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van Zoelen, Wendy; ten Brinke, Gerrit

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Thin films of complexed block copolymers

Wendy van Zoelen and Gerrit ten Brinke*

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Due to their ability to microphase separate into well ordered structures with periodicities on the nanometre scale, block copolymers have received widespread attention as building blocks for the fabrication of nanomaterials. In particular, thin films of block copolymers promise new technological breakthroughs in *e.g.* computer memory applications. This Review gives a short overview of progress that has been made in preparing suitable thin films of conventional coil–coil diblock copolymer systems, while the advantages as well as the complexities of using more unconventional systems such as triblock copolymers and supramolecular systems are emphasized.

Introduction

Since the emergence of the earliest computers, which could easily fill an entire room, vast improvements in lithographic techniques have made hardware sizes continuously smaller, at the same time resulting in higher speeds and less energy consumed per computing function. Current lithographic techniques have already reached a periodicity of less than 100 nm, however, as these techniques will eventually reach their limit with respect to costs and resolution, new methods to produce nanopatterns with a sub 100 nm periodicity are pursued in order to continue the downscaling trend. There are several new, “unconventional” techniques for nanofabrication including molding, embossing, printing, scanning probe lithography (SPL), edge lithography, and self-assembly.¹ Amongst these techniques, the self-assembly of block copolymers is widely considered as a feasible method, especially because of their low cost and ability to easily micro-

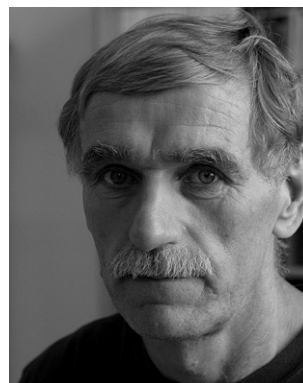
phase separate in ordered domains with length scales that are not available with lithographic techniques.²

Block copolymers are composed of two or more chemically distinct, and usually immiscible, polymer chains which are covalently bound together. In the case of two immiscible blocks, phase separation on the macro scale is no option as both blocks cannot detach from another and microphase separation in ordered microstructures with length scales of the order of ten to a hundred nanometres will occur instead. Depending on the (temperature dependent) Flory–Huggins interaction parameter between the monomer units χ , the length of the block copolymers N and the composition f , different structures are formed due to the balancing of the enthalpic interfacial energy between the blocks and the entropic chain stretching energy of the individual blocks. Body centered cubic (BCC) packed spheres, hexagonally packed cylinders and alternating lamellae are most common for conformationally symmetric diblock copolymers (Fig. 1). For weaker segregation ($\chi N \leq 40$) other morphologies, such as the bicontinuous gyroid or hexagonally perforated lamellae, can also be observed.^{3,4} Also in solution, block copolymer systems may form many interesting micellar structures depending on the

Laboratory of Polymer Chemistry, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands



Wendy van Zoelen received her MSc from the University of Groningen under the guidance of Professor Gerrit ten Brinke in 2004. In the same research group she is currently finishing her PhD research, which focuses on self-assembly and applications of hydrogen-bonded side-chain block copolymers. Her research interests include the behavior of these supramolecules in thin films.



Gerrit ten Brinke obtained his PhD in Statistical Physics from the University of Groningen, The Netherlands. He spent two years as a postdoctoral fellow at the University of Massachusetts at Amherst. In 1985 he became Associate Professor in the Polymer Department of the University of Groningen and in 1996 Professor. During 1994–1999 he was also part time Professor at the Helsinki University of Technology working closely together with

Olli Ikkala. His research interests are self-assembly in complex polymer systems.

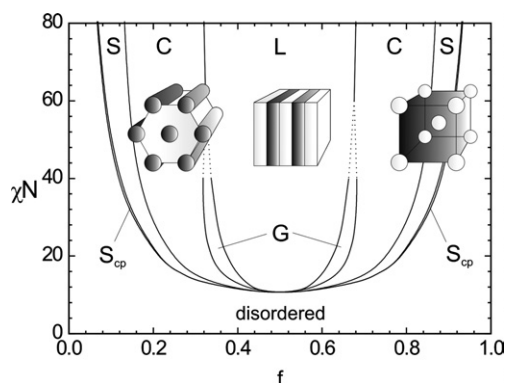


Fig. 1 A theoretical phase diagram for a conformationally symmetric diblock copolymer melt. S = spherical, C = cylindrical, L = lamellar, G = gyroid, S_{cp} = closely packed spherical. The perforated lamellar phase which is not addressed in the picture is believed to be a metastable state between G and L.

solvents used and preparation conditions,⁵ however this is beyond the scope of this Review.

The potential use of block copolymers for nanotechnology applications stems from the intrinsic differences between the microphase separated polymer blocks. For example, blocks may have different etch resistances to solvent or radiation. If the majority (matrix) block is selectively etched away, this results in nano-objects such as nanospheres and nanocylinders, however, more often the minority block is selectively removed, resulting in nanoporous structures. These may be used for microfiltration purposes, but also have a further use as templates for producing a wide range of functional materials.⁶ Also without selective etching, a variety of applications remains possible. For example, differences in electronic conductivity or dielectric contrast may be exploited for nano-electronics and photonics applications.^{7,8}

One of the biggest drawbacks that has been in the way of a large scale use of block copolymers for nanotechnological applications however, is the poor long range order of the microphase separated domains. Even though the alignment of these domains can be perfect over a length scale of up to several tens of microdomain periods, samples remain macroscopically isotropic. Methods that are used to improve long range order in bulk samples usually include flow fields such as oscillatory shear or extrusion, however, other methods such as electric field alignment have also successfully been used.⁹

Block copolymer thin films

Many interesting nanotechnological applications of block copolymers require the ordering of block copolymers in thin films. For example, a highly ordered hexagonal dot pattern obtained from a thin film of a cylindrically or spherically microphase separated block copolymer can be used in memory applications, whereas the inverse morphology can serve as a nanoporous membrane. At first sight, the reduction from three to two dimensions seems to be an advantage in tackling the above mentioned alignment issue, however, surface interactions very much complicate the phase behavior. The block that has the lower surface free energy will preferentially segregate at the air interface, whereas the block with the lowest interfacial energy,

which may be the same block, will segregate at the substrate interface, leading to a preferred parallel orientation of microdomains.^{10–13} However, if the thickness of the film is incommensurate with the microdomain period, for example because the film is confined between two rigid interfaces, or if it is simply kinetically trapped, the microdomains can be forced to orient perpendicularly or assume other non-equilibrium structures.^{14,15} Nevertheless, when an unconfined lamellar film is given the chance to equilibrate, for example by annealing at temperatures above the T_g of both blocks, it will usually form terraces with thicknesses that are a multiple of the microdomain period.^{10,16} In regions between terraces, the thickness is still incommensurate with the microdomain period, and other non-equilibrium structures are a possibility.

In case of symmetric wetting conditions, where both blocks wet the same interface, the thickness of a *lamellar* terrace is given by $d = nL$. For asymmetric wetting conditions, this changes to $d = (n + \frac{1}{2})L$. Only in the case of neutral surfaces, perpendicular lamellae will form spontaneously. This has been accomplished by using polymer blocks with similar surface properties or by adjusting the substrate, for example by coating it with a random copolymer brush.¹⁷ In the case of a neutral surface in combination with a strongly preferential surface, hybrid structures of parallel and perpendicularly oriented domains are also possible.¹⁴

For cylinder forming block copolymers, the structure formation behavior is excessively more complicated due to the possibility of surface reconstructions. Surface fields may be strong enough to change the surface morphology of a cylinder forming block copolymer to adapt to the planar symmetry of the substrate. These surface fields extend into the film to about 1.5 microdomain spacing deep and for a cylindrical $A_3B_{12}A_3$ triblock copolymer with symmetric wetting conditions the surface morphology has been found to change from a half lamellar wetting layer for an A attractive surface to perpendicular cylinders, parallel cylinders, perforated lamellae and finally full lamellae for a more B attractive surface.¹⁸ For very thin films, the effects of both surfaces combine and the transitions occur for weaker surface fields (Fig. 2). In the case of asymmetric wetting, thin films may possess a wide variety of hybrid structures such as cylinders with necks.¹⁹

The phase behavior of thin films of block copolymers forming a spherical morphology has not been extensively studied, but can be expected to be even more complex due to the three dimensional nature of the BCC morphology. Such systems are known to orient in a closely packed hexagonal (HEX) arrangement, because this morphology minimizes packing frustrations in thin films.²⁰ In three dimensions the BCC lattice reduces packing frustration, hence it is not strange that several studies in the group of Kramer have indicated packing transitions in these films. For example, a layering transition from HEX to FCO packing with an in-plane symmetry intermediate to that of the hexagonal lattice and the BCC (110) plane has been found upon increasing the film thickness of a spherical polystyrene-*block*-poly(2-vinyl pyridine) (PS-*b*-P2VP) block copolymer from 4 to 5 layers.^{21,22} In frustrated films, other packing morphologies such as face centered cubic (FCC) have also been found.²³ Furthermore, the spherical morphology does not contain any continuous block copolymer interfaces along which block copolymer chains

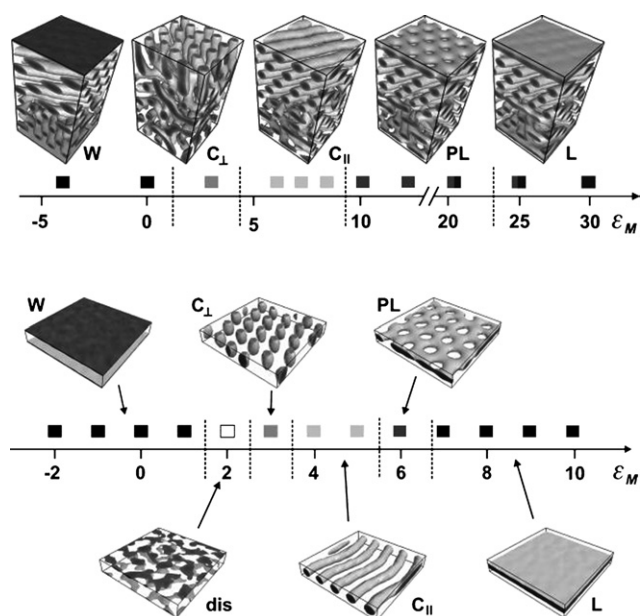


Fig. 2 Dynamic density functional theory simulation results for the effect of the strength of the symmetric surface field ϵ_M on microdomain structures and surface reconstructions of an $A_3B_{12}A_3$ melt for (top) a film with a thickness of 9 times the cylindrical period and (bottom) a film with a thickness of 1 cylindrical period. For a strongly A attractive surface (negative ϵ_M values), the surface is reconstructed to form a half lamellar wetting layer, which changes to perpendicular cylinders, parallel cylinders, perforated lamellae and finally a full lamella for a more B attractive surface. In very thin films, the effects of both surfaces combine and the transitions to non-cylindrical structures occur for weaker A or B attractive surface fields. Reprinted with permission from ref. 18. Copyright 2004, American Institute of Physics.

can redistribute, and in contrast to symmetric block copolymers, whose microdomains disorder directly into the homogeneous state through a single order disorder transition (ODT), these asymmetric block copolymers go through a series of transitions from spheres on an ordered lattice, to disordered spheres, to a homogeneous state. Both of these effects further influence their ordering mechanism in thin films.^{24–26} Together with the presence of possible surface reconstructions for strong surface fields, this provides a challenging puzzle for future research of block copolymer thin films with a spherical morphology.

Even less is known about the gyroid morphology in thin films. Due to its bicontinuous nature, alignment issues do not play an important role, which makes the gyroid an ideal candidate for membrane applications. However, although gyroid morphologies have been found to exist within relatively thick films,^{27–30} surface interactions are very likely to shift the morphology at the interfaces to the neighbouring cylindrical and (perforated) lamellar phases.³¹

A separate class of thin films are surface micelles. These are formed in ultrathin films, with a thickness much less than a microdomain spacing. The surface structures are a result of the absorption of single polymer chains on substrates, rather than of absorption of clusters of molecules.³²

Solvent annealing of thin films. Thin film behavior becomes even more complicated when instead of temperature annealing,

solvent annealing is used to improve the order in the films. For temperature annealing, the window between the highest T_g of the blocks and the lowest degradation temperature of the involved components might only be very small. When using solvent annealing, mobility is easily induced in the system without the danger of degradation, and the time scale of structure formation is significantly reduced.³³ In some cases, the long range order can even be greatly improved.^{34–36} However, the obtained structures most often do not correspond to the thermodynamic equilibrium morphology, as besides χ , N , f and the surface interactions, the morphology also depends on the selectivity of the solvent, the solvent evaporation rate and the vapor pressure. Fast solvent evaporation *directly after casting* of a film is known to kinetically trap non-equilibrium structures, which are usually not well ordered, whereas slower evaporation usually approaches the thermodynamic equilibrium morphology, depending on whether or not the polymer has enough mobility to form an ordered morphology at low solvent concentrations.³⁷ Solvent evaporation after annealing is therefore usually performed quickly, in order to retain the non-thermodynamic equilibrium but usually well ordered morphology that was obtained during annealing. Annealing in a selective solvent for example, results in preferential swelling of one of the domains, thereby changing the effective block composition and possibly also the “equilibrium” morphology at the used swelling ratio. It is obvious that high concentrations of a selective solvent change the effective block composition more drastically than lower concentrations, explaining why the morphology of a system may be changed from *e.g.* lamellar to cylindrical to spherical by increasing the vapor pressure of a matrix selective solvent.³⁸ Furthermore, a solvent may also change the interactions with the air interface, as the interface to be considered effectively changes from air to an air–solvent mixture. Therefore, high vapor pressures have been known to stabilize perpendicular morphologies due to balancing the surface interactions.³⁹ Furthermore, due to the higher mobility of a solvent swollen polymer compared to thermally annealed systems at a given χN value, classical defects such as dislocations and disclinations are more rapidly removed resulting in larger grains, however, new types of defects can be observed.⁴⁰

Templating with thin films

Neat alignment of the microphase separated structures is important for technical use. Due to the strong surface interactions, thin films can usually indeed be quite well aligned with respect to the surface,⁴¹ however, as surface fields usually induce a parallel orientation, while films with a perpendicular orientation of (especially cylindrical) microdomains offer the most interesting possibilities for fabrication of nanomaterials, a lot of effort has been given into redirecting the preferred microdomain orientation. This has been accomplished by the use of electric fields, solvent interactions, and confinement effects or surface modifications to yield neutral surfaces, of which a large number of examples can be found in ref. 9. Also the use of sufficiently rough substrates can induce a perpendicular orientation.⁴² Alignment in the other two dimensions parallel to the surface remains an important issue as well. Of course, techniques such as shear flow and electric fields can again be used, although

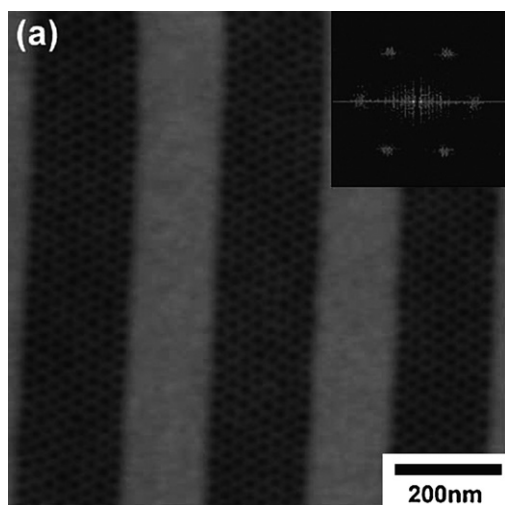


Fig. 3 An AFM height image of a binary mixture of polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) diblock copolymers on a patterned grating. In the grooves of the grating, well ordered perpendicular PMMA cylinders in a PS matrix can be observed. Reproduced with permission from ref. 47. Copyright 2007, WILEY-VCH Verlag GmbH & Co. KGaA.

applying shear to a thin film is not straightforward.⁹ However, the most promising alignment method still seems to be graphoepitaxy, whereby block copolymer self-assembly is guided along the features of a lithographic pattern (Fig. 3).^{43–52}

In such a case, the size limits of the lithographic pattern may seem to nullify the advantage of the high pattern density of the block copolymer, however, the length scale of the lithographic pattern may be many times larger than the microdomain spacing and by using asymmetric patterns (wide trenches and short raised areas) the pattern density can still be greatly increased. Furthermore, in a recent study, Bitá *et al.*⁵³ have even succeeded in incorporating the lithographic pattern into the polymer structure, by adjusting the surface chemistry of a hexagonal dot pattern to match one of the blocks of a spherical block copolymer. The hexagonally packed dots could replace one sphere in

the polymer pattern, resulting in highly ordered structures (Fig. 4).

Lithographic patterns in the form of an adjusted surface chemistry of the flat substrate have also been used, although in this case the pattern usually has the same periodicity as the block copolymer.^{54–57} Incommensurate patterns result in novel complex nanostructures,⁵⁸ whereas patterns with a multiple of the periodicity recently proved to be able to multiply the density of a pattern (Fig. 5).^{59,60}

It goes without saying that thin films of block copolymers have been used excessively as templates for the formation of nanostructured materials. Two extensive reviews on block copolymer thin films have addressed this issue,^{14,61} and also recent reviews on block copolymers in general address several thin film applications.^{6,9,62} We will therefore only highlight some representative examples.

Park *et al.* were the first to develop block copolymer lithography as an alternative to conventional lithography techniques.⁶³ They selectively removed the spherical PB block of a PS-*b*-PB microphase separated block copolymer thin film by ozonization, after which reactive ion etching was used to transform the pattern to silicon nitride. The exposed silicon nitride was etched away before the etch front had proceeded through the remaining PS matrix, resulting in holes in the silicon nitride. Also, they already developed the principle of increasing etch contrast by selectively staining the PB domains with OsO₄. In this case, RIE resulted in silicon nitride dots, as the PS matrix domains were etched away more quickly than the stained PB domains. In a more recent example Jeong *et al.*⁶⁴ were able to universally apply the etch process to a wide range of materials by applying them with a neutral organic monolayer before coating them with cylindrical PS-*b*-PMMA, which as a consequence oriented perpendicularly. PMMA was selectively removed, after which the nanoporous polystyrene was used as an etch mask to create the nanopatterned material (Fig. 6).

Besides as etch masks, the emptied pores of a block copolymer template have also often been used as nanoreactors to grow nanowires of other organic and inorganic materials, either electrochemically or by filling the pores with a precursor that reacts

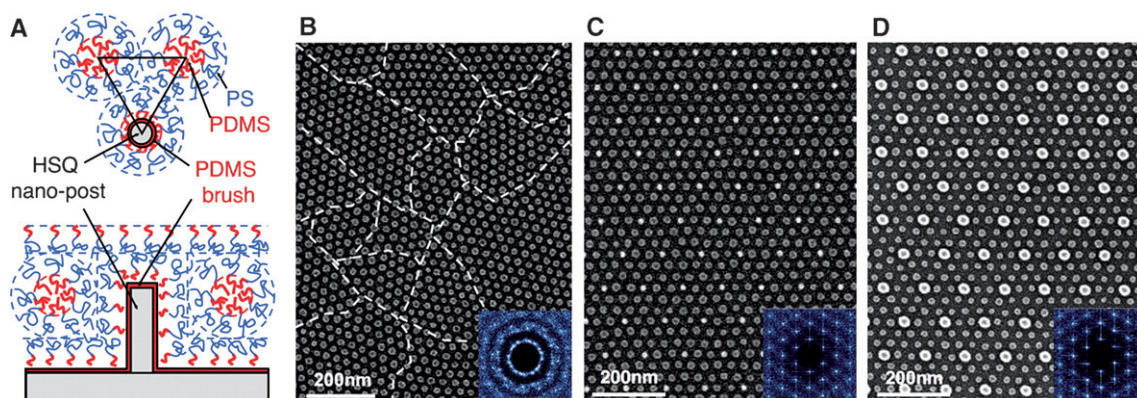


Fig. 4 (a) Top-down and side view schematics of polystyrene-*block*-polydimethylsiloxane (PS-*b*-PDMS) block copolymer chains surrounding a nanopost which is functionalized by a PDMS brush. (b) SEM image and Fourier transform of a poorly aligned monolayer of spherical microdomains (without templating). (c) SEM image and Fourier transform showing well ordered spheres formed within a lattice of nanoposts (brighter dots) functionalized with PDMS [as schematically shown in (a)]. (d) As (c), but now the nanoposts have been functionalized with PS chains. From ref. 53. Reprinted with permission from AAAS.

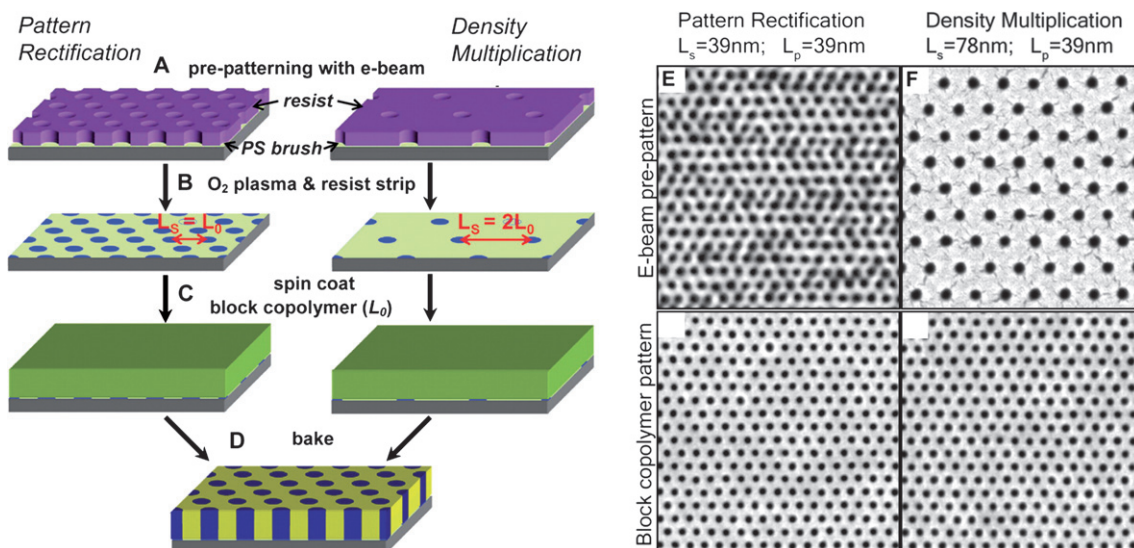


Fig. 5 Schematics showing the process to create lithographically defined prepatterned surfaces and subsequent self-assembly. The patterns are first applied to a PS brush by e-beam lithography (a), after which plasma etching produces chemical contrast on the substrate (b). When the spin-coated block copolymer layer (c) is annealed, the pattern is transformed to the polymer layer (d). Using a pattern with the same periodicity as the microphase separation results in a highly improved order (e), whereas using a double periodicity results density multiplication (f). From ref. 60. Reprinted with permission from AAAS.

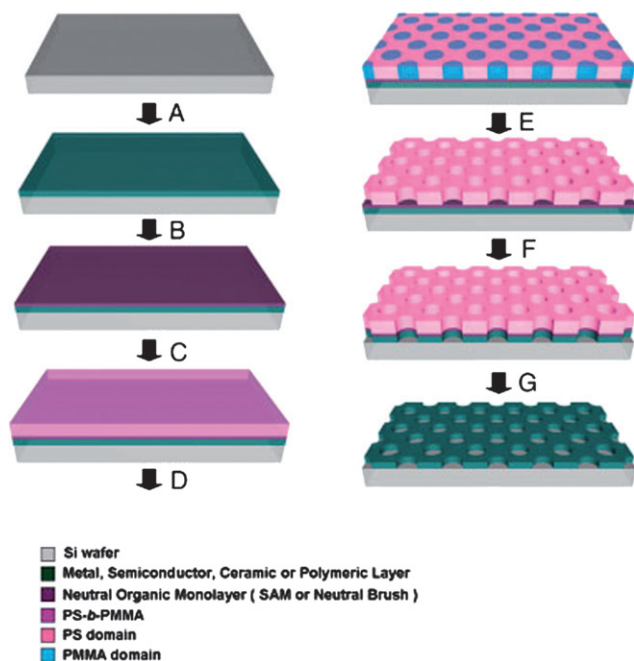


Fig. 6 A schematic representation of the universal block copolymer lithography process. (a) A target material film is deposited onto a silicon substrate. (b) The surface is functionalized with a neutral organic monolayer. (c,d) A PS-*b*-PMMA diblock copolymer is spin-coated on top of the modified substrate and thermally annealed to produce perpendicular PMMA cylinders. (e) PMMA is selectively etched away. (f) The nanostructured template is used as an etch mask. (g) Remaining polymer is removed, resulting in a nanopatterned surface. Reproduced with permission from ref. 64. Copyright 2008, WILEY-VCH Verlag GmbH & Co. KGaA.

to the desired component by exposing the pores to reactant vapors or radiation.^{65–69} Also, there still remain plenty of possibilities for creating nano-materials without first selectively removing one of the blocks. There are numerous examples of selective decoration, whereby one of the microphase separated polymer blocks selectively binds nanoparticles,^{70–79} which usually results in wire-like arrays of metallic nanoparticles.^{70–75} Continuous wires have recently been obtained by Chai *et al.* who selectively incorporated metal ions in the cylindrical P4VP blocks of a PS-*b*-P4VP block copolymer thin film, which after removal of the polymer by plasma treatment resulted in metallic nanowires (Fig. 7).^{80,81}

Of course, nanoparticles and precursors do not need to be incorporated *after* the block copolymer self-assembly has taken place. They can also be added in advance, and take part in the structure formation. In this case, they can influence phase behavior and interfacial interactions, which may be a great advantage, something which will be illustrated in the second part of this Review.

Much interesting work has also been performed on templating with thin films of block copolymer micelles. In this case however, if no post-annealing of the film is performed in a non- or partially-selective solvent, structure formation takes place in solution rather than in the thin film and casting of such films usually results in quasi hexagonal order. Hence we will pass over the subject here, only pointing out a review and several research papers to the reader.^{82–94}

Thin films of complex systems

Although the physics of simple coil-coil diblock copolymers are by now quite well understood, and many interesting applications have been investigated, the physics and applications of more complicated systems remain relatively unexplored. Especially

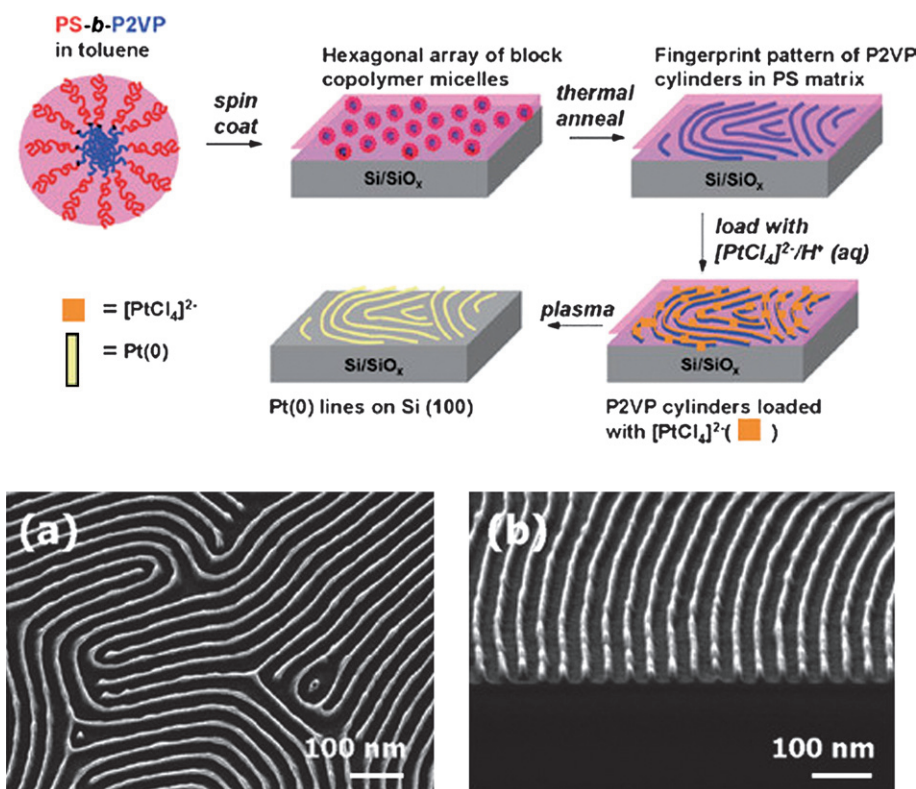


Fig. 7 A schematic showing the process of creating metallic nanowires. A micellar solution of PS-*b*-P2VP in toluene is coated onto a silicon substrate and is thermally annealed to form a single layer of parallelly oriented P2VP cylinders in a PS matrix. In an acidic medium, P2VP is selectively swollen due to protonation and pierces the PS layer, after which it is loaded with metal salts. The polymer is removed upon plasma treatment, resulting in continuous metal wires. SEM pictures of the wires are shown beneath. Reprinted in part with permission from ref. 81. Copyright 2008, American Chemical Society.

thin films of such systems may have several advantages over simple coil-coil diblock copolymers. For example, the use of triblock copolymers may lead to new thin film morphologies not available for diblock copolymers, while functional polymers for electronic and photonic applications are usually rod-like. Combining these rod-like polymers with a coil block may lead to block copolymer thin films with interesting electronic properties. Furthermore, additives may easily provide a system with desirable functionalities, while they may also be used to tune the interactions within a film, facilitating formation of the desired structure and/or orientation. However, thin film behavior of such “new” systems is far from well-known. The final part of this Review will therefore deal with the thin film behavior and applications of these more complex systems, notably supramolecular systems, in order to create a better understanding of these systems and highlight their advantages.

Functional block copolymers

We will start our list of complex systems with some examples of diblock copolymers that behave different from simple coil-coil systems, for example because one of the blocks is rod-like, or because the blocks are otherwise functionalized.

Most conducting polymers are rod-polymers, and control of the polymer morphology and structure on the 10 nm length scale of exciton diffusion can largely increase the efficiency of devices. This can be accomplished by using microphase separation of

rod-coil block copolymers. These systems exhibit extremely rich self-assembly behavior compared to traditional coil-coil block copolymers, due to the interplay between the microphase separation between the rod and coil block, and liquid crystalline alignment of the anisotropic rod blocks. The morphologies of these systems are susceptible to kinetic trapping, and thin film morphologies therefore also quite often depend on film deposition and processing conditions, leading to a variety of interesting structures, which are described in a thorough review on rod-coil diblock copolymers.⁹⁵ Recently however, Olsen *et al.* have been able to study the *equilibrium* self assembly of weakly segregated lamellar poly-2,5-di(2'-ethylhexyloxy)-1,4-phenylenevinylene-*block*-polyisoprene (DEH-PPV-*b*-PI). Comparable to coil-coil diblock copolymers, these systems also form holes and islands of parallelly oriented microdomains, due to preferential wetting of the substrate with PI. The perpendicular lamellae at the edges of islands are characterized by a long persistence length and break rather than bend at defect sites due to the high bending modulus of the liquid crystalline PPV domains. Therefore, islands have a highly irregular polygon shape, the straight edges being bounded by the perpendicular domains.⁹⁶ Only for coil fractions around 72 vol% coil block, square grains are formed as a result of the growth along orthogonal low-surface-energy directions induced by the tetragonal crystal lattice in the rod-rich nanodomains. Kinetic barriers at lower coil fractions and disordering of the lattice at higher coil fractions prevent these highly regular structures for a wider range of coil fractions (Fig. 8).^{97,98}

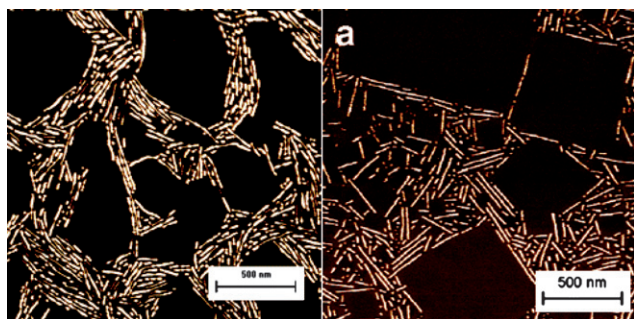


Fig. 8 AFM phase images of PPV-*b*-PI rod-coil diblock copolymers. Alternating light and dark regions represent lamellae oriented perpendicular to the surface, whereas large featureless regions represent parallel lamellae. The high moduli of the liquid crystalline nanodomains lead to out of plane lamellae with long persistence lengths, resulting in grains with irregular polygon shapes (left picture). Square grains are formed for a very small composition window and can be observed in the picture on the right. Reprinted in part with permission from ref. 96 and 97. Copyright 2007 and 2008, American Chemical Society.

Naturally, there are many more examples of functional blocks. For instance, block copolymers with an organometallic block naturally possess a large etch contrast and can therefore successfully be used as etch masks,⁹⁹ while simple heating may result in nanostructured ceramics.¹⁰⁰ If one of the blocks is functionalized with covalently attached liquid crystalline (LC) side-chains, a perpendicular orientation of microdomains may easily be stabilized by the tendency of the LC layers to orient parallel to the surface.^{101–104} Furthermore, the use of a crystallizable block leads to a variety of interesting observations, as the resulting morphology of these systems is an interplay between microphase separation, crystallization of the crystallizable block and thin film interactions (for examples see ref. 105 and references therein). And of course, the list of functional block copolymers is far from complete, as new polymerization techniques involving metal coordination, radical and ionic polymerizations have widely increased the possibilities for polymerizing different monomers,¹⁰⁶ creating novel opportunities to synthesize functional block copolymers.

ABC triblock copolymers

Due to the extra C component in triblock copolymers, the number of involved interaction parameters increases from 1 (χ_{AB}) to 3 (χ_{AB} , χ_{BC} and χ_{CA}). Therefore, in bulk, linear ABC triblock copolymers can exhibit a vast variety of microphase separated structures.^{107,108} These have been much less studied as tools for nanotechnology applications and especially investigations on thin film behavior are rare, even though they may potentially be more versatile than binary block copolymer morphologies due to the increased complexity. Can interaction with the interface already greatly enhance the variety of structures that can be obtained for AB diblock copolymers, this is certainly true if an extra component C is attached.¹⁰⁹ Some theoretical papers have dealt with triblock copolymer thin films.^{110–114} The most striking result found for a bulk lamellar triblock copolymer was that in the case of B attractive interfaces, any surface imbalance whatsoever could stabilize a perpendicular

orientation.^{112–114} This means that there is no need to confine the films, the perpendicular morphology will spontaneously form in a film simply spin coated onto a B attractive substrate. Given the fact that most nanotechnology applications require a perpendicular domain orientation, triblocks could therefore possess a distinct advantage over diblocks as there is no need to perform extra reaction steps in order to establish neutral surfaces. Many experimental work on ABC triblock copolymer thin films has been performed in the group of Krausch. For examples, Elbs *et al.* could facilitate identification of the different phases of a polystyrene-*block*-poly(2-vinylpyridine)-*block*-poly(*tert*-butyl methacrylate) (SVT) thin film by short treatment in different solvent vapors, and qualitatively proved the above mentioned theoretical results.¹¹⁵ Subsequent studies not surprisingly indicated a large morphology dependence on the annealing vapor and drying conditions.^{116–118} Rehse *et al.* demonstrated for the first time the presence of non-bulk surface-reconstruction morphologies using polystyrene-*block*-polybutadiene-*block*-poly-(methyl methacrylate) (SBM), polybutadiene-*block*-polystyrene-*block*-poly(methyl methacrylate) (BSM) and polystyrene-*block*-polybutadiene-*block*-poly(*tert*-butyl methacrylate) (SBT),¹¹⁹ and Ludwigs *et al.* systematically studied the phase behavior of SVT thin films and could match these results to simulations based on self-consistent field (SCF) theory.^{120,121} They concluded that confined systems are very sensitive to small changes in the energetic interaction between the different components, leading to a wide variety of possible surface reconstructed morphologies (Fig. 9).

Amongst other morphologies, they found a stable and highly ordered perforated lamellar phase, which could find use in membrane applications. The high order was presumably caused by the bicontinuous nature of the morphology. The perforated lamella phase is continuous in all three components, which aids chain diffusion within the film.¹²² Studies by other groups have also illustrated the large dependence of the thin film morphology on the substrate interactions, solvent annealing conditions and film thickness.^{34,123–126}

Supramolecular systems

The morphologies that can be obtained by incorporating additives which have specific interactions with one of the blocks are basically the same as those of diblock copolymers, as this effectively swells one of the blocks, however, the combination of supramolecular principles with microphase separation of diblock copolymers provides several other benefits for fabrication of nanomaterials.^{127,128} Especially in thin films, additives may lead to interesting new observations, as well as offer a variety of advantages for creating functional nanomaterials, as will be clarified in this final section.

Hydrogen-bonded side-chain block copolymers. Supramolecular interactions such as hydrogen bonding and ionic bonding between a diblock copolymer and a low molecular weight chain-like amphiphile for example, can result in so called structure-*within*-structures if there is sufficient repulsion between the polar backbone and the nonpolar alkyl tails.¹²⁹ Ruokolainen *et al.* first demonstrated the aforementioned concept by hydrogen bonding pentadecylphenol (PDP) to the P4VP block of a PS-*b*-P4VP

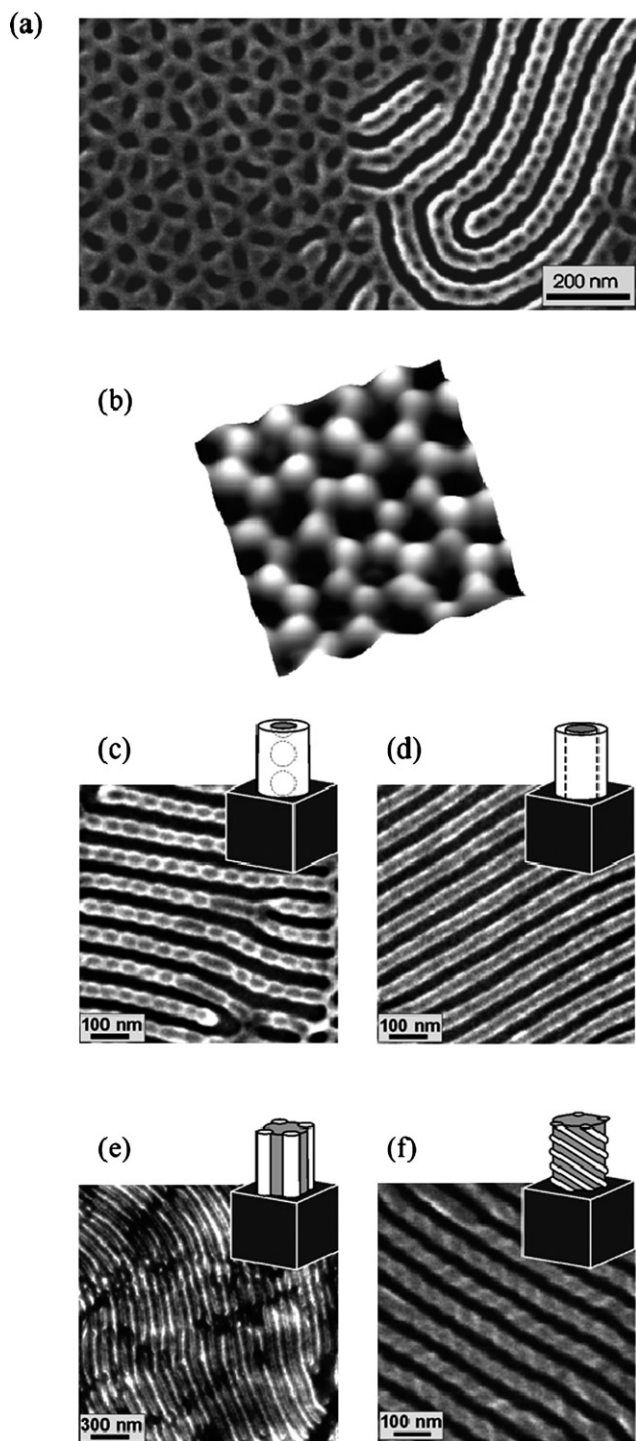


Fig. 9 SEM (a, c–f) and AFM (b) images of surface structures found in a single thin film of SVT triblock copolymer. Reprinted with permission from ref. 121. Copyright 2005, American Chemical Society.

diblock copolymer, forming comb-shaped supramolecules.¹³⁰ PDP microphase separates from the P4VP block, forming short length-scale lamellae with a period of ~ 4 nm below an ODT of ~ 60 °C for a 1 : 1 ratio of PDP : 4VP, while PS and P4VP microphase separate on a longer length scale, forming all the classical block copolymer phases, depending on the weight

fraction of PS and the P4VP(PDP) comb.¹³¹ Other ratios of PDP : 4VP are also possible, however, then the comb has a lower ODT.¹³² Several functional materials may be derived from these hierarchical structures. If the P4VP block of PS-*b*-P4VP is first transformed into a polysalt by complexing with a strong acid such as methane sulfonic acid (MSA) or toluene sulfonic acid (TSA), and subsequently hydrogen bonded with PDP, the hierarchically structured samples exhibit switchable protonic conductivity when heating and cooling the sample through an ODT between lamellae and cylinders.¹³³ Fast orientational switching of hydrogen-bonded side-chain liquid-crystalline block copolymers in an alternating current (AC) electric field has been reported by Chao *et al.*¹³⁴ The non-covalent nature of the bonds results in a considerably higher mobility of such systems, facilitating such orientational switching and the formation of ordered structures in general.¹³⁵ Furthermore, the effective swelling by the long side chains may lead to the large periodicities required for photonic bandgap materials,¹³⁶ and generally, by the addition of an extra component through non-covalent interactions the size of the microdomains and the morphology can easily be tuned by changing the amount of additive whilst using the same block copolymer. Furthermore, new functionalities can be incorporated,^{127,137} an additive may easily be washed away, resulting in nanoporous structures or nano-objects with hairy pore or object walls which may be further functionalized, and by choosing the right additive, surface interactions within thin films can be tuned. From a templating point of view, two morphologies, namely cylinders-*within*-lamellae and lamellae-*within*-cylinders are especially interesting, as they can easily be transformed to nanorods and nanoporous membranes, respectively, by simply washing away the additive (Fig. 10). In this case, the structure-*within*-structure morphology is not very important, however, in the case of PS-*b*-P4VP(PDP) comb-shaped supramolecules, the advantages of the increased mobility of the systems, possible functionalization of the P4VP coated cylinder or pore walls, and the easy adjustment of the nanorods or nanopore size by changing the amount of PDP remain.

Thin films of PS-*b*-P4VP(PDP) supramolecules have been investigated by van Zoelen *et al.* and Tung *et al.*^{138–140} In a study on solvent annealed systems of high molecular weight asymmetric comb copolymers with a small P4VP(PDP) block on silicon, the presence of PDP induced enough mobility to induce structure formation in the high molecular weight ($\sim 320\,000$ g mol⁻¹) block copolymer. Furthermore, it was found that as opposed to pure PS-*b*-P4VP diblock copolymers, which exhibit asymmetric wetting conditions (PS wets the surface and P4VP the substrate), the P4VP(PDP) comb wetted both the substrate and the air interface due to the low surface energy of PDP, which shielded P4VP from the surface. Because of the selectivity of chloroform towards PS, the morphology of the large length scale could be changed by annealing at different vapor pressures, which, for a specific strongly segregated system that was on the boundary between lamellar and cylindrical, resulted in terraces of metastable perpendicular lamellae.¹³⁸ The morphology of the short length scale was however not observed. In a different study, which focused on low molecular weight systems with a large P4VP(PDP) fraction, the short length scale was observed in the form of hierarchical terrace formation. During annealing, the P4VP(PDP) comb was above its ODT, and PS and P4VP

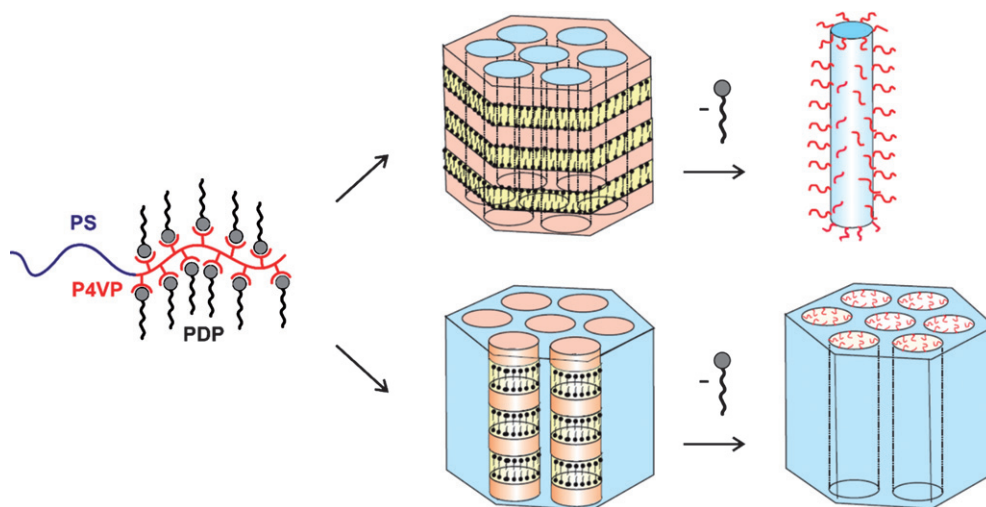


Fig. 10 Cylinders-*within*-lamellae and lamellae-*within*-cylinders formation of PS-*b*-P4VP(PDP) supramolecules. Washing away the PDP results in nanorods and nanoporous structures.

microphase separated in the normal parallel structures. After solvent evaporation the now phase separating combs quickly formed parallel layers within the terraces of the parallel block copolymer structure that were formed during annealing.¹³⁹ As opposed to the bulk systems, where the short and long length scale are oriented perpendicular to each other, both length scales were now oriented parallel with respect to each other (Fig. 11). This effect was only observed for high P4VP(PDP) fractions due to the higher conformational freedom of longer P4VP chains. Removal of the top layers of cylinders from these structures helped to identify the structure of the lowest terrace and for a specific composition resulted in a monolayer of ordered cylinders, which were used as templates to create ferroelectric nanorods by pulsed laser deposition.¹⁴¹

A study on identical PS-*b*-P4VP(PDP) systems at lower chloroform vapor pressures resulted in the classical structures, with the large length scale oriented perpendicular to the substrate for high P4VP(PDP) fractions.¹⁴⁰ In the case of P2VP-*b*-PEO hydrogen bonded with mesogenic groups, also able to form structures-*within*-structures, the preferred orientation of the liquid crystalline layers parallel to both interfaces stabilized a perpendicular orientation of the microdomains, comparable to the covalent counterparts in ref. 101–104.¹⁴²

Furthermore, in recent experiments the supramolecular approach was combined with novel triblock copolymers, creating materials that might be suitable for, *e.g.* charge-mosaic membrane applications.^{143,144} Notably, a core-shell gyroid phase has been found very recently in poly(*tert*-butoxy styrene-*block*-styrene-*block*-4-vinyl pyridine) complexed with PDP [PtBS-*b*-PS-*b*-P4VP(PDP)], in which the core channels were formed by the supramolecular P4VP(PDP) block.¹⁴⁴ Although it remains to be seen if the gyroid morphology can be recreated in thin films, these systems are certainly interesting material for future thin film research.

Most supramolecular interactions, however, do not lead to hierarchical structure formation. Studies on thin films of PS-*b*-P4VP diblock copolymers hydrogen bonded with a small molecule, not forming hierarchical structures, have been performed by Stamm and coworkers,^{145–153} who used 2-(4'-hydroxybenzeneazo)benzoic acid (HABA).^{148–152} Sidorenko *et al.* concluded that the orientation of a cylindrical PS-*b*-P4VP(HABA) assembly could be switched by annealing in different solvents. Annealing in chloroform resulted in terraces of parallel cylinders, whereas annealing in dioxane resulted in a perpendicular orientation.^{148,149} Washing away HABA from the perpendicular cylinders resulted in a porous

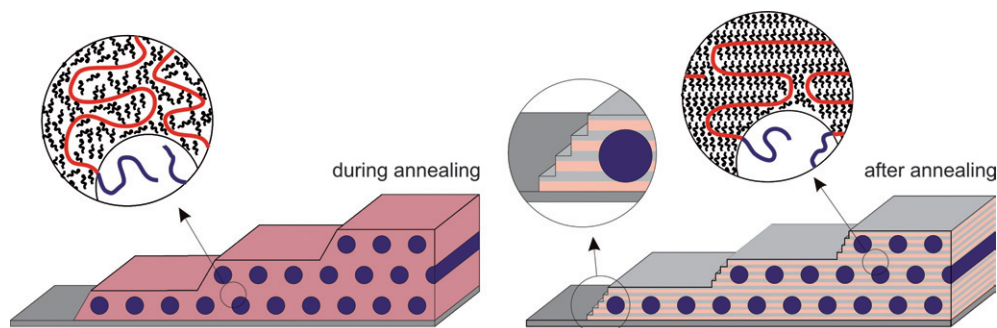


Fig. 11 Formation of terraces-*within*-terraces. During annealing, the P4VP(PDP) comb is above its ODT and the PS cylinders in the selectively swollen P4VP matrix orient in a parallel fashion. During the fast evaporation of the solvent, the P4VP and PDP also microphase separate in parallel layers. Reproduced with permission from ref. 139. Copyright 2008, American Chemical Society.

structure, which could be filled with metal to fabricate an array of nanodots.¹⁴⁸ Reactive ion etching (RIE) of the nanoporous structure on silicon produced patterned silicon,¹⁵⁰ and nanoporous films could also be carbonized by plasma immersion ion implantation.^{151,152} Liang *et al.* used complexation of resorcinol and the P4VP block of PS-*b*-P4VP to create PS cylinders in a P4VP(resorcinol) matrix. Slow evaporation after annealing in DMF–benzene vapor resulted in a perpendicular orientation of the cylinders. Subsequently, resorcinol was cross linked by exposing the film to formaldehyde vapor. After pyrolysis of the structures PS-*b*-P4VP was almost completely degraded, whereas resorcinol–formaldehyde resin is a good carbon precursor, resulting in well ordered porous carbon films, not easily obtainable with pure diblock copolymer systems because of the low carbon yields after pyrolysis.¹⁵³ In a similar study, Rodriguez *et al.* hydrogen bonded PS-*b*-P4VP with environmentally benign carbohydrates such as sucrose, turanose and raffinose. Annealing in a DMF–benzene vapor mixture resulted in a perforated lamellar structure, after which high temperature treatment removed PS fragments and carbonized the carbohydrates and partial P4VP fragments, resulting in a porous carbon structure, *e.g.* to be used in catalytic applications.¹⁵⁴ Very recently, Son *et al.* used a small amount of oleic acid (OA) to induce a perpendicular orientation in PS-*b*-PMMA thin films. As a surface active agent, OA segregated at the air interface, thereby providing neutral surface boundary conditions with respect to PS and PMMA. Combined with energetically neutral substrates, high aspect ratio perpendicular patterns could be obtained.¹⁵⁵

Supramolecular block copolymers. Another, in some respects even simpler, case of supramolecular interactions involves the presence of these interactions in the main chain. Instead of by covalent bonds, the blocks in *supramolecular* block copolymers are connected by non-covalent interactions such as hydrogen bonds or metal–ligand coordination. In metallo-supramolecular block copolymers, both blocks have a ligand end group, $-[$. Combining A- $[$ and B- $[$ blocks with a metal ion M results in A- $[$ M- $]$ B diblock copolymers. Research in the group of Schubert and Gohy has been devoted to self-assembly of systems, which have ruthenium ions as the metal, complexed with terpyridine ligands attached to PS and PEO.¹⁵⁶ In bulk, the electrostatic interactions between the metal–ligand complex (MLC) ions and their counterions drives them to form aggregates,¹⁵⁷ resulting in morphologies that are different from their covalent counterparts. Furthermore, different counterions lead to other morphologies.¹⁵⁸ A thin film morphology library of 16 PS- $[$ Ru- $]$ PEO block copolymers composed of 4 different PS multiplied by 4 different PEO blocks has been composed by Lohmeijer *et al.*¹⁵⁹ Thin films of systems that formed PEO cylinders in a PS matrix had a perpendicular orientation over a wide range of film thicknesses after spin coating, which could be improved by annealing in a polar solvent, due to the Ru acting as a middle block which is strongly incompatible with the other blocks and has a strong affinity to the substrate.¹⁶⁰ Reoxidation of Ru^{II} to Ru^{III} in aqueous medium resulted in washing away of the PEO, creating a nanoporous medium.¹⁶¹

Homopolymer addition. The simplest example of supramolecular interactions is the addition of homopolymer, by which the

size of the microdomains can be tuned by changing the amount and molecular weight of the homopolymer. In bulk, homopolymer with a considerably lower molecular weight than the corresponding block of the block copolymer tends to be solubilized throughout the corresponding domains, whereas higher molecular weights will result in segregation of the homopolymer in the middle of these domains. In the last case, the microdomain spacing increases more drastically, but in both cases, macrophase separation will eventually occur for high amounts of homopolymer.¹⁶²

The same behavior was found in thin films of lamellar PS-*b*-PMMA mixed with high and low molecular weight homopolymers.¹⁶³ In thin films of cylindrical PS-*b*-PMMA, Jeong *et al.* found an increased miscibility between PMMA homopolymer and the cylindrical PMMA block compared to bulk samples, and PMMA also seemed to be more localized in the middle of the domains. This increase in localization was even higher when poly(ethylene oxide) (PEO) homopolymer was mixed with PMMA.¹⁶⁴ Addition of PEO and PMMA homopolymer to a PEO cylinder forming PS-*b*-PEO diblock copolymer also resulted in easily tunable sizes and center-to-center distances of the microdomains.³⁵ When homopolymer was added to the corresponding majority block of cylindrical PS-*b*-PMMA, this led in both cases (PS cylinders and PMMA cylinders) to an increased tendency towards a perpendicular orientation. Addition of homopolymer induced conformational entropic relaxation of the block chains in the matrix due to the homopolymer filling up the spaces between cylinders, which stabilized hexagonal packing of the cylinders. The driving force for the cylinders to form a hexagonal lattice could overcome the requirement to achieve a minimum interfacial energy by other morphologies for incommensurable film thicknesses (Fig. 12).¹⁶⁵

In another thin film homopolymer miscibility study, Yoo *et al.* concluded that poly(vinylidene fluoride) (PVDF) was segregated in the middle of parallelly oriented PMMA lamellae of a PS-*b*-PMMA diblock copolymer. This was chosen as a model system because PVDF is a well known ferroelectric polymer, which could be used in nanoscale ferroelectric devices.¹⁶⁶ New morphologies can be achieved when instead of a homopolymer, a diblock copolymer is added. Guo *et al.* found various uncommon morphologies in thin films of binary mixtures of

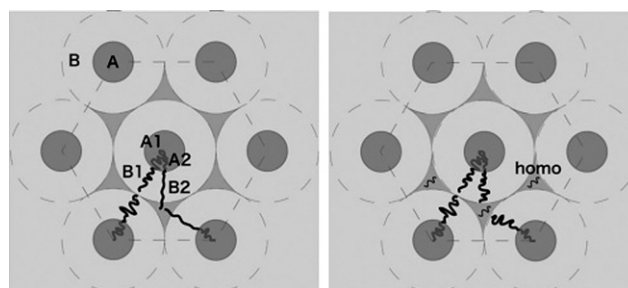


Fig. 12 Chain-packing model for (left, a) a diblock copolymer and (right, b) a diblock copolymer–homopolymer blend. The dented-triangular interstitial regions must be filled by the elongated block chains in (a), while they can be filled by the homopolymer chains in (b). Reprinted with permission from ref. 165. Copyright 2007, American Chemical Society.

polystyrene-*block*-polybutadiene (SB) diblock copolymers with comparable molecular weight but different composition annealed in several solvents and at different vapor pressures.¹⁶⁷ However, when using symmetric PS-*b*-PMMA block copolymers of comparable composition but different molecular weight, Mayes *et al.* found that parallel lamellae were formed with the short chains localized to the PS-PMMA interface and the long chains enriching the domain centers.¹⁶⁸

Nanoparticles. Finally, we turn to the addition of inorganics. As written in the introduction, block copolymers have been used excessively as templates to create arrays of nanoparticles, either by selective decoration of one of the microphase separated blocks after self assembly, or by first removing one of the blocks after which nanoparticles were deposited. Due to the highly ordered nanoscale arrangement of the nanoparticles, these nanoparticle-polymer composites can find abundant use in opto-electronic and microelectronic devices. However, nanoparticles do not need to be incorporated after self assembly, and can also be directly involved in structure formation.^{169–172} Surface modification of the nanoparticles is always necessary in order to prevent aggregation within the polymer matrix. The modification method then determines in which block the particle is preferentially segregated. Coating with, for example, a random AB-copolymer will drive the particles near the AB interface, whereas coating with homopolymer will preferentially drive the particles towards the corresponding block.¹⁷³ The spatial distribution can furthermore be tuned by the size and concentration of the particles. Large particles tend to be located at the center of the preferred block copolymer domain, due to the otherwise conformational entropy loss by the significant stretching of the corresponding blocks having to move around the particles, whereas smaller particles

are driven to the A-B interface, due to the higher translational entropy of the nanoparticles, this time not outweighed by the conformational entropy loss of the polymer chains.¹⁷⁴ The size of the nanoparticles,¹⁷⁵ as well as their concentration may also influence phase transitions.^{176,177}

In thin films, the nanoparticles may positively influence the surface interactions, resulting in the desired perpendicular structures. For example, in the case of hydrocarbon-coated CdSe nanoparticles which were selectively incorporated in the P2VP cylinders of a PS-*b*-P2VP diblock copolymer, the nanoparticles could induce a perpendicular orientation of the cylindrical microdomains. The carbon coated nanoparticles have a lower surface energy than P2VP, and hence shield P2VP from the surfaces, effectively balancing the surface interactions relative to the PS matrix, which has a comparable surface energy to the nanoparticles.¹⁷⁸ In a similar study where PEO-coated gold nanoparticles were incorporated in the cylindrical PMMA domains of PS-*b*-PMMA, annealing under high humidity provided neutral surface conditions between the PEO coated particles and PS, resulting in perpendicular structures.¹⁷⁹ In a theoretical study, Lee *et al.* concluded that confinement of a copolymer nanoparticle mixture could result in stable perpendicular lamellae due to a complex interplay of entropic and enthalpic interactions driving nonselective particles to localize at the hard walls and A-B interfaces.¹⁸⁰ Zhou *et al.* were able to achieve a relatively high loading of trioctylphosphine (TOPO) and polyethylene glycol (PEG) coated CdSe nanoparticles in the microdomains of a PS-*b*-P2VP diblock copolymer, only slightly affecting the self-assembly, while producing a high particle density.¹⁸¹ In a combined experimental and theoretical study, it was shown that the location of nanoparticles inside block copolymer domains can be tuned even more accurately by

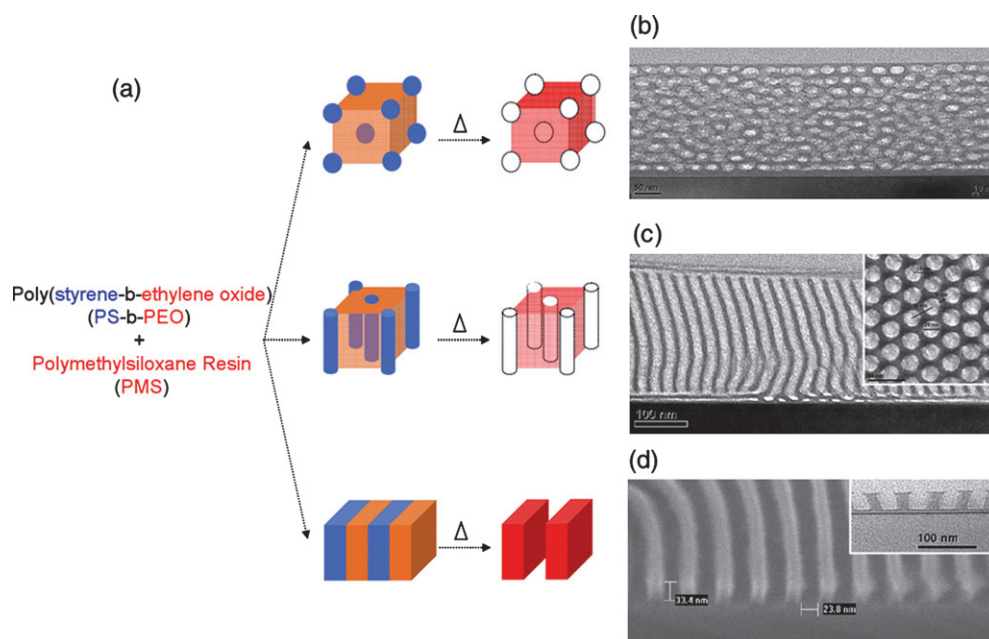


Fig. 13 (a) A schematic picture of the morphologies obtained for the PS-*b*-PEO(PMS) systems. The phase separated structure could be fixed by thermal treatment at 150–180 °C, and thermal treatment at high temperature (~450 °C) created porous nanostructures. (b) TEM of a cross-section of a thin PMS film containing spherical pores. (c) Cross sectional TEM and top-view (inset) of cylindrical pores. (d) Cross-sectional SEM and TEM (inset) of lamellar PMS resin. Reprinted with permission from ref. 186. Copyright 2008, IOP Publishing Ltd.

changing the period of a chemically patterned substrate used to guide the perpendicular orientation of lamellar microphases to values slightly higher than the equilibrium period or by adding homopolymer. In both cases a bimodal distribution of nanoparticles at the block interfaces was calculated, due to density changes in the polymer film.¹⁸² Li *et al.* used self assembly of Au nanoparticles in the P4VP domains of a PS-*b*-P4VP diblock copolymer spherical monolayer thin film to measure the collective electron transport behavior of the confined particles, and found an increased electron tunneling rate constant as compared to nanoparticles which were freely dispersed in a P4VP homopolymer thin film.¹⁸³

Inorganic precursors. Block copolymers have often been used as etch masks to pattern the inorganic substrate underneath, however, using inorganic precursors may also lead to nano-patterned inorganic materials, an example of which was already shown in Fig. 7, in which the precursor was loaded *after* self-assembly. In Kim's group, a mixture of PS-*b*-PEO with an oligomeric organosilicate precursor, silsesquioxane (SSQ), which was selectively miscible with PEO, was vapor annealed to form PS cylinders in a matrix of PEO(SSQ). Annealing ~300 nm thick films in chloroform for very long times (up to 314 h) finally resulted in reorientation of perpendicular cylinders to all parallel morphologies, illustrating the long annealing times which can be necessary to produce equilibrium structures. The parallel orientation started at both interfaces and proceeded through the film. Modification of the surface energy of the substrate by coating small layers of alkoxysilanes or Au and annealing in a mixed solvent vapor of chloroform and octane resulted in neutral interfaces and hence stable perpendicular morphologies. To produce porous organosilicate thin films, samples were heated at 450 °C, which cross-linked SSQ and decomposed PS-*b*-PEO.¹⁸⁴ A perpendicular lamellar morphology could be aligned by directed self assembly along lithographical patterns and was used as an etch mask to create patterned silicon (Fig. 13).^{185–187}

Another example of the precursor method is the use of thin films of PS-*b*-PEO with a titania precursor which selectively dissolves in the PEO domains to create arrays of titania nanoparticles by heat treatment.^{188–190} Furthermore, HAuCl₄ and PMMA homopolymer have been added to cylindrical PS-*b*-P2VP.¹⁹¹ In this case, the gold precursor could mediate interfacial interactions which led to a perpendicular orientation of cylindrical microdomains of PMMA-P2VP-HAuCl₃ in a PS matrix, after which the gold salt was reduced and PMMA washed from the film, resulting in a metallized nanoporous block copolymer film.

Summary and outlook

In this Review, we have attempted to illustrate the versatility of block copolymer thin films for fabrication of nanomaterials. The factors influencing the phase separation in thin films of simple coil-coil diblock copolymers have been summarized and several new developments in this field have been illustrated. Furthermore, we have tried to highlight the factors involved in using more complex block copolymer systems for thin film formation. Triblock copolymers exhibit much richer morphologies than simple diblock copolymers, especially in thin films, a feature

which may be exploited for creating more advanced nanomaterials. On the other hand, ordering functional block copolymers for electronic and photonic applications in thin films may greatly enhance their performances. Finally, the extra additives resulting in supramolecular systems may positively influence surface interactions, often leading to the so desired perpendicular structures for nanotechnology, while at the same time the number of steps to create a functional material can be reduced or simplified by incorporating an additive with the desired functionalities. Nevertheless, thin film studies of these more complex but versatile systems are relatively rare compared to those of "simple" diblock copolymers. More research could provide new information on how to exploit the functionalities of these systems in thin films, and by eventually combining novel functional polymers and polymer architectures with supramolecular chemistry in thin films, the advantages of these systems may simultaneously be exploited and new functional nanomaterials may easily be created with a minimum amount of effort.

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