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4.1 Introduction

For the last 30 years, block copolymers (BCP) have held the promises of new functional nanomaterials due to their fascinating spontaneous spatial organization as well as their complex properties, combining those of the individual blocks. The pathway is long, starting at the first synthesis mastered in the 1950s [1], travelling through full thermodynamics descriptions [2], the discovery of industrially viable synthesis technologies [3], and the first patents in one of the expected most appealing applicative fields [4]. This path still has obstacles and challenges ahead before block copolymer nanostructures really come out of the research laboratories. Until then, and for many more years, BCPs will keep researchers busy and amazed by their capacities to spontaneously produce chemically and topographically patterned surfaces [5]. Block copolymers nanopatterning is only one of the many opportunities offered by macromolecules at interfaces as detailed in the other chapters of this book, as well as previous enlightening literature [6]. But they indisputably present many advantages compared to alternative methods for the production of nanopatterned surfaces, including the tunability of size and morphologies of the domains, the ease of processing on many types of surfaces and the possibility to smarten the systems up with chemical functionalities. Theoretical and experimental tools have been readily derived from that developed for interfacial phenomena in mixed polymer systems [7]. The block copolymer thin film morphologies therefore offer a genuine technological platform for the generation of surface nanopatterns as well as ordered thin films, for a wide range of possible applications (cf. Fig. 4.1) mostly in optics, or based on their templating possibilities [8–10]. Two specific thin

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Fig. 4.1 Schematic of various applications of BCPs in nanotechnologies. Reprinted from ref. [8], Polymer 2003, **44**, 6725, Copyright 2003, with permission from Elsevier

film morphologies are particularly attractive, presenting high degree of order and uniaxial symmetry: the lamellar phase in parallel (homeotropic) alignment, which constitutes easily produced well-ordered and periodic multilayered slabs, and the phase of hexagonally packed cylinders in perpendicular orientation, from which can be obtained patterns of cylindrical nanodots or nanopores. The latter structures have attracted a lot of attention, with applications including high-density storage media [11, 12], lithographic masks [13–17], nanofluidics [18], separation membranes [19, 20], templates for nanorods synthesis [21, 22], enhanced patterned LEDs [23]. As it becomes obvious below, many research efforts have been devoted to the control of this orientation.

Extensive and excellent literature [24, 25], can be found on block copolymers and their microphase separation. After a brief reminder of some necessary bases, we will focus here on the conditions allowing to access specific patterns at the free surface of a thin film. This concerns mostly *really thin* films, a regime in which the film structure will be strongly affected by its interfaces on the one hand, and by the commensurability of the film thickness T with a (small) integer number of d_0 , the size of the microphase separation-induced period. This natural nanoscopic dimension d_0 constitutes a strong, almost inflexible constraint on the nanostructure of block copolymer materials, whatever their shaping, which will have specific consequences in the case of thin films.

4.2 Microphase Separation of Block Copolymers

Block copolymers are the result of covalently linking two or more polymer chains, each called a block. A diblock copolymer is $A-A-\dots-A-A-B-B-\dots-B-B$ or A_n-B_m , where the polymerization degrees n and m are typically between 10 and 10^5 . The nature of the monomers (A or B) can be chosen within a very wide range of chemical functions, made available by the development of many different synthetic techniques [26]. Thanks to the high degree of control of the copolymer synthesis techniques, block copolymers containing two distinct monomers A and B can also have various architectures, such as linear diblock (A_n-B_m), triblock ($A_n-B_m-A_n$), pentablock ($A_n-B_m-A_p-B_m-A_n$), multiblock (A_n-B_m)_p, and star diblocks (A_n-B_m)_pX. With a third ingredient C, linear $A_n-B_m-C_p$, $A_n-C_m-B_p$, and $B_n-A_m-C_p$ triblocks, multiblocks ($A_n-B_m-C_p-B_m-A_n$, etc. . .) and three-armed stars can be obtained, for instance. For the sake of simplicity, we will focus here on the cases of diblock copolymers, composed of two linear blocks of different chemical nature and linked covalently at one of their extremities. The properties of block copolymers with alternative architectures (multiblocks, branched copolymers, etc.) can be to some extent extrapolated from those of diblocks, although they are not nearly as well understood [24].

In the Flory–Huggins description of polymer melt thermodynamics, the interactions between segments, depending only on the local concentration of the different types of chemical functions, constitute the enthalpy contribution, whereas the entropy is a non-local contribution, depending on the number of allowed conformation of the entire copolymer chains [27, 28]. Entropy is related to elasticity and will be optimized when all tensions are released within the chains.

Most polymers are incompatible with one another and phase separate in a blend. This is also true for the distinct blocks of a block copolymer, but because they are covalently linked, they can segregate only as far as the size of the macromolecule itself: this is called the microphase separation and results in the formation of domains of each block [2, 29, 30], in the melt. They are called *microdomains*, although they actually present nanoscale dimensions: from a few nanometers to a few hundred nanometers depending mostly on the length of the copolymer chain. This segregation at equilibrium occurs when the enthalpic gain of avoiding contact between incompatible blocks overcomes the associated entropic loss. For a diblock A_n-B_m , the two terms in the free energy depend only on the dimensionless Flory–Huggins interaction parameter χ specific of each monomer pair (A,B) and characterizing their incompatibility, the total polymerization degree $N=n+m$ and the volume fractions of the blocks f_A and $f_B=1-f_A$. The balance of these two terms in the free energy defines a transition line, similar to the binodal in a blend, called the order–disorder transition (ODT). “Disorder” refers to the homogeneous solid in which all blocks are mixed, when χN is small and the entropy wins. Low values of χN can be obtained for any (A,B) pair when N is small; or at high temperature (since χ decreases when the temperature increases). Inversely, in order to reach high values of χN with short polymer

chains, strong incompatibility (high χ) is needed. “Order” refers to the segregated systems, in which the macrodomains form equilibrium organized structures.

In the case of the lamellar phase, the free energy can be approximated to two contributions, the stretching energy and the interfacial energy, respectively:

$$\frac{F_L}{kT} = \frac{3}{8} \left(\frac{d}{a N^{1/2}} \right)^2 + \frac{\gamma_{AB}}{kT} \Sigma \quad (4.1)$$

where the interfacial energy is

$$\gamma_{AB} = kT \left(\frac{\chi}{6} \right)^{1/2} a^{-2} \quad (4.2)$$

and the total interface area

$$\Sigma = 2 \frac{N a^3}{d} \quad (4.3)$$

with a the size of one segment of the chain, d , the layer thickness. Equating F_L with the disordered copolymer melt free energy $F_{\text{dis}} = f_A (1 - f_A) \chi N$, at the order-disorder transition (ODT), leads to $\chi N \sim 10$, independently of the chemical details of the considered system. Near this value lies the weak segregation limit, while far above $\chi N = 10$ is the strong segregation limit. In this latter regime, the interfaces between microdomains are sharp and well-defined [31].

The morphological phase diagrams of diblock copolymers present four equilibrium symmetries: body-centered cubic array of spherical cores (S-bcc), bicontinuous gyroid (G), hexagonally packed cylinders (C), and lamellae (L), which are selected mostly in relation with the volume fractions of the blocks f_A and $f_B = 1 - f_A$, due to interfacial curvature effects [2, 29]. These four phases exhibit long range order of dimension 3, 2, 3 and 1 respectively. With ABC triblocks, a much richer (more than 30) variety of phases [24] can be obtained in the bulk, as for example the striking 2D “knitting pattern” [32] (Fig. 4.2).

When the diblocks are close to being symmetrical ($f_A \sim f_B \sim 0.5$), the volumes occupied by both blocks on either sides of the interface are comparable, and the interface tends to be flat. This leads to a lamellar phase composed of a periodic stack of alternating slab-shaped microdomains extending infinitely in two directions. The period d_o of this stack, of the order of twice the extended length of the copolymer chain, correspond to the equilibrium conformation of the macromolecules and can hardly be modified for a given copolymer. This equilibrium period d_o is simply the result of the minimization of Eqs. (1–3), reading [33, 34],

$$d_o = 2N^{2/3} a \left[\frac{1}{3} \left(\frac{\chi}{6} \right)^{1/2} \right]^{1/3} \quad (4.4)$$

Fig. 4.2 (a) Transmission electron micrograph of a polystyrene-block-poly(ethylene-co-butylene)-block-poly(methyl methacrylate) (SEBM) triblock copolymer, stained with RuO_4 , presenting the morphology called the “knitting pattern.” Bar = 0.5 μm . (b) Schematic description of the triblock chain conformation within the unit cell. Adapted with permission from ref. [32], *Macromolecules* 1998, **31**, 135. Copyright 1998 American Chemical Society

The easiest way to vary d_o is certainly by changing the total polymerization degree N of the copolymer [35]. But playing with the Flory–Huggins parameter χ , either through temperature [34], or initial monomer choices, or diblock chemical composition is also considered [36]. Typically, d_o is easily obtained between 30 and 120 nm with commercially available BCPs, while going below 30 nm or beyond 120 nm may require tailor-made products.

4.3 Block Copolymer Thin Films

As was described before, the equilibrium nanostructures of BCP melt (dry) state are completely controlled by thermodynamics and do not depend on the processing or shaping of a sample. However, the pattern actually exhibited at the surface of a BCP thin film, and the nanostructure organization throughout the thickness of the film, can depend on the shaping and boundary conditions, even at thermodynamic equilibrium. Therefore, the control of orientation of ordered copolymer phases is an important part of the research effort aimed at developing functional surfaces or thin films [37]. This part of the research has benefitted from methodologies adapted from liquid crystal studies, in which the alignment of anisotropic liquids in thin films is required for both fundamental experimental work and applicative developments [38].

The equilibrium nanostructures, while presenting a high degree of order, typically extend over the size of grains, like in polycrystalline materials, leading to macroscopic isotropy. This grain size can be enlarged by annealing processes, but the application of external constraints is usually required to access macroscopic samples with no grain boundaries (monocrystals, or fully aligned samples).

In the case of thin films, meaning for thicknesses ranging from one time until typically ten times the equilibrium characteristic size of the nanostructure, surface effects act as efficient external constraints. It is indeed obvious that boundary conditions can influence the orientation of anisotropic materials in the vicinity of the boundaries and this is likely to affect the whole structure when the thickness of a film is small.

Thin films are usually produced by spin-casting from a relatively dilute solution ($< \sim 5$ wt%), or sometimes other casting techniques, and are rarely at equilibrium, due to the fast evaporation of the solvent leaving no time for the macromolecules to adjust their conformations. The copolymer chains are then either fully mixed (the film is said disordered or amorphous) or presenting some kinetically arrested metastable nanostructure [39], depending on the casting solvent (selectivity, saturation vapor pressure) and conditions (concentration, speed, etc). Bringing the film to equilibrium is usually done by thermal or solvent annealing. Elevated temperatures for several hours (above the glass transition temperatures of the constituent blocks and preferably in an inert atmosphere in order to avoid oxidative degradation), or solvent vapor swelling give the chains the necessary mobility for the system to evolve towards the equilibrium nanostructure. This evolution follows the minimization of the system energy, including the terms discussed in Sect. 4.1, leading to the formation of the microphase separated nanostructure, as well as the surface energy at the substrate and atmosphere surfaces. The two blocks, of different chemical nature, usually present a significant contrast in their interfacial energy at the contact of both the substrate and the atmosphere, which will induce a significant energy gain if the right domain is exposed at each interface. In the case of the lamellar structure, this selective alignment at the boundary produces a parallel alignment of the multilayered structure (cf. Fig. 4.3a), which then propagates throughout the thickness of the film.

4.4 Forcing the Perpendicular Alignment

As was said before, a strong motivation for reaching perpendicular alignment of nanostructured thin BCP films is the production of nanolithography masks [8, 11, 40] because they can reach sub-20 nm dimensions, at which classical lithography techniques cannot be applied and sophisticated variations including extreme UV technologies [41] are necessary. BCP are considered an interesting alternative, which motivates many of the research efforts in the search for alignment control.

Fig. 4.3 Schematic representation of various alignment situations: (a) and (b) show parallel alignment, (c) represents the elementary brick constituting parallel aligned films, (d) and (e) show perpendicular alignment, (f) shows a mixed alignment

4.4.1 Surface Energy Tuning

Rarely occurring naturally, the situation in which the contrast in interfacial energy at the contact of the substrate for the two blocks vanishes, can be induced by a proper surface treatment. This treatment needs to remain unaltered by the thermal or solvent annealing process, which will be used for the alignment step. A clever surface treatment insuring a neutral surface energy towards a given diblock copolymer consists in grafting the substrate with a *random* copolymer of same chemical composition than the diblock [42, 43], although this may induce interactions between the random brush and the block copolymer film, which go beyond a simple surface energy effect [44]. Other surface treatments can be employed, provided that they can be finely tuned, in order to access the proper balanced energy [45].

When the surface energy is neutral for a given diblock, entropic effects will lead to a perpendicular alignment of the nanostructure, due to a preferential conformation of the macromolecules lying along the substrate surface [46]. The Fig. 4.3d, e sketch successful achievements of perpendicular alignment at the substrate interface. Getting perpendicular alignment at the free surface of the film is more difficult, because most ambient conditions will present a preferential surface energy towards one of the blocks of any diblock. It is therefore common to obtain a hybrid alignment [47] (like shown in the Fig. 4.3f), unless the thickness of the film is restricted to a very small value, in which case geometrical constraints will prevent the deformation of the nanostructure to adjust from one orientation to the other. Hybrid orientation films, however, can be processed, by some etching techniques, in order to reveal the perpendicular pattern.

4.4.2 Other Surface Effects

4.4.2.1 Roughness

The effects of the substrate roughness on the orientation of BCPs in thin films have been studied experimentally [48, 49], and theoretically [50]. Typically, if the roughness characteristic lateral length is larger than the period of the copolymer nanostructure, the favored orientation will always be perpendicular, unless the roughness characteristic height is very small. Provided that the substrate roughness is not detrimental to the final use of the supported film, roughness can be an easy control knob for modifying the alignment of a nanostructured film. For instance, ITO-covered surfaces can be used as electrodes in organic electronic devices and double as conveniently rough surfaces.

4.4.2.2 Graphoepitaxy

Graphoepitaxy consists in using substrates with designed topographic features and was developed as a way to better control the effects of the substrate topography, rather than counting on sometimes ill-defined roughness. Substrates with templating grooves could, for instance, constrain a spherical BCP structure to adopt a highly ordered nanopattern [51, 52], when the template dimension is commensurate with the nanostructure characteristic size. The templates can be produced by “standard” lithography techniques because its dimensions are typically one order of magnitude larger than that of the BCP nanostructure. This combination of top-down (lithographic) technology at ~ 500 nm scale and bottom-up (BCP nanostructures) at ~ 50 nm scale is promising for well controlled nanosurfaces, if somewhat tedious. Other substrates with specific topographies were successfully used to produce perpendicular alignment of phases of hexagonally packed cylinders: faceted crystals [11] and interferometrically produced sinusoidal polymer gratings [53], are among the interesting examples. The former case proved appropriate for very thin films, whereas the latter requires a thickness above a threshold value of several times the pattern sinusoidal amplitude and the nanostructure period. Provided these structural features are compatible with a given desired structure, and the presence of the groove template is not problematic for the considered applications, these methodologies are interesting.

4.4.2.3 Chemically Patterned Surfaces

Besides topographically patterning the substrate, it can be useful to orient and possibly align PCB thin films with chemically patterned substrates. The propagation of surface patterns into the bulk was predicted to be possible [54], and some of these situations were demonstrated experimentally. For instance, Kim et al. [55]

Fig. 4.4 Effect of a chemical pattern on the alignment and azimuthal orientation of lamellar block copolymer nanostructure: top-view SEM images ($2\ \mu\text{m} \times 2\ \mu\text{m}$) of the nanostructure morphologies of thin films of lamellar copolymer with period $d_0 = 48\ \text{nm}$ onto chemically patterned substrates as a function of the pattern pitch and the composition of the random copolymer used to create the pattern. Adapted with permission from ref. [56], *Adv. Mater.* 2004, **16**, 1315. Copyright 2004 John Wiley and Sons

patterned a substrate using extreme ultraviolet interferometric lithography [41] to transfer alternating lines and spaces to a self-assembled monolayer (SAM) and studied the configurations of thin PS-PMMA films on top of such substrates. For this technique, sometimes referred to as epitaxy, commensurability constraints appear severe since the perpendicular alignment of lamellar microdomains by striped patterns can be obtained only with a pattern pitch equal to the BCP lamellar period within less than 5 % mismatch. The registry can have a slightly larger mismatch tolerance if the chemical pattern is produced with a random copolymer brush [56], supposedly because the interpenetration of the brush chains in the BCP film allows some variation of the lamellar period around the equilibrium value d_0 (cf. Fig. 4.4). Contrary to the graphoepitaxy patterning, the chemical template must have the same lengthscale than the structure to be aligned, meaning molecular scale, and therefore requires high-tech lithography techniques. This is why, although it is of fundamental interest to show the mechanisms of such alignment, it cannot claim the finality of an easy production of nanoscale patterns.

Real crystalline epitaxy has also been used to align BCP thin films, while using specific interactions between semicrystalline BCPs and crystalline substrates [57, 58], or directional crystallization [59].

4.4.3 Solvent Annealing

The effect of solvent swelling has become increasingly used in the last decade for the manipulation of block copolymer thin film textures. If a block copolymer thin film is swollen with a solvent, which is a true neutral solvent for the copolymer (meaning the affinities of the two blocks are exactly equal), the presence of the solvent will provide mobility to the copolymer chains and allow them to reach the equilibrium structure, then defined, as before, by the balance between conformation, incompatibility and surface energy effects. In that sense, it would usually produce the same effect as a thermal annealing, but specific effects can also be observed due to the evaporation process, like the presence of a solvent concentration gradient normal to the substrate plane and a subsequent ordering front from the film surface to the substrate, which will on the one hand induce a highly directional nanostructure, and on the other hand increase the impact of the interfacial energy conditions at the free surface (where the solvent concentration is the lowest).

In general, however, the solvent used is not genuinely neutral, which would usually lead to kinetically trapped nanostructures and alignments, especially if one or both blocks are glassy at room temperature [60]. Such metastability makes it possible to force the alignment of the nanostructures without tuning the energy balance, and the glassy nature of the final film insures the long-term absence of evolution of the pattern. Solvent swelling was proven to be a useful process to reach perpendicular alignment of cylinders in different systems [61–64] (cf. Fig. 4.5). This process is however still considered difficult to reproduce, mainly because reproducibility requires a precise mastering and controlling of many experimental

Fig. 4.5 Atomic force microscopy (AFM) phase image of the top surface of a thin film of poly (styrene)-*b*-poly(oxyethylene) diblock copolymer presenting a phase of hexagonally packed cylinders aligned perpendicular to the substrate after annealing in benzene vapor. The image contrast comes from the difference of elastic modulus between the domains. Adapted with permission from ref. [62], *Adv. Mater.* 2004, **16**, 226. Copyright 2004 John Wiley and Sons

details besides the choice of the solvent: film thickness [65], annealing time with characteristic times sometimes shorter than 1 min [63], vapor pressure and the rate of vapor removal [39, 66], glass transition temperature. All these can affect, often in coupled ways, the resulting metastable morphologies. The effects indeed involve different mechanisms including the modification of the interfacial energies of the swollen film as a function of the solvent loading, as well as hydrodynamic effects [62]. These non-equilibrium processes have not been easily considered by theory, but phase behavior and film patterns could be modeled in great detail by simulations [65] based on dynamic density functional theory. Nevertheless, solvent annealing is one of the most promising method, at this time, for the easy production of large-scale well-aligned nanopatterned thin films of block copolymers, while offering at the same time interesting scientific questions related to these non-equilibrium systems.

4.4.4 Other Fields

4.4.4.1 Electrical

The application of an external electric field, adapted from methodologies well optimized for liquid crystal systems, has been used with success [67–69] for large-scale alignment, although it often results in hybrid alignment situations (cf. Fig. 4.6). The electric field effect indeed competes with the surface effects, as was well documented theoretically [70, 71], while also taking into account the effects of mobile charged impurities in the films [72]. The nanostructure development and alignment could be followed by time-resolved X-ray scattering in the cases of initially disordered and ordered films [69, 73]. The reorientation of ordered films occurs by the fragmentation of the initial nanostructure into small domains, all eventually oriented along the field. The application of the field while the film is swollen by a neutral solvent proved beneficial for large scale alignment, and was satisfactorily described by simulations [74, 75].

Fig. 4.6 Cross-sectional TEM image of a ~ 700 nm PS-*b*-PMMA film annealed under ~ 40 V/ μ m electric field for 16 h. Scale bar: 100 nm. Reprinted with permission from ref. [47], *Macromolecules*, 2004, **37**, 2625. Copyright 2011 American Chemical Society

Fig. 4.7 (a) AFM image of a PS-PMMA film, 18 nm thick, shear-aligned at 40 kPa. (b) The same image after being Fourier-filtered. (c) Same image as in (b), with *small circles* added to mark the dislocation cores identified by an appropriate image treatment algorithm. Scale bars represent 500 nm, and the shear direction is oriented roughly diagonal (*upper right to lower left*) in all images. Adapted from ref. [81] with permission of The Royal Society of Chemistry

4.4.4.2 Flow

In bulk systems, shear induced alignment has proven the most successful, and has focused large research efforts, both experimentally [76, 77], and theoretically [78], which go beyond the scope of this chapter and are reviewed elsewhere [79]. Shear alignment of thin films was shown to be very efficient on spherical and cylindrical block copolymer phases, if it is performed at a temperature between the highest of the two glass transition temperature and the order–disorder transition temperature of the diblock [80]: $T_g < T < T_{ODT}$. In other cases, however, a good alignment is obtained with a high defect density [81] (Fig. 4.7).

Other alignment methodologies have been cited [82], including optical alignment of liquid crystalline block copolymers, and temperature gradients [83, 84], but are less general or practical.

4.5 Parallel Alignment

As was explained before, the parallel alignment is most of the time obtained spontaneously. For cylindrical nanostructures, this situation usually exposes at the free surface a homogeneous layer of the preferentially wetting block [85], meaning that here again, an etching step needs to be developed for nanopatterning purposes. For lamellar nanostructures, this alignment does not induce any exposed nanostructure-based pattern at the free surface. However, a complete alignment of the copolymer film (shown in Fig. 4.3a) is only possible if the total thickness of the film is commensurate with the lamellar period: $T = nd_o$ or $T = (n + 1/2)d_o$, where n is usually a small integer ($1 \leq n \leq 8$). The reason for that is that due to the free energy constraints on both the nanostructure alignment and the copolymer chain conformations, the nanostructured film has to be built as an assembly of the elementary brick (shown in Fig. 4.3c) composed of a copolymer layer of thickness $d_o/2$, corresponding to half of a bilayer of size d_o , the lamellar period. When deposited by a given casting technique, the film has a thickness controlled by the parameters of the casting (initial concentration and rotation speed and acceleration, for example in the case of spin-coating). While the fine tuning of these parameters, and therefore of the final film thickness, is in principle possible, it is more common to obtain a film with a thickness not exactly equal to nd_o or $(n + 1/2)d_o$. The layered structure of the copolymer then forces the film to present regions of different thicknesses, with the different regions satisfying one of the commensurability conditions [86, 87]. The film is therefore terraced, with a quantized surface topography: the step height of the terraces is d_o , so that the free surface exposes the same block domain on each terrace.

When the film thickness is close to and below the commensurability condition, the film lacks a little matter to reach a flat surface, and the terraces are shaped as holes, whereas when the film thickness is close to and above the commensurability condition, the film has a small excess of matter to reach a flat surface, and the terraces are shaped as islands [88]. This evolution is very obvious when a thickness gradient is produced on a lamellar copolymer thin film, as shown in Fig. 4.8. Interestingly, the film is flat on a finite range of thickness around the commensurability condition, showing that the copolymer layers are able to slightly adjust their surface chain density, so that the film can accommodate small discrepancies in thickness and avoid the cost of building a terrace edge.

The edges of the terraces concentrate the excess free energy related to a structural defect in the lamellar organization. These defect lines were shown to have a specific dynamics [89] and to present apparently stable structures [90], for some conditions of film T and bilayer d_o thicknesses. This allows for the relatively easy achievement of specific patterns, with a length scale one or two orders of magnitude larger than that of the copolymer nanostructure. Moreover, Li et al. have shown that these patterns can be somehow manipulated [91] as they present registry or anti-registry with underlying topographically patterned surfaces.

Fig. 4.8 True color optical micrograph of a continuous 26k PS-b-PMMA film with thickness gradient. The lower section is a continuation of the upper section. Film was annealed for 6 h at 170 °C, and the image shows the addition of four successive lamellae to the block copolymer film with increasing thickness, and the corresponding terraced patterns. *Labels* indicate when the film thickness verifies $h_s = (n + 1/2)d_o$, where $n = 2-6$. Reprinted with permission from ref. [88], J. Polym. Sci.: Part B: Polym. Phys. 2001, **39**, 2141. Copyright 2001 John Wiley and Sons

4.6 In-Plane Degeneracy and Single-Grain Formation

Beyond the formation of a specific alignment with regards to the substrate plane, ensuring the formation of a single-grain BCP lattice on large areas is critical in many cases. Also, in the cases of parallel oriented cylinders and perpendicular oriented lamellae, the orientation of the domains is azimuthally degenerate, and a complete in-plane alignment of the structure, usually desired in view of applications such as interconnects or light polarizers, requires some additional action.

An additional field can be applied orthogonally, which can be again of different nature. For instance, nicely ordered lamellar microdomains have been obtained by the combined application of a electric field and a flow field in a rather thick film [92]. Temperature treatment can also be combined with shear [93]. A combination of static and dynamic effects was successfully applied by Berry et al. [94], who used a graphoepitaxy and dynamic thermal annealing.

An intrinsically directional single field can align BCP patterns. As was mentioned before, chemically patterned surfaces, having the same length scale as the BCP nanostructure, apply a strong constrain on BCP thin films. It was shown to actually induce unidirectional orientation of perpendicular aligned lamellar phases [55, 56]. Graphoepitaxy alone can also unidirectionally align line patterns and organize spherical domains. Use of faceted surfaces [95] and 1D groove templates [52], due to entropic effects, as well as nanoimprint lithography [96, 97] (NIL), due to surface effects on the vertical groove walls, are efficient techniques to orient BCP nanostructures without requiring macromolecule-scale prior patterning. In the case of reconstructed sapphire surfaces, the atomic crystalline ordering of the

Fig. 4.9 (a) Top view of a SEM image of the BCP film after nanoimprinting with a NIL mold with main pitch $1.5\ \mu\text{m}$. The groove height is $50\ \text{nm}$. The perpendicularly lying BCP lamellae are further oriented along the groove long axis. (b) An enlargement of (a) where several lamellae (*left*) are well ordered in-plane. (c) An AFM top view of an enlarged section of the BCP film close to thin-thick boundary (the *middle vertical line*). To the *right*, the BCP film is thicker and is ordered by the groove vertical wall, whereas to the *left*, the BCP is thinner and less ordered. Reprinted with permission from ref. [96], *Macromolecules*, 2011, **44**, 2206. Copyright 2011 American Chemical Society

substrate can be transferred, over multiple length scales, to the block copolymer microdomains, via facets regular pattern. In the latter case, a micrometer-sized carved mold is imprinted onto the film, in order to guide the self-assembly of the BCP at the nanometer scale (cf. Fig. 4.9). Self-consistent field theory successfully accounted for the experimental results on NIL azimuthal alignment of lamellar domains, as shown in ref. [96].

Recent progress in the generation of large single-grain BCP thin films include zone processing, which induces sharp ordering front able to guide self-assembly (cf. Fig. 4.10). This can be found in a number of variations, like zone casting, using a scanning polymer deposition process [98], raster solvent vapor annealing [99], generating a localized solvent annealing zone with a scanning solvent vapor delivery nozzle, or thermal gradient zone processing [93, 100].

Device-oriented structures like sharp corners and curved patterns can be transferred into the BCP pattern [101]. In these studies, a small quantity of compatible homopolymer was added to the copolymer, which can redistribute in locations where it will compensate the mismatch between the pattern pitch and the natural lamellar domain d_o , thus allowing the copolymer pattern to follow even the sharp features of the underlying guide (cf. Fig. 4.11).

4.7 Experimental Techniques for the Structural Studies of the Nanopatterns

Atomic force microscopy (AFM) is a very useful technique to study the patterns exhibited at the surface of thin films. Used in tapping mode, which exploits the interaction of the tip with the surface during intermittent contacts between

Fig. 4.10 Zone casting of a lamellar BCP thin film. (a) Taping mode AFM phase image (*inset*: FT transform), and (b) GISAXS pattern of PODMA-*b*-PtBA-*b*-PODMA block copolymer films prepared by zone casting at 40 °C. *Arrow*: substrate withdrawal direction. (c) Scheme of the zone casting technique. Adapted with permission from ref. [98], J. Am. Chem. Soc. 2011, **133**, 11802. Copyright 2011 American Chemical Society

them, this scanning microscopy technique can provide topographic images of the free surface with a resolution allowing the observation of 10 nm features or sometimes less, but it can also provide images of chemical contrast between microdomains. Phase images, in particular, relate to the damping of the tip oscillations, which varies with the local elasticity and more generally with the type of tip-polymer interactions at play. This is very complementary to topographic images, specifically because the nanopatterns of block copolymers may sometimes coexist with relatively flat and smooth surfaces. AFM cannot report on in-depth nanostructure but is well suited for studies of top surface patterns and their evolution upon annealing. Defect mobility and annihilation can be imaged, for instance [102] as is shown on Fig. 4.12.

As for other organized soft matter systems with nanoscale characteristic sizes, *X-ray and neutrons scattering techniques* are very appropriate for the study of block

Fig. 4.11 Effect of a chemical pattern on the azimuthal orientation of lamellar block copolymer lamellar nanostructure: top-view SEM images ($2\ \mu\text{m} \times 2\ \mu\text{m}$) of the nanostructure morphologies of thin films of lamellar copolymer with period $d_o = 70\ \text{nm}$ onto chemically patterned substrates with a bent of 45° , 90° , and 135° as a function of the pattern pitch. Adapted from ref. [101]

Fig. 4.12 AFM images taken between repeated annealing treatments of a further hour at 523 K showing the evolution of a disclination pair. In each image, the repeat spacing of the microdomains is 50 nm. Adapted with permission from ref. [102], J. Chem. Phys. 2001, **114**, 4730. Copyright 2001 AIP Publishing LLC

copolymer self-assembled nanostructures. In the case of thin films, two main experimental configurations are of interest: the reflectivity [103] and the small-angle scattering at grazing incidence (GISAXS) [104–106]. These techniques provide a large foot-print of the beam on the samples, allowing the collection of data in spite of the sometimes minute thickness of the films. Reflectivity is sensitive to the ordering along the film normal, and is well adapted for layered films. It can also efficiently quantify roughness. GISAXS measures the off-specular signal and records both in-plane and out-of-plane order, giving access to the in-depth nanostructure. It presents a very good temporal resolution, allowing following in detail the nanostructure evolutions during solvent or thermal treatments.

Spectroscopic *ellipsometry* is an elaborate technique, which has been used as a robust and extremely sensitive tool for material characterization [107]. During the last decade, its domain of application has been extended to the study of nanostructured samples, although it is mostly appropriate for the determination of order along the film normal. Small refractive index contrast multilayer structures and birefringence can be experimentally accessed [108] in some conditions, but may require sophisticated models.

Emerging *new methods* include resonant X-ray scattering [109], for enhanced contrast, critical-dimension SAXS, giving access to a 3D reconstruction [110] of in-depth structural features in the films, and scattering infrared near-field microscopy [111], for nanoscale chemical analysis at surfaces.

4.8 Perspectives

Macroscopically aligned BCP thin films provide invaluable robust, versatile, chemically functionalizable nanopatterned surfaces. Due to the interplay between film thickness, nanostructure and alignment, careful and complex processes are required to reach large scale alignment monodomains. Moreover, with the multiplication of the actual possibilities in term of copolymer architecture, monomer choices, advanced substrates, high-tech deposition and treatment processes, as well as new time- or spatially resolved analysis techniques, the field of nanopatterned BCP thin films is still ready to provide remarkable model study subjects as well as routes for defect-free or tailor-made nanomaterials for technological applications.

Device-oriented structures with complex patterns will be obtained by the design and juxtaposition of guiding tiles on the substrates, as has been done by Chang et al. [112], who achieved patterns including dense bends, junctions, and lines with a simple and predictable topographic template (cf. Fig. 4.13).

Search for ever-smaller characteristic sizes, in order to reach the sub-20 nm limits desired for lithography applications, has involved the choices of new monomer combinations [13, 113], salt complexation [114], and exploration of the weak segregation regime [115]. However, this goal is conflicting with the need for defect-free patterns, since the energy cost of a defect formation typically scales as the third

Fig. 4.13 From *left to right*: template layout to fabricate complex patterns consisting of design patterns of posts. Each color represents the pattern templated by each arrangement; SEM images of the templates of posts to fabricate dense patterns of bends and terminations; SEM images of the PDMS patterns formed on the template shown on the left; SCFT simulation result showing the constant 50 % density surface of PDMS cylinders assembled with the template on the *left*. Scale bars are 50 nm. Adapted by permission from Macmillan Publishers Ltd: Nature Comm. 2014, **5**, 3305 (ref. [112]), copyright 2014

power of the nanostructure characteristic size [116]. Future research effort will be necessary to reach beyond this irreconcilability.

Other expected further studies will likely assess the nanopatterns and the mechanisms of their formation, in thin films of block copolymers with more complex architectures. For instance, the phase behavior of star copolymers is increasingly well described [117]. For enlarging the application openings, more advanced substrates will likely be implemented, like the curved surfaces theoretically considered in recent studies [118, 119]. Efforts will be devoted to the generation of reconfigurable and responsive surfaces, which can adapt to surrounding environments [120], as for instance thermoresponsive nanopatterned surfaces [121].

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