

Nanostructured colloidal particles by confined self-assembly of block copolymers in evaporative droplets

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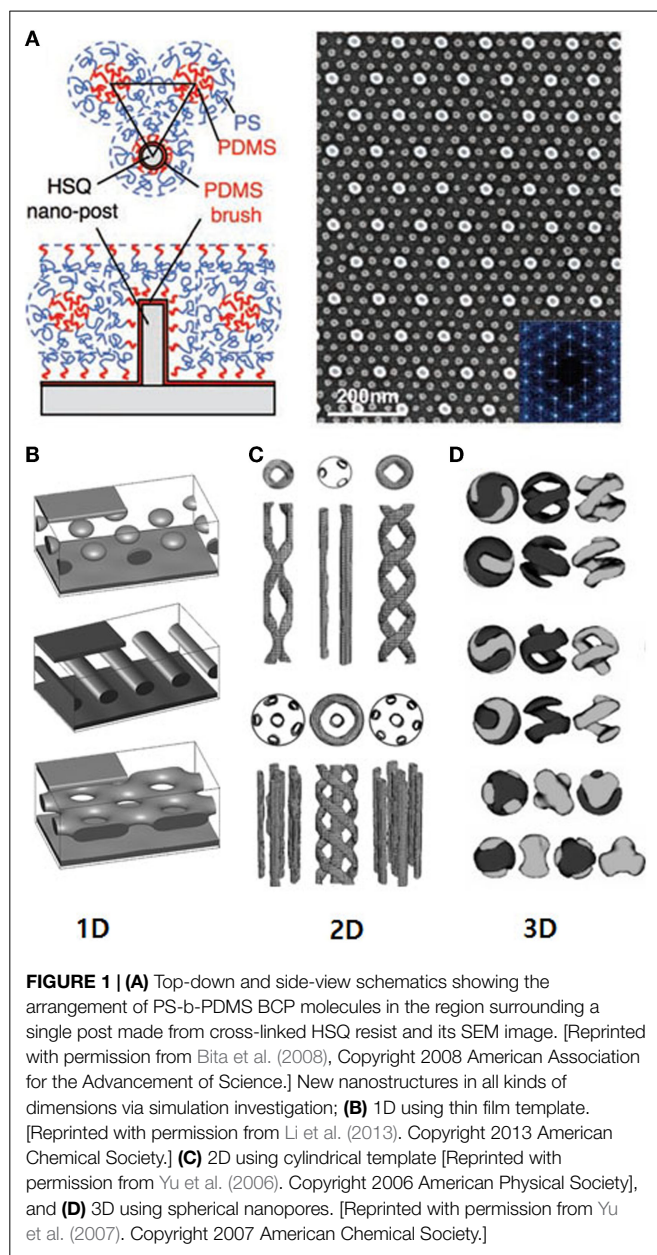
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Block copolymers (BCPs) can create various morphology by self-assembly in bulk or film. Recently, using BCPs in confined geometries such as thin film (one-dimension), cylindrical template (two-dimension), or emulsion droplet (three-dimension), nanostructured BCP particles have been prepared, in which unique nanostructures of the BCP are formed via solvent annealing process and can be controlled depending on molecular weight ratio and interaction parameter of the BCPs, and droplet size. Moreover, by tuning interfacial property of the BCP particles, anisotropic particles with unique nanostructures have been prepared. Furthermore, for practical application such as drug delivery system, sensor, self-healing, metamaterial, and optoelectronic device, functional nanoparticles can be incorporated inside BCP particles. In this article, we summarize recent progress on the production of structured BCP particles and composite particles with metallic nanoparticles.

Keywords: block copolymer particle, nanostructure, hybrid particle

What is Block Copolymer Particles?

Block copolymers (BCPs) have been widely used as templates for the nanostructured materials, since the BCPs can self-assemble to a variety of nanoscale morphologies like spheres, cylinders, and lamellar depending on their composition, volume fraction and molecular weight (Bates and Fredrickson, 1990; Hawker and Russell, 2005; Xiong et al., 2009; Mai and Eisenberg, 2012). The key to the use of BCPs for the complex nanostructures is to control the orientation and lateral order of the microdomains in the thin films. For instance, the use of solvent vapor can induce orientation of the BCP nanostructures (Malenfant et al., 2007). Kim and Libera (1998) carried out the effect of solvent on the morphological evolution of BCPs in the thin-film, resulting in perpendicular orientation of asymmetric poly(styrene-*block*-butadiene-*block*-styrene) (SBS) after solvent evaporation (Kim and Libera, 1998). Cavicchi and Russell (2007) reported a significant improvement on the lateral ordering of poly(isoprene-*block*-lactide) (PI-*b*-PLA) by solvent annealing in the casting film (Cavicchi and Russell, 2007). Besides the solvent annealing method, the orientation of BCP nanostructures can be also controlled by changing the surface properties of the substrate or the gap between the two substrates (Huang et al., 1998). For example, the periodic patterned substrates have been used to enhance or control the lateral order of microdomains in BCPs (Figure 1A) (Bita et al., 2008). Furthermore, various frustrated nanostructures inside confined geometry could be developed as shown in Figures 1B–D (Yu et al., 2007, 2006; Li et al., 2013). For one-dimensional (1D) confined geometry, it has been well known that perforated lamella phase can be formed instead of gyroid or bicontinuous phase (Figure 1B) (Koneripalli et al., 1995; Nikoubashman et al., 2014; Zhang et al., 2015a). In the case of cylindrical pores in anodized alumina oxide (AAO) membranes, various helical



structures were observed and they have been used as confining geometries (Lambooy et al., 1994; Dauphas et al., 2004; Wu et al., 2004; Xiang et al., 2004; Maiz et al., 2014; Hou et al., 2015). According to the theoretical prediction, more unusual morphologies like single helices, double helices, and meshes could be produced as shown in **Figure 1C** (Li and Wickham, 2006; Li et al., 2006; Yang et al., 2012; Bae et al., 2013; Xu et al., 2014; He et al., 2015; Zhang et al., 2015b; Zuo et al., 2015).

Likewise, in the case of three-dimensional (3D) confining geometries such as spheres, multi-shell, or onion-like structures or other morphologies as shown in **Figure 1D** could be developed (Yu et al., 2007). The nanostructures has been proved simulationally (Yu et al., 2007; Hao et al., 2014) and experimentally (Higuchi et al., 2012, 2008; Xu et al., 2015). These are practically important in a broad range of applications including the

production of impact-resistant polymers, composite materials, catalytic supports, coatings, and adhesives (Sundberg and Durant, 2003). For instance, dyed multi-shell particles have been used in high-density 3D optical data storage and security data encryption (Pham et al., 2004). Most of core-shell structured colloids have been employed in bio-application such as drug delivery and biosensor (Otsuka et al., 2003; Wang et al., 2011; Robb et al., 2012; Yu et al., 2014; Louage et al., 2015). The researchers have prepared the colloidal particles composed of the assemblies of spherical polymeric micelles, which have been employed to study stimuli-reactive delivery or sensor system. In addition, hollow particles have been used in bio-application such as self-healing. Mohwald group reported that hollow polymer particle with onion-like nanoshell structure can be employed in bio-related application such as nanocapsule and self-healing (Sukhorukov et al., 2005; Grigoriev et al., 2009; Delcea et al., 2011; Latnikova et al., 2012). Structured spheres with periodic radial variation of the refractive index have attracted much attention due to their potential uses as spherical dielectric resonators in cavity quantum electrodynamics, optical switches, and limiters (Babin et al., 2003; Gourevich et al., 2006; Petukhova et al., 2008; Zhang et al., 2008a; Burlak et al., 2012). Interestingly, by tuning the surface property of the BCP particles, ellipsoid-structured particles from spherical particles can be created (Deng et al., 2013; Klinger et al., 2014). The shape-controlled particles can be applied in the fields such as multi-responsive materials, optical device, and biomedical delivery device.

Furthermore, incorporating functional materials such as metal or semiconductor into the nanostructured BCP microsphere can produce novel inorganic nanostructures with new characteristics, which depend on their spatial and size distribution (Jeon et al., 2009; Connal et al., 2012; Ku et al., 2013). The composite BCP microspheres have been prepared by selective interaction between one block of the BCP and polymer-capped nanoparticles or infiltration of inorganic precursors into the one block. For example, Ku et al. (2013) have fabricated hybrid BCP-quantum dot (QD) microspheres by spatially isolating different-colored QDs into core-blocks of the BCP micelles, which can control Förster resonance energy transfer (FRET) between QDs, resulting in formation of multicolor emission colloidal particles.

This review focuses mainly on how BCP colloidal particles could be formed with unique internal structures and then describes how nanoparticles could be incorporated or decorated. Finally, we will discuss remaining issues or problems for future applications.

Synthesis of Structured Block Copolymer Particles

Structured BCP particles can be prepared synthetically using mini-emulsion polymerization method (Landfester, 2001a, 2009; Rao and Geckeler, 2011). In the method, two different kinds of monomers are dispersed in aqueous media with surfactants to stabilize the interface between the monomers and water. Polymerization is performed by an initiator dispersed in the aqueous phase, resulting in formation of random BCPs. More effective method to fabricate the particles has been

developed using radical polymerization (Smulders and Monteiro, 2004; Landfester, 2009; Wang and Zhang, 2012). For example, poly(*n*-butylacrylate-*block*-styrene) (PnBA-*b*-PS) particles were prepared by radical emulsion polymerization using a structural control agent (e.g., 1,1-diphenylethylene) or reversible addition-fragmentation chain-transfer (RAFT) agent, which is dispersed in the aqueous solution. Landfester et al. demonstrated that the particles, which have core-shell or hollow structures, can be used in the bio-application such as nanocapsules for drug delivery or self-healing materials (Landfester, 2001b, 2006; Landfester and Mailander, 2013; Lv et al., 2013; Vimalanandan et al., 2013). Moreover, hollow structured particles can be produced by layer-by-layer (LBL) assembly on colloidal particles as a template (Pastoriza-Santos et al., 2001; Coustet et al., 2014). The LBL technique is based on the consecutive assembly of oppositely charged polymer layers on a preformed charged spherical colloidal particle. After LBL assembly, the cores of the particles can be removed by selective dissolution or calcination, followed by formation of hollow particles. Mohwald et al. reported that the hollow particles were prepared by LBL assembly using charged polymer such as poly(diallyldimethylammonium chloride), poly(allylamine hydrochloride), or poly(styrene sulfonate) onto the charged silica or PS particles (Caruso et al., 1998a,b; Caruso and Mohwald, 1999; Shchukin and Mohwald, 2006). After removal of the cores in the particles, the hollow structured particles were obtained, which can be applied as biomaterials such as drug delivery carriers or self-healing (Peyratout and Dahne, 2004; Ma et al., 2005; Rivera Gil et al., 2008; Delcea et al., 2011; Latnikova et al., 2012; Yan et al., 2014). Although the structured particles prepared by mini-emulsion polymerization or LBL technique have narrow size distribution, the methods have been limited to control the inner nanostructure of the BCP particles.

On the other hand, BCP particles can be prepared directly from polymer solution by filling lithographically prepared voids and removing the template such as AAO template (Wu et al., 2004; Wang et al., 2008; Mei et al., 2011; Mei and Jin, 2013; Chu et al., 2014). Generally, a template is immersed in polymer solution during a constant time and then the template is picked up from the solution, resulting in formation of BCP nanotubes. After annealing of the BCP nanotubes, the template is selectively removed by etchant such as NaOH to release the nanotubes. Some groups demonstrated that the BCP particles were prepared by the templating method, which had spherical shape after exposure to neutral solvent for the BCP. Furthermore, mesoporous-structured BCP particles were fabricated by swelling of the BCP after exposure to a selective solvent which prefers one of the BCP (Mei et al., 2011; Mei and Jin, 2013).

Emulsion-encapsulation and solvent-evaporation method have been widely used for BCP particles, in which the polymer solution was dispersed in a non-solvent and the organic solvent inside emulsion was evaporated. Similarly, Thomas et al. (1990) experimentally demonstrated the formation of BCP particle using aerosol droplets as the confined geometry. Generally, BCP solution is atomized with an air jet atomizer, resulting in production of aerosol droplets. In nitrogen carrier gas, the droplets are transported to a heated tubular reactor where they are dried and heated for several seconds. After the droplets are cooled, the

dried BCP particles are finally collected. The method using the aerosol droplets would produce small particles ranging from sub-micrometers to a few micrometers after completely removing the solvent from the droplets (Lu et al., 1999). Later then, various structured BCP particles were prepared from aerosol droplets where poly(styrene-*block*-4-vinylpyridine) (PS-*b*-P4VP) or triblock copolymer with poly(3-triethoxysilyl)propyl block were included (Zhang et al., 2008a,b, 2010a; Rahikkala et al., 2013). However, the nanostructures inside the BCP particles could not reach to equilibrium state or significantly overlapped between the neighboring domains because of fast removal of the solvent from the aerosol droplets.

In case of using emulsion droplets as confining geometries (Figure 2A), well-defined BCP particles can be prepared by the evaporation-induced microphase separation of BCPs. BCPs are dissolved in organic solvent, which is not miscible to water and then dispersed in aqueous solution containing surfactant. After slowly solvent evaporation from the droplets, the structured BCP particles are produced. When symmetric BCPs were assembled, onion-like structure was observed and other morphologies were also obtained by adding homopolymers as shown in Figure 2B (Jeon et al., 2007). The microdomains of spheres, cylinders, and lamellae were structured in concentric arrangements due to the external spherical confinement provided by the emulsion droplets. Yu et al. (2007) reported the morphologies in BCP particles by Monte-Carlo simulations. It was shown that the morphologies in the BCP particles were dependent on the equilibrium spacing of the BCP structures in the bulk films (L_0) and the diameters of the microspheres (D) as shown in Figure 2C. Moreover, interfacial tension was controlled using a mixture of surfactants, for example, poly(styrene-*block*-ethyleneoxide) (PS-*b*-PEO) and poly(butadiene-*block*-ethylene oxide) (PB-*b*-PEO) (Jeon et al., 2008). As shown in Figure 3, single type of surfactant produced onion-like spherical particles, but mixture of surfactants produced ellipsoidal particles with stacked lamellae nanostructures.

Another method to fabricate the structured BCP particles directly from polymer solution is using re-precipitation (Yabu et al., 2005; Li et al., 2010; Yabu, 2013). The polymer solution is slowly added to a large amount of poor solvent for the polymer, which is miscible with the good solvent. After evaporation of good solvent into the polymer solution, structured BCP particles can be produced. To selectively evaporate the good solvent, its boiling point should be lower than that of the poor solvent. For example, Higuchi et al. prepared the nanostructured BCP particles by controlled precipitation from a tetrahydrofuran (THF)-water mixture (Higuchi et al., 2008). Through gradual evaporation of THF in the solvent mixture with symmetric poly(styrene-*block*-isoprene) (PS-*b*-PI), various nanostructures in the particles were produced.

Generally, the nanostructures of BCP in thin film have been developed during thermal annealing (Bates and Fredrickson, 1990; Winey et al., 1994; Park et al., 2003; Tang et al., 2004; Hawker and Russell, 2005; Xu et al., 2005; Ahn et al., 2009; Marencic and Register, 2010; Lee et al., 2011; Bai et al., 2013) above glass transition temperature (T_g) or solvent annealing (Li et al., 1996; Zhao et al., 2004; Kim et al., 2006; Bang et al., 2007; Cavicchi and Russell, 2007; Jung and Ross, 2007; Malenfant et al., 2007; Zhang

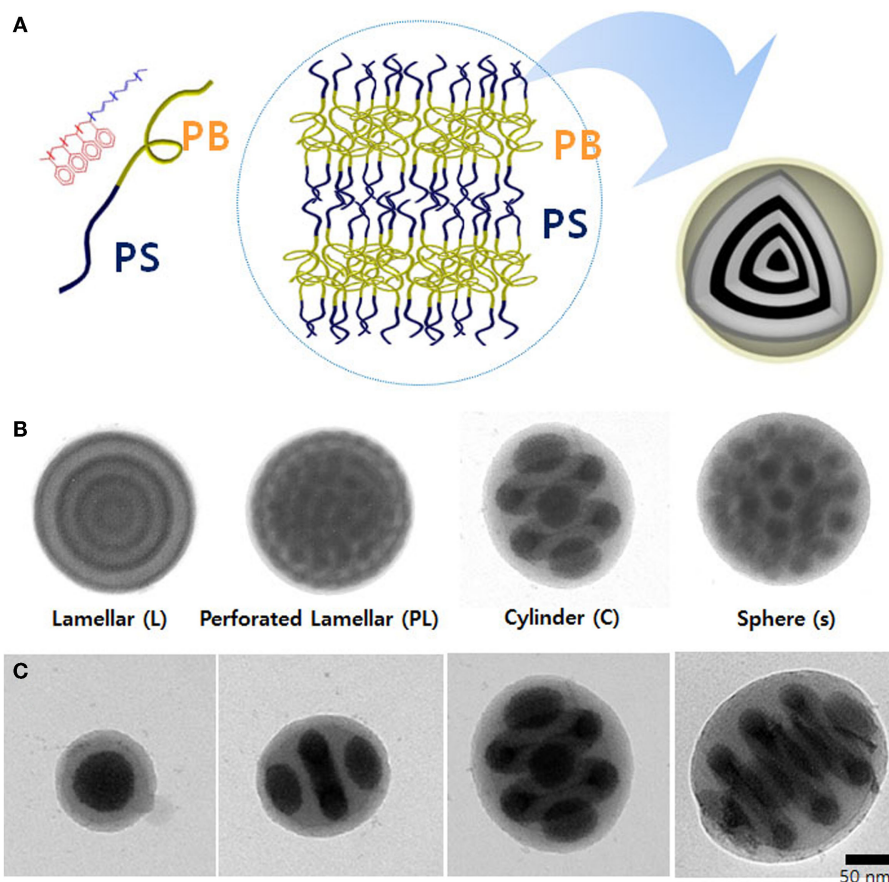


FIGURE 2 | 3D confinement effect of BCPs in emulsion droplet.

(A) Schematic illustration of preparation of PS-*b*-PB BCP particles with nanostructures in emulsion droplets. Morphological transition of the BCP

particles depending on (B) volume fraction of the BCP and (C) droplet size. [Reprinted with permission from Jeon et al. (2007). Copyright 2007 American Chemical Society.]

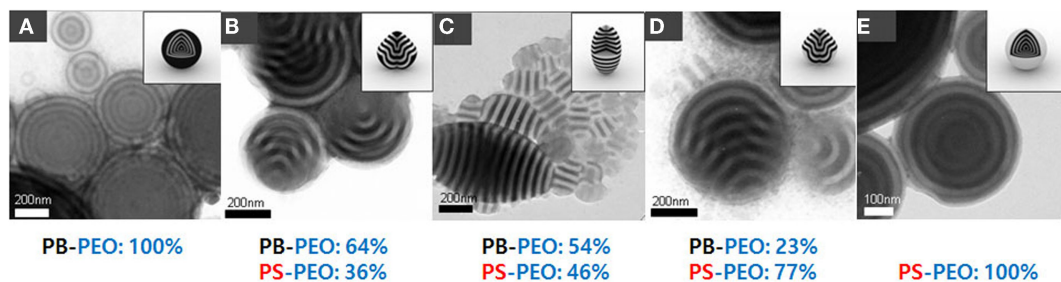


FIGURE 3 | TEM images of PS-*b*-PB colloidal particles depending on the volume ratio (f_s) of PS block in the mixed surfactant of PS-*b*-PEO and PB-*b*-PEO: (A) particles with onion-like morphology for $f_s = 0$. (B) "Tulip-bulb" particles for $f_s = 0.36$.

(C) Prolate particles for $f_s = 0.46$. (D) "Tulip-bulb" particles with inverted structure of the particles in (B) for $f_s = 0.77$. (E) Onion-like particles for $f_s = 1$. [Reprinted with permission from Jeon et al. (2008). Copyright 2008 Wiley-VCH.]

et al., 2007; Chang and Lo, 2011; Chu et al., 2014; Kao et al., 2014) in the presence of solvent below T_g . Solvent annealing uses solvent vapor to increase chain mobility of BCP unlike thermal annealing in which the film are heated above T_g . Similarly, the nanostructures in the BCP particles can be accomplished by solvent annealing method (Li et al., 2010; Chi et al., 2011; Deng et al., 2013; Yabu, 2013; Jin and Fan, 2014) because the particles have been

prepared from polymer solution. The morphological evolution of the BCP particle during solvent annealing has been reported theoretically and experimentally. Chi et al. studied solvent-induced self-assembly of BCPs under confinement via simulation (Chi et al., 2011). The self-assembled internal morphologies such as stacked lamellae, hexagonally packed cylinders, stacked toroids, or helices were predicted as functions of solvent-polymer interaction

and the monomer concentration. Experimentally, Russell group demonstrated solvent-driven morphology of BCP particles using re-precipitation method from THF/water mixture (Li et al., 2010). They used a symmetric PS-*b*-PI BCP and chloroform for evolution of the BCP nanostructures. Since chloroform is a good solvent for both blocks, it can swell and anneal the BCP particles, resulting in formation of onion-like nanostructures. Upon the extended annealing, the nanostructures are evolved to cylindrical morphology and finally core-shell spherical structure.

Recently, microwave annealing approach have been developed for rapidly inducing self-assembly of BCP, by which highly ordered patterns were achieved within 3 min (Zhang et al., 2010b; Mokarian-Tabari et al., 2014). The method is based on simultaneously solvent-driven and thermal-driven mechanism by adsorption of microwave radiation into BCP chains, resulting in generation of BCP nanostructures in minutes. The nanostructure of BCP particles can be also created by microwave annealing method. Higuchi et al. examined morphological transitions of PS-*b*-PI BCP particles depending on experimental conditions such as temperature and time during microwave annealing (Higuchi et al., 2013). Even though the BCP particles are dispersed in aqueous solution, which has a higher dielectric constant and absorb most of microwave radiation, a small amount of the radiation can evolve the BCP nanostructures.

In addition, it is possible to change the particle shape from sphere to ellipsoid by tuning surface property of the BCP particles. Jintao group prepared reversible transformed BCP particles by solvent-adsorption annealing (Deng et al., 2013). In the article, poly(vinyl alcohol) (PVA) was used as a surfactant, which is a critical role in determining the particle shape, and chloroform, which is a good solvent for both blocks was used to swell and anneal the ellipsoid particles to spherical particles with onion-like structures. Moreover, they reported to fabricate polymeric Janus particles with hierarchically structures by phase separation of PS-*b*-P4VP and homopolymer poly(methyl methacrylate) (PMMA) binary blend (Deng et al., 2014). The Janus particles were tuned by varying copolymer composition, blending ratio, solvent selectivity, and particle size and reversibly transformed by solvent-adsorption process. Hawker group developed a new strategy to prepare ellipsoid BCP particles using modified surfactants (Jang et al., 2013; Klinger et al., 2014). Jang et al. (2013, 2011) prepared PS-*b*-PI terminated Au-core/Pt-shell nanoparticles as a surfactant for poly(styrene-*block*-2-vinylpyridine) PS-*b*-P2VP droplets. Since the nanoparticles preferentially adsorb at the emulsion interface and modify the interfacial interactions between PS-*b*-P2VP domains, the BCP droplets can be transformed to ellipsoid particle with striped nanostructure. Besides the nanoparticle surfactant, they chemically modified cetyltrimethylammonium bromide (CTAB) to hydroxyl-terminated CTAB (CTAB-OH). Although CTAB has a good affinity to PS, CTAB-OH prefer to P2VP chains, which can be produced onion-structured particles with P2VP as the outermost layer. When the fraction ratio of CTAB-OH and CTAB was between 0.7 and 0.8, ellipsoid particle was prepared with an internal nanostructure of stacked lamellae morphology.

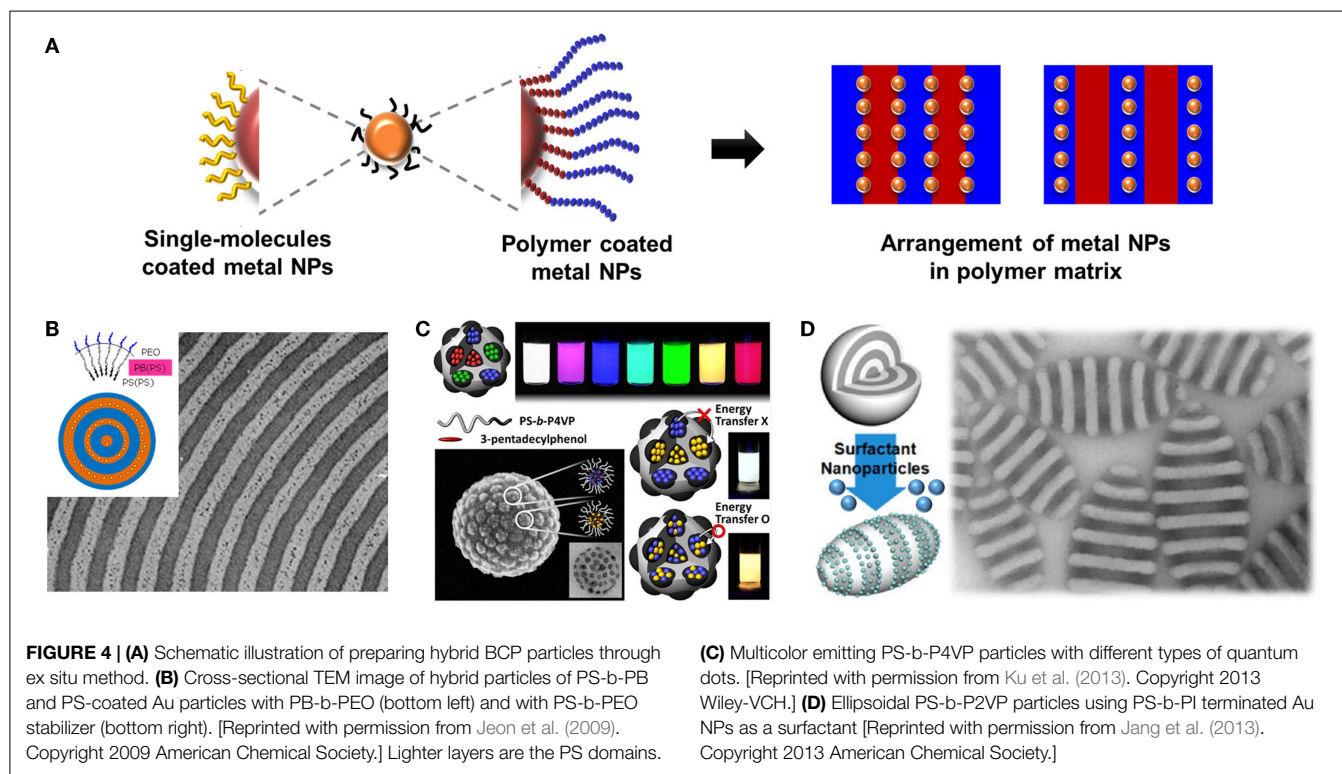
Briefly, those factors to control the morphology in the BCP particles can be summarized as follows; the effects of the molecular

weight and concentration of the BCP solution, the effect of the ratio of the particle diameter to the BCP structure period (D/L_0), the effect of the ratio of the good solvent to the poor solvent for the BCP on the microphase separation within the microspheres, and the effect of the interfacial tension between BCP solution and surfactants.

Composite Block Copolymer Particles

Block copolymer particles can be hybridized with functional inorganic, semiconductor, or metallic materials, to produce composite or hybrid BCP particles. There have been several different strategies for such a hybrid BCP particles, which can be categorized into chemical approach (MacLachlan et al., 2000; Manners, 2001, 2007; Korczagin et al., 2004; Whittell et al., 2011; Hudson et al., 2014; Zoetebier et al., 2015) using polymerization of metal-containing monomers and physical approach (Spatz et al., 1998; Kane et al., 1999; Tsutsumi et al., 1999; Lopes and Jaeger, 2001; Sohn and Seo, 2001; Boontongkong and Cohen, 2002; Bockstaller et al., 2003; Misner et al., 2003; Chiu et al., 2005; Kim et al., 2005; Yoo et al., 2010; Jang et al., 2011; Lim et al., 2011; Paek et al., 2011; Janczewski et al., 2014) such as *ex situ* and *in situ* approaches. The chemical approach is to use metal-containing monomer units. After living free-radical polymerization or ring-opening polymerization of the unit, metallopolymer can be produced. For example, Manner group reported a synthetic method to produce organo-metallic polymer. They performed ring-opening polymerization of spirocyclic silaferrocenophane as a monomer, resulting in formation of cross-linked Fe-containing polymer (MacLachlan et al., 2000). Moreover, they prepared fluorescent nanorod particles by micelle assembly of poly(ferrocenyldimethylsilane-*block*-(dimethylsiloxane-*random*-methylvinylsiloxane)) (PFS-*b*-(PDMS-*r*-PMVS)), which was synthesized by anionic polymerization (Hudson et al., 2014). The vinyl groups were then functionalized by photoinitiated hydrothiolation (thiolene-click reactions) with thiol reagents, providing primary hydroxyl or amino groups to which functional dyes may be attached. Vancso group reported a method to synthesize poly(ferrocenylsilane-*block*-methacrylate) (PFS-*b*-PMMA) by combined living radical polymerization. PFS was synthesized by anionic polymerization and PMMA was sequentially synthesized by ATRP, followed by production of PFS-*b*-PMMA (Korczagin et al., 2004). Although the chemical approach is to use inorganic precursor-containing monomers, it remains a challenge that the particles should be reduced as metal-polymer particles.

On the other hand, the physical approach to achieve hybrid BCPs is to use interaction between one block of BCPs and polymer ligands attached on the surface of NPs (*ex situ* method) or attraction between one block of BCPs and inorganic precursor (*in situ* method). The *ex situ* method is based on non-covalent interaction (e.g., van der Waals, π - π interactions or hydrogen bonding) or covalent linkage between each block and surface ligand of the NPs. For example, Bockstaller et al. (2003) reported alkanethiol-capped Au NPs localized at the interface between a symmetric poly(styrene-*block*-ethylene copropylene) (PS-*b*-PEP). Kim et al. (2005) studied PS-coated Au NPs self-assembled within

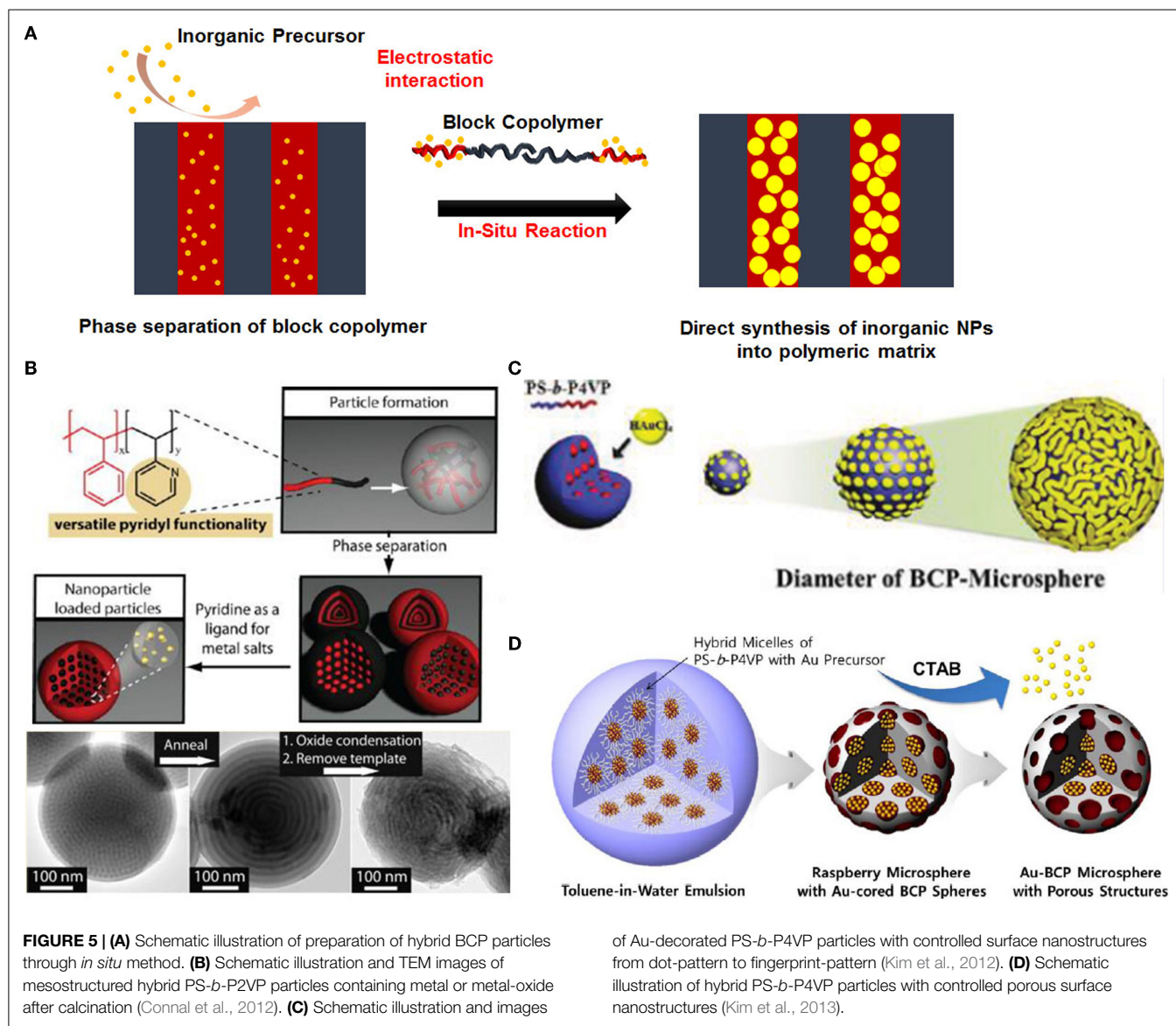


PS-*b*-P2VP. They found that the addition of NPs increased the effective volume fraction of the PS block and thus induced a lamellar-to-cylindrical phase transition. However, due to the steric hindrance between the core-shell type NPs and BCP chains, the density of NPs within the templates is expected to be much lower compared to the *in situ* approach. In addition, if the surface modification of NPs is necessary for such precise control, the intrinsic properties of NP can be deteriorated by increase in defect sites on the surface of NPs. The *in situ* method is based on electrostatic attraction between BCP chains and inorganic precursor. Generally, this approach has used Au, Pt, Pd, and Ag as inorganic precursors and poly(styrene-*block*-acrylic acid) (PS-*b*-PAA), and PS-*b*-P2VP as BCPs. For example, Chai et al. reported to fabricate linear metallic patterns using PS-*b*-P2VP (Chai et al., 2007). Since 2VP units of P2VP have been protonated under acidic condition, anionic metallic precursor (e.g., AuCl_4^- , PdCl_4^{2-} , PtCl_4^{2-}) interacted with the protonated 2VP units by electrostatic attraction. After their self-assembly on silicon substrate and metallization through chemical reduction, metallic patterns were produced, which can be extended toward increasing the conductance of the metallic nanowires and investigating the response of wire resistance to the environment for chemical and biosensing applications. In this section, we focus on *ex situ* and *in situ* approaches to produce hybrid BCP particles with nanostructures.

Ex Situ Method

The *ex situ* approach exploits the cooperative self-organization of pre-formed nanoparticles (NPs) and BCPs. The strategy for incorporating and controlling the location of NPs in a BCP or polymer blend involves tuning the surface properties of the NPs by functional polymer ligands, which play a critical role in particle

location (Figure 4). The *ex situ* method of controlling the structural characteristics of the sequestered component uses cooperative self-organization of pre-made NPs and BCPs. Through this method, NPs with desired size and shape coated with oligomers or polymers can be incorporated in the polymer matrix. Once phase separation of the copolymer has occurred, the NPs can be confined in one of the segregated domains. Some have studied the control of the position in polymer matrix after coating the surface of the NPs using organic molecules (Zhao et al., 2009; Li et al., 2011). For example, Jeon et al. (2009) have prepared hybrid onion-like PS-*b*-PB particles containing PS-coated Au NPs. Since Au NPs were sufficiently covered with PS ligands, all Au NPs were located near the center of PS domain as shown in Figure 4B. Ku et al. (2013) have fabricated multicolor emitting hybrid PS-*b*-P4VP particles using QDs; white-color emitting particles were produced when two different types of QDs were independently incorporated into isolated PS-*b*-P4VP micelles, while orange-color emitting particles when the QDs were concurrently incorporated into the same micelles (Figure 4C). Furthermore, the NPs incorporated into the BCP particles could be used as a surfactant, which resulted in tuning the particle shapes. Jang et al. (2013) have reported that the spherical BCP particles could be changed to ellipsoidal particles when polymer-coated Au NPs were used as a surfactant which tunes the interfacial tension of the particles (Figure 4D). In addition, Ku et al. (2014, 2015) have investigated the effect of NP size and aspect-ratio (AR) to control the interfacial tension of the BCP particles. They prepared oleylamine-capped Au NPs with different size or oleic acid/oleylamine-capped CuPt nanorods with different AR, which was used as a surfactant for the BCP particles. Using supramolecular assembly between the prepared NPs and the BCP domain into the emulsion droplets, the authors



demonstrated that convex-lens shaped PS-*b*-P4VP particles with defect-free and vertically ordered porous channels were created by tuning the interfacial tension.

Since the *ex situ* approach utilizes pre-made NPs that have desired size, shape, and uniformity, this approach is suitable for several applications that require inorganic and/or metallic NP with well controlled size and uniformity, for example, optoelectronic device (Ameri et al., 2009; Leventis et al., 2010; Yang et al., 2011; Liu, 2014), responsive sensor (Paek et al., 2011, 2014; Lee et al., 2013a; Yang et al., 2013), and catalyst (Campelo et al., 2009). Furthermore, the location of NPs within BCP matrix can be easily and precisely controlled by tailoring the surface properties of the NPs.

In situ Method

Another simple concept to incorporate the NPs into polymeric nanostructures is *in situ* method, followed by a chemical reduction step to obtain metallic nanoparticles (Figure 5). The *in situ*

approach is that NPs are directly synthesized within a BCP domain from metal precursors.

In that case, a specific and strong interaction between the precursors and the BCPs is required to guarantee the incorporation of metal precursors into the domain. In the *in situ* approach, preformed micelles of BCPs containing metal precursors are used as nanoreactors to synthesize NPs selectively in BCPs. Due to its chemical affinity, the salt selectively infiltrates the hydrophilic copolymer domain. The NPs are then formed selectively within the precursor-loaded domains upon reduction. The targeted types of application mainly depend on the properties and functionality of the hybrid materials, which are determined by their chemical composition as well as morphological and structural parameters, for example, catalyst (Shastri and Schwank, 1985a,b; Wan et al., 1999; Bonnemann et al., 2000; Guzzi et al., 2003), sensing device (Lee et al., 2013b; Choi et al., 2014), and metamaterials (Soukoulis and Wegener, 2011; Ramahi et al., 2012; Sheikholeslami et al., 2013).

Among the BCPs, polystyrene-*b*-poly (vinylpyridine) (PS-*b*-PVP) BCP has been widely used for preparing hybrid materials. This is because the nitrogen atoms in PVP block have unpaired electrons which interact strongly with metal precursor (Hayward et al., 2005; Chai et al., 2007). For example, Connal et al. (2012) have fabricated hybrid PS-*b*-P2VP particles by selectively infiltrating Au precursors (HAuCl₄) into the P2VP domain. In addition, they prepared mesoporous metal-oxide particles from PS-*b*-P2VP particles containing metal-oxide precursors after removing the BCP template by calcination. Furthermore, hybrid BCP particles with controlled surface nanostructures also have been reported (Kim et al., 2012, 2013). The prepared spherical BCP particles using spherical PS-*b*-P4VP micelles were investigated the surface nanostructures from dot pattern to fingerprint pattern depending on the size of the BCP particles after infiltrating Au precursors into the BCP particles. In addition, we prepared dot-pattern hybrid BCP particle using spherical PS-*b*-P4VP micelles with Au precursors. After removing Au precursor into the P4VP domain, we produced hybrid BCP particles with porous surface which was controlled by tuning the amount of the Au precursors into the P4VP unit.

Summary and Outlook

Using BCPs in confined geometries such as aerosol or emulsion droplets, many nanostructured BCP particles have been prepared after solvent annealing process. They show a variety of new nanostructures due to confinement effect and interfacial properties. According to the theoretical prediction, however, much more nanostructures could be developed by more precise control of particle size and interfacial properties. Complex architecture of BCP such as star shape or multi-BCPs would also be applied into these BCP particles. Recently, these colloidal particles were functionalized by combination of various nanoparticles. Nanoparticles were mixed with BCP before particles formation (*ex situ* method) or precursors for nanoparticles were added after preparing BCP particles (*in situ* method). As an alternative route, nanopores were produced by removing selectively one of blocks, using molecular

templates or selective swelling process, which were then backfilled with other functional materials. Due to their unique nanostructure, these particles would be useful in various nanophotonic applications when the particles were functionalized with optically active materials. Particularly, these would be the new types of metamaterials if one of the phases is replaced with metallic materials. In addition, when the particles were transformed into nanoporous materials, it would also be useful for catalytic or sensor applications due to their high surface-to-volume ratio and unusual well-defined pore structures. Although the nanostructured particles have been used in many applications such as drug delivery system, sensing device, self-healing, and optoelectronic device, it remains a challenge to scale-up monodisperse structured particles, which enable to investigate systematically the optical and electrical properties of the BCP particles with novel nanostructures.

Until now, the structured BCP particles have been prepared by high-mechanical force such as homogenizer, or sonicator, resulting in a broad range of the particle size. Polydisperse particles with different morphology and chemical heterogeneity can result in poor reproducibility and a variable property of the particles per batch. Some groups reported to fabricate uniform BCP particles using microfluidic method by which the particle diameters are ranged from hundreds nanometer to tens micrometer (Wang et al., 2010; Abate et al., 2011; Kuehne and Weitz, 2011), while other groups reported to prepare the structured BCP particles using membrane device (Tanaka et al., 2009; Connal et al., 2012; Deng et al., 2013), which enable a large-scale production of the particles but broader size distribution of the particles than that using microfluidic method. Therefore, it remains a challenge to produce large-scale and monodisperse structured BCP particles at sub-micrometer scale for practical application as mentioned above.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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