Hierarchical Assembly of Complex Block Copolymer Nanoparticles into Multicompartment Superstructures through Tunable Interparticle Associations

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A challenging aim in both materials physics and chemistry is the construction of complex and functional superstructures from designed nanoscale building units. Block copolymer nanoparticles with morphological variety and compositional complexity have been made with solution-based assembly. However, routine ability to build hierarchical superstructures by inter-nanoparticle association is not yet possible. A hierarchical assembly strategy of organizing pre-formed spherical block copolymer nanoparticles into superstructures, including linear, circular, and close-packed arrays, via tunable interparticle interactions is presented. Solution-state mixtures are made of two amphiphilic diblock copolymers, poly(acrylic acid)-*block*-poly(methyl methacrylate) (PAA-*b*-PMMA) and poly(acrylic acid)-*block*-polybutadiene (PAA-*b*-PB) with additional crown ether functionalities grafted onto 40 mol% of the AA repeat units on the PAA-*b*-PMMA diblock copolymer. Through kinetic control of the solution assembly process in aqueous/N,N-dimethylformamide (DMF) mixtures (4:1 water:DMF), spherical nanoparticles with compositional complexity confined in both the core and shell are obtained. Benefiting from host-guest chemistry, interparticle association is triggered and tuned by the addition of di-functional organoamines due to amine-crown ether complexation. The resultant multiparticle superstructures contain well-defined multicompartments within individual, constituent nanoparticles due to the local separation of unlike PB and PMMA hydrophobic blocks within the cores of the individual particles. Through competitive complexation with potassium ions, the superstructures are disassembled into individual multicomparment nanoparticles.

1. Introduction

Inspired by natural superstructure in biological systems, considerable efforts have been devoted to the understanding and manipulation of the hierarchical assembly behavior of diverse, non-natural, nanoscale units such as designed DNA nanotechnology[1] and colloidal crystal engineering.[2–4] Recent success in hierarchical assembly relies on two facets: complex particle construction and controllable particle-particle interactions. Nanoparticles constructed from synthetic, amphiphilic block copolymers provide the opportunity to control structure both within individual block copolymer nanoparticles as well as between multiple nanoparticles for hierarchical assembly.[5–10] We report here a strategy to construct spherical nanoparticles from the blending of two diblock copolymers, forced to reside in a common nanoparticle through kinetic control of solvent mixing. These blended, complex nanoparticles then can serve as hierarchical building units and assemble into desired superstructures including linear, circular, and close-packed arrays, by tuning the interparticle associations.

The development of nanostructures derived from block copolymer assembly has been studied intensively in the last decade. By taking advantage of synthetic methodologies to afford varied block copolymer structures,[11–14] and extensive exploration of molecular solution assembly,[5–10,15] block copolymer assemblies have exhibited prodigious morphological diversity at the nanoscale beyond traditional spheres, cylinders, and vesicles. Not only have particles been constructed with unique shapes, such as disks,[16,17] branched rods,[7,18] and toroids,[19] but new nanostructures with compositional complexity, or complex nanoparticles, such as anisotropic particles[20,21] that include patchy,[22,23] multicompartment,[14,24–26] and Janus particles,[26] also have been explored. Anisotropic particles created from block copolymer assemblies contain a non-centrosymmetric distribution of both compositions and properties within the core and/or on the surface of the particles. The compartments in the core are promising sites for multiple/selective loading, transport and

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release of a wide variety of compounds such as drugs/genes, dyes, inorganic nanoparticles, and catalysts.[8,26,28] The diversity of chemistry displayed from a particle surface provides patches that can be used as specific sites for organic or inorganic grafts[29,30] or interparticle associations.[31,32]

The importance of particle anisotropy has been realized recently in complex hierarchical structure assembly using larger length-scale colloidal systems[3,4,33,34] to produce novel structures beyond highly symmetric close-packed clusters assembled from hard spheres with short-range isotropic interactions.[35] Block copolymer nanoparticles with anisotropic cores, such as multicompartment micelles (MCMs), have been successfully fabricated from star terpolymer[14,36] or linear triblock terpolymer[10,19,37–39] assembly. These types of particles can also be made with mixtures of different block copolymers and variation of the ratio of molecules in the assembly mixture. Moreover, without being covalently linked in the same molecular backbone, components in the mixture are responsive to various external stimuli such as solvent exchange,[40] changes in temperature, pH,[41] ionic strength,[23] and assembly kinetics.[26] Also, the components are dynamic enough to demix internally into compartments of diverse sizes and geometries depending on the type and amount of block copolymers in the original mixture. Complex particles from block copolymer mixtures introduce opportunities for novel superstructures that are distinguished from rigid colloidal systems. However, significant challenges exist in how to precisely control the block copolymer nanoparticle-nanoparticle interactions due to their nanoscale size and dynamic nature.

Since block copolymer nanoparticles are usually isolated in solution due to steric or electrostatic intermicellar repulsions between the hydrophilic or charged corona in aqueous conditions, specific interparticle associations cannot be achieved until desired physical or chemical attractions are introduced in the shells. For example, by mixing with a specific unfavorable solvent for shell-forming blocks, solvent-phobic, hierarchical association between micellar shells can occur, giving rise to patchy spherical[10] or striped cylindrical aggregates.[8,37] This approach relies on critical solvent condition manipulation and block composition design. Herein, we report a new, post-polymerization chemical modification method for hierarchical interparticle assembly of block copolymer nanoparticles. Crown ether functionalities were grafted onto shell-forming hydrophilic blocks as active sites capable of controlled interparticle association and disassociation due to unique host-guest chemistry.[42]

In the present study, we selected a diblock copolymer pair of poly(acrylic acid)-*block*-poly(methyl methacrylate) (PAA-*b*-PMMA) and poly(acrylic acid)-*block*-polybutadiene (PAA-*b*-PB) with crown ether grafted to only the PAA-*b*-PMMA. Through kinetic control of the assembly process facilitated by solvent mixing, complex, spherical, micelle-like nanoparticles, with PMMA and PB mixed in the core and crown ether and PAA mixed in the shell, were assembled. As will be shown, tunable, subsequent interparticle association was achieved by diammonium-crown ether interparticle attractions after the addition of organic diamines.[42] Hierarchical formations, including one-dimensional micelle chains, two-dimensional micelle rings, and three-dimensional micelle aggregates, were obtained with easy manipulation of the extent of attraction by the amount of added diamines or blending ratio of the two diblock copolymers. The block copolymer nanoparticles that comprised the interparticle superstructures were dynamic internally to allow PMMA and PB to segregate into varying morphologies within the particle cores. By taking advantage of the reversible host-guest chemistry of crown ethers, disassembly of the hierarchical structures was then accomplished by the addition of potassium ion as a competitive guest. The ionic potassium competed with ammonium to associate with the crown ether in the shell of the nanoparticles, consequently cleaving the interparticle diammonium-crown ether bonds and resulting in individual, multicompartment nanoparticles.

2. Results and Discussion

First, we prepared PAA_{90}-*b*-$PMMA_{100}$ and purchased PAA_{75}-*b*-PB_{104} diblock copolymers. The two diblock copolymers consisted of a PAA block with similar chain length and two different hydrophobic blocks, PMMA or PB. A post-polymerization chemical modification was applied to the PAA block of PAA_{90}-*b*-$PMMA_{100}$ only, with functionalization of approximately 40% of the AA units with 18-crown-6 functionalities, to obtain 18-crown-6-grafted PAA_{90}-*b*-$PMMA_{100}$ ($P(crown_{0.4}$-*g*-$AA_{0.6})_{90}$-*b*-$PMMA_{100}$) (see the Experimental Section for a detailed description of the experiments and characterization data). The controlled solution-state assembly pathway for these amphiphilic diblock copolymers began with the dissolution of a desired amount of both of the diblock copolymers in *N,N*-dimethylformamide (DMF), a good solvent for all blocks. Subsequent fast addition of water had the combined effect of aggregating the hydrophobic PMMA and PB blocks into nanoparticle hydrophobic cores while concurrently swelling and solubilizing the hydrophilic blocks into the nanoparticle corona-like shell. Final spherical micelle-like particle formation was accomplished when water addition reached a volume ratio of 4:1, water:DMF in a rapid manner. Then, a certain amount of diamine, 2,2′-(ethylenedioxy)bis(ethylamine) (EDDA), was added into the particle solution. Amine groups in diamines are able to complex with both acid groups in acrylic acid side chains and the grafted crown ethers. It was found that diblock copolymer mixtures of PAA-*b*-PMMA and PAA–*b*-PB assembled into isolated spherical nanoparticles, confirmed by electron microscopy imaging with uranyl acetate negative staining (**Figure 1**A) or OsO_4 staining (Figure 1B, OsO4 selectively stained PB by reacting with double bonds). No clear, segregated PB-rich domains were observed in the nanoparticle cores after OsO_4 staining, indicating PMMA and PB chains were initially well mixed in the nanoparticle cores. Interestingly, the exact same solution conditions and assembly pathway produced unique superstructures, such as the chain- and ring-like arrays of spherical particles as displayed in Figure 1C,D, and Figure S1 (Supporting Information), when the PAA-*b*-PMMA diblock with the 18-crown-6 modification was used in the diblock blend. Along a single chain of nanoparticles or nanoparticle ring formation, the sizes of individual particles varied slightly, similar to the nanoparticles from copolymer mixtures without the 18-crown-6 modification, Figure 1B. Of note, the chains and rings here produced from interparticle assembly are different

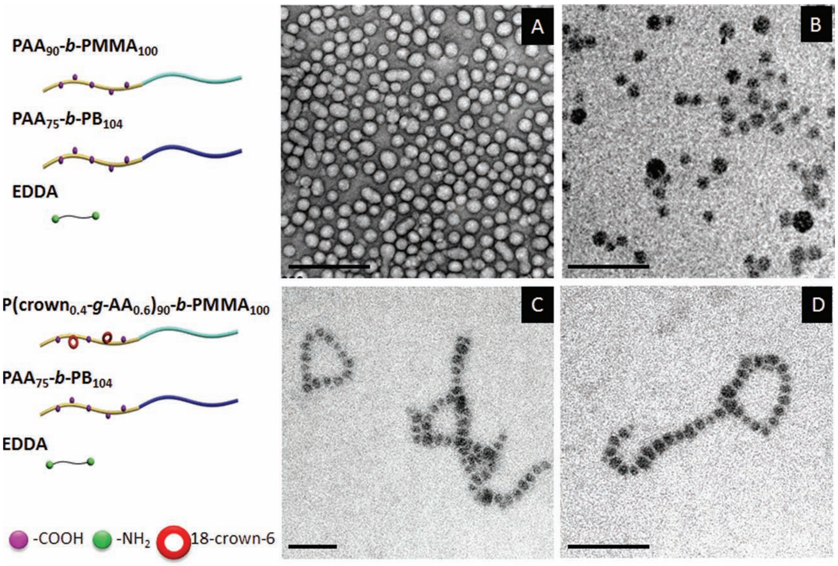

Figure 1. TEM images of isolated particles assembled from PAA$_{90}$-*b*-PMMA$_{100}$ and PAA$_{75}$-*b*-PB$_{104}$ diblock copolymer mixture in a 1:4 volume ratio of DMF and water mixture with added EDDA diamine (amine-to-PAA acid side chain molar ratio = 0.5:1.0), stained by A) uranyl acetate (negative staining the substrate) and B) osmium tetroxide (selective staining of double bonds in PB phase), respectively. Block copolymer mixing molar ratios is 1:1.5; C,D) are both OsO4 stained TEM images showing the nanoparticle chains and rings from P(crown$_{0.4}$-*g*-AA$_{0.6}$)$_{90}$-*b*-PMMA$_{100}$ and PAA$_{75}$-*b*-PB$_{104}$ mixture with added EDDA diamine (amine-to-PAA acid and crown ether side chain molar ratio = 0.5:1.0). Block copolymer mixing molar ratios is 1:1.5. Sample solutions were aged for 1 day before imaging. Scale bars = 200 nm.

from our earlier reported rods or toroids.[19] These earlier 1D and ring-like assemblies were co-assembled from diamines and PAA-containing block copolymers in dilute solution, in which the diamines complexed with intra-micellar acrylic acid side chains to tune the hydrophilic-hydrophobic interfacial curvature and nanoparticle geometry into cylindrical hydrophobic core/hydrophilic corona micelle-like particles. In the earlier assemblies without crown ether modifications, no associations between individual particles were found, consistent with the observations here in Figure 1A,B. Distinguished from all of our previous block copolymer assemblies,[8,18,19,26,42–46] in the current work the diamines were added into a preformed spherical nanoparticle solution of diblock copolymers at a controlled moment of choice to trigger the interparticle aggregation of particles.

In order to clarify the interactions driving the assembly, ^{1}H NMR studies were performed on small, model compounds under conditions that mimicked those used for block copolymer assembly. Acetic acid (modeling PAA) and diamine (EDDA) were mixed in D_2O at concentrations similar to the acid and base compositions present in the block copolymer assembly conditions. The signal at a chemical shift of 3.220 ppm refers to the amine-acid complex formation of $(CH_2OCH_2\mathit{CH_2}NH_3^+)_2$, in which the minority component amines were protonated by excess acid. This solution was then mixed with the D_2O solution of 18-crown-6 in a variety of ratios, and the chemical shifts of the $CH_2OCH_2\mathit{CH_2}NH_3^+$ peak (on the guest molecule EDDA) were monitored and plotted in **Figure 2**. The chemical shift kept changing until the ratio of crown ether to ammonium ion reached 1:1, where ammonium ions were all bound to crown ethers into 1:1 complexes. This observation demonstrated that the ammonium ion preferred to complex with crown ether over acetate due to the high stability of ammonium-crown ether complex structure. The crown ether:RNH_3^+ ratio of ≈0.4 in Figure 2 matches the crown ether:amine ratio present in the block copolymer assembly condition in Figure 1C,D. At this ratio, it is expected that all crown ethers were complexed with EDDA. Together with the TEM results, the NMR data suggest that the strong ammonium-crown ether binding enables interparticle associations. The strength of interparticle attraction is, thus, determined by the relative amount of crown ether functionalities as well as the added diamines.

Geometrical variation in the hierarchical superstructures due to tunable interparticle interactions could be accomplished by changing the amount of added EDDA or the mass blending ratios of diblock copolymers. In the absence of diamines, due to the electrostatic repulsion between the deprotonated PAA chains in the shell,[47] isolated spherical nanoparticles were obtained in water/DMF solution (**Figure 3**A). When added EDDA reached a 0.5:1 molar ratio of amine-to PAA acid and crown ether side chain, short chains of spheres and rings of spheres were obtained as shown in Figure 1C,D. Further addition of EDDA led to branched chains and chain networks (Figure 3B), and eventually to dense 3D aggregates (Figure 3C). Similar structural transformations from isolated spheres (Figure 3D) to sphere chains (Figure 3E) and sphere aggregates (Figure 3F) were achieved by simply varying the blending ratios of the two diblock copolymers with a constant amount of EDDA. For example, by increasing the fraction

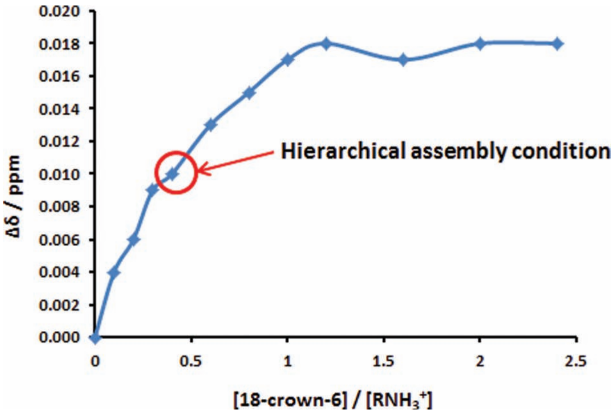

Figure 2. ^{1}H NMR titration curve for the solution of acetic acid and EDDA (acid: amine = 4: 2.5) with the solution of 18-crown-6, in which the shift of $CH_2OCH_2\mathit{CH_2}NH_3^+$ peak (at ca. δ = 3.22 ppm) is monitored. The molar ratio of acid:18-crown-6:amine was 4:1:2.5 in the circled point, modeling the solution assembly condition employed for the polymer system.

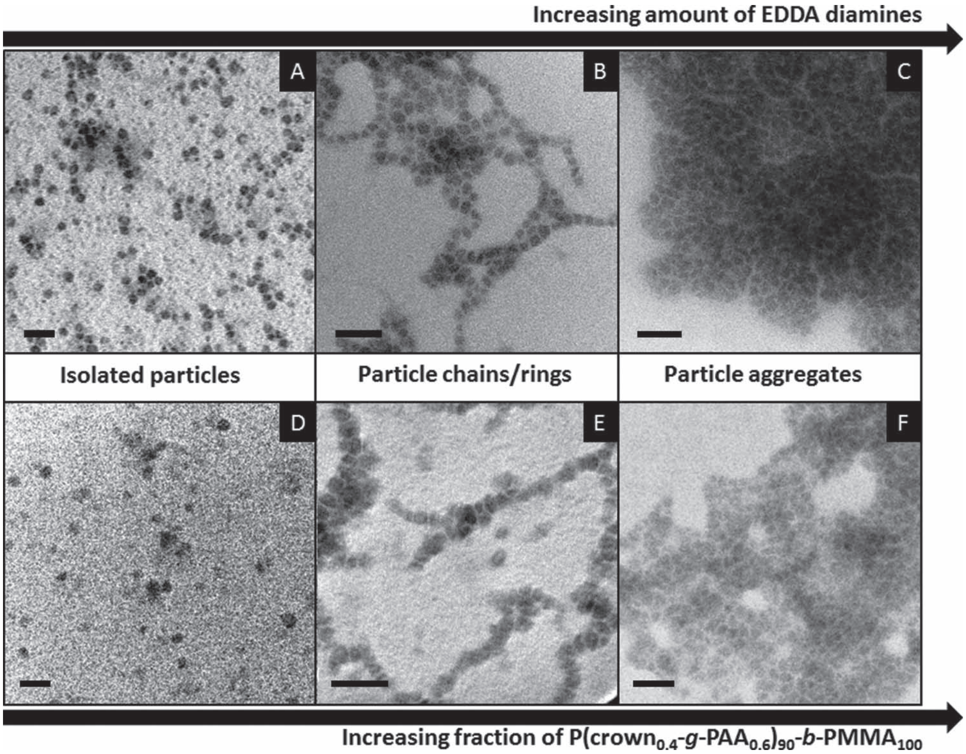

Figure 3. Morphological manipulation among isolated nanoparticles, particle chains/rings, and particle aggregates by differing the amounts of added diamine and diblock copolymer blending ratios. TEM images show the superstructures formed by P(crown$_{0.4}$-*g*-AA$_{0.6}$)$_{90}$-*b*-PMMA$_{100}$ and PAA$_{75}$-*b*-PB$_{104}$ mixed at a 1:1.5 molar ratio in a 1:4 volume ratio of DMF and water solution with EDDA at increasing amine to (acid + crown ether) ratios from A) 0, B) 1:1, to C) 2:1; At a fixed amine to (acid + crown ether) ratio of 0.5, varied superstructures were obtained from P(crown$_{0.4}$-*g*-AA$_{0.6}$)$_{90}$-*b*-PMMA$_{100}$ and PAA$_{75}$-*b*-PB$_{104}$ mixed at varied molar ratios from D) 0, E) 1:8, to F) 5:1. Samples were aged for 1 day and stained by OsO$_4$ before imaging. Scale bars = 100 nm.

of P(crown$_{0.4}$-*g*-AA$_{0.6}$)$_{90}$-*b*-PMMA$_{100}$ in the mixture, more crown ether groups in the particle shell improved the interparticle attraction and less acrylic acids reduced the charge repulsion.

On the basis of evidence described above, we propose an assembly mechanism responsible for the hierarchical formations as illustrated in **Figure 4**. The solvent mixing process gives rise to complex nanoparticles with PMMA and PB blocks from different diblock copolymers mixed in the core and crown ether and acid side chains mixed in the shell. The nanoparticles are initially separated in solution because PAA is a weak acid and becomes slightly negatively charged in aqueous mixtures. When the diamine EDDA is added to the solution, EDDA complexes with the acid side chains ubiquitous in the shells of the nanoparticles. However, as shown in the NMR measurements summarized in Figure 2, after protonation due to interactions with PAA acid side chains, the protonated amines can then interact strongly with crown ether functionalities also present in the shells of the nanoparticles. Only diamines that complex with crown ether groups from two neighboring particles can link the particles together as a nucleus from which further nanoparticles can connect to and grow into superstructures. As shown in Figure 4, the addition of a third particle can have three typical cases: linear packing, branched packing, and close packing, corresponding to position 1, 2, and 3. The final formations are determined by the relationship between charge repulsive forces due to deprotonated acid side chains in the shells of all nanoparticles and the attractions due to amine-crown ether interparticle bindings that are position dependent; for instance, the repulsive force at position 3 is approximately twice that at position 1 or 2.[48] The relative attractive forces are dependent on the fraction of crown ether-containing PAA present in the shell and available amine present that can complex with the crown ether and link particles together. Samples with less crown ether functionality or lower amount of amines will link in a linear fashion as highlighted in Figure 4 at position 1 or 2 for linear and branched packing with minor shell contact. Case 2 can occur with a slightly higher amount of crown ether-diamine complexation in a particle adding to a linear chain, but, as seen in Figure 1 and 2, occurs much less in frequently than case 1 attachment. Finally, if there is more crown ether and diamine present, additional spheres will tend to interact as closely as possible with growing domains in order to maximize shell contact. Therefore, 3D growth is preferred. As a result overall, one-dimensional chains of spheres, two-dimensional sphere rings, and three-dimensional sphere aggregates are three typical resultant formations correlated to the growth mechanisms of linear, branched and close packing, respectively.

Amphiphilic block copolymer assembles in solution are known as non-ergodic systems in which polymer chains are

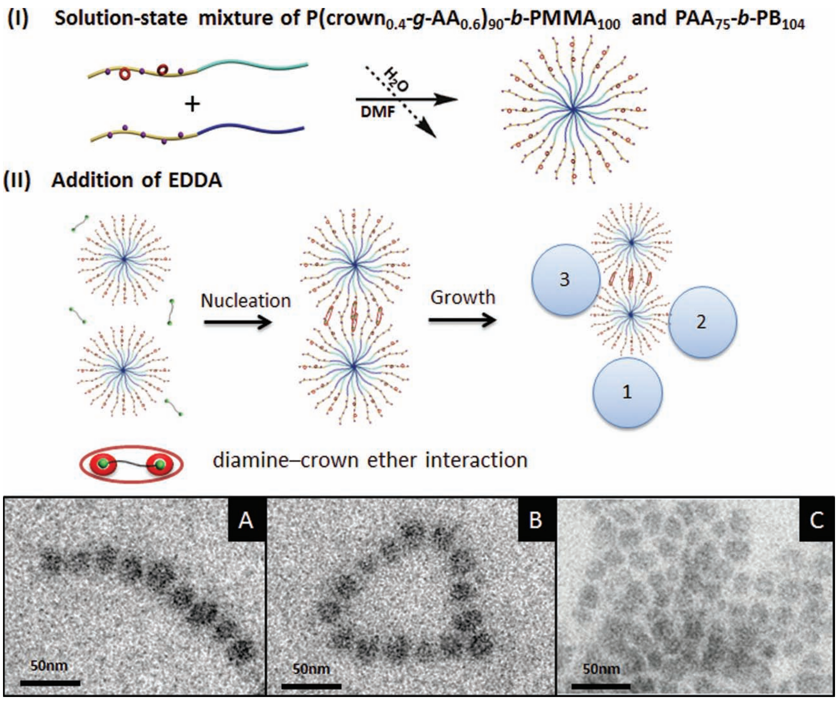

Figure 4. Hierarchical assembly process for superstructure formation consists of (I) nanoparticle assembly as building units, and (II) interparticle association. First, isolated nanoparticles were assembled from a diblock copolymer mixture of P(crown$_{0.4}$-*g*-AA$_{0.6}$)$_{90}$-*b*-PMMA$_{100}$ and PAA$_{75}$-*b*-PB$_{104}$ via fast water addition into DMF solution to a 4:1 volume ratio of water:DMF. Then, intermicellar association is triggered by addition of diamine, EDDA. Through a proposed growth process, superstructures, such as A) chains, B) rings, and C) 3-D aggregates were built with linear, branched, and close packing (corresponding to position 1, 2, and 3 in the illustration), respectively. TEM samples were stained by OsO_4.

dynamic primarily within assemblies. The inability of the global system to equilibrate over relatively brief periods of time allows the production of kinetically-defined structural diversity and manipulation. In dilute solutions, mobility of polymer chains is typically limited for inter-micellar exchange due to the high molecular weight and the physical characteristics of the polymer segments,[49] yet relatively fast for intra-micellar relaxation, inversion or segregation.[8] In case of isolated spherical micelles with PMMA and PB mixed core trapped within the same amine-PAA complexed shell, the initially well-mixed PMMA and PB blocks slowly phase-separated. As shown in **Figure 5**B, OsO_4 stained TEM image revealed dark semi-spherical PB-rich domains and light semi-spherical PMMA-rich domains in the particle cores. The volume ratio of the PB and PMMA subdomains well represented that of the original diblock copolymer mixtures. Directed by core phase separation, PAA blocks that are covalently linked to PB or PMMA blocks segregate in the shell as well. Therefore, in the case of interparticle association in chains, the mobility and segregation of core blocks are strongly affected by supramolecular interactions in the shell. The chains of nanoparticles (Figure 5D) assembled from P(crown$_{0.4}$-*g*-AA$_{0.6}$)$_{90}$-*b*-PMMA$_{100}$ and PAA$_{75}$-*b*-PB$_{104}$ with EDDA eventually evolved into striped cylinders as shown in Figure 5E. The dark stripes perpendicular to the cylinder axis indicate layers of PB-rich domains that are selectively stained by OsO_4. The light stripes are composed of PMMA segments and EDDA-complexed P(crown$_{0.4}$-*g*-AA$_{0.6}$)$_{90}$ blocks.

The morphological evolution of the hierarchical structure is considered as an interparticle interaction-directed phenomenon as shown in Figure 5F. Once the micelles linked together into linear chains due to crown ether-containing PAA residing predominately in between connected particles, unmodified PAA chains moved away from the neighboring micelles to avoid energetically unfavorable electrostatic contacts. As a result, more stable, sandwich-like distribution of hydrophilic blocks was slowly reached where PAA segments packed in the middle perpendicular to the particle chain axis and P(crown$_{0.4}$-*g*-AA$_{0.6}$) segments aligned along the chain axis. This shell morphology directed unlike PB and PMMA blocks to progressively segregate into sandwich-like core subdomains, accordingly.

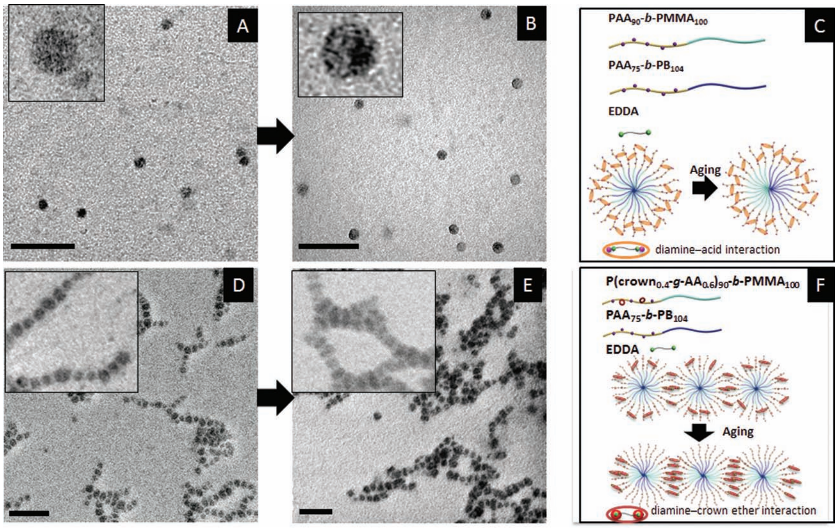

Figure 5. Morphological evolution of both isolated spherical nanoparticles and sphere chains. After 3 days aging, B) multicompartment spherical nanoparticles were obtained from A) mixed sphere of PAA$_{90}$-*b*-PMMA$_{100}$ and PAA$_{75}$-*b*-PB$_{104}$ in a 1:4 volume ratio of DMF and water mixture with additional EDDA diamine (amine-to-PAA acid side chain molar ratio = 0.5:1.0). After 7 days aging of D) sphere micelle chains from P(crown$_{0.4}$-*g*-AA$_{0.6}$)$_{90}$-*b*-PMMA$_{100}$ and PAA$_{75}$-*b*-PB$_{104}$ mixtures in a 1:4 volume ratio of DMF and water mixture with additional EDDA at an amine-to-PAA acid side chain molar ratio = 0.5:1.0, E) striped cylinders were obtained. The proposed shell interaction-directed mechanism is illustrated in (F). All block copolymer mixing molar ratios (PMMA to PB volume ratios) were 1:1.5 (1:1). Samples were stained by OsO_4. Scale bars = 200 nm.

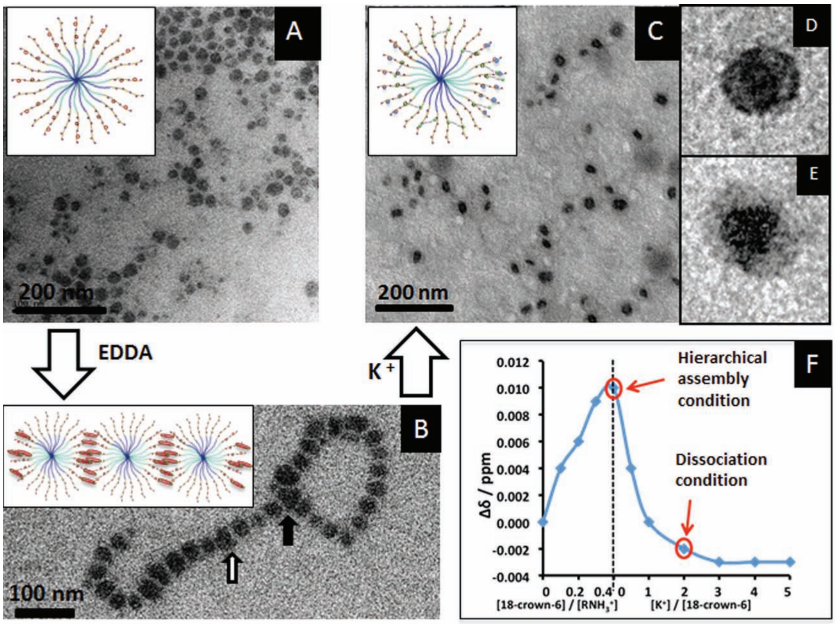

Figure 6. A) Isolated spherical nanoparticles were obtained from P(crown$_{0.4}$-*g*-AA$_{0.6}$)$_{90}$-*b*-PMMA$_{100}$ and PAA$_{75}$-*b*-PB$_{104}$ at a mixing molar ratio (PMMA to PB volume ratio) of 1:1.5 (1:1) via fast water addition into DMF solution. Subsequent addition of EDDA gave rise to nanoparticle chains (B) and rings with multiple segregated core domains after 3 days aging. Through addition of excess K$^+$ (2:1 molar ratio of K$^+$ to crown ether), the hierarchical superstructures were cleaved into separated nanoparticles (C). Both sandwich (D) and concentric triangle (E) shaped multicompartment particles were obtained, which are correlated to the micelles that existed on the backbone (white arrow) and junction points (solid black arrow) of the micelle chains and rings (B), respectively. Samples were stained with OsO$_4$. F) NMR shift of the CH$_2$NH$_3$$^+$ peak (at ca. $\delta = 3.22$ ppm) of guest molecule EDDA on the addition of 18-crown-6 and followed by the addition of K$^+$. The molar ratio of acid:18-crown-6:amine:K$^+$ was 4:1:2.5:2 in the lower cycled point, modeling the addition of K$^+$ ion to trigger the dissociation.

Disassembly of crown ether-ammonium linked superstructures was achieved by addition of competitive potassium ion (**Figure 6**).[42] Through addition of excess K$^+$ to break the linkage between the particle shells, the striped cylinders dissociated into separated nanoparticles (Figure 6C) that retained the separated PB and PMMA compartments in the cores. Both sandwich (Figure 6D) and concentric triangle (Figure 6E) shaped multicompartment particles were obtained that correlated with the precursor particles that existed in the backbone (hollow black arrow) and junction points (solid black arrow) of the striped cylinder particle morphologies (Figure 6B), respectively. To verify the proposed mechanism for the dissociation of the nanoparticles with the addition of potassium ions, an additional ^{1}H NMR study on the model compounds was performed. As shown in Figure 6F, at the assembly condition for striped cylinders, EDDA was present in an excess relative to the crown ether and was completely protonated by the excess acid, allowing for complete complexation of the minority crown ether functionalities. Upon the addition of potassium ion, which binds to crown ether 2 to 3 orders of magnitude more strongly than does the RNH$_3$$^+$,[50] the more weakly bound ammonium cation was released from the crown ether-ammonium complex. The addition of one equivalent of potassium ion was sufficient to complete this process to replace ammonium ion in the crown ether. The resultant isolated particles were stable and not able to link together upon further addition of diamines. The major advantage of using supramolecular chemistry for hierarchical assembly, apart from its relative ease, is the fact that the process can be a reversible one if under proper chemical selection, and the interparticle associations can be broken at a controlled moment of choice. This method opens the possibility of controlled release due to a transition between worm-like and spherical particles,[51] as well as a "top-down" method[52] to fabricate novel, complex nanoparticles.

3. Conclusions

We have reported a hierarchical assembly strategy of utilizing pre-formed block copolymer nanoparticles as building units to assemble into higher-ordered, multicompartment superstructures including 1D chains, 2D rings and 3D aggregates. The complex block copolymer nanoparticles were preformed through a simple rapid solvent mixing process from a blend of two diblock copolymers sharing the same PAA hydrophilic block chemistry and having either PB or PMMA as the hydrophobic segment. Crown ether moieties were incorporated into the PAA block of the PAA-b-PMMA copolymer, through a post-polymerization modification, to provide tunable interparticle interactions and hierarchical assembly processes with easy manipulation of added guest molecules (diamine or potassium ion) or the blending ratio of polymers. Interestingly, internal nanoparticle core morphological phase segregation of the PB and PMMA was affected by associations between the shells of different nanoparticles, driven by supramolecular crown ether-ammonium interactions facilitated by small molecule diamine additives. The hierarchical assemblies could then be disassembled by addition of potassium ion into multicompartment nanoparticles, including sandwich-like and concentric triangle-shaped structures. This combination of selective chemical modification and kinetically-controlled assembly demonstrates the great potential of complex block copolymer nanoparticles for hierarchical material construction by inter-nanoparticle association.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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