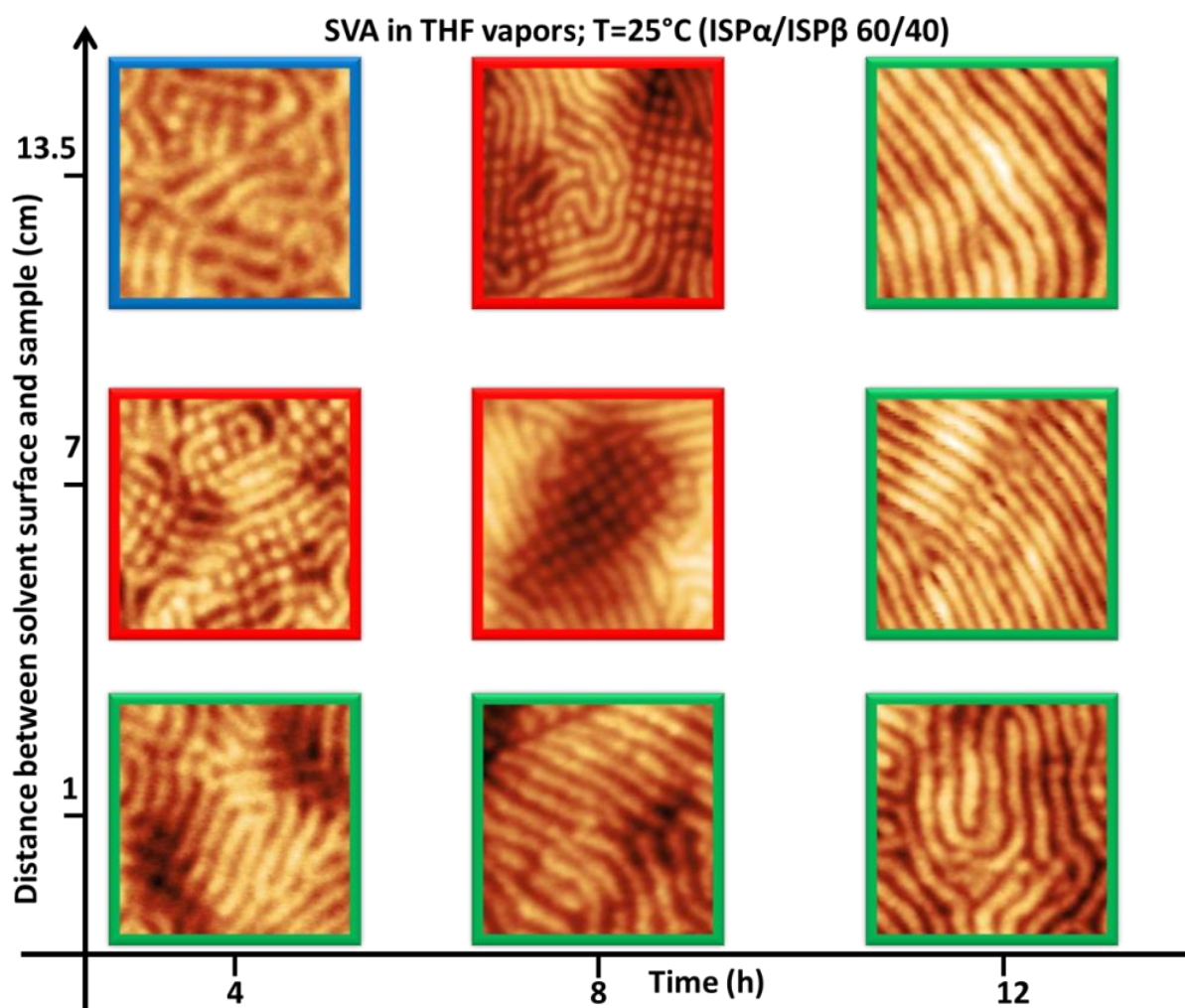


Figure 3-30. Structuration kinetics of ISP α / β (60/40) blends thin films in THF vapors at 25°C.

b. Moderate annealing time

AFM characterization

Figure 3-31 shows the AFM images of ISP α /ISP β (60/40) blend thin films. After 8h of THF exposure, as previously mentioned, AFM height image displays a mixture of lines and discrete features packed in a square array (Figure 3-31). We were able to select area where grains of square arrayed features were uniformly obtained (approx. 0.5 x 0.5 μ m, seen Figure 3-32a). We will focus on this kind of selected zones in the following paragraph.

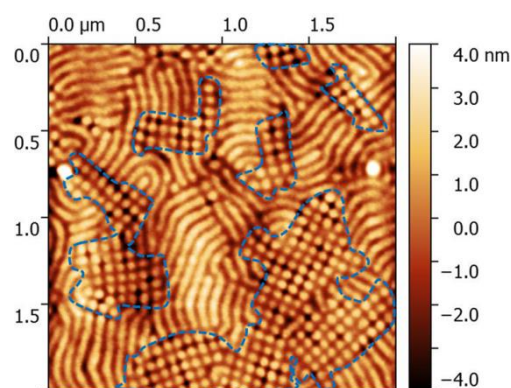


Figure 3-31. AFM height image of ISP α /ISP β 60/40 after 8 h of SVA in THF.

Selective elimination of PI and selective revelation of P2VP allow to describe the structure of the two minor phases (PI and P2VP) at film surface.

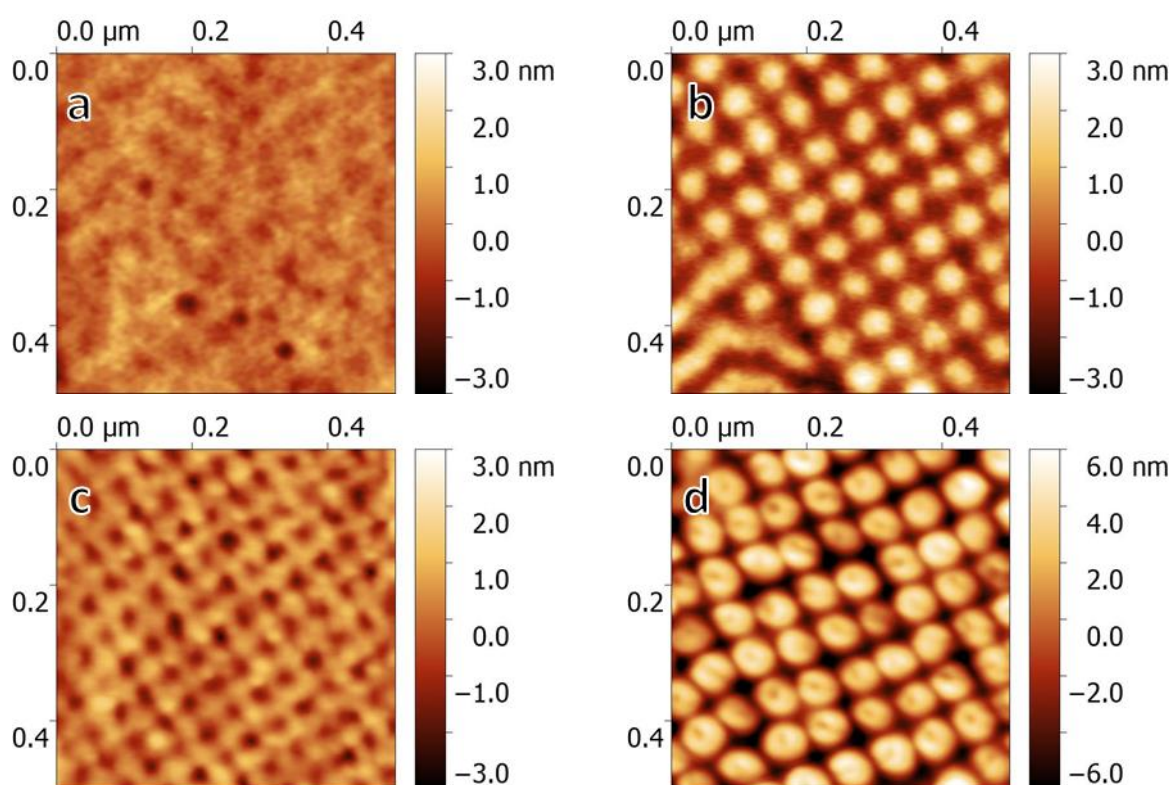


Figure 3-32. AFM topographic view of a blend of ISP α and ISP β (60/40) thin films: (a) after spin coating, (b) solvent annealing in THF, (c) after solvent annealing, and UVO (d) after solvent annealing and swelling in ethanol.

After UVO treatment, a distinct square packed pattern of holes was observed, suggesting that the parent PI domains occupied exactly the same locations. In a similar way, exposure to ethanol vapor resulted in selective swelling of the P2VP domains, highlighting their square arrangement (Figure 3-32d). From image analysis (Figure 3-32b), we measured a center-to-center distance of 65 nm, in good agreement with data obtained in the bulk for such composition (Asai et al. 2015) except for UVO treated sample where center-to-center distance decrease to 50 nm presumably due to a global shrinkage of lattice during the UVO

treatment. At that stage, shape of those features cannot be investigated by AFM, due to tip convolution effect. AFM confirms only square arrayed morphology on film surface.

TEM characterization

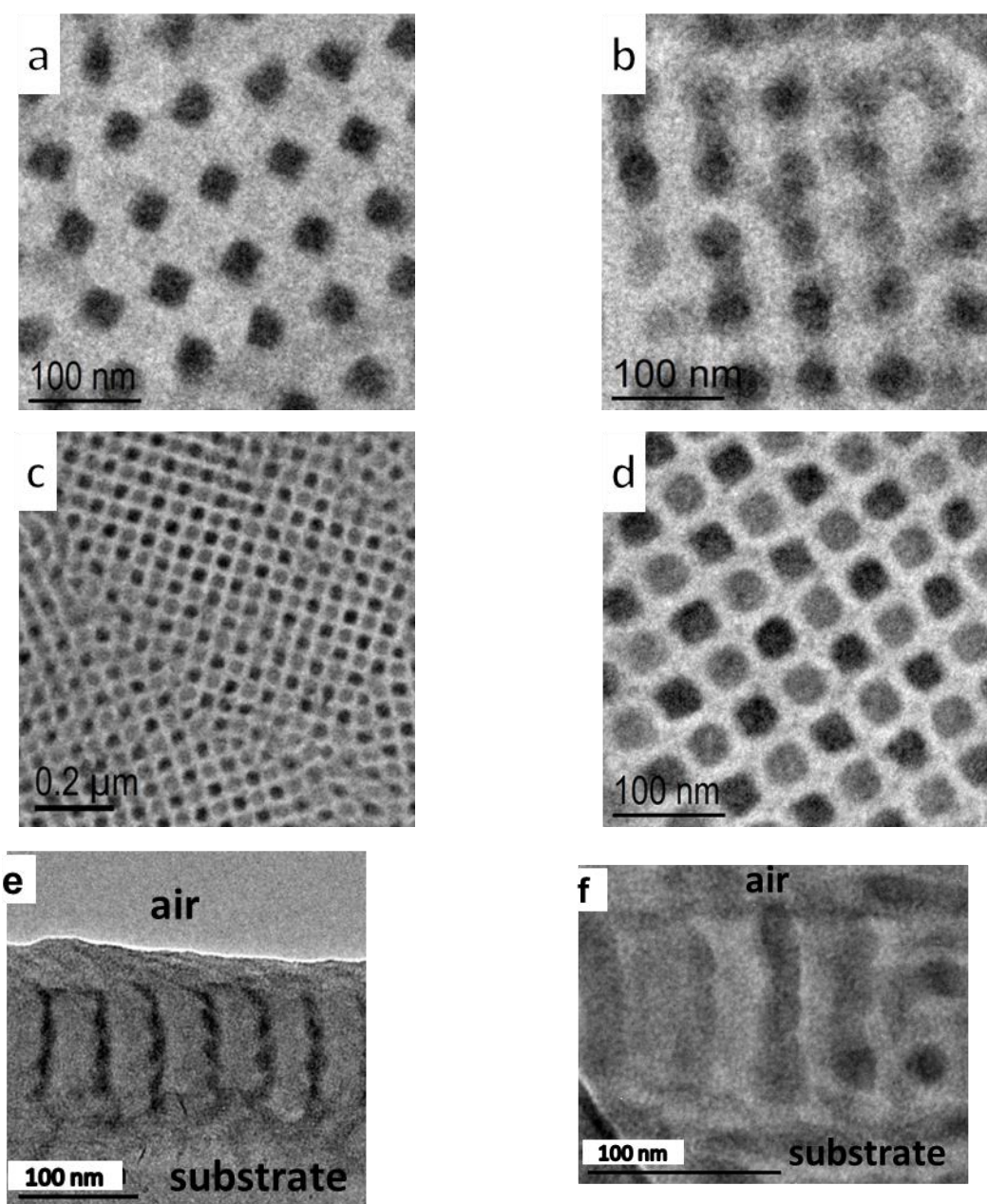


Figure 3-33. TEM images (a,b,c,d – top view and e, f section views) of blend of ISP α and ISP β (60/40) solvent annealed (THF) thin films: (a) after selective staining by OsO $_4$, (b) after selective staining by I $_2$, and (c), (d) after selective staining by OsO $_4$ and I $_2$ and section views of (e) after selective staining by OsO $_4$ and (f)) after selective staining by OsO $_4$ and I $_2$. Black, white, and gray domains represent I, S, and P blocks, respectively.

To obtain further information, TEM top-view observation (perpendicularly to the surface of the film) was firstly carried out after selective staining PI by OsO $_4$ (Figure 3-33a), P2VP by I $_2$ (Figure 3-33b) and staining both PI and P2VP (Figure 3-33c and 33d). After staining of one end block (PI or P2VP), a square array was observed on image. After staining PI and

P2VP, PS matrix appeared white, while PI and P2VP domains appeared darker revealing a square packed PI and P2VP domains. From TEM images, a center-to-center distance was measured for PI and P2VP domains of 70 nm which is similar to distance previously found in AFM.

TEM top-view images clearly demonstrate rectangular shape (non-CMC, flat interface) of domains oriented perpendicularly to the film surface. As proposed by Asai et al. (Asai et al. 2014) this very singular interface curvature result from 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 blend display different compositions of their PI and P2VP blocks (but the same chain length), introducing a molecular weight distribution in PI and P2VP domains and favoring a non-uniform placement of chains. This was of course not observed with ISP19, where the very limited distribution of molecular weight in PI and P2VP domains can only produces round interfaces.

As previously mentioned, TEM top-view images are not adapted to reveal internal structural inhomogeneities (like cylinder vs spheres in ISP19). Consequently, we performed TEM section-view imaging on stained samples (Figure 3-33e and 33f). Thin wetting layers of PI and P2VP at the two interfaces (air/film and film/substrate) were identified. In addition, these images indicate axial extension of minor domains through the entire film thickness. PI and P2VP can be seen as continuous rectangular rods oriented perpendicularly to the substrate and connecting the two interfaces.

GISAXS analysis

Figure 3-34 shows GISAXS pattern and profile of ISP α /ISP β (60/40) blend thin films after THF 8 h vapor exposure and UVO treatment due to the reasons already given earlier (low electronic density contrast of the three components). This led to observation of multiple diffraction peaks in in-plane direction. The lattice can be then considered as a simple tetragonal packing of pores (resulting from the PI elimination) in a homogenous continuous phase where all reflections of a cubic lattice are possible. A strong diffraction peak is observed at $q_0 = 0.0975 \text{ nm}^{-1}$. This allows to calculate center-to-center distance ($2\pi/q_0 = 65 \text{ nm}$). Figure 3-34b shows positions expected for high order diffraction peaks calculated from $q_0 = 0.0975 \text{ nm}^{-1}$ that fits quite well with the experimental positions. Unlike ISP19, where fluctuation of the Bragg rods were observed due to the spherical structure, for ISP α /ISP β blend, Bragg rods on GISAXS pattern are continuous in q_z direction and oscillations of diffraction spot was not observed. This confirms the axial extension of the rods due to cylindrical morphology.

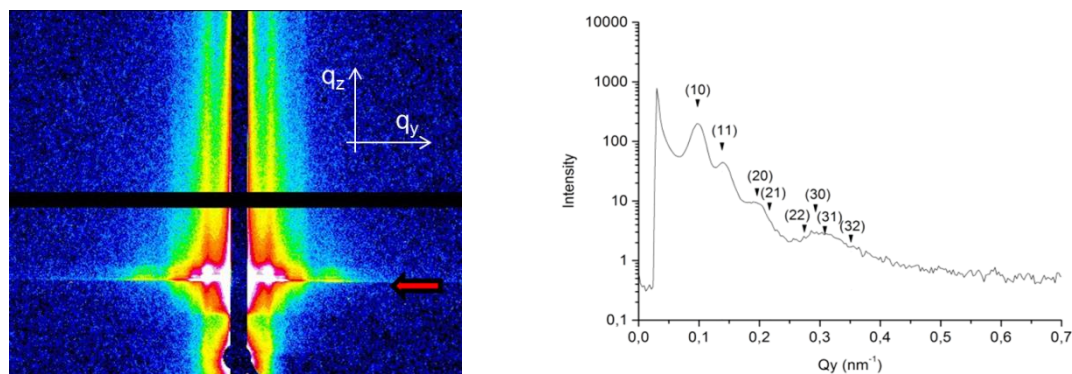


Figure 3-34. GISAXS pattern and corresponding in-plane profile of ISP α /ISP β (60/40) blend thin films in which tetragonal-packed structures of two different kinds of domains were observed by AFM and TEM after solvent annealing and UVO. Profile position is marked by an arrow on the pattern.

Partial conclusion

In summary, using the blend of ISP triblock terpolymer in thin films, we have demonstrated the possibility to achieve tetragonally packed rectangular rods of PI and P2VP, oriented perpendicularly to the film surface. Apart from creation of wetting layers at interfaces, we did not observe deviation of the morphology compared to the bulk for this blend. This suggests that the bulk morphology is energetically very stable, and not perturbed by the thin film configuration. These rectangular-shaped interfaces obtained from linear triblock blends in thin films constitute a major innovation of this work. As previously mentioned, it offers exciting potential for nanopatterning where need for rectangular-shaped features in a square symmetry is high (Tang et al. 2008; Chang et al. 2014; Ruiz et al. 2011).

c. Longer annealing time

AFM and TEM characterization

For longer SVA time in THF vapors, fingerprint morphology was observed on surface with lines with a periodic distance of 50 nm (Figure 3-35). This fingerprint morphology can be signature of lying cylinders or perpendicular lamellae. Former case can be explained by transition from perpendicular (obtained for moderate annealing time) to parallel rods. The latter case can be obtained from an order-to-order transition. In order to distinguish between these two possibilities, we performed TEM and GISAXS analysis.

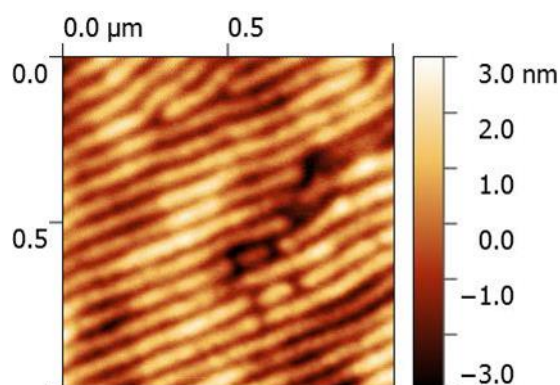


Figure 3-35. AFM height image after 24h SVA in THF.

After staining one of the minor components (PI or P2VP), TEM top-view images presented dark lines distant of 55 nm (Figure 3-36a). Staining PI and P2VP altogether led to alternating black (PI), white (PS) and gray (P2VP) lines that can again interpreted as lying cylinders or perpendicular lamellar morphology.

The morphology was fully addressed by cross-section TEM image as seen in Figure 3-36b, revealing circular discrete features and elongated lines (parallel to the surface) of PI and P2VP domains. This indicates that the fingerprint morphology corresponds to lying cylinders. Different shapes of PI and P2VP domains in this section-view (circular features and elongated lines) are in good agreement with mixed orientation of domains observed on TEM top-view image. In addition, it can be seen that all cylinders consisting of a given end component (PI or P2VP) are aligned along vertical direction (in good agreement with the top-view TEM images showing a three colored line pattern). Vertical and horizontal distances between two cylinders of PI (or two cylinders of P2VP) were equal to c.a. 60 and 50 nm. Such arrangement corresponds to a P2mm structure which has already presented for ISP23 systems. Again, as suggested in TEM cross section, wetting layers of PI at air/film interface and P2VP at substrate/film interface are present.

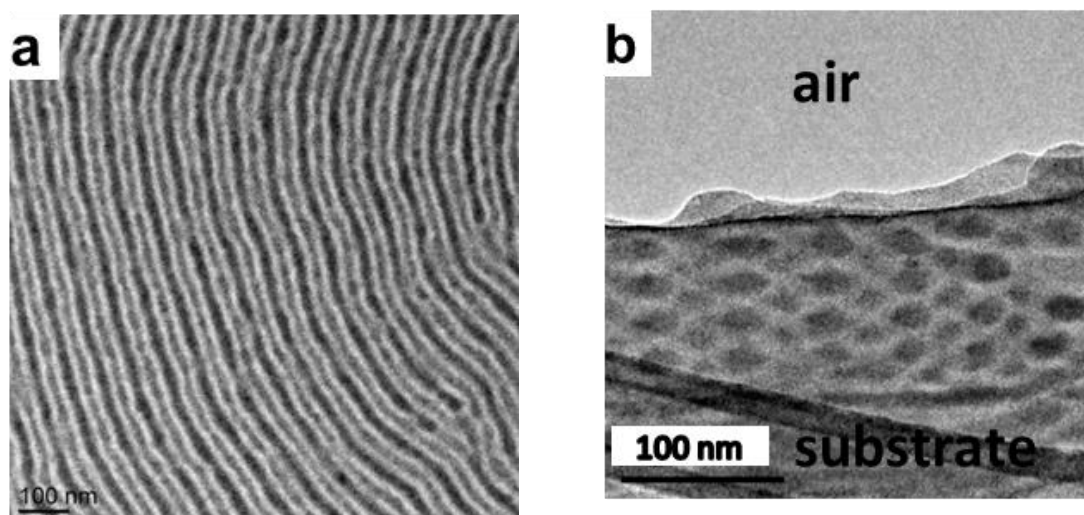


Figure 3-36. TEM (a) top and (b) section view images of ISP α /ISP β samples after 24 h SVA treatment in THF vapors.

Mechanism of transition of perpendicularly oriented cylinders to parallel oriented cylinders is known for BCP thin films (Suh et al. 2010; Sinturel et al. 2013; Aissou et al. 2013; Knoll et al. 2002). This is driven by blocks tendency to progressively wet interfaces (even in the situation of a surface energy mediation by solvent, a perfect nonselectivity toward 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 period of the self-assembly. Consequently, a perpendicular orientation is obtained for moderate annealing time (metastable) and progressively evolves toward a parallel orientation thanks to a self-adaptation of the film thickness (by polymer diffusion). A rapid drying of the swollen film freezes the new orientation. This was illustrated by Paik et al. in a GISAXS study focused on solvent swollen poly(α -methylstyrene)-*b*-poly(4-hydroxystyrene) block polymer thin films (Paik et al. 2010). Swelling a film containing perpendicularly oriented cylinders with high content of tetrahydrofuran led to morphological change and upon rapid removal of the solvent, the parallel orientation was preserved in dried film. On the Figure 3-37, optical microscopy data demonstrated that as-cast film thickness was uniform, however optical microscopy image of ordered thin film surface (after 6 h solvent annealing) depicted a typical topography consisting of islands and holes. These islands and holes formation can occur during annealing of block copolymer films due to incommensurability between polymer film thickness and formed structure with different orientation (in-plane and out-plane structure) (parallel orientation only observed on the islands).

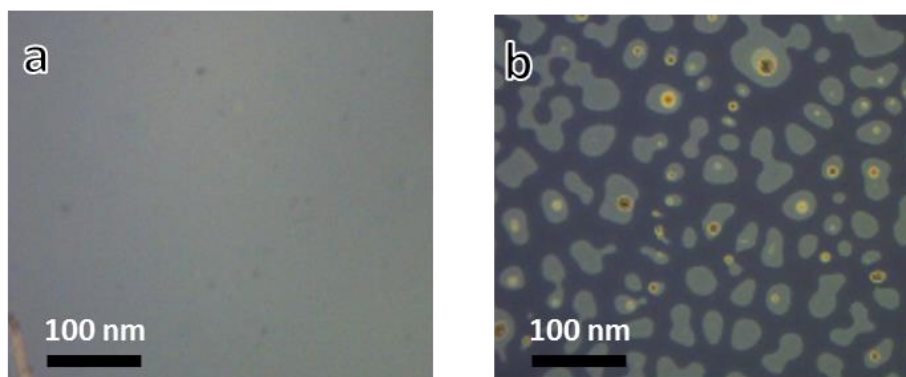


Figure 3-37. Optical image of a 100 nm thick thin film of ISP α /ISP β (60/40) blend (a) after spin coating; (b) after 6 h solvent annealing.

GISAXS analysis

Figure 3-38 shows GISAXS profile of ISP α /ISP β (60/40) blend after THF 24 h vapor exposure and elimination of PI by UVO treatment or staining of P2VP by I₂. The first diffraction peak is unchanged at $q_0 = 0.096 \text{ nm}^{-1}$ which allows to calculate the center-to-center distance ($2\pi/q_0 = 65 \text{ nm}$) and it is in good agreement with the AFM and TEM results. Second peak observed at 0.18 nm^{-1} follows the relation of $q/q_0 = 2$ which is indicative of lying cylinder morphology on GISAXS pattern.

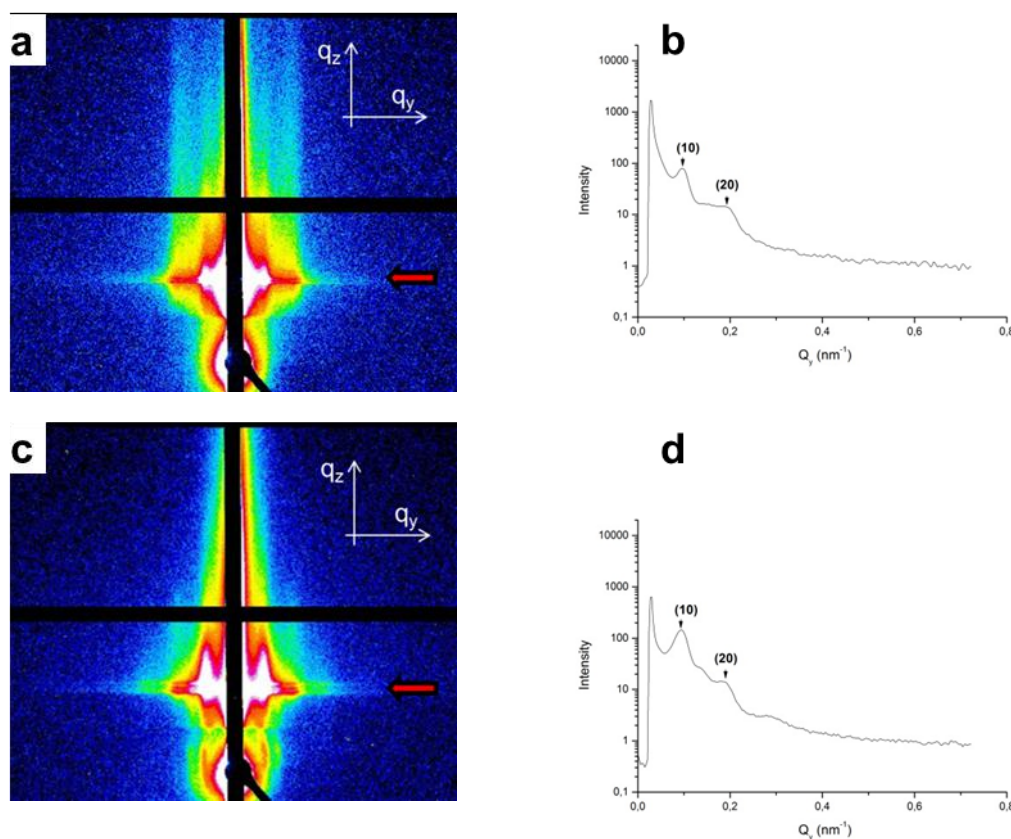


Figure 3-38. GISAXS pattern for the ISP α /ISP β samples after 24 h SVA treatment in THF vapors and (a, b) elimination of PI and (c, d) staining of P2VP.

Partial conclusion

In conclusion, after longer annealing, blend of ISP triblock terpolymer in thin films, give a tetragonally packed PI and P2VP rods, oriented parallel to film surface. Formation of wetting layers at the interfaces was observed on TEM section-view images. Change of morphology (order-order transition) was not observed, but due to thin film effect, the change of structure orientation (perpendicular – parallel) occurred for this blend.

d. Optimization of perpendicular orientation

In order to optimize the homogeneity of the perpendicular orientation, we have studied the influence of the initial thickness of the film and solvent nature.

Influence of initial film thickness on nanostructuration

Thin films with different thicknesses (between 45 nm and 250 nm) are shown in Figure 3-39.

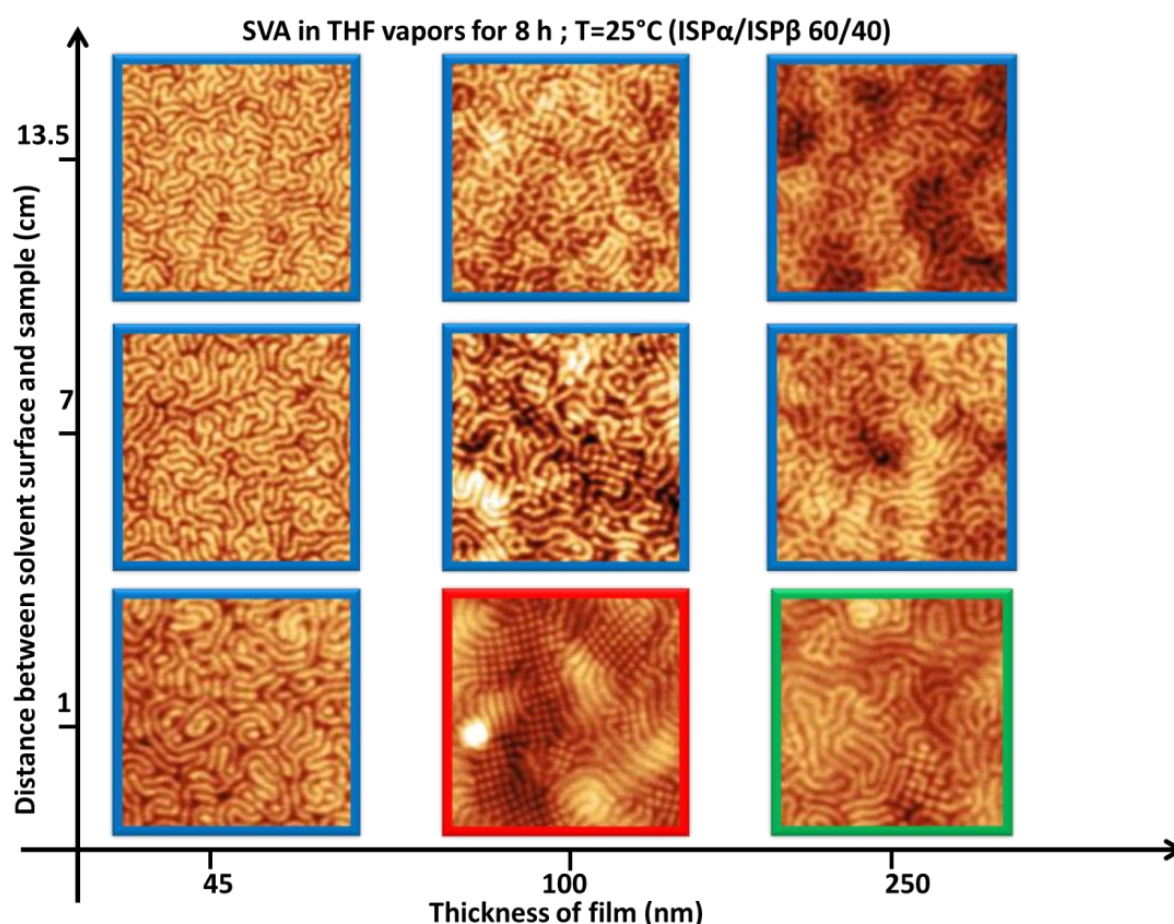


Figure 3-39. AFM height images of blend of ISP α / β (60/40) thin films with different thickness solvent annealed in THF for 8h at 25°C.

For the highest (13.5 cm) and second (7 cm) levels, films were not organized in all cases (45, 100 and 250 nm). On first level (1 cm), for 45 nm thick film, ordered structure was not observed. Film of 100 nm exhibited tetragonal packed nanostructuration on first level (1 cm) mixed with a parallel orientation. Finally, for 250 nm thick films, parallel oriented

pattern was obtained on first level with few perpendicular dots (smaller perpendicularly organized grains than for the 100 nm thick film). In conclusion, after THF SVA 8h, the optimal thickness to have perpendicular oriented cylinders is approximately 100 nm for ISP α /ISP β (60/40) blend thin films.

Influence of solvent nature on film nanostructuration

SVA treatment in toluene vapors was performed at 25°C and 30°C on different levels in the annealing chamber in order to obtain homogenous structure. Films thicknesses were about 100 nm. No ordered structuration (also no dewetting) was observed during SVA in toluene at 25°C as showed in Figure 3-40.

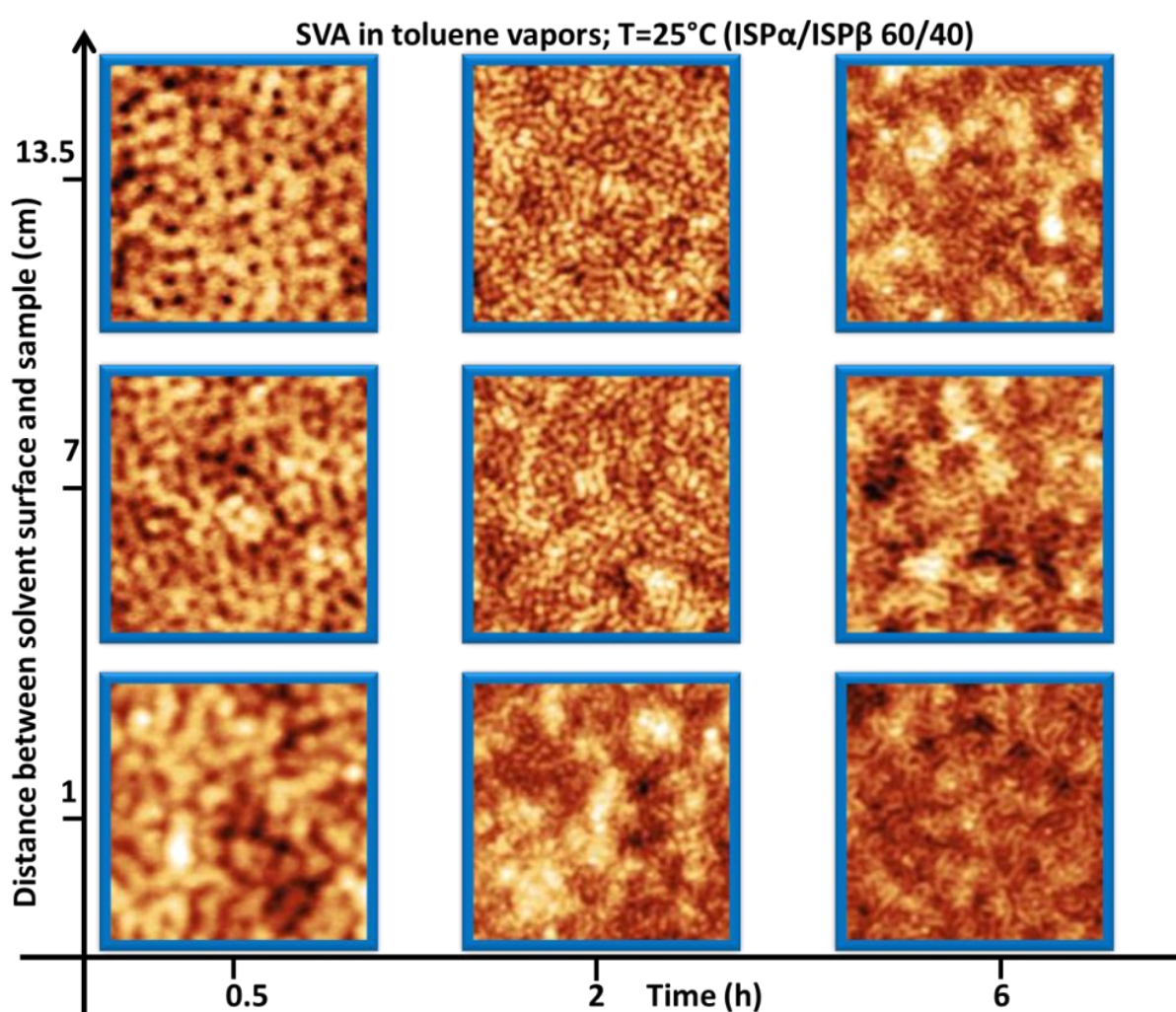


Figure 3-40. Structuration kinetics of ISP α / β (60/40) blends thin films in toluene vapors at 25°C.

For SVA in toluene vapors at 30 °C, no ordered structure (blue) was observed after 3 h of SVA for all sample positions (Figure 3-41). In contrast, films placed on the nearest (1 cm) and second (7 cm) level exhibited a perpendicular pattern (red) after 6 h SVA in toluene. In contrast to THF annealing, it is possible to obtain only perpendicular oriented morphology for SVA with toluene (no mixture of square and line features), however organized grains size

is smaller. For the highest level of system, films were not fully organized after 6 h (blue) due to the insufficient swelling ratio. Dewetting process was not observed under these conditions.

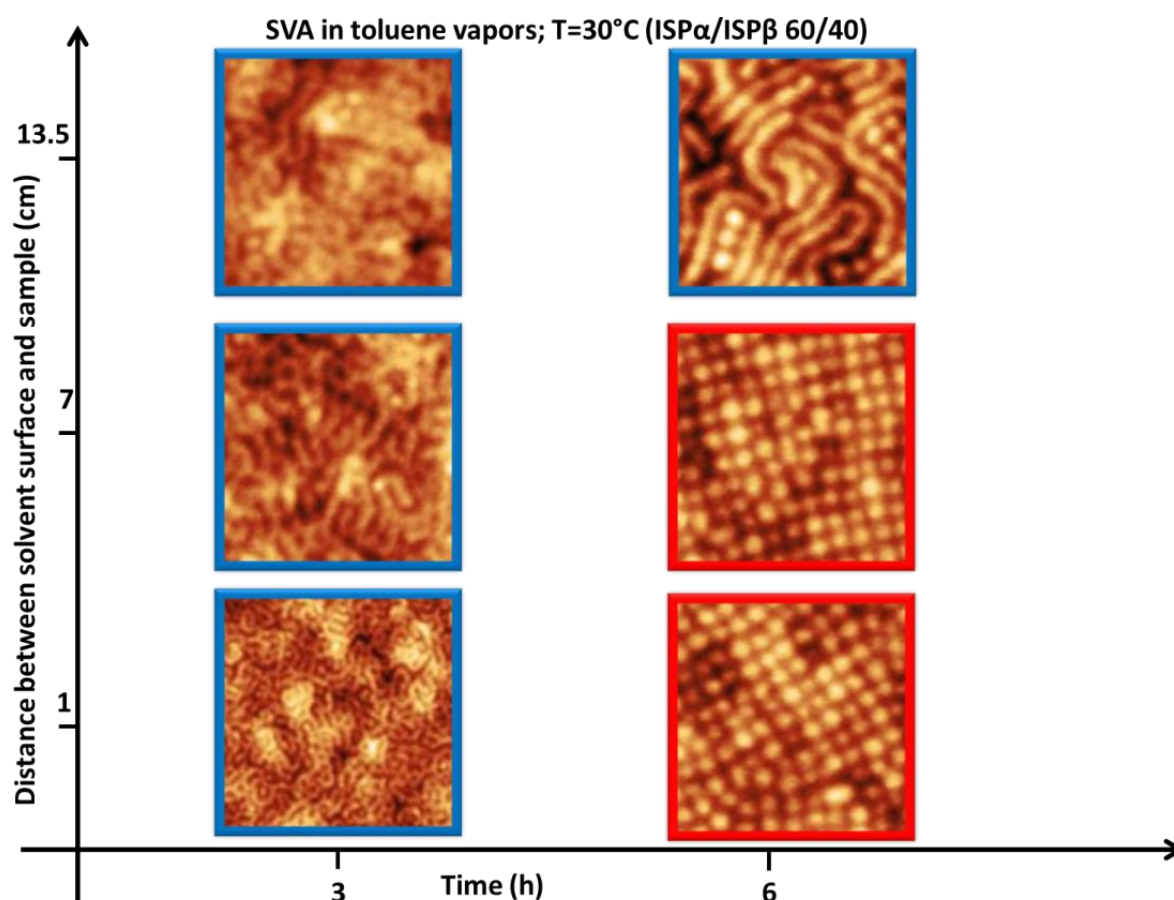


Figure 3-41. Structuration kinetics of ISP α / β (60/40) blends thin films in toluene vapors at 30°C.

In conclusion, we obtained the same type of nanostructuration after SVA in THF and toluene. As we mentioned, the same tetragonal packing nanostructure only based on perpendicular oriented features (no mixture of dots and lines) was obtained after SVA in toluene vapors, however the ordered grains had a smaller size in this case and for that reason, we focalised on morphology obtained for THF annealing.

To study internal structuration of film after toluene annealing, several UVO treatments were performed on the same sample (observation of PI holes after each UVO treatment) to eliminate successive layer (selectively PI but each time also 10 - 20% of PS and P2VP). The AFM images suggest the presence of continuous tetragonal cylinders from the film surface to the bottom of film, in accordance with the structuration depicted for THF SVA (Figure 3-42). Due to lack of time, TEM was not performed on films annealed in toluene vapors.

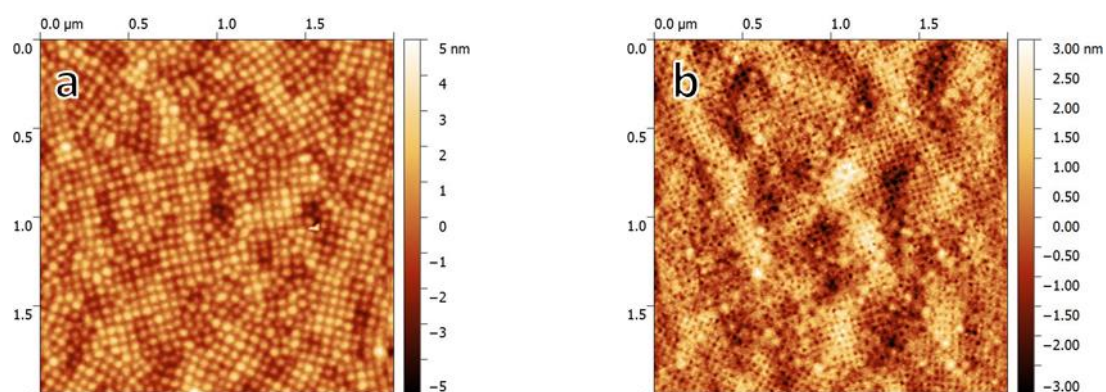


Figure 3-42. AFM topographic view of a blend of ISP α and ISP β (60/40) thin films: (a) after spin coating and solvent annealing in toluene and (b) after solvent annealing, and UVO treatment.

Partial Conclusion

In conclusion, tetragonally packed rectangular rods were obtained in toluene vapors for ISP α /ISP β (60/40) blend films. UVO treatment result suggests a similar nanostructure than this obtained after THF annealing (tetragonally packed rods). After THF annealing, a mixture of orientation was obtained in all cases, even on films with various thickness.

e. Conclusion

Tetragonally packed rectangular rods in thin film were observed as in bulk despite surface energy difference and confinement effect. However, a wetting layer on interface (air/film and film/substrate) and a transition of cylinders orientation were observed in thin film. By coupling different characterization methods (AFM, TEM and GISAXS), non-CMC interfaces of PI and P2VP domains were demonstrated clearly for this blend which can be explained by location of different types of chain in rods.

II.1.2. OTHER BLENDS

In this studies, thin films of $\text{ISP}\alpha/\beta$ blends from 35/65 to 80/20 (7 compositions in total) were studied. In the following, we will focus on 2 typical blends (48/52 and 40/60). Asai et al. showed these two blends could give morphologies (Figure 3-43) with original domain packing and domain shapes with non-CMC interfaces (Asai et al. 2015).

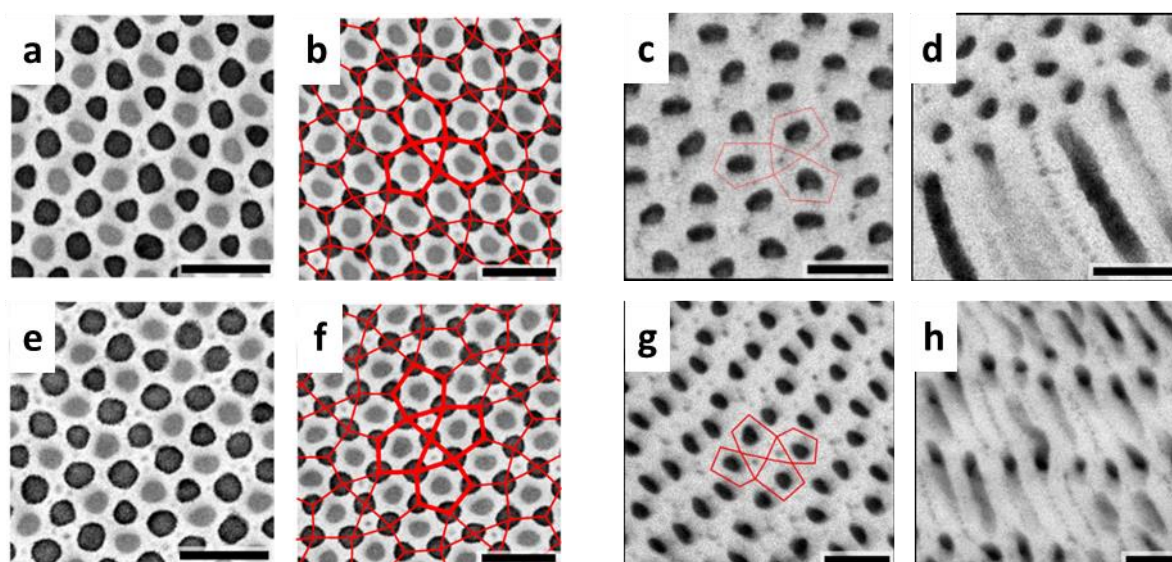


Figure 3-43. TEM images of the nanostructuration of $\text{ISP}\alpha/\text{ISP}\beta$ (48/52) blend (a - d) and (40/60) blend (e - h) in bulk. The images (c,d and g, h) described the structuration after selective staining of P2VP domain. The red line connects each PI domain showing the tiling pattern. Scale bars all represent 100 nm.

In bulk, the structure observed for (48/52) blend consists in rods of minor blocks (PI and P2VP) having different sizes and shapes, in a PS matrix Figure 3-43. These PI and P2VP rods were called “cylinders” in the original work of Asai (Asai, Takano, and Matsushita 2015), even if their shape is not uniformly circular as seen in Figure 3-43. A fraction of P2VP domains formed spheres. By connecting each PI domain, a tiling pattern consisting in one triangle and three pentagons was observed on the surface (P2VP cylinders being at the center of pentagons whereas P2VP spheres being in triangles). P2VP domains also create a deformed hexagonal pattern. The structure of (40/60) blend in bulk is a quite similar to the (48/52) blend morphology. In this case, tiling pattern composed of two triangles and four pentagons has been defined by connecting each PI domain.

Thin films (100 nm) of these two blends were treated in THF vapors for moderate annealing time (Figure 3-44). Dots and lines were observed on AFM images. Annex 5 shows AFM behavior of all series. Dots formed hexagonal pattern or square array. Center-to-center distance is c.a. 70 nm. Whatever the composition blend is, the pure pattern was never observed and always consisted in a mixture of dots and lines.

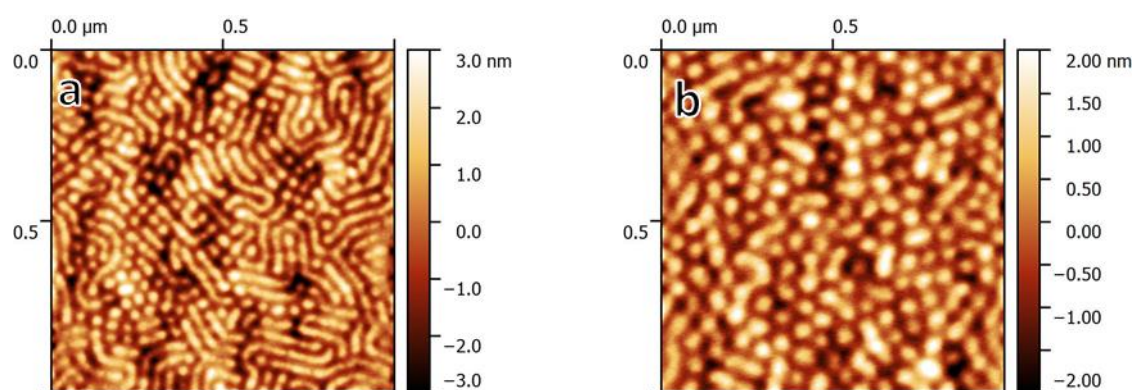


Figure 3-44. AFM topographic view of a blend of (a) ISP α and ISP β (48/52) thin films and (b) ISP α and ISP β (40/60) thin films after 6 hours solvent annealing in THF.

TEM top-view images are shown in Figure 3-45. After selective staining of PI, a mixture of hexagonally (zone1) and squared (zone2) packed white circles and elongated lines (zone 3) were observed. It reflected the mixed orientation composed of dots and lines observed by AFM. These non-stained domains revealed P2VP and PS blocks. The localization of PI as discrete domains is clear in zones 2 and 3, however, it is less obvious in zone 1. After selective staining of P2VP, a mixture of hexagonally packed black dots and lines were also observed.

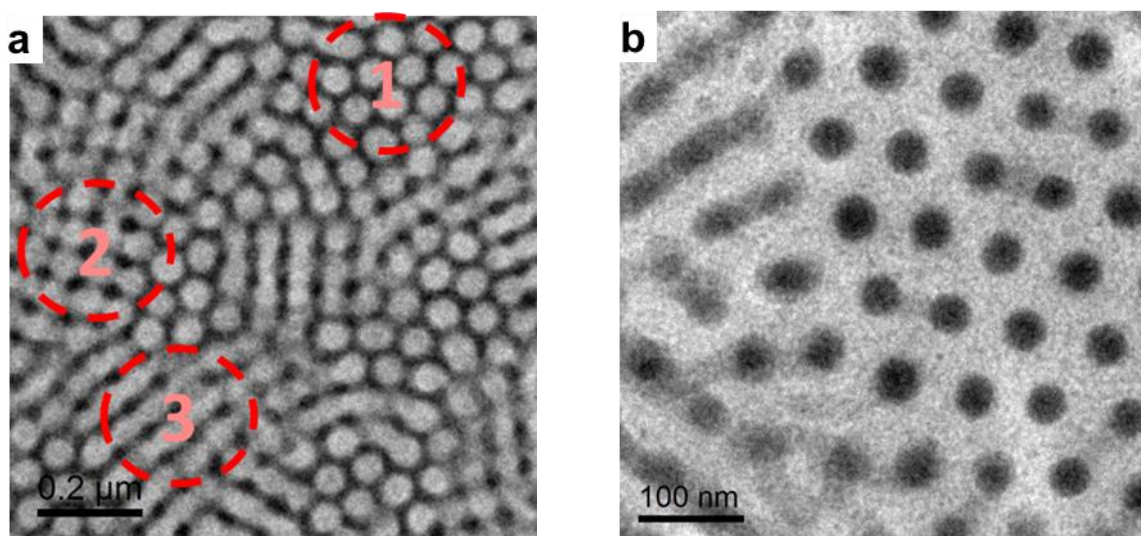


Figure 3-45. TEM images (top view) of blend of ISP α and ISP β (48/52) solvent annealed (THF) thin films: (a) after selective staining by OsO $_4$, (b) after selective staining by I $_2$.

On GISAXS pattern, the presence of one broad diffraction peak suggests a mixture of structures. Its position is in good agreement with center-to-center distance between dots domains measured by AFM and TEM.

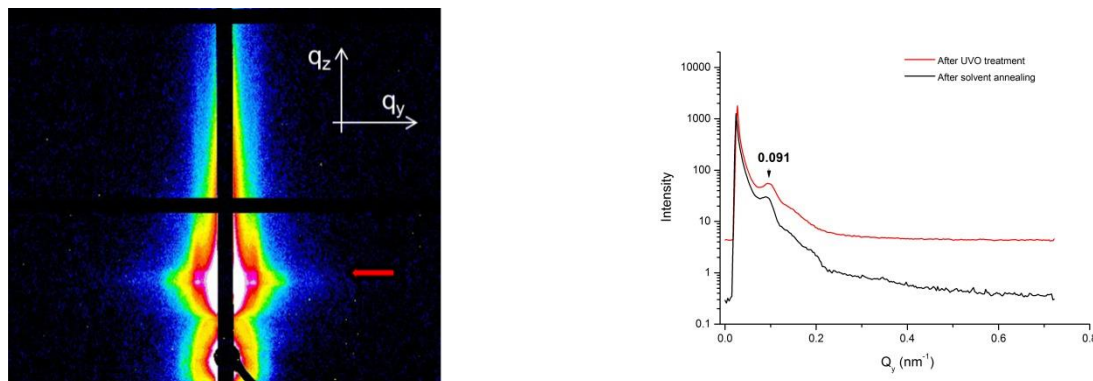


Figure 3-46. GISAXS result of a blend of ISP α and ISP β (48/52) thin films after UVO treatment.

This morphology differs from bulk morphology suggesting that the bulk morphology observed by Asai is energetically not as stable as the tetragonal structure observed previously. In this case, the morphology can be then easily destabilized by thin film configuration (surface energy, and also formation wetting layers which could artificially modify volume fraction of minority domains).

II.2.ISPX/ISPY BLENDS

Previously, we focused on triblock systems with number-average molar mass in the range from 90 to 124 kg/mol. In this part, thin films nanostructuration of blends of ISPX and ISPY (asymmetric chain lengths of two end-blocks) having respectively a number-average molar mass of 223 and 264 kg/mol, is presented (molar mass increases by a factor approximately 2 compared other systems).

In bulk, ISPX (0.12/0.67/0.21) exhibits a hierarchical structure with double hexagonal symmetry (centered hexagon of P2VP domains, each P2VP domain being surrounded by 6 PI domains). ISPY (0.42/0.56/0.02) forms a sphere-in-lamellae structure, in which PI and PS phases exhibit alternative lamellae and P2VP forms spheres inside PS lamellae. The 2 structures are described in Figure 3-47. (Asai et al. 2016)

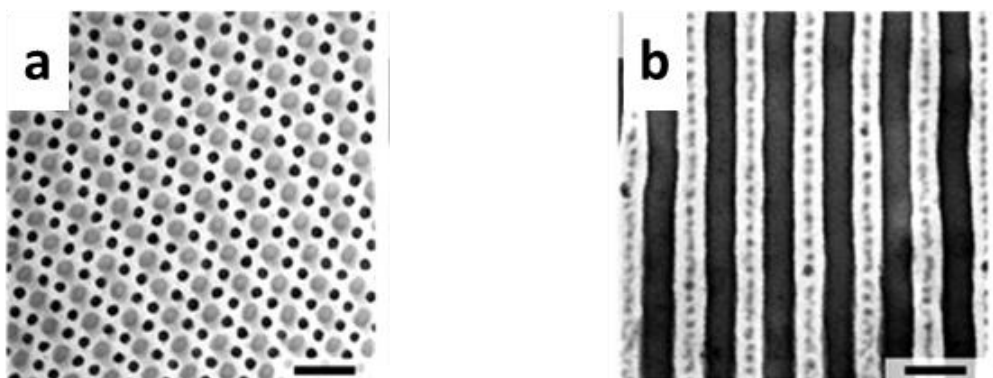


Figure 3-47. TEM images of ISPX (a) and ISPY (b) presented after selective staining of PI and P2VP by Asai. (Asai et al. 2016).

Asai has studied morphologies obtained from binary blends of ISPX and ISPY triblock terpolymer in bulk. (Asai et al. 2016) Tetragonal-packed rods have been observed in bulk for blends from 60/40 to 90/10. In this work, we will focus on (85/15) and (60/40) blends of ISPX/ISPY in thin film as presented in Table 9. For each system, two SVA treatments (in toluene and THF vapors) were performed.

Sample	Blend proportion	$\phi_{PI}/\phi_{PS}/\phi_{P2VP}$
ISPX/ISPY	85/15	0.17/0.65/0.18
	60/40	0.26/0.62/0.12

Table 9. Molecular characteristics of blend samples for ISPX/ISPY blend.

II.2.1.85/15 BLEND

Firstly, we focus on 85/15 blend of ISPX and ISPY triblock copolymers which gives a final composition with quite similar volume fraction of PI and P2VP minority domains. In bulk this blend presents tetragonally packed rectangular-shaped rods (with same diameter for PI and P2VP rods) as shown in Figure 3-48. (Asai et al. 2016).

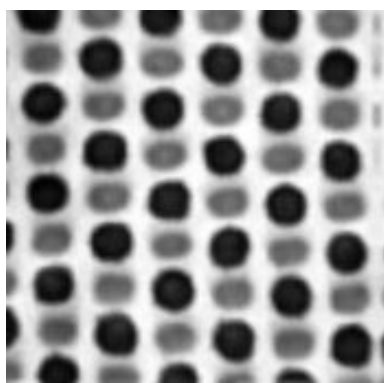


Figure 3-48. TEM image of 85/15 blend of ISPX/ISPY in bulk.

a. Structuration Kinetic

In this part, we will discuss results of SVA on ISPX/ISPY (85/15) blend thin films in THF and toluene vapors. After spin coating, non-organized film is obtained as shown in Figure 3-49.

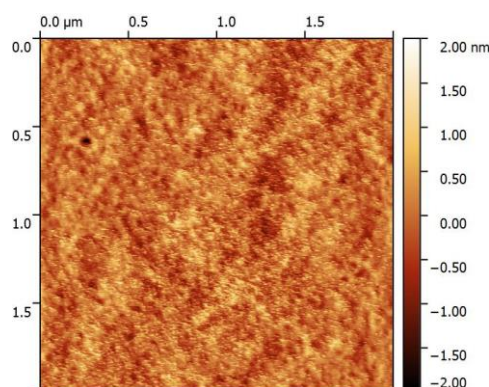


Figure 3-49. AFM height image of ISPX/Y (85/15) thin film after spin coating.

Firstly, SVA was performed in THF vapors at 25°C as presented in Figure 3-50. Films thicknesses were about 100 nm. After 3h SVA, an ordered hexagonal (violet) pattern was observed on films placed on the two highest levels (7 and 13.5 cm) and a fingerprint pattern (green) was obtained for the nearest level sample (1 cm). After 6 h, a hexagonal pattern (violet) was also again observed on the highest level (13.5 cm) and a fingerprint pattern (green) was obtained for the middle and the nearest level films (7 and 1 cm). Finally, line pattern (green) appeared on all levels after 9 h SVA in THF. Dewetting process was not observed.

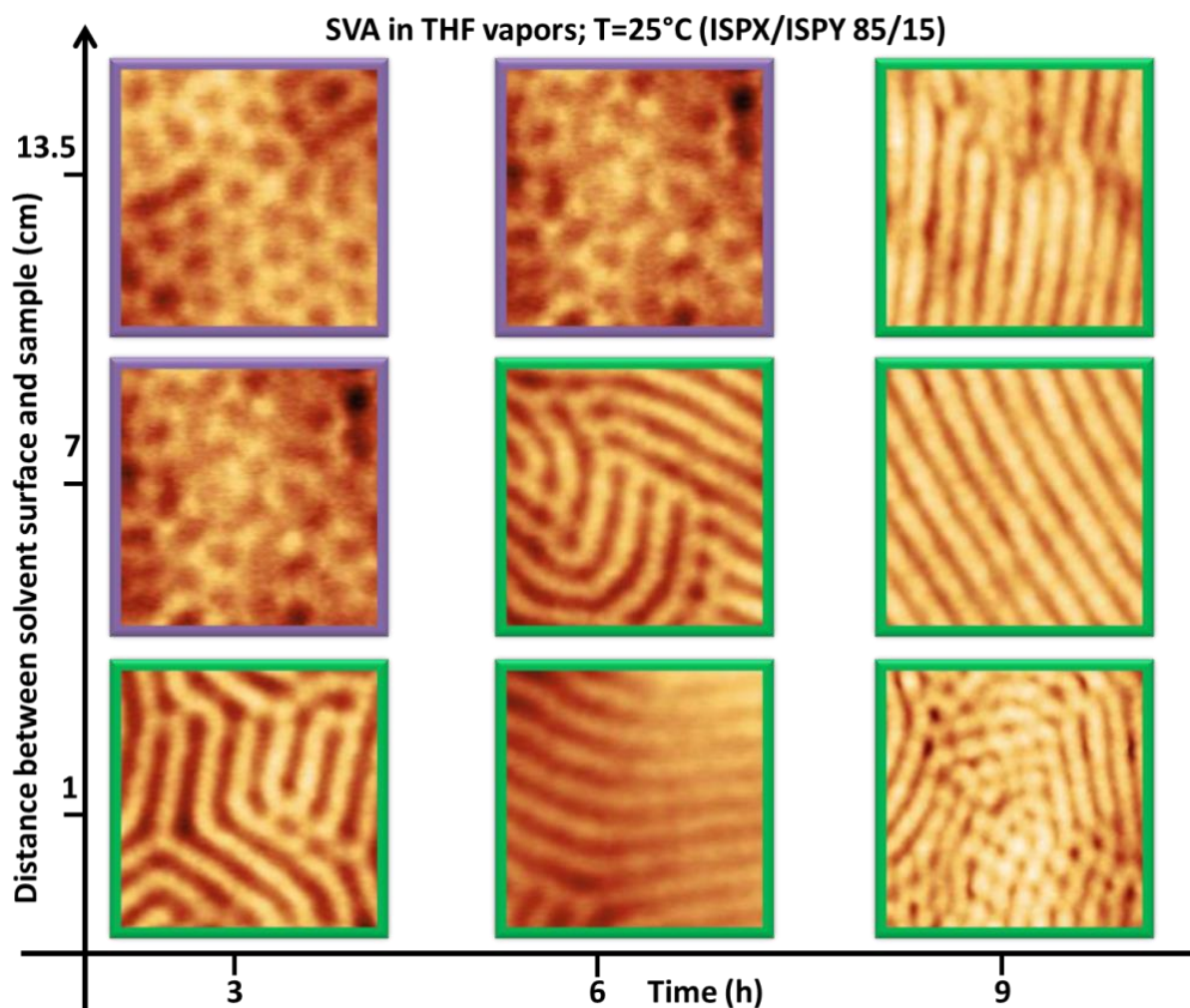


Figure 3-50. Structuration kinetics of ISPX/Y (85/15) blend thin films in THF vapors at 25°C.

Toluene

Figure 3-51 shows structuration kinetics obtained at 30°C (no structuration was observed at 25°C). After 5 h, hexagonal pattern was observed on the highest level (13.5 cm), square pattern started to be form on first level (1 cm). After 10 h and 15 h, square pattern was observed on the highest (13.5 cm) and second (7 cm) level but not on the first level (1 cm) where no ordered pattern was observed. Dewetting process was not observed under these conditions.

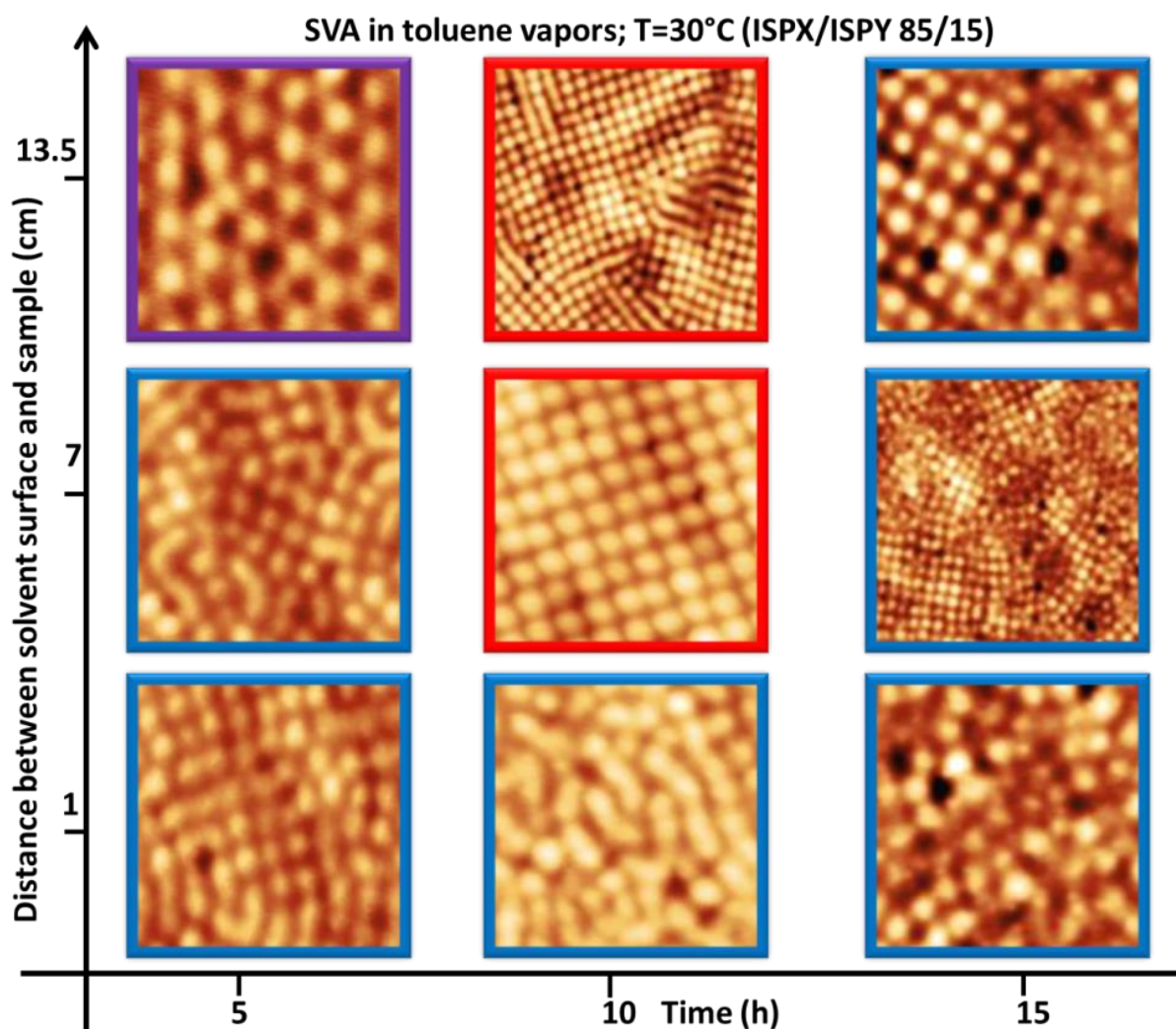


Figure 3-51. . Structuration kinetics of ISPX/Y (85/15) blend thin films in toluene vapors at 30°C.

THF and toluene SVA allowed to form three various types of morphology (hexagonal, square and fingerprint pattern) that will be studied in details in the following paragraph. The influence of the solvent nature will be also discussed.

b.Hexagonal pattern

Figure 3-52 shows a typical example of hexagonally packed dots obtained, in this case, after SVA in toluene vapors. Center-to-center between the features distance is 75 nm.

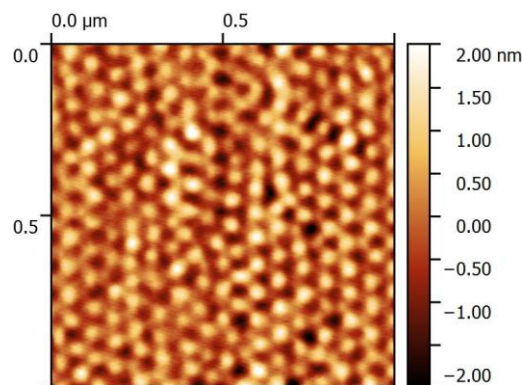


Figure 3-52. AFM height images of ISPX/Y (85/15) blend thin film after SVA in toluene.

TEM top view images clearly show a double hexagonal pattern (Figure 3-53) consisting in black (PI) and grey (P2VP) domains (on bright field TEM image, opposite color for dark field image) in a white (PS) matrix (Au nanoparticles deposited during the sample preparation appeared as small black dots on the figure). PI domains form a centered hexagonal pattern in which each PI dot is surrounded by six P2VP domains. Center to center distance between two PI domains and two P2VP domains are respectively 76 nm and 40 nm.

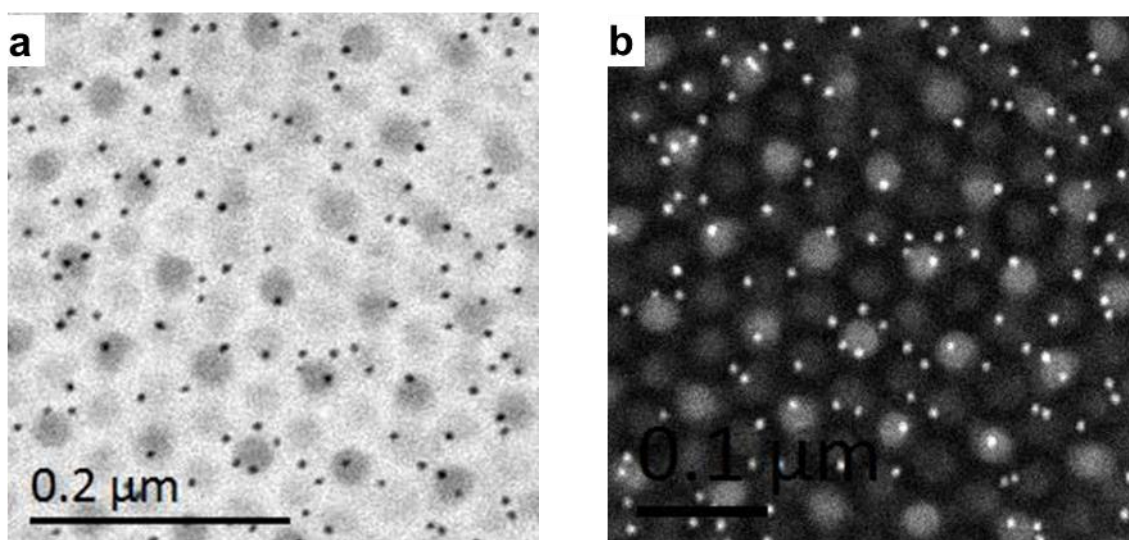


Figure 3-53. TEM image of ISPX/Y (85/15) with hexagonal structure (a) bright, (b) dark field images.

Figure 3-54 shows GISAXS profile of ISPX/ISPY blend after I_2 staining. Two strong diffraction peaks are observed at $q_0=0.093$ and $q_1= 0.16 \text{ nm}^{-1}$. These peaks can be attributed to the reflection of (10) and (11) planes of a hexagonal packing with the ratio of $q_1/q_0 = \sqrt{3}$. This allows to calculate the center-to-center distance ($2\pi/q_0 = 68 \text{ nm}$) which is in good agreement with AFM and TEM results.

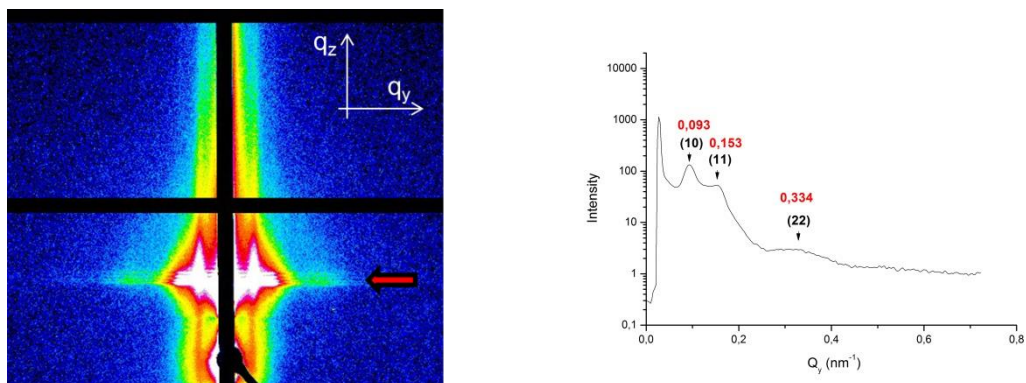


Figure 3-54. GISAXS pattern and corresponding in-plane profile of a blend of ISPX and ISPY (85/15) thin films in which hexagonal-packed structures of two different kinds of domains were observed by AFM and TEM after solvent annealing and selective staining by I_2 .

This morphology differs from the bulk one where tetragonally packed rods were observed.

c. Square pattern

Figure 3-55 shows the AFM and TEM images of square packed structure (obtained in this case after 3 hours SVA in toluene).

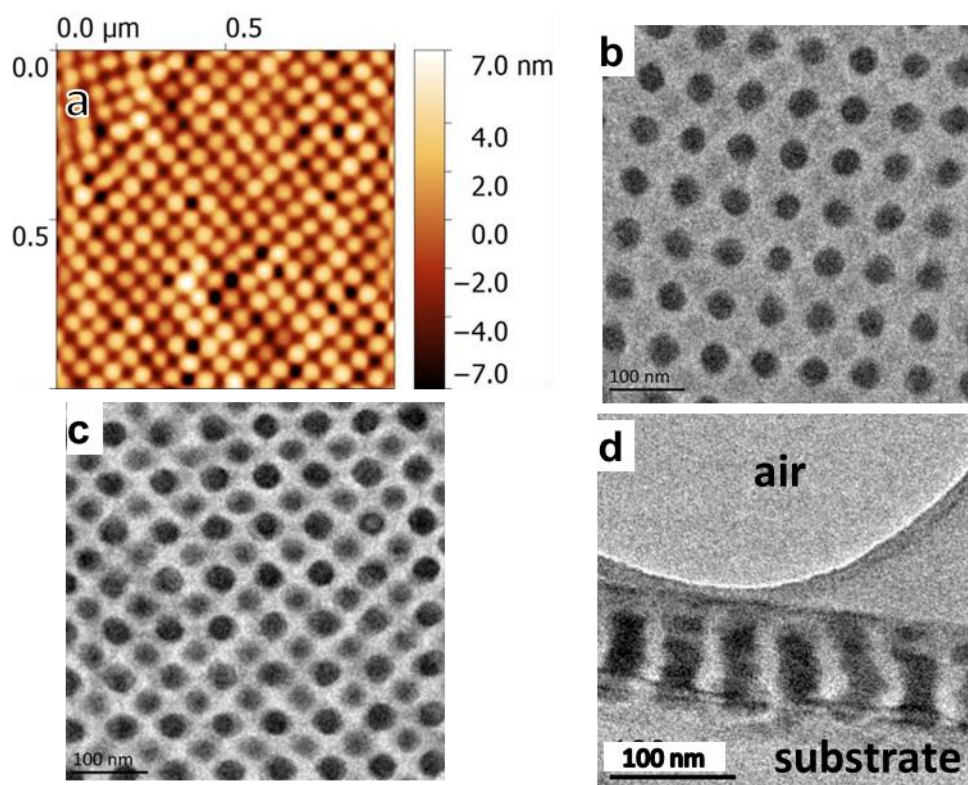


Figure 3-55. AFM and TEM top- and section-view images of ISPX/Y (85/15) blend thin films. (a) AFM image after SVA in Toluene; TEM top-view images (b) after staining of PI and (c) after staining of PI and P2VP; and TEM section-view image (d) after staining of PI and P2VP.

The center-to-center distance of domains is 70 nm. TEM top-view analysis after OsO_4 staining shows a well-ordered square array of PI domains. After selective staining of PI and P2VP, a square packed structure with two types of domains (PI and P2VP) having the same dimension (32 nm) was observed. The section-view showed stripes perpendicular to the

surface indicating that the morphology consists in rods that linked both interfaces. Consequently, we conclude that this morphology is similar to the bulk one (e.g. consisting in tetragonally packed rectangular-shaped rods).

The square morphology was confirmed by the GISAXS analysis. Figure 3-56 shows GISAXS profile of the ISPX and ISPY blend after selective staining. Strong diffraction peaks were observed at 0.093, 0.134 and 0.1841 nm⁻¹. These three peaks can be attributed to the reflection of the (10) (11) and (20) planes of a tetragonal packing. This allows to calculate the center-to-center distance ($2\pi/q_0 = 67.5$ nm) which is similar to AFM and TEM results.

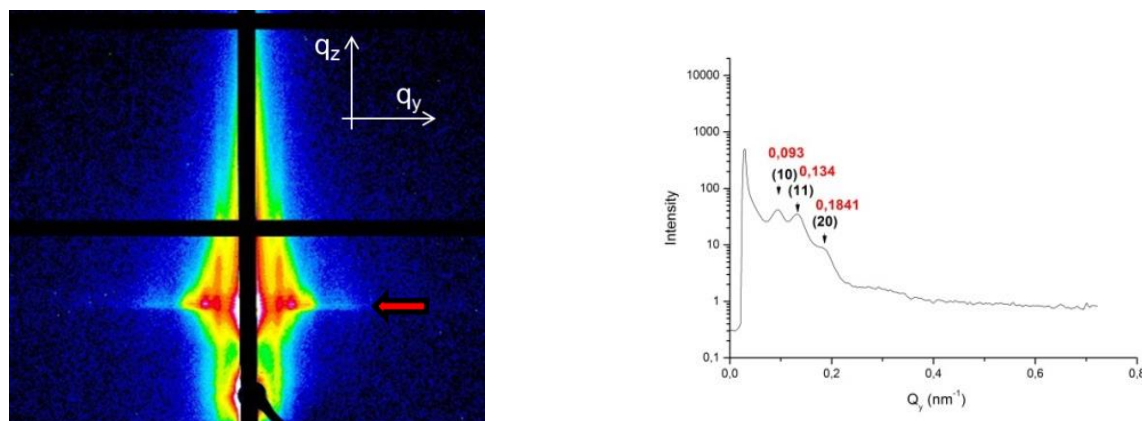


Figure 3-56. GISAXS pattern and corresponding in-plane profile of ISPX/ISPY (85/15) blend thin films: (a) and (b) after solvent annealing and staining by I₂.

d. Line pattern

Line pattern was observed only for solvent annealing in THF for longer SVA duration (9 h). AFM images were recorded and were displayed in Figure 3-57. The lines are distant of 75 nm.

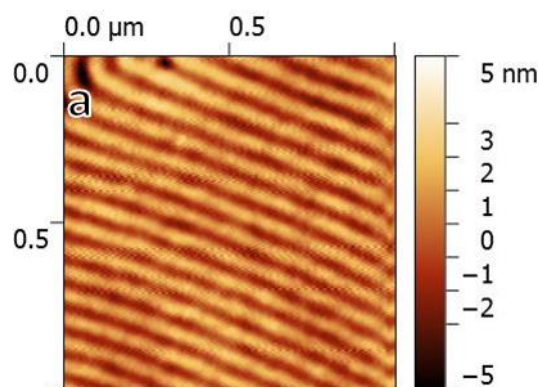


Figure 3-57. AFM height images of ISPX/Y (85/15) (a) after SVA in THF for 9 h.

TEM top-view image after OsO₄ and I₂ staining showed a three colored pattern composed of alternated lines of PI, P2VP and PS. The section-view shows a square pattern. The combination of these two observations leads to the conclusion that this morphology can be described as lying rods of PI and P2VP arranged in a tetragonal lattice. The presence of wetting layer is also observed at the two interfaces.

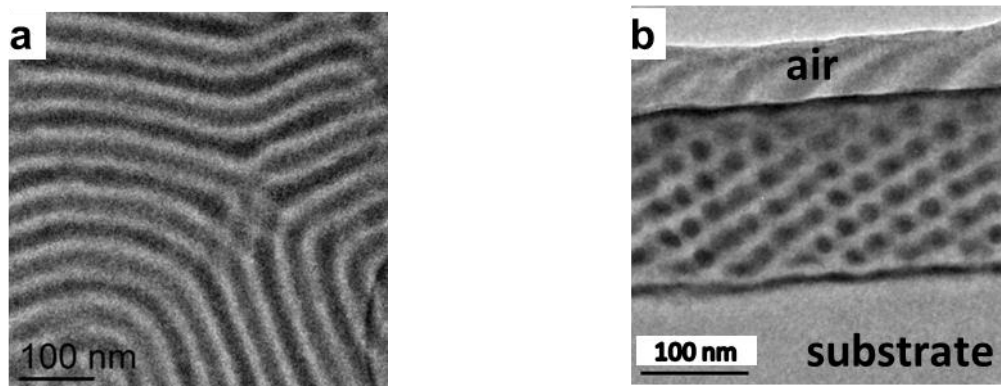


Figure 3-58. TEM (a) top- and (b) section-view images of ISPX/Y (85/15) blend thin films after staining of PI and P2VP.

This square arrayed parallel cylinders structuration was also confirmed by GISAXS analysis. Figure 3-59 shows experimental GISAXS patterns obtained for a nanostructured thin film after elimination of PI and GISAXS in-plane profile extracted from this GISAXS pattern. Two main scattering peaks observed for the film after treatment were at 0.084 and 0.17 nm^{-1} and correspond to scattering peaks of (100) and (200) planes perpendicular to the (001) surface. The observed values are in agreement with the lattice parameter $a = 75 \text{ nm}$ measured on AFM images and on TEM images structure.

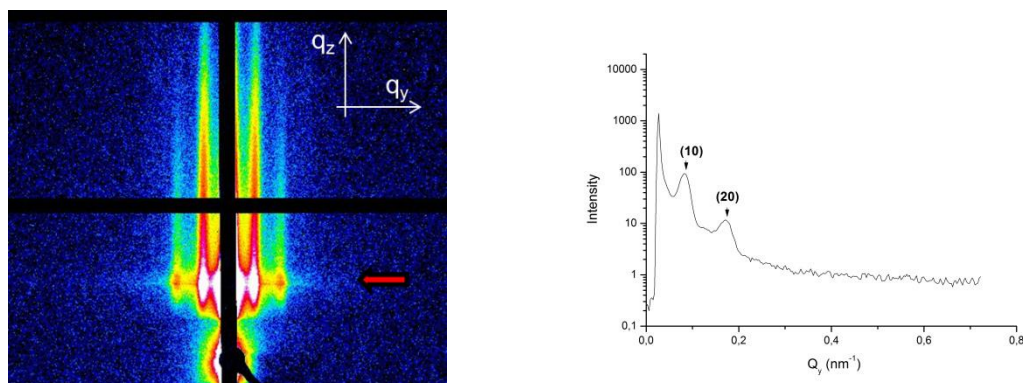


Figure 3-59. GISAXS pattern and corresponding in-plane profile of ISPX/ISPY (85/15) blend thin films.

e. Discussion on the morphology formation

As discussed above, three types of morphology were observed during SVA of ISPX/ISPY (85/15) blend: hexagonal, square and fingerprint patterns. Both square and fingerprint patterns correspond to the bulk structure (tetragonally packed rectangular rods respectively oriented perpendicularly and parallel to the surface). However, the hexagonal pattern is a new morphology for this blend. It is composed of a double hexagonal pattern with PI domains surrounded by six P2VP domains. Considering the higher incompatibility of PS/P2VP compared to PS/PI, this constitutes an unexpected result since this configuration creates more PS/P2VP interface.

It can be noted that the tetragonal packing of cylinders is normally the most stable configuration for triblocks. However, a double hexagonal packing can be also found when the BCP becomes asymmetric (like ISP X). Consequently, we assume that SVA artificially

modifies the relative volume fraction of the blocks (either by selective swelling or formation of a wetting layer). In this case, the hexagonal pattern is transient state which is only observed for moderate annealing time. It evolves toward square pattern, parallel or perpendicular depending of solvent nature. As previously demonstrated THF and toluene show different affinity toward the blocks. The exact phenomena involved in this complex morphological evolution is not yet fully understood and should deserve additional investigations.

II.2.2.60/40 BLEND

Now, we focus on the 60/40 blend of ISPX and ISPY which gives 0.26/0.62/0.12 composition with different volume fraction of PI and P2VP. In bulk this blend presents a tetragonally packed rectangular-shaped rods with a lattice parameter of 87 nm and diameter for PI and P2VP rods equal to 50 and 34 nm as shown in Figure 3-60 (Asai et al. 2016).

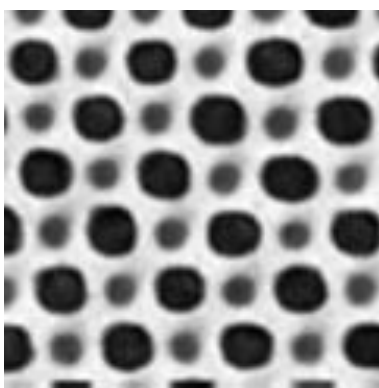


Figure 3-60. TEM image of 60/40 blend of ISPX/ISPY in bulk.

THF

Firstly we focus on the result of SVA treatment in THF vapors at 25 °C. The films thicknesses are about 100 nm.

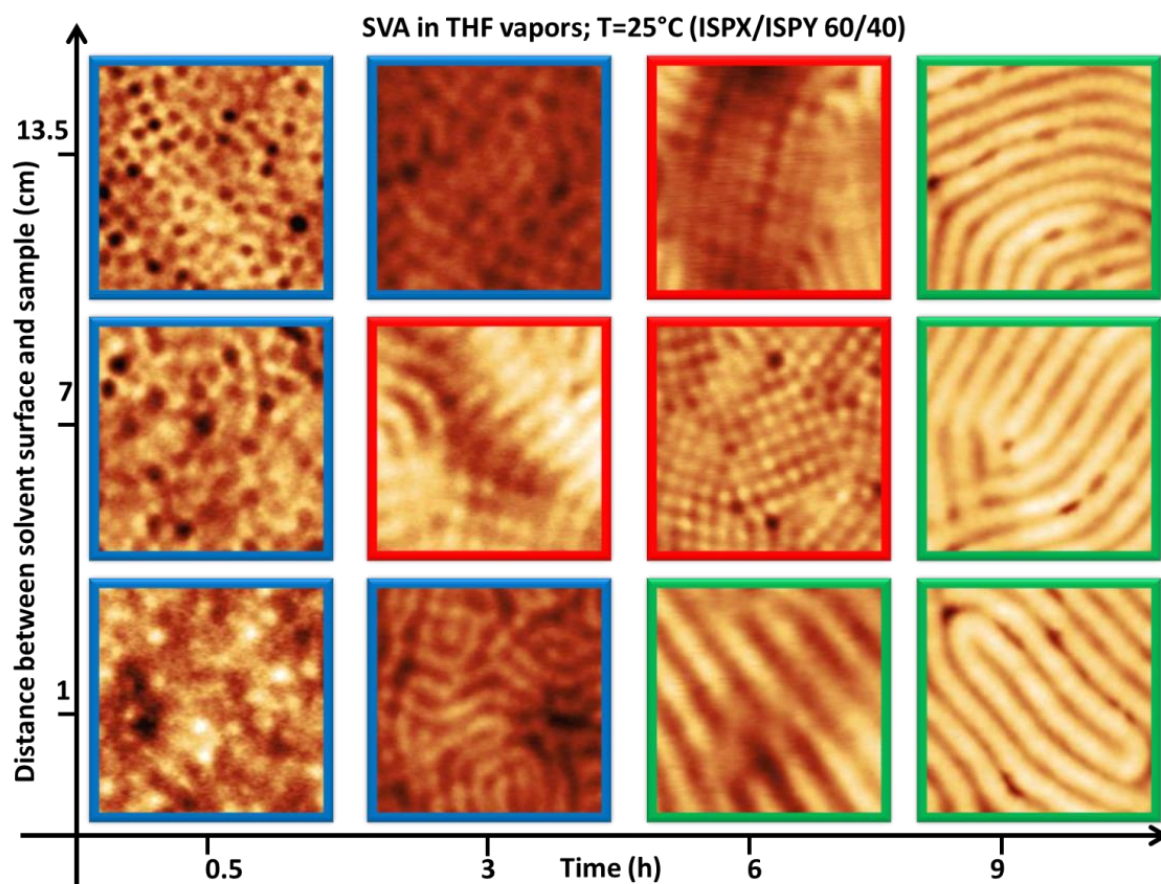


Figure 3-61. Structuration kinetics of ISPX/ISPY 60/40 blend thin films in THF vapors at 25°C.

A mixture of square array of dots and lines was observed on films after 3 and 6 h. After 9h, line structure appeared on all levels of systems. Dewetting process was not observed under these conditions. Dewetting of films occurs only after a few hours for SVA post-treatment at 30 °C and for that reason, the experiences at 30 °C were not realized.

Toluene

Firstly we focus on the results of SVA treatment in toluene vapors at 25 °C as illustrated in Figure 3-62. The films thicknesses are about 100 nm. No ordered structuration was observed during SVA in toluene at 25 °C, except for the longest SVA duration, the sample being closest to the solvent surface, where a square pattern was observed.

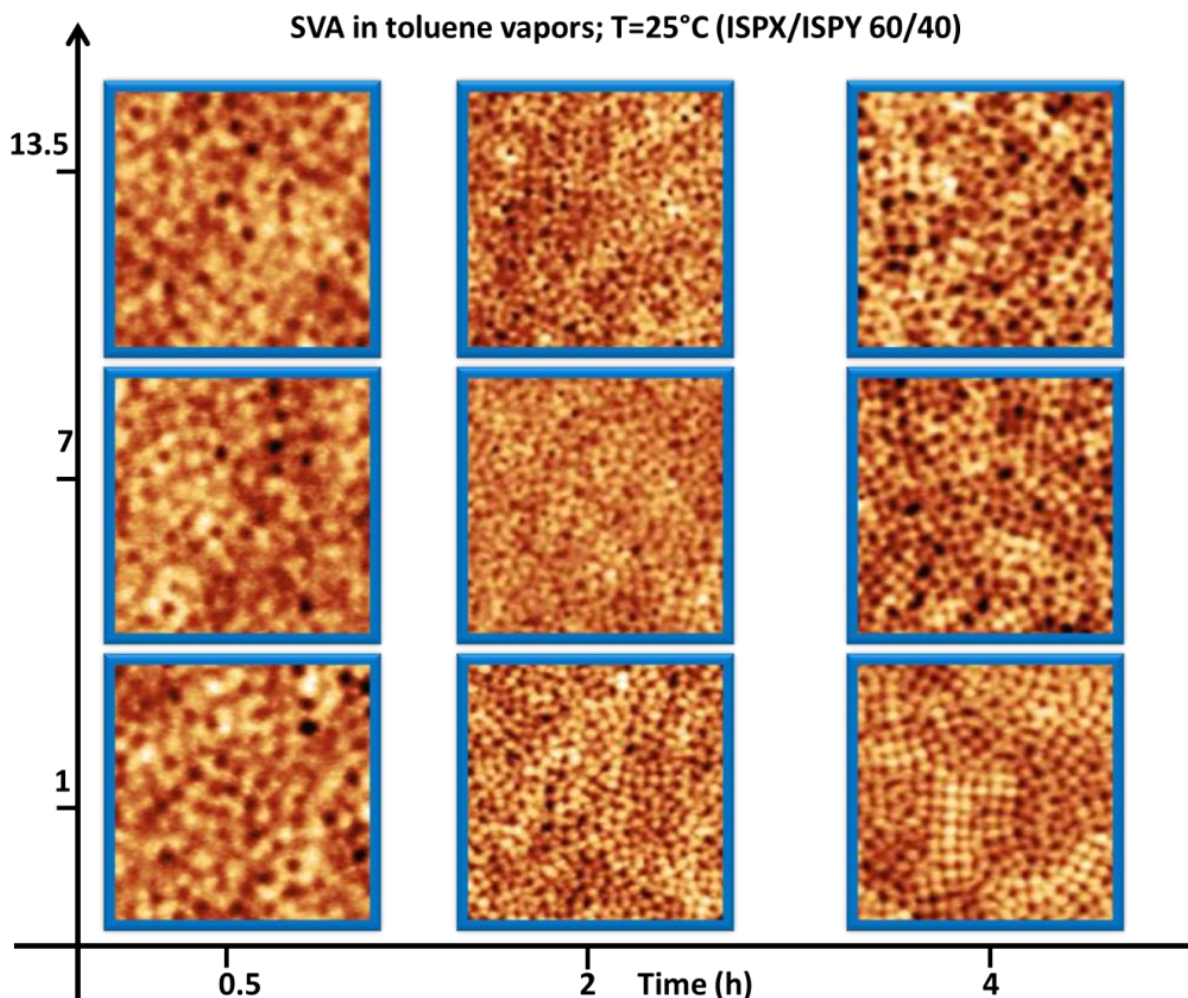


Figure 3-62. Structuration kinetics of ISPX/ISPY 60/40 blend thin films in toluene vapors at 25°C.

SVA treatment in toluene vapors at 30°C was performed for 5, 10, 15 and 24 h. After 5 h, there was no structuration. After 10 h, square pattern was observed on all levels, subsequently hexagonal structuration appeared on all levels after 15 h of SVA. Lastly, no organization was observed after 24 h treatment (in Figure 3-63). Dewetting process was not observed under these conditions.

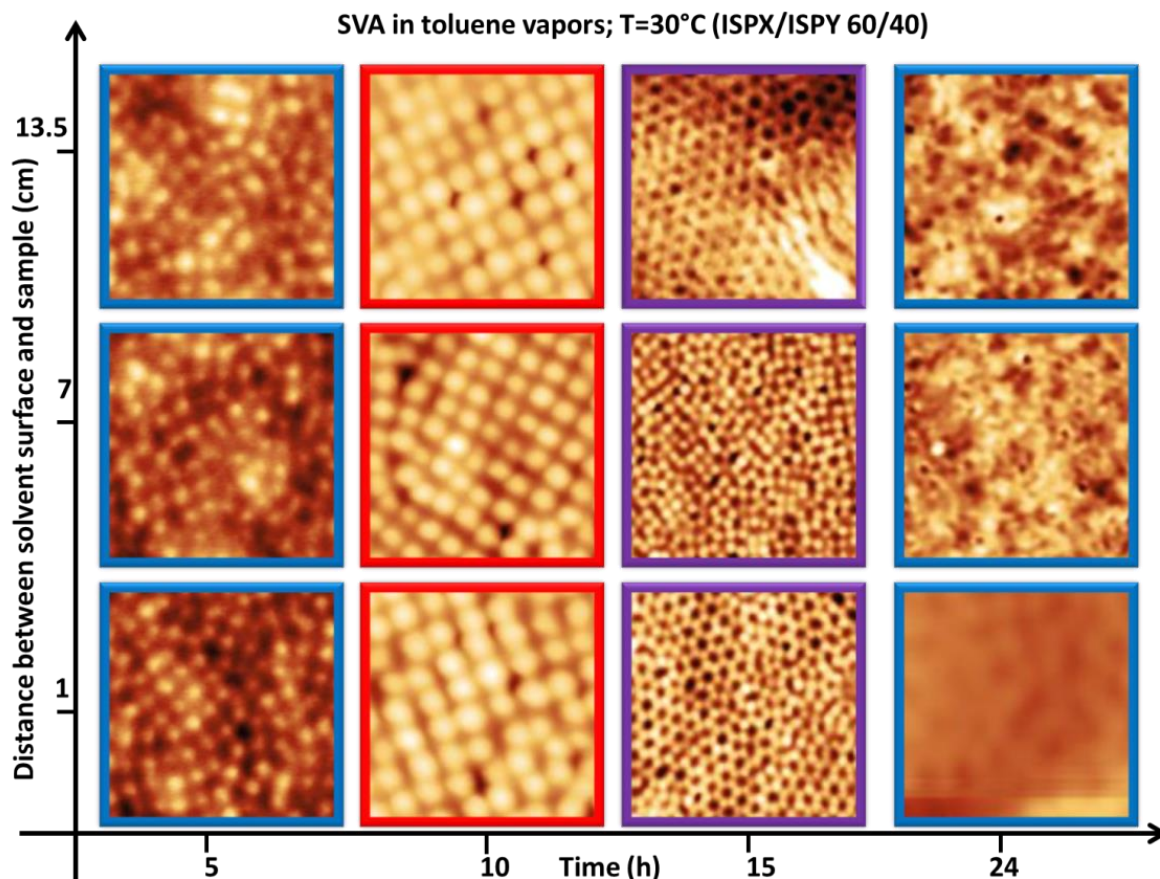


Figure 3-63. Structuration kinetics of ISPX/ISPY 60/40 blend thin films in toluene vapors at 30°C.

In this case, toluene SVA allowed to form two types of morphology (hexagonal and square pattern) that will be studied in the following paragraph.

a. Square pattern

AFM and TEM images are shown in Figure 3-64. AFM confirms the square packed pattern (both before and after UVO treatment). The center to center distance is evaluated to 80 nm. On TEM top-view image, tetragonal arrangement based P2VP domains is revealed after I_2 staining. Successive staining of PI and P2VP gives the four fold symmetry based on two different types of rods (PI and P2VP) with different sizes: PI domain has a diameter of 50 nm and P2VP domains a diameter of 30 nm. The center to center distance was evaluated to 80 nm. This morphology is similar to the bulk morphology.

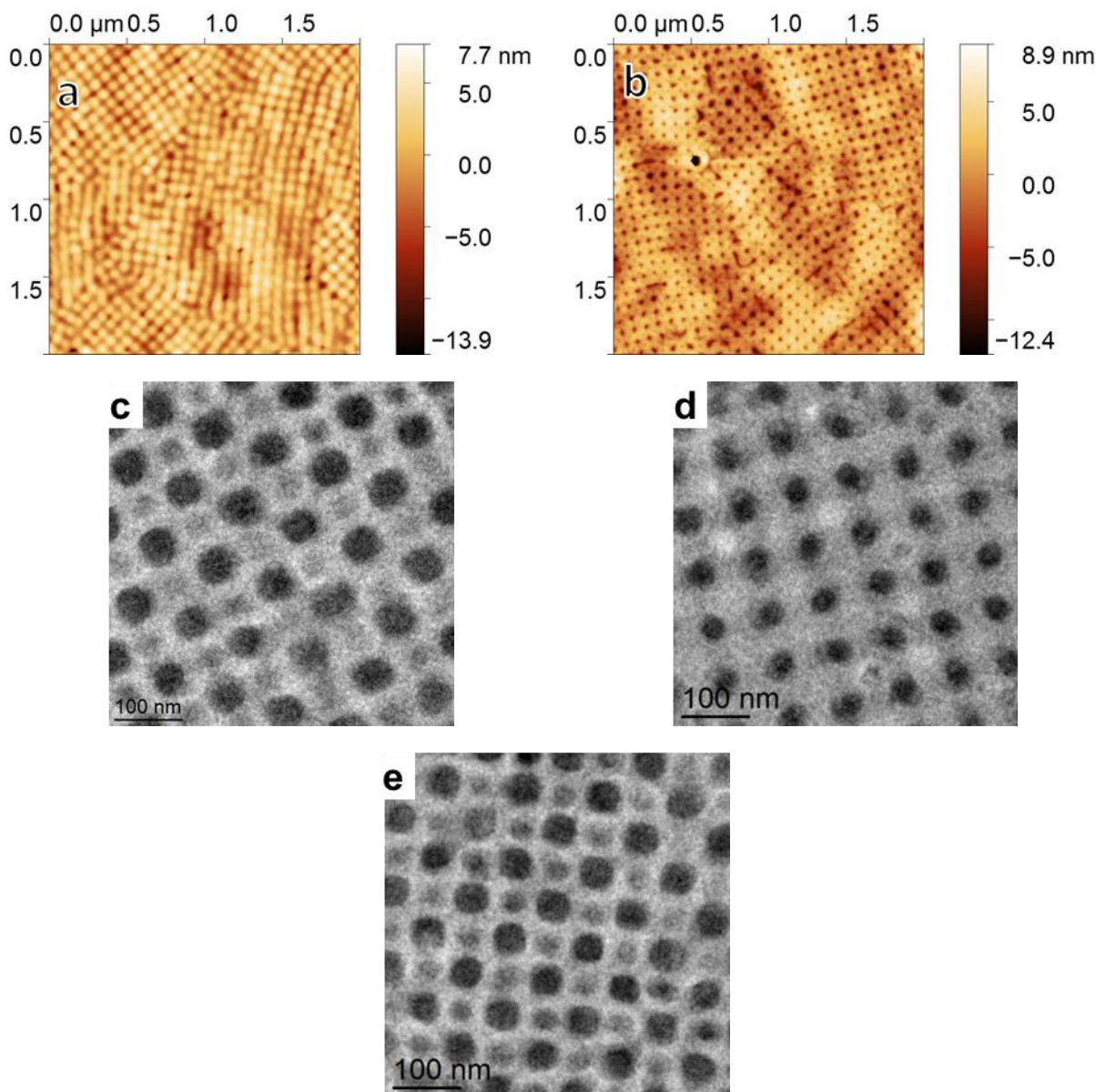


Figure 3-64. AFM and TEM top-view images of ISPX/Y (60/40) blend thin films. AFM height images (a) after SVA in toluene for 15 minutes; (b) after SVA in toluene and UVO treatment; (c) after SVA in toluene and swelling in ethanol; TEM top-view images (d) after selective staining of P2VP by I_2 (e) after selective staining of PI by OsO_4 and (f) after selective staining of PI and P2VP by OsO_4 and I_2 , respectively.

Figure 3-65 shows the GISAXS profile of the ISPX/ISPY (60/40) blend films with tetragonal pattern after UVO treatment (similar result was obtained after selective staining and shown in annex 6). Diffraction peaks are observed at $q_0 = 0.079, 0.113$ and 0.172 nm^{-1} . These three peaks can be attributed to the reflection of the (10) (11) and (20) plane of a tetragonal packing. This allows to calculate the center-to-center distance ($2\pi/q_0 = 79.5 \text{ nm}$).

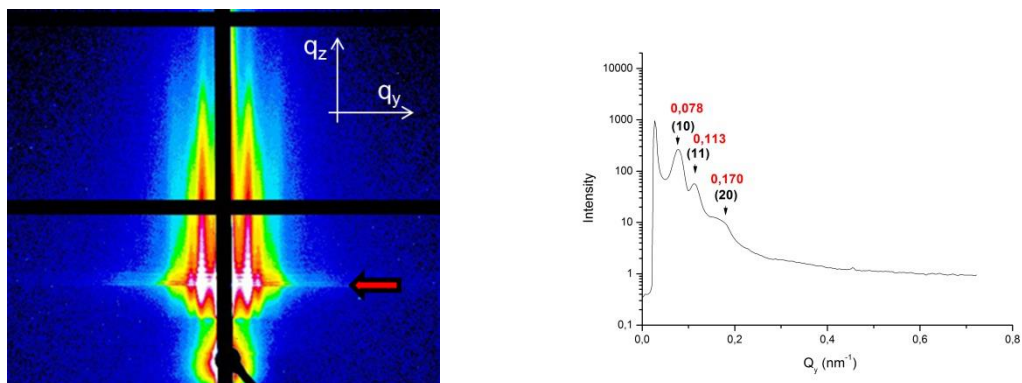


Figure 3-65. GISAXS pattern and corresponding in-plane profile of ISPX/ISPY (60/40) thin films: (a) and (b) after solvent annealing and UVO.

b.Hexagonal pattern

After longer SVA in toluene, AFM displays a new type of structuration with a hexagonal symmetry (Figure 3-66). After selective elimination of PI by UVO treatment, a centered hexagonal pattern formed by six holes (50 nm diameter) surrounded by six smaller holes (30 nm diameter) is observed. TEM top view images are presented in Figure 3-66. After PI staining, a centered hexagonal pattern was observed (domains size=50 nm, consistent with AFM). Six small domains surrounding the PI domains are also observed and attributed to P2VP due the natural contrast between PS and P2VP. In this case, and due to a lack of time, sample with both PI and P2VP stained was not obtained. Center to center distance between PI domains is c.a. 100 nm calculated from TEM image.

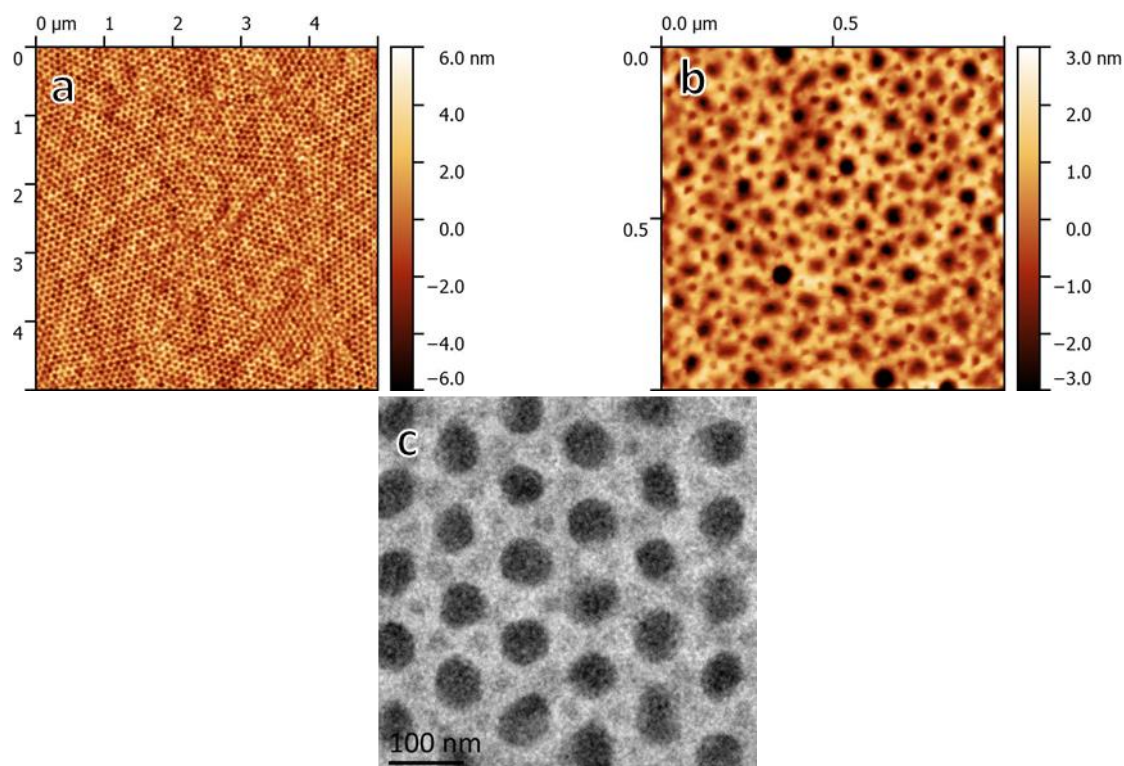


Figure 3-66. AFM and TEM top views images of ISPX/Y (60/40) blend thin films after SVA in toluene. AFM images (a) after SVA (b) after UVO treatment and (c) TEM top-view image after staining of PI by OsO_4 .

c.Line pattern

After 24 THF exposure, AFM height image displays lines with a periodic distance of 90 nm (Figure 3-67). TEM top-view results confirmed the same line morphology. The selective staining of PI and P2VP allows to observe separately the morphology of each PI and P2VP domain. The section-view analysis was not performed on these samples but we assume that as other blends, the line structure is a signature of the parallel oriented cylinders structure on substrate.

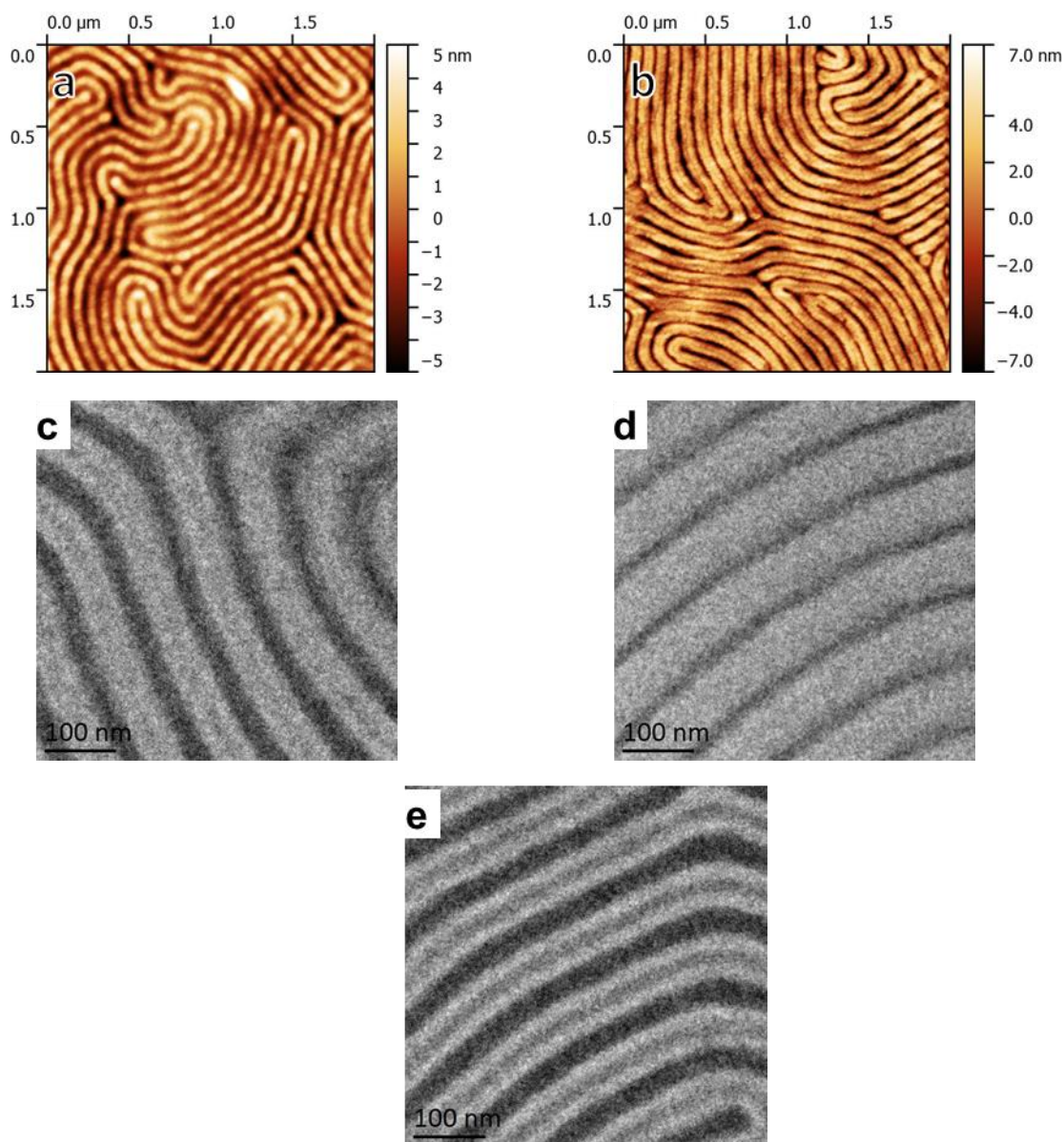


Figure 3-67. (a) and (b) AFM and (c), (d) and (e) TEM top view images for parallel oriented morphology: (a) after SVA (b) after SVA and UVO treatment, (c) after selective staining of PI by OsO₄; (d) after selective staining of P2VP by I₂ and (e) after selective staining of PI by OsO₄.

The parallel morphology was confirmed by GISAXS analysis. Figure 3-68 shows experimental GISAXS pattern obtained for a nanostructured thin film after elimination of PI and in-plane profile extracted from this GISAXS pattern. Scattering peaks at 0.067 and 0.138 nm⁻¹ were observed and correspond to scattering peaks of (100) and (200) planes perpendicular to the (001) surface. The observed value are in agreement with the observed lattice parameter $a = 93$ nm of the tetragonal structure.

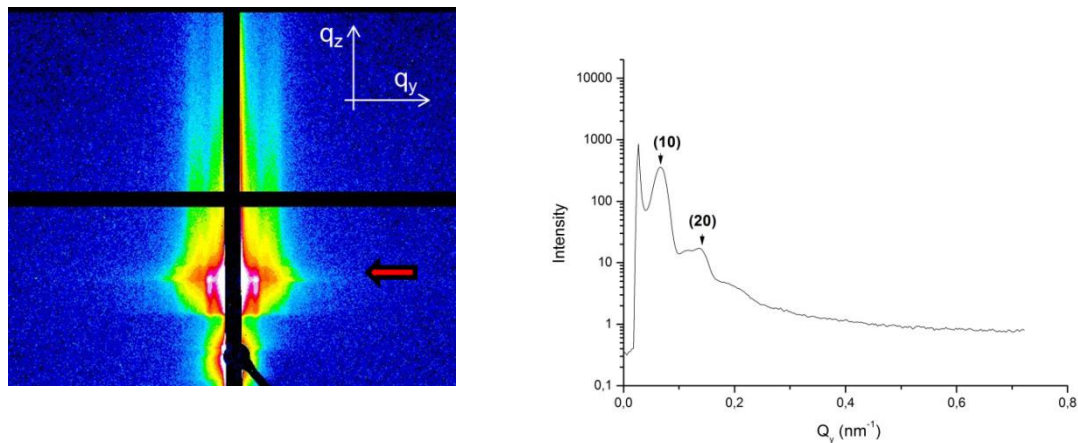


Figure 3-68. GISAXS pattern and corresponding in-plane profile of ISPX/ISPY (60/40) thin films.

d. Discussion on the evolution of the pattern as a function of time

ISPX/ISPY (60/40) blend has a global volume fraction of 0.26/0.62/0.12 which is typical for hexagonal pattern. However, a tetragonal pattern was firstly observed after SVA in toluene (as in bulk). For longer annealing time, a tetragonal to hexagonal transition is observed. Similarly to what we assumed in the case of the previous blend, the formation of wetting layer and/or selective swelling could lead to this transition. For example, it can be assumed that, as the solvent film interaction starts at the film/air interface, the PI wetting layer is firstly formed at the beginning of SVA post treatment. In this case, PI proportion decreases in total of film due to the formation of wetting layer and the proportion of end blocks “artificially” become equal in this step, which allows to form square packed morphology. Then, P2VP wetting layer also starts to form on the film/substrate interface. The diminution of P2VP proportion inside the film leads to its initial volume fraction which can explained the hexagonal pattern.

II.2.3. CONCLUSION

In conclusion, order-order transition was observed for ISPX/ISPY (85/15) and (60/40) blends in thin films and the presence of tetragonal and hexagonal pattern is confirmed by different characterization methods after SVA in THF and in toluene vapors. We observed structure reorientation (from perpendicular to parallel oriented cylinders) as well as order-order transition. The fine understanding of the phenomena driving this behavior is still not reached and would need further experiments. A possible scenario may be however proposed.

It can be explained by the swelling rate of polymers in different solvents. With the high pressure and the more important swelling ratio in THF, polymers have not enough time

to reorganize to all possible morphologies and the most thermodynamically stable orientation was obtained rapidly in THF vapors. In toluene case, the transition of different structure is observed due to the lower solvent vapor pressure and swelling rate of polymers than THF case. It is logical to obtain the hexagonal pattern as a “finally” structure (before parallel oriented cylinders) for 60/40 blend with a total volume fraction of (0.26/0.62/0.12) which is asymmetric (match with hexagonal structuration on phase diagram). The same hypothesis for 85/15 blend with a final volume fraction of (0.17/0.65/0.18) is confirmed by the experimental results. The sequence of morphology and the transition of structure were explained by the formation of wetting layers under thin film effect.

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4. CONCLUSIONS AND PERSPECTIVES

In this thesis, the confinement effect in thin films was systematically investigated on the nanostructuration of various ABC linear triblock terpolymer systems (neat or blend). Especially for the binary blend systems (ISP α /ISP β and ISPX/ISPY) several atypical morphologies were obtained which have never been observed experimentally in thin film. All developed structures were compared respectively to their bulk morphologies developed by Matsushita's team in University of Nagoya.

Chapter 2 allows to make a solvent choice for several crucial steps of nanostructuration: elaboration of films (solution solvent), Solvent Vapor Annealing (SVA) and identification of blocks (selective swelling of one block in ABC system). We have also developed methodologies for identification of the morphologies in GISAXS. GISAXS characterization was performed on UVO treated (PI selectively eliminated) or stained film (staining by I₂ for P2VP) to increase the electronic density contrast between different domains. This method has never been reported to our knowledge for the small-angle X-ray scattering study of block polymers. This could be very useful for structural characterization of BCP composed of segments with similar electronic densities.

In Chapter 3, nanostructuration of different ISP linear triblock terpolymer was investigated. For all systems (blend or neat polymer) a common feature was the formation of wetting layers at film/substrate (P2VP) and film/air (PI) interfaces and the transition of all morphologies to tetragonally packed cylinders oriented parallel to surface after a long SVA in THF.

Firstly neat triblock systems (ISP19 and ISP23) were studied. We observed that nanostructuration of ISP19 in thin film is more complex than bulk organization and it is not similar to bulk morphology developed by Mogi. Under thin film effect, CYL-SPH transition was observed which is facilitated by the position of ISP19 on phase diagram. After long solvent annealing, a tetragonally packed cylinder oriented parallel to surface was observed. For moderate annealing time, ISP23 forms a G_A morphology in thin film, similarly to bulk organization. However, we found that this thin film configuration leads to a preferential orientation of the G_A structure (with the (011) plane parallel to the surface) and a contraction of the lattice due to shrinkage. After longer solvent annealing, a transition from this structure to a P2mm structure with alternating cylinders of PI and P2VP was observed which has to our knowledge never been observed. For these neat triblocks, we obtained different structures compared to bulk morphology.

Then we focalized on blends of ISP triblocks, which constitute systems that are more complex. This part present blends of ISP α /ISP β with different proportion (60/40; 48/52; 40/60) which have already studied in bulk. ISP α /ISP β (60/40) exhibits a new structure with non-CMC in bulk which is very interesting to reproduce in thin film for potential application. As already proposed in the bulk, the formation of non-CMC interface could be explained by the localization of component polymer chains along domain interfaces (mix of short and long chains of end blocks). We demonstrated the possibility to achieve tetragonally packed rectangular rods of PI and P2VP, oriented perpendicularly to the surface in thin film. Apart

from creation of wetting layers at the interfaces, we did not observe deviation of morphology compared to the bulk one for this blend. This results suggests that the bulk morphology of rods is energetically very stable, and not perturbed by the thin film configuration. For long SVA in THF, orientations of cylinders were changed. We also investigated behavior of other blends of ISP α /ISP β (48/52) and (40/60). In contrast to the (60/40) blends, the obtained morphology differs from the bulk structure suggesting that morphology observed by Asai is energetically not as stable as the tetragonal structure observed previously. In this case, the morphology can be then easily destabilized by thin film configuration (surface energy, and also formation wetting layers which could artificially modify volume fraction of minority domains).

Eventually, we focused on blends of ISPX and ISPY which have a more important molecular weight comparing other ISP systems. We investigated two blend proportions (85/15 and 60/40) in thin film. These blends form tetragonally packed rods in bulk, however in thin films three types of morphologies were obtained: hexagonal, square and fingerprint patterns. The hexagonal pattern is a new morphology for this blend. Square and fingerprint patterns correspond to the bulk structure (tetragonally packed rectangular rods respectively oriented perpendicularly and parallel to the surface). Some hypotheses are presented for the formation of hexagonally packed cylinders for these blends. Because of the formation of wetting layer and selective swelling of blocks in solvent, it can be assumed that SVA artificially modifies the relative volumic fraction of the blocks and in this case, the hexagonal pattern is transient state which is only observed for moderate annealing time. We need more time to fully understand this morphological evolution. In short, an order-order transition was observed for ISPX/ISPY blends in thin films.

I. ONGOING WORK: ISP α /IS BLEND

In bulk, Ahn et al. 2017 investigated core shell gyroid (CSG) structure at highly asymmetric volume fractions obtained by blending a ISP triblock terpolymer and a IS diblock copolymer, as previously mentioned in Chapter I. This binary blend of ISP and IS with overall volume fraction of $\phi_I=0.12$ $\phi_S=0.79$ and $\phi_P=0.09$ exhibited CSG at highly asymmetric volume fraction, where P2VP having the smallest volume becomes a thin matrix (Ahn et al. 2017).

Blending of ABC asymmetric triblock (with sort A chains) with AB symmetric diblock has attracted our attention to obtain two types of interface (CMC (for C end block) and non CMC (for the blend of short and long A blocks)) in the same thin film. It was interesting also to observe if a tetragonally packed morphology could be obtained by blending diblock and triblock with a symmetric volume fraction in final (as a blend of ISP α /ISP β 60/40).

For that purpose, ISP α with IS were blended. As we discussed earlier, ISP α have short chains of PI (6% volume fraction) and long chains of P2VP (32% volume fraction) with 62% middle block PS. IS diblock is almost symmetric with 55% PI and 45% PS blocks. In this case we blended short and long chains of PI. As a majority block, PS will be matrix of the organization. Films were deposited by spin coating and the thickness of film was 100 nm. This blend has never been studied in bulk.

Figure 4-1 shows AFM and TEM top-view images of blend. After SVA, we observed a hexagonal pattern of dark domains. Successive staining by OsO₄ and I₂ showed a double

hexagonally packed morphology composed of hexagonally arrayed pattern of P2VP domains surrounded by six small PI dots. The diameters of domains are different (45 nm for PI and 75 nm for P2VP). The formation of different types of dots can be explained by the incompatibility of P2VP and PI with matrix (PS). To understand better, it is important to perform more analysis on this blend.

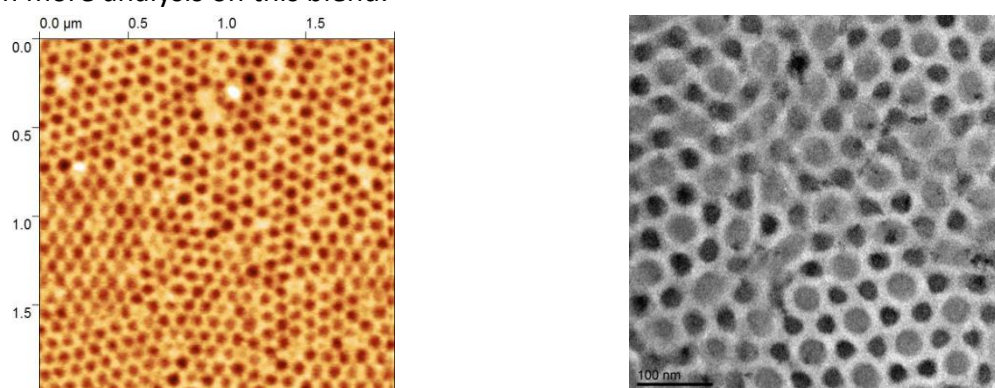


Figure 4-1. AFM and TEM top-view image of ISP70/IS blend

II. INORGANIC TEMPLATE

3D nanostructured inorganic materials appear as promising candidates for various practical applications (Vukovic, Brinke, and Loos 2013). Possibility of selective etching a block of system allows to obtain porous materials which can be a good candidate to form metal nanofoams (Vukovic, Brinke, and Loos 2013; Nguyen, Vayer, and Sinturel 2018). For example, when a thin film of ISP triblock copolymer is exposed to an UVO treatment, the unsaturated bonds along the PI backbone are cleaved, whilst the PS and P2VP is unchanged. (PS can even crosslink under the treatment condition). In this case, it is interesting to eliminate organized PI from system (for example tetragonally packed PI rods) and used PS and P2VP domains as a sacrificial mask for subsequent pattern transfer. (Nunns, Gwyther, and Manners 2013)

In a generally way, ordered BCP structure can be filled with inorganic materials (i.e. metals) to have more appealing properties. This process encompasses several steps (Vukovic, Brinke, and Loos 2013):

1. Selective removal of the sacrificial polymer block,
2. Backfilling of the porous structure with inorganic material (e.g., metal),
3. Removal of the remaining polymer template Figure 4-2.

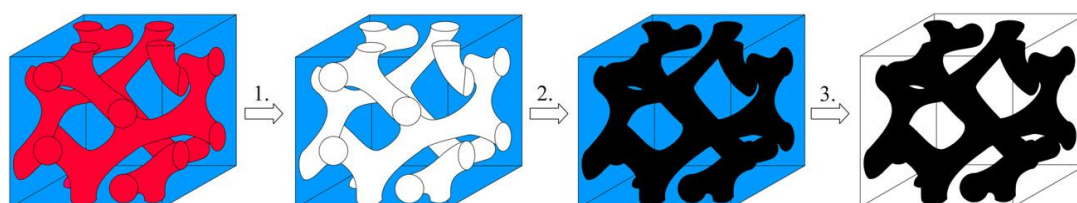


Figure 4-2. Block copolymer template directed preparation of ordered inorganic nanostructures: 1. selective removal of the sacrificial polymer block, 2. backfilling of the porous structure with inorganic material (e.g., metal), 3. removal of the remaining polymer template. (Vukovic, Brinke, and Loos 2013).

The tetragonally packed rods morphology (perpendicular and parallel to surface) based on ISP α /ISP β (60/40) thin films was subjected to inorganic replication in order to assess internal structuration of the film and fully confirm the morphology. After UVO treatment, the holes of PI were replicated by infiltration with sol-gel precursors followed by a brief thermal treatment in order to provoke precursors condensation and the polymer phase pyrolysis. After inorganic materials deposition, square packed dots and fingerprint morphologies were revealed as shown in Figure 4-3.

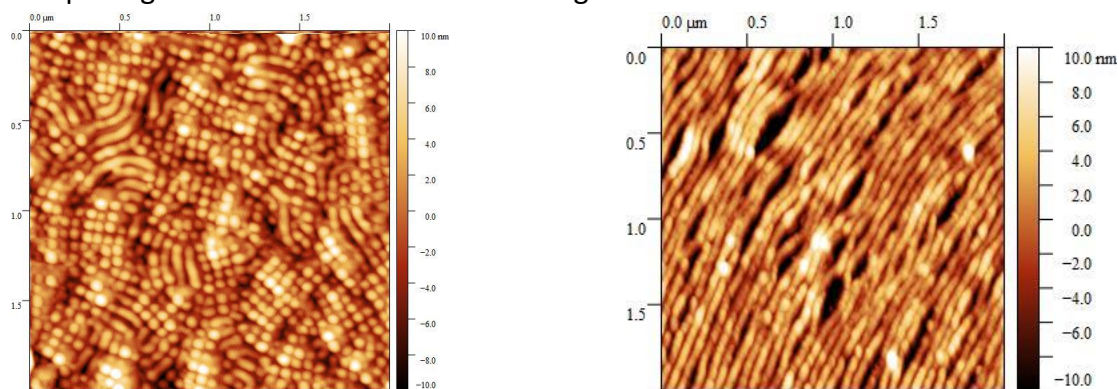


Figure 4-3. AFM image of the silica replica of the porous ISP α /ISP β (60/40) thin film obtained after Pi extraction for the dots.

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ANNEX

Annex 1. Calculation of solvent quantity for each system (Teflon box and Glass jar)

By using Antoine Equation Parameters (NIST Website)

$$\log_{10}(P) = A - (B / (T + C))$$

P = vapor pressure (bar)

T = temperature (K)

Volume of teflon box = 60 mL Volume of glass jar = 1000 mL

Molar mass of Toluene = 92 Molar mass of THF = 72

	M (g/mol)	T °C	Pression mmHg	Volume cm3	PV	n mole (PV/RT)	masse theor (g)
THF	72	25	163	1000	2,17E+01	8,7E-03	0,630
	72	25	163	60	1,30E+00	5,2E-04	0,038
	72	30	202	1000	2,69E+01	1,1E-02	0,767
	72	30	202	60	1,61E+00	6,4E-04	0,046
Toluene	92	25	29	1000	3,86E+00	1,6E-03	0,143
	92	25	29	60	2,31E-01	9,3E-05	0,009
	92	30	36,85	1000	4,90E+00	1,9E-03	0,179
	92	30	36,85	60	2,94E-01	1,2E-04	0,011

Figure 4. Calculation of solvent (THF and Toluene) quantity for each experimental chamber (Teflon box or glass jar) with different volume and for each temperature (25°C and 30°C)

Annex 2. Polymer-solvent affinity using the Hansen solubility parameters (HSP)

In Hansen's approach, total solubility parameter of compound is divided in three components: the energies from polar (δ_p) force between molecules, dispersion (δ_d) force between molecules and hydrogen bonding (δ_h) between molecules (Hansen 2000; Vayer, Vital, and Sinturel 2017). The equation is:

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$$

For estimation of the polymer-solvent affinity:

$$(R_a)^2 = 4 * (\delta_{D,S} - \delta_{D,P})^2 + (\delta_{P,S} - \delta_{P,P})^2 + (\delta_{H,S} - \delta_{H,P})^2$$

The Relative Energy Difference (RED) = R_a / R_0

RED < 1 the molecules are alike and will dissolve – in this case good solvent for polymer

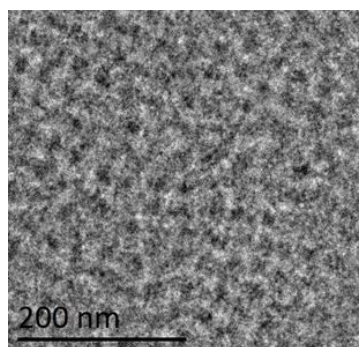
RED = 1 the system will partially dissolve – intermediate solvent

RED > 1 the system will not dissolve – non solvent

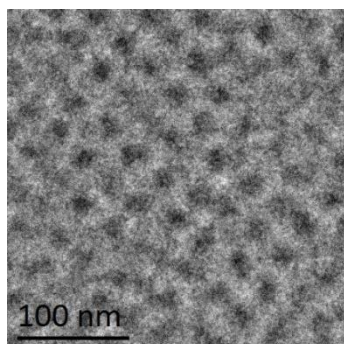
*Hansen, Charles M. 2000. *Hansen Solubility Parameters: A User's Handbook*. Boca Raton, Fla: CRC Press.

Vayer, Marylène, Alexane Vital, and Christophe Sinturel. 2017. 'New Insights into Polymer-Solvent Affinity in Thin Films'. *European Polymer Journal* 93 (August): 132–39. <https://doi.org/10.1016/j.eurpolymj.2017.05.035>.

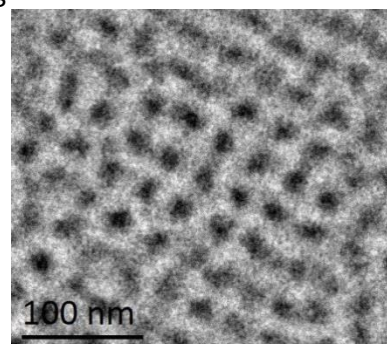
Annex 3. Optimization of staining by OsO_4 and I_2



Without staining

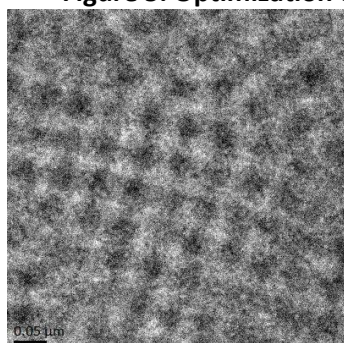


Staining by I_2 (0.1 g)

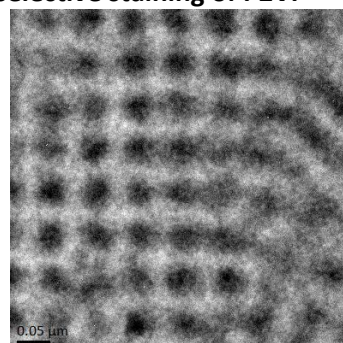


Staining by I_2 (0.5 g)

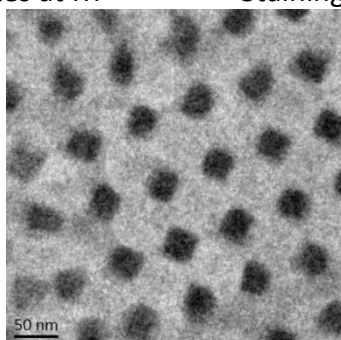
Figure 5. Optimization of iodine quantity for selective staining of P2VP



Staining by OsO_4 for 5 minutes at RT



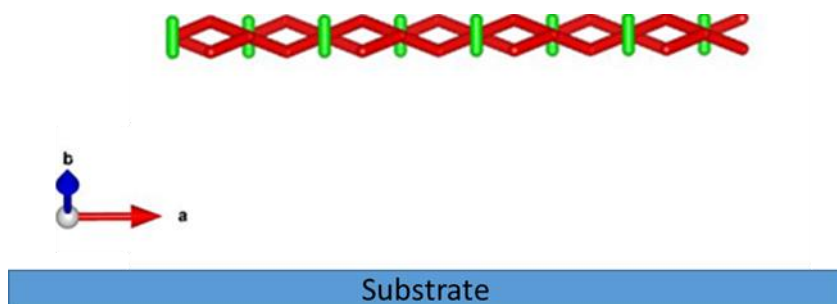
Staining by OsO_4 for 15 minutes at RT



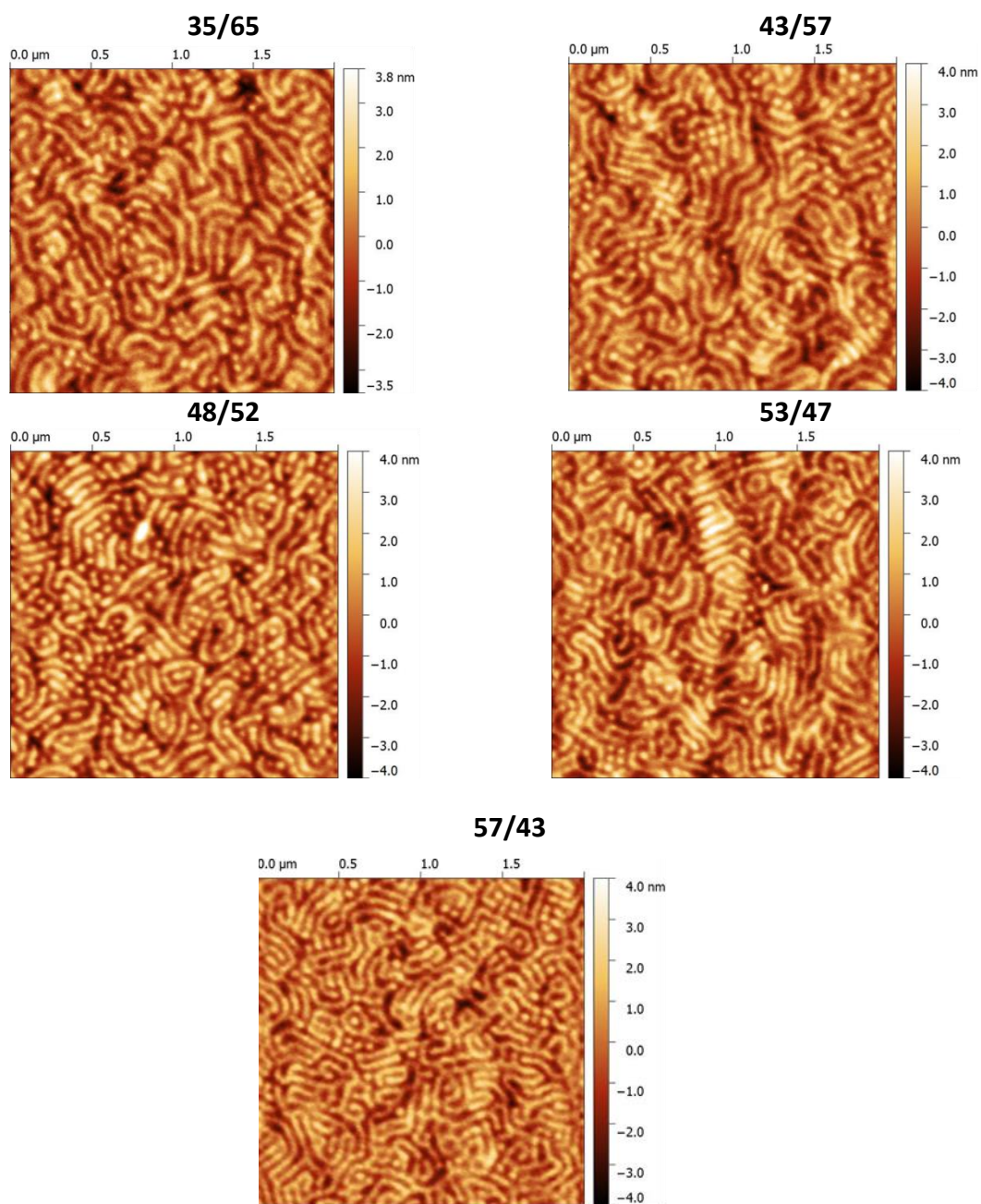
Staining by OsO_4 for 1 h at 50°C

Figure 6. Optimization of OsO_4 staining

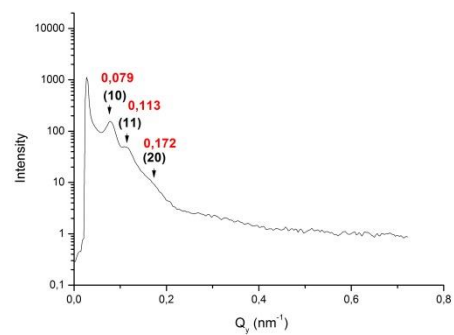
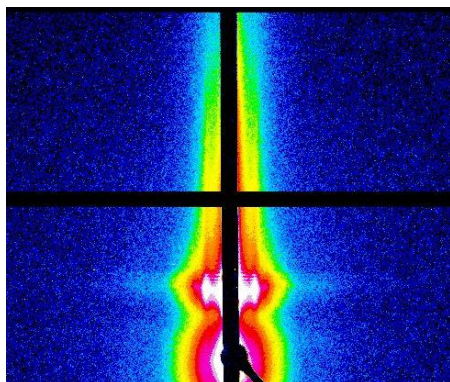
Annex 4. The thickness of this interfacial layer (15 nm) was estimated from side view created by Vesta for ISP23



Annex 5. AFM images of ISP α / β blends from 35/65 to 80/20

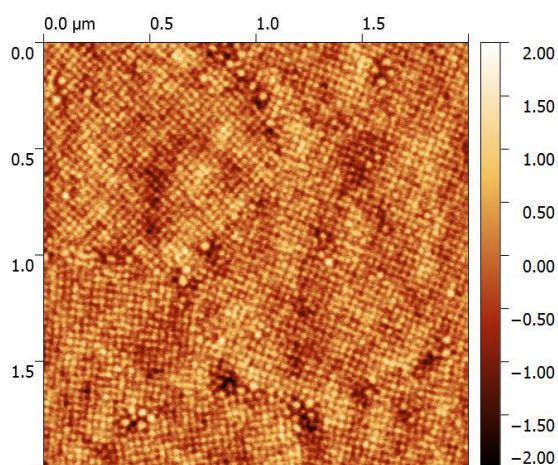


Annex 6. GISAXS pattern and corresponding in-plane profile of ISPX/ISPY (60/40) thin films after solvent annealing and selective staining by I₂.

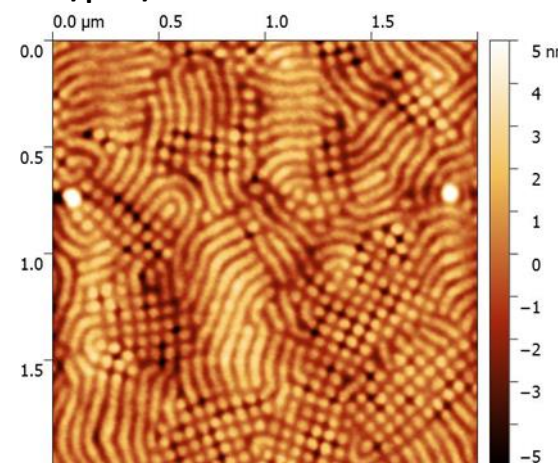


Other AFM images

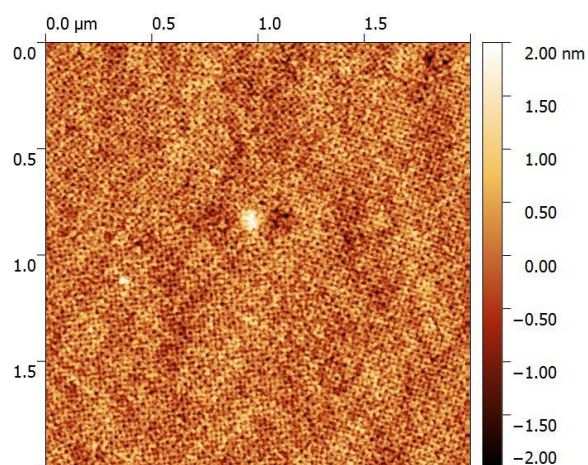
ISP19



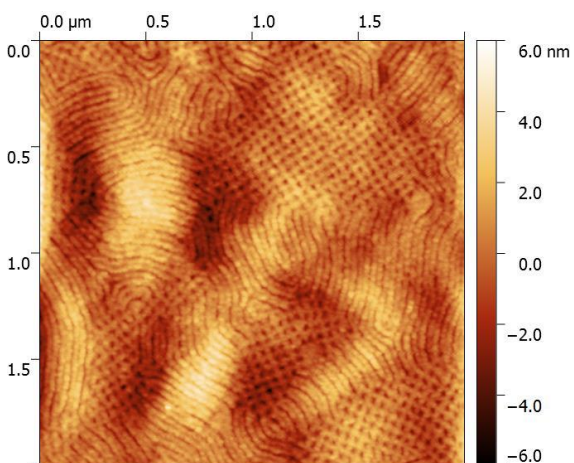
Solvent annealing in THF vapors
ISP α / β 60/40 blend



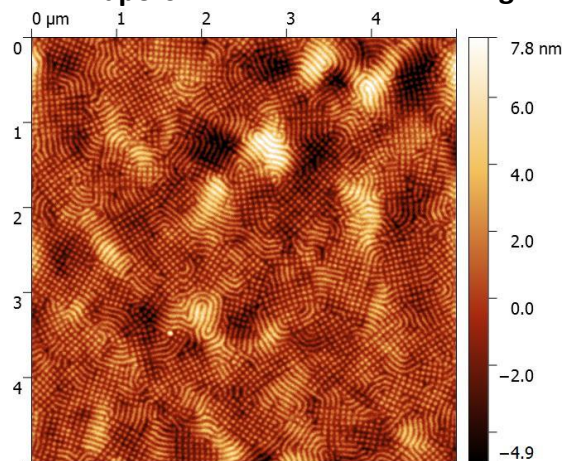
Solvent annealing in THF vapors



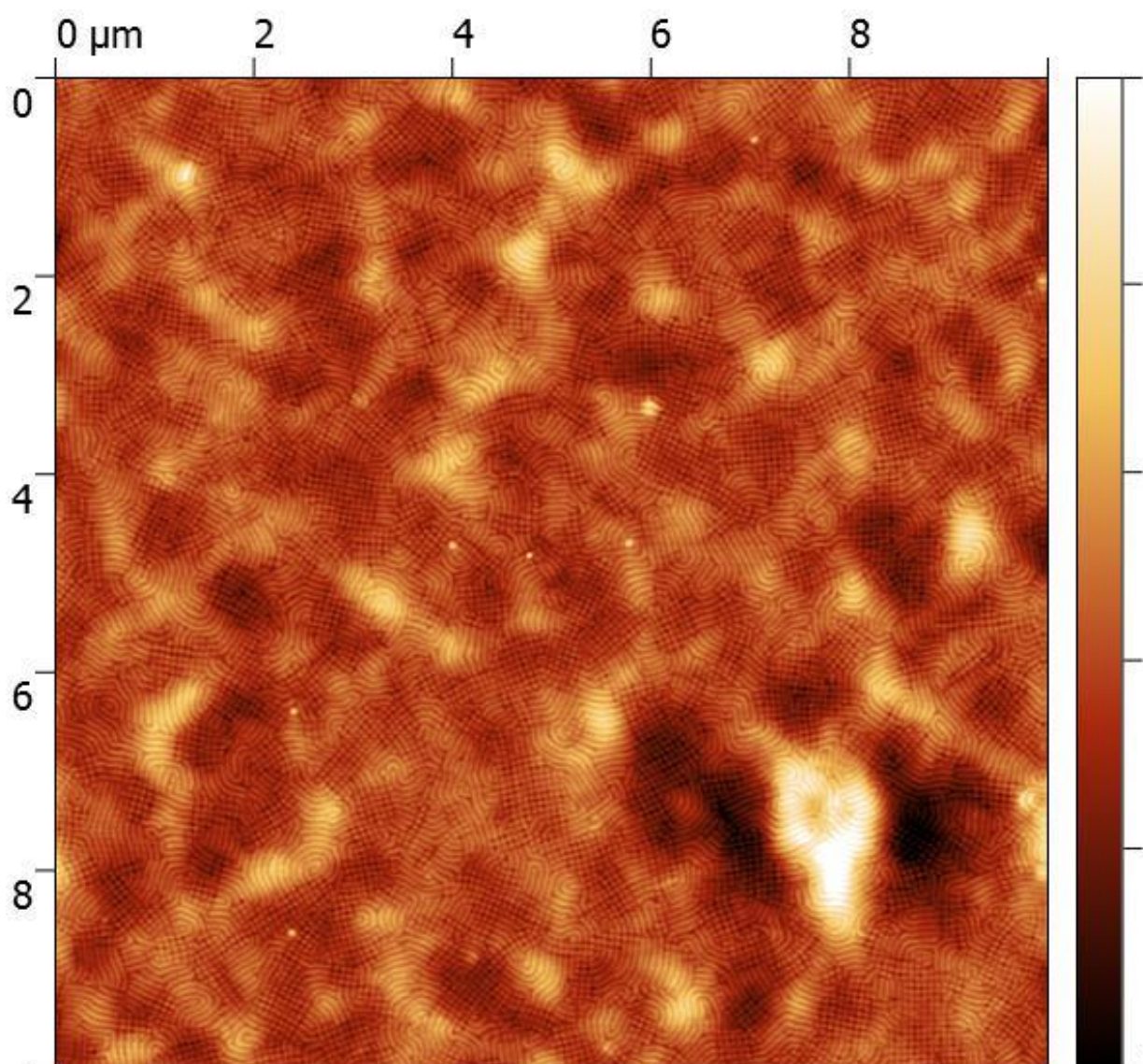
Solvent annealing in THF vapors + UV/Ozone



Solvent annealing in THF vapors + UV/Ozone

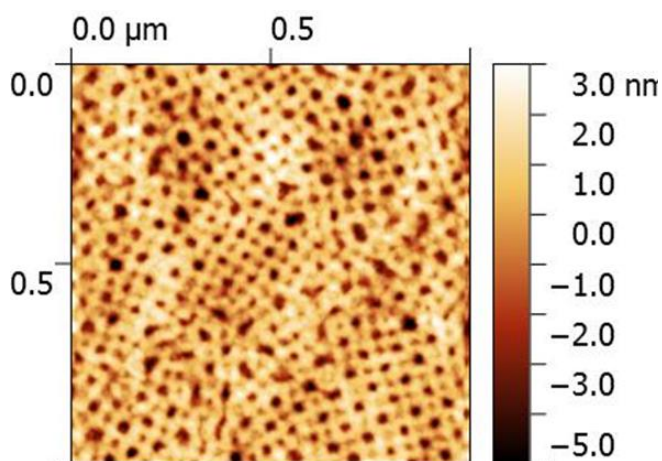
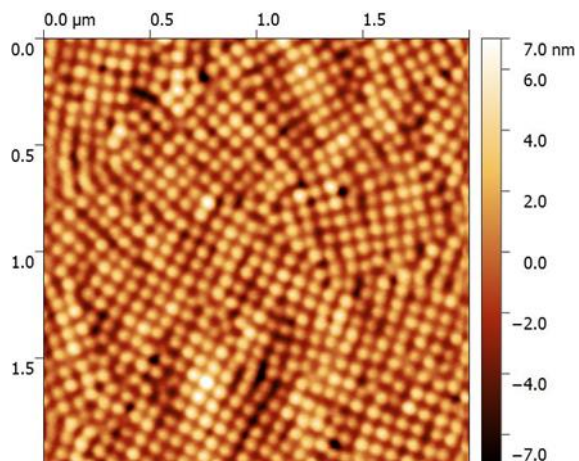


Solvent annealing in THF vapors

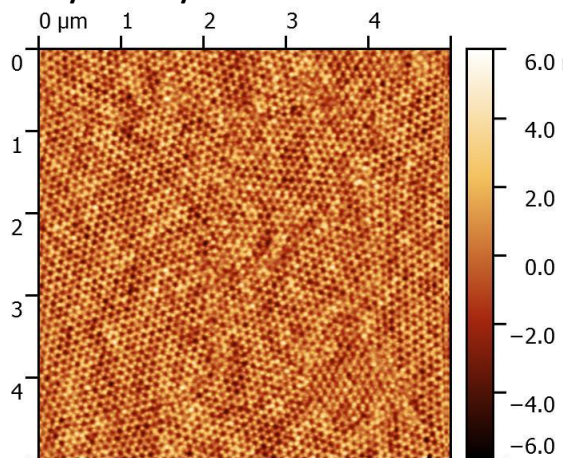


Solvent annealing in THF vapors

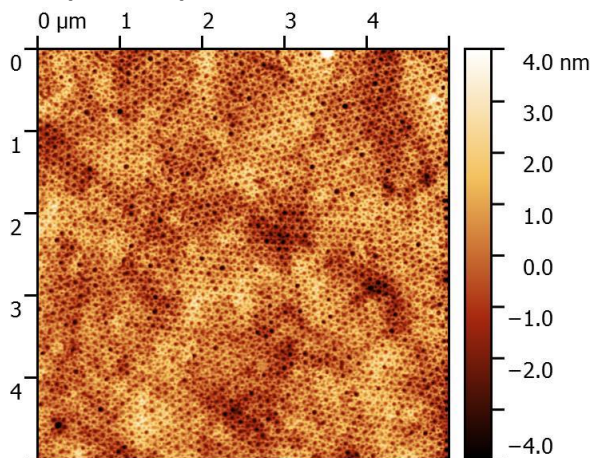
ISPX/ISPY blends



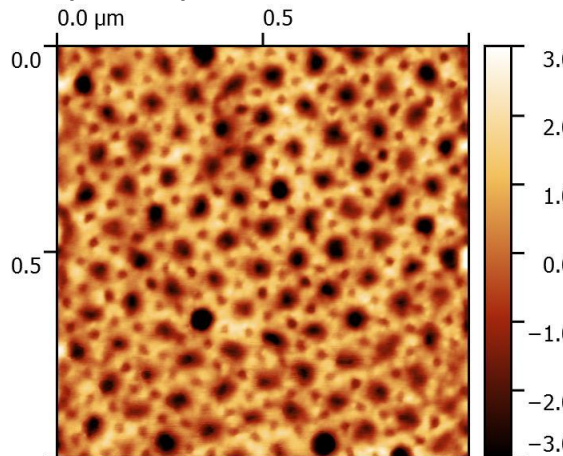
ISPX/ISPY 85/15 after SVA



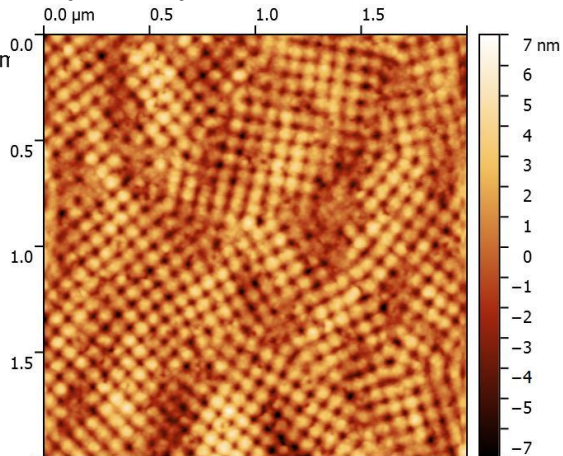
ISPX/ISPY 85/15 after SVA + UVO



ISPX/ISPY 60/40 after SVA



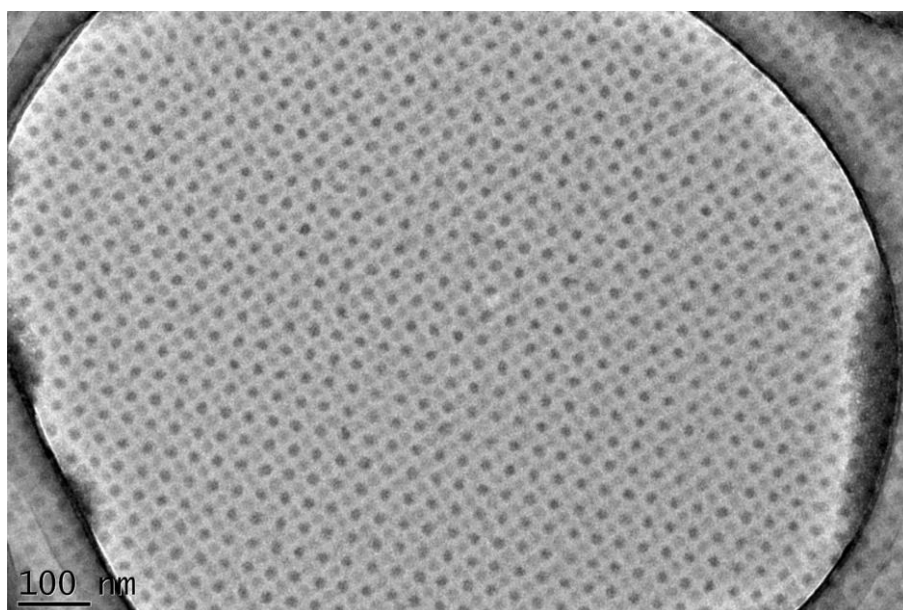
ISPX/ISPY 60/40 after SVA +UVO



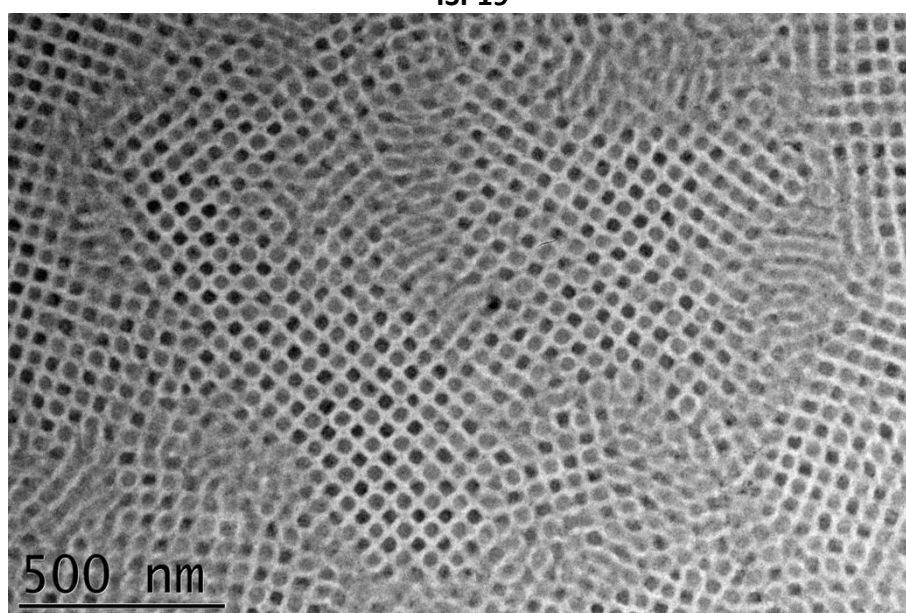
ISPX/ISPY 60/40 after SVA +UVO

ISPX/ISPY 60/40 after SVA +UVO+ EtOH

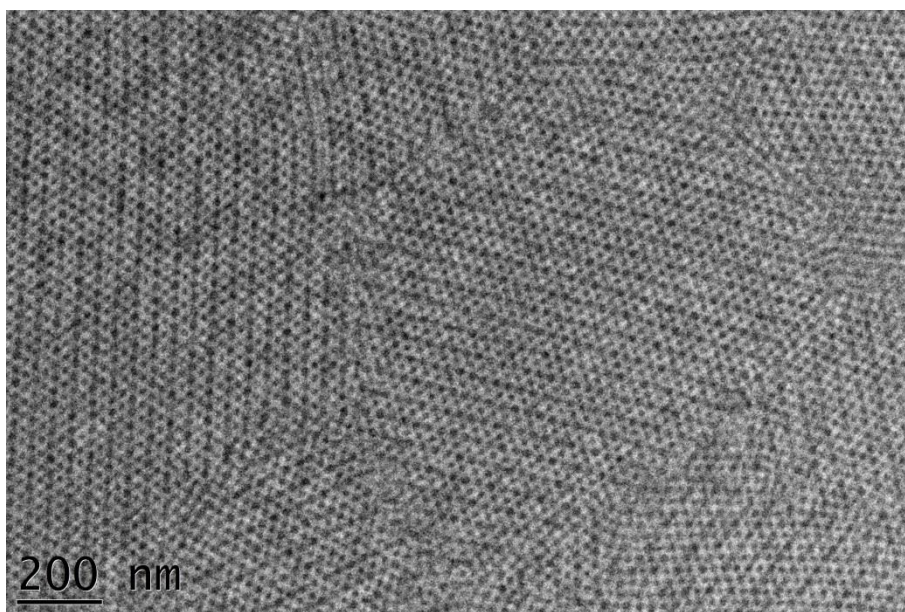
Other TEM images



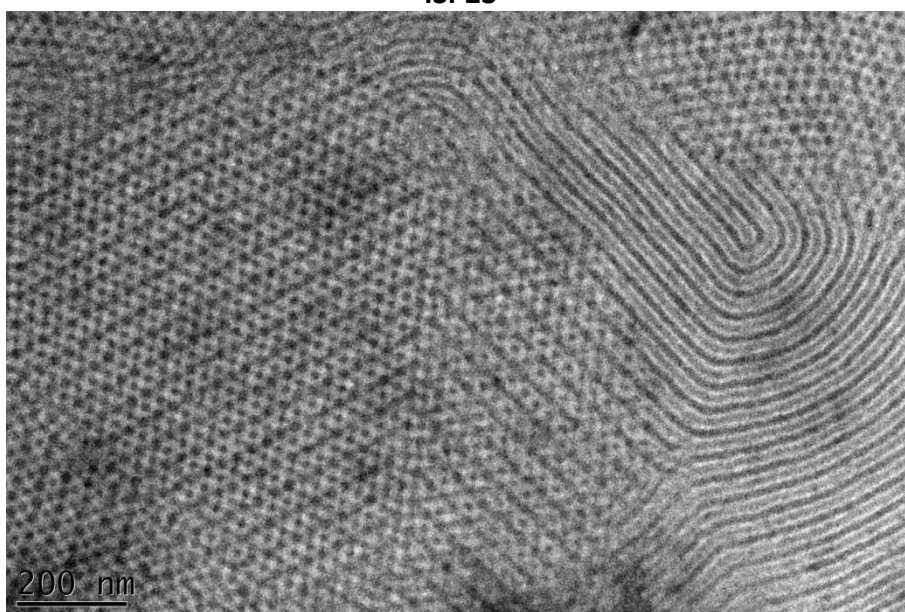
ISP19



ISP α / β 60/40 blend



ISP23



ISP23

Aynur GULIYEVA

Nanostructuration de terpolymères triblocs linéaires poly(isoprène-b-styrène-b-2-vinylpyridine) en film mince

Résumé :

Les travaux de thèse ont porté sur l'étude de copolymères triblocs linéaires ISP (PI-b-PS-b-P2VP) (seuls ou en mélanges) en films minces, déjà étudié en volume par un laboratoire partenaire de l'Université de Nagoya. Nous avons développé des méthodes de caractérisation adaptées à ce polymère en film mince, en particulier une technique originale de GISAXS reposant sur le marquage sélectif des blocs par des éléments lourds (iode, osmium). Ceci nous a permis de confirmer la structure interne et la forme de l'interface (rayon de courbure) des domaines minoritaires, d'observer des transitions structurales originales. La présence de couches de mouillage aux deux interfaces du film (film/air et film/substrat) est une caractéristique commune à tous les systèmes.

Tout d'abord, des triblocs seuls, se trouvant à la limite des différentes morphologies sur le diagramme de phase, ont été étudiés en film mince. Contrairement à ce qui a été observé en volume, des transitions structurales (CYL-SPH et GYD-CYL) ont été observées. Notamment, la transition d'une structure gyroïde alternée présentant une symétrie Q214 vers des cylindres avec une symétrie P2mm (pas d'arrangement typique hexagonal) représente, pour des terpolymères triblocs, un des résultats majeurs de la thèse. Le mécanisme de transition structurale a été élucidé par différentes techniques de caractérisation montrant une relation d'épitaxie entre les deux phases. Ensuite, nous nous sommes focalisés sur la nanostructuration de mélanges de triblocs. Nous avons montré la possibilité d'obtenir des domaines minoritaires de PI et P2VP présentant des interfaces rectangulaires, arrangés avec une symétrie tétragonale.

Mots clés : copolymères à bloc, film mince, auto-assemblage, nanostructuration, AFM.

Nanostructuration of poly(isoprene-b-styrene-b-2-vinylpyridine) linear triblock terpolymers in thin film

Abstract:

The thesis focused on the study of ISP linear triblock copolymers (PI-b-PS-b-P2VP) (neat or in blends) in thin films, already studied in volume by a partner laboratory of the Nagoya University. We developed adapted characterization methods to this type of polymer in thin film, such as an original method of GISAXS based on the selective staining of blocks by heavy elements (iodine, osmium). This allowed us to confirm the internal structure and the shape of interface of the minority domains and to observe original transitions between morphologies. The presence of wetting layers at both film interfaces (film / air and film / substrate) is a common feature for all systems.

Firstly, neat triblocks located on the boundary between different morphologies on the phase diagram, were studied in thin film. Contrary to what was observed in volume, structural transitions (CYL-SPH and GYD-CYL) were observed in thin film. Particularly, the transition from an alternating gyroid structure having a Q214 symmetry to cylinders with symmetry P2mm (no typical hexagonal arrangement) represents, for triblock terpolymers, one of the major results of the thesis. The structural transition mechanism was elucidated by different characterization techniques showing an epitaxial relationship between the two phases. Secondly, we focused on the nanostructuration of triblock blends. We showed the possibility to obtain minority domains of PI and P2VP with rectangular interfaces, arranged with tetragonal symmetry.

Keywords: block copolymers, thin film, self-assembly, nanostructuration, AFM.



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