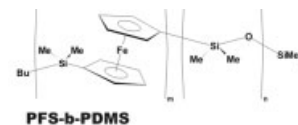
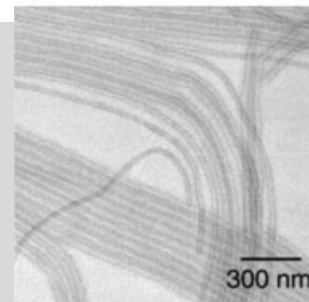


Block Copolymers as a Tool for Nanomaterial Fabrication**

By Massimo Lazzari*
and M. Arturo López-Quintela*



In this review the latest developments regarding the use of self-assembled copolymers for the fabrication of nanomaterials will be presented and their real potential evaluated. Most of the strategies reported so far are herewith classified under two main approaches: a) use of block copolymers as nanostructured materials, either “as they are” or through a selective isolation of one or more component blocks, and b) as templates for the synthesis of metallic or semiconducting nanomaterials. The problems of the orientation and large-scale order of self-organizing block copolymer mesophases will be also introduced, due to their importance as a route towards further improvements of the nanofabrication means.



1. Introduction

The fabrication of systems having characteristic dimensions smaller than 100 nm requires the ability to obtain, control, manipulate, and modify structures at the nanometer length scale, a step beyond microtechnology. It is well established that microstructured materials may be industrially prepared, e.g., by photolithography, but as the demand for smaller and smaller feature sizes always impose to lower the current state-of-the-art limits, further steps towards miniaturization have been raised in the last decade, focusing on different and more suitable strategies, which are based on both “top–down” and “bottom–up” approaches. Many methods for the fabrication of nanomaterials have been proposed, mainly to meet the de-

mand of the microelectronic industries, ranging from milling techniques to non-traditional photolithographic and chemical methods, with a strong prevalence of methods based on template synthesis.^[1] However, their main weakness still remain in the difficult and poor control of the final morphology of the produced nanostructures. In such a sense polymers represent ideal nanoscale tools,^[2] not only due to their intrinsic dimensions, ease of synthesis and processing, strict control of architecture and chemical functionality, but also because of their peculiar mesophase separation both in bulk and in solution, particularly in the case of block copolymers (BCs).^[3–5]

BCs may be considered as two or more chemically homogeneous polymer fragments, i.e., homopolymer chains, joined together by covalent bonds to form more complex macromolecules such as linear di-, tri-, or multiblock copolymers, and nonlinear architectures such as multiarm, starblock, or graft copolymers. In the frequent case of immiscibility among the constituent polymers, the competing thermodynamic effects give rise to different kind of self-assembled morphologies, depending both in structural and dimensional terms on composition, segmental interaction, and molecular weights, and having periodicity suitable for application in nanotechnology.^[6] The existence of some morphologies can be theoretically predicted within the self-consistent field theory,^[7] on the basis of the volume fraction of the components, the number of segments in the copolymer, and the Flory–Huggins interaction parameter, as is the case for the spherical, cylindrical, gyroid, and lamellar phases, which have been observed in the simplest amorphous diblock copolymers. Particularly in the case of more complex systems, differences from the theoretical predictions can, however, be expected, mainly because of chain

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fluctuations and conformational block asymmetries. Also for this reason, more recent efforts have focused on ordered structures obtained from BCs having both rigid and flexible segments,^[8] and also from triblock and even tetrablock copolymers, with the observation of a series of novel and unconventional morphologies such as zig-zag,^[9] core-shell double gyroid,^[10] spheres or rods between lamellae,^[11] helices around cylinders,^[12] and hexagonal double^[10] or triple^[13] coaxial cylinder structures. A few of these morphologies, the ones most frequently used for nanofabrication, are illustrated schematically in Figure 1.

Moreover, separation and orientation of domains are also influenced, especially in thin films, by surface-interfacial interactions as well as by the interplay between structural periodicity and film thickness.^[14] Such molecular self-assembly of block copolymers therefore allows one to obtain in a simple manner a large variety of highly regular mesostructures without any direct human intervention, in a way similar to processes occurring commonly throughout nature.^[15]

The potential technological application of such variety of mesostructures, and particularly of those formed in the case of thin films, can be easily appreciated by non-specialists alike and has been widely recognized, e.g., since the first successful attempts to use self-assembly strategy for the preparation of membranes with tunable nanochannels^[16] and the early block copolymer-based nanolithography,^[17] but only partially explored. In this review, the recent developments regarding the

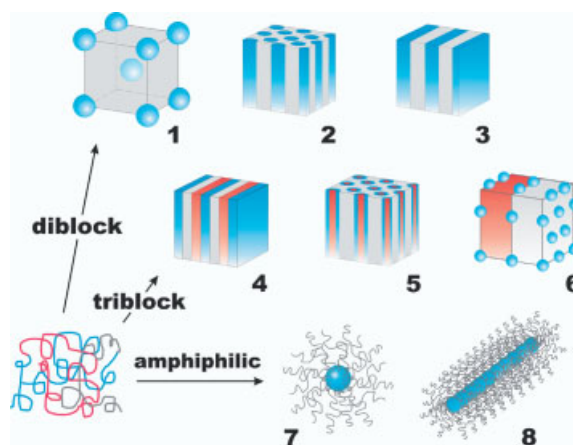


Fig. 1. Sketches of equilibrium morphologies from BC self-assembly, among the most frequently used for nanofabrication. For diblock copolymers in bulk: body-centered cubic-packed spheres (1), hexagonally ordered cylinders (2), lamellae (3). For triblock copolymers: lamellae (4), hexagonal coaxial cylinders (5), spheres between lamellae (6). For amphiphilic BCs in solution: spherical micelles (7), and cylindrical micelles (8). Periodicities, or micellar dimensions, are in the range 10–100 nm.

use of BCs as a tool for the fabrication of nanomaterials are presented, paying also attention to the possible application of amphiphilic BCs (Fig. 1), i.e., copolymers having both hydrophilic and hydrophobic blocks.^[18] Nanomaterial synthesis is herewith considered in its broader sense with the aim to include the most diverse aspects, from the direct use of self-as-



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sembled nanostructures, to processes based on BCs either in solution or as thin films for the fabrication of nanodevices or of metallic or semiconducting nanostructures, through the more general preparation of polymeric nano-objects as spheres, rods, or tubes. All of them are suitable for technological application or of remarkable interest as model objects, which can have fascinating properties or are simply intended as an academic exercise.

Most of the strategies developed so far may be classified into two different main approaches to nanomaterial fabrication, which are schematically discussed in the paper as follows: a) use of self-assembled copolymers as nanostructured materials, either “as they are” or through selective chemical isolation or processing of one or more components; b) via template formation, including both the use of copolymer films directly as the template and the fabrication techniques, which rely on the preliminary formation of the template through a first processing, followed by a nanoscale synthesis. Methods presenting original approaches or requiring innovative manipulation will be especially emphasized, also taking into account their potential for large scale applications.

As the scope of the review is limited by space, although also BC/ceramic hybrid materials^[19] and, more generally, BC nanocomposites^[20] are extensively researched subjects, their potential for the preparation of novel materials and nano-objects is not discussed here. However, it is possible to extend the applicability of the methodologies of fabrication herewith shown to any other BC-based material.

2. Block Copolymers as Nanomaterials

Direct use of the self-assembled BC morphologies without any further manipulation or processing appears quite intriguing, but so far only a few potential applications have been seriously explored, mainly taking advantage of the BC optical properties or of the electrical conductivity of at least one block. Fink et al.^[21] introduced the idea of using one-, two-, and three-dimensional (1D, 2D, and 3D, respectively) BC periodic structures (e.g., morphologies 2–5 in Fig. 1) as photonic crystals, namely materials in which the refractive index is a periodic function of space. For a rigorous analysis of the real promise that BC thin films can offer to photonic applications, as well as for the illustration of the major technological challenges still to overcome in order to achieve the desired photonic properties, the reading of two recently published reviews is suggested.^[22] Another potential direct application of BC nanostructures deals with the preparation of BCs containing conducting polymers or oligomer units. In particular, McCullough and co-workers have focused their investigation on a series of polythiophene-based BCs,^[23] which pave the way to utilize conjugated polymers for molecular level electronic devices.

2.1. Polymeric Nano-objects

Different types of self-assembling BCs have been used to prepare individual polymeric nano-objects, with each method having its advantages and limitations. In principle any of the mesostructures in bulk so far reported, and even those still not discovered, could be used to create well-defined objects with predetermined shapes, sizes, and compositions. For example, polymeric spheres, rods, or fibers are obtainable by some direct chemical isolation from the simplest spherical and cylindrical morphologies (Fig. 1, items 1 and 2, respectively).

The most complete investigation focused on this concept has been carried out by Liu et al., and is based on block copolymers, which contain crosslinkable moieties.^[24] Nanofibers can be easily prepared from poly(styrene)-*block*-poly(2-cinnamoethyl methacrylate) (PS-*b*-PCEMA)^[25] and poly(styrene)-*block*-poly(isoprene) (PS-*b*-PI)^[26] diblock copolymers, properly selecting samples which allow a hexagonally packed cylinder morphology (Fig. 1, 2) of the non-styrenic block dispersed in the continuous matrix of the PS block. Following Liu's strategy, the cylindrical domains of the minority block are locked in by crosslinking, either photoinduced or through chemical processes, on PCEMA and PI chains, respectively. After fixing the structure, nanofibers with PS hairs on their surface are easily separated via solvent dispersion in tetrahydrofuran (THF), i.e., a good solvent for PS, but they can retain their structural integrity in many other organic solvents. From the structural point of view, such BC nanofibers may be considered as the macroscopic counterparts of polymeric chains (suprapolymer chains) and, in principle, are suitable for characterization and fractionation through the techniques that have been developed for polymers. Among their peculiar solution properties^[27] it is worth mentioning the formation of lyotropic liquid-crystalline phases.^[25]

A similar but more complex procedure which applies a triblock copolymer is also suitable for the preparation of nanotubes having inner hydrophilic walls,^[28] as it is schematized in Figure 2. Self-assembly in thin films of poly(butyl methacrylate)-*block*-poly(2-cinnamoethyl methacrylate)-*block*-poly(*tert*-butyl acrylate) (PBMA-*b*-PCEMA-*b*-PtBA) triblock copolymers with higher content in PBMA formed hexagonally packed concentric cylinders of PtBA surrounded by PCEMA

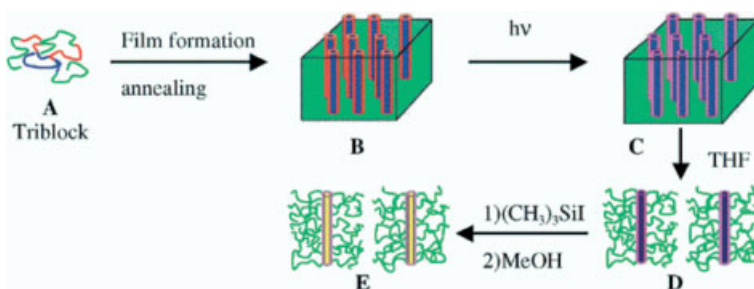


Fig. 2. Schematic representation of the process for the preparation of nanotubes from a PBMA-*b*-PCEMA-*b*-PtBA triblock copolymer (reprinted with permission from Yan et al. [28], copyright 2001 American Chemical Society).

and dispersed in the PBMA matrix (Fig. 1, 5). Once more the PCEMA shells are photo-crosslinked by UV irradiation, and the cylindrical domains separated from one another in THF, yielding nanofiber dispersions. Due to their core-shell structure these nanofibers may be further processed through a selective hydrolysis of *tert*-butyl groups of PtBA to yield poly (acrylic acid) (PAA)-lined nanotubes of PBMA-*b*-PCEMA. The location of acid groups inside the cores was elegantly demonstrated by reporting the production of γ -Fe₂O₃-impregnated nanotubes (Fig. 3) through a method based on the hydrophilic interaction with ferrous ions. This shows, at the same time, the potential offered by this synthetic route to prepare hollow nanostructures with an inner diameter of about 40 nm.



Fig. 3. Transmission electron micrograph of γ -Fe₂O₃-impregnated PBMA-*b*-PCEMA nanotubes with PAA-lined inner walls (reprinted with permission from Yian et al. [28], copyright 2001 American Chemical Society).

Other complex objects have been created via the synthetic detour through the bulk phase of triblock copolymer films which exhibit the so-called lamellae-sphere morphology, with spheres narrowly distributed at the interface of the lamellae (Fig. 1, item 6). Crosslinking in the bulk of the block that forms spherical domains leads to the conservation of the compartmentalization of the other blocks after dissolution in a selective solvent. Janus-type^[29] nanoparticles consisting of an interlocked core about 10 nm in radius and a corona with two well-separated hemispheres were synthesized from poly(styrene)-*block*-poly(2-vinylpyridine)-*block*-poly(butyl methacrylate) (PS-*b*-PVP-*b*-PBMA)^[30] and poly(styrene)-*block*-poly(butadiene)-*block*-poly(methyl methacrylate) (PS-*b*-PB-*b*-PMMA)^[31] of tailored compositions through crosslinking of the PVP and PB blocks, respectively.

It is finally worth mentioning that polymeric nanofibers have also been prepared from self-organizing supramolecules (also called supramolecular BCs).^[32] Poly(4-vinylpyridine)-*block*-poly(styrene) (P4VP-*b*-PS) diblock copolymers were stoichiometrically (with respect to the number of pyridine groups that act as hydrogen bonding acceptors) combined with a low molecular weight amphiphile, namely pentadecylphenol (PDP), to yield P4VP(PDP)-*b*-PS supramolecules.^[33] Proper selection of the volume ratio between the P4VP(PDP) complex and the PS block allowed the formation of a morphology of PS cylinders inside a P4VP(PDP) matrix (see

Fig. 1, 2-like). Subsequent removal of PDP with ethanol, which is a good solvent for the P4VP block as well, yields PS nanofibers. The straightforward merit of this proposal is that the simple choice of different alkylphenols or other amphiphilic additives would allow tuning of the supramolecular BC self-organization and therefore controlling the shape of the isolable objects, without the requirement of a time consuming new BC synthesis. Moreover, countless many BC-amphiphile pairs with different morphologies can easily be envisaged, thus illustrating a facile concept of fabrication aimed to introduce novel design principles for the prediction of nanostructures.

A further type of processing, which can in principle be considered as specular to the isolation of polymeric nano-objects from thin films, is that leading to porous nanostructures. It is well known that commercially available membranes for ultrafiltration purposes can easily be prepared by track-etching from polymeric sheets.^[34] However, the resulting nanopores (diameter as small as 10 nm) are not regularly packed and their density is low, whereas in the case of BC thin films, the selective degradation of e.g., cylindrical domains in morphology 2 (Fig. 1), may result in the formation of more homogeneous membranes. For example, membranes with regularly spaced nanochannels with diameters of 20–30 nm and periodicities of around 50 nm have been prepared from PCEMA-*b*-PtBA (through hydrolysis of the PtBA minor block),^[35] and bicontinuous nanoporous networks from PS-*b*-PI (via ozone degradation of the PI minor block).^[16] 3D nanostructured films have also been produced from silicon-containing triblock copolymers films through the selective removal of the hydrocarbon block and the conversion of the silicon-containing block to a highly stable silicon oxycarbide ceramic.^[36] As these highly ordered nanoporous membranes have also been extensively investigated as templates, the last developments regarding their preparation and the solution of the non-trivial problem of the orientation of the domains will be discussed in detail in Section 3.

Another general approach for the preparation of nano-objects is based on amphiphilic BCs.^[18] In a solvent that preferentially dissolves one block, often an aqueous media or a polar solvent, these copolymers form well-defined micelles with a core consisting of the less soluble block(s) and a highly swollen corona of the more soluble block.^[37] Depending on the degree of swelling of the corona and the relative composition of the copolymer, spherical (Fig. 1, 7) and worm- or rod-like (Fig. 1, 8) micelles are formed, as well as more complex polymer vesicles^[38] and compound micelles.^[39] A specific case is that of the so-called crew-cut aggregates, which are formed by amphiphilic BCs having a short hydrophilic block.^[40] Aggregates are prepared by first dissolving the BC in a good solvent for both blocks, and subsequently adding water or decreasing the temperature to cause aggregation of the hydrophobic block into a variety of morphologies, which resemble those of typical micelles.

Although only crew-cut micelle-like aggregates directly refer to objects existing under non-equilibrium conditions, also

the stability of micellar associates in thermodynamic equilibrium depends on phenomena that involve basic molecular interactions, as such “soft” assemblies are held together essentially by weak undirected forces (van der Waals forces, hydrophobic effects). As a consequence, all the structures constructed with these macromolecular amphiphiles are not only non-permanent, but even a relatively slight change in the physical conditions that resulted in the original self-assembly can completely disrupt them. For this reason, notwithstanding micelles and crew-cut aggregates have been a popular subject of research activity, the impossibility to fractionate these nano-objects make them far from the philosophy of nanomaterial fabrication that this review aims to highlight. Only the development of tailored amphiphile-based materials that are less sensible to environmental perturbation will therefore be documented in detail.

Successful approaches for the preparation of stable micelles consist of the use of amphiphilic BCs that either have reactive functional groups or a block which can crystallize, in both cases with the final aim to fix the micellar structures.^[41] Since the first systematic works on crosslinked micelles,^[42] increasing interest has been focused on the chemical fixation of more and more complex structures,^[43] up to triblock micelles with surprising characteristics such as tunable hydrophilic or hollow cores. For example, Armes and co-workers^[44] has developed an efficient synthesis of micelles with pH-responsive cores from a series of poly(ethylene oxide)-*block*-poly[2-(dimethylamino)ethyl methacrylate]-*block*-poly[2-(diethylamino) methacrylate] (PEO-*b*-PDMA-*b*-PDEA) triblock copolymers (Fig. 4). The micelles formed in aqueous solution at > pH 7.3 consist of a PEO corona, a PDMA innershell, and a

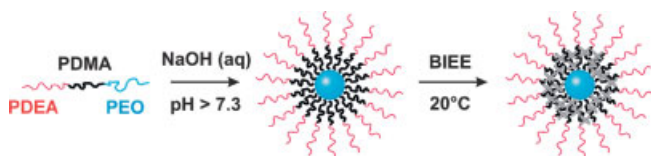


Fig. 4. Schematic illustration of the formation of “hard” micelles from PEO-*b*-PDMA-*b*-PDEA triblock copolymers by crosslinking of the PDMA inner shells with 1,2-bis(2-iodoethoxy)ethane (BIEE) [44].

PDEA core, and show a degree of (de)swelling strictly dependent on the degree of inner-shell crosslinking, PDEA block length, and solution pH. Furthermore, Underhill and Liu reported the preparation of hollow triblock nanospheres^[45] following an approach based on the methodology already presented in Figure 2. A PI-*b*-PCEMA-*b*-*Pt*BA, with 370 isoprene, 420 CEMA, and 350 *t*BA units, was used to form three layer “onion-like” micelles in THF comprising PI-hydroxylated coronas, solvent insoluble PCEMA shells, and *Pt*BA cores. The structures were locked by photo-crosslinking the PCEMA shell to yield “hard” nanospheres. The core was cavitated and made compatible with inorganic species by removal of the *tert*-butyl groups through controlled hydrolysis. A similar approach has also been used for the preparation of nanotubes, i.e., hollow cylindrical micelles, in methanol from a dif-

ferent PI-*b*-PCEMA-*b*-*Pt*BA.^[46] The PCEMA shell of the cylindrical micelle was photo-crosslinked, in this case followed by the complete degradation of the PI core through ozonolysis. The dispersion medium for the whole structure was provided by the high molecular weight *Pt*BA corona.

Fixation of non-spherical micelles to get individual macromolecular objects with molar masses several orders of magnitude greater than those of conventional polymers has been mainly investigated by Bates and co-workers, around 20 years later the first impressive images of collapsed BC worm-like micelles.^[37b,c] Self-assembly of a low molecular weight poly(ethylene oxide)-*block*-poly(butadiene) (PEO-*b*-PB) containing 50 wt.-% of PEO gave rise to the formation of worm-like micelles at low concentration in water (<5 wt.-%), while the presence of reactive double bonds in the PB cores allowed the use of a conventional water-based crosslinker without disruption of the cylindrical morphology (Fig. 5).^[47] The authors also pointed out the irreplaceable utilization of these covalently bonded giant macromolecules as model nano-objects, thus investigating their peculiar rheological properties.^[48] In our opinion, such results represent the best example of a direct comparison between the properties of “living”, less stable, micellar systems and those of “permanent” micelles.

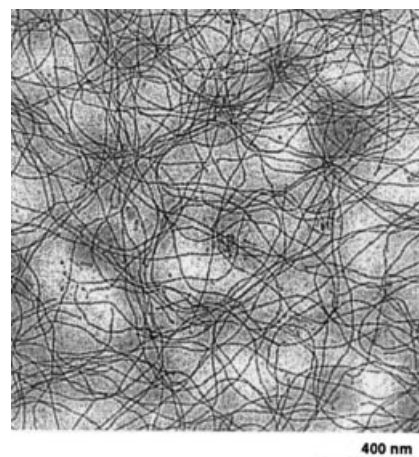


Fig. 5. Cryo-transmission electron micrograph of a 0.05 wt.-% solution in water of crosslinked worm-like micelles of PEO-*b*-PB (reprinted with permission from Won et al. [47], copyright 1999 American Association for the Advancement of Science).

Also the intrinsic properties of amphiphilic rod-coil diblock copolymers have been exploited for the fabrication of “hard” micelles. These polymers, consisting of a flexible block attached to a rigid or semi-rigid second block, present morphologies that result from the competition between microphase separation of the immiscible blocks and aggregation of the rod-segments into crystalline domains. Those polymers, in which the crystalline blocks are also insoluble, may self-assemble into micelles, whose core structure depends on the strong crystal packing forces. Manners and Winnik have investigated the structures formed from poly(ferrocenylsilane)-*block*-poly(dimethylsiloxane) (PFS-*b*-PDMS) in hydrocarbon solvents in which the PFS block is insoluble. Some of these co-

polymers formed long, thin, relatively flexible cylindrical micelles having a crystalline PFS core,^[49] while in the case of the highly asymmetric PFS-*b*-PDMS with a block ratio of 1:12 the samples generated a tubular morphology.^[50] In the latter case, when aggregation occurs, the short PFS block crystallizes to form a shell with a central cavity, surrounded by a solvent swollen PDMS corona. These equilibrium structures are stable in a wide range of temperatures, and their structure was confirmed by the encapsulation of Pb(*n*-Bu)₄. The tubes formed are up to 100 μm long and have both wall thickness and interior cavity of ca. 10 nm (Fig. 6). As the authors suggested, the potential of these copolymers is intriguing, not only for encapsulation purposes but particularly because PFS is a red-ox material with semiconducting properties, which can also serve as ceramic precursor.^[36]

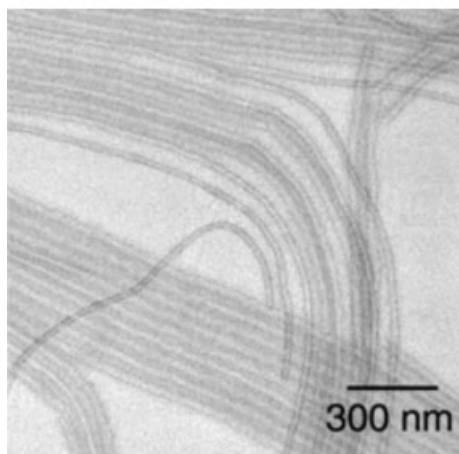
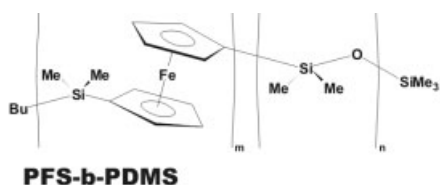


Fig. 6. Chemical structure of PFS-*b*-PDMS and transmission electron microscopy image of its assemblies formed in *n*-decane (reprinted with permission from Ruez et al. [50], copyright 2002 American Chemical Society).

3. Block Copolymers as Templates

Many polymer systems have been successfully employed as templates for nanofabrication,^[1c,d,g,h] and among them, all the above mentioned self-organizing BC systems may play a crucial role, mainly because of the variety of tunable matrixes at nanoscale level that they offer, ranging from micelles to 3D structures. Since the remarkable number of related works published in journals of many different fields, e.g., chemistry, physics, materials science, and engineering, and the possibility of scale-up for industrial applications, a special emphasis will first be placed on the sophisticated procedures to arrive at continuous arrays of metallic or semiconducting objects from BC thin films. The most common methods are those based on

the use of 2D-ordered morphologies from diblock copolymer films, which are processed through the eventual removal of one of the blocks, and using the film as a mask for subsequent deposition steps or etching through the film to transfer the BC motif pattern to a substrate. This part will be followed by an overview on the potential of amphiphilic BCs in solution as templates.

3.1. Nanolithography

A prime satisfactory example of the utilization of BC thin films as templates for lithography under conventional reactive ion etching (RIE) techniques was provided by Park et al.,^[17b] who managed to transfer the spherical microdomain pattern of a PS-*b*-PB monolayer to the underlying silicon nitride. Notwithstanding, further refinement of this technique, the two processing approaches reproduced in Figure 7 still exemplify the potential offered by nanolithography well. In general, as the etching rates of different organic polymers are almost identical, it is first necessary to resort to some manipulation for enhancing the etching selectivity between the different regions. One approach involves the selective removal of one

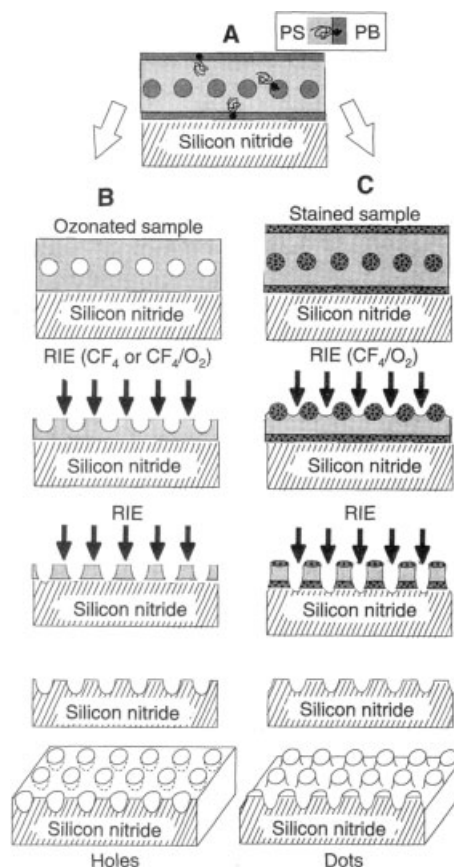


Fig. 7. Fabrication processes of silicon nitride dot (B) and hole (C) arrays via a nanolithography template consisting of a uniform monolayer of hexagonally ordered PB spheres in a PS matrix (cross-sectional view in A). PB wets the interfaces with the air and the silicon nitride substrate due to preferential interactions (reprinted with permission from Park et al. [17b], copyright 1997 American Association for the Advancement of Science).

block component before etching. For example, in Figure 7 (processing flow B) the spherical PB domains ordered in a 2D hexagonal lattice are ozone degraded, leading to regular voids in the PS matrix and hence to a variation in the thickness of the mask. Once exposed to the etchings, the thinner parts of the mask underneath the removed domains yield holes on the substrate. Other procedures achieve etching contrast by loading one of the microphase separated blocks. In the case that one block contains double bonds, it can selectively incorporate compounds containing transition metals possessing reactivity for unsaturated double bonds. In the processing shown in Figure 7C, OsO_4 staining PB reduces the etching rate of such domains, producing an etching selectivity under CF_4/O_2 -RIE of PS to stained PB of approximately 2:1. When the plasma is applied, the regions below PB domains are partially masked, resulting in the production of dots. Similar procedures have also been performed on PS-*b*-PI monolayers, in both cases with the production of etched features on silicon, silicon nitride, and germanium with a periodicity of 30–40 nm, corresponding to a density of around 10^{11} cm^{-2} , and an aspect ratio of about one.^[17b,51] More recently, the combination with other microfabrication techniques has permitted the creation of dense arrays of GaAs nanocrystals^[52] and gold dots.^[53] The first were made through selective growing of GaAs into ordered holes patterned as reported above on a silicon nitride–GaAs bilayer, while the latter were produced by combining BC nanolithography with a trilayer resist technique, hence transferring the pattern by different etching techniques from the BC film to the underlying layers, down to the gold layer. The real advantage this trilayer pattern-transfer method offers, despite its apparent complexity, is a viable route of general applicability for nanoscale patterning of different materials on arbitrary surfaces. Moreover, the high aspect ratio holes that are generated can be used for other applications, e.g., electroplating and elastomer molding.^[54]

A simplification of the nanolithography process has consisted in approaches where “imageable” BCs are used, in which one of the blocks already contains components that provide a barrier to etching, thus eliminating the preliminary step, consisting of either the loading with inorganics or the selective removal of one block. Silicon-containing polymers, and in particular BCs based on PFS (chemical structure in Fig. 6),^[55] have been proposed as good candidates, since they can form a thin $\text{Si}_x\text{O}_y\text{Fe}_z$ layer on the surface when exposed to an oxygen plasma (O_2 -RIE). This results in a lower etching rate and therefore in an etching selectivity that is as high as 50:1, in comparison with organic polymers. As an example, Figure 8 shows the fabrication of a cobalt magnetic dot array by lithography using a PS-*b*-PFS monolayer.^[56] The first O_2 -RIE step removes the organic part of the polymer and converts the PFS into the non-volatile iron–silicon oxides. The spherical features of the template are transferred sequentially through the silica, then the tungsten, and finally the cobalt, with the formation of patterns A–D shown in Figure 9.

The main restriction for a wider use of all the above lithography processes is the limited aspect ratio and long-range or-

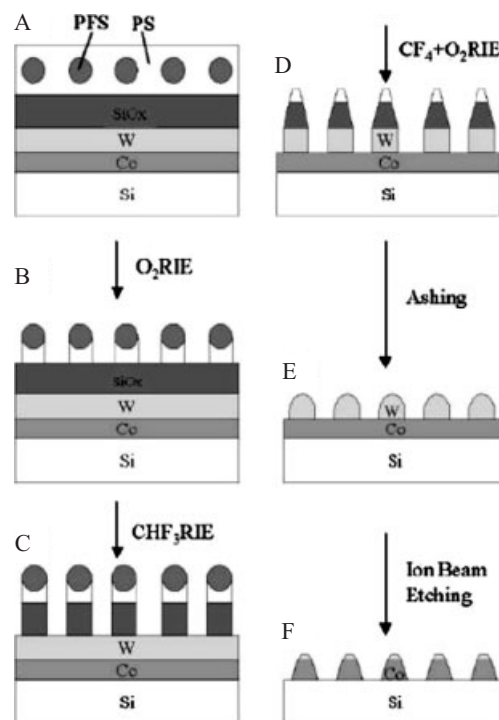


Fig. 8. Nanolithography fabrication of a cobalt dot array from PS-*b*-PFS. A) Cross-sectional view of the spherical microdomain monolayer consisting of PFS spheres ordered in a 2D hexagonal lattice on a multilayer of silica, tungsten and cobalt. B) Formation of the mask through the O_2 -RIE process. C) Silica patterning using CHF_3 -RIE. D) Tungsten patterning using CF_4/O_2 -RIE. E) Removal of silica and residual polymer by further CF_4/O_2 -RIE at high pressure. F) Final formation of cobalt dots by ion beam etching [56].

der of the features fabricated by such monolayer masks. A practical difficulty for the creation of higher (or deeper) features arises from the necessity to use thicker BC films with suitable patterns, as might be the case with surface-perpendicular lamellae or cylinder morphologies (e.g., Fig. 1, items 2–5). As mentioned in the introduction, the orientation of domains is not at all a trivial problem, since their disposition and long-range order are dependent upon the interaction with the surfaces (usually a substrate and a free surface). Noteworthy efforts to understand and control the domain alignment in BC morphologies have been carried out by several groups through the investigation of the effect of external fields and surface energy boundary conditions on the self-assembly process. These include the use of applied mechanical or electrical fields,^[57,58] applied temperature gradients,^[59] solvent evaporation or crystallization,^[60,61] and patterned or neutral surfaces.^[62,63] The best results obtained so far, in terms of large-area ordering of domains and efficiency of orientation in thicker films (up to few micrometers), were achieved from directional crystallization of a solvent^[61a] and application of an electric field,^[58a–c] respectively.

Despite of these promising results, the use of highly ordered BC templates for nanolithography application is so far limited to a surprisingly low number of cases, essentially based on very thin films (< 50 nm thickness). In most investigations, PS-*b*-PMMA films with PMMA cylinders normal to the surface

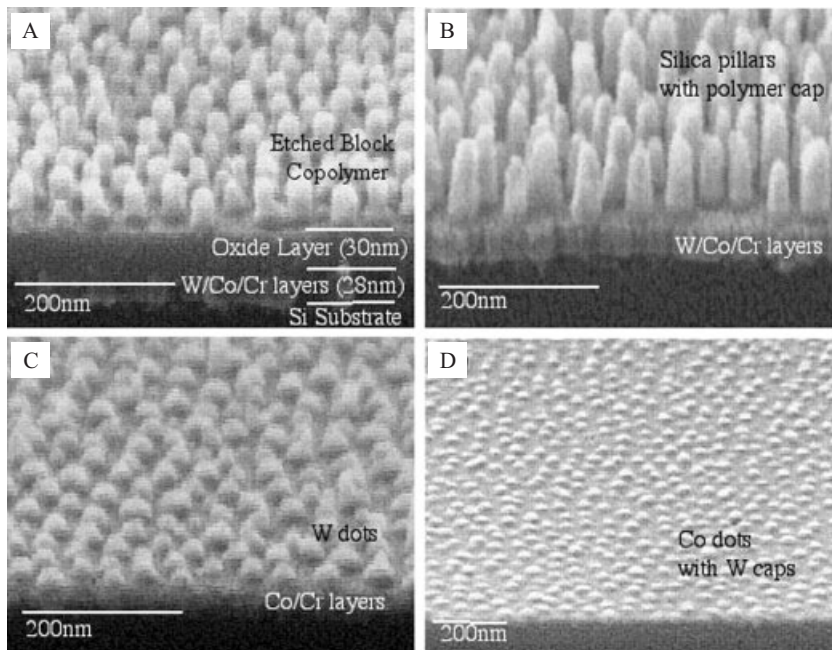


Fig. 9. Tilted scanning electron microscopy image of the intermediate stages of the PS-*b*-PFS nanolithography. A–D) Images correspond to the different patterns after the stages B,C,E,F as schematized in Figure 8 [56].

and dispersed in the PS matrix were obtained by deposition onto a neutral surface,^[63a] and subsequently transformed into a nanoporous template by elimination of PMMA domains via UV degradation. Such masks have found applications for transferring the pattern (Fig. 10) over full silicon wafers and into various substrate materials^[64] including antiferromagnet-ferromagnet bilayers, such as a FeF₂-Fe bilayer.^[65]

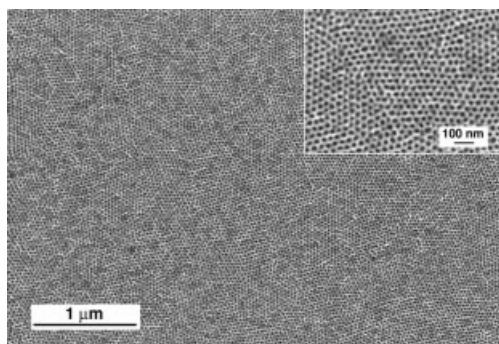


Fig. 10. Scanning electron microscopy images of a nanoporous template formed from a 40 nm thick film of PS-*b*-PMMA self-assembled in a hexagonally ordered cylinder morphology normal to the surface. Dark regions correspond to the pores (<20 nm diameter) from which PMMA microdomains were removed by UV degradation (reprinted with permission from Guarini et al. [64a], copyright 2001 AVS—The Science & Technology Society).

And finally, BC nanolithographic techniques certainly offer unprecedented feature dimensions and densities well below the photolithographic resolution limits, but this may not be the only key advantage of BCs in the near future. At least as important is that the feature sizes may be realized over macroscopically larger areas than by standard top-down approaches.

3.2. Membrane-Based Synthesis

At the same time, the tuning of the procedure for the preparation of nanoporous films with controlled spatial orientation (essentially carried out by Russell and co-workers)^[66] has also constituted a decisive step forward in membrane-based nanofabrication.^[1d,i] Synthesis of nano-objects via chemical- or electrodeposition^[67,68] into particle track-etched polymeric membranes are performed with well established procedures, and the introduction of a versatile and robust route to the fabrication of densely packed nanoporous arrays (as those shown in Fig. 10) certainly opened up novel unprecedented developments.^[69] Two groundbreaking papers have recently reported the electrodeposition of ferromagnetic cobalt nanowires,^[70] and the chemical deposition of nanoscopic SiO₂ posts^[71] into nanoporous films used as scaffolds. In both cases, a template was used, which was generated by selective removal of PMMA domains from PS-*b*-PMMA films with hexagonally packed cylinder morphology and oriented normal to the surface either by application of an electric field^[58b] or deposition onto a neutral substrate.^[63a] The corresponding processing flows are shown in Figures 11,12 (the steps are described in detail in the captions), while images of the arrays of

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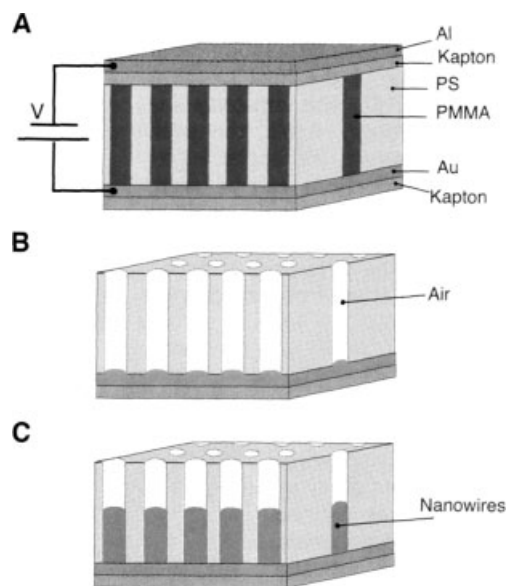


Fig. 11. Process of fabrication of cobalt nanowire arrays with densities in excess of 1.9×10^{11} wires cm^{-2} . A 1 μm thick film of PS-*b*-PMMA is annealed above the glass-transition temperature of both blocks between an electric field, in order to form a hexagonally ordered cylinder morphology normal to the electrodes (A). After removal of PMMA microdomains by UV degradation a nanoporous film (B) is left, which is used for the controlled electrodeposition of nanowires (approximate diameter 15 nm, C), thus forming an array of nanowires within the PS matrix (reprinted with permission from Thurn-Albrecht et al. [70], copyright 2000 American Association for the Advancement of Science).

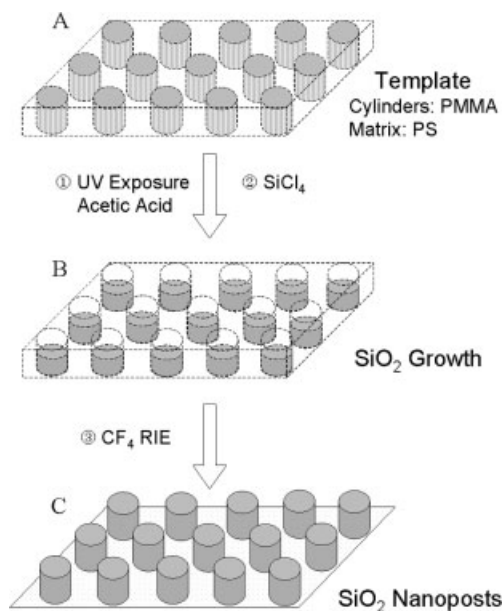


Fig. 12. Process of fabrication of SiO₂ nanoposts. A PS-*b*-PMMA thin film (A) is selectively degraded to form a nanoporous template like that in Figure 10. SiO₂ is grown within the nanoporous (B) by SiCl₄ hydrolysis with atmospheric water, then SiO₂ nanoposts are left after removing PS matrix with CF₄-RIE (C, Kim et al. [71]).

SiO₂ are presented in Figure 13. In any case, the impact of these highly ordered templates might be much broader, as they offer different practical means of producing tailored nanostructures. More recent publications demonstrated few other likely routes, such as processing to high-density arrays of chromium, and layered gold–chromium nanodots and nanoholes by evaporation onto nanoporous templates.^[72] In addition, such nanoporous membranes have been proposed for the creation of nanoelectrode arrays.^[73]

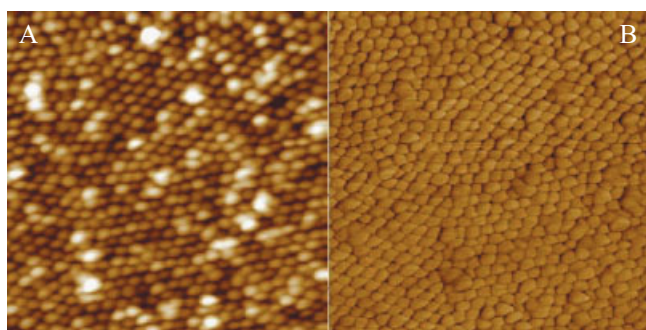


Fig. 13. Atomic force microscopy height (A) and phase (B) images of the SiO₂ nanoposts fabricated as schematized in Figure 12 (adapted from H.-C. Kim et al. [71]). The size of the images is approximately 1 μm × 1 μm.

3.3. Amphiphilic Block Copolymer Templates

The formation of ordered patterns is also possible by assembling BC micelles upon casting,^[74] with a major interest in terms of potential applications in nanotechnology placed on

laterally ordered hexagonal array of spherical micelles (Fig. 1, item 7, with dimensions falling in the approximate 10–100 nm range) deposited into a monolayer film. Furthermore, long-range positional order and orientation of these BC domains can be efficiently controlled by the application of graphoepitaxy,^[75] in which the surface-relief structure of the substrate directs epitaxial growth of the overlying micelles.^[76]

Micellar cores offer unique microenvironments (“nanoreactors”) in which inorganic precursors are loaded and then processed by wet chemical methods to produce comparatively uniform nanoparticles, in a similar way as it is usually done with microemulsions.^[11] BC-nanoparticle hybrids present peculiar magnetic, electro-optical, and catalytic properties arising primarily from single inorganic colloids,^[19a] but even more fascinating are the possibilities, offered by their self-assembly, as templates. Synthesis of different single-metal nanoclusters within microphase separated domains of amphiphilic diblock copolymers has been already reviewed,^[19a] and need not to be repeated here. Further developments that have been reported are, for example, the ordered deposition of gold and silver nanoclusters from micellar PS-*b*-PVP^[77] and PS-*b*-PAA (Fig. 14)^[78] films, respectively. The versatility of this procedure is such that it allows the use of various different amphiphilic BC, with the only requirement to form reverse micelles in a

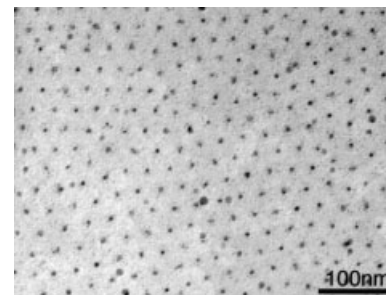


Fig. 14. Transmission electron microscopy image of a PS-*b*-PAA monolayer (film thickness 22 nm) containing silver nanoclusters. Silver was loaded as silver acetate in aqueous solution and reduced in a hydrogen atmosphere (reprinted with permission from Boontongkong and Cohen [78], copyright 2002 American Chemical Society).

non-polar solvent. A large variety of inorganic compounds can be loaded in the micellar polar cores and, in principle, their chemical transformation can be performed either before or after film deposition. At the same time, a large number of substrates can be used. It is also worth mentioning that the polymer can be removed after deposition, leaving on the substrate an inorganic nanopattern suitable for other applications, such as nanolithographic masks. Möller and co-workers reported the application of this approach for the fabrication of quantum structures with a very high aspect ratio of 1:10 and dimensions down to 10 nm.^[79] The metal cluster mask resulting from a monolayer of Au-loaded PS-*b*-PVP micelles has been used in a chlorine dry etching process to etch free-standing cylinders in GaAs and its alloys on In and Al. This combination of standard and bottom-up lithography can be applied on virtually any semiconductor material and could widen the possibility of technological application of quantum dot devices.

4. Summary and Outlook

Self-assembly of block copolymers into highly regular morphologies has been investigated by chemists for several decades^[57a] but it is only in the last ten years that multidisciplinary groups have focused their research efforts on the use of BCs as a tool for nanomaterial fabrication, following a wider scientific and technological trend towards miniaturization. Diverse methods of fabrication have been presented throughout the review, with the final aim to provide an overview of the potential applications offered by BC mesostructures (Table 1 summarizes the main research reported so far).

It has been shown that relatively simple processing of self-assembled BCs in bulk or in solution permits the creation of individual polymeric nano-objects with different shapes, such as spheres, hollow spheres, fibres, and tubes. A better tailoring of intrinsic properties and control of dimensions of such objects, as well as optimization of fabrication methods currently available do not appear as too difficult challenges. However their use for practical applications, as chemical or biological sensors or for encapsulation purposes, e.g., as carriers, is possibly hindered by the limited efforts so far focused on the development of efficient and reliable fractionation techniques.^[26,27] Moreover, a tremendous, almost unexplored potential is likely to reside in the development of processes based on the controlled pyrolysis of polymeric nano-objects, as well as of self-assembled BC films as a whole,^[80] to yield nanostructured carbons.

The preparation of templates from BC thin films has already been performed by a relatively large number of research groups through similar approaches, even though the key point for a wider application of these films is still represented by issues such as long-range order and control of domain orientation. Just few works have reported the application of large-area, highly oriented thin films as templates, using methodologies that only apply to PS-*b*-PMMA, while promising results can be also obtained from the use of ordering procedures, based on the deposition onto substrates neutralized with substances that do not present preferential interactions with any hydrocarbon polymers, such as carbon-coated surfaces.^[82] Notwithstanding many applications do not

require long-range order, e.g., preparation of individual nano-objects or direct use of nanoporous films as membranes, only the tuning of a reproducible orientation procedure applicable with different BCs will permit more flexible fabrication of very sharp, highly dense features, independently from the production either by nanolithography or via a templated synthesis, thereby pointing towards a route for further technological developments of applications such as in addressable ultra-high density recording media. If one could template through a reproducible and robust process with those nanostructures arrangements of single grain magnetic bits, storage densities of more than 5 Tbit cm⁻² could be achieved, which are two orders of magnitude larger than the actual and most recent developments of announced storage densities.

In addition, amphiphilic BC templates have demonstrated their potential through the preparation of dense metal nanoclusters from as-cast monolayers of loaded micelles. Thus following a procedure that could become an alternative, at least in terms of ease of processing and reproducibility, to the fabrication from nanoporous templates.

And finally, although polymer synthesis did not represent a priori the limiting factor for further growth of interest in the use of BCs for the fabrication of nanomaterials, it is worth pointing out that a new field has been opened by the availability of mesostructures through reactive blending of homopolymers.^[83]

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- [1] For early papers see: a) G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **1991**, 254, 1312. b) G. A. Ozin, *Adv. Mater.* **1992**, 4, 612. c) C. R. Martin, *Science* **1994**, 266, 1961. d) C. R. Martin, *Chem. Mater.* **1996**, 8, 1739. For more recent reviews or books on nanomaterial synthesis see, e.g.: e) Y. Xia, J. A. Rogers, K. E. Paul, G. M. Whitesides, *Chem. Rev.* **1999**, 99, 1823. f) Special issue on Nanoscale Materials, *Acc. Chem. Res.* **1999**, 32, Issue 5. g) A. Huczko, *Appl. Phys. A* **2000**, 70, 365. h) M. M. Alkaisi, R. J. Blaikie, S. J. McNab, *Adv. Mater.* **2001**, 13, 877. i) T. Liu, C. Burger, B. Chu, *Prog. Polym. Sci.* **2003**, 28, 5. l) M. A. López-Quintela, *Curr. Opin. Colloid Interface Sci.* **2003**, 8, 137. m) H. S. Nalwa, *Handbook of Nanostructured Materials and Technology*, Vol. 1–5, Academic Press, San Diego **2000**. n) K. J. Klabunde, *Nanoscale Materials in Chemistry*, Wiley, New York **2001**.

Table 1. Summary of the nanomaterials that may be obtained from microphase separated block copolymers (BCs) [a].

BC tool	As nanomaterials		As templates	
	direct use	through processing	direct use	after processing
BCs in bulk [b]	photonic crystals [21,22]	individual polymeric nano-objects: spheres, fibers, tubes [24–28,30–32]	nanolithographically patterned materials: cobalt [56]	nanolithographically patterned materials: silicon, silicon nitride, gold, others [17,51–53,64,65]
	conducting BCs [23]	nanoporous membranes [16,35,36,66,73] nanostructured carbons [80]	hierarchically self-assembled metal nanowires [81]	high density arrays of metallic or semiconductor materials: cobalt, silica, chromium, others [70,72]
amphiphilic BCs		individual polymeric nano-objects: spheres, hollow spheres, cylinders, tubes [44–50]	metal nanoclusters [19a,77,78] inorganic colloids [19a]	nanolithographically patterned materials [79]

[a] Applications of BC nanocomposites and more specifically of BC/ceramic hybrids are not included because they are beyond the scope of the present review.
[b] Mainly as amorphous thin films.

- [2] a) H. Li, W. T. S. Huck, *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 3. b) K. Ishizu, K. Tsubaki, A. Mori, S. Uchida, *Prog. Polym. Sci.* **2003**, *28*, 27.
- [3] For an overview on the last developments on polymer synthesis: a) K. Hatada, T. Kitayama, O. Vogl, *Macromolecular Design of Polymeric Materials*, Marcel Dekker, New York **1997**. b) T. E. Patten, K. Matyjaszewski, *Adv. Mater.* **1998**, *10*, 901. c) N. Hadjichristidis, M. Pitsikalis, S. Pispas, H. Iatrou, *Chem. Rev.* **2001**, *101*, 3747. d) K. Matyjaszewski, T. P. Davis, *Handbook of Radical Polymerization*, Wiley, New York, **2002**. For more specific examples on the preparation of complex polymer structures see e.g.: e) M. Lazzari, K. Hatada, T. Kitayama, M. Jančo, *Macromolecules* **2001**, *34*, 5734. f) P. Dumas, C. Delaite, G. Hurtrez, *Macromol. Symp.* **2002**, *183*, 29. g) D. Charalabidis, M. Pitsikalis, N. Hadjichristidis, *Macromol. Chem. Phys.* **2002**, *203*, 2132. h) R. Francis, N. Lepoittevin, D. Taton, Y. Gnanou, *Macromolecules* **2002**, *35*, 9001.
- [4] a) I. W. Hamley, *The Physics of Block Copolymers*, Oxford University Press, Oxford **1998**. b) D. Y. Ryu, U. Jeong, J. K. Kim, T. P. Russell, *Nat. Mater.* **2002**, *1*, 114.
- [5] The potential of BCs for the preparation of supramolecular materials has been discussed in a previous review: H.-A. Klok, S. Commandoux, *Adv. Mater.* **2001**, *13*, 1217.
- [6] I. W. Hamley, *J. Phys.: Condens. Matter* **2001**, *13*, R643.
- [7] M. W. Matsen, F. S. Bates, *J. Chem. Phys.* **1997**, *106*, 2436.
- [8] For a recent example of non-predicted morphologies, formed by introducing highly flexible block segments into a BC, see: M. H. Uddin, C. Rodriguez, M. A. Lopez-Quintela, D. Leisner, C. Solans, J. Esquena, H. Kuniyeda, *Macromolecules* **2003**, *36*, 1261.
- [9] J. T. Chen, E. L. Thomas, C. K. Oberle, G.-P. Mao, *Science* **1996**, *273*, 343.
- [10] H. Elbs, C. Drummer, V. Abetz, G. Krausch, *Macromolecules* **2002**, *35*, 5570.
- [11] R. Stadler, C. Auschra, J. Beckman, U. Krappe, I. Voigt-Martin, L. Leibner, H. Elbs, *Macromolecules* **1995**, *28*, 3080.
- [12] H. Elbs, C. Drummer, V. Abetz, G. Hadziioannou, G. Krausch, *Macromolecules* **2001**, *34*, 7917.
- [13] K. Takahashi, H. Hasegawa, T. Hashimoto, V. Bellas, H. Iatrou, N. Hadjichristidis, *Macromolecules* **2002**, *35*, 4859.
- [14] a) M. J. Fasaloka, A. M. Mays, *Annu. Rev. Mater. Res.* **2001**, *31*, 323. b) G. Krausch, R. Magerle, *Adv. Mater.* **2002**, *14*, 1579.
- [15] G. M. Whitesides, B. Grzybowski, *Science* **2002**, *295*, 2418.
- [16] T. Hashimoto, K. Tsutsumi, Y. Funaki, *Langmuir* **1997**, *13*, 6869.
- [17] a) P. Mansky, P. Chaikin, E. L. Thomas, *J. Mater. Sci.* **1995**, *30*, 1987. b) M. Park, C. Harrison, P. M. Chaikin, R. A. Register, D. H. Adamson, *Science* **1997**, *276*, 1401.
- [18] P. Alexandridis, B. Lindman, *Amphiphilic Block Copolymers*, Elsevier, Amsterdam **2000**.
- [19] a) S. Förster, M. Antonietti, *Adv. Mater.* **1998**, *10*, 195. b) M. Breulmann, S. A. Davis, S. Mann, H. P. Hentze, M. Antonietti, *Adv. Mater.* **2000**, *12*, 502. c) P. F. W. Simon, R. Ulrich, H. W. Spiess, U. Wiesner, *Chem. Mater.* **2001**, *13*, 3464. d) R. Ulrich, J. W. Zwanziger, S. M. De Paul, A. Reiche, H. Leuninger, H. W. Spiess, U. Wiesner, *Adv. Mater.* **2002**, *14*, 1134.
- [20] a) R. B. Thompson, V. V. Ginzburg, M. W. Matsen, A. C. Balazs, *Macromolecules* **2002**, *35*, 1060. b) K. A. Mauritz, R. F. Storey, D. A. Mountz, D. A. Reuschle, *Polymer* **2002**, *43*, 4315. c) S. Yang, Y. Horibe, C.-H. Chen, P. Mirau, T. Tatry, P. Evans, J. Grazul, E. M. Dufresne, *Chem. Mater.* **2002**, *14*, 5173. d) M. R. Bockstaller, Y. Lapetnikov, S. Margel, E. L. Thomas, *J. Am. Chem. Soc.* **2003**, *125*, 5276.
- [21] Y. Fink, A. M. Urbas, M. G. Bawendi, J. D. Joannopoulos, E. L. Thomas, *J. Lightwave Technol.* **1999**, *17*, 1963.
- [22] a) A. C. Endrington, A. M. Urbas, P. DeRege, C. X. Chen, T. M. Swager, N. Hadjichristidis, M. Xenidou, L. J. Fetters, J. D. Joannopoulos, Y. Fink, E. L. Thomas, *Adv. Mater.* **2001**, *13*, 421. b) M. Maldovan, A. M. Urbas, N. Yufa, W. C. Carter, E. L. Thomas, *Phys. Rev. B* **2002**, *65*, 165123.
- [23] J. Liu, E. Sheina, T. Kowalewski, R. D. McCullough, *Angew. Chem. Int. Ed.* **2002**, *41*, 329.
- [24] For a general view of this approach, see also other examples not illustrated in this review: a) G. Liu, L. Qiao, A. Guo, *Macromolecules* **1996**, *29*, 5508. b) G. Liu, *Adv. Mater.* **1997**, *9*, 437.
- [25] G. Liu, J. Ding, L. Qiao, A. Guo, B. P. Dymov, J. T. Gleeson, T. Hashimoto, K. Saijo, *Chem. Eur. J.* **1999**, *5*, 2740.
- [26] G. Liu, X. Yan, S. Duncan, *Macromolecules* **2002**, *35*, 9788.
- [27] G. Liu, X. Yan, X. Qiu, Z. Li, *Macromolecules* **2002**, *35*, 7742.
- [28] X. Yian, F. Liu, Z. Li, G. Liu, *Macromolecules* **2001**, *34*, 9112.
- [29] The Roman mythological term "Janus" describes the property of having two faces and was first used in chemistry by C. Casagrande, M. Veysié, *C. R. Acad. Sci., Ser. II: Mec., Phys., Chim., Sci. Terre Univers* **1988**, *306*, 1423.
- [30] R. Saito, A. Fujita, A. Ichimura, K. Ishizu, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2091.
- [31] R. Erhardt, A. Böker, H. Zettl, H. Kaya, W. Pyckhout-Hintzen, G. Krausch, V. Abetz, A. H. E. Müller, *Macromolecules* **2001**, *34*, 1069.
- [32] See for example: a) J. Ruokolainen, G. ten Brinkle, O. Ikkala, *Adv. Mater.* **1999**, *11*, 777. b) O. Ikkala, G. ten Brinkle, *Science* **2002**, *295*, 2407.
- [33] K. de Moel, G. O. R. A. Van Ekenstein, H. Nijland, E. Plushkin, G. Ten Brinkle, *Chem. Mater.* **2001**, *13*, 4580.
- [34] P. Apel, *Radiat. Meas.* **2001**, *34*, 559.
- [35] a) G. Liu, J. Ding, A. Guo, M. Hertford, D. Bazett-Jones, *Macromolecules* **1997**, *30*, 1851. b) G. Liu, J. Ding, *Adv. Mater.* **1998**, *10*, 69. c) G. Liu, J. Ding, T. Hashimoto, K. Kimishima, F. M. Winnik, S. Nigam, *Chem. Mater.* **1999**, *11*, 2233.
- [36] V. Z.-H. Chan, J. Hoffman, V. Y. Lee, H. Iatrou, A. Avgeropoulos, N. Hadjichristidis, R. D. Miller, E. L. Thomas, *Science* **1999**, *286*, 1716.
- [37] For an introductory view on the formation of micelles by BCs, see: a) C. Price, D. Woods, *Eur. Polym. J.* **1973**, *9*, 827. b) C. Price, *Pure Appl. Chem.* **1983**, *55*, 1563. c) C. Price, E. K. M. Chan, A. L. Hudd, R. B. Stubbersfield, *Polym. Comm.* **1986**, *27*, 196. For a recent comprehensive paper see: d) J. S. Pedersen, C. Svaneborg, *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 158.
- [38] For recent investigations see: a) H. Shen, A. Eisenberg, *Angew. Chem. Int. Ed.* **2002**, *39*, 3310. b) D. E. Discher, A. Eisenberg, *Science* **2002**, *297*, 967.
- [39] a) K. Yu, A. Eisenberg, *Macromolecules* **1998**, *31*, 3509. b) L. Zhang, A. Eisenberg, *Macromolecules* **1999**, *32*, 2239. c) H. Y. Zhao, E. P. Douglas, B. S. Harrison, K. S. Schanze, *Langmuir* **2001**, *17*, 8428.
- [40] a) L. Zhang, A. Eisenberg, *Science* **1995**, *268*, 1728. b) L. Zhang, K. Yu, A. Eisenberg, *Science* **1996**, *272*, 1777. c) T. Imae, H. Tabuchi, K. Funayama, A. Sato, T. Nakamura, N. Amaya, *Coll. Surf. A* **2000**, *167*, 63. d) J. C. Riegel, A. Eisenberg, C. L. Petzhold, D. Semios, *Langmuir* **2002**, *18*, 3358.
- [41] It should be noticed that stable aggregates can be synthesized with traditional surfactants replacing the alkyl chains by rigid skeletons or connecting the head groups through intermolecular interactions: G. Li, W. Fudickar, M. Skupin, A. Klyszcz, C. Draeger, M. Lauer, J.-H. Fuhrhop, *Angew. Chem. Int. Ed.* **2002**, *41*, 1828.
- [42] a) K. B. Thurmond, T. Kowalewski, K. L. Wooley, *J. Am. Chem. Soc.* **1996**, *118*, 7239. b) J. Tao, G. Liu, J. Ding, M. Yang, *Macromolecules* **1997**, *30*, 4084.
- [43] For other recent related examples not illustrated in this review see: a) S. Stewart, G. Liu, *Chem. Mater.* **1999**, *11*, 1048. b) Q. Zhang, E. E. Remsen, K. L. Wooley, *J. Am. Chem. Soc.* **2000**, *122*, 651. c) Z. Zhang, G. Liu, S. Bell, *Macromolecules* **2000**, *33*, 7877. d) Q. Ma, E. E. Remsen, T. Kowalewski, J. Schaefer, K. L. Wooley, *Nano Lett.* **2001**, *1*, 651. e) M. L. Becker, E. E. Remsen, K. L. Wooley, *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 4152. f) J. Y. Zhou, Z. Li, G. J. Liu, *Macromolecules* **2002**, *35*, 3690. g) G. J. Liu, J. Y. Zhou, *Macromolecules* **2002**, *35*, 8167.
- [44] S. Liu, J. V. M. Weaver, Y. Tang, N. C. Billingham, S. P. Armes, K. Tribe, *Macromolecules* **2002**, *35*, 6121.
- [45] R. S. Underhill, G. Liu, *Chem. Mater.* **2000**, *12*, 2082.
- [46] S. Stewart, G. Liu, *Angew. Chem. Int. Ed.* **2000**, *39*, 340.
- [47] Y.-Y. Won, H. T. Davis, F. S. Bates, *Science* **1999**, *283*, 960.
- [48] Y.-Y. Won, K. Paso, H. T. Davis, F. S. Bates, *J. Phys. Chem. B* **2001**, *105*, 8302.
- [49] J. Massey, K. Temple, L. Cao, Y. Rharbi, J. Raez, M. A. Winnik, I. Manners, *J. Am. Chem. Soc.* **2000**, *122*, 11577.
- [50] J. Raez, I. Manners, M. A. Winnik, *J. Am. Chem. Soc.* **2002**, *124*, 10381.
- [51] C. Harrison, M. Park, P. M. Chaikin, R. A. Register, D. H. Adamson, *J. Vac. Sci. Technol. B* **1998**, *16*, 544.
- [52] R. R. Li, P. D. Dapkus, M. E. Thompson, W. G. Jeong, C. Harrison, P. M. Chaikin, R. A. Register, D. H. Adamson, *Appl. Phys. Lett.* **2000**, *76*, 1689.
- [53] M. Park, P. M. Chaikin, R. A. Register, D. H. Adamson, *Appl. Phys. Lett.* **2001**, *79*, 257.
- [54] Y. Xia, G. M. Whitesides, *Annu. Rev. Mater. Res.* **1998**, *28*, 153.
- [55] a) R. G. H. Lammertink, M. A. Hempenius, J. E. van den Enk, V. Z.-H. Chan, E. L. Thomas, G. J. Vancso, *Adv. Mater.* **2000**, *12*, 98. b) J. Y. Cheng, C. A. Ross, E. L. Thomas, H. I. Smith, G. J. Vancso, *Appl. Phys. Lett.* **2002**, *81*, 3657.
- [56] J. Y. Cheng, C. A. Ross, V. Z.-H. Chan, E. L. Thomas, R. G. H. Lammertink, G. J. Vancso, *Adv. Mater.* **2001**, *13*, 1174.
- [57] a) A. Keller, E. Pedemonte, F. M. Willmouth, *Nature* **1970**, *225*, 538. b) R. J. Albalak, E. L. Thomas, *J. Polym. Sci., Part B: Polym. Phys.* **1993**, *31*, 37. c) D. Maring, U. Wiesner, *Macromolecules* **1997**, *30*, 660. d) B. S. Pinheiro, K. I. Winey, *Macromolecules* **1998**, *31*, 4447.
- [58] a) T. L. Morkved, M. Lu, A. M. Urbas, E. E. Ehrichs, H. M. Jaeger, P. Mansky, T. P. Russell, *Science* **1996**, *273*, 931. b) T. Thurn-Albrecht, J. DeRouchey, T. P. Russell, H. M. Jaeger, *Macromolecules* **2000**, *33*, 3250. c) A. Boker, A. Knoll, H. Elbs, V. Abetz, A. H. E. Müller, G. Krausch, *Macromolecules* **2002**, *35*, 1319. For theoretical works: d) G. G. Pereira, D. R. M. Williams, *Macromolecules* **1999**, *32*, 8155. e) B. Ashok,

- M. Muthukumar, T. P. Russell, *J. Chem. Phys.* **2001**, *115*, 1559. f) Y. Tsori, D. Andelman, *Macromolecules* **2002**, *35*, 5161.
- [59] J. Bodycomb, Y. Funaki, K. Kimishima, T. Hashimoto, *Macromolecules* **1999**, *32*, 2075.
- [60] a) K. Fukunaga, H. Elbs, R. Magerle, G. Krausch, *Macromolecules* **2000**, *33*, 947. b) Z. Lin, D. H. Kim, X. Wu, L. Boosahda, D. Stone, L. LaRose, T. P. Russell, *Adv. Mater.* **2002**, *12*, 1373.
- [61] a) C. De Rosa, C. Park, B. Lodz, J.-C. Wittmann, L. J. Fetters, E. L. Thomas, *Macromolecules* **2000**, *33*, 4871. b) C. De Rosa, C. Park, E. L. Thomas, B. Lodz, *Nature* **2000**, *405*, 433. c) C. Park, J. Y. Cheng, M. J. Fasolka, A. M. Mayes, C. A. Ross, E. L. Thomas, C. de Rosa, *Appl. Phys. Lett.* **2001**, *79*, 848. d) C. Park, C. de Rosa, L. J. Fetters, B. Lodz, E. L. Thomas, *Adv. Mater.* **2001**, *13*, 724. e) C. Park, C. de Rosa, E. L. Thomas, *Macromolecules* **2001**, *34*, 2602.
- [62] a) J. Heier, J. Genzer, E. J. Kramer, F. S. Bates, S. Walheim, G. Krausch, *J. Chem. Phys.* **1999**, *111*, 11 101. b) X. M. Yang, R. D. Peters, P. F. Nealey, H. H. Solak, F. Cerrina, *Macromolecules* **2000**, *33*, 9575. c) L. Rockford, S. G. J. Mochrie, T. P. Russell, *Macromolecules* **2001**, *34*, 1487.
- [63] a) E. Huang, T. P. Russell, C. Harrison, P. M. Chaikin, R. A. Register, C. J. Hawker, J. Mays, *Macromolecules* **1998**, *31*, 7641. b) R. G. H. Lammermintink, M. A. Hempenius, G. J. Vancso, K. Shin, M. H. Rafailovich, J. Sokolov, *Macromolecules* **2001**, *34*, 942. c) B. Sundrani, S. J. Sibener, *Macromolecules* **2002**, *35*, 8531.
- [64] a) K. W. Guarini, C. T. Black, K. R. Milkove, R. L. Sandstrom, *J. Vac. Sci. Technol. B* **2001**, *19*, 2784. b) C. T. Black, K. W. Guarini, K. R. Milkove, S. M. Baker, T. P. Russell, M. T. Tuominen, *Appl. Phys. Lett.* **2001**, *79*, 409.
- [65] K. Liu, S. M. Baker, M. T. Tuominen, T. P. Russell, I. K. Schuller, *Phys. Rev. B* **2001**, *63*, 060 403(R).
- [66] a) T. Thurn-Albrecht, R. Steiner, J. DeRouche, C. M. Stafford, E. Huang, M. Bal, M. T. Tuominen, C. J. Hawker, T. P. Russell, *Adv. Mater.* **2000**, *12*, 787. b) T. P. Russell, T. Thurn-Albrecht, M. T. Tuominen, E. Huang, C. J. Hawker, *Macromol. Symp.* **2000**, *159*, 77.
- [67] a) C. J. Brumlik, V. P. Menon, C. R. Martin, *J. Mater. Res.* **1994**, *9*, 1174. b) S. Demoustier-Champagne, M. Delvaux, *Mater. Sci. Eng., C* **2001**, *15*, 269. c) C. R. Martin, M. Nishizawa, K. Jirage, M. S. Kang, S. B. Lee, *Adv. Mater.* **2001**, *13*, 1351. d) M. Barbic, J. J. Mock, D. R. Smith, S. Schultz, *J. Appl. Phys.* **2002**, *91*, 9341. e) M. Wirtz, M. Parker, Y. Kobayashi, C. R. Martin, *Chem. Eur. J.* **2002**, *8*, 3573.
- [68] a) A. Blondel, J. Meier, B. Doudin, J.-P. Ansermet, K. Attenborough, P. Evans, R. Hart, G. Nabiyouni, W. Schwarzacher, *J. Magn. Magn. Mater.* **1995**, *148*, 317. b) S. Dubois, A. Michel, J. P. Eymery, J. L. Duval, L. Piroux, *J. Mater. Res.* **1999**, *14*, 665. c) A. K. M. Bantu, J. Rivas, G. Zaragoza, M. A. Lopez-Quintela, M. C. Blanco, *J. Non-Cryst. Solids* **2001**, *287*, 5. d) M. E. T. Molares, V. Buschmann, D. Dobrev, R. Neumann, R. Scholz, I. U. Schuchert, J. Vetter, *Adv. Mater.* **2001**, *13*, 62. e) A. K. M. Bantu, J. Rivas, G. Zaragoza, M. A. Lopez-Quintela, M. C. Blanco, *J. Appl. Phys.* **2001**, *89*, 3393. f) J. Rivas, A. K. M. Bantu, G. Zaragoza, M. C. Blanco, M. A. Lopez-Quintela, *J. Magn. Magn. Mater.* **2002**, *249*, 220.
- [69] a) U. Jeong, H.-C. Kim, R. L. Rodriguez, I. Y. Tsai, C. M. Stafford, J. K. Kim, C. J. Hawker, T. P. Russell, *Adv. Mater.* **2002**, *14*, 274. b) K. W. Guarini, C. T. Black, S. H. I. Yeung, *Adv. Mater.* **2002**, *14*, 1290.
- [70] T. Thurn-Albrecht, J. Schotter, G. A. Kästle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C. T. Black, M. T. Tuominen, T. P. Russell, *Science* **2000**, *290*, 2126.
- [71] H.-C. Kim, X. Jia, C. M. Stafford, D. H. Kim, T. J. McCarthy, M. T. Tuominen, C. J. Hawker, T. P. Russell, *Adv. Mater.* **2001**, *13*, 795.
- [72] K. Shin, K. A. Leach, J. T. Goldbach, D. H. Kim, J. Y. Jho, M. T. Tuominen, C. J. Hawker, T. P. Russell, *Nano Lett.* **2002**, *2*, 933.
- [73] E. Jeoung, T. H. Galow, J. Schotter, M. Bal, A. Ursache, M. T. Tuominen, C. M. Stafford, T. P. Russell, V. M. Rotello, *Langmuir* **2001**, *17*, 6396.
- [74] M. Breulmann, S. Förster, M. Antonietti, *Macromol. Chem. Phys.* **2000**, *201*, 204.
- [75] H. I. Smith, D. C. Flanders, *Appl. Phys. Lett.* **1978**, *32*, 349.
- [76] a) R. A. Segalman, H. Yokoyama, E. J. Kramer, *Adv. Mater.* **2001**, *13*, 1152. b) J. Hahn, S. E. Webber, *Langmuir* **2003**, *19*, 3098.
- [77] J. P. Spatz, S. Mössmer, C. Hartmann, M. Möller, T. Herzog, M. Krieger, H.-G. Boyen, P. Ziemann, B. Kabius, *Langmuir* **2000**, *16*, 407.
- [78] Y. Boontongkong, R. E. Cohen, *Macromolecules* **2002**, *35*, 3647.
- [79] a) J. P. Spatz, T. Herzog, S. Mößmer, P. Ziemann, M. Möller, *Adv. Mater.* **1999**, *11*, 149. b) M. Haupt, S. Miller, K. Bitzer, K. Thonke, R. Sauer, J. P. Spatz, S. Mößmer, C. Hartmann, M. Möller, *Phys. Status Solidi B* **2001**, *224*, 867. c) M. Haupt, S. Miller, A. Ladenburger, R. Sauer, K. Thonke, J. P. Spatz, S. Riethmüller, M. Möller, F. Banhart, *J. Appl. Phys.* **2002**, *91*, 6057.
- [80] a) T. Kowalewski, N. V. Tsarevsky, T. Matyjaszewski, *J. Am. Chem. Soc.* **2002**, *124*, 10 632. b) T. Kowalewski, R. D. McCullough, K. Matyjaszewski, *Eur. Phys. J. E* **2003**, *10*, 5.
- [81] a) W. A. Lopes, H. M. Jaeger, *Nature* **2001**, *414*, 735. b) W. A. Lopes, *Phys. Rev. E* **2002**, *65*, 031 606.
- [82] M. Lazzari, M. C. Blanco, J. Rivas, M. A. López-Quintela, unpublished.
- [83] H. Pernot, M. Baumert, F. Court, L. Leibler, *Nat. Mater.* **2002**, *1*, 54.