**Review:** Block copolymers are the focus of a great deal of research activity in contemporary macromolecular science. This is attributable to a range of fascinating fundamental issues associated with understanding self-assembly processes in both solution and in bulk, coupled to an adventitious convergence of substantial progress in synthetic versatility, developments in molecular and structural characterization, understanding of the factors that control phase behavior, and elucidation of the response of copolymer materials to external fields. It is argued that due to the rapid progress in these areas block copolymers now stand on the verge of a new generation of sophisticated materials applications, in which particular nanostructures will play a crucial role. This may be contrasted with the current billion dollar annual market for block copolymer materials, in which no substantial advantage is taken of any particular nanostructure. A variety of persistent challenges are identified that stand between block copolymers and widespread success in novel applications; foremost amongst these are issues concerned with processing.

# Block Copolymers: Past Successes and Future Challenges

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## 1 Introduction

Block copolymers represent a subject of broad current research emphasis across the full spectrum of macromolecular chemistry and physics, ranging from development of new synthetic strategies and molecular architectures to application of advanced theoretical and computational methods. Almost fifty years after the preparation of the first laboratory samples by living anionic polymerization, scientific interest in these materials continues to grow, as does the global market for block copolymer materials. The aim of this article is to provide an individual perspective on this particular facet of macromolecular science, touching both on historical aspects of the field as well as promising future directions. In so doing, I also hope to convey some sense of, and justification for, the excitement that drives academic research in this arena. At the same time this is not intended as a thorough review, and space limitations preclude discussion of many interesting topics.

It will be helpful to introduce some terminology at the outset. Block copolymers containing two distinct monomers A and B have various architectures, such as linear diblock (AB), triblock (ABA), pentablock (ABABA), multiblock or segmented copolymers $(AB)_n$, and star diblocks $(AB)_nX$. When a third ingredient is added, linear ABC, ACB, and BAC triblocks can be prepared, and also three-armed stars. The total degree of polymerization (in terms of a common reference segment), $N$, is proportional to molecular weight, and the composition of the copolymer is expressed in terms of the volume fractions of the blocks $f_A(=N_A/N), f_B$, etc. The thermodynamic interaction between any two dissimilar monomers is given by the dimensionless interaction parameter $\chi_{AB}$ (or simply $\chi$), which is inversely proportional to temperature. It is worth noting an important distinction between the ‘‘theorist's $\chi$’’ and the ‘‘experimentalist's $\chi$’’. The former quantity is a strictly energetic quantity, defined in the spirit of regular solution theory by the exchange energy required to interchange two dissimilar monomers, divided by thermal energy $kT$. The latter quantity is a parameter obtained by fitting some experimental observations to a theoretical relation. As the experimental system is likely to violate one or more assumptions inherent in the theory, the resulting $\chi$ values reflect the influences of the various non-idealities present in addition to the expected exchange energy contribution.

The central thesis of this paper is that the future importance of block copolymers will be founded on two already recognized aspects of their behavior: access to exquisite control over self-assembly, and advanced, ‘‘non-scalar’’ application of the resulting nanostructures. Block copolymers are the pre-eminent self-assembling materials, for the following five reasons:

(i) *Precise control over lengthscale*. Block copolymer microstructures have domain dimensions that can be

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varied continuously from approximately 5 to 50 nm, through the simple expedients of changing molecular weight, monomer structure, and temperature. Dilution with other polymers or solvents can extend this range beyond 100 nm.

(ii) *Control over morphology.* Pure diblock copolymers exhibit four different equilibrium symmetries: lamellae (L), hexagonal cylinders (C), bicontinuous gyroid (G), and body-centered cubic arrays of spherical micelles ($S^{bcc}$). These four span the range of the possible dimensional connectivity of the dividing interfaces: 2, 1, 3, and 0, respectively. In the bulk state the selection of morphology is dictated primarily by composition, but temperature, diluents, and changes in architecture can also be used to modulate the equilibrium structure. By extending to three components, as in ABC triblocks, a much richer variety of phases can be accessed; over 30 have been identified to date, with no obvious limit in sight.[1]

(iii) *Control over domain functionality and properties*. Advances in synthetic techniques allow almost complete freedom in selecting the polymer for each block. This, in turn, allows each block to have properties tailored for ultimate applications.

(iv) *Quantitative prediction of equilibrium structures*. The highly developed self-consistent mean-field (SCMF) theory provides accurate calculations of free energies and composition profiles for the various ordered states. This unprecedented success of a mean-field approach in condensed matter is due to the relative weakness of the thermodynamic interactions ($\chi \ll 1$) combined with the large number of interchain contacts ($\approx N$).

(v) *Retention of the traditional advantages of polymeric materials*. The features that endow polymers with such widespread utility, including cost effectiveness, flexibility, toughness, low density, optical clarity, permeability control, etc., extend naturally to the copolymer case.

The current large-volume applications of block copolymers are ‘‘scalar’’ in the sense that they do not take advantage of any particular nanostructure; rather, they are useful because they retain important features of their constituent homopolymers while suppressing macroscopic phase separation. For example, thermoplastic elastomers such as polystyrene-*block*-polyisoprene-*block*-polystyrene are important in a variety of applications, but it is primarily the microphase separation of the styrene and isoprene segments that leads to robust and reusable elastomeric behavior, rather than any particular ordered structure.[2] Although the material properties do depend on the copolymer composition, and therefore on the ordered state morphology, it is certainly the case that current applications do not rely on any long-range organization of a given morphology. However, the markets for such materials, although growing in volume, are relatively mature. Future new applications are much more likely to be ‘‘vectorial’’ in nature, relying not only on the properties of the components, but also on the particular spatial extent, connectivity, and orientation of the nanodomains. Accordingly, new commercial implementations are more likely to be in high-value-added, specialty markets rather than as commodity polymers.

The remainder of this paper is organized as follows. In the next section we address the following question: how have the research developments of the last 40 years or so brought block copolymers to the brink of a new era of applications? The answer is subdivided into highlights concerning synthesis (Section 2.1), molecular and structural characterization (2.2), experimental and theoretical descriptions of phase behavior (2.3), and rheology and

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processing (2.4). The final section discusses some of the challenges that are the focus of a good deal of current research.

## 2 Developments

### 2.1 Synthesis

The preparation of well-defined block copolymers requires a chain-growth polymerization mechanism that can be conducted in the absence of undesired transfer and termination steps. The anionic polymerization of styrene and isoprene was the first successful demonstration of this approach,[3] although both the precedence and initial impact of this work has been questioned.[2] If the "living" carbanion end of the polymer can be used to initiate polymerization of a second monomer, then an AB diblock can be prepared by sequential addition of monomers. This was one of the original motivations for developing living anionic polymerization (LAP), and remains a key potential advantage of any living polymerization protocol. Diblock copolymers can also be formed by coupling of two appropriately end-functionalized chains. Extension to ABA triblocks was accomplished in the pioneering work of Szwarc,[3] and this architecture represents the majority of commercial materials.[2] There are three possible routes to the ABA structure; in addition to sequential addition of monomers and coupling of two living AB diblocks, a difunctional initiator can be use to grow the chain from the middle outwards. Note that preparation of linear diblocks dates back at least to 1938,[4] and that graft copolymers had been prepared by a wide variety of means prior to the advent of anionic polymerization.[5,6]

Extension of sequential living polymerization techniques to other architectures followed closely the initial introduction of ABA triblocks. For example in 1960 Schlick and Levy reported sequential polymerization of styrene and isoprene (from a difunctional initiator) to prepare $(AB)_nA$ and $(BA)_nB$ with $n = 1, 2, 3$, and 4, i.e., tri-, penta-, hepta-, and nonablock copolymers.[7] The first star block copolymer contained four styrene/butadiene arms.[8] A variety of linear ABC and ABCBA materials were reported in the early 1970s,[9–11] but the first ABC star ("miktoarm") copolymers were not described until 1992.[12,13] Four-component (ABCD) linear[14,15] and miktoarms,[16] and ring-shaped or cyclic block copolymers have also been prepared.[17]

LAP has since been demonstrated for dozens of different monomers, which greatly expands the resulting properties beyond the prototypical styrene/diene materials.[18,19] From the point of view of fundamental studies, one can access most of the major polymer types in this manner, e.g. thermoplastics (styrenes, methacrylates), elastomers (dienes, siloxanes), crystallizable blocks (ethylene oxide), water-soluble blocks (ethylene oxide), anionic blocks (*tert*-butyl methacrylate followed by hydrolysis) and cationic blocks (2-vinylpyridine followed by quaternization). These last two examples introduce a further important concept in the preparation of block copolymers, that of post-polymerization chemical modification. The chain length, composition, and architecture can be fixed by the initial LAP, but the chemical identity of one or more blocks can subsequently be transformed. Ideally the transformation reaction will be sufficiently mild to avoid chain degradation, crosslinking, or unwanted side reactions, but facile enough to permit 100% conversion. The primary example of this approach is the catalytic hydrogenation of polydienes, for example to form poly(ethylene-*alt*-propylene) in the case of 1,4-polyisoprene. Other interesting possibilities, besides the transformation to ionic groups alluded to above, include fluorination,[20] and the introduction of photoactive groups or mesogenic moieties.

Chemical modification is one of two general strategies for overcoming the primary limitation of LAP for block copolymers, namely the restriction to a minority of all interesting or otherwise useful monomers. The other strategy, that of using alternative living or controlled polymerization protocols, has also been highly successful. A variety of block copolymers have been prepared by cationic, group transfer, metallocene and metathesis routes,[21] but it is probably fair to say that the biggest advance along these lines has come with the advent of controlled radical polymerization (CRP) techniques.[22,23] As free radical polymerization is by far the most commonly employed chain-growth scheme, one may reasonably anticipate an increasing role for CRP in block copolymer technology. As a further important point, one is by no means limited to a single mechanism for producing a particular copolymer; the strategy of changing mechanism in mid-stream (i.e., using one block as a macroinitiator for another) is by now well-established. In fact, it pre-dates LAP in the context of graft copolymers, but for model diblocks a pioneering example was the crossover from anionic polymerization of styrene to the cationic polymerization of THF.[24] As multicomponent block copolymers (ABC, ABCA, . . .) grow in importance, the likelihood that all three or four desired monomers may be polymerized sequentially by a single mechanism diminishes, and change of mechanism approaches should become even more attractive.

### 2.2 Solution Characterization

At the time of the first model block copolymers, the primary routes to characterizing molecular architecture were osmometry, light scattering, viscometry, and chemical analysis.[25] While osmometry is in principle unaffected by the copolymer nature of the chain (in a common good solvent for all blocks), the indirect connection of viscosity to molecular weight was potentially problematic (i.e., the individual Mark-Houwink parameters for the blocks could be quite different). Similarly, light scattering was complicated by the multiple component refractive index increments, and the unknown chain-to-chain compositional heterogeneity.[26] Furthermore, there was a longstanding controversy about the conformation of a single block copolymer in solution; could ''segregated'' or ''collapsed block'' conformations occur?[27] Chemical composition could be determined by various chemical analysis schemes, but these were often rather laborious. The advent of NMR spectroscopy as a routine tool for copolymer chemical composition and microstructure,[28,29] and size exclusion chromatography (SEC) for molecular weight distribution,[30] facilitated matters greatly. If the chromatogram indicated a narrow distribution and plausible molecular weight, and if the expected composition was confirmed by NMR spectroscopy, one could be reasonably confident of the molecular structure. If a sample of the first block was extracted during synthesis for later characterization, then a very robust analysis could be performed. Indeed, this combination of NMR spectroscopy, SEC, and extraction of intermediate blocks remains the preferred method of analysis. However, this approach can be limited under certain circumstances. For example, SEC is difficult if a common good solvent cannot be found. Similarly it is challenging to extract information about the distribution of composition independent of the distribution of molecular weight. As the number or type of blocks increases (ABABA, ..., ABC, ...) the extraction of intermediate chains becomes tedious, and potentially hazardous to the integrity of the overall synthesis.

When block copolymers are dispersed in solvents that are selective, and in particular if the solvent (or solvent mixture) is near or below the theta temperature for one of the blocks, micelles will form. Such self-assembled structures, which are typically spherical with aggregation numbers of order 100, have been the focus of intense study ever since the pioneering work.[31–33] The phenomenon of micellization was already well-established for soaps and surfactants, but block copolymers offered potential advantages such as ready access to the critical micelle temperature (cmt), extremely low critical micelle concentrations (cmc), larger and more robust assemblies, and micellization in any desired organic or aqueous solvent. Light scattering is particularly sensitive to micellization, and was the characterization tool of choice prior to the introduction of dynamic light scattering.[34,35] The latter technique, by adding the additional experimental dimension of time, provides crucial information about particle size distributions, which is essential to thorough studies of micellization. More recently, electron microscopy and small-angle scattering (X-rays and neutrons) have provided exquisitely detailed information about micellar morphology and internal structure.[36,37]

Topics of interest in block copolymer micelles beyond structural characterization have included differences in association behavior between diblocks and triblocks, between BAB and ABA triblocks in a B selective solvent, solubilization of homopolymers and other ''guest'' molecules, and the phenomenon known as ''anomalous micellization''.[36,37] More recently emphasis has been placed on amphiphilic block copolymers, and copolymers with polyelectrolyte blocks.[38] Furthermore, a wide variety of non-spherical morphologies have been reported, with worm-like micelles[39,40] and vesicles[41–43] being the most prevalent.

## 2.3 Phase Behavior

The development of the current understanding of the phase behavior of block copolymers has been reviewed in some detail.[37,44] The observation of elastomeric-like properties in ABA systems (and also in multiblock or segmented copolymers) was attributed to ''microphase separation'' of the blocks in the 1960s, but the nanoscopic domain dimensions precluded characterization by optical techniques.[2] The application of transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS), beginning in the later 1960s, enabled both the confirmation of nanoscopic domains of the components and the identification of particular symmetries. The evolution of phases from spheres to cylinders to lamellae to inverted cylinders and inverted spheres was established relatively early,[45] although the bcc symmetry of the sphere phases was not established until later. The extensive work of the Hashimoto group on bulk and solution systems,[46] and of the Strasbourg group in solutions,[47] was particularly influential. The initial emphasis was on mapping the phase behavior as a function of bulk composition and solution concentration, and on the dependence of domain dimensions on molecular weight. Beginning in the 1980s interest grew in the location and characterization of the order-disorder transition (ODT) as a function of temperature, and the observation of thermally accessible order-order transitions (OOT) between phases. The richness of the phase diagram in the vicinity of the ODT, including the presence of an additional phase, the gyroid, and the rheological signatures of the various transitions, became topics of great interest beginning in the later 1980s.[44,46,48]

The first molecular description of the microdomain structure in ordered block copolymers was developed by Meier,[49] and incorporated the essential conceptual ingredient, the competition between interfacial tension and chain stretching. This approach was made more quantitative by Helfand and coworkers,[50,51] who adapted the self-consistent mean-field (SCMF) scheme that Edwards had earlier applied to the excluded volume problem.[52] Similar results were obtained via an analytical theory due to Semenov.[53] In Helfand's version of SCMF the assumption of a narrow interface between microdomains played a central role, which limited the applicability of the theory to the so-called strong segregation limit ($\chi N \gg 10$).

Consequently, thermally induced OOTs between different phases, and the ODT to the disordered melt, could not be treated. Leibler addressed the opposite extreme,[54] the weak-segregation limit, ($\chi N \ll 10$) and adapted the random phase approximation of deGennes[55] to find the limit of stability of the disordered phase. For a symmetric diblock the ODT was predicted to occur at $\chi N \approx 10.5$, and for all other compositions the ODT connected the $S^{bcc}$ and disordered phases. OOTs from $S^{bcc}$ to C and from C to L with increasing $\chi N$ were anticipated. However, many experiments, inspired in part by Leibler's theory, demonstrated the essentially non-mean-field character of the ODT and the nearby disordered state;[44] a quantitative treatment of this so-called "fluctuation regime" remains elusive. In the ordered state, however, the numerical SCMF theory has undergone a series of improvements to the point where it is now considered to be almost quantitatively reliable.[56,57] Computer simulations have also played an important role, and will continue to do so, especially when issues of dynamics are of concern.[48,58]

The interplay of experiment and theory, and some of the difficulties attendant on each, has been rather nicely illustrated by the story of the gyroid (G) phase (space group $Ia\bar{3}d$). Electron micrographs of a structure that was clearly not S, C, or L were first presented by Aggarwal; the name ‘‘wagon-wheel’’ was employed.[59] Thomas and coworkers conducted careful SAXS and TEM measurements on a variety of copolymers, and established the thermodynamic stability of a bicontinuous cubic phase referred to as the ordered bicontinuous double diamond (OBDD, space group Pn3m).[60] At the same time the Hashimoto group obtained similar TEM pictures of a phase dubbed the ‘‘tetrapod network’’.[61] Work on small molecule surfactants had established several bicontinuous phases, including G, OBDD, and the ‘‘plumber's nightmare’’ (Im3m).[62] It was therefore an interesting question as to why block copolymers seemed to favor just one of these. Various attempts to calculate the stability of such phases failed to find that the OBDD structure had the lowest free energy. Ultimately, re-examination of old SAXS patterns, and measurements on new systems, suggested that in fact the observed phase was G.[63,64] Then, the SCMF in the version developed by Matsen and Schick found G to be preferred among the various bicontinuous cubic phases, and indeed under some conditions to be stable relative to S, C, and L.[65] However, the calculations also indicate that with increasing $\chi N$ the G phase should eventually yield to either C or L; this aspect of the experimental picture is not yet clear, partly due to equilibration difficulties with increasing segregation.

### *2.4 Rheology and Processing*

As current large-volume applications of block copolymers are scalar, and furthermore because in many such applications block copolymers are minor ingredients in elaborate formulations, processing strategies are not profoundly different than for other polymeric materials. However, it has been recognized for some time that block copolymer microstructures are quite susceptible to alignment by flow, and more recently that electric fields can also be effective in generating desired alignment, particularly in thin films. The pioneering work was that of Keller's group, which demonstrated the high degree of alignment possible by extruding cylinder- and lamellae-forming styrene/diene copolymers.[66] This theme was advanced when Hadziioannou and Skoulios developed a parallel plate shear device and investigated the alignment process in more detail.[67] More recently there has been a spate of activity, with at least a dozen groups involved,[68] largely inspired by the remarkable observation of Koppi et al. that under different flow conditions lamellae could orient either parallel or perpendicular to the shear planes.[69] In general diblocks and ABA triblocks appear to exhibit similar responses to flow, which gave the impression that chain architecture does not play a major role. However, recent experiments on ABABA pentablocks convincingly refute this notion; the near absence of the parallel orientation, combined with success in producing the ‘‘forbidden’’ transverse orientation, demonstrate that multiblock architectures can yield particular processing advantages.[70,71] The different diblock morphologies ($S^{bcc}$, C, G, L) all exhibit some degree of susceptibility to flow orientation, but even in the linear viscoelastic limit there are clear and useful differences in the response.[72] Consequently, changes in low frequency dynamic moduli are often the most accessible route to characterizing thermally induced OOTs and the ODT.[48]

The application of electric fields to induce net orientation of a block copolymer microstructure was explored in the bulk by Amundson et al.,[73] and in thin films by Morkved et al.[74] The relatively high field strengths required to induce substantial domain alignment (on the order of 100 kV/cm), and the typically sluggish kinetics of domain re-orientation, combine to favor thin film applications for this approach, but success with thicker samples has recently been achieved.[75] A particular exciting development has been the ability to induce block copolymer cylinders to ‘‘stand up’’ normal to the substrate plane under the action of an electric field;[76] this orientation is clearly favorable for potential applications in lithography, patterning, displays, and information storage media.

## 3 Current Challenges

We begin this section by re-iterating the two principal theses: block copolymers are the pre-eminent self-assembling materials, and we now stand on the brink of a new era of ‘‘vectorial’’ applications for block copolymers, that will rely on the nature and orientation of particular nanostructures.

### 3.1 Synthesis and Preparation of Materials

The case can be made that synthetic techniques have advanced to the point where almost any conceivable block copolymer architecture can be made, and furthermore that the chemical composition of each block can be selected as desired. Nevertheless, many interesting challenges remain. Clearly, even if a particular copolymer can be made, its applicability will rely on developing a synthetic route that is sufficiently simple, robust, and scalable to produce commercial quantities. Further development of chemical modification schemes appear particularly promising in this regard, as they offer the potential for tailoring properties of the final materials simply by controlling the extent of modification from one parent batch polymer.

Another class of block copolymers or ‘‘block copolymer analogous’’ materials that offer great promise may be termed ‘‘conformational hybrids’’, i.e., copolymers in which not all blocks are random coils. Examples that have been prepared to date include rod/coil, rod/dendrimer, and rod/inorganic cluster hybrids.[77–81] In addition to accessing new morphologies and providing enhanced properties, such materials can facilitate the integration of particular functionality into the non-coil nanodomains.

An emerging class of applications for block copolymers are as templates for porous materials, such as membranes, catalysts, delivery devices, etc.[82,83] The underlying concept is straightforward to express, but has so far proven rather difficult to achieve: use a block copolymer to form a particular nanostructure, and then remove one block by chemical degradation. The degradation step could be by depolymerization, by cleavage of a pre-placed sacrificial group, or by chemical digestion; examples of all three have been demonstrated. What has proven particularly difficult, however, is to achieve full degradation in a macroscopic sample,[84] as opposed to in a very thin film. Among the difficulties are transport limitations in the nanopores, and defects in the structure that block penetration or escape of the necessary reagents. At the same time, it would also be desirable to develop new methods for fixation of the non-digestible scaffold. Although vitrification is simple enough and adequate for some applications, chemical crosslinking or crystallization that does not perturb the nanostructure would be preferable in many cases.

### 3.2 Discrete Nanostructures

Block copolymer micelles have long been touted for many potential applications, and some have indeed been realized. However, the current advanced state of the art is focused rather heavily on spherical micelles, whereas many more opportunities exist. Spherical micelles of AB copolymers are bounded in size by limits on practical block molecular weights; this restriction is easily lifted with worm-like micelles, disks, or vesicles. The key challenge is to understand how to form such structures on demand, and particularly in the case of disks and vesicles to control their size. Micelles formed from copolymers with only two block types are also restricted to dividing space into two domains, i.e. an ‘‘inside’’ and an ‘‘outside’’. Micelles formed from ABC copolymers offer the potential to form ‘‘structured micelles’’,[85] i.e., assemblies with internal segregation; the past five years has witnessed an explosion of activity along these lines. As one simple illustration of the potential utility of such structures, consider a core-shell-corona or ‘‘onion’’ micelle formed from ABC copolymers as a delivery vehicle. In this case the target molecule could be sequestered in the inner core, with the B shell thickness or permeability designed independently to control the release rate. Another interesting approach is to crosslink one microdomain of an ABC copolymer in the bulk, and then disperse the resulting aggregates; when the B domain formed spheres at the A/C interface, the assemblies are dubbed ‘‘Janus’’ micelles.[86]

### 3.3 New Nanostructures

As noted above, a rich variety of nanostructures have been produced, and especially with ABC copolymers. However, presumably many more structures remain to be prepared and characterized. A key issue becomes to adopt ‘‘structure searching strategies’’ that transcend brute force exploration. For example, in an ABC system there are many parameters that can be varied: total $N, f_A, f_B, \chi_{AB}, \chi_{AC}, \chi_{BC}$, sequence (ABC vs ACB vs BAC) and architecture (linear versus star). Consequently it would be prohibitively time-consuming to map out the entire phase diagram. In concert with this, SCMF has so far been restricted to computing free energies of *proposed* structures; it has no mechanism for predicting structures *a priori*. Furthermore, as the structures become more complex, the calculations become quite time consuming. Some field theoretic schemes towards this end have recently been proposed.[87] Other routes to complex nanostructures, such as blending of AB and BC diblocks, have so far received rather little experimental attention.[88] One potentially important breakthrough in this regard is the development of non-centrosymmetric lamellae by the judicious blending of an ABC with an AC.[89]

The molecular weights of typical block copolymers lead to periodicities in the range of 10–20 nm. For many applications an increase in lengthscale by an order of magnitude or more would be desirable. Although in principle this can be done by increasing $N$, it is not generally practical because molecular weights well in excess of $10^6$ would be required, which incurs both synthesis and processing problems. Consequently, blending and dilution strategies are more promising. An alternate route to larger domain sizes, and indeed to new structures, is to access the so-called super-strong segregation regime.[90] If $\chi$ is made sufficiently large interfacial tension completely overwhelms the chain stretching penalty, and domain dimensions should scale linearly with $N$ (in contrast to the $N^{2/3}$ dependence characteristic of strong segregation). The most direct route to this regime is through the use of ionomeric or polyelectrolytic blocks. Systematic studies of such materials are lacking, as is theoretical treatment at the SCMF level.

### *3.4 Processing*

Although many of the challenges identified above are substantial, it is fair to say that promising routes by which they may be overcome are generally apparent. On the other hand, the challenges in the processing arena are potentially more problematic. Five examples of such issues are the following:

(i) *Preparation of defect-free nanostructures*. A finite population of defects is almost inevitable in any self-assembled copolymer system, because the energy associated with certain defects is quite small. A key *processing* strategy will be to minimize defects by whatever means, whereas a key *design* strategy will be to reduce the liability of the material performance to defects. A related challenge is to develop characterization tools for quantifying and monitoring small populations of defects.

(ii) *Preparation of forbidden orientations*. Some orientations are "natural", e.g. cylinders aligned along the extrusion direction or in the plane of a thin film. Others may be more desirable, but harder to achieve, e.g., cylinders in the circumferential direction of the extrudate, or perpendicular to a substrate plane.

(iii) *Generation of irregular three-dimensional nanostructures*. Copolymer self-assembly provides a natural way to pattern a two-dimensional substrate, or to generate a periodic three-dimensional array. But by analogy to printed circuit boards, or even to certain biological assemblies, it is also desirable to be able to vary the structure aperiodically along a particular direction.

(iv) *Accelerating the kinetics of ordering processes*. Although self-assembly is a promising strategy for producing nanostructured materials, and although in many cases the development of long-range order represents a thermodynamically downhill trajectory, there is no guarantee that the process will be rapid. As a case in point, the development of a well-defined $S^{bcc}$ phase upon cooling from disorder sometimes takes weeks.[91] Methods are therefore required to facilitate the formation of particular phases. One such is to take advantage of order-order transitions, such as $C \rightarrow S^{bcc}$. A sample can be rapidly aligned in C, and the heated into $S^{bcc}$, where the epitaxy provides almost immediately a highly organized cubic structure.[92]

(v) *Decoupling processing and thermodynamic constraints*. Suppose a given application requires a particular nanostructure and particular chemical identities for the blocks; this amounts to specifying $f$ and $\chi$. Furthermore, suppose that processing must be done in the liquid state, before cooling into the nanostructure. This requires that the ODT lie at a convenient temperature, thereby specifying $N$. At this stage there are no degrees of freedom left, but it may well be that the relative rheological properties of the blocks will determine the macroscopic orientation. Consequently, there is a need for ways to modulate the rheological properties of the microdomains without affecting the thermodynamics.

Although these processing challenges and others not discussed here are likely to prove substantial, there is every reason to anticipate success. This optimistic stance is based in no small measure on the fact that research efforts heretofore have been directed disproportionately towards the other areas of interest: synthesis, characterization, and phase behavior. When a greater share of the community's attention is directed to processing issues, rapid progress should ensue.

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