

Advances in self-ordering macromolecules and nanostructure design

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Nanostructured macromolecules, such as block copolymers, elucidate the fundamental principles governing self-organization in soft condensed matter. Significant experimental and theoretical advances regarding complex morphology development in bulk copolymers and their homopolymer blends have recently been achieved. New equilibrium block copolymer morphologies have been reported for copolymers in the super-strong segregation regime, and the pathways by which bicontinuous morphologies in copolymers and copolymer blends form have been identified. Emerging research directions target chemically tailored copolymer systems as designer templates for uniform ceramic nanostructures and field-responsive devices with switchable molecular orientation.

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Introduction

Self-ordering macromolecules include those materials capable of forming supramolecular (many chain) aggregates, nanostructures or mesophases, which can, under the right set of conditions, exhibit long-range periodicity [1]. Block copolymers can be envisioned as two or more chemically dissimilar, yet covalently linked, homopolymers, and constitute one of the most widely studied classes of self-ordering macromolecules due to their ability to organize spontaneously into a wide range of nanostructural elements in the same manner as low-molar-mass surfactants [2*,3]. Since the chemical identity of each contiguous repeat unit sequence can be judiciously selected prior to copolymerization, these examples of 'soft' condensed matter also provide numerous opportunities to produce multifunctional materials molecularly tailored for use in specific applications. Most block copolymers are synthetically derived

from the precursors of commodity homopolymers (e.g. polystyrenes, polyacrylates, polydienes and polyolefins), but recent evidence provided by Waite and co-workers [4**,5] indicates that tricomponent (ABC) block copolymers composed of collagen, silk fibroin and elastin likewise occur naturally, in the byssal threads of the mussel *Mytilus edulis*.

Due to their far-reaching versatility and universal self-ordering behavior, block copolymers have fascinated researchers for more than 30 years, and the past year has been no exception, witnessing a steady rise in the number of publications related to these materials. To maintain a manageable focus in the present work, we begin by restricting discussion to only non-solvated, non-ionic block copolymer systems (a second review targets copolymers in the presence of one or more selective solvents). Moreover, while tremendous advances have been realized over the past year in (surface-patterned) thin films, diffusion dynamics, shear-induced alignment and architecture design, several of these topics have been addressed as the subjects of reviews elsewhere [6*,7**] and are therefore not included here. Instead, we concentrate on progress achieved in elucidating the ordering mechanism and morphology stability of block copolymers and their blends, as well as on exciting new technological uses of nanostructured block copolymers in the development of either hybrid or wholly inorganic materials. It must be realized, however, that, despite the narrower focus of this review, not all accomplishments reported in this blossoming field since December 1997 can be mentioned.

Ordering in (non)traditional block copolymers Bicomponent copolymers

The principal molecular factors governing morphology equilibrium in microphase-ordered diblock copolymers are well established [8*,9*,10*] and include measures of monomer pairwise interaction and asymmetry, as well as molecular composition, architecture and chain length. An additional consideration that has been previously shown [11] to influence microphase ordering is hydrostatic pressure. Pressure-induced microphase ordering under isothermal conditions has been reported by Steinhoff et al. [12*] and Ladynski et al. [13], suggesting that the compressible nature of block copolymers may not be negligible in accurately describing block copolymer phase behavior [14**]. Complementary studies by Balsara et al. [15**] and Hashimoto et al. [16*] of ambient-

pressure ordering in copolymers exhibiting hexagonally packed cylinders reveal that morphological development induced by a quench from the disordered state into the ordered state proceeds by nucleation and growth of ordered grains, with the rate of grain growth being proportional to the degree of supercooling. Supporting results have been obtained [17^{••}] for a symmetric (lamellar) diblock copolymer, and have led [18[•]] to the identification of an equilibrium order–disorder transition temperature that is likewise dependent on quench depth due to ordered grains of variable size and shape. A theoretical framework proposed by Newstein et al. [19] to relate grain growth during microphase ordering to scattering patterns indicates that, depending on the quench conditions, copolymer ordering can occur by either single grains or grain clusters, with the latter producing characteristic scattering peaks attributable to intergrain correlations.

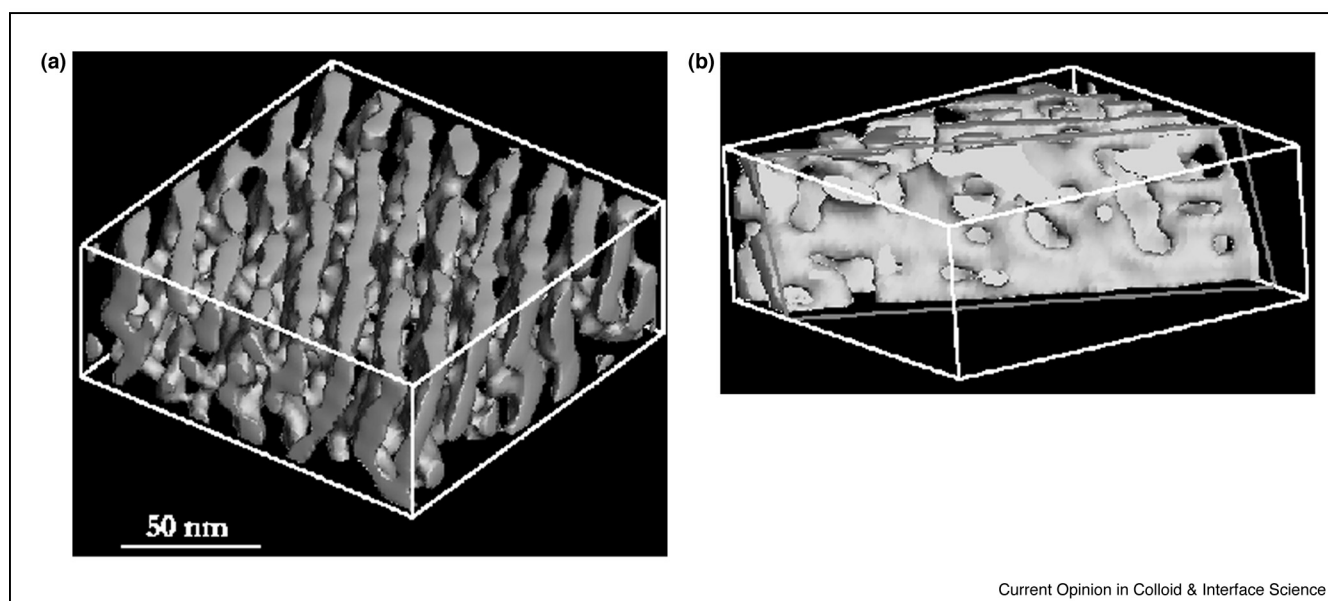
One of the interesting and unexpected real-space observations made by Sakamoto and Hashimoto [17^{••}] is that the embryonic lamellae in a symmetric copolymer quenched from the disordered state into the ordered state initially appear perforated and subsequently solidify. The stability of the perforated lamellar (PL) morphology, shown as a transmission electron microtomograph [20^{••}] in Fig. 1, remains a topic of keen interest, since it was first believed [21] to represent an equilibrium morphology, but was later found [22[•]] to represent a long-lived metastable nanostructure. Recent efforts by Hamley et al. [23[•]] are consistent with the earlier

results of Hajduk et al. [22[•]], and indicate that perforated lamellae may be conveniently accessed through quenching and post-annealing. An exquisitely detailed study examining the morphological transition from the lamellar to gyroid (G) morphologies has been conducted by Hajduk et al. [24^{••}], who have shown that a direct transition between these two morphologies, occurring via nucleation and growth, is energetically unfavorable due to epitaxial mismatch along grain boundaries, and therefore proceeds by way of an intermediate PL morphology. Matsen [25[•]], on the other hand, predicts a direct epitaxial transition from the G morphology to hexagonally packed cylinders. Contrary to this and related [26[•],27[•]] morphological evidence, as well as theoretical predictions for moderately–strongly segregated diblock [28[•]], triblock [29^{••}] and starblock [30[•]] copolymers, Groot and Madden [31[•]] report that, according to dissipative particle dynamics simulations of diblock copolymer microphase separation, the PL, not the G, morphology is stable. Furthermore, super-strongly segregated block copolymers composed of polystyrene and fluorinated blocks have been found [32[•]] to order into two new stable morphologies, one described as quadratically PL (schematically depicted in Fig. 2) and the other as sanidically degenerate cylinders. These new observations suggest that the current understanding of self-ordering in even simple AB diblock copolymers may not yet be complete.

Tricomponent copolymers

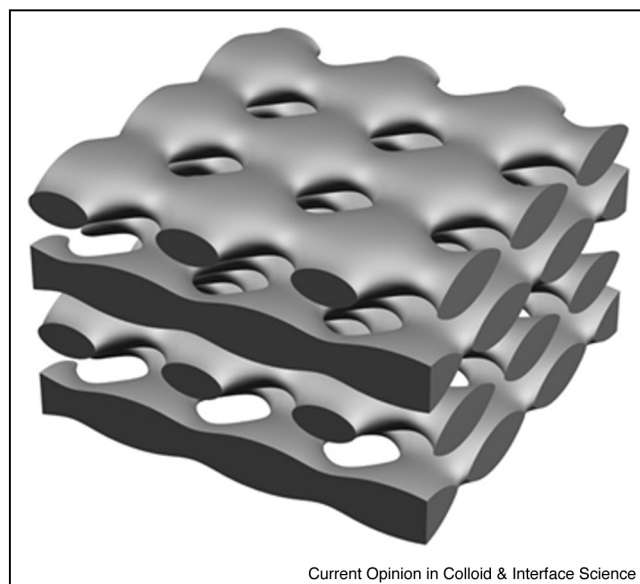
Researchers intrigued by the numerous and concatenate

Figure 1



Transmission electron microtomographs (3-D transmission electron microscopy images, described elsewhere [20^{••}]) of perforated lamellae formed in a triblock copolymer annealed at a temperature just below the order–disorder transition. The image in (b) is a cross-sectional view of the three-dimensional volume element displayed in (a) and clearly reveals the existence of nonperiodic perforations in a lamella.

Figure 2



Schematic diagram of the quadratically perforated lamellar morphology recently reported by Burger et al. [32•] for a copolymer composed of polystyrene and fluorinated blocks in the super-strong segregation regime. (Courtesy of C. Burger.)

morphological possibilities in ABC triblock copolymers were greatly saddened this past year by the sudden and tragic passing away of Prof. Dr Reimund Stadler (Bayreuth, Germany), a visionary and pioneer in this field. He, as well as his benchmark contributions to the field of block copolymers, will certainly be sorely missed. Recent efforts by Stadler and co-workers [33••] have, for example, demonstrated that a ‘knitting pattern’ morphology with an interface of non-constant mean curvature can be induced by hydrogenating the midblock of a poly(styrene-*b*-butadiene-*b*-methacrylate) (SBM) triblock copolymer that initially orders into a lamellar morphology prior to hydrogenation. This morphology has become one of the most exemplary in the block copolymer literature, as it beautifully illustrates the ability of block copolymers to order into elegant (and sometimes unexpected) morphologies. In a related study of an ordered SBM copolymer of different composition, Brinkmann et al. [34] have observed a hexagonally ordered bicylindrical morphology composed of coexisting S and M cylinders in a B matrix. An issue of considerable interest in this vein of research is the nature of the tricontinuous morphologies formed in ABC copolymers. While Mogi et al. [35•] previously reported the existence of the ordered tricontinuous double-diamond morphology, Matsen [29•] and Phan and Fredrickson [36] predict that the gyroid morphology is more stable than the double-diamond in ABC copolymers, even in the limit of strong segregation. These predictions are consistent with the recent findings of

Matsushita et al. [37••], who employed transmission electron microscopy, small-angle scattering and computer simulation to discern that both interfaces in a microphase-ordered poly(isoprene-*b*-styrene-*b*-2-vinylpyridine) copolymer most closely resemble Schoen surfaces (e.g. the G morphology) with threefold symmetry.

Impact of copolymer liquid crystallinity

Over the past few years, an increasing interest in block copolymers exhibiting an additional level, or hierarchy, of supramolecular order has emerged. While the block copolymers discussed in the previous sections have all possessed isotropic blocks that stretch upon microphase ordering, liquid crystalline (LC) block copolymers consist of at least one isotropic block and one block capable of ordering into a nematic or smectic mesophase. The mesogens comprising the LC block can be positioned along the backbone (to form a main-chain LC block) or as side groups along an isotropic backbone (to form a side-chain LC block). Pospiech and co-workers [38,39] have succeeded in synthesizing perfectly-alternating (AB)_n multiblock copolymers that exhibit nematic LC textures due to main-chain mesogens, whereas Yamada et al. [40•,41] have focused on synthesizing well-defined side-chain LC diblock copolymers in which lamellae of a styrenic moiety alternate with lamellae of a smectic A liquid crystal. It is noteworthy that, according to X-ray analysis, the mesogens in the side-chain LC copolymers lie parallel to the lamellar interface, indicating that the smectic layers comprising the LC lamellae are oriented along the lamellar normal.

Matsen and Barrett [42•] have proposed a self-consistent field formalism to predict the phase behavior of main-chain LC diblock copolymers exhibiting a smectic C mesophase. The mesogen tilt angle is predicted to depend on the competition between interfacial tension and isotropic block stretching. By lowering the fraction of the isotropic block (and, hence, the degree of stretching), it is found that a smectic A mesophase (with zero tilt angle) becomes stable. Ferri et al. [43•] have incorporated the main-chain and side-chain LC block copolymer designs into a single diblock molecule, and report that the blocks microphase-order into segregated smectic microdomains. The mesogenic units in each microdomain could, however, be highly aligned upon exposure to a magnetic field, but they retained a distribution of orientations during mechanical alignment.

One of the most exciting developments in this field is the synthesis of LC block copolymers in which the LC segments order into a smectic C* mesophase. Zheng and Hammond [44•] have synthesized a series of such diblock copolymers varying in composition and find that, in low-molecular-weight LC-rich copolymers, the order–disorder transition of the copolymer corresponds

Figure 3

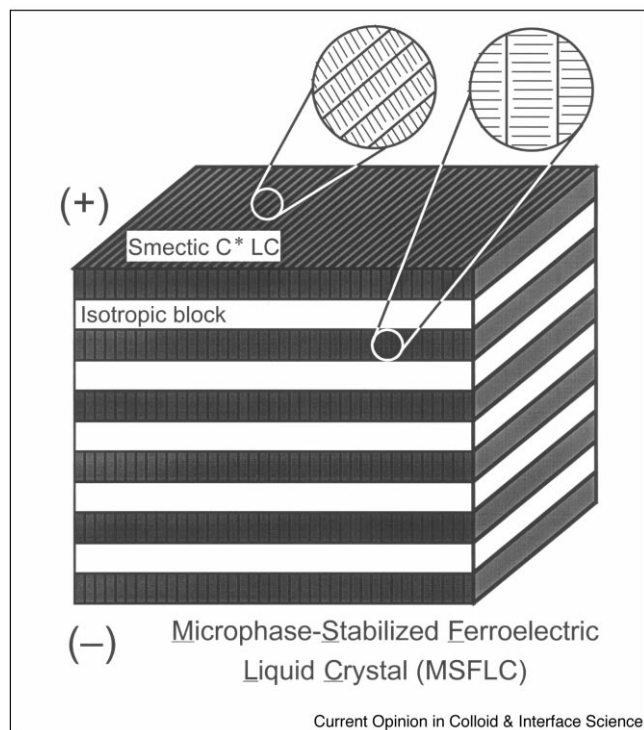


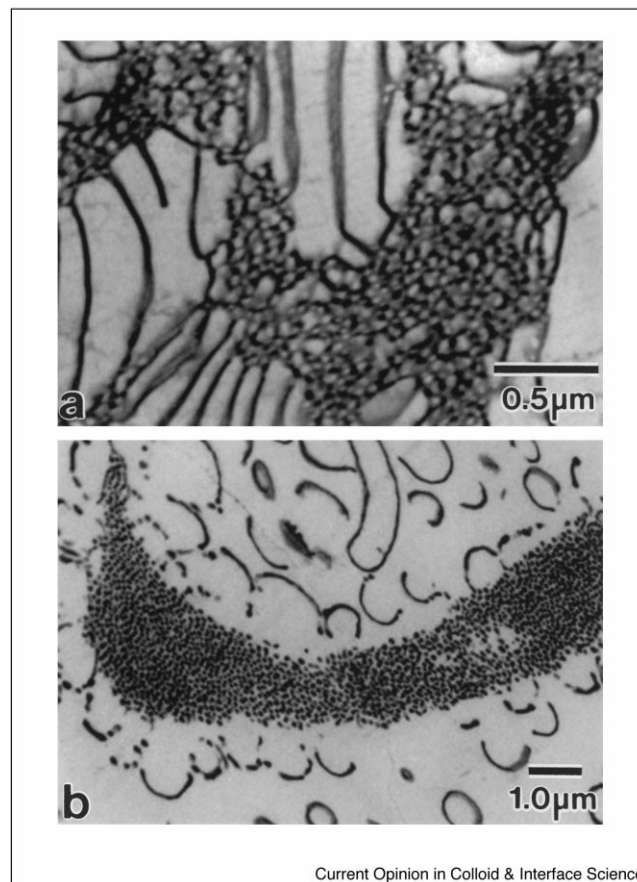
Illustration of the molecular arrangements required for a microphase-stabilized ferroelectric liquid crystal (MSFLC) device [46••] in response to an imposed electric field.

to the clearing temperature of the LC block. It is of interest to note that, in this same vein, Sanger et al. [45•] previously documented a spherical–cylindrical order–order transition induced by the onset of liquid crystallinity in a nematic LC block copolymer. Development of novel materials such as these is keenly driven by the desire to create switchable polymer devices, which has been recently achieved by Mao et al. [46••]. They have successfully shown that the orientation of the ferroelectric smectic C* mesogens in a side-chain LC block copolymer can be reversibly switched, which they attribute to unwinding of the smectic C* pitch. In addition to providing fundamental insight into hierarchical ordering and molecular reorientation in a molecularly constrained environment, this investigation constitutes a technological breakthrough by demonstrating that a ‘microphase-stabilized ferroelectric liquid crystal’ (MSFLC), illustrated in Fig. 3, can be fabricated.

Advances in contemporary copolymer blends

As in unmodified block copolymers, pairwise monomer interactions, molecular weight considerations and copolymer/blend compositions all play crucial roles in the development and stability of morphologies in copolymer/homopolymer blends. Interactions are often collectively expressed in terms of a temperature-

Figure 4



TEM images of a binary ABC triblock copolymer/homopolymer blend [48] demonstrating the existence of (a) the bicontinuous (bilayered) sponge morphology and swollen lamellae at 80 wt./homopolymer, and (b) dispersed micelles and detached bilayers at 90 wt./homopolymer.

dependent Flory–Huggins χ parameter. Maurer et al. [47••], however, contend that, on the basis of small-angle neutron scattering results obtained from polyolefin blends and homologous diblock copolymers, a single χ functionality is insufficient to represent accurately the interactions in copolymer-containing systems due to block stretching and polarization in proximity to the order–disorder transition. Another consideration in the development of morphology in copolymer/homopolymer blends is interfacial modification. In the study reported by Laurer et al. [48], tricomponent block copolymers possessing a random poly(styrene-*r*-isoprene) midblock, along with polystyrene and polyisoprene end-blocks, have been synthesized to alter interfacial packing. These copolymers order into vesicles or a randomly connected, bicontinuous, bilayered ‘sponge’ morphology (see Fig. 4), depending on midblock fraction, in a series of homopolymer-rich blends in which the homopolymer molecules are of sufficiently low molecular weight to wet the compatible copolymer block.

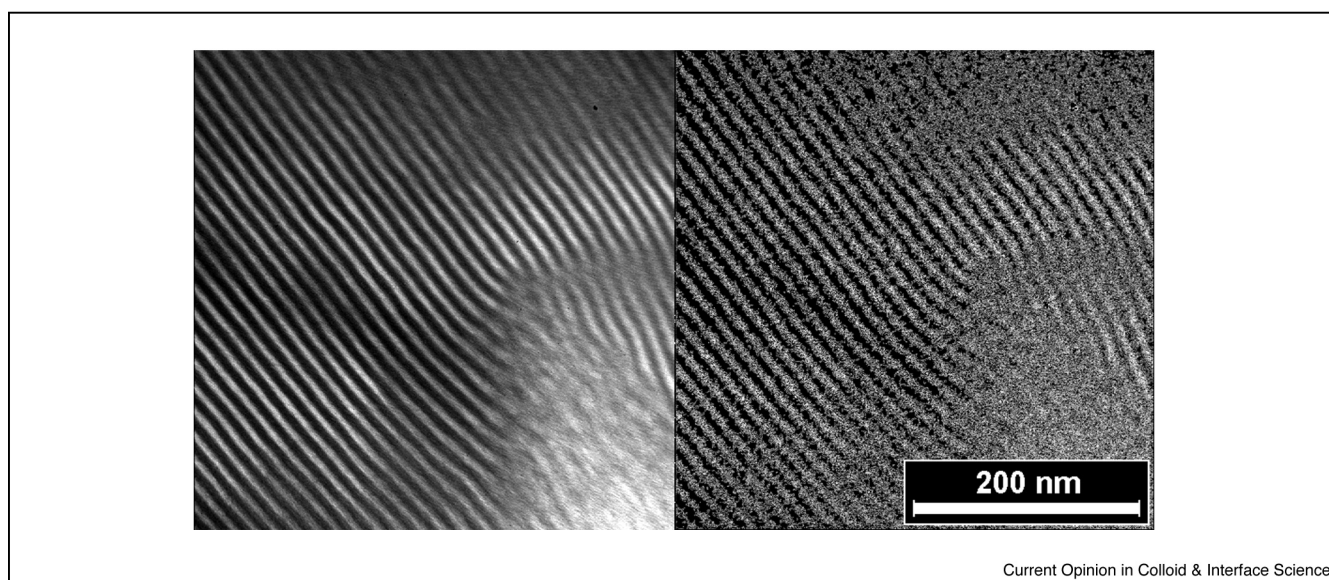
Sponge-like polymeric microemulsions likewise form [49•] in ternary block copolymer/homopolymer blends, and a recent investigation by Lee et al. [50•] describes the time-dependent evolution of microemulsion formation by small-angle neutron scattering. It is found that large-scale defects coarsen, whereas periodic elements comprising the microstructure become more refined with time. Interfacial considerations remain an important topic in the study of compatibilized blends and reveal that copolymer architecture constitutes an important variable in the design of such blends. Cigana and Favis [51•] have shown that, at sufficiently low copolymer concentrations (which preclude formation of copolymer micelles), ABA triblock copolymer molecules are more effective than the corresponding AB diblocks in promoting emulsification. Diblock copolymers produced in-situ during concurrent reactive chain coupling and early-stage spinodal decomposition are, however, predicted [52•] to promote compatibilization more effectively than triblock or graft copolymers under identical conditions. The relative importance of homopolymer wetting along the copolymer-rich interface of compatibilized blends on emulsion stability has been examined by Erukhimovich et al. [53]. This issue is also addressed by Laradji and Desai [54], who investigated the elastic properties (i.e. interfacial bending rigidity) of compatibilized blends and find that this rigidity, unlike that of binary homopolymer blends, can either increase or decrease, depending on copolymer incompatibility and the

molecular weight ratios of the homopolymers to the corresponding copolymer blocks.

Conclusions

Diverse nanoscale structural elements can be systematically and uniformly produced upon macromolecular self-organization in systems containing block copolymers. The major achievements realized in this field during the past year (e.g. identification and analysis of the nucleation-and-growth mechanisms responsible for several order-disorder and order-order transitions) clearly reflect the increasing fundamental and technological importance of this class of 'soft' materials. A contemporary challenge for researchers investigating block copolymers is to apply the ability of block copolymers to self-organize (into periodic nanostructures) to problems at the nanoscale. Clearly, fabrication of MS-FLC devices [46••] constitutes a major step in this direction. Another emerging use of nanostructured block copolymers as templating media is the sol-gel synthesis of nanoporous silica. Silica possessing uniform pores ranging in size from 1 to over 30 nm have been reported by Kramer et al. [55••] and Chmelka, Stucky and co-workers [56••,57••]. Avgeropoulos et al. [58••] have produced complex nanoporous structures by oxidizing triblock copolymers possessing one or more pentamethyldisilylstyrene blocks and exhibiting the gyroid morphology. Instead of producing nanoporous materials, Templin et al. [59••] and Massey et al. [60•] have

Figure 5



Energy-filtered electron microscopy images of the nanostructured aluminosilicates produced by swelling the hydrophilic lamellae of a poly(isoprene-*b*-ethylene oxide) block copolymer with a ceramic precursor and thermoforming the ceramic within the poly(ethylene oxide) microdomains [59••]. The image on the left shows OsO₄-stained polyisoprene lamellae (dark), whereas the one on the right reveals the net silicon distribution (light). (Courtesy of U. Wiesner and A. Du Chesne.)

successfully demonstrated that discrete nanostructures, such as molecular-scale wires and sheets (see Fig. 5), could be produced either from aluminosilicates or ferrosilicates through the use of block copolymer templating. Achievements such as these, coupled with a more thorough understanding of the fundamental factors governing block copolymer ordering (especially in the presence of a liquid crystalline block or a block-selective additive), hold tremendous promise for the facilitated design of uniform organic, inorganic, hybrid and functionalized nanostructures.

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