

Hairy Core–Shell Polymer Nano-objects from Self-Assembled Block Copolymer Structures

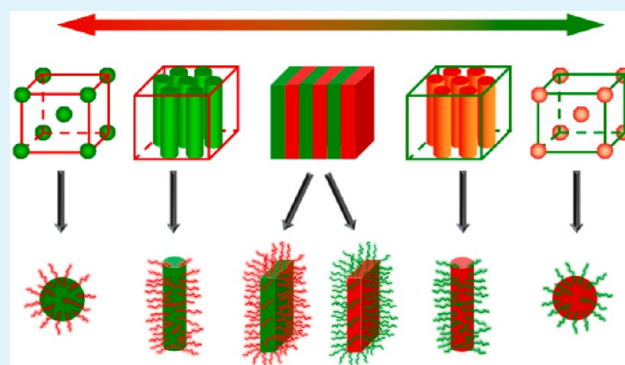
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ABSTRACT: Fabrication of core–shell polymer nano-objects with well-defined shape and hairy shell has been a subject of immense interest in polymer chemistry for more than two decades now. Different approaches such as those involving synthesis (grafting approaches) and block copolymer self-assembly (solution as well as bulk) have been used for the preparation of such nano-objects. Of these approaches that involving bulk self-assembled structures of block copolymers have been of special interest because of the simplicity and range of shape and structures possible. The present review focuses on the advances which have been made in this direction using diblock and triblock self-assembled structures. It will be shown that this approach allows to fabricate hairy nano-objects of not only simple shapes such as spheres, rods, and sheets but also those with more complex shape and morphology such as multicompartment micelles, which are not possible to obtain with synthetic or solution self-assembly approaches. Furthermore, interesting structures such as Janus nano-objects could also be fabricated using this approach. The review further highlights the use of such nano-objects for templating applications.

KEYWORDS: block copolymer, self-assembly, template, nano-objects, functionality



1. INTRODUCTION

In recent years, lot of interest has been shown in shaped nanometer-sized objects—such as nanoparticles, nanotubes, nanorods, nanosheets, etc. These nano-objects have at least one dimension in the range of 1–100 nm. The interest in the nano-objects mainly originates from the fact that they have unique optical, electrical, thermal, and mechanical properties.¹ Moreover, the physical characteristics of these nano-objects can be rationally tailored by manipulating their shape, size, and composition. Though most of the research in this area has been directed toward inorganic nano-objects, recently the nano-objects composed of polymers have also generated tremendous interest.² Whereas the inorganic nano-objects are mostly hard and stiff, the polymeric nano-objects are soft, deformable, and exhibit viscoelastic properties as could be expected of these materials. Furthermore, they are more easily dispersible/soluble in common solvents than their inorganic counterparts and also can be easily functionalized with desired functionalities. Additionally, polymer nano-objects may also exhibit stimuli responsive properties by changing the composition, environment, chemical structure, etc., which makes these materials even more interesting. Hence, the organic (polymer) nano-objects have potential applications in many crucial technologies such as drug delivery, medical diagnosing and imaging/optical probes, catalyst carriers, etc.³ They can also serve as templates for the fabrication of pure inorganic and organic/inorganic

hybrid nano-objects, which further extends the scope of applications of such materials in different fields.

The nano-objects we would like to discuss here include those having an inner compact polymeric core and a densely tethered/grafted and chemically different polymeric shell. Because of the chain stretching, the outermost densely tethered/grafted polymeric shell is essentially hairy in nature, and hence, these nano-objects could be referred to as hairy core–shell nano-objects. The shape of these core–shell nano-objects could be spherical, cylindrical, planar or more complex such as disc, toroid, etc. Several attempts have been made in the past to prepare such shaped hairy polymeric nano-objects.³ The more widely reported approach, at least for the spherical and cylindrical polymer nano-objects, has been those utilizing grafting chemistry principles.^{4–7} In these approaches, a single polymer chain or an organic nanogel network is used as the rigid core and via grafting-to and/or grafting-from methods, polymer chains are grafted on the rigid core resulting in the formation of what is more commonly known as cylindrical or spherical molecular brushes.^{8–12} This approach, of course, is

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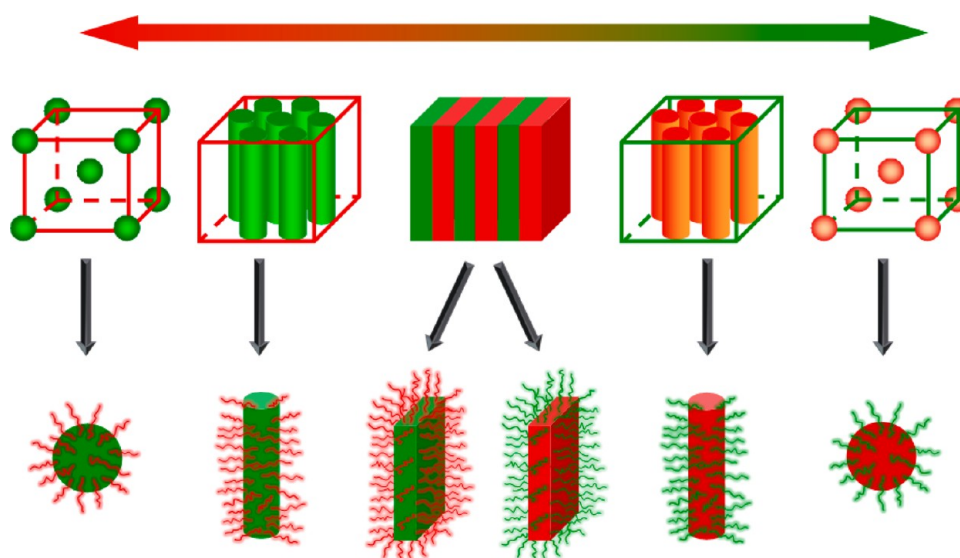


Figure 1. Schematic illustration for the isolation of hairy polymer nano-objects of different geometric shape from the self-assembled morphologies of the block copolymers.

not that straightforward. It involves tedious synthetic chemistry and, moreover, is difficult to upscale for application purpose. In addition, the synthetic approach limits the length/diameter of such cylindrical/spherical molecular brushes that could be prepared.³

The use of block copolymers for the preparation of polymer nano-objects is another interesting approach that has recently attracted significant attention.³ Block copolymers typically consist of two or more chemically dissimilar polymer chains that are covalently bound. The competition between the inherent incompatibility of the constituent polymer blocks and their chemical linkage leads to a self-assembling process with structure sizes in the range of 5–100 nm. The resulting self-assembled pattern formed is determined by the volume fraction of the components, and length scale of the nanoscopic domain is defined by the molecular weight of the copolymer and the strength of the segmental interaction between the blocks. The typical morphological patterns observed for diblock copolymers in bulk include body-centered-cubic (BCC) packed spheres, hexagonally packed cylinders, bicontinuous cubic (gyroid), and 1D stacked alternating lamellae.^{13–15}

The morphology behavior of BCP thin films is more complex as compared to the bulk and depends on a number of additional parameters, such as surface fields, as expression for the interactions of the blocks to the surfaces in the environment, film thickness, substrate polarity, environmental conditions, or sample preparation history, etc.^{16,17} For instance, for the BCP thin films, both substrate-parallel and substrate-perpendicular domain orientation can be realized and governed by variation of the BCP film thickness.¹⁸ On the other hand, domain orientation and domain ordering can be altered using solvent annealing,^{19,20} mechanical flow,^{21,22} by applying external electric field,²³ or exploiting effects provided by the substrates (substrate field effects),^{24,25} or otherwise using chemically or topographically patterned substrates.^{26,27}

There are two basic approaches for preparing hairy polymer nano-objects from the block copolymers. The first approach involves the use of block copolymer solution in selective solvent such that the copolymer forms micellar structures in which nonsoluble block forms the core and the soluble block

forms the shell. Depending on the solvent concentration and the composition of the block copolymers, theoretically spherical, cylindrical, or sheetlike nano-objects can be prepared.^{28–32} Though the principle is simple, the micellar approach to prepare cylindrical and sheetlike polymer nano-objects is not that straightforward. This is attributed to the requirements that have to be matched to produce such nano-objects, i.e., the block copolymers should form micelles of required shape in solution, and the core forming segments must be stabilized.³ Suitable block copolymers for such purpose are still very few because of a narrow window of block copolymer composition to form cylindrical or lamellar micelles. Moreover, as will be discussed later, this approach may not be used for the fabrication of some nonregular/complex nano-objects compared to the other approach discussed below.

The second approach involves the bulk morphology of the microphase-separated block copolymers and is more robust. The reason is that the block copolymers form well-ordered lamellar, cylindrical, and spherical morphologies in a relatively wide range of component windows, and moreover, no solvent interaction needs to be considered. In this approach, the self-assembled structures achieved in the bulk state are dispersed in a solvent selective for the matrix block. Figure 1 schematically shows how the microphase-separated morphologies of the block copolymers could be used to extract individual hairy polymer nano-objects.

The present review focuses on these approaches for fabrication of nano-objects. We will first describe various methods that have been adopted for isolation of nano-objects using self-assembled BCP structures and then review the work which has been done for using these isolated hairy nano-objects for templating applications. Finally, we will outline the future scope of research in this area and challenges ahead.

2. FABRICATION OF HAIRY NANO-OBJECTS FROM SELF-ASSEMBLED BCP STRUCTURES

The approach involves a two-stage process in which first formation of the well-ordered microphase-separated structure of block copolymer is achieved and then, using a selective solvent, the self-assembled domain is isolated. The main

requirement here is that during solvent treatment, the self-assembled domains should not undergo any distortion/deformation. Hence, the solvent used should be strongly selective for the matrix-forming block and have minimal affinity for the minority block that constitutes the nanodomains. Because even in a selective solvent the cylindrical and lamellar domains could readily undergo structural transformation to spherical micelles, these domains need to be stabilized before they are isolated. This has been done mostly using a chemical fixation approach where the minority block forming the self-assembled domains is stabilized by cross-linking. However, this requires the presence of a reactive minority block and, in some cases, may also induce undesired changes in the copolymer properties. Hence, more recently, there have been reports on block copolymer systems where for isolating the nanodomains the cross-linking step is not required. Here, we review both the approaches for preparation of the polymer nano-objects.

2.1. Core-stabilized Nano-objects via Cross-linking.

This approach has been the most widely used for obtaining nano-objects from self-assembled block copolymer structures. The block constituting the core-forming domains to be isolated (spheres, cylinders, sheets) is cross-linked first and then the BCP is swollen in a solvent, selective for the second matrix-forming block. The nano-objects so isolated are stable for a long period of time. The approach was first used by Ishizu and Fukutami, who obtained polymer nanospheres from a sphere forming PS-*b*-P4VP block copolymer.³³ In this case, the P4VP block which constituted the spherical microdomains was cross-linked using 1,4-dibromobutane vapors. The sample was then exposed to an organic solvent (1,1,2-trichloroethane/nitrobenzene, 10/1) selective for the PS block, which resulted in the isolation of the nanospheres with cross-linked P4VP core and hairy PS shell. Subsequently, Liu and co-workers did a significant amount of work in this direction utilizing the core cross-linking approach.

For instance, they used polystyrene-*block*-poly(2-cinnamoyl ethyl methacrylate) (PS-*b*-PCEMA) with UV-cross-linkable cylinder forming PCEMA block (Figure 2a), from which the nanofibers could be isolated.^{34–36} After the microphase-separated structure has formed in bulk, the block copolymer was irradiated with UV light to cross-link the PCEMA block. Subsequently, the bulk samples were swollen by immersion in THF and disintegrated to form the individual hairy nanofibers suspended in THF (Figure 2b). The nanofibers so isolated consisted of UV cross-linked PCEMA as a core and PS as a hairy shell. Later, Liu and co-workers also used polystyrene-*block*-polyisoprene (PS-*b*-PI) block copolymer for producing hairy nanofibers.^{37–39} In this case, the cylinder forming PI block was cross-linked using sulfur chloride before isolating the hairy nanofibers in THF.

Subsequently, following similar approach, Liu and co-workers also fabricated hairy nanotubes by utilizing a triblock copolymer (TBC) instead of diblock.^{40–42} Figure 3 shows the schematic illustration of the procedure adopted. Authors used polystyrene-*block*-poly(2-cinnamoyloxyethyl methacrylate)-*block*-poly(*tert*-butyl acrylate) (PS-*b*-PCEMA-*b*-PtBA) with volume fractions of constituent blocks so adjusted that PtBA and PCEMA formed concentric core-shell cylinders embedded in continuous PS matrix. The TBC solid film was irradiated with UV light to cross-link the PCEMA cylinder shell. The PS-*b*-PCEMA-*b*-PtBA nanofibers were obtained after separation of the cross-linked cylinders by solubilization of the PS chains in THF. Subsequently, the nanofibers were converted into the PS-

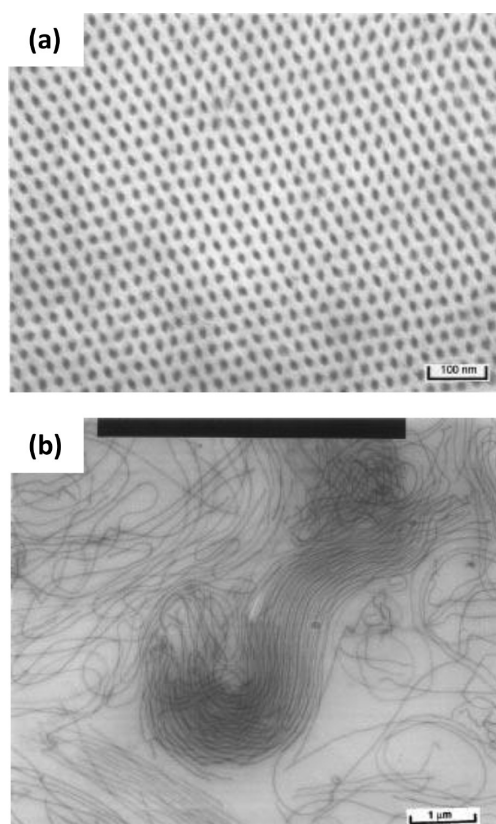


Figure 2. (a) Ordered domain structure of bulk PS-*b*-PCEMA; (b) TEM micrograph of the nanofibers isolated from bulk PS-*b*-PCEMA. Reprinted with permission from ref 34. Copyright 1996 American Chemical Society.

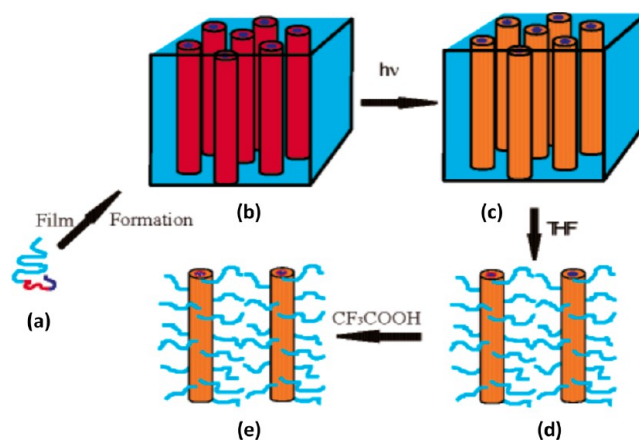


Figure 3. (a) PS-*b*-PCEMA-*b*-PAA TBC; (b) PS-*b*-PCEMA-*b*-PAA TBC solid films with concentric core-shell cylinders composed of PtBA and PCEMA block, respectively, embedded in continuous PS matrix; (c) the TBC solid film after UV irradiation to cross-link the PCEMA shell of cylinders; (d) PS-*b*-PCEMA-*b*-PtBA nanofibers obtained after separation of the cross-linked cylinders by solubilization of the PS matrix chains in THF; (e) PS-*b*-PCEMA-*b*-PAA nanotubes obtained after the hydrolysis of the *tert*-butyl groups of the PtBA cores. Reprinted with permission from ref 42. Copyright 2004 American Chemical Society.

b-PCEMA-*b*-PAA nanotubes after the hydrolysis of the *tert*-butyl groups of the PtBA cores.

Following similar approach of cross-linkable core, Chen and co-workers fabricated hairy nano-objects with controlled shapes

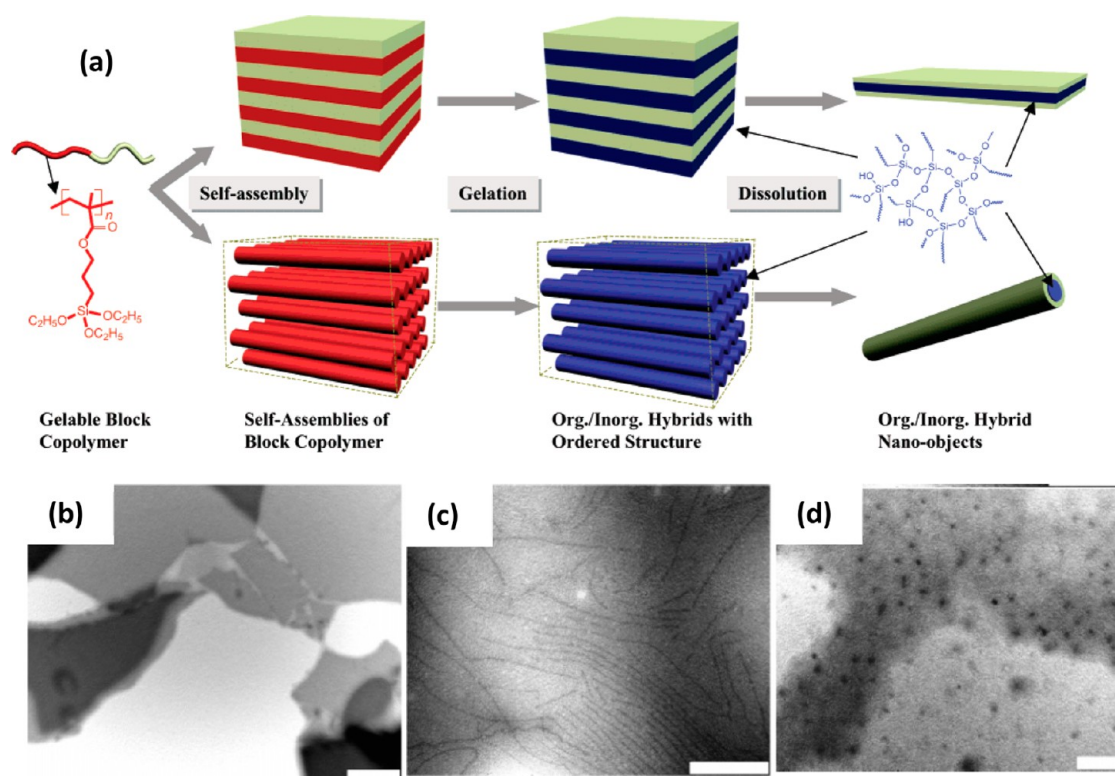


Figure 4. (a) Scheme depicting fabrication of ordered organic/inorganic hybrid materials by self-assembly of gelable PTEPM-*b*-PS block copolymer in bulk and isolated hybrid plates and cylinders (Red, PTEPM block; yellow, PS block; blue, PTEPM + silica network); (b–d) TEM micrographs of the hybrid nano-objects obtained through dispersing the bulk samples in THF after gelation. Scale bar: (a) 1000, (b) 500, and (c) 200 nm. Reprinted with permission from ref 43. Copyright 2007 American Chemical Society.

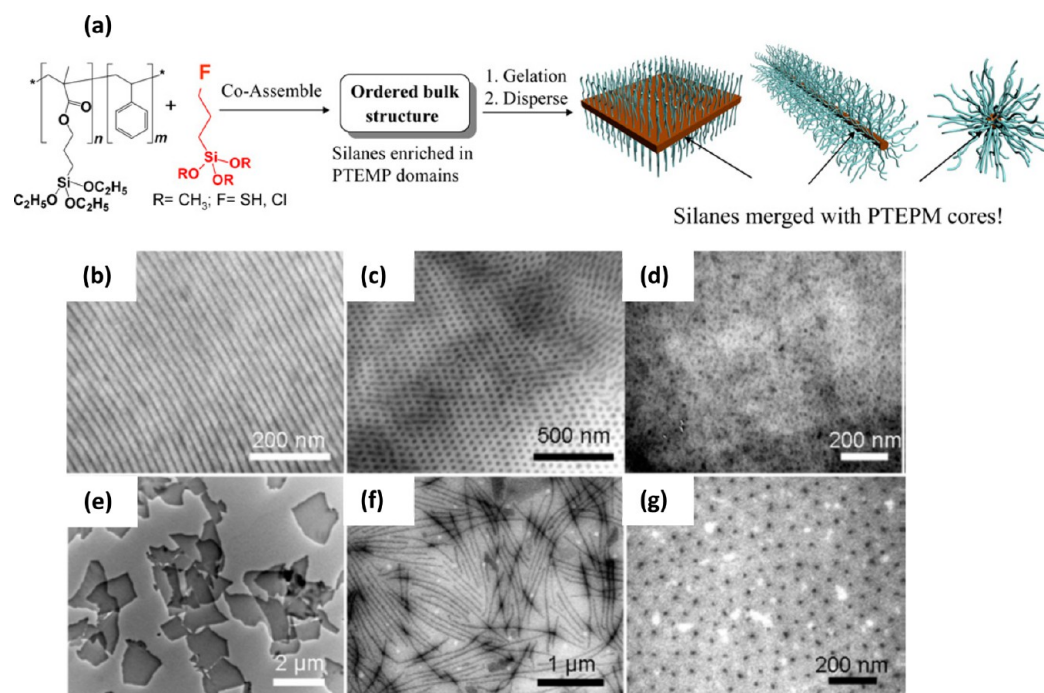


Figure 5. (a) Scheme depicting fabrication hairy polymer nano-objects of different shapes by coself-assembly of PTEPM-*b*-PS block copolymers and functional silanes; (b–d) TEM images of microtomed slices of gelled bulk materials from PTEPM-*b*-PS of different compositions; (e–g) their corresponding hybrid nano-objects by dispersing bulk samples in THF. Reprinted with permission from ref 44. Copyright 2011 Elsevier.

including sheets, cylinders, and spheres.⁴³ However, their concept was slightly distinct because they used block copolymers with a core-forming block, which could be cross-

linked using sol–gel approach. The gelable block copolymer used was poly(3-(triethoxysilyl)propyl methacrylate)-*block*-polystyrene (PTEPM-*b*-PS). By changing the volume fraction

of PTEPM block from 0.38 to 0.20 to 0.11, three different morphologies, i.e., lamella, hexagonally packed cylinders, and liquidlike spheres, were obtained. After the microphase-separated structure had formed, the gelation was carried out in situ in acidic conditions to cross-link the PTEPM phases. Subsequently, the gelled materials were dispersed in THF to isolate the nano-objects with defined shapes, including plates, cylinders, and spheres with PS hairy shell (Figure 4).

It was also shown that the shape of the nano-objects could be appropriately tuned using a single PTEPM-*b*-PS copolymer.⁴⁴ In this case, the morphology of the block copolymer was altered by mixing silanes, such as (3-mercaptopropyl)trimethoxysilane or (3-chloropropyl)trimethoxysilane, with the block copolymer where the silanes selectively enriched into the discontinuous PTEPM microdomains (Figure 5). In a separate work, the same group also demonstrated the fabrication of hairy nano-objects from PTEPM-*b*-P2VP block copolymer.⁴⁵ In this case, the hairy nano-objects so formed had a shell composed of hairy P2VP block and hence depicted stimulus responsive to the pH change.

The nano-objects dispersed well at pH 3 because of the protonation of P2VP chains and by deprotonation at higher pH they were precipitated from the solution (Figure 6). The behavior was completely reversible with changing pH.

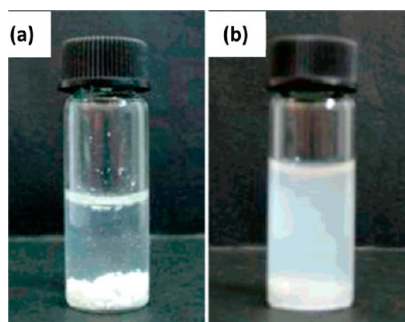


Figure 6. Photographs of the pH-responsive PTEPM-*b*-P2VP nanoplates dispersed in water: (a) pH 9 and (b) pH 3. Reprinted with permission from ref 45. Copyright 2008 American Chemical Society.

In another work, Chen and co-workers used poly(*tert*-butyl acrylate)-*block*-poly(glycidyl methacrylate) (PtBA-*b*-PGMA) block copolymer with the PGMA as a cross-linkable segment and the PtBA as a hydrolyzable segment for isolating nano-objects (Figure 7).^{46,47} First, the microphase-separated PtBA-*b*-PGMA films were exposed to ethylenediamine (EDA) or propargylamine (PA) vapors to chemically cross-link epoxy groups of the PGMA block. The samples were then dispersed in a good solvent (dichloromethane) for PtBA to generate the polymeric nano-objects of plates, fibers, and spheres having cross-linked PGMA cores and PtBA coronas. After hydrolysis of the PtBA segments, the core-cross-linked nano-objects were dispersed in basic water and showed reversible pH responsiveness. Moreover, the pendant alkyne groups of the propargylamine were applied to anchor anthracenes to the cross-linked nano-objects by click reaction with 9-(azidomethyl)anthracene (9-AMA).

Chen and co-workers have also used poly(2-(dimethylamino)ethyl methacrylate)-*block*-poly(3-(triethoxysilyl)propyl methacrylate) (PDMAEMA-*b*-PTEPM)

block copolymer to produce nano-objects with sheetlike, cylindrical, and spherical shapes.⁴⁸

Müller and co-workers have used polybutadiene-*block*-poly(2-vinylpyridine) (PB-*b*-P2VP) with PB as the domain forming block for preparing hairy nanorods.⁴⁹ In this case, the cylinder forming PB block was UV-cross-linked to stabilize the cylindrical domains and, subsequently, the hairy nanorods were isolated in THF or acetone. Similarly, hairy nanofibers were obtained using a cylinder forming polystyrene-*block*-poly(allyl methacrylate) (PS-*b*-PAMA) diblock copolymer.⁵⁰ The minority PAMA block was UV-cross-linked before isolating the cylindrical domains in THF. The hairy PS shell of the isolated nanofibers were further sulfonated to poly(styrene sulfonic acid).

The cross-linking strategy was also used extensively in several other similar works, which primarily were focused on the isolation of nano-objects with more complex shape/structure and have been discussed in later sections separately.

2.2. Nano-objects without Cross-Linking. The approaches used for fabrication of nano-objects from microphase-separated structures of block copolymers, as described above, require the (chemical) stabilization one of the blocks, usually done via cross-linking. In many cases, this makes the process tedious and also limits its applicability to selected block copolymers. In recent years, other approaches have been used which do not necessitate the use of additional domain stabilization step. These approaches involve either the use of block copolymers with high glass transition temperature (T_g) domain forming block or mixing (complexing) block copolymers with easily removable low-molecular-weight additives (LMWA). We now review the work that has been done utilizing these approaches.

2.2.1. BCP with High T_g Domain Forming Block. The principle behind this approach is that the nano-objects prepared from block copolymers have one (i.e., domain-forming) block with sufficiently high T_g , which remain stable for a reasonable time in solvents, selective for the second (i.e., matrix forming) block. Chen and co-workers were the first to demonstrate the applicability of this approach utilizing poly(*tert*-butyl acrylate)-*block*-polystyrene (PtBA-*b*-PS) in which the PS block had $T_g \approx 100$ °C.⁵¹ They showed, that after microphase separation, sheetlike, rodlike, and spherical nano-objects can be isolated in methanol from the self-assembled BCPs with lamellar, cylindrical and spherical bulk morphologies, respectively. It was noted that the polymeric sheets and nanorods obtained from lamellar and cylindrical PtBA-*b*-PS via bulk microphase separation, though thermodynamically unfavorable in methanol, remained “frozen” because of the glassy PS cores, but convert into thermodynamically more stable (favorable) spherical micelles during refluxing in methanol, as traced by TEM (Figure 8). It was observed that during the reflux, dispersed sheets first transform into nanorods and then into spheres, whereas the nanorods gradually convert into spheres. It was also shown that the hairy PtBA shell of these nano-objects can be hydrolyzed to poly(acrylic acid), which provides the possibility of further functionalization of such nano-objects. Hence, this approach makes it possible to obtain different shaped nano-objects and functional nanomaterials starting from the same block copolymer.

Recently, our group has extensively used this approach for fabrication of functional nano-objects from block copolymers.^{52,53} Utilizing this approach, we prepared hairy nanorods/nanofibers starting from a PS-*b*-P4VP diblock copoly-

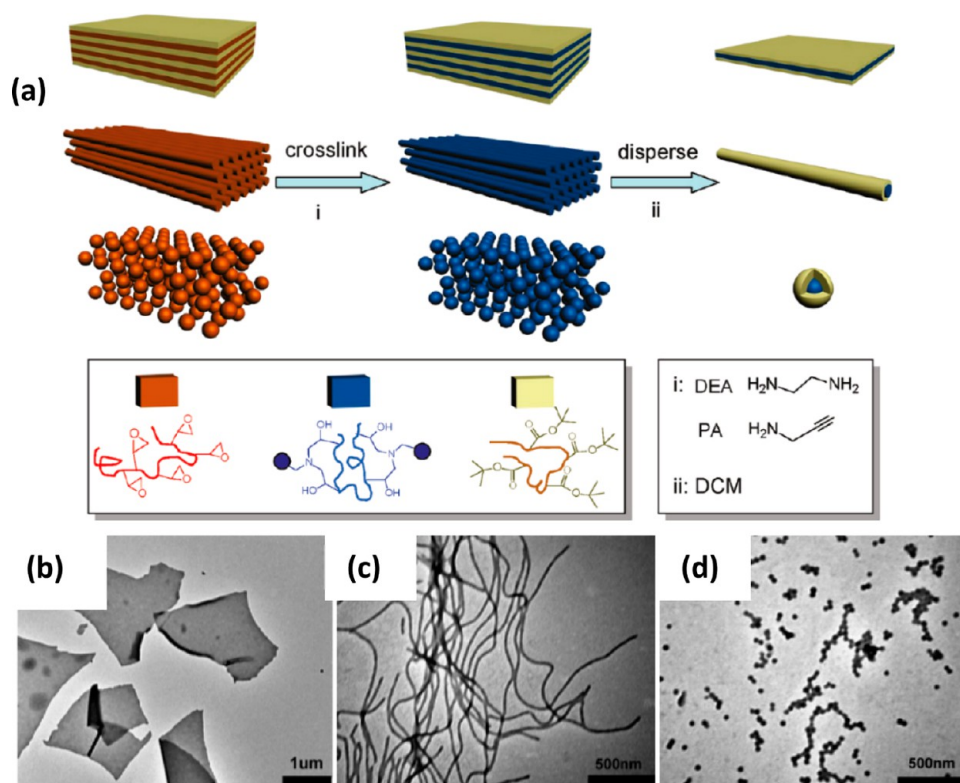


Figure 7. (a) Scheme depicting preparation of functional nano-objects with different morphologies from the microphase-separated PtBA-*b*-PGMA block copolymers via cross-linking of PGMA domains and dispersing in PtBA selective solvent; (b–d) TEM images of the nano-objects obtained from corresponding bulk structures of PtBA-*b*-PGMA after cross-linking the PGMA domains. Reprinted with permission from ref 46. Copyright 2010 American Chemical Society.

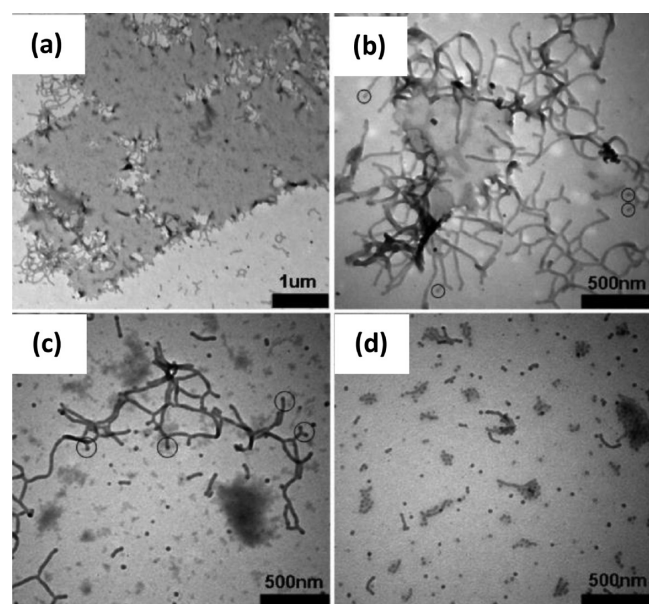


Figure 8. Morphology evolution of the polymer nanosheets obtained from a lamellae forming PtBA-*b*-PS block copolymer by refluxing in methanol for (a) 2, (b) 5, (c) 10, and (d) 24 h. Reprinted with permission from ref 51. Copyright 2010 American Chemical Society.

mers.⁵² The dispersion of cylinder forming PS-*b*-P4VP BCPs in methanol, a selective solvent for P4VP, results in the formation of cylindrical nanofibers composed of PS core covered with hairy P4VP shell (Figure 9). Importantly, these nanofibers in dispersed state are stable enough to be utilized as templates to

generate functional hybrid nano-objects or hollow nanostructures (see Section 5 for more details). Furthermore, the diameter of the nanofibers could be tuned either by utilizing block copolymers of different molar masses, maintaining an appropriate block ratio, or alternatively, by mixing PS-*b*-P4VP with PS homopolymer to swell cylindrical PS domains of the BCP.

2.2.2. Approaches Based on Supramolecular Assemblies. The supramolecular assembly approach involves the use of the block copolymers in combination with low molecular weight additives (LMWA), for instance, small organic molecules. In this approach, first a supramolecular complex is formed via selective noncovalent binding of LMWA to one of the blocks, which ultimately constitutes the matrix phase of the self-assembled morphology. The supramolecular complex thus formed is then allowed to undergo microphase separation to form the self-assembled structures typical for block copolymers. Subsequently, the LMWA is extracted using a selective solvent and, in this process, the self-assembled block copolymer domains get dispersed in the solvent.

The first attempt in this direction was made by ten Brinke and co-workers.⁵⁴ They used a symmetric PS-*b*-P4VP block copolymer and pentadecylphenol (PDP) as the LMWA. On mixing the two in appropriate ratio, the PDP selectively binds to the P4VP block via hydrogen bonding and hence creates compositional asymmetry in the diblock supramolecular assembly. The supramolecular complex thus formed was allowed to self-assemble into a structure where the PS block formed the cylindrical domains whereas the matrix was composed of P4VP(PDP) complex. Dissolution of PDP using

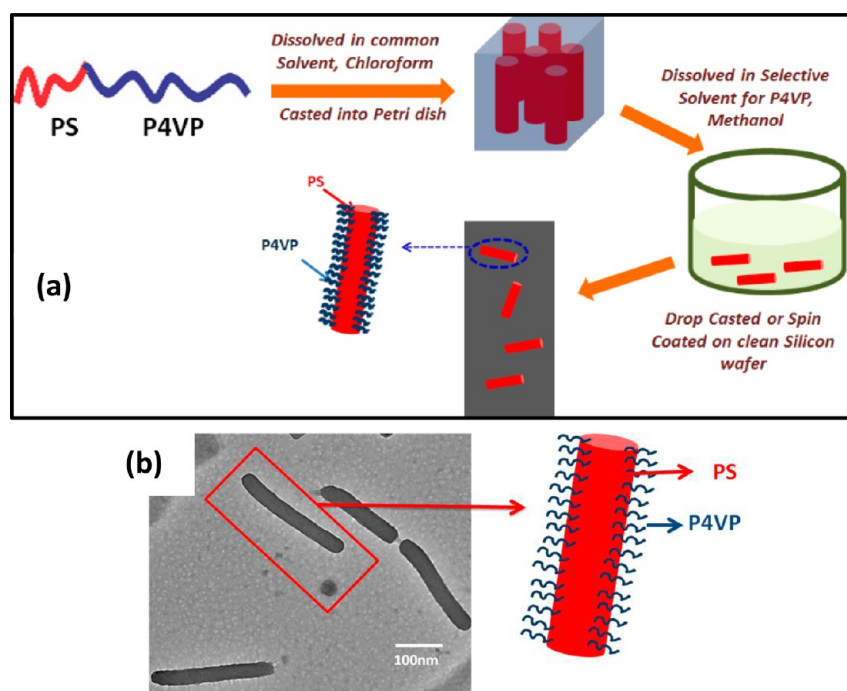


Figure 9. (a) Schematic illustration of isolation of polymer nano-objects from PS-*b*-P4VP bulk structure without any cross-linking; (b) TEM image of the nanofibers obtained. Reprinted with permission from ref 52. Copyright 2012 Royal Society of Chemistry.

ethanol resulted in the isolation of individual nanofibers composed of PS core and P4VP shell (Figure 10).

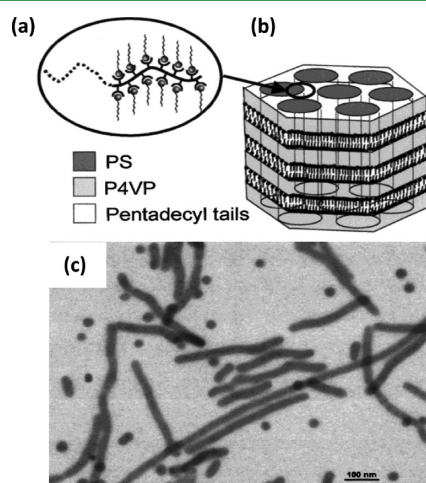


Figure 10. (a) Schematics to form the supramolecular assemblies from a PS-*b*-P4VP diblock copolymer and low molecular weight additive (PDP); (b) the initial self-assembled hexagonal structure before the removal of the PDP; (c) STEM picture of cylindrical nano-objects obtained from the bulk cylindrical morphology. Reprinted with permission from ref 54. Copyright 2001 American Chemical Society.

Stamm and co-workers also used the PS-*b*-P4VP(PDP) supramolecular assembly system to isolate hairy nano-objects.^{55–58} Authors were successful in isolation of nanosheets from ultramicrotomed sections prepared from bulk samples. Furthermore, using melt extrusion and large amplitude oscillatory shear, they obtained nanofibers with very high aspect ratio because of the alignment of the cylindrical microdomains along the flow direction. Recently, Zhu and co-workers have also extensively used the PS-*b*-P4VP(PDP)

system for fabricating functional nano-objects which will be discussed in later sections.^{59–61} Lee et al. used supramolecular assemblies of PS-*b*-PEO and dodecylbenzenesulfonic acid (DBSA) for isolation of hairy nano-objects from spin-coated PS-*b*-PEO/DBSA thin films.⁶² Both cylindrical as well as spherical nano-objects were isolated with PS as a core and PEO as corona (Figure 11). Cylindrical nano-objects were isolated both from thin film structures in which the orientation of cylinders was either parallel or perpendicular to the substrate. Whereas the length of the cylindrical nano-objects obtained from substrate-perpendicular cylinders could be altered by changing the film thickness, that for substrate-parallel morphology was found dependent on the kinetics of the structure formation (Figure 11b, c).

3. NANO-OBJECTS WITH COMPLEX SHAPES

Most of the work in this area has been directed toward isolation of nano-objects with shapes, which are typical for self-assembled domains formed by diblock copolymers. Hence, there is a lot of work where the nano-objects shape is spherical, cylindrical, or sheetlike as discussed in previous sections of this article. However, there are also reports in literature on preparation of nano-objects with more complex shape and structure. In this section we intend to discuss the work done on fabrication of such nano-objects.

There are mainly two approaches to generate such complex structures. The first concept is to use the block copolymers that could self-assemble to form such complex morphologies. For example, ABC-type TBCs, which display a much richer spectrum of phase morphologies than AB diblocks, can be used for such purposes. The second option is to allow the block copolymers to undergo self-assembly under cylindrical or spherical confinement. It has been shown that under confinement, the diblock copolymer can self-assemble to the morphologies that are much more complex than that observed in bulk.

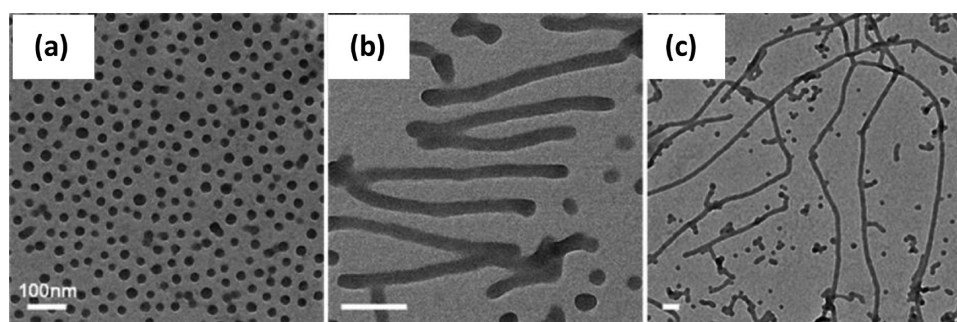


Figure 11. TEM images of the nano-objects prepared from PS-*b*-PEO/DBSA complexes with EO:DBSA stoichiometric ratios of (a) 0.5 yielding with spheres and (b, c) 1.0 yielding with cylinders, obtained after eliminating DBSA from the complexes. The nano-objects in parts b and c were obtained from the PS-*b*-PEO/DBSA thin films with cylinders oriented perpendicular and parallel to the surface, respectively. Reprinted with permission from ref 62. Copyright 2010 American Chemical Society.

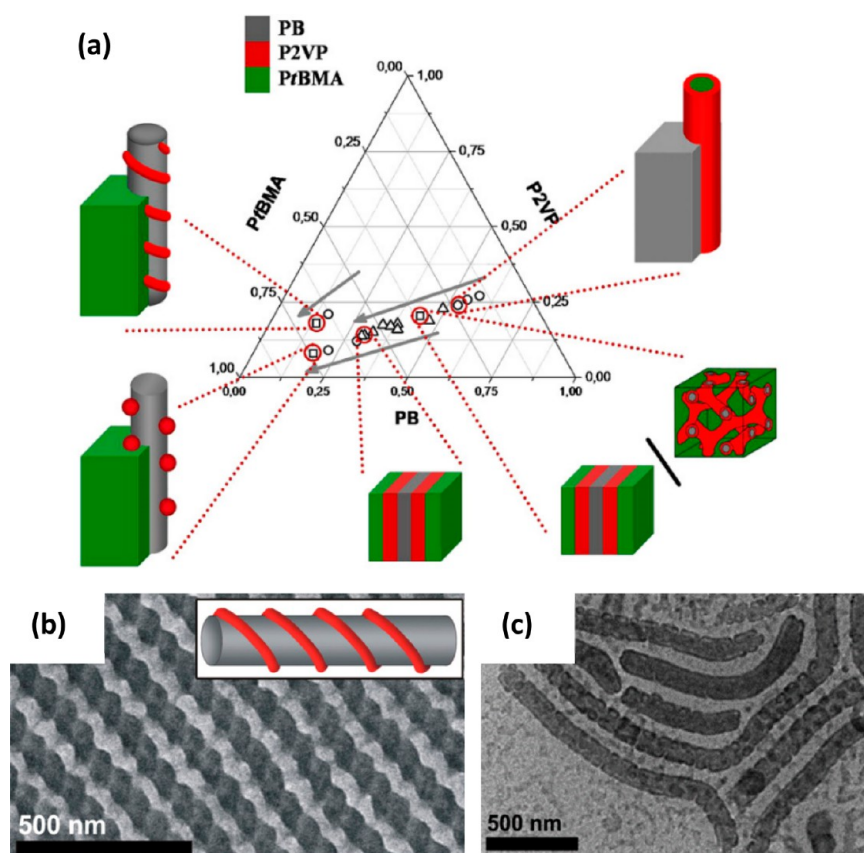


Figure 12. (a) Ternary phase diagram obtained for several series of BVT block terpolymers: the gray phase resembles polybutadiene, the red phase poly(2-vinylpyridine), and the green phase poly(*tert*-butyl methacrylate); morphologies are lamellar, cylindrical, or either mixtures or unusual structures (spheres on cylinders or helices on cylinders); (b) TEM micrograph of B14 V18T68 cast from THF after staining with OsO₄; the inset depicts the plausible bulk morphology with PB cylinders (gray) carrying a P2VP helix (red) embedded in a PtBMA matrix; (c) TEM micrograph for B14 V18T68 after 5 min sonication and drop-coating onto a TEM grid. Reprinted with permission from ref 64. Copyright 2010 Elsevier.

Among others, Müller and co-workers have done some very interesting and comprehensive work in this direction. They used TBCs of different composition and architecture to generate what they called “multi-compartment self-assembled nano-objects”.^{63–67} In one such work, they studied the self-assembly of polybutadiene-*block*-poly(2-vinylpyridine)-*block*-poly(*tert*-butyl methacrylate) (PB-*b*-P2VP-*b*-PtBMA; BVT) TBCs of varied block ratios.⁶⁴ Thus, 18 different BVT terpolymers with different volume fractions of the blocks were synthesized and characterized in terms of bulk morphology using SAXS and TEM, unveiling mostly lamellar

patterns or hexagonally arranged cylindrical structures (Figure 12).

Some polymers displayed a partial gyroid structure coexisting with lamellar parts or cylinders with a noncontinuous shell around the PB core, which served as interesting template for the facile generation of multicompartmental self-assembled structures. In one case, the middle block, P2VP, formed a helix around the cylindrical PB core embedded in PtBMA continuous phase. Cross-linking of the polybutadiene compartment was performed in bulk using UV-photoinitiator, followed by sonication-assisted dissolution of the aggregates.

In another work, using BVT terpolymer, but with different composition, they found that the particular TBC had a bulk microstructure of PtBMA-embedded PB cylinders surrounded by a P2VP double helix (Figure 13).⁶⁵

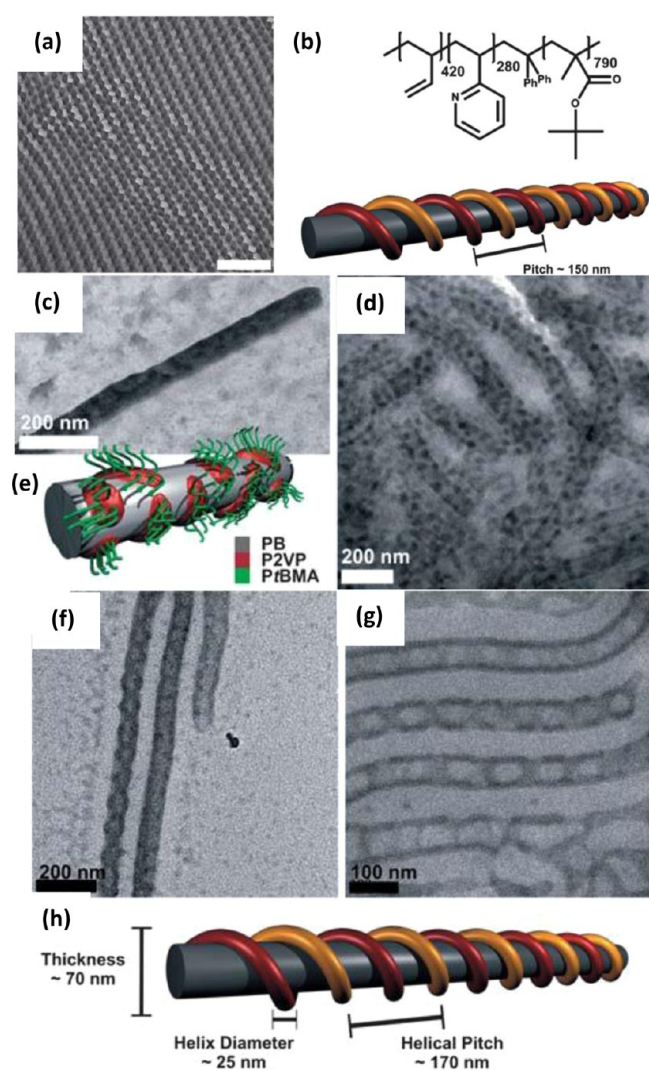


Figure 13. (a) TEM micrograph showing the bulk morphology of B420 V280T790, the scale bar corresponds to 500 nm; (b) structure, composition, and schematic bulk morphology, depicting a P2VP double helix with a pitch of roughly 150 nm; (c) TEM micrographs of BVT cylinders after staining with iodide; (d) cryo-TEM micrograph of BVT in THF after cross-linking and sonication; (e) proposed solution structure of the block terpolymer particles; (f) TEM micrograph of core-cross-linked and quaternized BVqT cylinders cast from THF:MeOH 80:20 mixture; (g) cryo-TEM image of the same sample; (h) proposed solution structure highlighting important distances, the two strands of the P2VPq double helix are shown in yellow and red for easier visualization. Reprinted with permission from ref 65. Copyright 2011 Royal Society of Chemistry.

Hence, after the PB cylinders were selectively cross-linked using UV-photoinitiator (Lauricin-TPO), subsequent sonication-assisted dissolution and chemical modifications (i.e., quaternization of P2VP and hydrolysis of PtBMA) resulted in core-cross-linked amphiphilic cylinders soluble in both organic and aqueous media. Authors studied the influence of cross-linker concentration and sonication treatment on size and shape of the cylindrical aggregates, revealing that cylinders

always exhibit a compartmentalized corona. Under certain conditions (e.g., quaternization of P2VP in mixtures of THF and MeOH), the helical arrangement of the P2VPq shell was also preserved in solution, whereas in most other cases, randomly distributed P2VP/P2VPq patches were observed.

Another interesting work published by the same group refers to the BVT terpolymer having tetragonally perforated lamellar structure in bulk, which was used for fabrication of well-defined porous sheets with tunable pore size. The cross-linking of the central perforated PB lamella with UV-photoinitiator followed by sonication-assisted dissolution in nonselective solvents like THF led to an isolation of micrometer-sized lamellar sheets with tetragonally arranged pores.⁶⁶

Later, the same group also demonstrated the preparation of highly periodic nanoporous sheets and core-shell cylinders from a stimuli-responsive triblock terpolymer, polybutadiene-*block*-poly(*tert*-butyl methacrylate)-*block*-poly(2-(dimethylamino) ethyl methacrylate) (PB-*b*-PtBMA-*b*-PDMAEMA).⁶⁷ Here, they tuned the morphology by blending terpolymer with either PtBMA or PDMAEMA homopolymers. This resulted in the formation of a variety of bulk morphologies, including rarely found examples, such as tetragonally perforated lamellae and double gyroid networks. Selective cross-linking of the PB domains followed by sonication-assisted dispersion allowed the preparation of well-defined nanostructures in nonselective solvents. Because of the PDMAEMA corona, the cross-linked structures were soluble in aqueous media. The high regularity of the pore diameter in combination with a tunable pore permeability by two external stimuli, pH and temperature, render such perforated lamellae particularly appealing for potential applications as membrane materials (Figure 14).

Müller and co-workers have also shown that cross-linking of the bulk structure of a miktoarm star terpolymer based on PB, P2VP and PS leads to novel polymeric multicompartiment cylinders (MCCs) with a very desirable distribution of the compartments parallel to the cylinder long axis. The complex structure of MCCs so isolated could hardly be imagined to be recreated by a solution self-assembly approach.⁶³

Zhang et al. used poly(2-vinylpyridine)-*block*-poly(3-(triethoxysilyl)propyl methacrylate)-*block*-polystyrene (P2VP-*b*-PTEPM-*b*-PS) TBC to generate nanofibers with three concentric layers.⁶⁸ The nanofibers had the middle layer composed of gelable PTEPM block, whereas the core and the shell were composed either of PS or P2VP. Moreover, they used the same triblock to generate also Janus nanosheets, which will be discussed in the next section. Zhang et al. also were able to fabricate a novel sandwichlike nanoplates from P2VP-*b*-PS-*b*-PTEPM terpolymer, consisting of an inner PTEPM layer sandwiched first by PS and then by P2VP layers.⁶⁹

As discussed earlier, the other interesting approach for fabricating complex shaped nano-objects is from the self-assembled block copolymer morphologies generated under confinement. The diblock copolymers under a cylindrical or spherical confinement could produce a variety of self-assembled morphologies depending on the degree of confinement and interaction between the diblock and confining surface. There are some excellent reviews summarizing some of structures possible under confinement.^{70,71} The earliest work dealing with the isolation of polymer nano-objects obtained from self-assembled block copolymer structure in confined geometry was reported by Zhang et al.⁷² In this work, PTEPM-*b*-PS block copolymer was first converted to aerosol form composed of spherical particles with the size in micrometer range. On self-

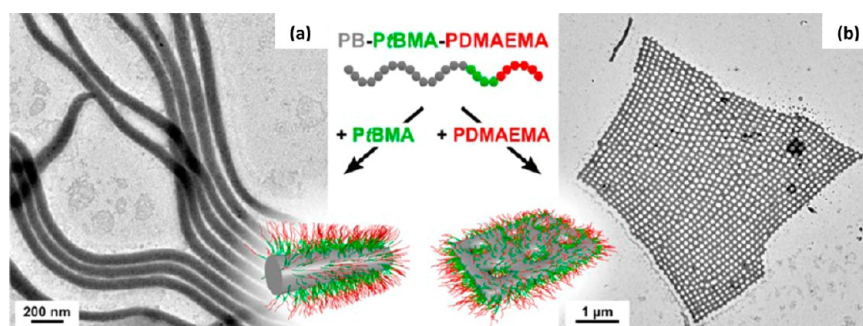


Figure 14. TEM micrographs of core-cross-linked cylinders obtained from B37T24D39 blends with 10 vol % PtBMA after swelling of the films in THF. The inset in (a) shows a schematic representation of the core-cross-linked cylinders in THF; (b) TEM micrographs of cross-linked perforated sheets obtained from B37T24D39 blends with 10 vol % PDMAEMA after sonication for 7 min. The inset in b shows a schematic representation of the cross-linked perforated sheets in THF. Reprinted with permission from ref 67. Copyright 2014 American Chemical Society.

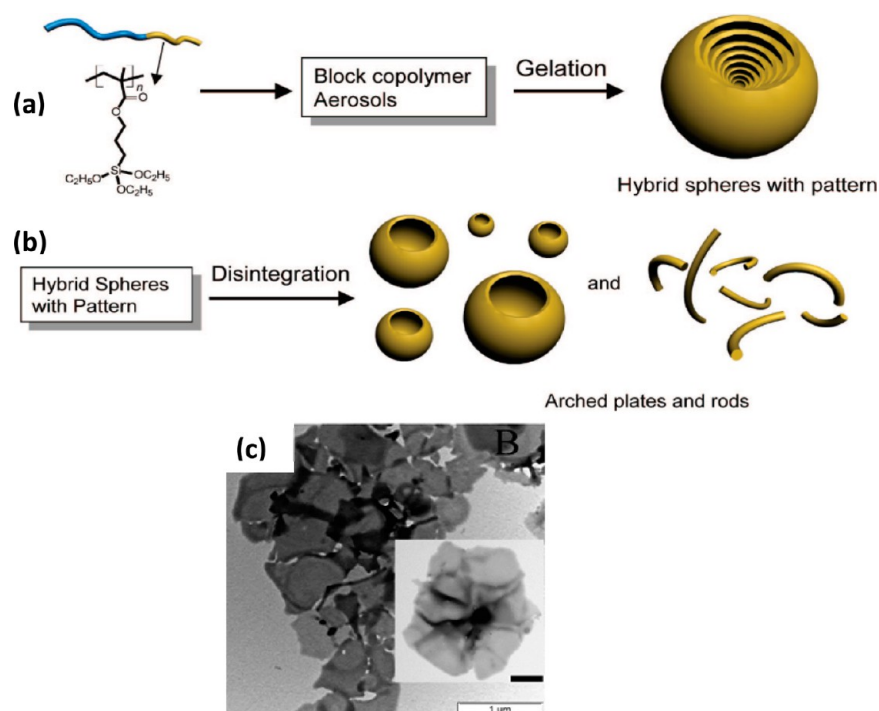


Figure 15. (a) Self-gelation of block copolymer assembly in aerosols to produce mesostructured spheres of organic/inorganic hybrid; (b) disintegration of the spheres with internal pattern into individual arched organic/inorganic hybrid nano-objects; (c) TEM images of the hybrid curved nanoplates obtained by dispersing the disintegrated hybrid spheres in THF; the inset in B is a single plate (bar: 500 nm). Reprinted with permission from ref 72. Copyright 2008 American Chemical Society).

assembly, the spherical particles of block copolymer with different internal patterns, such as onionlike, lamella, and curved cylinder, were obtained. After cross-linking of the gelable PTEPM block, the hybrid spheres were further disintegrated by dispersion in a good solvent (THF) for PS. As a result, novel nano-objects such as arched plates and cylinders were prepared (Figure 15). In another work, the same group used a TBC, poly(3-(triethoxysilyl)propyl methacrylate)-*block*-polystyrene-*block*-poly(2-vinylpyridine) (PTEPM-*b*-PS-*b*-P2VP) to produce the nano-objects of with curved geometry.⁷³ Similarly to a diBCP case, the onion-like microspheres, but now with three alternate layers were obtained by aerosol-assisted self-assembly. The PTEPM layers of the highly ordered concentric curved lamellar structure were cross-linked and, by dispersion in acidic water, the onionlike polymeric spheres were broken yielding sandwichlike curved nanoplates.

Recently, Deng et al. combined the block copolymer supramolecular assembly and spherical confinement to obtain complex hairy polymer nano-objects.⁷⁴ The supramolecular assembly was formed by PS-*b*-P4VP and PDP where the P4VP to PDP molar ratio was varied to tailor the morphology. Supramolecular particles with various shapes and internal structures were prepared by confining PS-*b*-P4VP(PDP) in emulsion droplets such that PS formed the dispersed phase, whereas P4VP(PDP) formed the continuous phase. Subsequent disassembling of supramolecular complex by breaking the hydrogen bonds disintegrated the particles to generate individual nano-objects with tunable shape, including nanocups, nanodiscs, nanotoroids and superaggregates. The nano-objects consisted of a PS core and P4VP corona, were dispersible in alcohol or acidic aqueous media and exhibited pH-stimuli responsiveness. Besides, pyridine group could also induce a favorable growth of other materials such as inorganic shell and

metallic nanoparticles (NPs) to extend the composition and the microstructure of the nano-objects as discussed in next section (Figure 16).

4. JANUS NANO-OBJECTS

Janus nano-objects are bicompartimentalized, noncentrosymmetric objects where the two sides or surfaces have different chemical and/or physical properties. They have gained significant interest in recent years and a number of reviews related to their preparation and properties have appeared in the

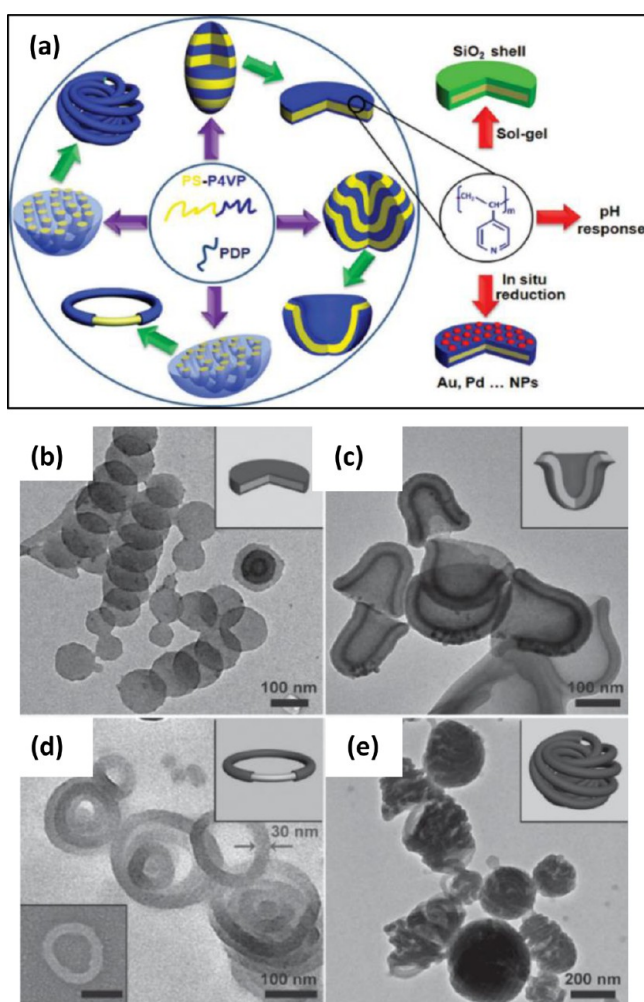


Figure 16. (a) Illustration showing the synthetic strategy toward the nanostructured particles through self-assembly of PS-*b*-P4VP(PDP)_{*x*} under 3D soft confinement (indicated by the purple arrows) and the corresponding nano-objects derived by disassembling of the parent nanostructured particles (indicated by the green arrows), as well as the favorable growth of other functional species onto the nanoobject surface (indicated by the red arrows); (b–e) Bright-field TEM images of the nano-objects of various shape and internal structure obtained via disassembly of PS-*b*-P4VP(PDP)_{*x*} supramolecular complexes under 3D confinement: (b) nanodiscs from the ellipsoids with stacked discs after disassembling with ethanol; (c) nanocups from bud-like particles with stacked cups; (d) nanotoroids from ellipsoids with stacked toroids inside. Inset is the scanning electron microscopy (SEM) image of a nanotoroid; (e) SAs from PS-*b*-P4VP(PDP)_{0.8} supramolecular particles with internal tortuous cylindrical structures. Insets in the upper right are the cartoons displaying the core–corona structure of the nano-objects. Reprinted with permission from ref 74. Copyright 2013 Wiley–VCH.

past few years.^{75–78} The noncentrosymmetric architecture provides Janus particles with unique properties that are not accessible for homogeneous analogues. For instance, their broken symmetry leads to the formation of a variety of complex superstructures, which cannot be obtained from simple particles, thus representing fascinating building blocks for the construction of hierarchical assemblies and materials.⁷⁸ Block copolymer self-assembly has been one of the approaches used for obtaining Janus nano-objects. This approach mainly utilizes the self-assembled structures formed by ABC-type TBCs and was pioneered by Müller and co-workers.^{78–86} The rich phase diagram of such TBCs is well-known where the self-assembled structures depend on the volume fraction of the blocks and relative incompatibilities between the respective blocks. Figure 17 shows the phase diagram for polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) (SBM), one of the most widely studied triblock terpolymer system.⁷⁸ The approach essentially involves tuning the bulk morphology in such a way that the outer A and C blocks are nearly symmetric, thus forming lamellar phase, whereas fraction of the middle B block is varied so as to tune the morphology of B domains from spheres to cylinders to lamellae. Once the terpolymer assembles into the desired morphology, the structure is locked by cross-linking the middle block. From such middle-block locked structures Janus nano-objects can be prepared very easily by dispersion in a suitable solvent and typically have nearly monodisperse size and shape.⁷⁸ Moreover, the shape and size could easily be engineered by varying the volume fraction and molecular weight of the blocks, respectively.

The very first work in this direction was done almost simultaneously by Saito et al.⁸⁷ and Erhardt et al.⁷⁹ In both works, the isolation of spherical Janus nano-objects from self-assembled ABC TBC system was reported. Saito et al. used polystyrene-*block*-poly(2-vinylpyridine)-*block*-poly(*tert*-butyl methacrylate) (PS-*b*-P2VP-*b*-PtBMA).⁸⁷ The terpolymer casted from a toluene solution self-assembled to form spherical P2VP domain embedded in lamellae formed by PS and PtBMA blocks. The spherical P2VP domains were cross-linked using 1,4-diiodobutane and subsequently isolated in THF where the two opposing sides of the nanospheres were capped with hairy PS and PtBMA chains. In a similar work and almost concurrently, Erhardt et al. isolated spherical Janus nano-objects (i.e., Janus micelles) using PS-*b*-PB-*b*-PMMA terpolymer.⁷⁹ In this work, the cross-linking of the PB spherical domains was accomplished using S₂Cl₂ or radical polymerization via a cocast radical initiator. The Janus micelles so isolated could be transformed into strongly amphiphilic and water-soluble Janus micelles via alkaline hydrolysis of the PMMA part into poly(methacrylic acid) (PMAA). Furthermore, both species showed remarkable hierarchical self-assembly behavior in solution.^{79,80} These Janus nanospheres were used recently by Müller and co-workers as effective supracolloidal dispersant for carbon nanotubes.⁸⁶ The same strategy was also used to prepare Janus discs and Janus cylinders.^{81,82} For Janus discs, a PS-*b*-PB-*b*-PtBMA terpolymer with full lamellar morphology was used and PB block was cross-linked after the BCP self-assembly. Subsequently, Janus sheets were released by sonication of the self-assembled structure. Under sonication, the particle size decayed in an exponential fashion, and a fragmentation of the Janus sheets into significantly smaller ones occurred. The average sizes could be tuned from the micrometer level down to the nanometer scale. It was found that the smaller particles revealed rather

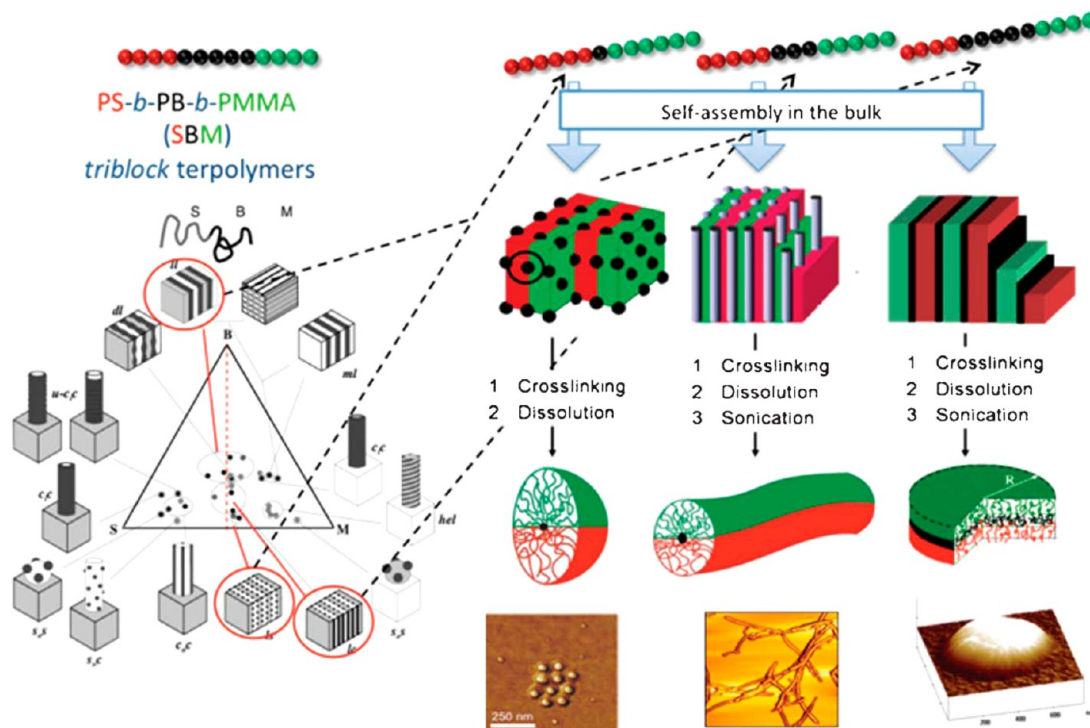


Figure 17. Janus nano-objects of different architectures prepared via the selective cross-linking of the middle block of triblock terpolymer bulk phases and subsequent dissolution. Left: Phase diagram of SBM. Right: Synthetic strategy toward Janus spheres, Janus cylinders, and Janus discs. Reprinted with permission from ref78. Copyright 2013 American Chemical Society.

circular appearance, which was suggested to originate from sonication-induced rounding off. These Janus discs were also rendered strongly amphiphilic via facile acidic hydrolysis of PtBMA into PMAA, resulting in water-soluble Janus discs with one PS and one PMAA side.⁸² The Janus cylinders were obtained by using a PS-*b*-PB-*b*-PMMA terpolymer assembled into cylinder-in-lamellae morphology.⁸¹ The cylinder-core forming PB block was cross-linked before dispersing it in a solvent (THF) using sonication. It was revealed that the length of the Janus cylinders could be adjusted by both the amplitude and the duration of a sonication treatment from the micro- to the nanometer length. Furthermore, the Janus cylinders were also found to form superstructures in selective solvents (THF/chloroform).^{81,84}

Recently, Müller and co-workers also demonstrated that the careful choice of the solvent and cross-linking conditions can be used to manipulate triblock terpolymer bulk structures in a way that allows to prepare three different types of nonspherical Janus particles as well as spherical ones from one single triblock terpolymer.⁸⁵ They used poly(*tert*-butoxystyrene)-*block*-polybutadiene-*block*-poly(*tert*-butyl methacrylate) (tSBT), from which Janus sheets, Janus cylinders, and an intermediate new structure, Janus ribbons, were isolated. The microphase-separated structures were manipulated with selective solvents and different cross-linking conditions (UV/S₂Cl₂) which allowed us to tailor the various morphologies. The Janus ribbons with exactly two Janus cylinders connected along their long axis were obtained by trapping a metastable state during a phase transition. Fully water-soluble Janus cylinders with a pH-responsive poly(hydroxystyrene) side and a permanently water-soluble PMAA side were obtained after hydrolysis of the protecting groups.

Foldable Janus sheets were prepared by Gao et al. from P2VP-*b*-PTEPM-*b*-PS terpolymer.⁸⁸ The terpolymer had an all

lamellar morphology, where the PTEPM lamellar domain was cross-linked following sol-gel route. The nanosheets obtained after dispersion in solvent (THF) had one side tethered with PS chains and the other side with P2VP. These Janus sheets were found to be foldable by the addition of acidic water to their dispersion in THF. When acidic water was added to mixture of sheets and PS spheres in THF, dumpling-like complexes of two different nano-objects were obtained by wrapping the spheres with the sheets (Figure 18).

Recently, Deng et al. prepared Janus nanodiscs from a diblock copolymer.⁸⁹ The self-assembled block copolymer precursor structure consisted of alternating lamellar layers of

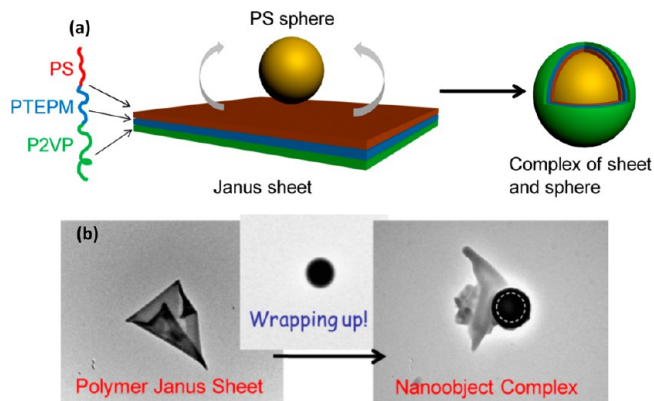


Figure 18. (a) Schematic illustration of a foldable Janus sheet, PS sphere, and the formation of dumpling-like complex driven by the hydrophobic interactions. (b) TEM images depicting wrapping of nanosphere by Janus sheet to form the nanoobject complex. Reprinted with permission from ref 88. Copyright 2012 American Chemical Society.

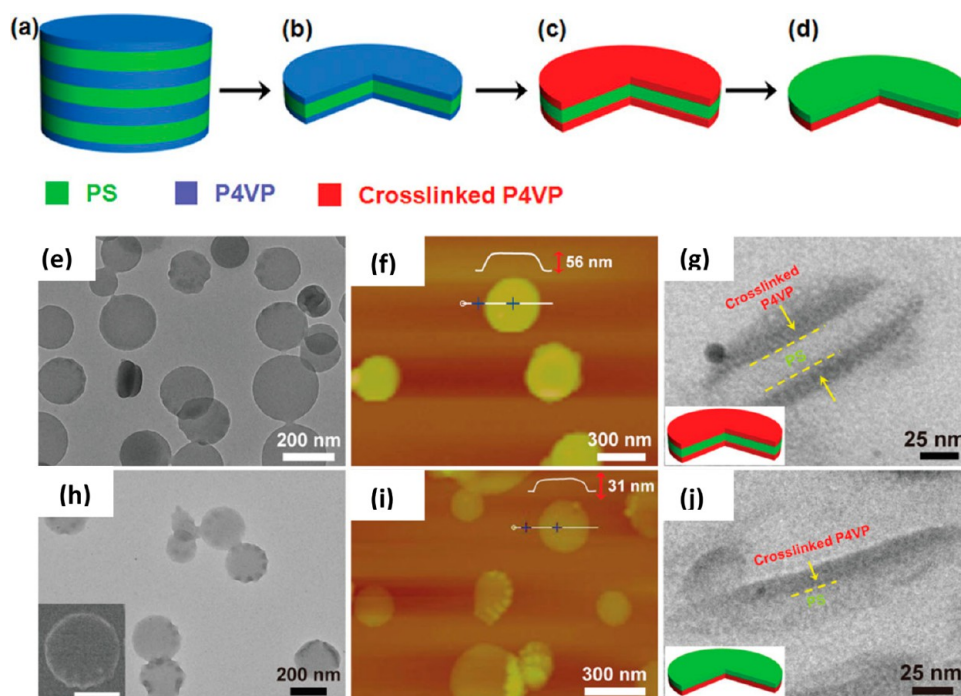


Figure 19. (a–d) Illustrative synthesis of the Janus nanodiscs. (a) Disc-stacked particles of PS-*b*-P4VP diblock copolymer by emulsion droplet confined self-assembly; (b) P4VP/PS/P4VP sandwiched nanodiscs by selective disassembling the P4VP layer of (a) using a P4VP selective solvent; (c) cross-linking both the top and bottom P4VP layers of (b) with 1, 5-diiodopentane; (d) Janus nanodiscs by selectively disassembling PS intermediate layer of (c) using a PS selective solvent; (e) TEM image and (f) AFM image of the cross-linked sandwiched nanodiscs; (g) cross-section TEM image of the cross-linked sandwiched nanodiscs; (h) TEM image and (i) AFM image of the Janus nanodiscs after complete selective disassembly from the intermediate PS layer; (j) cross-section TEM image of the Janus nanodiscs. Reprinted with permission from ref 89. Copyright 2014 Wiley–VCH.

PS and P4VP were formed by emulsion droplet confined assembly of PS-*b*-P4VP solution. Using P4VP selective solvent (e.g., ethanol), the droplets are partially disassembled into P4VP/PS/P4VP sandwiched nanodiscs. Both the top and bottom P4VP layers are then cross-linked with 1,5-diiodopentane, ensuring integrity of the Janus nanodiscs after disassembling the intermediate layer with a PS-solubilizing solvent, for example chloroform (Figure 19).

5. POLYMER NANOOBJECTS AS FUNCTIONAL TEMPLATES

The hairy polymer nano-objects of various shapes, as described above, have been used for hosting/directing inorganic and/or organic/inorganic hybrid nano-objects of various geometries. This involves either loading the functionality in the dense core of the polymer nano-objects or functionalization of the hairy shell. Below we review the two approaches separately.

5.1. Hairy Shell as Host for Functionality. The primary requirement for hosting functionality in the shell is that the polymer block constituting the shell should be chemically active i.e. should be capable of strong interaction with the guest molecules/particles. From all the works discussed in previous sections, the most widely used polymeric shell as host have been PAA and P2VP(P4VP). Both pyridine, as well as acrylic acid moiety have strong ability to coordinate with metal salts/nanoparticles etc. Zhang et al. used the polymer nano-objects obtained from PTEPM-*b*-P2VP block copolymer to support and organize inorganic nanoparticles (Figure 20).⁴⁵

The Au NPs were organized on the nano-objects of different shapes by binding them onto the P2VP hairs. Because the P2VP block is pH sensitive, the hybrid nano-objects obtained

also demonstrated pH responsiveness.⁴⁵ In another work, core-cross-linked PB-*b*-P2VP block copolymer nanofibers were used as templates for the synthesis of Keggin-type heteropolyoxometalate (POM) nanostructures by grafting [SiMo₁₂O₄₀]⁴⁻ Keggin ions on the template.⁴⁹ The produced POM exhibited high dispersion and improved surface area and are thus expected to be useful in catalytic, electrochemical, and biotechnology-related applications. Mullner et al. used the hairy nanofibers obtained from cylinder forming PS-*b*-PAMA diblock copolymer to template titania nanorods (Figure 21).⁵⁰

The minority PAMA block in this case was photo-cross-linked before isolating the cylindrical domains in THF. The hairy PS shell of the isolated nanofibers were sulfonated to poly(styrene sulfonic acid) (PSS) and then infiltrated with presynthesized positively charged titania nanocrystals. The nanowires disperse well in polar solvents and arranged into porous nonwoven mesostructures with high surface area upon drying, which keep their shape after calcination.

Recently, we also have demonstrated that hairy nano-objects, such as nanofibers and nanospheres, can be functionalized if they are prepared from BCPs without core or shell cross-linking step.^{52,53} Thus, nanofibers and nanospheres isolated from self-assembled asymmetric PS-*b*-P4VP using P4VP-selective solvent (methanol) were stable enough to be functionalized with silica shell or with gold nanoparticles attached to the P4VP shell. Similarly, non-cross-linked PS nanofibers with P4VP hairy shell obtained via SMA approach were prepared by Fahmi et al. and further converted to metallized nanowires. The P4VP shell, in this case, was used as the reactor to synthesize and host Pd nanoparticles.⁵⁶ In other work, presynthesized CdSe nanoparticles were directly adsorbed onto the P4VP shell of the

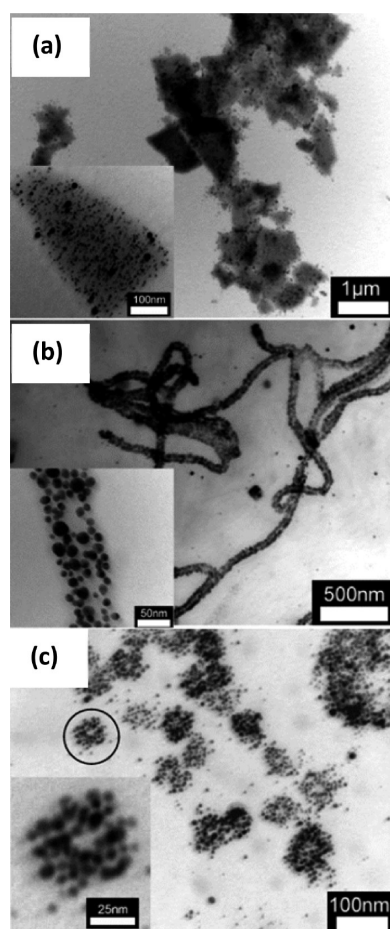


Figure 20. TEM micrographs of the hybrid nano-objects loaded with gold nanoparticles dispersed in water (pH 3). The BCPs used were: (a) PTEPM₃₈-*b*-P2VP₄₇₄, (b) PTEPM₃₇-*b*-P2VP₅₄₀, and (c) PTEPM₃₅-*b*-P2VP₁₃₆₀; here, the subscripts denote degree of polymerization of each BCP, whereas the insets on each image are the magnified parts of particular nano-objects bearing gold nanoparticles. Reprinted with permission from ref 45. Copyright 2008 American Chemical Society.

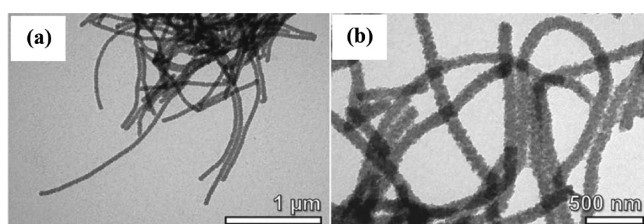


Figure 21. TEM images of as-synthesized titania nanorods obtained using nanofibers, isolated from PS-*b*-PAMA, as templates. Reprinted with permission from ref 50. Copyright 2012 Royal Society of Chemistry.

nanofibers.⁵⁵ More recently, Deng et al. also used the self-assembled structure formed by PS-*b*-P4VP(PDP) SMA confined in emulsion droplets to produce nanodiscs with double side P4VP hairy shell which were further functionalized with SiO₂ and Au NP (Figure 22).⁷⁴ The Au NP-functionalized nanodiscs showed the plasmon absorption peak in UV-vis, whereas the presence of P4VP chains also made the nano-objects pH responsive.

Müller and co-workers used the nano-objects of more complex shape and morphology for templating the growth of

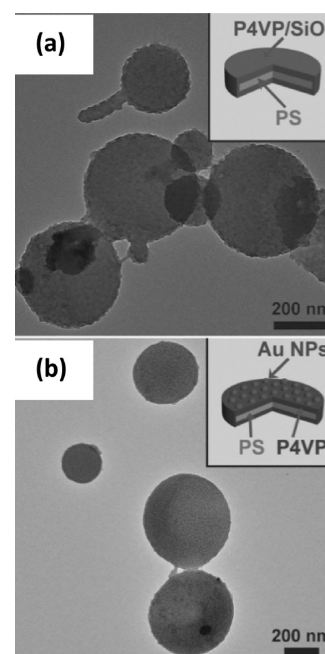


Figure 22. Bright-field TEM image of (a) PS-*b*-P4VP/SiO₂ core-shell nanodiscs and (b) PS-*b*-P4VP/Au hybrid nanodiscs with Au NPs (size: 5.2 ± 1.7 nm) dominantly loaded on their surfaces. Insets in a and b are the cartoons showing the structure of the hybrid nano-objects. Reprinted with permission from ref 74. Copyright 2013 Wiley-VCH.

functionalities on their shell.⁶³ The multicompart ment cylinders (MCCs) obtained from the bulk structure of a miktoarm star terpolymer based on PB, P2VP, and PS were used to template the growth of Au, Ag, and CdS NPs in the P2VP compartment. The amphiphilic and solvent-responsive character of the PS and P2VP blocks forming the corona compartments allowed us to tune the distribution of the nanoparticles within MCC corona simply by changing the solvent selectivity. For example, in THF, the P2VP-attached Ag NPs appeared predominantly located within the two side compartments, with a small amount of NPs also located in the center because of the incomplete phase segregation of the compartments in THF. When THF was replaced with toluene, the nanoparticles underwent a drastic rearrangement. The hybrid MCCs exhibited a strong compartmentalization and confinement of the nanoparticles within the two cylindrical domains at the sides induced by swelling of PS and collapse of P2VP compartments in toluene. On the contrary, in ethanol, the nanoparticles get redistributed within the whole corona of the MCCs as the PS arms collapsed and the P2VP arms spread around the full corona. Importantly, the extent of compartmentalization can be tuned by the solvent choice and manipulated by changing the solvent quality (Figure 23).

More recently, the compartmentalized cylinders obtained by Schacher et al. from linear PB-*b*-P2VP-*b*-PtBA were also used for templating the growth of the NPs.⁶⁵ In this case, the compartmentalized cylinders consisting of cross-linked PB core were first converted to an intramicellar polyelectrolyte complex by quaternization of P2VP and hydrolysis of PtBA counterparts and then functionalized with various types of in situ synthesized metal nanoparticles, such as Au, Pt, and Pd. Interestingly, Au and Pt NPs were found to be homogeneously distributed along the cylinder long axis, whereas Pd NPs were found to from

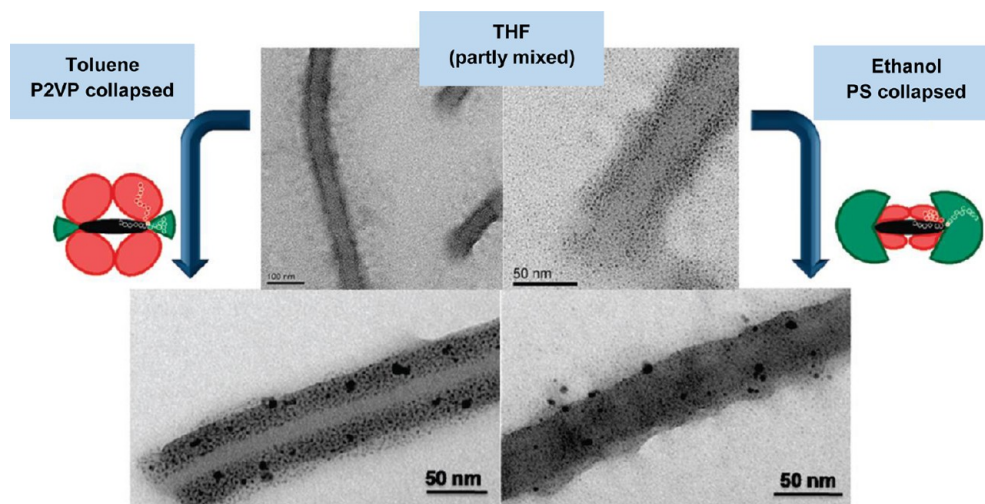


Figure 23. Structural changes of the nanoparticle-decorated MCC bearing compartmentalized corona upon exposure to selective solvents. TEM micrographs of Ag-loaded hybrid MCCs deposited from THF (top), toluene (lower left), and ethanol (lower right). Reprinted with permission from ref 63. Copyright 2009 American Chemical Society.

patches along the PB core (Figure 24). This suggested that Au and Pt nanoparticles bind to both quaternized P2VP blocks and hydrolyzed PtBA block, whereas the Pd NPs preferably bind only to the former.

5.2. Nano-object Core as Host for Functionality. Most of the work on polymer nano-objects, utilizing the approaches being discussed in this review, has been done on copolymers where the core forming block has been chemically inert and/or was cross-linked to stabilize the nano-objects in solution. Hence, incorporation of functionalities in the core of such nano-objects is more tedious. Nevertheless, there are several reports in literature which demonstrate that functionalization of nano-objects can be also achieved through the modification of the nanoobject's cores. The earliest work in this direction was carried by Weisner et al., who used polyisoprene-*block*-poly(ethylene oxide) (PI-*b*-PEO) block copolymer to prepare aluminosilicate nano-objects.^{90–93} The PI-*b*-PEO copolymer with minority PEO block was mixed with metal alkoxides ((3-glycidyloxypropyl)trimethoxysilane and aluminum sec-butoxide) which enriched the PEO phase. By varying the metal alkoxide loading, the effective volume fraction of PEO was varied such that different morphologies were generated using a single block copolymer (Figure 25).^{90,91} The PEO domain enriched with metal alkoxides was then cross-linked by sol-gel route and the nano-objects with hairy PI shell and PEO/poly(metal alkoxides) core were isolated by dispersing the bulk samples in THF. Calcination of the resulting organic/inorganic hybrid nano-objects led to the formation of aluminosilicate based ceramic nano-objects. Following a similar approach Weisner et al. also prepared iron oxide-aluminosilicate nano-objects. For this purpose, Iron(III) ethoxide was used as the iron oxide precursor and mixed with the PI-*b*-PEO block copolymer together with the 3-(glycidyloxypropyl)-trimethoxysilane and aluminum sec-butoxide.⁹² Calcination of these materials propagates the nucleation and growth of a magnetically active γ -Fe₂O₃ crystalline phase within the amorphous aluminosilicate matrix (Figure 25). Yan et al. used a TBC, PS-*b*-PCEMA-*b*-PtBA, to prepare superparamagnetic nanofibers.⁹⁴ In this case, the nanofibers isolated after the self-assembly of the terpolymer had PtBA block as the core, cross-linkable PCEMA block as the middle layer and PS as the hairy

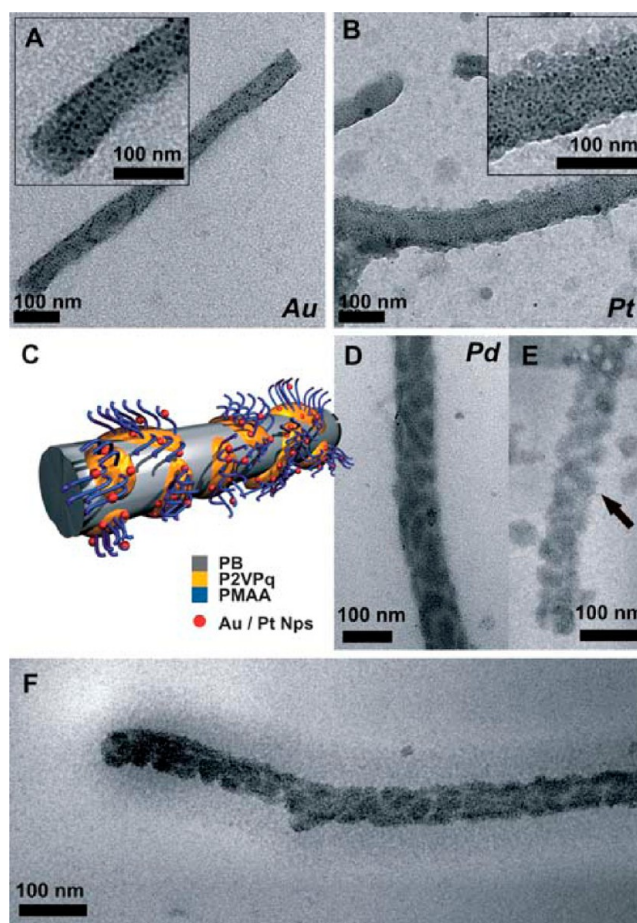


Figure 24. TEM micrographs of cylindrical BVqMANa/NP hybrids deposited from aqueous solution and decorated with (A) Au, (B) Pt, and (D) Pd nanoparticles, (C) the proposed solution structure of compartmentalized cylinders; (E, F) cryo-TEM images from Pd@BVqMANa. Reprinted with permission from ref 65. Copyright 2011 Royal Society of Chemistry.

shell. The PtBA was chemically modified to PAA and loaded with γ -Fe₂O₃. The hybrid nanofibers were found to align in the direction of the magnetic field. Zhang et al. used PTEPM-*b*-PS-

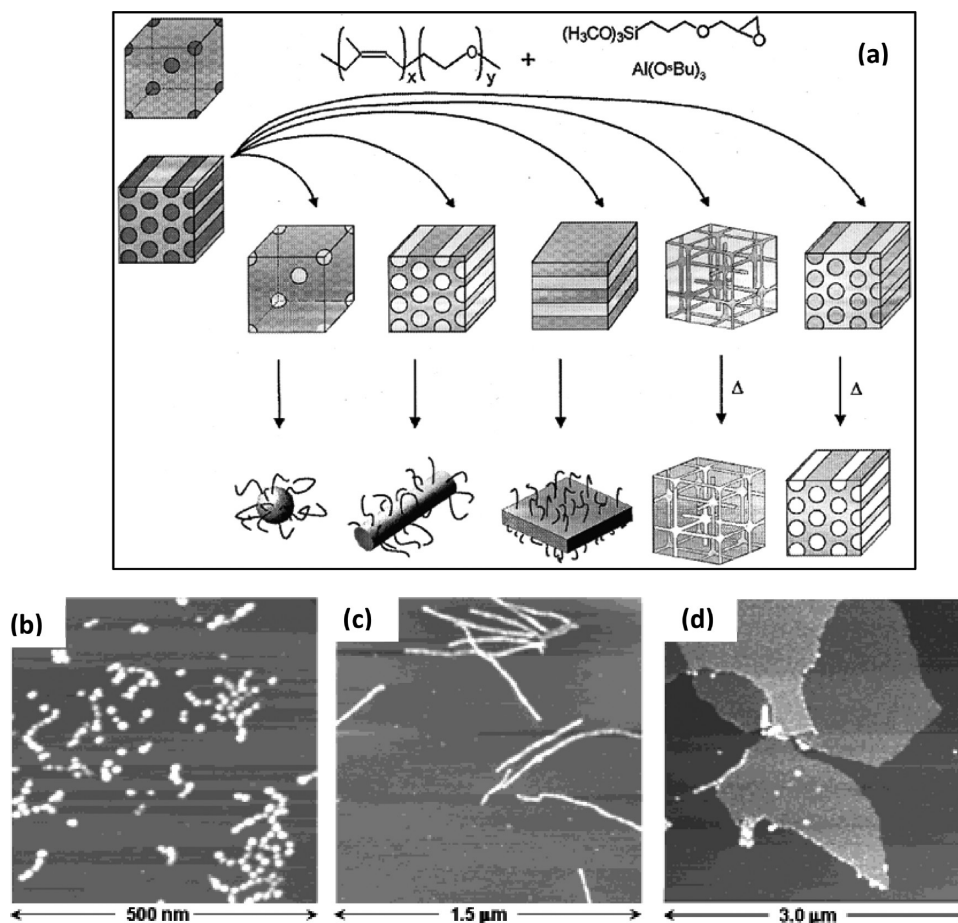


Figure 25. (a) Schematic drawing of the approach used for synthesis of metal alkoxide loaded single nano-objects with controlled shape, size, and composition, and SFM images of the iron oxide-aluminosilicate (b) spheres, (c) cylinders, and (d) plates obtained from polymer nano-objects as template on mica. Reprinted with permission from refs 91 and 92. Copyright 2001 and 2003 American Chemical Society.

b-P2VP terpolymer to isolate a trilayer nanofiber where the inner P2VP core was used to host Au NPs.⁶⁸

Supramolecular assembly route was used by Zhu and co-workers to selective incorporation of gold NPs into the PS domains with spherical, cylindrical, or lamellar morphologies from PS-*b*-P4VP(PDP) SMA complexes in bulk (Figure 26).^{59–61} The gold nanoparticles used were grafted with PS homopolymer to make them compatible within the PS domain. Hence, the nano-objects with Au NP encapsulated within PS cores were obtained by selective removal of PDP in ethanol. The loading of Au NPs in each-type nano-objects was effectively raised by increasing the content of NPs with simultaneous adjustment of the 4VP/PDP ratio. Thus, the balance between the NP loading (increasing the volume fraction of PS part) and the PDP fraction (increasing the volume fraction of PVP(PDP) part) led to the same morphology while achieving high NP loading. Moreover, the hydrogen bonding between PDP and 4VP units increased the effective Flory–Huggins interaction parameter of the whole system to maintain the strong segregation, leading to the formation of ordered structures. It was also shown that the NPs start to self-assemble within a spherical domain once their volume fraction increase beyond a critical value. Later on, the same group also demonstrated the encapsulation of PS-grafted Au nanorods within the PS cores of a hairy nanofibers obtained from PS-*b*-P4VP(PDP) SMA complexes.⁶¹

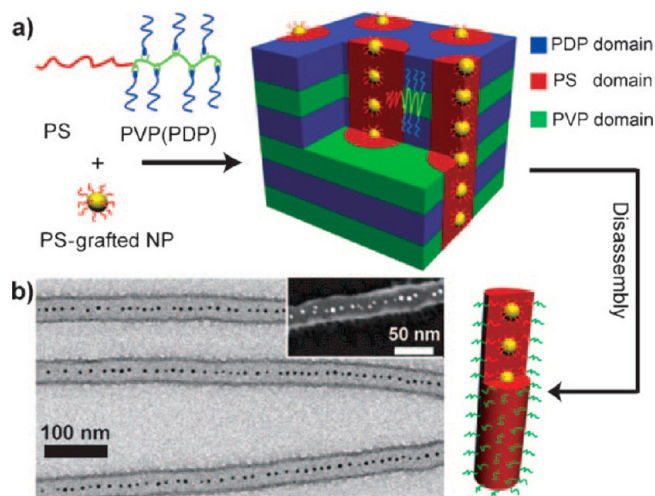


Figure 26. (a) Illustration of comb-coil supramolecular assembly (SMA) based on PS-*b*-P4VP(PDP)_{1.0} ($\phi(\text{PS}) = 23\%$), the hierarchical structures formed by coassembly of the PS-*b*-P4VP(PDP) SMA and PS-grafted Au NPs, and isolated hybrid cylindrical micelles obtained by solvent-assisted disassembling of the Au NP-loaded PS-*b*-P4VP(PDP) SMA. (b) Bright-field TEM image of isolated PS-*b*-P4VP wormlike micelles with encapsulated 6.5 nm Au NPs; the inset shows the dark-field TEM image. Reprinted with permission from ref 59. Copyright 2011 Wiley–VCH.

Recently, we demonstrated the fabrication of polymer nano-objects with densely packed AgNP in the PS core of PS-*b*-P4VP block copolymer.⁹⁵ The PS-grafted AgNP selectively goes into the PS cylindrical domains of the PS-*b*-P4VP copolymer on self-assembly. More significantly, we found that under the experimental conditions used, the AgNP pack in a helical morphology inside the PS cylinder (Figure 27). Hence, the

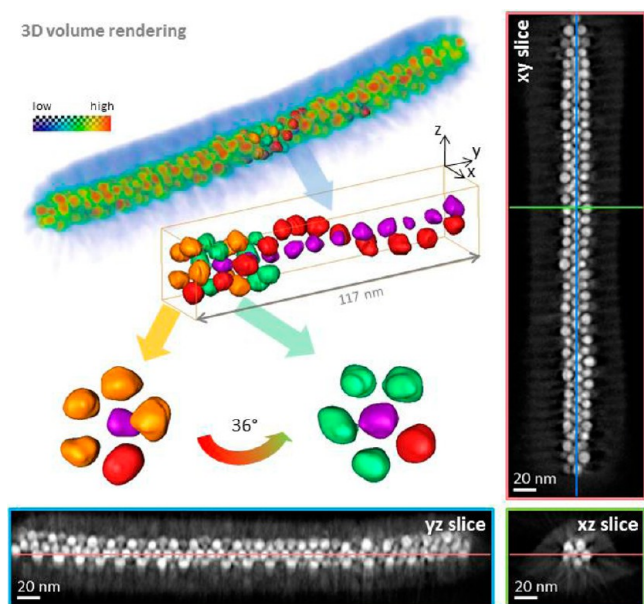


Figure 27. 3D TEM tomography reconstruction of AgNP packed inside the isolated nanofiber formed by the PS-*b*-P4VP block copolymer. The 3D volume rendering shows the entire structure, in which the reconstructed density is color-coded according to the color bar, i.e., the AgNPs appear red (high density) and the BCP appears blue (low density). From the tomogram some of the AgNPs are segmented to visualize their spiral arrangement. The slices show sections through the center of the 3D volume in the three spatial directions. Reprinted with permission from ref 95. Copyright 2014 Wiley–VCH.

isolated hairy nanofibers had the AgNP arranged in a helical packing inside the core. Although the ability of uniform particles to form well-ordered closely packed structures is well-known, recent theoretical estimations have also shown that under cylindrical confinement, uniform spherical particles can form a wide spectrum of densely packed morphologies whose geometry strongly depends on the particle-to-cylinder diameter ratio.^{96–98}

With respect to the nanoparticle dispersed in BCP, an existence of such NP superstructures, including the helical one, was predicted by Ginsburg and Ballazs, though very rare and unstable, and thus not observed before.^{99,100} Experimental results demonstrate that, similar to rigid-wall hollow cylinders, flexible cylindrical microdomains of self-assembled BCPs can also provide confinement conditions to induce nanoparticle self-assembly to form complex superstructures, such as helices as shown in Figure 27. Moreover, such superstructures can be isolated in the form of individual nanofibers, which because of the NP- and structure-specific properties could be an interesting future area of research.

Recently, the core–shell polymer nano-objects have been used in more interesting applications. Li et al. demonstrated that reverse-amphiphilic core/shell polymeric nano-objects with

lamellar, cylindrical, and spherical morphologies derived from PGMA-*b*-PnBMA BCP could be used as nanocapsules to encapsulate anionic hydrophilic dyes.⁴⁷ The shaped nano-objects with electropositive hydrophilic cores and hydrophobic PnBMA hairs were used as nanocapsules to transfer calmagite, an anionic hydrophilic dye, from water into the cores. It was found that the specific area of the interface between the cores and shells of the nanocapsules determined by the geometric shapes of the nanocapsules had a great influence on their loading capacities. Spherical nanocapsules exhibited the highest number loading ratio because of the large specific area of the interface followed by cylindrical and lamellar, respectively. The spherical nanocapsules with electropositive cores and polymeric shells could also be suitable for the separation of dyes with different charges and the uniform coloration of shell-compatible homopolymers. In another application specific work, Yao et al. reported a procedure to fabricate antibacterial core/shell polymer nano-objects with sheetlike, cylindrical, and spherical shapes.⁴⁸ These shaped nano-objects with chemically cross-linked polysiloxane cores and densely grafted polyammoniums shells were prepared by dispersing cross-linked microphase-separated PDMAEMA-*b*-PTEPM BCP. Then the tethered PDMAEMA shells were further quaternized with *n*-octyl bromide. The antibacterial activities of these quaternized nano-objects were assessed against bacteria *Escherichia coli* and was found to be nearly ten times higher than that of quaternized PDMAEMA homopolymer because of the higher quaternary ammonium density.

6. CONCLUSION AND FUTURE OUTLOOK

The present review shows that significant progress have been made on preparation of polymer nano-objects from self-assembled block copolymer morphologies. The uniqueness of the method lies in the robustness and simplicity in terms of precise control on block copolymer morphologies in bulk and easiness of disassembly of the self-assembled structures, e.g., using selective solvents. Moreover, the fact that nano-objects with fascinating shape and structures have been isolated via this approach, some of which are difficult to obtain through any other approach known so far, further enhances the appeal of the method. However, there are still many fascinating aspects of this approach which could be explored in the future. Because the bulk morphology of block copolymers becomes more intriguing as the number of chemically distinct blocks increases and/or the architecture of the copolymer becomes more complex, the possibility of finding a variety of other complex nano-objects is enormous. Furthermore, it has also been shown that bulk morphology of block copolymers becomes further rich and different if they are self-assembled in cylindrical or spherical confinement. This has already been used as a tool to obtain complex shaped nano-objects. However, significantly more possibilities exists to discover a variety of other structures. The other interesting area of future research could be on the stability of nano-objects in dispersion especially in the case where the core is not cross-linked. In this case, it has been found that a sheetlike nano-objects obtained from a lamellar morphology could be converted to cylinder and spherical structures. The transient structure during these structural transitions could be investigated in more detail because it might provide a pathway for more complex structures. Furthermore, routes to improve aspect ratio of nano-objects such as nanofibers by combining the traditional tools available for

improving block copolymer anisotropic ordering such as shear alignment also needs to be looked into.

The use of nano-objects as templates to grow functional nanoparticles also presents enormous possibilities. Properties of nanoparticles loaded on the nano-objects have not been studied in detail, especially with respect to the effect of nano-object shape. Furthermore, the discovery of superstructures of nanoparticles inside the block copolymer domain opens a new area of research where a variety of other superstructures could possibly be explored both in the bulk as well as in isolated nanoobjects. Moreover, by combining the nanoparticle deposition in shell and core, a range of multifunctional nano-objects of different shape could be fabricated where two different functional properties could be combined in a single nanoobject. The use of Janus nano-objects for fabricating such multifunctional nano-objects could further enrich the research opportunities. Apart from the templating applications, the use of polymer nano-objects as drug-delivery carriers could also hold promising future. In this case, the influence of the shape of polymer nano-objects on such biomedical applications may also be interesting to investigate.¹⁰¹ The biomedical application could further be extended by functionalizing the polymer nano-objects with fluorescent dye or superparamagnetic particles.^{102,103}

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Notes

The authors declare no competing financial interest.

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