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# 1.1 Block Copolymers as Useful Nanomaterials

# 1.1.1 Introduction

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Despite our best efforts to chemically design functional nanomaterials, we cannot yet match the brilliance of Nature. One striking example of this fact comes from a tethering structure known as a byssus created by the bivalve, Mytilus edulis. Byssal threads are the highly evolved materials that M. edulis uses to provide secure attachments to rocks and pilings during filter feeding. The threads begin at the base of the mussel's soft foot and attach to a hard surface by an adhesive plaque. Under strong tidal forces, an ordinary material would not be able to withstand the contact stresses that would result from the meeting of such soft and hard surfaces. Recent studies have shown that M. edulis solves this materials design problem through the creation of a "fuzzy" interface that avoids abrupt changes in the mechanical properties by gradually changing the chemical composition of the thread [1]. The chemistry that it uses to accomplish this graded material involves the elegant use of collagen-based self-assembling block copolymers (BCPs) [2]. The ventral groove of the mussel's foot contains several pores that act as channels for a reaction-injection-molding process that creates the copolymer. For this, central collagen blocks are mixed with a gradient of either elastin-like (soft) blocks, amorphous polyglycine blocks (intermediate), or silk-like (stiff) threads to form "diblock" copolymers of gradually decreasing mechanical stiffness as M. edulis moves farther away from the rock interface. Spontaneous self-assembly of the biopolymer seems to occur by the metal-binding histidine groups found in between each block interface that may act as ligands for metal-catalyzed polymerizations. The transition metals used for these polymerizations, such as Zn and Cu, are extracted from the ambient water through filter feeding.

*M. edulis* byssal thread is not the only example of a self-assembling chemical system found in Nature that seems perfectly suited to its environment. Self-assembly such as that found in *M. edulis* can be found in nearly every level of

nature, from cellular structures such as lipid bilayers [3], the colonization of bacteria [4], and the formation of weather systems [5]. The concept of self-assembly is defined by the automatic organization of small components into larger patterns or structures [6]. As small components, nature often uses various molecular interactions, such as hydrophilic/hydrophobic effects and covalent, hydrogen, ionic and van der Waals bonds to construct nanomaterials with specific macroscale functionalities. As scientists, we have learned an extraordinary amount about how to construct better synthetic materials from careful studies of how structure fits function in natural materials [7].

In the field of soft matter, one type of self-assembling synthetic material that has already been introduced in the *M. edulis* example is the BCP. BCPs are composed of different types of polymer connected by a covalent bond [8]. Apart from their interesting physical properties that have resulted in their use in byssal threads, upholstery foam, box tape, and asphalt [9], BCPs are also interesting due to the ability of each polymer block, or *phase*, to physically separate on the nanometer scale into various self-assembled morphologies such as spheres, cylinders, and sheets. These structures are attractive to scientists for several reasons.

- First, if one of the phases is removed from the periodic, ordered lattice, then thin films of the material could be used as stencils to etch patterns into semiconductor substrates such as silicon or gallium arsenide. This application is of great interest to the semiconductor industry, which is currently searching for alternative technologies for sub-20 nm lithography.
- Second, chemists are interested in BCP templates because they provide the power to carry out chemical reactions within specific phases of the material. This ability opens up many new areas of chemistry for nanomaterial design, including the growth of functional nanoparticle arrays for catalytic applications, the selective sequestration of chemicals for drug delivery, and the creation of mesoporous monolithic structures as low-*k* dielectric materials.
- Third, chemical functionalities attached to one phase within BCPs can be driven to segregate to the surface, where they can be affected by external stimuli such as ultraviolet (UV) light. These *surface-responsive* materials could be lithographically patterned to control the selective adsorption of biomolecules for biosensor applications.

All of the above applications use *phase-selective chemistry* to effect changes to the BCP microstructure and create useful nanostructured materials. In this chapter, we will discuss not only the recent investigations in these areas but also many other new and interesting applications.

The chapter is organized into three sections. In the first section we will discuss the basics of BCP self-assembly, and include a more detailed analysis of the morphologies possible with this class of material, along with an overview on how they are made and modified. The second section will provide a literature review of relevant studies in the field, including descriptions of BCPs as lithographic materials, as *nanoreactors*, as photo-crosslinkable nanobjects, and as surface-responsive materials. The third section will conclude with a summary of the most important contributions, together with a few additional insights on the future direction of the field of phase-selective BCP systems.

# 1.1.2 Self-Assembly of Block Copolymers

The thermodynamics of polymer mixing plays a large role in the self-assembly of BCPs [10]. In typical binary polymer mixtures, it is entropically unfavorable for two dissimilar homopolymers to mix homogeneously, as both components feel repulsive forces that result in the formation of large "macrophases" of each component in the mixture, akin to the mixing of oil and water. In diblock copolymers, however, the two component polymer "blocks" are chemically attached with a covalent bond. Here, the covalent bond acts as an elastic restoring force that limits the phase separation to mesoscopic length scales, thus resulting in "microphase" separated structures. The size of these phases, which are also known as microdomains, scale directly as the two-thirds power of the copolymer molecular weight [11]. The specific shape of the microdomains relies on a number of factors that control how each of the blocks interacts with each other. In the simplest argument, if there are equal amounts of each polymer, the microdomains will form into distinct layers with planar interfaces. However, if there is more of one block than the other, then curved interfaces will result. This curvature minimizes the repulsive interfacial contact between the A and B block, which also minimizes the free energy of the system. The bend that forms can be characterized by the curvature radius, R, as shown in Figure 1.1. Therefore, the equilibrium morphology of the BCP can usually be predicted based on differential geometry.

Other, more complicated, 'self-consistent mean field' theoretical treatments can be used to calculate the equilibrium morphology of the BCP. These theories sum the free energy contributions between (i) the repulsive polymer-polymer interactions versus (ii) the elastic restoring force energy for a particular microphase structure. The microphase structure with the lowest free energy sum will be the final equilibrium morphology. These theoretical equilibrium morphologies can be mapped out on a phase diagram, as shown in Figure 1.2. A typical BCP phase diagram plots the product  $\chi N$  on the ordinate versus the volume ratio,  $f_A$ , on the independent axis.  $\chi$  is known as the Flory-Huggins interaction parameter, which quantifies the relative incompatibility between the polymer blocks, and is inversely related to the temperature of the system. N is called the degree of polymerization, which is the total number of monomers per macromolecule. The volume fraction is represented by  $f_A = N_A/N$ , where  $N_A$  is the number of A monomers per molecule. For very low concentrations of A monomer, no phase separation will occur and the two polymers will mix homogeneously. However, at slightly higher compositions, where  $f_A \ll f_B$ , the A blocks form spherical microdomains in a matrix of B. The microdomains arrange on a body-centered cubic (BCC) lattice. Increasing the volume fraction to  $f_{\rm A} < f_{\rm B}$  leads to an increase in the connectivity of the microdomains, triggering the spheres to coalesce into cylinders that arrange on a hexago-

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$$N_{\rm A} > N_{\rm E}$$



Figure 1.1 (a) Equal volume fractions of A and B blocks form layered structures called lamellae with curvature radius approaching infinity. Unequal volume fractions of A and B cause a curvature at the intermaterial dividing surface (IMDS) to minimize interfacial

contact between the blocks and cause decrease of the curvature radius; (b) Schematic representing the application of this model in a sphere-forming (PS-*b*-PMMA) block copolymer system. Adapted from Ref. [29].

nal lattice. A roughly equal amount of both A and B blocks ( $f_A \approx f_B$ ) will result in the formation of alternating layered sheets, or lamellae, of the A and B blocks. Any further increase in  $f_A$  ( $f_A > f_B$ ), will cause the phases to invert, which means that the B block forms the microdomains in the matrix of A.

Thus, by tailoring the relative amount of A, the chemist can control the connectivity and dimensionality of the global BCP structure: spheres essentially represent zero-dimensional points in a matrix; cylinders represent one-dimensional lines; and lamellae represent two-dimensional sheets. Additionally, narrow regions of  $f_A$  exist in between the cylindrical and lamellar phase space where the two morphologies interpenetrate each other to form three-dimensional (3-D) "gyroid" [12, 13] network structures. Some reports of these morphologies have been published, and efforts have been put forth to take advantage of the added dimensionality with new applications [14, 15].

# 1.1.3

# **Triblock Copolymers**

Adding extra polymer blocks to the BCP chain introduces additional levels of complexity into the self-assembled phase behavior. Core–shell morphologies [16], "knitting pattern" [17] and helical structures (Figure 1.3) are just a few of the exotic



**Figure 1.2** Phase diagram for linear AB diblock copolymers, comparing theory and experiment. (a) Self-consistent mean field theory predicts four equilibrium morphologies: spherical (S), cylindrical (C), gyroid (G), and lamellar (L), depending on the composition f and combination parameter  $\chi N$ . Here,  $\chi$  is the Flory–Huggins interaction parameter (proportional to the heat of mixing A and B segments) and N is the degree of polymerization (number of monomers of all

types per macromolecule); (b) Experimental phase portrait for poly(isoprene-*block*-styrene) diblock copolymers. Note the resemblance to the theoretical diagram. One difference is the observed perforated lamellae (PL) phase, which is actually metastable; (c) A representation of the equilibrium microdomain structures as  $f_A$  is increased for fixed  $\chi N$ . Reprinted with permission from Ref. [8]; © 2006, American Institute of Physics.

structures that have been found experimentally using triblock copolymers. Even more of the so-called "decorated phases" of tri-BCPs [18] have been predicted on a theoretical basis, but not yet found experimentally (Figure 1.4), offering a plethora of structures available to the chemist based on this template. In these cases, the phase behavior depends on two compositional variables and three relative incompatibility parameters ( $\chi_{AB}$ ,  $\chi_{AC}$ ,  $\chi_{BC}$ ), and thus the sequence of the components in the chain becomes important. For example, a poly(styrene-*block*-ethylene*block*-butadiene) BCP may have completely different phase behavior than a poly(styrene-*block*-butadiene-*block*-ethylene) BCP at the same relative volume ratios. It is also possible to synthesize more than three blocks in the polymer chain–for example, a tetrablock terpolymer [19]. A more detailed look into the phase behavior and morphology of these complex systems is offered in a review by Abetz [20].



**Figure 1.3** (a) Scanning electron microscopy image of the first layers of cylinders of a thin film of a triblock copolymer containing 17% styrene, 26% vinylpyridine, and 57% *tert*-butyl methacrylate after THF vapor exposure. The surface structures indicate a helix/cylinder



morphology; (b) Transmission electron microscopy cross-section of a bulk sample of a triblock copolymer containing 26% styrene, 12% butadiene, and 62% *tert*-butyl methacrylate (MW = 218000 g mol<sup>-1</sup>).



**Figure 1.4** Morphologies for linear ABC triblock copolymers. A combination of block sequence (ABC, ACB, BAC), composition and block molecular weights provides an

enormous parameter space for the creation of new morphologies. Reprinted with permission from Ref. [8]; © 2006, American Institute of Physics.

## 1.1.4 Rod–Coil Block Copolymers

There are essentially two types of BCP, both of which highlight interesting avenues for BCP self-assembly. "Coil-coil" BCPs, which are the most commonly studied, contain A and B blocks that can both be theoretically modeled as flexible chains. "Rod-coil" BCPs, on the other hand, have one polymer chain that is best represented as a rigid rod due to its stiff nature and anisotropic molecular shape. Rod-type molecules, also known as mesogens, can be incorporated into the main chain of a polymer backbone or appended from the polymer backbone as a side-chain substituent. Both types of rod-coil BCP have been shown to exhibit liquid crystalline (LC) behavior when placed in solution [21, 22]. These solutions are known as *lyotropic* solutions, which means that their phase behavior changes at different polymer concentrations. Initially, the polymers exhibit a disordered state called the *isotropic* phase; however, when the solution reaches a critical concentration, the molecular chains become locally packed and are forced to orient in a particular direction (nematic phase) due to the anisotropy of their shape. They can also arrange into several types of well-defined layers (smectic phases). By creating a BCP with a combination of a rod-like polymer block and a flexible polymer block, molecular level ordering characteristic of liquid crystals can be combined with the microphase-separated behavior typical of BCPs to produce hierarchical levels of self-assembly [23].

In a groundbreaking study on poly(hexylisocyanate-*block*-styrene) (PHIC-*b*-PS)–where the PHIC block represents the "rod" and the PS represents the "coil" block–it was found that, with increasing concentration of the polymer, isotropic, nematic and smectic LC phases each developed before the polymer adopted its final microphase-separated state [24]. As the PHIC chain was much longer than the PS chain in this case, the PHIC chain axis tilted with respect to the layer normal and interdigitated with the PS in order to accommodate the strain, resulting in wavy lamellae and never-before-seen zigzag and arrowhead morphologies. Electron diffraction experiments revealed ~1 nm spacings between the PHIC chains and a smectic layer repeat distance of approximately 200 nm. Furthermore, shearing a nematic solution of the polymer on a glass substrate induced over 10 $\mu$ m of perfect long-range ordering of the layers, thus powerfully illustrating the multiple levels of ordering possible with LC-BCPs.

In further studies conducted by Mao and coworkers [25], a LC side group was attached as a pendent unit to a modified poly(styrene-*block*-isoprene) BCP. In this material, the phase transitions occurred in the opposite direction. The microphase separation of the classical lamellae and cylinders developed first, after which smectic layering of the LC blocks developed *within* the BCP microdomains due to constraint by the intermaterial dividing surface (IMDS) (Figure 1.5). Again, by incorporating a rigid block into a BCP framework, a hierarchy of ordering is observed. Unique chemical properties such as LC behavior may turn out to be crucial for future self-assembled synthetic materials.



Figure 1.5 (a) A model showing the hierarchical levels of self-assembly using rod–coil block copolymers exhibiting liquid crystalline behavior in a lamellar morphology. (b) Structures can also form in the cylindrical morphology. Adapted from Ref. [25].

# 1.1.5 Micelle Formation

If the BCP is dissolved in a dilute solution with a solvent that dissolves only one of the blocks, the BCP will act as a surfactant molecule and micelle formation will occur. These materials are referred to as "amphiphilic" due to their dual polar/nonpolar chemical nature, and can thus dissolve partially in polar or nonpolar media. In dilute solutions, the soluble block "corona" will wrap itself around the insoluble "core" to minimize the repulsive contact forces between the insoluble block and the solvent, as illustrated in Figure 1.6. These micelles form structures with a defined size and shape, depending on the relative molecular weight of the blocks and the ionic strength of the solution. BCPs with large soluble block typically form spherical micelles due to small curvature radii, but smaller soluble block lengths can also form cylindrical micelles due to their greater curvature radii. The similarity of these micellar structures to biological cell vesicles [26] and liposomes



Figure 1.6 Schematic showing micelle structure. Amphiphilic block copolymers form micelles when dissolved in block-selective solvents. The soluble block "corona" stretches the relative volume fraction of the blocks.

out into the solvent and masks the solvophobic "core". Cylindrical (and other) morphologies can be formed by tuning

has prompted many investigators to explore their use as templates [27], encapsulating agents [28], or drug delivery systems [29].

# 1.1.6 Synthesis of Block Copolymers Using Living Polymerization Techniques

BCPs are produced by the sequential addition of monomers into a "living" polymerization system [30]. Living polymerizations are characterized by a rapid initiation of the reactive chain end (e.g., carbanion, organometallic complex, etc.) and the lack of side reactions (e.g., chain termination or chain transfer) during growth of the polymer chain. In other words, a living polymer is a macromolecular species that will continue to grow as long as the monomer supply is replenished. The reactive chain end is then quenched to terminate further growth of the polymer during precipitation and purification.

A precise control of molecular weight is possible through living polymerization strategies. The degree of polymerization (N) is directly related to the molar amount of monomer (M) and the molar concentration of initiator, [I], as shown in Equation 1.1:

$$N = \frac{[M]}{[I]} \tag{1.1}$$

The living reaction will also be characterized by a narrow distribution of molecular weight, or polydispersity  $(M_w/M_n)$ , of usually between 1.02 and 1.1, which means that that there is less than 30% standard deviation in the degree of polymerization of each of the chains. Many possible synthetic techniques are available to the

Polymerization technique	Monomers available
Anionic	Styrenes, vinylpyridines, methacrylates, acrylates, butadiene, isoprene, <i>N</i> - carboxyanhydrides (amino acids), ethylene oxide, lactones, hexamethylcyclotrisiloxane, 1,3-cyclohexadiene, isocyanates
Cationic ring-opening	Epoxides, siloxanes, tetrahydrofuran
Group transfer	Methacrylates, acrylates, nitriles, esters, butadienes, isoprenes
Ring-opening metathesis	Norbornenes
Stable free radical	Styrene, methacrylates, acrylates, acrylamides, dienes, acrylonitrile
Atom transfer radical	Styrenes, methacrylates, acrylates, acrylonitriles
Reversible addition – fragmentation chain transfer	Methacrylates, styrene, acrylates

Table 1.1 Common living polymerization techniques for the preparation of block copolymers.



chemist wishing to prepare a BCP, each with its own advantages and disadvantages. The types of polymerization suitable for each type of monomer are listed in Table 1.1. The most common techniques used to synthesize and modify BCPs are summarized briefly in the following paragraphs.

#### 1.1.6.1 Anionic Polymerization

Anionic polymerization has become the most common technique in the synthesis of BCPs with narrow polydispersity [31]. The polymerization proceeds through the highly reactive carbanion chain end, usually created by an alkyl lithium initiator such as *sec*-BuLi or *n*-BuLi (Scheme 1.1). Due to the high reactivity of the chain end with other compounds, extremely stringent conditions must be met in order to avoid unwanted side reactions. Therefore, the polymerization must be carried out without any trace of oxygen or water, and all monomers and solvents must be extensively dried, degassed, and purified before use [32, 33]. The other main dis-

advantage to anionic polymerization is the limited range of monomers available for synthesis. Although the standard styrenes, methacrylates, butadiene, isoprene, ethylene oxide, vinylpyridines, and amino acids can all be synthesized using this technique, monomers with reactive functional groups cannot be used because they will interfere with the anionic chain end. Such monomers must therefore be protected before synthesis and then later deprotected. In some cases, such as the polymerization of acrylates, the reactions must be carried out at very low temperatures (–78 °C) in order to avoid terminating side reactions such as intrachain cyclization or "backbiting", caused by the reaction of the anionic center with a carbonyl group on the monomer.

For BCPs containing two distinctly different monomer types, such as the polymerization of polystyrene and polyethylene oxide, attention must be paid to the order of polymerization in order to maximize the efficiency of the reaction. For example, whilst a polystyryl lithium "macroinitiator" enables the rapid initiation of ethylene oxide, lithium-activated ethylene oxide will not efficiently initiate the polystyrene monomer and the reaction may not go to completion. This is due to the difference in relative reactivity between the oxyanion and carbanionic species.

There are, of course, many advantages to anionic polymerizations, besides the fact that they produce polymers with the lowest polydispersity. One advantage is that the chain end can be terminated with functional groups or coupling agents to produce telechelic polymers or complex macromolecular architectures, respectively. Examples of complex BCP architectures include ABA tri-BCPs, star, or graft BCPs [34].

#### 1.1.6.2 Stable Free Radical Polymerizations

The amount of growth in the area of stable free radical polymerizations (SFRPs) during the past 20 years has been astounding. Although the model for SFRP was introduced by Otsu during the early 1980s [35], more recently, alkoxyamine initiators generated by the research group of Hawker [36] at IBM have led to dramatic improvements in the technique as introduced by Georges [37, 38] at Xerox during the early 1990s. These types of initiator contain a thermally cleavable C–O bond attached to a nitroxyl radical species. Running the reaction at high temperatures (80–90 °C) causes a reversible capping of the nitroxyl radicals, and allows monomer addition to the polymer chain only when the nitroxyl radical is in its detached state (Scheme 1.2). An advantage to SFRP is that the chemical rate of this detachment drops almost to zero at room temperature. Therefore, decreasing the temperature



Scheme 1.2 The general mechanism of stable free radical polymerizations.

of the polymerization reactor essentially "switches off" the polymerization and allows the chemist to expose the first block to air, without terminating the reactive chain end. After precipitation, purification, and molecular weight characterization, the first block can be dissolved and heated in the presence of the second monomer to form the final product. There is a wide range of monomers available using SFRP, including styrenes, methacrylates, (meth)acrylonitriles, among others. Unfortunately, the polydispersities of the free radical polymerization process are not quite as low as anionic polymerization, and stereochemical control is not possible.

1.1.6.3 Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization

The RAFT process is a variation of the living radical process that instead uses the thermal lability of a C–S bond to provide the insertion of monomer units [39]. A general scheme of the monomer addition/fragmentation step is shown in Scheme 1.3. RAFT is used for the polymerization of methacrylates, styrenes and acrylates, and can also be successfully applied to narrow polydispersity BCPs. Interestingly, in species with dithiocarbamate end groups, such as tetraethyldithiuram disulfide, Otsu and coworkers found that the C–S bond could photochemically dissociate, offering the possibility of initiating polymerizations purely with UV light [40]. This technique was subsequently used to produce several types of BCP [41–45]. The thiocarbonyl end group can be removed by aminolysis or reduction with tri*n*butylstannane to leave a saturated chain end, or by thermal treatment to leave an unsaturated chain end. It may also be functionalized with amino or carboxy-functionalized end groups [46].

#### 1.1.6.4 Atom Transfer Radical Polymerization

Atom transfer radical polymerization (ATRP) is another rapidly maturing technology that easily allows the production of end-functionalized and low-polydispersity polymers. It has also been shown to be a highly versatile reaction for the production of a wide variety of polymer architectures such as stars, combs, and tapered BCPs [47]. The mechanism (Scheme 1.4) functions in similar manner to typical



R-X + Mt<sup>n</sup>-Y/ligand 
$$\xrightarrow{k_{act}}_{k_{deact}}$$
  $\xrightarrow{R}$  + X-Mt<sup>n+1</sup>-Y/ligand  
Monomer

Scheme 1.4 The general mechanism of atom-transfer radical polymerization (ATRP).

living free radical processes, except that the active radical species undergoes a reversible redox process that is catalyzed by a transition metal complex attached to an amine-based ligand. The main disadvantage of ATRP is that these transition metals are difficult (if not impossible) to remove completely from the polymer after polymerization. ATRP has a wide range of monomers available for synthesis, however, including (meth)acrylates, (meth)acrylamides, styrenes, and acryloni-triles. Initiators for the process are usually alkyl halide species (R–X), and their presence at the end of the polymer chain allows for easy substitution reactions with functional groups.

#### 1.1.6.5 Ring-Opening Metathesis Polymerization

Ring-opening metathesis polymerization (ROMP) is typically used for the ringopening polymerization of cyclic olefins such as norbornenes and cyclooctadiene [48]. A general mechanism is presented in Scheme 1.5. ROMP also uses a metal catalyst that is usually composed of titanium, tungsten, or ruthenium attached to an aluminum ligand. Based on the results obtained by Robert Grubbs and coworkers, a selection of functional group-tolerant ruthenium catalysts has been synthesized, opening up new opportunities for structurally diverse BCPs, such as amphiphilic copolymers [49] used to coat chromatographic supports, water-soluble/conducting self-assembling materials [50], and flourescent BCPs for use in light-emitting devices [51].

#### 1.1.6.6 Group Transfer Polymerization

Group transfer polymerization (GTP) is best suited for the polymerization of methacrylate and acrylate polymers [52]. A general mechanism is shown in Scheme 1.6. Esters, nitriles, styrenes, butadienes, isoprenes, and most other  $\alpha$ , $\beta$ -unsaturated



Scheme 1.5 The general mechanism of ring-opening metathesis polymerization (ROMP).



Scheme 1.6 The general mechanism for group transfer polymerizations.

compounds can also be prepared [53]. One interesting monomer that is typically prepared by GTP is poly(2-(dimethylamino)ethylmethacrylate) (PDAEMA). When polymerized with a hydrophobic methacrylate species, Billingham and coworkers found that the resulting amphiphilic BCP would easily form micelles in aqueous solution due to the water solubility of the PDAEMA block [54, 55]. Initiators often include silyl ketene acetal-type structures. Trace amounts of nucleophilic catalysts such as TASHF<sub>2</sub> are necessary to activate the silicon catalyst, along with large amounts of Lewis acids such as  $ZnX_2$  (X = Cl, Br, I) to activate the monomer. A key advantage of GTP is that it can be performed at room temperature. Moreover, functionalized polymers can easily be added by the use of either: (i) a functionalized initiator or end-capping agents for functional groups attached to the end of the chain; or (ii) a functionalized monomer for functional groups evenly distributed throughout the polymer chain.

#### 1.1.7

# Post-Polymerization Modifications

Today, living polymerization techniques are available for a wide range of monomer types, and the possibilities are expanding daily. However, alternative routes are still necessary for the preparation of BCPs with highly specialized solubilities and functionalities, and this often requires post-polymerization modification steps such as active-center transformations and polymer-analogous reactions.

## 1.1.7.1 Active-Center Transformations

Often, one type of polymerization mechanism may not be suitable for both types of monomer used in the BCP. In this case, following formation of the first block, it is possible to alter the polymerization mechanism to suit the efficient addition of a second monomer to the chain. The active center can be modified either by in situ reactions or by isolation of the first block, followed by chemical transformation of the active center with a separate reaction; the polymerization can then continue after addition of the second monomer. For example, an SFRP mechanism can be transformed into an anionic ring-opening system for the polymerization of poly(styrene-block-ethylene oxide). First, the styrene undergoes SFRP in the presence of mercaptoethanol, a chain-transfer agent. The hydroxyl functionalized PS is then used as a "macroinitiator" for the anionic ring-opening polymerization of ethylene oxide [56]. Active center transformation has been used for the formation of poly(norbornene-block-vinylalcohol) BCPs through a combination of ROMP and aldol GTP [57], while a combination of cationic (not discussed) and anionic procedures have been used to polymerize poly(isobutylene-block- methyl methacrylate) BCPs [58]. Finally, each of the above mechanisms can also be transformed into an ATRP process, as described in a review by Matyjaszewski [59].

## 1.1.7.2 Polymer-Analogous Reactions

As we have seen, the creation of BCPs through living polymerization mechanisms restricts the number of monomers available for use. Additionally, functionalized

polymers feature delicate protecting groups that may be unsuitable for the highly reactive initiators used in living polymerizations. Polymer-analogous reactions can create copolymers that could not have been synthesized within a living polymerization. These modifications are carried out on previously synthesized, or "precursor" BCPs such as poly(styrene-block-isoprene) with known molecular weights and narrow molecular weight distributions. Chemical transformation of the precursor polymer can be carried out selectively on individual blocks, on the entire copolymer, or on each block in sequence. Here, careful selection of the reaction conditions is vital to avoid any harmful side reactions such as degradation or crosslinking of the original polymer. If carried out successfully, the degree of polymerization, molecular weight distribution, and main chain architecture of the precursor polymer will remain the same, but the solubility and physical properties of the polymer may be altered completely. Examples of polymer analogous reactions include hydrogenation [60], epoxidation [61], hydrolysis [62], sulfonation [63], hydroboration/oxidation [64, 65], guaternization [66], hydrosilylation [67], and chloro/bromomethylation [68, 69]. Further details for each of these reactions is also available [71].

In this section, we have set the foundation for understanding how the chemistry of block copolymeric materials relates to the physics of their unique self-assembling properties. In the remainder of the chapter, it will become clear how these novel chemical strategies are used to effect practical physical applications.

# 1.2 Block Copolymers as Lithographic Materials

#### 1.2.1 Introduction to Lithography

A modern integrated circuit is a complex, 3-D network of patterned wires, vias, insulators, and conductors. In order to transfer these patterns onto the silicon substrate it is first necessary to write the pattern, and for this the technique of photolithography is used, in which radiation-sensitive polymers play an integral role. Standard photolithography consists of essentially two steps: (i) writing of the pattern into a radiation-sensitive polymer thin film (resist); and (ii) transferring the pattern by etching into the underlying substrate [72]. A schematic of the traditional lithographic process is shown in Figure 1.7a. As photolithography and its associated technologies will become a recurring theme in this chapter, a brief primer on the subject will be useful at this point.

During the exposure process of a polymeric photoresist, UV radiation passes through a quartz photo mask that only allows a particular pattern of radiation to pass through and strike a thin film of photoresist. A chemical change is effected in the exposed regions of the polymer, which allows its subsequent development in a solvent, similar to the way in which photographic film is exposed and developed in a darkroom. The mechanism of the chemical change involves the forma-



Figure 1.7 (a) Schematic of a traditional photolithography using positive-tone or negative-tone resist chemistry. (b) Schematic of block copolymer lithography, using a combination of positive-tone and negative-tone resist chemistry.

tion, rearrangement or breaking of bonds within the polymer chain. A resist's *sensitivity* is a measure of how efficiently it responds to a given amount of radiation, and might be compared to the ASA or ISO rating of a photographic film. A resist with a higher sensitivity will allow a satisfactory image to be produced for a smaller absorbed *dose* of radiation. The *resolution* of a photoresist is the size of the smallest structure that can be cleanly resolved after pattern development using standard microscopy techniques. This structure will then be used to efficiently pattern into the underlying substrate, assuming that the photoresist has sufficient *etch resistance* to withstand the harsh pattern transfer step. In this step, the patterned resist must withstand high-energy plasma sources that are designed to etch into silicon wafers. Polymers containing more carbon have stronger dry-etch resistance than those with lower amounts of carbon, whilst polymers containing high amounts of oxygen are etched easily. Even etch-resistant polymers may lose

a small amount of material during the etching step, but maintaining the structure of the pattern is important for high resolution. If less than a  $\pm 10\%$  change in the finest feature size of the polymer is etched into the substrate, the pattern transfer step is deemed successful [73]. This presents a huge challenge for the resist designer, who must tune the chemical components of the photoresist to satisfy two diametrically opposed requirements: to design a resist that is very responsive to ultraviolet radiation, but which, after the initial exposure, becomes highly resistant to the specific type of radiation and heat involved in the pattern transfer step. This is often achieved through the copolymerization of more than one type of monomer, each having its own functionality in the photoresist.

The realm of photolithography is split into two families of chemistry, based on the different physical properties possible for the exposed photoresist:

- *Positive-tone* resist chemistry refers to a photoresist that becomes *more soluble* after exposure to UV light. This can happen because of chemical deprotection, bond rearrangement, or chain-scission mechanisms.
- *Negative-tone* resist chemistry refers to a photoresist that becomes *less soluble* through the formation of crosslinked networks after exposure to UV light.

In this chapter, we will highlight the many approaches that have been used for one or both of these types of chemistries, in order to fabricate functional nanoscale-sized structures using BCPs.

# 1.2.2 Block Copolymers as Nanolithographic Templates

The lithography community has been extremely successful in its ability to pack progressively more circuit elements into a chip, as governed by the benchmark pace first predicted by Gordon Moore in 1989, which states that the transistor density of semiconductor chips will double roughly every 18 months [74]. Since then, new technologies have enabled this march down to smaller feature sizes. Photoresists with smaller pixel sizes such as molecular glass resists [75, 76], new processes such as nanoimprint lithography and step and flash lithography [77], as well as the development of smaller wavelength exposure sources [78], have catalyzed the production of feature sizes down below 50 nm.

The exposure wavelength, however, has become the rate-determining step in our ability to pattern small feature sizes. Extremely small wavelength sources such as electron beams (e-beams) and X-rays do not have wavelength limitations, but e-beam systems can only write features in a slow serial process that is not amenable to large-scale commercial processes. The high cost of the incorporation of these tools into a clean room is another disadvantage to their use. X-ray lithography requires the extremely high power of synchrotron sources, or electron storage rings, which are found in only a handful of locations around the world. Both, therefore, have proven to be impractical in a production setting. It seems that extreme ultraviolet (EUV) radiation sources can carry the lithography community down to 20 nm structures, but beyond that the semiconductor industry sees a need for innovative patterning strategies [79].

Design for modern integrated circuits usually requires a motif of several of different types of feature that may include-but are not limited to-regular patterns of straight and jogged lines and spaces, circular holes for contact openings, Tjunctions, and columns of ferromagnetic media for data storage and memory applications. Interestingly, the shape of these features relate very well to the various geometries involved in BCP self-assembly (refer back to Figure 1.2). Furthermore, BCP microdomains form features that are much smaller than the current state-of-the-art standard photolithographic techniques. If one of the blocks in a BCP could be selectively degraded (i.e., positive tone chemistry), while the other block is crosslinked (i.e., negative tone chemistry) or has sufficient etch resistance, the result would be an ordered, nanoscale "stencil" that could be used to pattern circuit elements into a substrate. Theoretically, a density of over 10<sup>11</sup> elements per square centimeter could be achieved over a large area with this technique [80]. Starting with the pioneering work of Lee in 1989 [81], the field of BCP lithography has exploded during the past ten years. Several excellent reviews on the subject are available [82-84].

Several obstacles stand in the way of BCP lithography becoming an industrially useful technology. First, when a BCP thin film is created, the microdomains will often seem disordered, appearing in randomly oriented grains along the sample surface. Long-range ordering of the BCP nanodomains is often necessary for a few of the possible applications of BCP lithography, such as in the creation of addressable, high-density information storage media. Second, the nanodomains tend to arrange parallel to the sample surface due to preferred interfacial interactions between one of the blocks and the substrate. However, in order to be lithographically useful as etch masks that are able to transfer patterns into a wafer, nanodomains such as lamellae and cylinders must be arranged perpendicularly so that they are physically and continuously connected from the polymer/air interface through to the substrate, as shown in the plan-view and cross-sectional scanning electron microscopy (SEM) images shown in Figure 1.8. Third, the thickness of the BCP must be carefully controlled. It has been shown that, for a lamellar PS-b-PMMA BCP, if the initial film thickness t is thicker than the natural period of the lamellae  $L_0$  and  $t \neq (n + \frac{1}{2}) L_0$  (n an integer), then islands or holes of height L<sub>o</sub> will form at the surface of the film and damage the homogeneity of the surface morphology. In the case where  $t < L_0$ , the situation becomes more complicated, as the lamellar chains will arrange perpendicular to the substrate due to the large entropic penalty associated with the chains having to compress to fit into the parallel orientation [85]. Other hybrid morphologies (Figure 1.9) have been found as the film thickness changes, due to the competition of several forces such as strong surface interactions, slow kinetics, and the thermodynamic driving force to arrange in layers commensurate with the height  $L_0$ . The physical complexity of block copolymer systems is staggering, and orientational control over these systems has developed into a field of its own [86]. Many research groups have achieved success in controlling the orientation of



**Figure 1.8** Field-effect scanning electron microscopy images obtained from a thin film of PS-*b*-PMMA after removal of the PMMA block. (a) Top view of the film; (b) A cross-sectional view. Reprinted with permission from Ref. [90]; © 2006, Wiley-VCH.



**Figure 1.9** (a,b) Tapping-mode atomic force microscopy phase images of thin poly(styrene*block*-butadiene-block-styrene) (PS-*b*-PB-*b*-PS) films on Si substrates after annealing in chloroform vapor. The surface is covered with an 10nm-thick PB layer. Bright regions correspond to PS microdomains below the darker top PB layer. Contour lines calculated from the corresponding height images are

superimposed; (c) Schematic height profile of the phase images shown in (a, b); (d) Simulation of a block copolymer film in one large simulation box with increasing film thickness. Reprinted with permission from Knoll A., Horvat, A., Lyakhova, K.S. *et al.* (2002) *Phys. Rev. Lett.*, **89**, 035501-1; © 2006, American Physical Society.

the self-assembled structures through special processing strategies; these include techniques such as thermal annealing [87], electric fields [88–90], mechanical shear [91–93], exposure to solvent vapor [18, 94, 95], physical confinement [96], neutral surfaces [97, 98], chemically nanopatterned surfaces [99–101], or a combination of any of the above [102].

# 1.2.2.1 Creation of Nanoporous Block Copolymer Templates

Once a high degree of long-range ordering has been achieved on a BCP thin film, a final processing step is necessary to create the nanolithographic template. A schematic of BCP lithography is shown in Figure 1.7b. Upon exposure to UV, chemical, or reactive ion etching (RIE), these systems are designed so that one of the blocks will be selectively degraded relative to the other block(s). In fact, the second block should ideally become photochemically crosslinked and thus highly immobile during the subsequent pattern transfer step in order to avoid distortion of the photo pattern. Both "wet" and "dry" chemical processes can be used during the pattern transfer step. Wet chemical etching involves the dissolution of the first block in an aggressive acid or base solvent, whereas "dry" chemical processes refer to exposure of the film to high-energy reactive ions and plasmas such as CF<sub>4</sub>, O<sub>2</sub>, SF<sub>6</sub>, Cl<sub>2</sub>, or argon gas. The etching process results from the combination of the kinetic energy of the ions (causing sputtering) and ion-induced chemical reactions that create volatile byproducts. The etching process affects polymers to different extents, depending on the chemical composition of the block. Several different types of BCP systems have been used as nanolithographic templates, such as poly(styrene-blockbutadiene), poly(styrene-block-methyl methacrylate), poly(styrene-block- ferrocenyldimethylsilane), poly(styrene-*block*-lactic acid) and poly(α-methylstyreneblock-hydroxystyrene). The structures of the most commonly used sacrificial blocks are listed in Table 1.2.

Poly(Styrene-block-Butadiene) One of the first applications in this area also provides a model example of the concept of BCP lithography. Chaikin and coworkers [80, 111] created a thin film of microphase-separated poly(styrene-block-butadiene) (PS-b-PB), as shown in Figure 1.10a. Figure 1.10b shows how ozone was used to eliminate the PB spherical minority phase and open up windows in the PS matrix. In this instance, the minority PB block acts as a positive-tone resist due to its vulnerability to ozone chemical attack. The resulting spherical pores in the film provided less RIE resistance than the continuous PS matrix, thus creating a periodic array of 20 nm holes spaced 40 nm apart on a silicon nitride substrate. In the opposite strategy, illustrated in Figure 1.10c, the PB block was stained with osmium tetroxide vapor, which caused the PB block to exhibit a greater etch resistance than the PS block. In this case, the PB block acts like a negative-tone resist, resulting in removal of the PS matrix after RIE with CF<sub>4</sub>. Therefore, the negativetone system creates a pattern of raised dots on the substrate, instead of holes. This concept can easily be extended to create nanosized metal dots on any type of substrate for high-density information storage applications [127], or substrates such

Name	Structure	Method of removal	Reference(s)
Poly(methyl		Photolysis	[103–107]
methacrylate)	( ) n = 0 0 CH <sub>3</sub>	Etch selectivity	[108–110]
Poly(butadiene)	(	Ozonolysis	[80, 111, 112]
Poly(isoprene)	$f \rightarrow f$	Reactive ion etching	[113, 114]
	/ / / n	Ozonolysis	[14, 111, 115]
Poly(α- methylstyrene)	()	Heat/Vacuum	[116, 117]
Poly(L-lactide)	( 1 )	Aqueous base dissolution	[118–121]
Poly(4-vinyl pyridine)	$($ $)_n$	Reactive ion etching	[96]
Poly(ethylene oxide)	( )	Water dissolution	[122]

 Table 1.2 Commonly used sacrificial blocks for block copolymer templates.

Name	Structure	Method of removal	Reference(s)
Polystyrene	()	Reactive ion etching	[123, 124]
Poly(perfluorooctyl ethyl methacrylate)	$(CH_3)$ $(H_2)$ $(H_2)$ $(CF_2)$ $(CF_2)$ $(CF_2)$ $(CF_3)$	Reactive ion etching	[125, 126]

#### Table 1.2 Continued.

as gallium arsenide can be patterned, opening up new avenues for the production of quantum dot (QD) structures [128].

Poly(Styrene-block-Methyl Methacrylate) Poly(styrene-block-methyl methacrylate) (PS-b-PMMA) has been the workhorse of the field of BCP lithography for several reasons. First, it is relatively simple to produce using anionic polymerization techniques, and is commercially available [129]. Second, PMMA acts as a readily degradable positive-tone resist on exposure to deep ultraviolet (DUV) or e-beam radiation. In fact, PMMA is already well established in the semiconductor industry as a positive-tone e-beam resist. The PMMA chain breaks up into oligomers through a chain scission mechanism (Scheme 1.7), and can then be removed from the matrix through dissolution in acetic acid. Third, in the same DUV exposure step, the polystyrene matrix acts as a weak negative-tone resist, becoming photochemically crosslinked through oxidative coupling, as shown in Scheme 1.8 [130]. Immobilizing the matrix phase through crosslinking strategies is very important in the creation of nanoporous materials. The huge increase in surface area that results from the removal of the minority domain creates a concomitant increase in surface free energy. A driving force for the minimization of this free energy creates a strong tendency for the nanopores to collapse, which would result in distorted etched patterns. A high glass transition temperature  $(T_{o})$  relative to the processing temperature represents another means of stabilizing the nanoporous



view of a nanolithographic template consisting of a uniform monolayer of PB spherical microdomains on silicon nitride. PB wets the air and substrate interfaces; (b) Schematic of the processing flow when an ozonated copolymer film is used, which produces holes in silicon nitride; (c) Schematic of the processing flow when an osmium-stained copolymer film is used, which produces dots in silicon nitride. Reprinted with permission from Ref. [80]; © 1997, American Association for the Advancement of Science.

template; however, there must be a clear pathway in the film for the removal of degraded minority component (e.g., vertical cylinders). Otherwise, the low-molecular-weight products permeate through the matrix, leading to a decrease in  $T_g$  and collapse of the pores.

Stoykovich and colleagues in the Nealey group have substantially improved the directed self-assembly of lamellar microdomains of PS-*b*-PMMA. Traditional lithographic techniques were used to create a chemically nanopatterned surface that preferentially wets the PMMA domain. By using this preferential attraction,

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Scheme 1.7 Chain scission mechanism of PMMA.



Scheme 1.8 Ultraviolet irradiation byproducts of polystyrene.

Stoykovich *et al.* were able to steer the vertically oriented lamellar morphologies through various bend angles, from 45° to 135° (Figure 1.11). The high curvature of these patterns induces a great deal of stress in the in the polymeric material, and leads to the formation of defects in the structure. It was found that, by blending small amounts of PMMA homopolymer, the homopolymer selectively swelled the PMMA block in the areas of high curvature (Figure 1.11b); this alleviated the stress in the material and in turn reduced the pattern defects [131].

Several successful applications of PS-*b*-PMMA as a nanolithographic template have already been achieved, with C. T. Black and coworkers at IBM being among

the first to demonstrate the industrial feasibility of this technology. After optimization of the process window for maximum ordering of perpendicular-oriented nanodomains [132, 133], Black's group demonstrated the successful fabrication of metal-oxide-silicon (MOS) capacitors (Figure 1.12) [133–135], multinanowire





**Figure 1.11** (a) A top-down SEM image of angled lamellae in a ternary PS-*b*-PMMA/PS/ PMMA blend. The chemical surface pattern is fabricated with a 70nm line spacing to match the natural period of the copolymer; (b) Theoretical concentration map of the distribution of the homopolymers on the surface. The homopolymers concentrate and swell the polymer at the bend area of the patterns to prevent the formation of defects. Reprinted with permission from Ref. [131]; © 2006, American Association for the Advancement of Science.



**Figure 1.12** The process flow for MOS capacitors. (a) Polymer template formation on silicon surface; (b) RIE pattern transfer of PS template into silicon, followed by removal of the PS matrix; (c)  $SiO_2$  growth followed by top A1 gate electrode deposition; (d) SEM image

at a 70° tilt after RIE etch. The remaining PS template is shown at the top. At the bottom, the nanoscale hexagonal array has been transferred into a Si counter electrode. Reprinted with permission from Ref. [134]; © 2006, American Institute of Physics.



**Figure 1.13** Cross-sectional transmission electron microscopy image obtained from a PS-*b*-PMMA film (800 nm) annealed in an electric field of  $25 V \mu m^{-1}$ . The block copolymer film is lying on top of a dark Au-film, which was used as the lower

electrode. The upper electrode has been removed. Cylinders oriented normal to the substrate pass all the way through the sample. Reprinted with permission from Ref. [90]; © 2006, Wiley-VCH.

silicon field effect transistors [136], and FLASH memory devices [137]. The creation of high-aspect ratio patterns has always been problematic due to the difficulty of achieving a single microdomain orientation in thick BCP films. In this area, Thurn-Albrecht and coworkers reported that the application of a strong electric field, in combination with thermal annealing, creates 500 nm-long, vertically oriented PMMA cylinders that physically connect to the substrate, as shown in Figure 1.13. After PMMA removal, the underlying conducting substrate was used for the subsequent deposition of copper into the holes to form a matrix of continuous nanowires [90].

Asakawa and coworkers from the Toshiba Corporation were the first to pattern magnetic media for hard disk applications, by using a PS-*b*-PMMA template. In these investigations, the group took advantage of the large difference in etch resistance between the aromatic and acrylic polymer to produce the BCP template using dry etching techniques [108, 109]. Spiral-shaped circumferential grooves were imprinted into a hard-baked photoresist using a nickel master plate. The spherical PMMA microdomains then aligned within the walls of the grooves, and the PMMA was preferentially etched by oxygen plasma to create holes which connected to an underlying magnetic cobalt platinum film. The size of these holes could be adjusted by changing the molecular weight of the PS-*b*-PMMA. The holes were then filled with etch-resistant spin-on-glass, which acted as a mask while the remaining PS polymer and the underlying magnetic media were patterned by ion milling. After removal of the spin-on glass, the disk featured magnetic nanodots arranged in a spiral pattern.

PS-*b*-PMMA has proved to be an excellent system to perform studies on the ability of BCPs to act as nanolithographic stencils, although doubts persist regarding its potential to enter into industrial, high-volume production. For example, as noted previously, crosslinking the matrix phase of the BCP is necessary to prevent pore collapse during the rough pattern transfer and etching step. PS, however, cannot be crosslinked (or patterned) efficiently upon exposure to UV light. A combination of different photochemical processes, such as random chain scission, oxidative coupling and crosslinking, all occur at the same time during UV expo

sure, as shown previously in Scheme 1.8. Several groups have taken steps to correct this problem, with Hawker and coworkers [103] having randomly copolymerized thermally crosslinkable benzocyclobutene (BCB) groups with polystyrene (PS-*ran*-BCB). The degree of crosslinking can be tuned by increasing the amount of the BCB in the random copolymer. Microdomain ordering was induced by thermally annealing the matrix at 160 °C. Raising the temperature to 220 °C caused the matrix to be crosslinked, and the PMMA was exposed and developed in the normal manner.

**Poly(Styrene-block-Lactic Acid)** Poly(styrene-*block*-lactic acid) (PS-*b*-PLA) is another copolymer that has been developed as a nanolithographic template. To synthesize this polymer, hydroxyl-terminated PS (prepared through anionic polymerization) was treated with triethylaluminum to form the corresponding aluminum alkoxide macroinitiator. This species was able to efficiently polymerize D,L-lactide through a ring-opening process [118]. The advantage of using this BCP as a nanolithographic template is that PLA undergoes main-chain cleavage simply by soaking it in an aqueous methanol mixture containing sodium hydroxide at 65 °C. The PS matrix is not affected at all by this treatment. Zalusky and coworkers have also published a complete phase diagram and characterization of PS-*b*-PLA [119]. Leiston-Balanger and coworkers used the benzocyclobutene crosslinking strategy explained in Section 1.2.2.1.2 but with PLA as the minority component, thus eliminating the photoprocessing step [138]. The group noted that, if a thermally degradable minority component were to be used, then a robust nanoporous template could be produced by using a completely thermal process.

**Poly(Styrene-block-Ferrocenyldimethylsilane)** BCPs containing organometallic elements can also function very well as nanolithographic etch masks, as shown by the studies of Thomas and coworkers [113, 114, 139]. Thomas' group was able to synthesize a BCP of poly(styrene-*block*-ferrocenyldimethylsilane) (PS-*b*-PFS) that organized into lamellar and cylindrical microdomains by using an anionic ringopening polymerization. The PFS block contained elemental iron and silicon, which made it highly resistant to dry-etching processes due to the creation of iron and silicon oxides during oxygen etching. The resulting etching ratio between PS and PFS was estimated to be as high as 50:1. Thus, by etching through the polystyrene, the BCP patterns were transferred into the underlying substrate in only one step. By using this polymer as a masking layer, Thomas *et al.* further demonstrated that an array of cobalt single-domain magnetic particles could be created through a tri-level etching strategy (Figure 1.14). Moreover, the magnetic properties and thermal stability of the dots could be tuned simply by changing the copolymer composition and etch depth into the cobalt [123, 140].

**Poly**( $\alpha$ -**Methylstyrene–block-Hydroxystyrene)** Studies conducted by the present authors' group have focused on poly( $\alpha$ -methylstyrene-*block*-hydroxystyrene) (P $\alpha$ -MS-*b*-HOST) that allows not only an efficient crosslinking of the hydroxystyrene matrix phase but also the ability to lithographically pattern the nanoporous tem-



**Figure 1.14** Tilted SEM images of the intermediate stages of lithographic processing. (a) An O<sub>2</sub>-RIE-treated block copolymer thin film on a multilayer of silica, the metallic films, and the silicon substrate; (b) Pillars of silicon oxide capped with oxidized PFS after CHF<sub>3</sub>-RIE; (c) Patterned

tungsten film using  $CF_4 + O_2$ -RIE on top of a cobalt layer after removing the silica and residual polymer cap; (d) W-capped cobalt dot array produced by ion beam etching (note the different magnification). Reprinted with permission from Ref. [123]; © 2006, Wiley-VCH.

plates on select areas of the wafer [116, 117]. In these studies, traditional chemical amplification strategies [141], which have been recognized among the photoresist community for over 20 years, were used in combination with BCP lithography. An overview of the processing scheme is presented in Figure 1.15. The key to chemical amplification strategies is the use of cationic catalysts known as photoacid generators (PAGs); these produce a strong acid when exposed to DUV radiation (248 and 193 nm). Triflic acid generated by the PAG molecule (triphenylsulfonium triflate) was used to catalyze a condensation reaction [142] between the hydroxyl groups of the poly(hydroxystyrene) and a crosslinking species tetramethoxymethyl glycoluril (TMMGU; Powderlink 1174) to produce, in turn, a highly crosslinked network of the matrix phase (Scheme 1.9). The areas of the wafer where nanoporous templates are not needed are washed away with a solvent development step. The crosslinked regions of PHOST contained standing, 20 nm-diameter cylinders of poly( $\alpha$ -methylstyrene), a polymer that can be depolymerized and removed from the matrix with additional UV irradiation, heat,



**Figure 1.15** Novel nanofabrication process of obtaining spatially controlled nanopores. (a) Spin-coating of a P $\alpha$ MS-b-PHOST/PAG mixture onto a silicon wafer to form vertical cylinders of P $\alpha$ MS in the PHOST matrix; (b) Irradiate using a 248 nm stepper with a photomask and bake; (c) Develop with a mixed solvent to form micron-sized patterns on top of the substrate; (d) Irradiate using a 365 nm lamp under vacuum; (e) Form patterns with nanoporous channels. Reprinted with permission from Ref. [117]; © 2006, American Chemical Society.

and high vacuum. Thus, by using standard lithography procedures, it was possible to generate 450nm resolution patterns of crosslinked PHOST containing 20nm nanoporous substructures, as shown in Figure 1.16. Further processing of this polymer in order to maximize the degree of long-range ordering is currently under way [143]. It is believed that this combination of traditional "topdown" positive- and negative-tone lithography techniques, in combination with the power of "bottom-up" BCP self-assembly, holds much promise for the future of lithography.

# 1.2.3 Multilevel Resist Strategies Using Block Copolymers

The constant drive for smaller and smaller circuit device features with higher aspect ratios and more complex substrate topographies has caused many photolithographic engineers to rethink traditional single-level resist-processing strategies. As sub-100 nm feature sizes become the norm, artifacts arising from the lithographic process that were recently deemed insignificant have now become



**Scheme 1.9** Proposed crosslinking mechanism of PαMS-*b*-PHOST with TMMGU. After Roschert, H., Dammel, R., Eckes, C. *et al.* (1992), *Proc. SPIE-Int. Soc. Opt. Eng.*, **1672**, 157.

major problems. One such artifact that limits resolution is the creation of the "standing wave effects" which occur when UV light reflects off the substrate surface after passing through the resist [73]. As a result, multilevel resist chemistries have been developed to incorporate polymeric planarizing layers to eliminate substrate topography variability and anti-reflection coatings to eliminate standingwave patterns in photoresists. Commonly used multilevel strategies employ a photoresist imaging layer on top of the planarization layer. The resist used for the imaging layer is designed to provide high sensitivity to UV light exposure by providing a large number of photosensitive functional groups, and must be highly etch-resistant to the extremely harsh conditions imposed by the oxygen reactive ion-etching step. Organosilicon-containing polymers have been demonstrated to be excellent candidates as etch-resistant photoresists, due to their ability to form a protective SiO<sub>2</sub> ceramic upon exposure to oxygen plasma, as shown by Taylor and Wolf [144, 145]. The only disadvantage of these polymers is that their bulky side groups result in very low  $T_g$ -values, which make them susceptible to viscous flow and excess swelling during the development step. Photoresist engineers typically counter the problem of low  $T_{\rm g}$  values by randomly copolymerizing the etch



**Figure 1.16** Atomic force microscopy height images showing: (a) the 450 nm photopattern produced through the crosslinking of the PHOST matrix; and (b) the 20 nm-diameter porous substructure generated after removal of the  $\alpha$ -methylstyrene block.

resistant, low- $T_{\rm g}$  polymer with a photosensitive polymer that also has a high  $T_{\rm g}$ . The copolymerization of the two monomers is necessary to avoid the inevitable macrophase separation that results when two homopolymers are mixed together. This composite style approach thereby simultaneously satisfies the requirements for high etch resistance, high sensitivity and high  $T_{\rm g}$ , resulting in the best-performing photoresists.

BCPs seem to be a perfect fit for multilevel resist chemistries, due to their ability to segregate into chemically distinct levels and their intrinsic ability to avoid

macrophase separation. It is well known that a BCP film will self-assemble such that the lower surface energy block is presented at the polymer/air interface. This principle can in turn be used to design layered systems of different functionality, as will be seen in the creation of semi-fluorinated BCPs for low-surface energy applications (see Section 1.6.1). For example, to create the imaging layer a polymer containing photosensitive tert-butyl functional groups may be used along with an etch-resistant organosilicon polymer (Figure 1.17). Conveniently, the tert-butyl groups contain three low-energy methyl groups that drive the segregation of the photoactive compound to the surface, where it is most effectively exposed to UV light. The surface-segregating properties are not limited to the *tert*-butyl group, however; many other protecting groups could be used. Moreover, the functional, chemically distinct polymers used in photoresists will exist in a microphase-separated state if they are incorporated into a BCP. The microdomains form with diameters within one radius of gyration of the polymer chain, which usually is about 5-30 nm. Therefore, a patterned lithographic feature on the BCP photoresist, currently approximately 100-200 nm, will contain numerous domains of the photosensitive and etch-resistant functionalities incorporated within it to ensure optimal performance of the photoresist.

The microphase separation of BCPs also means that each one of the polymer chains is confined to its own respective domain, and can be thought of as being artificially crosslinked. Thus, in negative-tone resists, less UV light is required to cause the polymers to become insoluble compared to a homopolymer of a similar molecular weight. BCPs have also been shown to be twice as sensitive to nonphase-separated random copolymers using the same monomer units and molecular weight, due to this confinement effect [146]. Confinement might also mean that the PAG moieties used in these resists might be clustering selectively inside one of the microdomains, and this effect might be magnified if the PAG is miscible in only one of the BCP microdomains [147]. Moreover, if the usually hydrophilic photoacid segregates inside the block containing the acid-labile functional groups, the effective concentration of the acid will be increased, which means that a higher percentage of the protecting groups will be converted to base-soluble –OH groups.

Hartney and coworkers [148] developed the first application for BCPs as bi-level e-beam resists in 1985, when they prepared a BCP of poly(chloromethylstyrene) for sensitivity and high  $T_g$ , and poly(dimethylsiloxane) (PDMS) that forms etch-resistant silicon oxide upon exposure to oxygen plasma and has a low  $T_g$ . Bowden *et al.* subsequently prepared a PDMS BCP grafted to PMMA that acted as a negative-tone resist [149, 150], while Jurek *et al.* created a novalac oligo-PDMS resist



Figure 1.17 Multilevel resist strategy using block copolymers. Adapted from Ref. [148].

which showed resolutions of 500 nm and etch rates which were 36-fold slower than hard-baked novalac [151]. Gabor and coworkers attached a PDMS graft to the double bonds of an isoprene block in a styrene-*block*-isoprene BCP to create a negative-tone resist. In this way, Gabor *et al.* achieved line-space patterns of 200 nm using e-beam lithography, and demonstrated oxygen etching rates which were 42-fold slower than for polyimide [152]. Other resists which have incorporated PDMS for etch resistance in both block and graft copolymer architectures have also been reviewed [153].

Gabor and coworkers also prepared block and random copolymers of poly(tertbutyl methacrylate) and a silicon-containing methacrylate (poly(3-methacryloxy) propyl pentadimethyldisiloxane) (Figure 1.18) via group transfer polymerization for applications in 193 nm photolithography [154]. The BCP architecture allowed Gabor's group to incorporate a larger amount of the hydrophobic siloxane component for a high-oxygen RIE resistance, while maintaining solubility in an aqueous base developer. In fact, the BCPs were found to have a better development behavior in aqueous base than their random copolymer counterparts (Figure 1.19). Gabor et al. hypothesized that the exposed polymeric regions formed micelles in the aqueous base developer, with the silicon-containing block forming the core and the soluble methacrylic acid group forming the corona. In contrast, random copolymers would not have the ability to form these micellar structures; that is, the entire copolymer would need to be soluble in order for development to occur. However, the development behavior of these BCPs was far from perfect, presumably due to segregation of the PAG away from the surface of the film. Although their performance does not exceed commonly used industrial photoresists, the concept of using BCP architectures for multilevel photoresists is enticing, and there may be much more to learn from these types of systems.



**Figure 1.18** Block copolymer designed as a multilevel photoresist: *t*-butyl methacrylate (*t*-BMA)-*block*-3-methacryloxy-propylpentamethyldisoloxane (SiMA).



**Figure 1.19** (a) A block copolymer photoresist poly(*tert*-butyl methacrylate-*block*-[3-(methacryloxy)propyl]pentamethyldisiloxane) with 10.0 wt% silicon, formulated with 5 wt% PAG. An exposure dose of 2 mJ cm<sup>-2</sup> was used, and the resist was developed for 20s in a mixture of 27% 0.21 N tetramethylammonium hydroxide (TMAH) and 73% iso-propyl alcohol; (b) Random copolymer with 9.7 wt% silicon, formulated

with 5 wt% PAG, after  $1.2 \,\mu$ m features are exposed to 19 mJ cm<sup>-2</sup> and developed using the same conditions. While the random copolymer is insoluble, pinholes form during development and are thought to originate from phase-separated acid, which is removed by the developer. Reprinted with permission from Ref. [154]; © 2006, American Chemical Society.

# 1.3

#### Nanoporous Monoliths Using Block Copolymers

# 1.3.1

# Structure Direction Using Block Copolymer Scaffolds

Besides the potential uses of BCPs as lithographic materials, their inherent microphase separation and chemical dissimilarity of the blocks also leads to other applications. For example, BCPs can serve as structure-directing agents for the formation of mesoporous monolithic materials through phase-selective chemistry. Monolithic nanoporous structures have a large surface : volume ratio, which means that there is a large amount of functionalizable surface area within a small volume of material. In one of the pioneering efforts in this area, Hashimoto and coworkers created a bicontinuous morphology with poly(styrene-*block*-isoprene) and selectively removed the minority isoprene domain with ozonolysis [115]. The group showed that coating the bulk structure with nickel metal does not completely block the nanopores. Rather, metal catalysts such as nickel are known for their ability to adsorb and split  $H_2$  molecules for large-scale industrial reactions such as hydrogenation. The high surface : volume ratio of porous bicontinuous BCP morphologies make them excellent candidates for catalytic applications; indeed, one day they may even be used to make your margarine!

The BCPs used as structure-directing "scaffolds" to create mesoporous silicate structures could also be used as dielectric materials. Silicon dioxide  $(SiO_2)$  is typically used as a dielectric material to reduce undesired capacitive coupling between neighboring elements of an integrated circuit, due to its low dielectric constant (*k*)

of approximately 4.5. Air, however, has one of the lowest dielectric constants (~1); hence, the dielectric constant of SiO<sub>2</sub> can be dramatically decreased by filling it with voids, while maintaining good mechanical properties. So-called 'low-k' materials are highly desired by the semiconductor community because they allow faster switching speeds and lower heat dissipation in computer chipsets. Early studies conducted by Nakahama and coworkers led to the creation of monoliths of bicontinuous BCPs through a spin-coating process. This synthesis included a silylcontaining matrix block and an isoprene-based minority phase. Processing the film entailed hydrolytically crosslinking the silyl-containing block to prevent pore collapse, and ozonolysis to eliminate the isoprene minority domain [155]. Another group subsequently discovered a one-step, room-temperature UV irradiation/ ozonolysis treatment to transform the matrix into a silicon oxycarbide ceramic and eliminate the polydiene minority phase. The silicon oxycarbide ceramic was stable at temperatures up to 400°C, and adjustment of the volume fraction of the BCP afforded an inverse bicontinuous phase to produce a nanorelief structure [14]. These mesoporous materials have also proved useful in the creation of photonic band gap materials [156], due to the possibility of tailoring the dielectric constant of the optical waveguides by sequestering optically active particles inside the matrix phase [157].

Watkins and coworkers have also demonstrated a novel technique to create mesoporous silicate structures by performing phase-selective chemistry inside one of the blocks [158]. In these studies, a tri-BCP of poly(ethylene oxide-block-propylene oxide-block-ethylene oxide) (PEO-b-PPO-b-PEO; also known as Pluronics<sup>®</sup>) was mixed with p-toluene sulfonic acid (pTSA) in an ethanol solution. Upon spincasting the BCP onto a Si wafer, the BCP microphase separated into an ordered morphology containing spherical PPO microdomains. The pTSA catalyst segregated preferentially to the hydrophilic PEO matrix phase. The polymer was then placed in a chamber with humidified supercritical CO2, so as to swell the polymer and allow the infiltration of a metal alkoxide, tetraethylorthosilicate (TEOS), into the polymer. The segregated acid in the hydrophilic domains then underwent a condensation reaction with the TEOS to form a silicon oxide network. Due to the phase selectivity of the acid segregation, no condensation reaction took place within the hydrophobic domains. The alcohol byproducts of the condensation reaction were quickly removed by the supercritical solvent, which rapidly pushed the condensation reaction to complete conversion. Finally, a calcination step in air at 400 °C removed the organic block copolymer framework, leaving an inorganic silicon oxide replica of the original BCP (Figure 1.20). The process could also be carried out in standing cylindrical P(aMS-b-HOST) BCPs [159]. Eventually, the ability to pattern these monolithic silicate structures will lead to their use in future semiconductor fabrication paradigms.

Ulrich and coworkers reported the use of poly(isoprene-*block*-ethylene oxide) (PI-*b*-PEO) as a structure-directing agent for silica-type ceramic materials [160]. A mixture of prehydrolyzed (3-glycidyloxypropyl) trimethoxysilane (GLYMO) and aluminum *sec*-butoxide (Al(OBu)<sub>3</sub>) was added to a solution of the PI-*b*-PEO and cast in a Petri dish. The Al(OBu)<sub>3</sub> triggered ring opening of the epoxy group that made the 3-glycidyloxypropyl ligand of the silane precursor compatible with the



**Figure 1.20** A scanning electron microscopy image showing the cross-section of a highly ordered mesoporous silicate film exhibiting a cylindrical morphology. The film was prepared by infusion and condensation of TEOS within a preorganized triblock PEO-*b*-PPO-*b*-PEO BCP film dilated with supercritical CO<sub>2</sub>. The

image reveals a preferential alignment of cylinders at the interfaces and grains of random orientation within the bulk of the film. Reprinted with permission from Ref. [158]; © 2006, American Association for the Advancement of Science.

PEO block [161]. Thus, addition of the inorganic material led to an increase in the volume fraction of the PEO block and the formation of multiple morphologies, depending on the concentration of the inorganic content in the solution. Spherical, cylindrical, lamellar and a novel type of bicontinuous morphology–called the "Plumber's Nightmare" morphology [162]–was found and characterized using transmission electron microscopy (TEM). Surprisingly, this phase did not occur in the neat PI-*b*-PEO BCP, indicating a radical transformation of the phase space through the addition of the inorganic content, possibly through a dramatic increase in the incompatibility ( $\chi$  parameter) between the blocks. Additionally, calcination of the hybrid materials at 600 °C removed the organic phase and led to the creation of isolated nano-objects such as ceramic cylinders of the inorganic ruthenium dye complex, these nano-objects could be used as fluorescent biomarkers in the field of nanobiotechnology [163].

## 1.3.2 Nanopore Size Tunability

Nanoporous BCP films can also be used as separation membranes or filtration devices [164, 165]. According to C.J. Hawker, "...the lateral density of pores in films prepared from block copolymers is nearly two times greater than that of aluminum oxide membranes and an order of magnitude greater than that of track-etched membranes" [82]. This increase in porosity corresponds to an ability to handle a higher flux of liquid, and thus a higher throughput filter. Furthermore, size-specific separation is possible because the nanopore size will be constant if a polymer with a low polydispersity is used. There is, however, a thermodynamic limit to how small the nanopores can be, this lower bound being based on the

position of the order–disorder transition on the phase diagram relative to  $\chi N$  (refer back to Figure 1.2). Since small molecular weights are desired for smaller microdomains, a highly immiscible pair of polymers (corresponding to a greater  $\chi$  value) is required to decrease their size. If  $\chi N$  falls below this lower bound, the copolymer will mix to form a single phase [166]. To date, structures below 12 nm have been difficult to achieve [167], although in order to tune the size of the nanopores to smaller dimensions, numerous processing methodologies have been developed.

Jeong and coworkers developed a method to alter nanopore size in PS-b-PMMA nanoporous films [168]. Their technique allowed the formation of two discrete sizes of nanopores, depending on the processing strategy used. A 10% blend of low-molecular-weight PMMA homopolymer into a PS-b-PMMA BCP resulted in the solubilization of the homopolymer into the center of the PMMA block. As the PMMA homopolymer was of a lower molecular weight than the PMMA block, it dissolved first when the film was washed with acetic acid (which is a selective solvent for PMMA). This led to the production of nanopores which were 6 nm in size, as determined by atomic force microscopy (AFM) measurements. DUV radiation, in combination with an acetic acid wash, allowed the removal of both the PMMA homopolymer and the PMMA block in the BCP matrix, which resulted in 22nm-sized nanopores. Thus, two different size scales of nanoporous structures-6nm and 22nm-were created using different processing schemes. Jeong et al. noted that the size of the smaller length-scale nanopores could be decreased if homopolymers of smaller molecular weights were used to infiltrate the PMMA block.

In an interesting approach to the preparation of nanoporous films, Ikkala and coworkers have incorporated alkylphenols, such as pentadecylphenol (PDP), into poly(styrene-*block*-4-vinylpyridine) (PS-*b*-P4VP) to create comb–coil supramolecular structures. Here, the phenol group of the PDP forms a strong hydrogen bond with the nitrogen donor on the pyridine group of the P4VP. The hydrogen bonding introduces an additional repulsive interaction that leads to the formation of "comb-like" layered structures of the PDP side chains inside the cylindrical P4VP microdomains. By using this approach, Ikkala *et al.* witnessed hierarchical structure formations such as lamellar-within-lamellar, lamellar-within cylinders, and lamellar-within-sphere morphologies [169, 170]. This was similar to the effects seen in liquid crystalline BCPs, except that the PDP side chains could easily be dissolved in methanol to create porous membranes [171].

The tunability of nanoporous monolithic structures has also been reported through the selective infusion of supercritical  $CO_2$  inside the fluorinated block of poly(styrene-*block*- perfloro-octylethyl methacrylate) (PS-*b*-PFOMA) [125, 126]. Supercritical  $CO_2$  has been shown to have a high affinity for fluorinated polymers [172]. After selective swelling of the  $CO_2$  inside the PFOMA domain, quenching at 0°C to lock in the PS matrix, and controlled depressurization at 0.5 MPa min<sup>-1</sup>, nanocell formation was noted in the BCP film. It was also found that the nanocell diameter could be tuned from 10–30 nm by adjusting the saturation pressure of the  $CO_2$  solvent, with low saturation pressures corresponding to small cell

diameters, and *vice versa*. All of these approaches represent innovative means of decreasing the size scale of nanopores beyond that of the neat BCP.

# 1.3.3

#### **Functionalized Nanoporous Surfaces**

In nanoporous material, it may be very useful to control the chemical functionality of the nanopore wall for applications that require aqueous environments, such as microfluidic devices, water filtration, biocatalysis, or other chemical reactions that take place within the pore. In microfluidic devices, for example, compatibility between the substrate (pore wall) and the filler fluid (analyte) that passes through the nanoporous channels is necessary. Hydrophilic moieties such as hydroxyl groups attached to the pore wall will permit conduction of the aqueous solution through the membrane, as opposed to hydrophobic substrates that would hinder the flow of solution through the pores.

Several strategies are available for functionalization of the pore wall, three of which are shown in Figure 1.21. The first strategy (Figure 1.21a) is to introduce a functional group "spacer" between the covalent junction of the matrix and



**Figure 1.21** Possible routes to nanoporous materials with controlled pore-wall functionality. (a) A functional group is incorporated into the junction between the matrix and sacrificial blocks, and is exposed upon template degradation; (b) A functionalized mid-block is inserted between the matrix and sacrificial end block, producing a functional polymer brush at the pore wall upon removal of the template; (c) An AB/AC

diblock copolymer blend is formed in which the common A block serves as the matrix, the B and C blocks are miscible, and only one of the two blocks is susceptible to degradative removal. In this manner, a functionalized nondegradable block can be introduced as a diffuse brush along the pore interior. Reproduced with permission from Ref. [176]; © 2006, Royal Society of Chemistry. sacrificial blocks. This telechelic functionality can easily be introduced to the end of the living polymer chain during BCP synthesis, following addition of the first monomer and before addition of the second monomer. When the sacrificial block is removed through standard degradation procedures, the functional spacer will then line the pore wall. This approach has been demonstrated recently by Zalusky and coworkers [118, 119], Wolf and Hillmyer [120], and Hawker and coworkers [138]. Each of these groups made use of the hydroxyl-terminated poly(styrene) or poly(cyclohexylethylene) remaining when the PLA block had been removed. Degradation of the PLA left behind hydroxyl groups at the pore surfaces after removal, as proven by the reaction with trifluoroacetic anhydride and subsequent nuclear magnetic resonance (NMR) and infrared (IR) spectroscopic analyses. The only disadvantage to this relatively simple approach is the low density of functional groups that results, since only one -OH group exists per polymer chain. Zalusky et al. calculated the areal density of the hydroxyl groups to be approximately one -OH per 4 nm<sup>2</sup> for a sample with 22 nm-diameter pores [118].

Clearly, the solution to the low density of the functional groups would be to increase their number by polymerizing the functional unit, as shown in Figure 1.21b. In other words, a tri-BCP could be synthesized in which a functional center block (B) existed between the matrix (A) and the sacrificial (C) block. The success of this strategy, of course, would depend on the morphology of the tri-BCP, which can be difficult to predict. The ideal morphology, in this case, would be a hexagonally packed core–shell cylindrical morphology, with the functional block forming a shell around the sacrificial core, surrounded by a crosslinkable matrix. The first attempt at the formation of this morphology was demonstrated by Liu *et al.* with PI-*b*-PCEMA-*b*-PtBA (CEMA = cinnamoyloxyethyl methacrylate, *t*BA = *tert*-butyl acrylate) [173]. The *tert*-butyl group was removed by hydrolysis to form gas-permeable poly(acrylic acid) nanochannels. The research results of Liu and colleagues will be presented in greater detail in Section 1.4.

Recent investigations conducted by the group of Hillmyer have demonstrated great success in functionalizing nanoporous monoliths. A poly(styrene-block-polydimethylacrylamide-block-polylactide (PS-b-PDMA-b-PLA) tri-BCP was synthesized by a combination of controlled ring-opening and free-radical polymerization techniques [174]. Aqueous base removal of the PLA minority phase and hydrolysis of the PDMA domain left carboxylic acid groups coating the pore wall, and these were used to chemically attach allylamine through carbodiimide coupling chemistry. <sup>1</sup>H NMR spectra of the dissolved polymer film verified a successful attachment of the N-allylamide group, and proved that the pore wall surface was chemically active. The same group was also successful in binding other functional groups such as a pyridine, a chiral hydroxyl, and an alkene in high yields. Other studies with PS-b-PI-b-PLA triblocks [175] by the Hillmyer group have produced an isoprene shell coating the pore wall following removal of the PLA phase by treatment with NaOH solution. These studies led to the production of a beautiful AFM image of a core-shell morphology (Figure 1.22) which was due to the differing mechanical contrasts between the PS matrix and PI shell. A tri-BCP containing



**Figure 1.22** Tapping mode AFM phase image acquired from a PS-*b*-PI-*b*-PLA thin film. The scale bar at the lower right is 200 nm. The inset at upper right is  $250 \times 250$  nm. Reprinted with permission from Ref. [175]; © 2006, American Chemical Society.

two selectively etchable blocks, such as PI and PLA, opens up the possibility of forming hollow "nanoring" donut-shaped structures through removal of the matrix and core-forming phases. The creation of coaxial nanowires would then be conceivable through the sequential electrodeposition of metals.

The third approach to add functionality to nanoporous BCP films, as shown in Figure 1.21c, is through the blending of two diblock copolymers. This idea is based on the use of two BCPs (AB and AC), in which the A blocks mix to form the matrix phase, and the B and C blocks must be selected to be miscible with one another to form a single cylindrical domain. If either one of the B or C blocks is degradable, it is possible to form nanopore walls coated with the nondegradable block. For example, if B is degraded by UV light, C will still be attached to its parent A molecules and will form a brush extending out towards the center of the nanopore containing the end-group functionality. This approach was championed in a recent investigation by Mao and coworkers, who blended a parent PS-b-PLA BCP with PS-b-PEO to form the blended PLA/PEO microdomains in a PS matrix [176]. The PLA was degraded through hydrolysis in an aqueous methanol/NaOH solution, leaving a PEO polymer brush (containing a hydroxyl end group) which extended into the nanopore. As a test to prove the success of their strategy, Mao et al. floated blended (PS-b-PEO/PS-b-PLA) and nonblended (PSb-PLA) films on a water surface. The blended film proceeded to sink, which meant that the pores within the film had imbibed water. In contrast, the nonblended PS-b-PLA BCPs floated on the water surface for an indefinite period. Chemical functionalization strategies such as these will become increasingly important as the field of BCPs moves away from fundamental science and into the realm of practical applications.

#### 1.4 Photo-Crosslinkable Nano-Objects

The design and fabrication of nanometer-sized structures with well-defined size and shape has recently aroused much interest, much of which has stemmed from the need for smaller electronic devices that are not possible to produce using conventional lithographic techniques. Indeed, small nano-objects could also be useful as biosensors capable of molecular recognition. A number of groups have emerged as front-runners in this field, with their use of photoactive BCP domains to fix unique microphase-separated structures. The Liu research group, for example, has been very prolific in this area, with the majority of their investigations lying in a variety of applications stemming from the unique photocrosslinkable polymer, poly(2-cinnamoyloxyethyl methacrylate) (PCEMA). Through a dimerization process involving a [2 + 2] cycloaddition of two double bonds in neighboring chains (see Scheme 1.10), the PCEMA becomes photochemically crosslinked. An amphiphilic BCP containing PCEMA will form micelles when placed in a solvent that dissolves only one of the blocks. The shape and size of the micelles can then be changed by altering the relative chain lengths of the soluble and insoluble blocks, to produce spherical [177], cylindrical





[178, 179], vesicular [180], or donut-shaped [181] structures. These structures can then be fixed with UV light through the dimerization process to form permanent "nano-objects" that are stable in a wide variety of solvents. In an assortment of creative syntheses using this polymer, Liu's group has developed a wide range of structures, including nanotubes [182], porous [183], "shaved" and "hairy" nanospheres [184–187], nanospheres with crosslinked shells [188], crosslinked polymer brushes [189], nanofibers [184, 190–192], and nanochannels in polymer thin films [193, 194].

As an example of the power of their photocrosslinking strategy, nanotubes with hydrophilic nanochannels have been formed using the tri-BCP PbMA-*b*-PCEMA-*b*-PtBA (PbMA = poly(butyl methacrylate); see Figure 1.23) [195]. Bulk films (~0.2 mm thick) were produced by slow evaporation of the polymer in toluene. After an annealing step, the PtBA formed the hexagonally packed cylindrical core, surrounded by a shell of PCEMA in a PbMA matrix. The PCEMA is first photocrosslinked, after which the PtBA cylinders are hydrolyzed in methanol to yield nanochannels filled with poly(acrylic acid) (PAA) brushes. Subsequent dissolution of the PbMA matrix in tetrahydrofuran (THF) led to the production of free-floating, functionalized nanotubes. These rod-like nanotubes were also shown to exhibit LC properties in solution [196].



**Figure 1.23** (a) A triblock copolymer of PbMA-*b*-PHEMA-TMS-*b*-PtBA was synthesized via anionic polymerization, deprotected, and then reacted with cinnamoyl chloride to form PbMA-*b*-PCEMA-*b*-PtBA; (b) Self-assembly of cylindrical morphologies

developed upon spin-coating; (c) The PCEMA shells were crosslinked through a [2+2] cycloaddition upon exposure to UV light; (d) The PbMA matrix was dissolved in THF to free the cylinders; (e) The PtBA was hydrolyzed to form PAA-functionalized nanotubes; (f) Schematic of the chemical "nanovalve" effect. At low pH, low water permeability was found, whereas at high pH an increased permeability was found. Adapted from Ref. [195]. These studies also had ties to the creation of functionalized nanopores (see Section 1.3.3). In what was termed a "chemical valve effect," the permeability of the channels within the nanotubes could be tuned due to the swelling effect of the PAA brushes in water at different pH values. At low pH, the PAA chains formed a gel due to hydrogen bonding between the AA units, and prevented the flow of water through the pores. At high pH, the AA groups were converted to sodium acrylate, which did not form hydrogen bonds, and the ionized carboxyl groups were readily solvated by water. This allowed a high permeability of water through the tubes.

An obvious application for these type of functionalized material would be as a pH-sensitive membrane for filtration devices [70], although the hydrophilic PAA nanochannels may also act as hosts for the growth of inorganic nanoparticles. To demonstrate such capabilities, the authors were able to grow inorganic particles of CdS, an interesting semiconductor material, and a magnetic material, Fe<sub>2</sub>O<sub>3</sub>, by adding the appropriate metal salts and a reducing agent (see Section 1.5) [197, 198]. The Fe<sub>2</sub>O<sub>3</sub> metal-impregnated nanofibers were found to be super-paramagnetic; that is, they were attracted to each other when a magnetic field was applied, but demagnetized when the field was turned off [199].

Taking their technology one step further, Liu's group has been successful in physically connecting the floating nanotubes to other structures, such as nanospheres. Here, a thick PS-*b*-PCEMA-*b*-PtBA film formed PtBA hexagonal cylindrical cores surrounded by a PCEMA shell and a PS matrix. After crosslinking the PCEMA, the PS was dissolved in THF to break the film up into nanotubes. Subsequent ultrasonication caused a shortening of the nanotubes and exposed the PtBA core chains at the ends, which were then hydrolyzed using trifluoroacetic acid to form PAA. The AA ends of the nanotubes were then grafted to polymeric spacers containing multiple amine groups on both ends. These amine-functionalized nanotubes were coupled with PCEMA-*b*-PAA nanospheres bearing surface carboxyl groups [183] through an amidation reaction, the result being the formation of "ball and chain" structures (see Figure 1.24) [182]. When a nanosphere



**Figure 1.24** Transmission electron microscopy images of nanotube and nanosphere coupling products. (a) Singular nanotubes connected to nanospheres; (b) Two nanotubes connected to a nanosphere. Reprinted with permission from Ref. [182]; © 2006, American Chemical Society.

became attached to two nanotubes (see Figure 1.24b), Liu suggested that if the nanotubes were loaded with super-paramagnetic  $Fe_2O_3$  particles they might act as "fingers," with an opening and closing motion induced by a magnetic field. In this way they could form the chemical basis of a magnetic "nano-hand!"

# 1.5 Block Copolymers as Nanoreactors

The directed self-assembly of inorganic nanoparticles into BCP templates can result in structures with interesting and useful electronic, optical, and magnetic properties. We have already seen the long-range ordering possible with BCP thin films. Yet, rather than selectively removing one of the blocks, it is also possible to use the ordered BCP pattern as a template for chemical reactions within one phase, leading to patterned clusters of functional nanoscale functional materials over large areas. Various types of functional nanostructures that could, in theory, result from these approaches include metal catalyst particles for fuel cell applications, ferromagnetic particles for high-density storage media [200], doped semiconductor clusters [201], QD structures [202, 203], and core–shell structures [204].

There are two approaches towards the use of BCPs as nanoreactors [205]. The first, most common approach uses an "*in situ*" production of metal nanoclusters inside BCP nanodomains [206]. Figure 1.25 shows a schematic of a cylindrical BCP that contains a functional group "receptor" which is located within the minority phase and is capable of selectively binding positively charged organometallic salts. Once the metal ions have been loaded, a subsequent reduction step can convert the metal ions into oxide, chalcogenide or zerovalent metal clusters, thus regenerating the receptor moiety [205]. The BCP can then accommodate repeated loading/reaction cycles [207] with the same or different metal salt.

In the second approach, the inorganic element is incorporated into an organometallic monomer, which can then be synthesized directly into the parent BCP. The previously mentioned PS-*b*-PFS (see Section 1.2.2.1.4) is an example of this type of polymer. This approach has been reviewed by Cummins *et al.* [208]. These BCPs self-assemble normally to leave an array of "pre-loaded" nanoreactors, ready and waiting for further chemical processing to form the inorganic clusters. This approach eliminates the metal salt loading step, which can take up to two weeks for bulk films, and may lead to nonselective sequestering of the reagents. However, the synthesis of new organometallic monomers for every application also presents huge challenges for the chemist.

#### 1.5.1

#### Polymer-Metal Solubility

The solubility of inorganic compounds inside an organic matrix is made possible by careful adjustment of the polymer–metal bonding energy. Pearson's Hard–Soft, Acid–Base (HSAB) principle effectively describes the bonding behavior [28]. The



**Figure 1.25** A typical scheme for the use of a block copolymer as a template for the selective growth of nanoparticles. Adapted from Ref. [205].

HSAB theory states that only chemicals of similar "hardness" will bond to each other; that is, soft acids will only bind to soft bases, and hard acids will only bind to hard bases. This hardness value is proportional to the difference between the materials' highest occupied molecular orbital (HOMO) energy and the lowest unoccupied molecular orbital (LUMO) energy, which also relates to the band gap of the material. Metals are conductors and have smaller band gaps, and so are classified as chemically "soft." Conversely, polymers are insulators with large band gaps and are classified as chemically "hard." Therefore, hard polymers cannot bind to soft metals unless functional groups are attached to the polymer that change the bonding energy and make it chemically softer. In block copolymers, poly(vinylpyridine) (PVP), containing the electron pair-donating nitrogen species, is most commonly used to effectively solubilize metal salts. The typical design for the loading step is to choose a weakly coordinated metal salt, such as Pd(OAc)<sub>2</sub>, in which the transition metal acts as the soft acid bonded to a hard acetate base. According to the HSAB principle, this hard-soft bond is highly unstable, such that when the soft metal (Pd) encounters the functionalized soft polymer (PVP), a more stable soft-soft bond is created so as to encapsulate the metal within the block.

#### 1.5.2

#### **Cluster Nucleation and Growth**

After block-selective loading of the metal salt, the next step is to reduce the salt to create the nanoparticles within each domain. Different applications may require different nanoparticle sizes and different numbers of clusters within each domain, as shown in Figure 1.26. For example, investigators in the field of electro-optics may only be interested in one nanoparticle per microdomain, whereas those in the field of catalysis might aim for a large number of nanoparticles to present a higher degree of functional surface area for subsequent chemical reactions. Formation of the nanoparticles proceeds through a nucleation and growth process. In typical nucleation and growth schemes, if the colloidal species has enough free energy to aggregate to sizes above a certain critical radius,  $R_c$ , then the particle will continue to grow; if not, the particle becomes unstable and falls apart to minimize the surface free energy. The critical radius is proportional to the interfacial tension of the polymer/particle interface ( $\gamma$ ) and the degree of supersaturation ( $c/c_o$ ), as shown in Equation 1.2 [28]:

$$R_{\rm c} \propto \frac{\gamma}{\ln(c/c_{\rm o})} \tag{1.2}$$

Thus, one way to adjust the size and number of the particles is by adjustment of the degree of supersaturation of the reducing agent, which depends on the rate of chemical reaction of the reduction step [209]. Fast chemical reactions with strong



**Figure 1.26** (a) Transmission electron microscopy (TEM) image showing multiple gold nanoclusters in each domain. Scale bar = 500 Angstroms. Reprinted with permission from Chan, Y., Ng Cheong, Schrock, R.R. and Cohen, R.E. (1992) *Chem.* 

(b)



Mater., 4, 885–894; (b) TEM image showing single nanoparticles in each domain. Reprinted with permission from Klingelhofer, S., Heitz, A., Greiner, S. *et al.* (1997) *J. Am. Chem. Soc.*, **119**, 10116; © 2006, American Chemical Society.

reducing agents such as lithium aluminum hydride (LiAlH<sub>4</sub>) lead to high supersaturations, which in turn will mean a low critical radius for nucleation and a higher probability for particle nucleation within the microdomain. This would result in a large number of particles per domain, as shown in Figure 1.26a. In the reverse case, the use of weak reducing agents such as alkylsilanes would result in low supersaturation values. This will increase the critical radius for nucleation and decrease the probability that a nucleating event will occur, resulting usually in only one particle per microdomain, as shown in Figure 1.26b. Another way to control the critical radius is by changing the interfacial tension ( $\gamma$ ) between the particle and the polymer, which can be achieved through the selection of different metalbinding blocks.

# 1.5.3 Block Copolymer Micelle Nanolithography

Building on the nanoreactor approach, nanoscale devices will require the precise placement of functional materials in one- or two-dimensional arrays on semiconductor interfaces. Increased levels of control over the exact location of these inorganic nanoparticles can come from a top-down approach using UV light or e-beam lithography, as shown from a series of reports from Spatz and coworkers. Their approach, which is known as "block copolymer micelle nanolithography" [210], is shown schematically in Figure 1.27a. As an example of their strategy, poly(styrene*block-*2-vinylpyridine) (PS-*b*-P2VP) is dissolved in a selective solvent for PS to form



Figure 1.27 Application of monomicellar films as a negative e-beam resist on glass cover slips. (a) Schematic representation; (b) Monomicellar layers after lift-off; (c) Au-nanodots of 7 nm diameter after hydrogen plasma treatment. The white arrows

point to holes which are characteristic for glass coverslips. Reprinted with permission from Glass, R., Moeller, M and Spatz, J.P. (2003) *Nanotechnology*, **14**, 1153–1160; © 2006, Institute of Physics.

micelles with P2VP cores and PS coronas. The diameter of these micelles is controlled by the molecular weight of the minority block and the interaction between the polymer blocks and the solvent. The micelles are then loaded with a metal salt of tetrachloroauric acid (HAuCl<sub>4</sub>), which complexes with the P2VP core. The loaded micelles are deposited as a monolayer film onto a silicon wafer. The film then is exposed to a focused electron beam that oxidizes the polymer, creating carboxylic acids, ketones, aldehydes, and ethers on the polymer surface. These reactive groups bind to the silanol groups on the Si wafer, fixing the exposed area to the substrate, while the unexposed areas are washed away in a sonicating bath. Hydrogen plasma is then used to remove the underlying polymer layer and reduce the HAuCl<sub>4</sub>, leaving gold dots in the same shape as the previous electron beam pattern (see Figure 1.27b). It was found that the size of the gold nanoparticles could be tuned by adjusting the concentration of metal salt in the BCP solution. These gold clusters are highly mechanically stable structures, and are being pursued for applications in immobilizing single proteins for biosensor applications, or as coatings for lenses [211].

# 1.6 Interface-Active Block Copolymers

#### 1.6.1

#### Low-Energy Surfaces Using Fluorinated Block Copolymers

Molecular-level control over the surface properties of polymer films has become increasingly important in current research and development strategies. Polymers with tailored surface energies are used in a wide variety of applications, from planarizing or dielectric layers for semiconductor device fabrication to nonstick cookware and surfaces for combinatorial chemistry. In each of these applications, properties such as adhesion, wetting, lubrication and adsorption behavior must be carefully tuned so as to optimize performance. In the past, scientists toiled on the effects of individual molecular interactions such as entropic frustration between polymer blocks, hydrogen bonding, molecular shape anisotropy, coulombic interactions, and surface segregation. Now, we have learned how to combine these molecular interactions to produce powerful synergistic effects on materials structure.

Semi-fluorinated polymers attached to polymer backbones are often used as surface coatings for their hydrophobic and lipophobic behavior due to the highly chemically resistant nature of the C–F bond. They can also be used as surfactants, lubricating agents, emulsifiers, or photoresists. It has been found that the semifluorinated mesogens segregate to the polymer/air interface due to their low surface energy, and are often tilted with respect to the surface normal [212]. One problem with these highly hydrophobic materials, however, is the tendency for surface reconstruction to occur when placed in a highly polar solvent such as water (see Figure 1.28a). Surface reconstruction severely impairs the hydrophobic properties of the material.

#### 1.6 Interface-Active Block Copolymers 49



**Figure 1.28** (a) Lamellar morphologies of a block copolymer consisting of hydrophobic and hydrophilic blocks self-assembled with the hydrophobic block situated at the air interface due to its lower surface energy. Exposure of the film to water causes a surface reconstruction that brings the hydrophilic block into contact with the water; (b) Block

copolymers containing a hydrophobic fluorinated mesogen resist surface reconstruction due to the formation of a highly stable liquid crystalline smectic phase at the surface. Adapted from Gabor, A.H., Pruette, L.C. and Ober, C.K. (1996), *Chem. Mater.*, **8** (9), 2282–2290.

BCPs provide a solution to the problem of surface reconstruction. It has been found that the incorporation of semi-fluorinated chemical groups into microphase-separated BCPs produces materials that resist surface reconstruction due to the formation of a stable liquid crystalline smectic phase at the surface (as shown in Figure 1.28b). Since this discovery, semi-fluorinated BCPs have become very popular candidates as longlasting, nonbiofouling surface coatings for marine vessels, due to the inability of aquatic organisms to stick to their surfaces [65, 213]. A recent report showed that the surface hydrophobicity of fluorinated BCPs can be enhanced with supercritical CO<sub>2</sub> annealing due to a thickening of the smectic layer [214]. According to Langmuir's *Principle of Independent Surface Action*, the unique hydrophobic properties of a surface depend on: (i) the *nature*; and (ii) the *physical arrangement* of the atoms populating the surface energy of block copolymer films have been manipulated by changing these two variables.

#### 1.6.2 Patterning Surface Energies

The facility to alter the hydrophobicity of a polymer in precise patterns would be a highly desirable trait for the formation of biologically active surfaces. This would allow the selective adsorption of biomolecules [216] or recombinant proteins [217] onto specific locations of a polymer film, which could then be used for biosensors

or other "lab-on-a-chip" applications. By definition, the patterning of a photoresist readily accomplishes this solubility switch (see Section 1.2.1). Hayakawa and coworkers synthesized a hydroxylated poly(styrene-*block*-isoprene) BCP using polymer-analogous chemistry, followed by the grafting of a semi-fluorinated side chain onto the hydroxylated isoprene block [218]. The surface-segregated semifluorinated chains were capped with an acid-labile *tert*-butoxycarbonyl (TBOC) protecting group that masks a hydroxyl functionality at the end of the chain. To tailor the surface energy of the polymer surface layer, a chemical amplification strategy was used. A photoacid generator mixed into the polymer thin film produced a photoacid that deprotected the TBOC groups, such that the nonpolar methyl end group from the TBOC switched to a polar hydroxyl group during photoprocessing. This resulted in a decrease in the advancing and receding water contact angles by 14° and 15°, respectively. Annealing the film also induced a greater degree of surface ordering of the semi-fluorinated chain and increased the hydrophilicity of the exposed material by a small amount.

Other similar approaches have been used to accomplish the same effect. Böker *et al.* demonstrated that the highly hydrophobic perfluorinated side chains grafted to a hydroxylated poly(styrene-*b*-isoprene) BCP became completely removed after thermal annealing to dramatically alter the surface properties of the film [219]. Annealing at 340 °C for 15 min in a vacuum oven caused a thermal ester cleavage that resulted in decomposition of the perfluorodecanoyl side chains, but left the parent polymer backbone intact. This resulted in a considerable change of the advancing contact angle of the film, from 122° to 87°. As thermal heating could also be carried out locally on a polymer film, the author suggested that this approach could be used to pattern hydrophobic and hydrophilic regions on the master template of a printing press to control the dispersion of aqueous inks.

In a similar approach, Yang et al. used group transfer polymerization to synthesize a variety of methacrylate-based BCPs with semi-fluorinated chains functionalized with protecting groups, with the intent to use them as surface-active materials as well as photoresists [220]. Due to their transparency under 193 nm wavelength light, the semiconductor industry has shown great interest in fluorinated methacrylate polymers as 193 nm wavelength photoresists. Prior studies have also shown that fluorine-containing BCPs can outperform their random copolymer counterparts [154], and are able to develop in environmentally friendly supercritical CO<sub>2</sub> [221]. To investigate the effect of BCP microstructure on wetting behavior, an assortment of volume ratios for these copolymers were synthesized to provide a wide range of different microstructures and solubilities, but these did not have any effect on the surface energy of the films. The polymers with six -CF<sub>2</sub>- units and a  $-CF_3$  end group showed the lowest critical surface tension, at approximately 7mNewtons per meter. Rather than the commonly used tert-butyl protecting group, the acetal-type tetrahydropyranyl (THP) protecting group was used on the basis of its more polar and labile nature. Thermal deprotection of the THP groups formed acid and left -OH groups on the polymer chain ends that reduced the advancing water contact angle by 30°. After a period of annealing, it was also reported that that the free acid caused by the THP deprotection interacted with the Si–OH substrate and led to the formation of highly stable, nonreconstructing surfaces.

# 1.6.3 Photoswitchable Surface Energies Using Block Copolymers Containing Azobenzene

It is well known that polymers containing azobenzene groups attached to one of the blocks can exhibit light-responsive effects [222]. These chemical structures undergo a reversible *cis*-*trans* isomerization upon exposure to specific wavelengths of light (Figure 1.29), which also changes the molecular orientation of the LC azobenzene mesogens. It has also been found that the mesogens align perpendicular to the incident light polarization, which means that they will align in the film plane and along the direction of the propagation of radiation. Therefore, if the irradiation source is slanted at a given angle, the mesogens then align at the same angle within the film. This field is full of exciting potential for applications in the fields of holographic data storage, optical signal processing, and optical switching.

Light-induced molecular reorganization can also be used to tailor surface properties. Returning to the principle of independent surface action, there are two ways to change the wettability of a surface: (i) to change the nature of the end-group atoms; or (ii) to change the molecular orientation of the end-group atoms. Expanding on the latter point brings us to the topic of photoisomerizable fluorinated mesogens. Thin films of BCPs containing LC fluorinated mesogens have been shown to segregate into well-organized smectic layers on the surface, due to the low energy of the fluorinated block (see Section 1.6.1). Recently, the details have been reported of azobenzene BCPs with semi-fluorinated alkyl side chains that would allow structural modification of the fluorinated mesogens at the surface,



*trans* isomer *cis* isomer **Figure 1.29** The chemical structure of an azobenzene chromophore and the reversible photoisomerization between *trans* and *cis* isomers.

and thus selective patterning of the films' wetting behavior [223]. It has also been shown that the copolymers with longer fluoroalkyl chain lengths resulted in a high degree of orientational order, but were highly resistant to molecular restructuring with photoisomerization. The copolymers with short fluoroalkyl segments showed a small change in advancing/receding contact angle measurements upon exposure to UV light, corresponding to changes from a hydrophobic to a slightly less hydrophobic surface.

Möller and coworkers have also investigated the behavior of a BCP consisting of a PHEMA block and a poly(methacrylate) block with 4-trifluoromethoxyazobenzene side groups for photoswitchable wetting applications [224]. The group found that the photoswitchable effect depended heavily on the packing density of the chromophores, which are higher in the *trans* state than in the *cis* state. Films that were switched to the *cis* state before film formation had a lower packing density and were more susceptible to photoinduced motions, due to the increased free volume in the film. Another group reported an 8° difference in water contact angles between the *cis* and *trans* states in 4-trifluoromethylazobenzene-containing BCPs [225].

#### 1.6.4

## Light-Active Azobenzene Block Copolymer Vesicles as Drug Delivery Devices

Tong and coworkers have shown that amphiphilic, azobenzene-containing BCP micelles are highly responsive to UV light [226]. In their ATRP synthesis, the hydrophobic block is a methacrylate-based, azobenzene-containing LC polymer, and the hydrophilic block is a random copolymer of poly(tert-butyl acrylate-coacrylic acid). The BCP forms micelles in solution. Under UV light, the azobenzene groups in the core undergo a *trans-cis* photoisomerization that induces a change in the dipole moment in the BCP vesicle. This shift in the delicate hydrophilic/ hydrophobic balance between the chains causes dissociation of the micelle. Subsequent exposure to visible light irradiation switches the azo molecule back to its trans state, restores the thermodynamic balance, and causes the micelles to reform (Figure 1.30). Tong et al. note that other groups [227] had found little effect of UV light irradiation on other azo-based amphiphilic BCPs, but hinted that the success of their system might be due to the thermodynamic lever made possible by the tunability of the hydrophilic random copolymer block. Combined with the ability for micelles to solubilize anticancer drugs [228] and to act as carriers for the site-specific transport of drugs [229], these UV light-responsive micelles are very exciting.

#### 1.6.5

#### Azobenzene-Containing Block Copolymers as Holographic Materials

In the effort to store data on smaller and smaller length scales, volume holographic data storage has become an area of intense study in the scientific community. Recently, attention has turned to BCPs as a potential holographic material. In



**Figure 1.30** Changes in transmittance for a vesicle solution of PAzo74-*b*-(*t*BA46-AA22) exposed to UV (360 nm, 18 mW cm<sup>-2</sup>) and visible (440 nm, 24 mW cm<sup>-2</sup>) light irradiation. The vesicles are formed by adding 16% (v/v) of water in a dioxane solution with an initial polymer concentration of 1 mg ml<sup>-1</sup>. (a–c) Typical SEM images for samples cast from the solution at different times: (a) before and (b) during UV light exposure, while (c) shows their reformation after visible light

exposure. For comparison, also shown is the transmittance of the diblock copolymer solution in dioxane (no water added to induce the aggregation) subjected to the same conditions of UV and visible light irradiation. The abscissa of time is shifted to have the origin correspond to the application of UV irradiation. Reprinted with permission from Ref. [226]; © 2006, American Chemical Society.

order to understand where they fit in, some background into the technology will be necessary. Holography is a revolutionary technique to store and view data in which an optical interference pattern is produced by the intersection of two coherent laser beams. At the point of intersection, the phase and amplitude of the wave fields induce a chemical or physical change in the material, and are thus "recorded" onto the holographic material [230].

High-capacity holographic data storage requires precise, 3-D control over the index of refraction of the material. Among many potential candidates for holographic materials, azobenzene-containing polymers seem to be the best suited for

holographic data storage for several reasons, including their high diffraction efficiency, resolution, and sensitivity, but mainly for the nematic–isotropic phase transition that occurs when the rod-like *trans* isomer is switched to the contracted *cis* isomer (refer to Figure 1.29). The disruption of LC ordering in the molecule takes place on a time scale of about 200 $\mu$ s, which is a reasonable period for writing data. In 1995, in a landmark study conducted by Ikeda and coworkers [231], this phenomenon was used to record holographic gratings inside the bulk of a polymer film.

One drawback to the use of azobenzene-containing homopolymers and random copolymers is the astonishing formation of surface relief gratings [232]. Here, the polymer becomes physically displaced in the areas of the most intense illumination, due to a massive macroscopic motion of the azo-polymer chains. Despite an increased diffraction efficiency created by these photopatterned ridges, surface relief structures are permanent physical effects that are highly detrimental to the angular selectivity and rewritability required for volume holograms.

BCPs containing azobenzene side chains do not form surface relief gratings due to the confining effect of the microdomains on the azobenzene side chains [233]. This confinement effect, however, seems to have detrimental effects on the speed and magnitude of the *cis–trans* photoisomerization [234]. Häckel *et al.* synthesized a series of BCPs containing a polystyrene block and a polybutadiene block containing the photo-addressable azobenzene components [235]. The photo-addressable phase consisted of a statistical distribution of azobenzene side groups and benzoylbiphenyl side groups. The latter rod-type mesogen was introduced to increase the difference in refractive index between the illuminated and nonilluminated areas of the volume and to improve the stability of the orientation. Different azo: mesogen ratios were used to identify the polymer with the highest degree and stability of molecular reorientation. The polymer containing 35% of the mesogenic side groups showed a slight increase of the refractive index modulation over the period of a year. This strategy posted remarkable improvements over the stability of the recorded orientations.

# 1.7 Summary and Outlook

In this chapter we have brought to light many interesting chemical and physical applications possible using BCP-directed self-assembly (see Table 1.3). Unfortunately, however, many other fascinating applications have been omitted in the interest of space. An extraordinary amount of progress has been made in our ability to manipulate and optimize BCP structural ordering in various forms, including thin films, micelles, and monolithic bulk structures. The ordered microdomains may contain chemical functionality that can be used in a variety of fashions, such as templates for the nucleation and growth of inorganic nanoparticles, chemical valves inside cylindrical pores, monolithic nanoporous structures, or as removable components to form lithographic stencils. We have also seen how BCPs

Table 1.3 Block copolymers used for phase-selec	ctive chemistry.	
Name	Structure	Function
Poly(styrene- <i>block</i> -isoprene) modified with 4-perfluoroalkyl azobenzene side groups	$B_{u} \xrightarrow{f} B_{u} \xrightarrow{h} H \xrightarrow{h}$	Photoswitchable surface engineering
Poly(styrene- <i>block</i> -methyl methacrylate)	$+ \underbrace{cH_2 - cH_1 - cH_2 - cH_3}_{CH_3}$	Nanolithogaphic patterning
Poly(styrene- <i>block-</i> 4-vinyl pyridine)	$\frac{1}{1000} CH_2 - CH \frac{1}{1000} CH_2 - CH \frac{1}{10000} CH_2 - CH \frac{1}{10000000000000000000000000000000000$	Micelle nanoreactors, nanolithographic patterning
Polystyrene- <i>block</i> -butadiene	$+$ $cH_2 - cH \rightarrow n$ $+$ $cH_2 - cH = CH - CH_2$	Nanolithographic patterning

1.7 Summary and Outlook 55





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can behave as multilevel photoresists due to their ability to combine different polymers without macrophase separation. BCPs have also been used for their ability to segregate into distinct chemical levels for the tailoring of surface properties. Lastly, we have seen how the incorporation of LC moieties such as fluorinated mesogens or azobenzene chromophores into BCPs widens their repertoire to lowenergy surface patterning and holographic data storage applications.

In all of these studies, novel chemical strategies have been used to generate functional results. Chemistry is at the heart of every physical effect arising from BCP self-assembly. Using myriad living polymerization strategies in combination with polymer-analogous reactions, BCPs with a vast range of functionalities can be synthesized with low polydispersity and well-defined molecular weights. Exquisite levels of control over the BCP can be achieved by altering the degree of polymerization of each of the blocks, through which the chemist can dial in any type of morphology from spheres, cylinders, bicontinuous networks, and lamellar phases. Even more morphologies are possible through micellization strategies, such as spherical, cylindrical, or onion-like structures. The physical and functional likeness of these structures to biological vesicles and lysosomes is uncanny. Moreover, these technologies are just starting to see the first of their applications as containers for drug delivery, and excellent reviews have been produced that highlight this area [29, 236].

In the field of BCP lithography, we have just begun to see the first practical uses emerge from all of the fundamental studies. The formation of cobalt magnetic dot arrays, flash memory devices, and MOS capacitors are only the "tip of the iceberg" of applications that can arise from this technology. Whilst industry has not overlooked these results, several key requirements are required in order for the semiconductor industry to take directed self-assembly seriously. Among these requirements are "improved long-range dimensional control … improved resolution and linear density by at least a factor of two over that achieved by top down lithography [~11 nm by 2010] … fabricated features with multiple sizes and pitches in the same layer in different regions of a chip …." and so on [79]. If improvements in these areas are not made in the next four years, the field of directed selfassembly may miss its chance for widespread industrial use.

In the future, nothing stands in the way of our ability to pattern individual, isolated lines of perpendicular lamellar morphologies. To this end, the work of Ober and coworkers with the P( $\alpha$ MS-b-HOST) system, in combination with small molecular additives that undergo phase-selective photocrosslinking chemistry, seems very promising. One day, the rapidly growing field of organic electronics may converge with BCP lithography, and the ability to create patterned, well-ordered arrays of conducting nanowires may become possible [237–239]. In theory, the chemical nanopatterning approach mastered by the Nealey group should allow us to effectively control BCP self-assembly by forcing microdomains to organize into any type of lattice, such as simple cubic lattices. It should also be possible with chemical nanopatterning to pattern some of the more complicated features in semiconductor device components, such as nested and embedded jog structures, and t-junctions. Furthermore, if we consider the immense 3-D complexity

of protein molecules, which are formed from various combinations of the 20 amino acids, we have only begun to scratch the surface of the dimensional control made possible by block copolymers. The incorporation of multiple blocks, hydrogen-bonded [240] and LC blocks [21] will be immensely rewarded by the ability to manipulate and exert control over multiple length scales of molecular self-assembly. Nor should we be constrained by the type of BCP that we use. PS-*b*-PMMA is a great lithographic system, but other, better-performing BCP systems may be on the horizon. New and improved chemistry will be vital for improvement in this field. It will certainly be exciting to follow the field of BCP research as it reaches its full maturity in the coming years.

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