# Solvent Vapor Annealing of Block Polymer Thin Films

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**ABSTRACT:** This Perspective provides a critical analysis of the current knowledge concerning solvent vapor annealing (SVA) of block polymer thin films. Herein, we identify key challenges that will be important to overcome for future development of SVA as a practical, reliable, and universal technique for the valorization of block polymer thin films in a wide range of technologies. The Perspective includes a brief background on thin film block polymer self-assembly, a historical account of the SVA technique, an overview of the SVA fundamentals that are necessary to develop a more comprehensive picture of the overall process, and summaries of relevant and important contributions from the recent literature. We also offer our outlook on SVA and suggest important future directions.
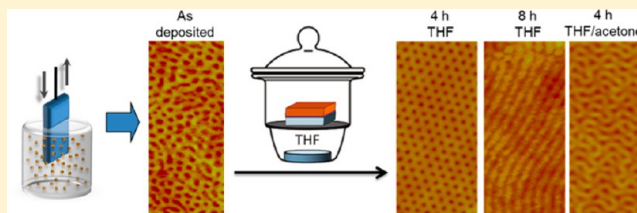
In a 1995 publication entitled "Monolayer films of diblock copolymer microdomains for nanolithographic applications", Mansky et al. launched the concept of exploiting block polymer self-assembly for lithographic templates.[1] They pointed out that the highly defined structural arrangements resulting from microphase segregation can be used to form nanopatterns similar to the elements defined in conventional lithographic processes used in microelectronics fabrication. Since the publication of this paper, interest in block polymer thin films has grown considerably with much of the work driven by use of block polymers for self-assembly approaches to advance lithography and generate other functional nanostructures.[2−4] The hope of reducing pattern and device feature sizes beyond the characteristic length limits imposed by conventional device fabrication techniques, for example 193 nm UV lithography in the microelectronics industry fabrication, has spurred and motivated further advances in this area.[5,6] The decrease of feature sizes using block polymer approaches has also been explored in other technologies such as separation membranes,[7,8] nanofluidics,[9,10] photonics,[11] and biological scaffolds.[12]

Microphase segregation of block polymers is a thermodynamically driven process that leads to periodic nanoscale structures. The most practical applications of self-assembled block polymers generally rely on thin film formation since this is the most appropriate form to create a surface pattern that can be transferred to a substrate for the creation of functional nanoscale devices. However, when block polymer thin films are cast from a solvent onto a substrate, they generally become kinetically trapped in nonequilibrium, disorganized, and ill-defined structures. To adopt the highly regular structures predicted at equilibrium, the mobility of the polymer chains must be sufficient to allow for structural reorganization. In some systems, simple thermal treatments above the limiting glass transition temperature $(T_g)$ of the system can be successfully used to facilitate the attainment of the equilibrium structure. However, for many high molar mass systems thermal treatments alone are not very effective, and very long anneal times are often required.[13] To combat such long annealing periods, another annealing process known as *solvent vapor annealing* (SVA) has been shown to be generally much more effective.[14] In SVA, as-prepared block polymer thin films are exposed to vapors of one or more solvents, at temperatures typically well below the bulk $T_g$ of both blocks to form a swollen and mobile polymer film atop the substrate. On subsequent solvent evaporation, polymer chains can form more well-organized nanostructures. Despite its widespread use and proven capability to produce controlled morphologies with long-range-order, a comprehensive understanding of the phenomena involved in SVA has not been established. Two principal reasons for the lack of understanding of this important process are that (i) the connection between the nanostructure formed in the swollen film and the final dried film has not been rigorously established in most cases and (ii) no standardized SVA method has been developed. Although an inherently simple technique, understanding, controlling, studying, and quantifying the conditions within a solvent exposure chamber can be quite difficult.

In this Perspective we aim to provide analysis of critical issues in SVA, demonstrate how the understanding of this process is incomplete, and provide some key challenges to overcome for future development of SVA as a practical, reliable, and general tool for enhancing the applicability of block
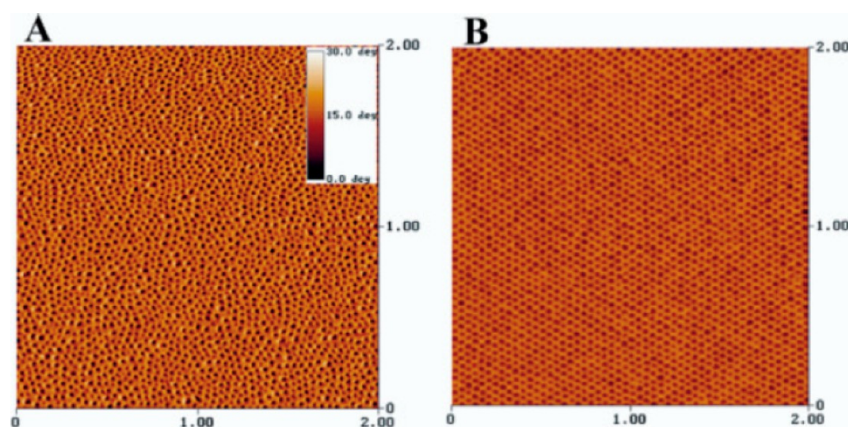
**Figure 1.** As-cast (A) and solvent vapor annealed (B) thin films of poly(styrene)-*b*-poly(ethylene oxide) block polymers. Reproduced with permission from ref 30. Copyright 2004 Wiley-VCH.

polymer thin films for technological use. The Perspective is presented in four sections. In the first, we provide an overview of block polymer thin film self-assembly and briefly discuss the emergence of the SVA technique. In the second section, we will present some fundamentals of SVA that are necessary to develop a more comprehensive overview of the process. In the third section, we highlight several important and recent contributions from the literature that connect simple solvent swelling concepts to a more complete understanding of block polymer film structure postannealing. Finally, we present an outlook on SVA of block polymer thin films and suggest important future research directions.

## I. CONTEXT AND BACKGROUND

The ability of block polymers to form ordered nanostructures arises from the thermodynamic incompatibility between their constituent blocks.[15] The covalent bond between the blocks prevents macroscopic phase separation and leads to microphase segregation into domains of macromolecular length scale, for example, from a few to several tens of nanometers depending on the molar masses of the blocks, and their incompatibility. In bulk samples at equilibrium, it is well established how morphology, periodicity, and the microdomain dimensions are determined by the composition, the overall degree of polymerization ($N$), and the Flory–Huggins interaction parameter ($\chi$) which is a measure of the degree of incompatibility between the blocks.[16] The morphology of these materials has been experimentally studied and theoretically described for numerous compositions, architectures, incompatibilities, and molar masses.[17]

Many of the possible applications of block polymers require the development of thin films where the self-assembled pattern is used to create surface topography or chemical composition variation for applications where structural and compositional nanoscale surface engineering is required.[18] Consequently, since the late 1980s significant research focused on the behavior of block polymer films with thicknesses ranging from a few nanometers to several times the natural period of the block polymer morphology.[19,20] Through these studies, kinetic, surface, and commensurability effects were shown to significantly impact the self-assembly process.[21–25] Among all the efforts that have been made to produce highly ordered assemblies of block polymer thin films, the SVA approach has emerged as one of the most convenient.

One of the very first examples reporting an improvement in long-range order in block polymer films using solvents was by Albalak et al. in 1998.[26] In this work, solvent swollen roll-cast films of poly(styrene)-*b*-poly(butadiene)-*b*-poly(styrene) triblock polymers with cylinder and lamellar morphologies were studied upon preferential (toluene) and nonpreferential (methyl ethyl ketone (MEK) and hexane) solvent exposure using small-angle X-ray scattering. The microphase-separated pattern formed was found to be similar in structure and degree of order as seen by a thermal annealing approach but was achieved in significantly reduced times. They suggested that the SVA methodology favored mobility of the polymers in the swollen state, allowing the system to reach the thermodynamically preferred, nanostructured arrangement. Also in 1998, Kim and Liberia studied films of a cylinder forming poly(styrene)-*b*-poly(butadiene)-*b*-poly(styrene) triblock polymers cast from toluene and showed how the evaporation rate within the as-cast films influenced their final morphological state.[27] Despite the fact that SVA as a structure forming technique was not specifically highlighted in this landmark work, the complexity of the transition from a film of a block polymer solution toward a solid film was established. The block polymer films produced at more rapid solvent evaporation rates were "kinetically constrained" in a disordered arrangement since the evaporation rate of the solvent was fast compared to the diffusion of the macromolecules. Slow evaporation rates lead instead to an ordered organization with vertical (i.e., perpendicular to the surface plane) cylinders, and even slower evaporation rates gave in-plane (i.e., parallel) cylinders. Works published by Fukunaga et al. in 2000[28] and Knoll et al. in 2002[29] were also informative and important early examples demonstrating how solvent vapor exposure can enable morphological rearrangements from as-cast disorganized states.

Because of the considerable potential of the method, a great deal of work was subsequently dedicated to technical improvements to the SVA process. Particularly relevant is the work of Kim et al., who demonstrated in 2004 that poly(ethylene oxide)-containing block copolymers can form highly oriented and ordered arrays upon prolonged SVA in benzene (Figure 1).[30] In this important paper, phenomena occurring during the drying were shown to have a prominent influence on the final structure in the dried film. The authors suggested that evaporation of the solvent at the free surface generated an ordering front that propagates from the interface

through the film thickness, thereby defining the orientation of the domains in a direction perpendicular to the solvent front.

Work carried out to date on SVA represents extensions of these early models and centers on the subtle interplay between thermodynamic considerations associated with block polymer self-assembly (in the presence and absence of solvent) and kinetic considerations associated with the transition from a solvent swollen state to the final dried film. When the film is exposed to a solvent atmosphere, the process can be separated in two stages. In the first, the extended period of solvent exposure leads to the formation of a swollen state that may or may not be equilibrated, whereas in the second the most commonly applied removal of the samples from the solvent atmosphere (deswelling/evaporation) represents a rapid and nonequilibrium process in most cases. Practically, great care and control must be exercised in both regimes to achieve the highest degree of structural order in the microphase-separated film. In the following sections we provide our perspective of work to date and identify the key issues associated with better understanding of block polymer films in the swollen state and identification of the parameters most important for controlling the morphology in the final dried state.

## II. FUNDAMENTAL CONSIDERATIONS

When preparing a block polymer thin film that will ultimately be subjected to SVA, there are several important factors that influence the final state of the film postannealing. All of the factors discussed below can impact the efficacy of the annealing process. The relative sensitivities, however, can vary dramatically; some aspects do not impact the overall process in any meaningful way, and other aspects are highly sensitive to even minor perturbations. It is therefore important to consider each of the factors when developing a new process or using new block polymer structures to reveal these sensitivities. A schematic depicting the overall process is shown in Figure 2.

**Block Polymer Selection.** The choice of the block polymer has obvious implications. The room temperature morphology of the bulk material should be determined through appropriate scattering and microscopy experiments. This is a starting point that will identify not only the ordered-state symmetry but also the principal domain spacing that can be
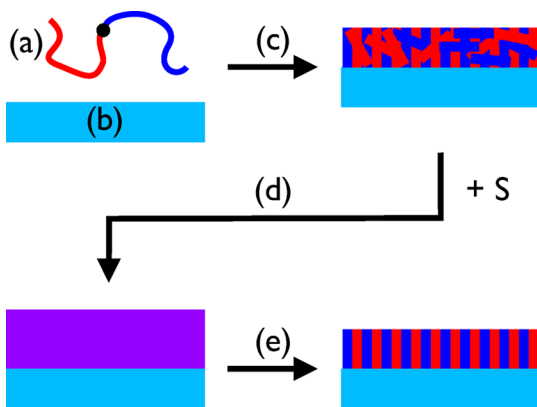


**Figure 2.** A schematic showing the five major considerations for SVA of block polymer thin films: block polymer selection (a), substrate preparation (b), film formation [a disorganized but ordered structure depicted] (c), solvent (S) exposure [a homogeneous, swollen film shown] (d), and deswelling by solvent evaporation [to a perpendicular cylindrical structure as an example] (e).

compared to the thin film observations. The $T_g$'s of the component blocks should also be determined so that dynamic considerations can be addressed. Typical systems such as poly(styrene)-$b$-poly(methyl methacrylate)[31] contain two glassy, amorphous blocks at room temperature. However, others contain blocks that are rubbery or semicrystalline at room temperature. The state of the particular component when exposed to solvent can influence the rate of solvent uptake and can ultimately dictate how rearrangements occur from the dry state to the solvent swollen state. While one might expect the swollen state of the film to be in equilibrium right after solvent exposure, metastable swollen states can however be formed and in turn impact the final ordered state upon drying. Thus, the dynamics of solvent uptake and removal can be important.

Overall molar mass (proportional to the polymerization degree $N$) and the interaction parameter ($\chi$) between the two blocks should also be considered as they are tied to both the degree of segregation of the block polymer and diffusion in the swollen state. High molar mass systems that are strongly segregated will take longer to come to equilibrium relative to lower molar mass systems due to chain diffusion and interfacial width considerations. Consequently, the time in the swollen state can influence the ultimate arrangement as the steady state or equilibrium situation may take longer to achieve than expected. Also, knowledge of $\chi$ for the blocks within the polymer is important since this can provide understanding of how a particular solvent used in the annealing process mitigates the interactions between the two blocks.

The composition of the block polymer is the main factor that dictates the ordered state symmetry in both the bulk and thin film. For example, in the case of typical cylinder forming AB diblock copolymers there is a range of about 20 vol % over which the cylinder phase is predicted to be experimentally stable (at moderate to strong degrees of segregation).[32] The behavior of block polymer thin films during SVA, however, can be sensitive to composition even though the bulk morphology is constant. We have observed this experimentally in thin films of poly(styrene)-$b$-poly(lactide) block copolymers. Furthermore, one must be careful to fairly compare systems as compositional changes are often accompanied by changes in molar mass and thus segregation strength due to synthetic protocols used. Changing composition at fixed degree of segregation requires detailed knowledge of the relevant $\chi$ parameter(s).

The interfacial energies between the constituent blocks and the solvent vapor are critical parameters that influence the tendency for one of the blocks to present itself at the film/vapor interface. The state of the swollen film prior to drying is important, and as the drying proceeds from the top of the film to the bottom, the deposition of the constituent blocks near the film vapor interface is a factor that should be considered. This typically requires knowledge of the $\chi$ parameter between the blocks and the solvents utilized. The effective $\chi$ parameters in the swollen state depend on the solvent content.[33,34] However, as the solvent vapor is far from the bulk density of the solvent, the use of interaction parameters determined between polymers dissolved in a liquid solvent has limitations since there will likely be a solvent vapor pressure dependence on the preference for a particular block being at the surface. This has not been studied to the best of our knowledge but could have implications for the final ordered state of the films. In the case of low molar mass systems, the nature of the end groups could also be important for such interfacial phenomena.

**Substrate Effects.** The key aspect of any substrate choice is the nature of the substrate surface and the interface it forms with the polymer. For example, a silicon wafer typically has a native oxide (SiO$_x$) layer at the surface. This can be etched to generate a silicon surface with functionality dependent on the etching conditions used which can be modified by, for example, silane coupling agents or polymer brushes that can alter the substrate surface energy.[35] The substrate can also be coated with metals or other materials. A common treatment is the attachment of a polymer layer to the substrate surface that "tailors" interactions with the block copolymer. A typical example is the use of a functionalized random copolymer that can lead to a neutral surface condition. However, the use of polymer brushes and other surface modification processes is not always facile.[36] Any surface treatment influences subsequent film deposition and SVA processing steps. For example, the hydrophilicity of the substrate surface can influence the wettability and impact the coating process and in turn the film thickness and uniformity; the ability to consistently deposit a film of a precise thickness can be compromised due to wettability considerations. During the coating process, one constituent of the block polymer may have a preferential affinity for the substrate surface, and if this is a particularly strong interaction, the addition of a solvent may not lead to detachment of a block polymer monolayer at this interface. This will modify the nature of the substrate polymer interface in the dried film.

A main factor requiring careful control of the surface chemistry is how the block polymer pattern will ultimately be transferred to the underlying substrate via selective inclusion (templating) or block removal (etching). For some systems, protective coatings on, for example, easily oxidized metals may be preferred, and for others, bare silicon may be required. Unfortunately, the pattern transfer requirements may not always be compatible with the preferred orientation of the block polymer thin film, and thus adjustments will need to be considered. All of these issues are important for the ultimate efficacy of the entire process. In addition, the surface roughness of the substrate and more precisely the topography of the substrate can have significant influence.[37]

**Polymer Deposition Process.** By far the most common method for deposition of block polymer thin films is spin-coating a dilute solution of the polymer onto a substrate surface. This is a simple and easily managed process for converting a block polymer solution into a thin film. The key parameters are the nature of the solvent used for the coating process, the block polymer concentration, the spinning process including speed and acceleration, and the environmental conditions. Higher concentrations and slower spinning speeds lead to thicker films. The more volatile the solvent, the less control there is over the spinning process. Low boiling solvents such as methylene chloride and tetrahydrofuran are often less desirable than higher boiling solvents such as chlorobenzene and toluene. The solvent choice will however depend on the block polymer structure. With proper combinations of solvent, speed, and concentration smooth films with thicknesses of 10s to 100s of nanometers can easily be deposited on a variety of substrates. As with most coating operations, rigorous avoidance of dust and other impurities during coating is desirable. However, for screening studies, benchtop coating conditions can be adequate.

In most cases, the solvent used will dissolve all the blocks in the block polymer leading to a homogeneous solution. Upon rapid drying during spin-coating, the block polymer will often microphase separate to give a disorganized but self-assembled structure. However, in some cases faster drying rates can lead to organized structures directly (Figure 3).[38] In cases where the
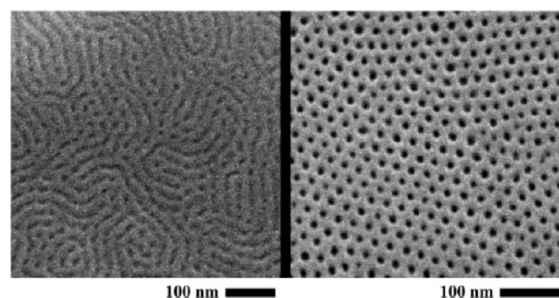


**Figure 3.** Influence of the evaporation speed on the orientation of cylinders forming poly(styrene)-b-poly(lactide) in thin films (left: slower drying; right: faster drying). Reproduced with permission from ref 38.

solvent used for spin-coating is a nonsolvent for one of the blocks, a micellar solution can be formed. In this case, coating can lead to a monolayer or multilayers of micelles (e.g., spherical micelles packed on a lattice).[39] These two different states of order prior to SVA can influence the rate of structural reorganization.

There are other coating methods that can be used to deposit block polymer thin films over large areas. Draw down coating, spray coating, and dip coating are three examples. Dip coating block polymer thin films has been shown to be quite effective for the formation of smooth and uniform thin films,[40] and this technique can be quite useful for generating thickness gradients. In this case, the withdraw speed, temperature, solvent volatility, and environmental conditions all play a role. In general, the technique used should give reproducible thicknesses with low levels of macroscopic defects.

By far the most important parameter in the coating process is the thickness of the final dried film. This thickness should always be considered in terms relative to the natural domain periodicity for the block polymer being coated (Figure 4).[29] In the case of cylinder forming block polymers, thicknesses that are integral units of the natural domain period tend to give
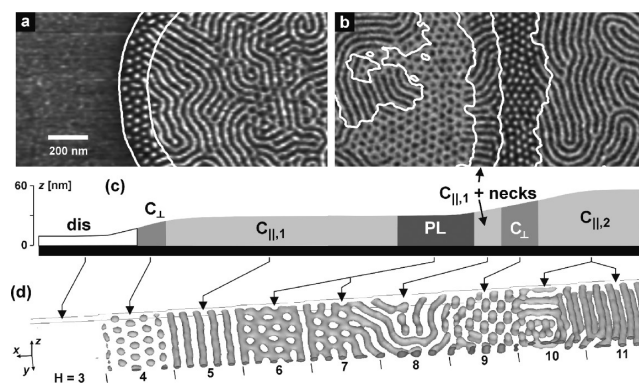


**Figure 4.** (a, b) Tapping mode scanning force microscopy phase images of thin SBS films after annealing in chloroform vapor. Bright (dark) domains correspond to poly(styrene) [poly(butadiene)] microdomains. (c) Schematic height profile of (a, b). (d) Simulated morphology. Reproduced with permission from ref 29. Copyright 2002 American Physical Society.

structures that are parallel to the substrate surface plane.[41] In the case of nonintegral thicknesses, terracing (island and hole formation) can occur so as to locally adjust the polymer film thickness to the natural period. Although this effect is most commonly observed in thermally annealed systems, it should most certainly be considered in SVA processes, where the thickness in the swollen state becomes an additional parameter of interest. As the natural period of the block polymer changes upon swelling, a systematic study of the effect of film thickness and the swelling ratio on the SVA process should be carried out early in any SVA study. Combinatorial methods using thickness gradients with controlled dip-coating processes can greatly facilitate such studies.[42] The thickness should also be considered in terms of the relative importance of the surface field (Figure 5).[29] A thinner film will emphasize the
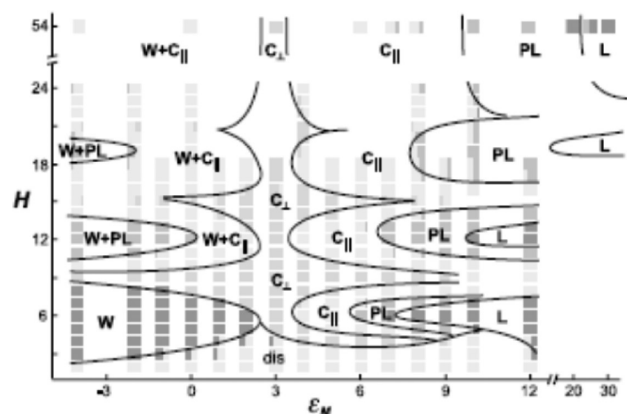


**Figure 5.** Simulated phase diagram of a triblock polymer showing the dependence with the thickness ($H$) and the strength of the surface field ($\varepsilon_M$). Reproduced with permission from ref 29. Copyright 2002 American Physical Society.

thermodynamic and dynamic importance of the two interfaces. With extremely strong surface fields and/or ultrathin films these effects can dominate.

**Solvent Vapor Annealing.** Once the block polymer of interest has been deposited on the substrate of choice, the substrate/film laminate is then subjected to SVA. In many cases, the final thin film assembly is very sensitive to the exact SVA conditions, and several factors are important to consider in any experimental protocol. First and foremost is the selection of the solvent.[43] The most common solvent used for SVA of block polymers is one that is either neutral or only slightly selective for one of the blocks. The swollen state is effectively a block polymer "solution" of some thickness (concentration) sitting atop the underlying substrate that is typically characterized by the block polymer concentration. The selectivity of the solvent is certainly related to the selectivity observed in the bulk mixtures of block polymers and solvents but is also subject to interfacial phenomena associated with both the solution/vapor and the solution/substrate interfaces. The solvent uptake of each component is affected by the solvent compatibility with the block and by the physical state of the block (e.g., glassy, rubbery or semicrystalline). This can result in a differential swelling of the blocks and consequently an effective variation of the block volume fractions that can have direct impact on the resultant ordered state symmetry.

Once the dry block polymer film is subjected to the solvent vapors, the film will swell due to thermodynamic driving forces

associated with the entropy of mixing and dilution of the unfavorable interfaces between blocks (and between the polymer and the surface in some systems). The swelling will continue until the chemical potential of the solvent in the film equals that of the solvent in the vapor phase. Flory–Huggins theory can be used to model swelling with reasonable accuracy.[44,45] Because of diffusion limitations, a solvent front will travel from the vapor interface through to the substrate, and these mass transport effects can control the time needed for the film to reach a steady (swollen) state.[46,47] In a model suggested by Hui et al., it is assumed that swelling is driven by differences in osmotic pressure across the polymer/vapor interface.[46,47] In this way the vapor pressure of the solvent controls the thickness of the swollen film and thus the relative concentrations of polymer and solvent in the film. The vapor pressure of the solvent used for annealing should be precisely controlled since the structure adopted by the block polymer/solvent mixture prior to drying can and often does influence the outcome postannealing structure (but note that the degree of swelling at a given vapor pressure can also depend on the thickness of the initial state[48]). During the transient state, solvent swelling can occur in two reasonably well-separated kinetic processes known as case 1 and case 2 diffusion.[49] In case 1 diffusion, the solvent swelling kinetics result in a mass uptake dependence that varies with the square root of time. Here the polymer chain relaxation processes are much faster than the time taken for the solvent vapor to diffuse into the film. In case II diffusion the reverse is true, and mass uptake changes linearly with time. Case I is seen for rubbery systems, and case II is seen for glassy systems. Understanding the swelling process at early times is likely important for short annealing times.

The solvent vapor pressure acting on the thin film can be controlled by mass flow controllers, temperature, or other means. The Antoine equation (derived from the Clausius–Clapeyron relation) can be used to predict the vapor pressure of a particular liquid at a given temperature.[50] Because of the nonlinear form of this equation, the vapor pressure of a liquid is quite sensitive to temperature near the boiling point of the liquid. Thus, when using volatile solvents such as tetrahydrofuran, small changes in temperature can lead to large changes in the solvent vapor pressure and consequently changes in the thickness of the swollen block polymer film. This should be taken into consideration when developing a SVA process. Direct measures of the swollen film thickness during the process are recommended for consistency (see below).

Once in the solvent swollen state, the block polymer film adopts a steady state thickness that can be simply correlated to the composition of the solution; the thicker the film, the more dilute the block polymer. An interesting aspect of the swollen state is that it comes from the initially dried state of the film postdeposition. The level of organization in the dried state can potentially impact the initial ordered state in the solvent-swollen thin film. Parameters that are important are the time taken to reach the swollen state and the time in that swollen state prior to solvent removal (since the swollen state can be metastable in nature). Depending on the molar mass of the block polymer being studied, the reorganization of the structure in the swollen state can be slow, and thus the ultimate equilibrium state may not be achieved over typical annealing times.

The structure adopted in the swollen state will be reasonably connected to the final structure of the dried film provided that

the solvent uptake is not too great. One simple connection that should be considered is the structure adopted in solutions of the block polymer as a function of solvent concentration. There have been several phase behavior studies on block polymers in solvents of varying selectivity, and these can be used as a first guide to the lyotropic structure of the block polymer solution in the solvent swollen thin film.[51] Drying from a cylindrical state or a spherical state will likely lead to different levels and degrees of organization than, for example, a disordered state. Precise knowledge of the structure in the swollen state is highly desirable when trying to understand how to connect the block polymer solution structure to the dried polymer film structure. The evolution of the system in the swollen phase diagram with respect to order−order and order−disorder transitions is of great importance. Examples are shown in Figure 6 for a poly(styrene)-b-poly(vinylpyridine) supramolecular assembly in various solvents[52] and in Figure 7 for a poly(styrene)-b-poly(isoprene) diblock in dimethyl phthalate (DMP).[51]



**Figure 7.** Phase diagram for poly(styrene)-b-poly(isoprene) in dimethyl phthalate (DMP). Reproduced with permission from ref 51.
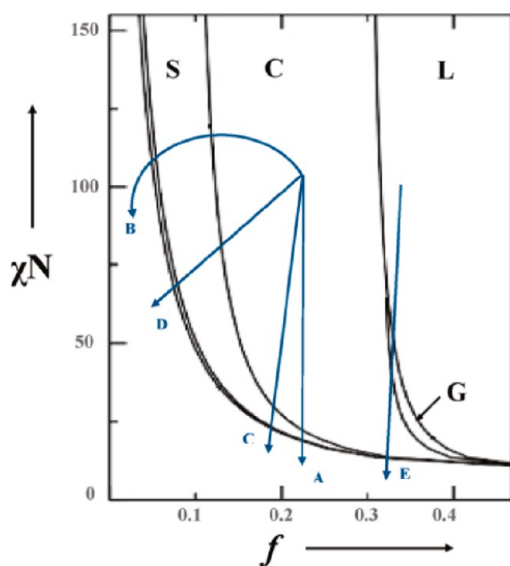


**Figure 6.** Schematic phase diagram showing the trajectory induced by the swelling of a poly(styrene)-b-poly(vinylpyridine) supramolecular assembly in a nonselective solvent (A), in a strongly PS selective solvent (B), in chloroform (C), and in 1,4-dioxane (D). (E) represents the trajectory in chloroform for another composition. Reproduced with permission from ref 52.

All SVA parameters need to be carefully documented and considered when embarking on SVA studies. These include the size of the annealing chamber, temperature, purity of solvent, leak rate (if applicable), and time in the swollen state. Of course, precise knowledge of steady solvent vapor pressure is the one parameter that would be useful to know precisely; however, in most benchtop laboratory frameworks this is not something that is typically measured or controlled. Thus, annealing chamber size and other such facets (e.g., proximity of the sample to the liquid surface) should be documented and carefully controlled as they all can influence the steady state vapor pressure and the time it takes to achieve this pressure. There are several examples in the literature where seemingly inconsequential aspects of the SVA apparatus must be carefully controlled to achieve reproducibility. As an example, relative humidity changes (seasonal, geographic), which are not
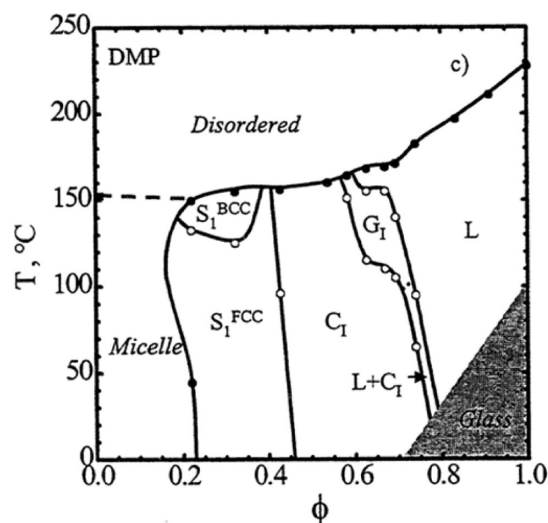
controlled in simple systems with a leak valve open to the atmosphere, may significantly impact the process.

**Solvent Removal.** It is important to stress that the method of conversion of the swollen state to the final dried state is critical and is often neglected in many studies. Recent studies show that solvent removal rates can strongly affect film morphology at the free surface but not at the film/substrate interface.[53] After solvent exposure and subsequent removal from the environment, the solvent evaporates from the swollen film. Rapid evaporation of the solvent can "freeze in" the organization of the swollen state. Solvent evaporation can also direct the ordering of the film through the formation of an "ordering front" as shown in Figure 8.[30] The deswelling results
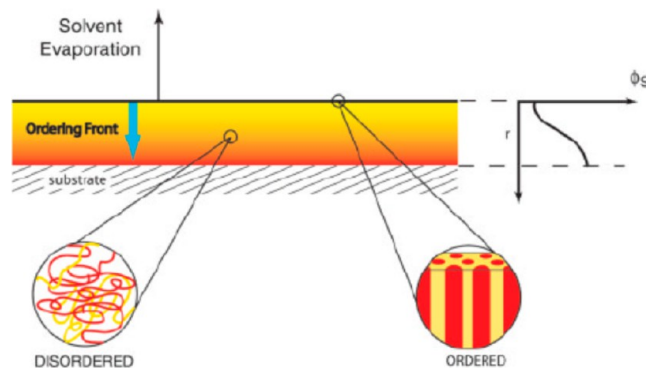


**Figure 8.** Schematic view of the solvent evaporation in a thin block polymer film illustrating the concept on an ordering front that propagates through the film. Reproduced with permission from ref 30. Copyright 2004 Wiley-VCH.

in collapse of the swollen microdomain arrangement and can also lead to structural transitions. Going from the swollen state to the dried state requires transition from a lyotropic state to a thermotropic state, and this can be path dependent considering polymer dynamics and lyotropic transitions that can occur when concentrating the system.

Also, because there is a gradient in solvent concentration formed when drying, this field can influence how the state of order propagates through the film upon solvent removal. This drying can induce significant strain in the films which can affect

the dimensions of phase-separated structure and shape of the domains. There are documented cases of very fast solvent evaporation and very slow evaporation leading to highly organized structures. Thus, both dynamic and thermodynamic considerations come into play, and they will clearly depend on the specific system being explored. Fast evaporation may be desirable for one system and not for another. Control of the evaporation is an important parameter to consider when designing an experimental SVA system.

**Analysis of Thin Films (Dried and Swollen State).** Techniques used to analyze thin films of block copolymers pre- and postannealing (i.e., in the dried state) are very well documented. Block polymer thin film morphology is typically defined by the surface, interior, and substrate/film structures. These can be the same for ultrathin films[43] or could be completely different for thicker films. The commonly used techniques for their characterizations are atomic force microscopy, scanning electron microscopy, grazing incidence X-ray and neutron scattering, and ellipsometry. While atomic force and electron microscopies are the most used techniques, they give rather local information. Atomic force microscopy is simple to carry out and nondestructive, and in the majority of studies data are recorded as topographical or phase images with the instrument in tapping mode. Topographical atomic force microscopy imaging can be limited because variation in height from domain to domain can be small and on the order of the surface roughness.[54] Thus, tapping mode atomic force microscopy phase imaging is most commonly used for flat samples with large mechanical contrast between the blocks. Moreover, atomic force microscopy images can be highly dependent on the imaging parameters.[55] The same problem of distinction between the two blocks can be encountered in scanning electron microscopy, and charging effects can be problematic. Some sample treatments such as selective staining or removal of one block can be used to enhance contrast.[56]

Scanning electron microscopy or transmission electron microscopy examination of film cross sections allows for the characterization of the interior of film, but lack of contrast generally prevents direct imaging without staining or removal of one block. Another way to access 3D information is the "step by step" layer removal and surface imaging approach.[57] Scanning electron microscopy imaging of inorganic replica of one block network can also be used to investigate the interior of a film.[58]

The interface between the film and substrate is more difficult to characterize. However, this is very important to establish since many nanopattern transfer techniques are reliant on clear and continuous connections from the top of the film to the bottom. Techniques used to access this information are not simple to carry out in many cases, and 3D studies of block copolymer films are limited. Possible methods include peeling (or floating) off the film and microscopic examination of the back of the film.[13,59,60]

Grazing incidence small-angle X-ray or neutron scattering can be used to probe the long-range lateral ordering in the sample with the in-plane vector component and the ordering in the depth direction with the out-of-plane vector component. This technique provides information averaged over a macroscopic portion of the sample. Fine adjustment of the incident angle can lead to differential information on the ordering on the surface, the interior, and the substrate/film interface.[61,62] Finally, ellipsometry and other interferometric techniques (e.g., spectral reflectance) quantify the film thickness without

tedious preparation of the film and are nondestructive. Spectroscopic ellipsometry is most often used in this regard.[63] Combining adsorption/desorption techniques with ellipsometry of films after the removing of one block of copolymer can also provide an access to porosity and pore shape.[64] This method is based on the measurement of the refractive index and thickness variations induced by the adsorption and condensation of solvent vapors in the pores of the analyzed sample.

The knowledge of the morphology during the SVA process is of fundamental importance. Characterization of the film as it swells, equilibrates, deswells, and goes through thickness and morphology changes is critical in extending our understanding of the SVA method. During SVA and solvent evaporation, the swelling of the film can be followed by ellipsometry or reflectometry. The deduced swelling ratio is one of the key parameters of the SVA process and is needed for critical comparison of SVA methods. Only a few experiments have been reported that follow the morphology by atomic force microscopy during SVA since the main issue in this case is the swollen state of the film and its mechanical state.[65] The swelling related morphology evolution is generally studied by small-angle scattering. The information given by these grazing incidence small-angle X-ray scattering (GISAXS) experiments combined with the swelling ratio given by ellipsometry is in our point of view the key to generate a more complete understanding of the SVA process.

## III. CONTEMPORARY RESEARCH AND SVA PROCESS INSIGHTS

In the first part of this section, we focus on the relationship between the morphology in the swollen state and the final structure in the dried state. The second part is dedicated to alternative annealing conditions and techniques, and the third part describes advanced annealing experiments that have been recently described to enhance the control (and/or the understanding) of the SVA process. Finally, we highlight some recent characterization work on the morphology in the dried state, allowing the solvent vapor annealed block-polymer films to be implemented in nanotechnological applications.

**Morphology in the Swollen State and Its Transformation to a Dried Film.** The structure adopted by a block polymer film after SVA results from successive phenomena occurring during swelling, time in the equilibrated swollen state, and deswelling. Complete control of the final morphology requires a full understanding of all the structural transitions accompanying these processes. This effort is however quite rare, and most of the studies focus on the final dried state. *In situ* measurements continuously carried out during the experiment are critical to attain a more complete picture of the entire process. Below we discuss some recent studies that are nice illustrations of this approach.

To assess the morphology in the swollen state, *in situ* GISAXS measurements are perhaps the most valuable and readily applied. Although such experiments are not always easy to perform because of the relatively low contrast between the scattering domains, there are significant advantages because the samples are probed remotely and instrumentation is not directly exposed to aggressive environments. GISAXS should be considered as one of the most powerful tools to allow for a full understanding of the SVA process. Among the earliest work on the subject, the studies on the morphology of swollen poly(isoprene)-*b*-poly(lactide) thin films by Cavicchi et al. are
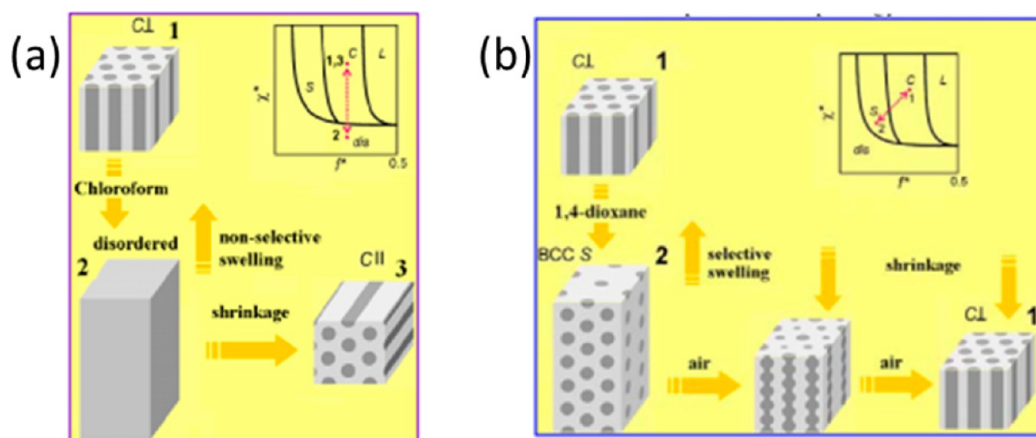
**Figure 9.** Schematic representation of microdomain reorientation during swelling of poly(styrene)-*b*-poly(4-vinylpyridine) film in nonselective solvent (a) and selective solvent (b) vapors. Reproduced with permission from ref 68. Copyright 2010 Springer.
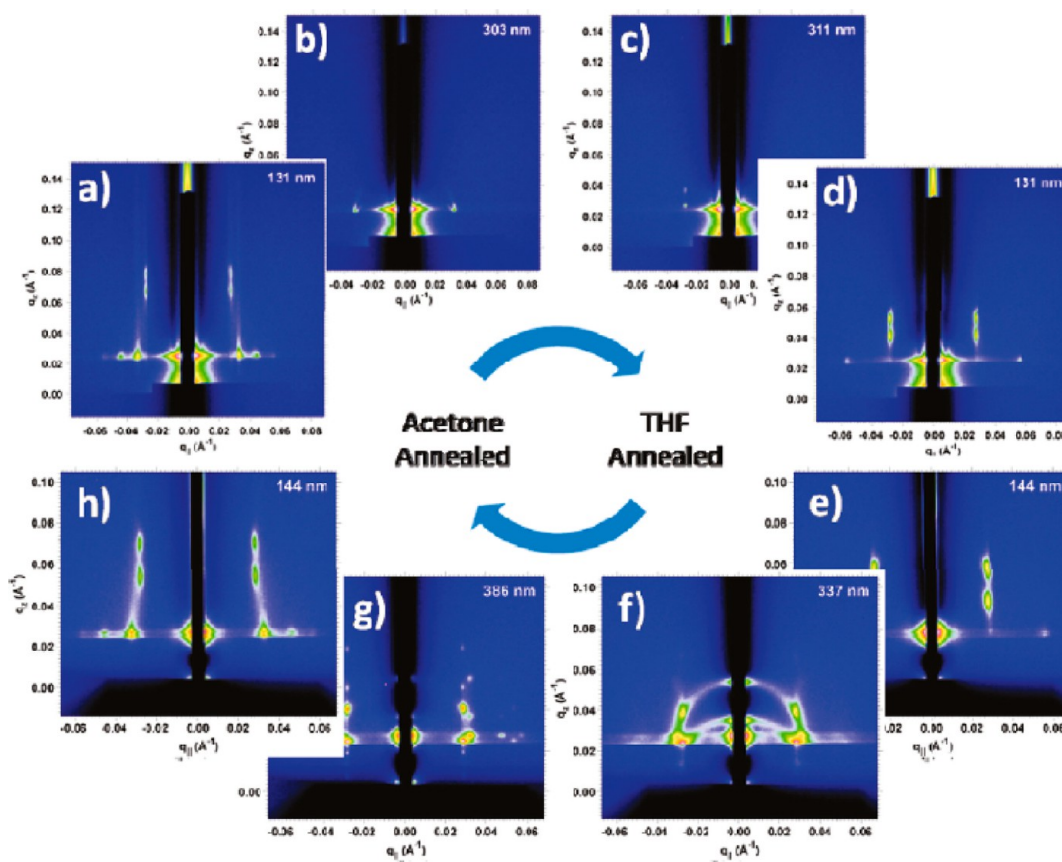


**Figure 10.** Illustration of real time *in situ* GISAXS analysis of the morphology changes of poly($\alpha$-methylstyrene)-*b*-poly(4-hydroxystyrene) thin films upon solvent swelling. A reversible change from spherical morphology under acetone vapor to parallel cylinders under THF annealing is showed. Reproduced with permission from ref 70.

worth noting.[66,67] In a more recent study by Gowd et al., investigations of the orientation changes of cylindrical poly-(styrene)-*b*-poly(4-vinylpyridine) thin films were performed using time-resolved *in situ* GISAXS, during annealing with nonselective (chloroform) and selective (1,4-dioxane) solvents.[68] Swelling of perpendicular cylinder arrangements produces parallel orientation in the case of nonselective solvent, whereas the orientation remains perpendicular in the case of the selective solvent. Such behavior was related to the difference of morphology within the swollen state. In the case

of the nonselective solvent, a disordered state was produced as seen by the diminution of the intensity of the scattering peaks: an order−disorder transition, provoked by the mediation of the unfavorable segmental interactions, was produced in this case. In contrast, the swollen state remains microphase separated in the case of the selective solvent, and the selective swelling of the poly(styrene) block induces an order−order transition as observed on the GISAXS patterns (a body-centered cubic phase was formed). Upon drying, the cylindrical morphology is recovered in the two cases, but their orientations were different.
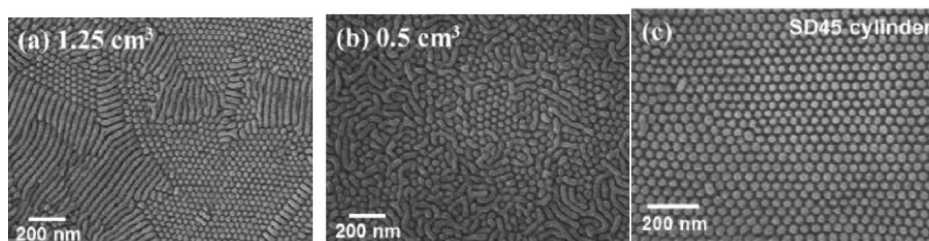
**Figure 11.** Scanning electron microscopy images of 45 kg mol$^{-1}$ cylindrical poly(styrene)-*b*-poly(dimethylsiloxane) block copolymer films. The films ~300 nm thick were treated with 30 s of 450 W $CF_4/O_2$ RIE and then 30 s of 90 W $O_2$ RIE. Annealed with (a) 1.25, (b) 0.5, and (c) 0.75 cm$^3$ of chloroform. Reproduced with permission from ref 73.

In the fully disordered state, the cylinders grow from a homogeneous state, and a more energetically favored parallel orientation was obtained. In contrast, a perpendicular orientation was preserved for the other case due to the existence of kinetic constraints that "freeze" the in-plane joining of the spheres required for a parallel reorientation; thus, the metastable perpendicular orientation was re-formed. The two pathways are illustrated in Figures 9a and 9b.

In addition, the rate of evaporation from the same swollen state can play a central role. For example, Kim et al. studied thin films of cylinder-forming poly(styrene)-*b*-poly(ethylene oxide) samples. A fully disordered swollen state was determined by *in situ* SAXS, but in this case, the dried state exhibited a dense array of perpendicular cylinders.[30] It was thought that rapid solvent evaporation causes an ordering front that forces the cylindrical domains to orientate in the direction of the solvent gradient. In another work, Bosworth et al. observed a cylinder−sphere phase transition upon annealing a poly(α-methylstyrene)-*b*-poly(4 hydroxystyrene) thin film in a selective solvent.[69] In this system the cylinders were not recovered upon drying because the BCC structure was kinetically trapped in the dried state, due to the fast evaporation of the solvent (acetone).

The morphology in the swollen state depends on the solvent vapor pressure and selectivity. 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.[70] Swelling a film containing perpendicularly oriented cylinders with low content of tetrahydrofuran did not lead to any morphological change and the film returned it to its original state. At higher contents of solvent, however, new signals were observed in the solvent swollen film consistent with parallel oriented cylinders. Upon rapid removal of the solvent the parallel orientation was preserved in the dried film. The authors claim that at low levels of solvent the polymer film does not have enough mobility, but with enough solvent the interfacial preference of the blocks leads to a parallel morphology. In the case of tetrahydrofuran, the authors posit that there is no change in morphology upon swelling, but in the case of the more selective solvent acetone an order−order transition occurs. Again, sufficient acetone is necessary for this to occur, and the authors attribute this mainly to a polymer mobility limitations based on glass transition arguments. In the case of sufficient acetone the GISAXS data were consistent with a face-centered orthorhombic packing of spheres that is preserved upon rapid drying. By alternating between acetone and tetrahydrofuran, the morphology of the dried films could be reversibly switched (Figure 10). This publication empha-sized the need to have sufficient mobility in the swollen films to induce structural reorganizations. In this particular example it

seems that in both cases the swollen films remain ordered at high (>200% of the original film thickness) swelling extents.

One feature commonly reported in many SVA experiments is the time dependence of annealing on the final dried morphology. This phenomenon can be related to the morphology in the swollen state (ordered or disordered). Indeed, if the swollen state is disordered, further annealing should have no effect, and the final morphology will be entirely driven by the solvent evaporation step (see below). On the other hand, if the swollen state is ordered (microphase-separated), orientation changes and/or order−order transitions may occur as a function of annealing time. This has been verified in our group where an ordered morphology was observed by *in situ* GISAXS (even at high swelling degrees) for poly(styrene)-*b*-poly(lactide) block polymers,[71] and the final dried morphology was dependent on the annealing time.[72]

The above observation is also in line with a 2012 study of Son et al. in which SVA was used organize cylinder-forming poly(styrene)-*b*-poly(dimethylsiloxane) block copolymers.[73] In that work, the ratio of solvent surface area to SVA chamber volume was used to parametrize the process. The solvent (acetone or chloroform) was allowed to slowly leak from the chamber over a multihour period; changing the initial amount of solvent in the chamber resulted in controllable annealing. Wetting layers of parallel cylinders were formed in both thermally annealed samples and solvent annealed samples. However, in the solvent annealed samples, the perpendicular orientation of the cylinders was apparent below the top ~100 nm of the film. In this study, all the films swelled within a few minutes and retained a swelling ratio that was nearly independent of both initial solvent volume and initial film thickness. Importantly, the films deswelled at over about 1 h in all the samples due to the leak in the chamber. A key observation in this work was that the annealing time was critical in determining the quality of the perpendicular orientation. As show in Figure 11, the perpendicular cylinders were achieved in the case of 0.75 cm$^3$ of solvent, but poor quality films were obtained at both 0.5 and 1.25 cm$^3$ of chloroform. This strongly suggests that the time in the solvent swollen state is important since all three of these solvents volumes are expected to have similar swelling and deswelling rates. Again, this particular feature is related by the authors to the existence of microseparated system in the swollen state. It is interesting to note that the authors also observed that slow drying was critical to achieve a well-ordered perpendicular orientation indicating that evaporation also play a determinant role.

As mentioned above, the disordered swollen state may produce various morphologies in the dried state depending on solvent evaporation rate. In 2010, Phillip et al. attempted to capture the salient features of SVA/evaporation that give

perpendicularly ordered cylindrical structures using a theoretical approach and provided a fresh insight into the SVA process.[38] Under most coating situations, the solution of block polymer used to generate thin films is devoid of any specific microstructure because of the high dilution. Upon evaporation, the block polymer solution concentrates and passes through an order−disordered transition concentration that first occurs near the surface of the film in contact with the solvent vapor. After nucleation of the ordered phase, it will grow in the film as the solvent continues to evaporate. The authors posit that the solvent concentration profile at this nucleation point is critical to determining the microstructural orientation upon subsequent solvent removal. As growth of the ordered phase is the product of a thermodynamic driving force and a kinetic term associated with polymer relaxation rate, the way these two terms change with vertical position in the film will determine orientation of the microstructure. If the growth rate increases with position into the film (i.e., if the polymer relaxation rate increases with position faster than the driving force decreases), the growth of an ordered structure is able to "accelerate" into the film, forming perpendicular cylinders. A more balanced situation between driving force and relaxation rate occurs deeper into the film, considering that the solvent concentration increases further from the vapor/solution interface; higher concentration of solvent lowers the driving force for growth of a particular ordered state but also results in faster chain dynamics. Thus, it is the product of these two terms that is the key determinant; if the product of driving force and growth rate is larger at a position "deeper" into the film from some initial position where the ordered structure growth has begun, then the cylindrical structure can grow faster and further into the film and perpendicular cylinder arrangements will result. Through a detailed theoretical analysis involving prediction of solvent concentration profiles and driving forces for ordered structure growth, Phillip et al. proposed a critical concentration of solvent at which the transition from perpendicular to parallel cylindrical structures occurs. Above this concentration, parallel cylinders will grow. This would typically be observed under slow evaporation conditions and result from the absence of a steep concentration gradient in the thickness of the film. However, when the ordered structure nucleates below this critical concentration, upon solvent evaporation perpendicular structures are preferred since the driving force for growing cylinders into the film is typically high. This situation occurs during rapid drying (Figure 3). However, in very thin films or under very rapid drying, there is not enough time for the polymer chains to reorganize as the drying time is much shorter than the characteristic ordered structure nucleation time, and disorganized structures typically result.

For some systems, this relationship of the SVA process to structural orientation can be very complex. Mokarian-Tabari et al. recently found a direct link between the degree of swelling of the film, the solvent content, and orientation in a poly-(styrene)-b-poly(ethylene oxide) block copolymer that formed hexagonally arranged poly(ethylene oxide) cylinders in a poly(styrene) matrix.[74] Using atomic force microscopy, a swelling-dependent reorientation of the cylinder direction but also a cyclic variation or flipping of the orientation (from cylinders vertical to the surface plane to cylinders perpendicular to the plane) was observed. These flips could be seen for several cycles of fixed period. An *in situ* time-resolved light scattering device combined with an environmental cell was used to correlate the structural changes with the film thickness

variation. These effects were simply based on volume changes of the film. A parallel orientation of cylinders is typically favored at thicknesses corresponding to the domain spacing, suggesting that at a key degree of solvent swelling this critical thickness was attained, and the perpendicular orientation would flip to the parallel orientation. Since the two orientations had slightly different swelling characteristics (the solvent used was selective and the surface composition was different in each orientation), it allows the cyclic morphology changes to be seen. This was verified by studying different film thicknesses and confinement effects that allowed the complex relationship between kinetics and equilibrium states to be defined.

**Alternative Annealing Processes.** Health and safety concerns have led to significant changes in the use and selection of solvents in industry environments.[75] Because carbon dioxide is abundant, nontoxic, and inflammable, compressable fluid phases and, in particular, the supercritical (sc) state of this gas have led to its use as an environmentally friendly solvent.[76] Further, the solubility parameter of sc-$CO_2$ can be tuned with small variations in pressure and/or temperature.[77,78] The use of sc-$CO_2$ as a solvent in SVA of block copolymer films may thus be seen as attractive for large-scale manufacturing. Early work on the use of carbon dioxide to anneal block polymer thin films was reported by Ramachan-draRao in 2001.[79] Sc-$CO_2$ may have particular relevance because while it is generally a poor solvent for polymers,[80] it can have high diffusivities in polymers and can swell common polymers such as poly(styrene)[81] and poly(methyl methacrylate)[78] effectively. The high diffusivity and moderate sorption properties lead to sc-$CO_2$ being a very effective solvent for enhancing chain mobility well below the glass transition temperature.[82] Importantly, the small size and chemical inertness of $CO_2$ also suggest it can be controllably removed from films. It may also find practical application because sc-$CO_2$ processing of large silicon wafers is more tractable than using typical organic solvents since homogeneous exposure and condensation avoidance can be achieved over large areas.

Perhaps the most complete explanation of the effect of sc-$CO_2$ (and a very useful exposition on solvent−block polymer interactions in general) was provided by O'Driscoll et al. in a recent paper[83] where they combined a very thorough experimental examination of the effect of various solvents including $CO_2$ on the microphase segregation of a hydroxyl-functionalized poly(styrene)-b-poly(methyl methacrylate) diblock system using self-consistent field theory models. In this system, the hydroxy-functionalized block was chemically grafted to the surface. In general, they showed that SVA is not effective for generation of ordered morphologies because the solvent improves the miscibility of the two polymer blocks, leading to an effective decrease of the interaction parameter with increasing solvent content. In line with our views, the authors point out that careful consideration of solvent−polymer interactions that is needed to understand the role of solvent in the SVA approach. Sc-$CO_2$ was not effective in inducing microphase segregation but could facilitate removal of solvent from the films. This is because sc-$CO_2$ is a poor solvent for both poly(styrene) and poly(methyl methacrylate) but does swell both polymers[84] which facilitates solvent removal. The authors also show by considering several solvents and comparing experiment and theory that the microphase-separated morphology can be changed by the relevant solubility of the solvent in the blocks. Changes in effective compositions caused by selective swelling of one block can lead to ready

changes in the structure and correspondingly shift the expected phase boundaries.[85]

Other block copolymer films show more encouraging results than those noted for the poly(styrene)-*b*-poly(methyl methacrylate) system.[86] For example, thermal annealing of poly(ethylene oxide)-*b*-poly(1,1-dihydroperfluorooctyl methacrylate) results in only disordered structures in the temperature range 80−180 °C. However, annealing in supercritical $CO_2$ reveals an order−disorder phase transition between 116 and 145 °C. No clear, direct imaging analysis is provided to support the observation of ordered phases, but indirect evidence is seen for a structure consisting of poly(ethylene oxide) spheres embedded in a matrix of poly(1,1-dihydroperfluorooctyl methacrylate) above a brushlike layer of poly(ethylene oxide) molecules. The authors once again note the importance of proper consideration of the solvent-modified interaction parameters and volume composition changes that result from polymer swelling. In this case, the $CO_2$ is selective for the poly(1,1-dihydroperfluorooctyl methacrylate) block. To date, the most convincing evidence for a well-ordered periodic structure in the swollen state was reported for a rod−coil system, poly(dimethylsiloxane)-*b*-poly{2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene}.[87] In this case sc-$CO_2$ is selective for the poly(dimethylsiloxane) block. Small-angle X-ray scattering evidence for lamellar and hexagonal structures was presented and a range of block compositions studied. This allowed observation of an order−disorder phase transition between the hexagonal and lamellar structures depending on the degree of swelling.

As shown, while some work has been carried out that provides a fundamental understanding of the basis and potential of supercritical sc-$CO_2$ SVA (and it should be noted that no other compressible fluid has been studied to the best of our knowledge), the work is very much in its infancy. Little evidence of highly regular, long-range, periodic structures has been presented. The paucity of data may reflect the success of conventional SVA and the limited number of researchers with access to the necessary equipment. However, the need to develop SVA equipment that can be used for large substrates may ensure that the technique is investigated considerable more.

**Contemporary SVA Techniques.** Since the very first SVA experiments, a great variety of experimental environments have been developed in order to manipulate the process parameters. From the crude conditions consisting of placing the block copolymer covered substrate in a closed chamber (like a beaker or desiccator) containing a given volume of solvent, experimental devices have progressively evolved to more sophisticated systems using accurate control of the vapor pressure, dynamic flux, mixture of solvent vapors, microwave technology, etc. Additionally, *in situ* probes like interferometry, ellipsometery, quartz crystal microbalance, and other techniques were also introduced to follow the evolution of the characteristics of the system upon annealing. In this section we will provide selected examples of recent experimental systems that illustrate more "advanced" SVA techniques.

One of the main issues of the standard experimental setups is related to the time required to obtain the desired ordered system and low defect morphology. In 2010, Zhang introduced a novel solvothermal annealing process that significantly reduced the time needed to generate highly organized thin films of cylinder-forming poly(styrene)-*b*-poly(2-vinylpyridine) and poly(styrene)-*b*-poly(methyl methacrylate) on unpatterned

and patterned Si wafers.[88] In this approach, the block polymer film was simultaneously exposed to solvent vapor by the presence of the selected solvent in the bottom of a sealed vial containing the coated substrate (Figure 12a) and heated using a
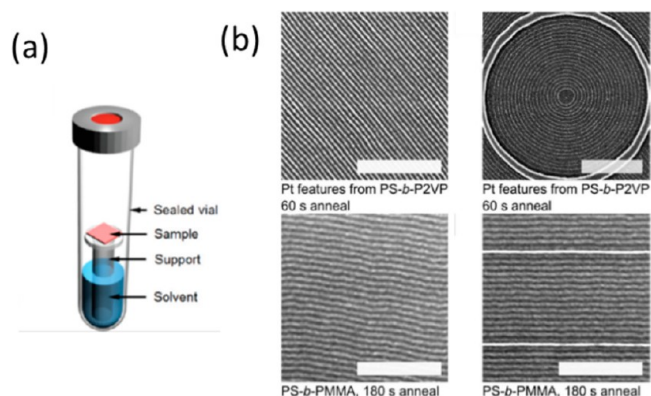


**Figure 12.** Experimental device (a) and observed morphology (b) in a microwave assisted solvo-thermal annealing process. Reproduced with permission from ref 88.

microwave reactor. In their experimental conditions, the sample temperature ranged between 60 and 260 °C. Within selected conditions, this process allows very high-speed reorganization with unusually low defect densities of less than two defect pairs per square micrometer. The effects of the sample temperature, exposure time, molar mass, solvent nature, and the substrate resistivity on the ordering defined by the defect density were explored. Within these experimental conditions, pressures in the vial as high as 8 bar were measured, suggesting a very high vapor solvent concentration in the vapor phase and also in the film. However, no dewetting was observed. All the samples presented cylinders oriented parallel to the surface (Figure 12b). Increasing the temperature decreased the defect density, and even a 2 s annealing time led to decrease of defect density compared to as-spun films. Lower substrate resistivity induced greater microwave absorption and a higher substrate temperature for the same microwave energy and consequently a lower defect density. Although no mechanism was identified for such impressive ordering, it can be anticipated that the combined effects of the elevation of the temperature, the energy brought by the microwaves, and the high vapor pressure in the vial favored this behavior.

As previously described, the nature of the solvent vapor is of prime importance in the final morphology. This is why numerous solvents and then mixtures of solvents have been studied to tune the process. However, it is experimentally challenging, expensive, and time-consuming to study a wide range of solvent mixture compositions. In 2011, Albert et al. designed, fabricated, and used a new type of microfluidic device to perform SVA (Figure 13) with different solvent vapor compositions in a single experiment.[89] In this experimental setup, comprising six annealing chambers and one isolated chamber for reference, they were able to mix two gas streams enriched in two different solvent vapors. The device included apparatus for real-time monitoring of film thickness for measuring solvent uptake by the film. SVA of a cylinder-forming poly(styrene)-*b*-poly(isoprene)-*b*-poly(styrene) block copolymer with a mixture of *n*-hexane (which is poly(isoprene) selective) and tetrahydrofuran (a neutral solvent for both blocks) was performed. The *n*-hexane mole fraction in the
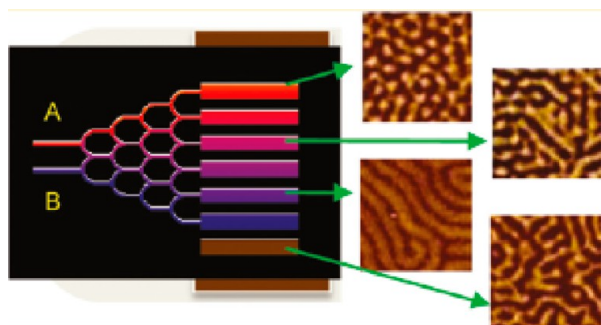
**Figure 13.** Microfluidic SVA device and obtained morphologies. Reproduced with permission from ref 89.

chambers varied from >0.99 to 0.69, and the solvent concentration in the film varied from 60 to 40% v/v. Morphological transformations from spherical arrangements to perpendicular cylinders, parallel cylinders, and dewetting were observed as a function of the *n*-hexane fraction and were related to the selective swelling of the poly(isoprene) block by *n*-hexane. This device with its multisample approach represented a significant contribution to improving our understanding of SVA phenomena as it allowed simultaneous monitoring of film thickness and also the morphology determination by GISAXS. The work also explicitly showed that the use of solvent mixtures (versus a single solvent) can help to tune solvent selectivity and to obtain the desired block copolymer morphology.

Another nice example of a sophisticated continuous flow system was reported by Gotrik et al. in 2012.[90] In this system, inert gas flows containing solvent saturated vapors were produced by bubbling a carrier through the liquid solvents (Figure 14). The gas flows were mixed together with inert gas
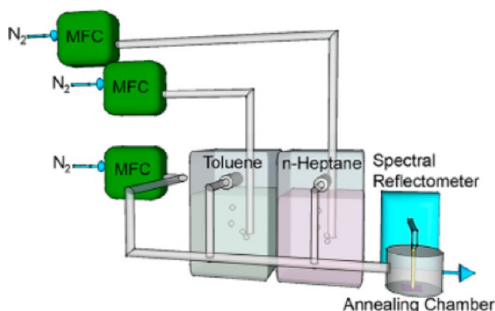


**Figure 14.** Continuous flow system for SVA. Reproduced with permission from ref 90.

to produce a gas flow containing a given vapor concentration at a given total pressure. In this study cylinder-forming poly-(styrene)-*b*-poly(dimethylsiloxane) thin films were exposed to nitrogen gas flow containing poly(dimethylsiloxane)-selective heptane and poly(styrene)-selective toluene. The morphologies of the samples were recorded as a function of total pressure and solvent composition and compared to those obtained on the same films annealed using a simple static solvent reservoir. The results showed that the flow device produced a much richer array of microphase-separated structures than the reservoir system with, for example, observation of an unusual discontinuous in-plane lamellae arrangement. Self-consistent field theory (SCFT) simulations were performed to model the morphology changes that occur during SVA and understand the

observed changes in microdomain morphology and orientation. This work provided a very flexible but robust system for understanding the SVA process with *in situ* film swelling control and solvent vapor pressure control. These techniques and information should enable the design of the processing conditions so as to precisely control specific morphologies.

**Applications Using Solvent Vapor Annealed Films.** Potential applications of block polymer thin films in nano-lithography or device fabrications often require a perfect control of the annealed morphology. We have summarized in the previous sections a number of analytical techniques that can be used to analyze the top, the bottom, or even inside the film, with their associated advantages and drawbacks. We herein would like to report two methods from our groups that can be applied to block polymers where one of the blocks can be selectively removed, leading to the formation of a porous network. Several excellent reviews on the utility of highly organized block polymer films are in the literature, and we refer the reader to those for a more complete coverage of this important area.[91−93]

The first method is based on the preparation of high fidelity SiO$_2$ replicas of porous thin films that can be obtained from microphase-separated block copolymer systems.[58] Porous films, obtained from the SVA of a cylinder-forming poly(styrene)-*b*-poly(lactide) block copolymer containing a sacrificial block (poly(lactide)) that can be readily and selectively removed, were first infiltrated by silica precursors using a chemical solution deposition process, before being exposed to a brief thermal treatment to promote inorganic condensation and elimination of the poly(styrene) template. In a very simple experiment, the porous film on a silicon wafer is immersed in a solution containing the silica precursors and withdrawn at an appropriated speed using dip-coating. The film/substrates were then dried and calcined at high temperature to cross-link and densify the silica components. Scanning electron microscopy observations of the obtained replica gave a three-dimensional view of the internal topology of the porosity, offering an ideal tool to characterize the topology of porous networks in supported polymer thin films. This method can be generalized to any type of porous polymer media where one block can be selectively removed allowing the visualization of the internal topology with valuable details in the bulk of the film as well as at the substrate and air interfaces.

The second methodology uses environmental ellipsometric porosimetry (EEP) which is based on the measurement of the refractive index and thickness variations induced by the adsorption and condensation of solvent vapors in the pores of the analyzed sample. This technique allows gas adsorption−desorption isotherms to be collected to allow accurate determination of the pore-size distribution and mechanical properties of films ranging from a few nanometers to micrometers thick. This method, initially developed for the characterization of inorganic or hybrid supported layers, was used to probe the internal porosity of nanoporous polymer thin films.[64] In this work, the measurements were performed with isopropanol on a poly(styrene) film exhibiting a well-defined porosity obtained from the selective etching of a solvent vapor annealed poly(styrene)-*b*-poly(lactide) sample. It was shown that classical adsorption−desorption isotherms could be obtained from the refractive index variations of a porous polymer film in equilibrium with vapors of the liquid. The calculation of the pore size distribution using a modified Kelvin equation in both isotherm branches (adsorption and

desorption) led to a pore size consistent with that extracted from the microscopic study of the film and supporting GISAXS measurements.

A more detailed analysis of the EEP data revealed that the topology of the porous structure was more complex than a simple picture of vertically oriented nanochannels. Adsorption−desorption isotherms displayed hysteresis that suggests the existence of cylindrical pores opened at both ends. This indicates that instead of being completely perpendicular with a circular base anchored at the surface of the substrate, some adjacent pores are connected at the substrate/film interface. This method can be generalized to any type of porous polymer system, including those with more complex topology, including the gyroid structure which is relevant for many practical applications.[94] For each porous sample, the crucial parameter will be the selection of an appropriate liquid to probe the porosity, dictated by the polymer/solvent interactions and the pore wall functionality.

The practicality of solvent vapor annealed block polymer templates for pattern transfer was recently demonstrated by Baruth et al.[95] Using poly(styrene)-*b*-poly(lactide) diblock polymer thin films approximately one and a half times as thick as the principal domain spacing for the cylinder-forming microstructure, the authors showed that "uncontrolled" annealing with tetrahydrofuran vapor led to moderately well-organized structures on hydrophobically modified silicon wafers. To attain better control over the SVA process, they used a climate controlled, all-metal SVA chamber that gave much more precise control over annealing conditions (e.g., absolute and partial pressures, humidity, and annealing/evaporation times). Using only a 10 min annealing process with very rapid (<1 s) evaporation times, very well organized arrays of hexagonally packed features were reproducibly obtained; lateral correlation lengths on the order of 2 $\mu$m were evident. Through this SVA process, subsequent poly(lactide) removal through a hydrolytic process, and a brief plasma etch, the resultant nanoporous templates were used to pattern NiFe nanodots using a combined additive/subtractive "Damascene" type process. The nanodots obtained with these more highly ordered templates were much less dispersed in size and spacing compared to the structures prepared under the less well-controlled SVA conditions (Figure 15). The authors point out that high fidelity pattern transfer using solvent vapor annealed block polymer templates has not received as much attention as the templates themselves. This study, which delves deeply into the magnetic characterization of the patterned NiFe, is a rigorous demonstration of how solvent vapor annealed block polymer templates can be very useful for



**Figure 15.** A schematic of the Damascene process used to generate a pattern of metal nanodots from a SVA annealed block polymer thin film. Reproduced with permission from ref 95.

generation of high precision nanostructures. Furthermore, this work demonstrates how more careful control of the SVA conditions can be critical for the generation of highly organized templates.

## IV. OUTLOOK

As we have described, SVA of block polymer thin films capable of microphase separation is a powerful technique that allows for the generation of highly organized nanostructures in a simple manner. The process is typically carried out at or around ambient temperature and can be used for tuning of the nanostructural features by controlling solvent vapor composition and pressure, and can be effective over very short time frames (seconds or minutes). For these reasons of convenience and the fact that the resultant nanostructured films hold tremendous promise in a variety of advanced nanotechnologies, the practical implementation of SVA is a subject of critical importance and certainly warrants future study and development. We have confidence that proper fundamental understanding, coupled to appropriate engineering developments, SVA of block polymer films will go beyond the laboratory and find a place in the manufacture of nanostructured materials. In recent work, the use of SVA techniques to generate highly regular films with lithographic quality patterns over large substrate areas has been demonstrated.[96,97]

In this Perspective we have given our point of view on the important aspects of SVA and highlighted some recent and particularly relevant examples from the literature. While we are optimistic about the future of SVA, the process is not without its limitations of course. As discussed, careful control of operational parameters is critically important for reproducibility. This can complicate experimental apparatus and indeed requires more advanced systems than the simple laboratory systems often described in the literature. While we did not focus on issues associated with dewetting of the thin film in the swollen state, the mechanical instability of a liquid film supported on a surface and the subsequent development of macroscopic defects stemming from dewetting phenomena are critical challenges in manufacturing large area nanostructured thin films using these techniques.[98] The solvent can mitigate interfacial adhesion with the substrate and result in local or gross delamination of films. And, unlike thermal annealing, the use of the volatile organic solvents that are typically employed can lead to hazardous conditions from a health and safety perspective. Going forward, these and other issues will have to be tackled. Nonetheless, these technical considerations will benefit from a better and more fundamental understanding of the details of the entire SVA process. Below we identify three important areas that we believe will require more attention to advance SVA technologies.

First, carefully controlled SVA chambers should continue to be developed to improve reproducibility. This will require systems that allow for precise control over solvent vapor composition, absolute pressure, humidity, temperature, and solvent vapor introduction/removal rates. All of these experimental parameters should be meticulously defined in an ideal process. We recognize that simple systems can be effective (e.g., as outlined above, a vial with a slow leak rate has been demonstrated to be highly effective for small area substrates), but it has been our experience in three different laboratories in three different countries that subtle and sometimes unrecognizable differences in conditions can lead to irreproducibility. This, of course, renders proper scientific investigations aimed at
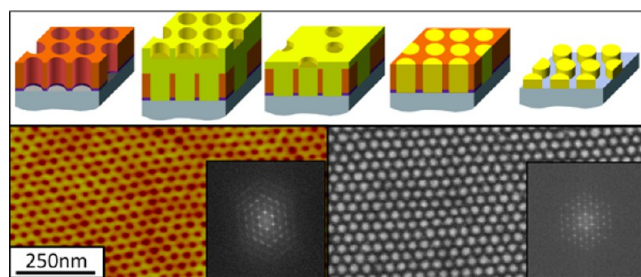
uncovering fundamental aspects of SVA frustrating and unproductive. In addition, advanced SVA apparatus should allow for *in situ* detailed investigation of the block polymer films in both the swollen and dried state. Grazing incidence small-angle X-ray scattering, ellipsometry, and interferometry are three important techniques that allow for a better under-standing of the thickness, state of microphase segregation, and nanostructure orientation before, during, and after SVA. This will require the fabrication of more elaborate and sophisticated annealing systems, but the payoff from studies in the literature and from unpublished work in our laboratories with respect to understanding the overall processes has been tremendous. More efforts along these lines are encouraged.

Self-consistent mean field theory has been very important to the understanding of block polymer structure in thin films. However, the application of theory to the SVA process has been limited. Understanding the origin and form of the equilibrium structure has been of tremendous benefit to the development of block polymer based technologies, but work is required to understand the kinetic development of equilibrium and metastable phases. Such calculations are critical to develop, for example, models for determining defect formation and annihilation as well as defining kinetic barriers to a desired structure. In SVA, the inclusion of small molecules introduces a second component that can interact with one or more blocks as well as any interfaces present (for thin films) introduce challenges into modeling studies. The changes that occur in the equilibrium solvent swollen state and the changes during solvent removal and deswelling are pivotal in defining structural morphology and the size and shape of the microphase-separated domains that result.

Finally, we feel that it is imperative that more emphasis be placed on the actual implementation of solvent vapor annealed block polymer films for lithography, pattern transfer, or other intended applications. While the images of the nanostructures in a solvent annealed block polymer film may be consistent with a highly organized and high fidelity structure, the true proof of utility requires actually going beyond the initial characterization stage and to demonstrate efficacy for the desired application. This can reveal limitations of what appears to be a functional material. In our experience, interfacial wetting layers, film/substrate adhesion, film stability, and other issues can reveal themselves when attempting to translate the nanopattern into another material. Going beyond surface characterization using microscopy post-solvent vapor annealed films will become more and more important for technological demonstration purposes.

Despite the challenges that exist, there is significant potential for the SVA methodology. Recognizing these challenges represents a maturity in the science and understanding of the approach. SVA (as opposed to simple thermal processing) will almost certainly be highly desirable for systems of high interaction parameter that offer the opportunity to develop nanostructures of the lowest dimension. In addition, the use of triblock terpolymers or other more complex multiblock polymers, which has been largely ignored in this Perspective article, will certainly receive more attention in the future.[99] Despite the fact that SVA of these polymers is even more complicated to understand and control, the new possibilities offered by such complex architectures will offer new opportunities, such as introduction of new functionality, fine-tuning of the orientation, and more complex morphologies. While we normally consider these materials for high-tech

applications, the methods afford development for more traditional applications such as adhesive, hydrophobic and antireflective surfaces, and textile applications that have wide-ranging implications. SVA offers the opportunity to develop large-scale nanostructures and nanopatterned surfaces with broad applicability at low cost.

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**Notes**
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Marylène Vayer graduated from the Chemical Engineering School of Strasbourg (France) in 1987 and received her Ph.D. in Materials Science (1989) from the University of Nancy II (France). She spent one year at the University of Liverpool as a Postdoctoral fellow before joining the laboratory of Surface Chemistry and Catalysis in Strasbourg as Centre National de la Recherche Scientifique (CNRS) research scientist. She moved to the Centre de Recherche sur la Matière Divisée, a joint research institute of the CNRS and the

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Michael Morris received his B.Sc. and Ph.D. in Surface Science (1983) from Liverpool University. He spent 2 years at Imperial College London as a Postdoctoral Fellow before taking up Lectureships at the University of Strathclyde in Glasgow and Cardiff University in Wales. In 1989, he became an Industrial Research Scientist at Imperial Chemical Industries in Teesside, Co., Durham in the UK with a main interest in using surface science methods to improve catalyst characterization by developing surface engineering approaches towards "tuning" activity. In 1994, he moved to University College Cork (UCC) in Ireland and developed self-assembly methods to create nanomaterials and nanopatterned substrates. He has been developing block copolymer lithography techniques in collaboration with industrial collaborators for 10 years. He is currently the Professor of Inorganic Chemistry at UCC and also leads the Nanoelectronics theme at CRANN in Trinity College Dublin where he is an Adjunct Professor.



Marc A. Hillmyer received his B.S. in Chemistry from the University of Florida in 1989 and his Ph.D. in Chemistry from the California Institute of Technology in 1994. After a postdoctoral research position in the University of Minnesota's Department of Chemical Engineering and Materials Science, he joined the Chemistry faculty at Minnesota in 1997. He is currently a Distinguished McKnight University Professor of chemistry and leads a research group focused on the synthesis and self-assembly of multifunctional polymers. In addition to his teaching and research responsibilities, Marc also serves as an Associate Editor for the ACS journal *Macromolecules* and is the director of the National Science Foundation funded Center for Sustainable Polymers at the University of Minnesota. During the 2012−2013 academic year, Marc was a LE STUDIUM research fellow at the Université d'Orléans/Centre National de la Recherche Scientifique (CNRS) in the CRMD.

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