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Publication Date
2015

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Manipulating Supramolecular Nanocomposite Self-Assembly via Entropy Modulation

By

Peter Jin Bai

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Engineering - Materials Science and Engineering in the Graduate Division of the University of California, Berkeley

Committee in charge:

Professor Ting Xu, Chair
Professor Andrew Minor
Professor Felix Fischer

Spring 2015
Manipulating Supramolecular Nanocomposite Self-Assembly via Entropy Modulation

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by

Peter Jin Bai
Abstract

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Peter Jin Bai

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University of California, Berkeley

Professor Ting Xu, Chair

A grand challenge in materials science is to create materials with complex, rationally designed structures and functionalities. Self-assembly is a promising route to fabricate these materials with nano-scale precision, and efficiency in terms of cost and time. Nanocomposites comprised of block copolymer (BCP)-based supramolecules and nanoparticles (NPs) represent a promising platform to access nanostructures of various structures, chemistries, and functionalities. The thermodynamic landscape, and thus self-assembly behavior, of these supramolecular nanocomposites is dominated by entropic factors. While entropy is often considered a detrimental factor that prevents the formation of ordered phases and the co-assembly of BCPs and NPs, it can also be harnessed to stabilize nanostructures that are not accessible to traditional BCPs. This dissertation will focus on controlling the self-assembly of supramolecular nanocomposites by manipulating the entropy in these systems.

In bulk and thin films of supramolecular nanocomposites, self-assembly is governed by a balance between NP translational entropy and supramolecule chain conformational entropy. By systematically varying the NP size within these systems, this entropic balance can be perturbed, leading to a change in NP spatial distribution within the nanocomposite and the stabilization of cubic and anisotropic microphases that are unique from traditional BCP morphologies, as confirmed by TEM, TEM tomography, and small angle X-ray scattering techniques.

Geometrically confining supramolecular nanocomposites into cylindrical pores introduces boundary conditions that impose additional entropic frustration to the composite system, leading to exotic nanostructures such as NP stacked rings and single and double helices. The single helical structures are also demonstrated, via dark field scattering and finite integration technique simulations, to possess strong chiral plasmonic
properties due to the chiral arrangement of NPs and strong plasmonic interparticle coupling.

Finally, replacing alkyl side groups of the supramolecules with liquid crystalline side groups further increases chain rigidity and presents another avenue towards entropic modulation. These modified supramolecules and their associated nanocomposites are thoroughly investigated for their self-assembly behavior. It is observed that the liquid crystalline small molecule side chains introduce hierarchical smectic ordering and thermally triggered, non-reversible order-order transitions to the supramolecular nanocomposite.

These studies demonstrate entropic modulation in supramolecular nanocomposites to be an important tool in creating uniquely structured and functional materials with potential applications in memory storage, energy transport, and metamaterials.
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Acknowledgments

I would like to extend my sincere gratitude for everyone who graciously supported me during my graduate years. Obtaining a doctorate degree was beyond my dreams when I first embarked on my studies in science, and achieving this honor would be impossible without their contribution.

First and foremost, I would like to thank Prof. Ting Xu, my researcher advisor, who took me under her wing. She provided me with invaluable opportunities to tackle many intriguing scientific problems and always challenged me to think critically and creatively. She also granted me the freedom to pursue my research interests, and introduced me to many brilliant colleagues and collaborators whom I had the privilege to work with. I am grateful for her guidance and cultivation throughout the years.

I also would like to thank everyone in the group whom I had the pleasure to spend these past 5 years with. They are not only my colleagues in lab but also my dear friends in life. Joseph Kao was a great mentor who set high standards for academic rigor and professionalism, and was a great friend who never hesitated to share a joke, a laugh, and a drink. Kari Thorkelesson and Ben Rancatore are also my dear colleagues who, along with Joseph and I, spent countless hours together at beamlines and conferences. Our interactions together are some of my happiest times in grad school, and make me proud to be a part of the nanoparticle subgroup. Beverly Zhang and Nikhil Dube were always there to offer support in dealing with the ups and downs of scientific research. Their dedication and perseverance to research is a great inspiration to me. I also appreciate the help and company of Joseph Chang, He Dong, Yunfeng Qiu, Yeling Dai, and Tao Li, as well as collaborators from other groups, Sui Yang, Wei Bao, Peter Ercius, Joseph Strzalka, and Zhang Jiang. I have learned much from them, both professionally and personally.

Finally, I offer my sincere gratitude to my parents, Anna and David, who started my education even before bringing me into this world, and continued ever since. More importantly, they enlightened me to the importance of being not only a good scholar, but also a good person who genuinely respects and cares about other people. They offered me their unconditional love and support for my academic pursuit, and encouraged me to overcome many difficulties as they arise. I cannot wait to receive this incredible academic honor as they bear witness.
Chapter 1

Entropy Driven Self-Assembly in Block Copolymer and Block Copolymer based Nanocomposites

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§ 1.1 Introduction

The macroscopic world that we live in is permeated by an almost infinite diversity of materials, each with distinct physical properties, that govern every aspect of our daily lives. However, such diversity is afforded by a collection of a little more than one hundred different types of atoms, of which a even smaller subset are employed in routine applications. The key to the diversity of materials lies in the nano-scale, where the interaction and arrangement among different atoms dictate their collective macroscopic properties. In the past centuries and millennia, understanding of this nano- to macro-scale correlation is limited. Thus, new materials development has been slow, often relying on naturally occurring materials, accidental discoveries, and trial-and-error. With the advent of modern science and technology, it has become increasingly feasible to alter material properties by rationally manipulating their nano-scale structure and composition, leading to rapid advancement in chemistry and materials science. Currently, a grand challenge in materials science is to create a new class of structurally and functionally complex materials with arbitrarily designed physical properties.

Nanoparticles (NPs), or clusters of 100 to 10,000 atoms\textsuperscript{1-5}, are ideal building blocks for constructing these new materials. NPs are often regarded as “artificial atoms”\textsuperscript{6} as they exhibit unique optical, electronic, magnetic and mechanical properties due to inter-atomic coupling and quantum confinement effects. Precise, hierarchical assembly of NPs into 1-D, 2-D and 3-D nanostructures is often required to translate the nanoscopic properties of NPs into desired macroscopic properties via interparticle coupling \textsuperscript{6-16}. Traditionally, NPs are assembled via “top-down” approaches, in which the desired patterns are lithographically defined in the form of topographical trenches\textsuperscript{17-19} or chemical patterns\textsuperscript{20, 21}, and NPs introduced to these systems conform to the trenches via physical capillary forces or chemical affinity. While these approaches are highly versatile in the variety of nanostructures accessible, they also suffer several shortcomings, as the definition of the patterns is a time consuming and cost ineffective process. In addition, the patterns are limited in resolution to tens of nm due to the resolution limit of current lithography technology, and are largely confined to flat substrates. These drawbacks are major bottlenecks towards the large scale exploration and manufacturing of NP-based nanostructures towards next-generation advanced functional materials for applications in diverse technological fields such as energy production, storage and transport, medicine, memory storage, and information technologies.

To address the issues associated with top-down NP assembly, another class of NP assembly techniques known as “bottom-up” assembly has been developed and actively researched. The main concept of “bottom-up” assembly is to enable the self-assembly of nanoscale building blocks into desired structures without the need of preexisting guiding patterns. These approaches rely on manipulating the thermodynamic energy landscape of the materials system such that the desired structure represents a thermodynamically stable
or metastable state of that system. To date, NPs have been assembled using “bottom-up” approaches such as controlled drying\textsuperscript{22-24}, DNA templating\textsuperscript{4, 8, 25, 26}, and block copolymer (BCP)-directed assembly techniques\textsuperscript{27-31}. While these techniques possess some advantages in comparison to “top-down” techniques, they also possess shortcomings. Controlled drying techniques, while highly simple and scalable, are limited to simple 2-D superlattice patterns. DNA-templating approaches, while able to surpass “top-down” approaches in terms of structural versatility and resolution, are prohibitively expensive due to the cost of DNA synthesis.

BCPs, which are polymers with two or more chemically distinct segments, or blocks, are especially interesting for directed assembly of NPs as they are low-cost, easily scalable, and versatile in the variety of nanostructures accessible in di-, tri-, and multiblock systems\textsuperscript{32}. However, this approach is not without limitations. The directed assembly of NPs within BCPs relies on the chemical affinity of NPs to a specific block of the BCP via van der Waals\textsuperscript{33-36}, dipole-dipole\textsuperscript{31}, or hydrogen bonding interactions\textsuperscript{37-39}. Therefore, the assembly of NPs with different chemistries often requires complex chemical modifications to either the NP surface ligand chemistry or the BCP chemistry. Another limitation, which will be discussed in further detail in the remainder of this chapter, is that the incorporation of NPs within the BCP matrix will induce entropic penalty which increases with increasing NP size, thus disrupting the self-assembly of large NPs within the BCP and limiting the effective range of this assembly technique to small NPs of ~10 nm in diameter or less.

A BCP-based supramolecular approach has been developed to address the first issue of BCP/NP chemical compatibility. A BCP-based supramolecule comprises a BCP in which one or more blocks contain side chains that are non-covalently linked to the polymer backbone by hydrogen bonding\textsuperscript{40-44}, ionic complexation\textsuperscript{45-49}, metal coordination\textsuperscript{50}, \(\pi-\pi\) interactions\textsuperscript{51}, and combinations of these non-covalent forces\textsuperscript{52}. The non-covalent nature of the side chain allows the side chain chemistry to be easily modulated, thus circumventing the need for complex chemical modifications to tune the BCP/NP interactions. By hydrogen bonding small molecules with long alkyl chains as the supramolecule side chains, a wide variety of metallic, semiconducting, and insulating NPs can be readily incorporated and assembled within the supramolecule due to the favorable van der Waals interaction between the alkyl groups of the supramolecule side chain and NP ligands\textsuperscript{53}. Since a wide variety of inorganic NPs employ alkyl ligands to maintain colloid stability in solutions, the supramolecular approach is a highly versatile approach for NP assembly. Furthermore, the side chain chemistry can be readily modulated to accommodate other types of NP surface chemistries.

The second issue of entropic penalty is fascinating in that it is both detrimental and potentially beneficial to BCP and supramolecule directed NP assembly. On one hand, the increasing entropic penalty as a function of increase in NP size disrupts the self-assembly of NPs with diameters that represent a significant fraction of the BCP
microdomain size. This represents a significant obstacle towards the application of BCP and supramolecule directed NP assembly towards technological applications, as larger NPs exhibit stronger interparticle coupling. On the other hand, modulating the entropic penalty within the BCP matrix may also alter the thermodynamic equilibrium states within the composite system, thus leading to nanostructures that are not accessible in typical BCPs. Thus, a comprehensive understanding of the role entropy plays in the self-assembly of BCPs and BCP-based nanocomposites is requisite to utilize entropic modulation in rational materials design. The following sections review the current knowledge and state of the art in the role of entropy in the self-assembly of BCPs and BCP/NP nanocomposites in bulk, thin film, and geometric confinement conditions. This will be followed by a discussion of how the supramolecular nanocomposite system presents a valuable opportunity to not only create chemically versatile composite materials, but also to investigate the effect of entropic modulation on the self-assembly behavior and nanostructure control of these materials.

§ 1.2 Role of entropy in block copolymer/nanoparticle composites

The tendency of a BCP to microphase separate is governed by a balance between enthalpic (H) and entropic (S) driving forces that together constitute the Gibb’s free energy (G) \(G = H - TS\),

\[
G = H - TS
\]

where T is the temperature. The chemically distinct blocks in a BCP may be thermodynamically incompatible with each other due to the low entropy of mixing that scales inversely with molecular weight, and the enthalpic Flory-Huggins interaction parameter \(\chi_{AB}\),

\[
\chi_{AB} = \left(\frac{z}{k_B T}\right)\left[\varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})\right]
\]

where \(z\) is the number of nearest neighbors per atom, \(k_B T\) is the thermal energy, and \(\varepsilon_{AB}\), \(\varepsilon_{AA}\) and \(\varepsilon_{BB}\) are the interaction energies between AB, AA and BB monomer pairs, respectively. The interaction parameter is positive when the A and B monomers are incompatible (i.e. when the creation of two A-B pairings at the cost of a A-A and B-B pairing). The total interaction enthalpy of the A and B blocks is given by \(\chi_{AB}N\), where \(N\) is the total number of monomers per polymer chain. For \(\chi_{AB}N > 10.5\), the enthalpic tendency to phase separate dominate the entropic tendency to phase mix, resulting in phase separation between the two blocks \(55\).

Besides enthalpic contributions, entropy also plays an important role in BCP phase behavior \(32\). Although the entropy of mixing is low for BCPs, the A and B blocks
cannot completely macro-phase separate due to the covalent bond between the A and B blocks. Instead, the blocks micro-phase separate to minimize the enthalpically unfavorable A-B interfacial area. However, phase separation also requires the BCP chains to stretch beyond their most preferred coiled conformations. This chain stretching induces an entropic penalty that is a function of the relative volume factions of the A and B blocks. The final thermodynamically stable micro-phase separated morphology of a BCP is therefore a balance between the enthalpic and entropic factors that leads to a minimization of the overall Gibb’s free energy. As the relative volume fractions between A and B blocks change, four different types of morphologies can be accessed. They are, in order of increasing volume fraction of the minority block: body centered cubic packed spheres, hexagonally packed cylinders, double gyroid networks, and lamellae (Figure 1.1)\textsuperscript{56-58}. For ABC triblock terpolymers, a much wider variety of morphologies exist\textsuperscript{59}.

\textbf{Figure 1.1.} Phase diagram (top) and morphology illustrations (bottom) of a diblock copolymer. For $\chi N > 10.5$, as the volume fraction of the yellow block increases from 0 to 1, the morphology transitions from disordered to bcc spheres (CPS/Q\textsuperscript{229}), hexagonally packed cylinders (H), cubic bicontinuous gyroid (Q\textsuperscript{230}), lamellar, and their inverse analogues. Adapted with permission from Wiesner \textit{et al.} Chem. Soc. Rev., 2011, 40, 522. Copyright 2011 Royal Society of Chemistry.
The entropic contributions and overall thermodynamic landscape of BCPs can be further complicated by additional perturbations to the materials system. Examples of these perturbations include addition of NPs, geometric confinement, and modulation of side chain stiffness. As will be discussed in the following sections, these complexities are sometimes problematic, but more often present opportunities to enhance BCPs in terms of functionality, versatility, and morphological diversity.

1.2.1 Role of entropy in bulk block copolymer/nanoparticle composites

The effect of entropic modulation in polymeric systems can best be demonstrated in the simplest polymer/NP hybrid system, that of homopolymer (HP)/NP composites. In these systems, the change in the overall Gibb’s free energy upon NP incorporation, \( \Delta G_{HP/NP} \), is given by

\[
\Delta G_{HP/NP} = \Delta H_{HP/NP} - T(\Delta S_{\text{trans}} + \Delta S_{\text{con}})
\]

where \( \Delta H_{HP/NP} \) is the HP/NP interaction enthalpy, \( \Delta S_{\text{trans}} \) is the NP translational entropy, and \( \Delta S_{\text{con}} \) is the polymer conformational entropy. Given favorable \( \Delta H_{HP/NP} \), small NPs embedded in the polymer matrix are uniformly dispersed to maximize \( \Delta S_{\text{trans}} \). As the NP size increases, the polymer chains are forced to stretch around the NPs to accommodate their incorporation. However, this deviation from ideal chain conformation decreases \( \Delta S_{\text{con}} \), in effect creating an entropic penalty that increases \( \Delta G_{HP/NP} \) and destabilizes the composite system. As the NP size approaches and exceeds the radius of gyration \( R_g \) of the polymers, the entropic penalty dominates the overall free energy balance, and the NPs are expelled from the polymer matrix in order to relax the chain conformation and reduce the conformational entropic penalty. This effect is demonstrated both computationally and experimentally in HP/NP composites containing cracks. As the composites are heated above the glass transition temperature \( T_g \) of the polymer matrix, small NPs remain uniformly dispersed within the matrix, while larger NPs are expelled out of the matrix and localized in the cracks to reduce the entropic penalty.

The thermodynamics of bulk BCP/NP nanocomposites is slightly more complex than HP/NP composites. The Gibb’s free energy of a bulk BCP/NP nanocomposite, \( \Delta G_{BCP/NP} \), is given by

\[
\Delta G_{BCP/NP} = \Delta H_{BCP/NP} - T(\Delta S_{\text{trans}} + \Delta S_{\text{con}} + \Delta S_{\text{geo}})
\]

where \( \Delta S_{\text{geo}} \) represents the polymer chain conformational entropy as a result of the geometric arrangement of the BCP microdomains. Similar to HP/NP composites, NPs in BCPs introduce large conformational entropic penalties upon incorporation within the polymeric matrix. Balazs et al pioneered the detailed theoretical study of the entropic effect in BCP/NP nanocomposites using a combination of Self-Consistent Field Theory (SCFT) and Density Functional Theory (DFT) calculations. It was determined that in an AB diblock copolymer, NPs with chemical affinity to the A block, yet small in radius \( R_{NP} \) compared to the \( R_g \) of the BCP \( R_{NP} = 0.2R_g \), form uniform dispersions within the
A microdomain to maximize $\Delta S_{\text{trans}}$. Larger NPs ($R_{NP} = 0.3R_g$) are found to localize at the center of the A microdomain, where the polymer is able to accommodate the NPs with minimal conformational entropic penalty (Figure 1.2). These results are later corroborated by O’Shaughnesssey et al., who used analytical scaling theory to study the phase behavior of NPs in BCP brushes. The theoretical predictions are supported by subsequent experimental studies, in which the $R_{NP}/R_g$ ratio is systematically varied by either changing NP size or changing the BCP molecular weight. While large NPs are sequestered in the center of the A microdomains, smaller NPs distribute more uniformly throughout the microdomain. However, as NP loading increases, even the small NPs begin to localize to the center of the microdomain, as the increase in NP translational entropy can no longer offset the decrease in polymer chain conformational entropy.

![Figure 1.2. Simulated concentration profiles of a) large NPs ($R = 0.3 R_g$) with 0.15 volume fraction loading, b) large NPs ($R = 0.3 R_g$) with 0.03 volume fraction loading, and c) small NPs ($R = 0.2 R_g$) with 0.15 volume fraction loading. The illustrates in the insets further clarify the spatial distribution of the NPs within the BCP microdomain. Adapted with permission from Balazs et al. Science, 2001, 292, 2470. Copyright 2001 American Association for the Advancement of Science.](image)

While entropic penalty is often considered as a negative factor preventing NP assembly within BCPs, it can also be harnessed to promote the formation of thermodynamically stable and morphologically complex BCP/NP nanocomposites. An interesting observation is made in the high energy tilt and twist grain boundary defects within the BCP/NP nanocomposites, where the conformational entropic penalty increases as a function of increasing defect tilt angle. Large NPs tend to localize to the high energy omega and T-junction defects to relieve the chain stretching and hence decrease the entropic penalty. NPs are even observed to alter the self-assembly characteristics of the BCP template due to exceptionally large entropic penalty induced by large NP size or high NP loading, dictating the morphology of the BCP microdomains. Simulations by Balazs et al. predicted that increasing the radii of NPs...
embedded in a cylindrical BCP from $0.1R_g$ to $0.3R_g$ resulted in a cylindrical to lamellar morphological transition of the BCP matrix, as the NPs disproportionately swell the A and B blocks to create a morphology with reduced AB interfacial area (Figure 1.3)\(^7^7\). Liang et al demonstrated this phenomenon experimentally, as increasing the size of CdS NPs embedded in a poly(styrene-block-4-vinylpyridine) (PS-\(b\)-P4VP) matrix resulted in a cylindrical to lamellar phase transition\(^7^9\).

Figure 1.3. Two dimensional density plots for BCPs containing a) small NPs ($R = 0.1R_g$) and b) large NPs ($R = 0.3R_g$) obtained from SCFT/DFT simulations, showing NP size induced morphological transition of BCP/NP composites. The left panels denote A block density distribution and the right panels denote NP density distribution. A phase diagram relating NP size to $\chi N$ is shown in c). Adapted with permission from Balazs et al. Macromolecules, 2002, 35, 4857-4858. Copyright 2002 American Chemical Society.

### 1.2.2 Role of entropy in thin films of copolymer/nanoparticle composites

While bulk BCP/NP nanocomposites demonstrate a wide variety of chemically and structurally tunable compositions, many applications require thin film geometry to comply with device specifications and/or existing manufacturing infrastructure. In thin films of BCP/NP nanocomposites, the energetic contributions become more complex due to the introduction of additional interfaces\(^7^4\), and the overall Gibb’s free energy of a BCP/NP nanocomposite thin film $\Delta G_{BCP/NP}$ is given by

$$\Delta G_{BCP/NP} = \Delta H_{BCP/NP} + \Delta H_{NP/Air} + \Delta H_{NP/Sub} - T(\Delta S_{trans} + \Delta S_{con} + \Delta S_{geo})$$

where $\Delta H_{NP/Air}$ and $\Delta H_{NP/Sub}$ are the interaction enthalpy between the NP ligands with the film/air and film/substrate interfaces, respectively.

As evident in the above equation, the entropic terms are the same for both bulk and thin film composite systems. However, with the presence of interfacial interactions in
thin film, the effect of entropic penalty on NP spatial distribution is altered. Bang et al conducted SCFT simulations on neutral Au NPs embedded within poly(styrene-block-methylmethacrylate) (PS-<i>b</i>-PMMA) thin films with lamellar morphology oriented perpendicular to the underlying substrate. They observed that larger NPs are expelled to the film/air interface instead of the center of the BCP microdomains. This occurs because the BCP chains are able to reduce the entropic penalty further by completely expelling the NPs from the matrix. Experimentally, Hamdoun et al used neutron scattering techniques to investigate the assembly of Fe₂O₃ NPs in deuterated poly(styrene-<i>b</i>-butylmethacrylate) thin films. They observed that smaller 4 nm NPs dispersed near the d-PS-<i>b</i>-PBMA interfaces, while larger 6 nm NPs localized in the center of the PS microdomain, a result similar to what was observed in the bulk. The absence of NPs expelled to the thin film surface may be due to the relatively small size of NPs used in this study. Green et al investigated the assembly of PS-coated Au NPs in poly(styrene-<i>b</i>-n-butyl methacrylate) lamellar thin films, and observed that while smaller NPs localized throughout the PS microdomain, larger NPs segregated to the edge dislocations within the film. The reason for this size dependence is that for smaller NPs, the gain in translational entropy for uniform dispersion outweighs the loss in conformational entropy, while for larger NPs the conformational entropic penalty dictates NP spatial distribution.

When the composite thin film is confined between two substrates, entropic penalty caused by the NPs can be large enough to alter the orientation of the BCP morphology. Balazs et al demonstrated this effect via simulation of a BCP with symmetric AB blocks confined between two A-like surfaces. Without NP addition, the BCP forms lamellae morphology parallel to the surfaces when the film thickness is commensurate with the distance between surfaces. However, when large neutral NPs are introduced to the system, the lamellae oriented perpendicular to the surfaces. This phenomenon is again due to the expulsion of NPs to the film/substrate interfaces, which effectively neutralizes the film/substrate interaction and energetically promotes the perpendicular orientation of the lamellae. This theoretically predicted result was experimentally corroborated by Russell et al, who used tri-<i>n</i>-octylphosphine oxide-(TOPO)-covered CdSe NPs embedded in poly(styrene-<i>b</i>-2-vinylpyridine) (PS-<i>b</i>-P2VP) to demonstrate the reorientation of the cylindrical BCP microdomains from parallel to perpendicular relative to the P2VP-selective Si substrate upon thermal annealing.

The theoretical and experimental investigation of BCPs and BCP/NP nanocomposites in bulk and thin film configurations clearly demonstrate the significance of entropic considerations during the rational design of these materials systems. While entropic penalty is often problematic for the stable incorporation of large NPs within BCP templating matrices, it can also be harnessed to stabilize the composite system via the intentional incorporation of low entropy defects. In fact, the significance of entropy transcends the stabilization of composite nanostructures in bulk and thin film. As will be discussed in the next section, even greater perturbations to the conformational entropy via...
2-D and 3-D external geometric confinement can potentially lead to the stabilization of BCP morphologies that are far from equilibrium phases in bulk and thin film.

§ 1.3 Role of entropy in block copolymers and block copolymer/nanoparticle composites under geometric confinement

Although BCPs are promising candidates for templating NP assemblies into unique nanostructures, the morphological diversity in bulk BCPs is limited to four main types of morphologies. Extensive research in thin film BCP systems has revealed that thermodynamic boundary conditions may significantly alter equilibrium BCP morphologies. For example, tuning the enthalpic interaction between film and substrates leads to transitions in the microdomain orientation between parallel and perpendicular to the substrate. Varying the film thickness introduces changes in the polymer chain conformational entropy, such that when the film thickness is not an integer multiple of the BCP equilibrium domain periodicity, significant entropic penalty in maintaining the symmetric morphologies causes the creation of asymmetry in the BCP thin film morphology, such as island and hole formation.

Thin film systems represent the simplest case of geometric confinement, that of 1-D confinement. Higher degrees of confinement, such as 2-D cylindrical confinement and 3-D spherical confinement, cause even greater entropic penalty to the confined BCP. The confining surfaces and the BCP interact strongly to produce the final morphology. In most cases, the domain spacing and interface curvature of the BCP microphases must deviate significantly from bulk values in order to satisfy the confining surface, especially as the dimensions of the confinement volume approaches the BCP microdomain size. As a result, numerous novel equilibrium morphologies are created, such as the perturbation of cylinders to helices or networks, concentrically nested structures, and other structures containing equilibrium defects. As these new morphologies greatly expand the library of accessible BCP self-assembled nanostructures, numerous recent theoretical and experimental publications have been devoted to this subject. The following sections will provide a review on this subject, with a particular focus on cylindrical confinement.

1.3.1 Block copolymers under geometric confinement: theory and simulation

Similar to 1-D confinement in thin films, BCP morphology under geometric confinement deviate from bulk morphologies due to two factors: enthalpic BCP/surface interactions ($\Delta H_{BCP/Sub}$) and entropic commensurability conditions ($\Delta S_{con}$). Here, the term commensurability relates to the ratio of the confinement dimensions and BCP bulk periodicity, and thus is an indication of the degree of entropic frustration in the chain packing. The simplest case of cylindrical confined BCPs is that of symmetric BCPs with A-B lamellar morphology, which behaves analogously to thin film lamellar BCPs. Simulations by Shi et al on cylindrically confined lamellar BCPs revealed that if the pore surface is strongly selective to one of the two blocks, concentric lamellae will be formed.
if the lamellae are commensurate with the confining pores (i.e. the pore radius is approximately an integer multiple of the lamellar periodicity), with the pore surface being wetted by the attracted block. Small deviations from this commensurability condition will result in changes in thickness of the concentric lamellae, while larger deviations in the pore radius will result in A or B block “holes” in the innermost cylinder. This is similar to hole formation in incommensurate BCP lamellar thin films, except the holes are filled with the other block in this case. For neutral pore walls, the lamellae will orient perpendicularly to the pore axis, forming alternating circular A and B disks, analogous to perpendicular lamellae in BCP thin films on a neutral substrate. In this case, incommensurability can still occur if the length of the pore is not an integer value of the lamellar periodicity, and novel morphologies such as single helices, double helices, triple helices, catenoid cylinders, and a gyroidal structures may form.

For asymmetric cylinder forming BCPs, the commensurability conditions are more complex, as the packing of cylinders are two dimensional in nature with three natural periodicities, $L_{10}$, $L_{20}$, and $L_{30}$ (Figure 1.4), which are related to the BCP periodicity $L_0$ as follows:

\[
L_{10} = L_{20} = L_0 \\
L_{30} = \frac{\sqrt{3}}{2} L_0
\]

In comparison, the lamellar geometry is one dimensional in nature with only one natural periodicity.

**Figure 1.4.** Schematic of the characteristic distances between cylinders. The rectangular cross-section signifies a commensurate condition, while the circular cross-sections all signify incommensurate conditions. Adapted with permission from Shi et al. Soft Matter, 2013, 9, 1407. Copyright 2012 Royal Society of Chemistry.

In terms of 2-D confinement, the commensurability condition in cylindrical BCPs is only satisfied if the confining surface is a rectangle with one side being an integer multiple of $L_0$ and the other side being an integer multiple of $L_{30}$. Hence, for cylindrical
confinement, the commensurability condition is never satisfied for BCPs with parallel cylindrical morphology (*i.e.* when the pore wall is selective to one of the blocks). This incommensurate confinement condition induces high conformational entropic penalty, leading to a wide variety of theoretically predicted morphologies that cannot be obtained in bulk or thin film systems as the pore radius is varied. It is important to note, though, that the parallel cylinder morphology is still accessible for certain pore radii that sufficiently approximate commensurate confinement conditions. For BCPs with perpendicular cylindrical morphologies (*i.e.* when the pore wall is neutral to both blocks), commensurability is dictated by a bounding rectangle with one side equal to the long axis of the confining pore, and the other side equal to the pore diameter. In general, simulations predict that when commensurability conditions are satisfied, BCP cylinders oriented perpendicular to the pore axis will form. When the confinement conditions are incommensurate to the BCP periodicity, asymmetric morphologies such as stacked toroids and helices will form to release the structural frustration and reduce entropic penalty.

For more complex confined systems, such as BCPs with gyroid morphology, multi-block copolymers and other confinement geometries (*i.e.* triangle/square pores, 3-D confinement etc.), determination of the resulting morphologies is even more complex, and are generally predicted via simulation and limited experimental works. A partial selection of theoretically predicted BCP morphologies under geometric confinement are give in Figure 1.5.
Figure 1.5. A sampling of theoretically predicted BCP morphologies under a) 2-D cylindrical and b) 3-D spherical confinement, as a function of confinement parameter (D/L). Adapted with permission from Shi et al. Soft Matter, 2013, 9, 1402-1405. Copyright 2012 Royal Society of Chemistry.

1.3.2 Block copolymers under geometric confinement: experiment

Experimentally, 2-D cylindrical confinement conditions can be satisfied using either porous anodic aluminum oxide (AAO) membranes as hard templates\textsuperscript{109-117}, or using electrospinning\textsuperscript{96, 118-123}. The experimentally observed confined BCP morphologies are largely in agreement with theoretically predicted results. For BCPs that form lamellar morphology in the bulk, a wide variety of morphologies are observed as a function of decreasing cylinder radius, including concentric circles\textsuperscript{109, 110, 112, 113, 115, 117-119, 121, 122}, a torus-like morphology\textsuperscript{115}, lamellae oriented perpendicular to the cylindrical axis\textsuperscript{109, 112, 117}. 
and finally a single wetting layer of the surface-preferential block surrounding the other block\textsuperscript{109, 112, 115}. The concentric circle morphologies also underwent significant deviations in periodicity as the radius of the concentric cylinder is changed, with the value ranging from $0.8 \leq L_0 \leq 1.6$\textsuperscript{115}. One important insight gained from experimental studies is that the kinetics of self-assembly also plays an important role in the morphological evolution of the BCP. A study by Yoo \textit{et al} on electrospun poly(styrene-block-isoprene) (PS-\textit{b}-PI) revealed that the confined BCP underwent several metastable phases before reaching the final theoretically predicted morphology\textsuperscript{120}.

BCPs that form cylinders in the bulk assume a wider variety of morphologies under cylindrical confinement, due to the inherent asymmetry of the BCPs. Russell \textit{et al} comprehensively investigated cylinder forming BCPs under confinement within AAO membrane pores (Figure 1.6). When the majority block preferentially wets the confining surface, the following morphologies are observed as the confining cylinder radius decreases: cylinders parallel to the long axis\textsuperscript{115}, single helices surrounding a cylinder\textsuperscript{115}, double helices\textsuperscript{115}, single helices\textsuperscript{115}, and circular layers and tori\textsuperscript{115}. When the minority block preferentially wets the confining surface, the following morphologies are observed as the confining cylinder radius decreases: cylinders parallel to the long axis\textsuperscript{112}, a single layer of minority block surrounding the majority block\textsuperscript{112}, a mixture of parallel cylinders and disordered microphase separation\textsuperscript{112}, one central minority block cylinder\textsuperscript{112}, and finally a minority block wetting layer surrounding the majority block\textsuperscript{112}.

Sphere-forming BCPs confined within cylindrical pores present the simplest morphology, retaining their spherical morphology in which the spheres are arranged in lines parallel to the pore axis. The number of lines increases with increasing pore radius\textsuperscript{115, 123}. Gyroid-forming BCPs, on the other hand, present the most complex morphologies under cylindrical confinement. There have been very sparse experimental studies done on this system, revealing highly variable and complex morphologies under cylindrical confinement\textsuperscript{96}.

Finally, 3-D spherical confinement conditions can also be realized for BCPs using a variety of techniques, including micelle formation in solvent followed by solvent evaporation\textsuperscript{124}, precipitation of BCPs in a poor solvent\textsuperscript{125, 126}, and creating aerosols of BCPs\textsuperscript{127}. In spherically confined lamellar BCPs, the morphologies are investigated extensively by Shimomura \textit{et al}, demonstrating that increasing the degree of spherical confinement resulted in the following observed morphologies: striped lamellae parallel to one axis of the sphere, a three-armed structure formed by one block surrounded by the other block, two small spheres of one block on both “poles” of the sphere surrounded by the other block, a “wheel” or “mushroom”-like structure, and janus morphology\textsuperscript{126}. For cylinder forming BCPs under spherical confinement, the morphologies are comprehensively investigated by Manners \textit{et al}. When the majority block wets the confining surface, concentric lamellae were formed. On the other hand, when the minority block wets the sphere surface, structures containing spheres of minority domain...
embedded in a majority block matrix were observed. For a neutral confining surface, the morphology resembled the majority domain encaged in a network of minority cylinders arranged into pentagons and hexagons\textsuperscript{128}.

Figure 1.6. A partial collection of cylindrically confined BCP morphologies, clockwise from top left: stacked disks, stacked rings, single helix around central cylinder, triple helix, single helix, and double helix. Adapted with permission from Russell \textit{et al.} Macromolecules, \textbf{2009}, 42, 9086. Copyright 2009 American Chemical Society.

1.3.3 Block copolymer/nanoparticle composites under geometric confinement

The rich morphological diversity of 2-D and 3-D confined BCPs provide ample opportunities as templates to create complex nanostructures. Some of the research on this subject achieved the nanostructures by directly functionalizing one of the blocks. For example, Stucky \textit{et al} infused a sol-gel precursor into an ABA triblock copolymer,
followed by cylindrical confinement within AAO membrane pores and calcining to remove the organic phase and preserve the silicate phase. By varying the pore size, nanostructured silica with stacked ring, and single, double and triple helical morphologies can be created\textsuperscript{111}. Steinhart et al used cylindrically confined asymmetric PS-\textit{b}-P2VP as templates for atomic-layer deposition of semiconductor materials, creating single and double helical hollow structures of ZnO\textsuperscript{116}.

To better take advantage of the quantum effects of nanomaterials, it is requisite to assemble preformed NPs within geometrically confined BCP templates. This is a challenging yet intriguing prospect, as the incorporation of NPs introduces additional entropic considerations into an already entropically frustrated system. Because of the complexity of this system, the amount of theoretical and experimental work devoted to this area is relatively sparse. Zhu et al conducted the first theoretical simulations of a cylindrically confined BCP/NP nanocomposite system using a hybrid SCFT/DFT approach. The composite system comprises a symmetric AB diblock copolymer and NPs that are neutral to both blocks. It was observed that when the ratio of the confining cylinder radius $R$ to the $R_g$ of the BCP is below 8, both the NP translational entropy and BCP conformational entropy decrease with tighter confinement. This implies that the nanocomposite self-assembly under cylindrical confinement is strongly entropy dominated. For $R/R_g > 8$, the conformational entropic terms decrease due to enthalpic interactions between blocks. As NP loading increases, the nanocomposite morphology transitions from a concentric lamellar to a cylindrical phase\textsuperscript{129}. Joo et al used coarse-grained molecular dynamics (MD) simulations to study the coassembly of NPs and asymmetric BCPs under cylindrical confinement. It was revealed that while NPs neutral to both blocks tend to be placed near the interface between radially alternating layers of A or B domains, NPs selective to one block swell the corresponding phase, inducing discrete asymmetrical morphologies\textsuperscript{130, 131}. The theoretically predicted self-assembled nanostructures were confirmed experimentally using Au or Fe$_2$O$_3$ NPs confined within electrospun PS-\textit{b}-PI\textsuperscript{131}. Li et al used dissipative particle dynamics to simulate double hydrophilic BCP/NP mixtures within cylindrical confinement, and found that the assembled structures of the composite system are different from those of pure BCP, implying that NPs play a significant structure directing role rather than a passive role within cylindrical confinement\textsuperscript{132}. Recent research by Hawker et al discovered that PS-\textit{b}-P2VP/Au NP nanocomposite micelles in chloroform created 3-D confined striped or janus ellipsoidal particles, with NPs sequestered at the PS/P2VP interface\textsuperscript{133}.

The myriad of research conducted on BCP and BCP/NP composites under geometric confinement suggest entropic frustration to be a promising approach in inducing unique BCP morphologies and expand the library of accessible nanostructures. However, the incorporation of NPs within these systems remains a significant challenge, and is an issue that is just beginning to be explored.
§ 1.4 Effect of polymer chain architecture on entropy

Besides NP incorporation and geometric confinement, the chain architecture of BCPs also significantly affects the conformational entropy. In BCPs containing flexible, linear chains, the chain segments orient randomly in space, creating Gaussian coils that resemble spheres with radii of $R_g$. These BCPs are referred to as coil-coil BCPs. In many cases, however, the chain architecture of BCPs is more complex. In BCPs where one block contains π-conjugation along the polymer backbone, helical secondary structures, aromatic groups, or rigid side groups, that particular block adopts an extended, rigid chain conformation that is no longer coil-like. These BCPs are often referred to as “rod-coil” or “coil-comb” BCPs.

The thermodynamic landscape and self-assembly behaviors of these BCPs deviate from coil-coil BCPs for two reasons. Firstly, the rigid block does not have the same conformational entropy as the coil block, which restricts its ability to pack within self-assembled microdomains. Secondly, the anisotropic nature of the rigid block leads to anisotropic interactions between the blocks, which could lead to unique, liquid crystalline microphases. These effects have been observed in a number of experimental studies. In a study on a rod-coil poly(hexylisocyanate-block-polystyrene) (PHIC-b-PS) system, Mao et al observed a number of unique phases not observed in coil-coil BCPs, such as arrowhead, wavy lamellar, and zig-zag morphologies. Mezzenga et al also discovered exotic, distorted lamellar, cylindrical and spherical morphologies in a rod-coil BCP containing poly(2,5-diethylhexyloxy-1,4-phenylenevinylene) (DEH-PPV) rod blocks and P4VP coil blocks. Segalman et al conducted a series of experiments on a (PI-b-DEH-PPV) system to map the equilibrium phase behavior of rod-coil BCPs as a function of temperature, molecular weight, and coil fraction. They identified liquid crystalline nematic phases between microphase separated and isotropic phases for all the samples containing a rod block volume fraction above 0.2.

The entropic effect of polymer chain architecture also extends to BCP-based supramolecules. Ikkala et al have extensively studied the phase behavior of supramolecules comprising BCPs with non-covalently bond small molecule side chains. This class of materials possesses a coil-comb chain architecture due to the comb-like structure of the rigid block. The rigidity of the comb-block promote the formation of hierarchical morphologies with organization on two length scales: that of the overall BCP and that of the comb-block, resulting in a wealth of unique morphologies such as lamellar-within-lamellar, lamellar-within-spherical, lamellar-within-cylindrical, lamellar-within-hexagonally perforated lamellae, gyroid-within-lamellar, cylindrical-within-lamellar, and spherical-within-lamellar. Monte carlo simulation studies of supramolecular coil-comb BCPs demonstrate that the comb structure significantly increases the chain rigidity and conformational characteristics of the chains. This change in chain rigidity has a dramatic effect on the chain conformational entropy, as Xu
et al have observed that when NPs are incorporated into coil-comb supramolecules, both small and large NPs localize to the center of the comb block microdomain to relieve chain conformational entropy, demonstrating the significant difference in the role of entropy between coil-coil BCPs and coil-comb supramolecules\textsuperscript{53} (Figure 1.7).

**Figure 1.7.** Self-assembly of ~4 nm NPs within a lamellar forming supramolecule, showing the precise sequestration of NPs to the center of the microdomain, forming chains 1 NP in width, even though the NP radii are only about 10\% of $R_g$. Adapted with permission from Xu et al. Nat. Mater., 2009, 8, 979. Copyright 2009 Nature Publishing Group.

The effect of chain architecture in coil-comb supramolecular systems is an interesting issue, as the rigidity can be easily tuned by modulating the non-covalently bond side chain, and the morphological behavior of these materials within composites have yet to be thoroughly explored.
§ 1.5 Conclusions and Outlook

Entropy is a problematic issue yet also a powerful tool in the self assembly of BCPs and BCP-based nanocomposites. The balance between NP translational entropy and BCP chain conformational entropy in bulk, thin film, and 2-D/3-D confinement geometries, as well as in rod-coil/coil-comb BCPs, have led to a wide variety of nanostructures that cannot be obtained from pure BCPs. While the effect of entropic modulation has been extensively explored in pure BCP and BCP/NP composite systems, it has only been scarcely investigated in BCP-based supramolecular nanocomposites. The exploration of entropic modulation in supramolecular nanocomposites is an important endeavor for several reasons. Firstly, the coil-comb architecture of supramolecules significantly changes the entropic landscape of the nanocomposite system due to the increased chain rigidity, thus may potentially lead to entropic effects and equilibrium structures not observed in BCP/NP composite systems. Secondly, the side chain chemistry can be readily tuned in supramolecules due to the non-covalent bonding, thus allowing the accommodation of a wide variety of NPs as well as the modulation of the side chain functionality.

In bulk and thin film supramolecular nanocomposites, the effect of NP size on the overall composite morphology have yet to be thoroughly explored. The stabilization of hierarchically structured, self-assembled nanostructures comprising functional NPs, especially large (> 10 nm) NPs, cannot be readily achieved in BCP/NP systems, and may lead to opportunities in creating electronically or plasmonically active materials due to the strong interparticle coupling within this NP size regime. The creation of unique stable morphologies due to the different entropic landscape is also an intriguing prospect that awaits exploration.

The self-assembly of supramolecules and supramolecular nanocomposites under geometric confinement also presents an exciting avenue for exploration, as the thermodynamic behavior of these material systems have never been investigated, both experimentally or theoretically. It is expected that the chain rigidity of supramolecules will magnify the effect of conformational entropic penalty in a system that is already entropically frustrated. This may lead to the stabilization of more exotic morphologies not previously observed in geometrically confined BCP systems. The stabilization of these exotic morphologies may be translated into exotic materials properties via the introduction of NPs, if they also conform to these morphologies. Of particular interest are chiral nanostructures such as helices, as materials with chiral structures may possess chiral physical properties.

Finally, modulating the supramolecule side chain chemistry may also significantly alter the entropic landscape of the material, leading to changes in the self-assembly behavior. Introduction of rigid side chains, such as liquid crystalline small molecules, may further increase the comb block rigidity, and its effect on the overall self-assembly
remains an interesting issue awaiting investigation. The interplay between the liquid crystalline phase behavior of the small molecules and BCP self-assembly could potentially lead to unique hierarchical co-assemblies of these materials and the incorporation of novel material properties.

A thorough study on the effect of entropic modulation on the self-assembly of supramolecular nanocomposites will enable a further degree of structural control in this promising material system. The myriad of unique nanostructures generated \textit{via} entropic modulation will greatly expand the library of structures accessible to supramolecular nanocomposites. The diversity in the chemistry, structure, and physical properties of these nanostructured materials may potentially find a wide variety of applications in modern technologies.

\section*{§ 1.6 General Approach and Synopsis of Subsequent Chapters}

The work described in this dissertation investigates the effect of entropic modulation in bulk, thin film, and 2-D cylindrically confined supramolecular nanocomposites (Figure 1.8). It begins in Chapter 2 with the self-assembly of bulk supramolecular nanocomposites as a function of increasing NP size. This work is followed up in Chapter 3, which extends the investigation of the effect of NP size to thin film supramolecular nanocomposite systems. Chapter 4 explores the assembly and physical properties of supramolecules and supramolecular nanocomposites under cylindrical confinement. Finally, Chapter 5 is focused on the bulk self-assembly of supramolecules and their composites containing rigid liquid crystalline side chains.
Figure 1.8. Schematic synopsis of Chapters 2-5, revolving around entropic modulation in supramolecular nanocomposites.
Chapter 2

Entropy Modulation in Bulk Supramolecular Nanocomposites

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Co-assemblies of block copolymer (BCP)-based supramolecules and nanoparticles (NPs) provide a versatile platform to generate hierarchically structured nanocomposites with tunable composition, nanostructure, and properties. Previous theoretical and experimental studies into BCP/NP and supramolecule/NP composite systems reveal that BCPs and BCP-based supramolecules behave as templates to direct NP assembly in conformity with existing BCP morphologies. In addition, the entropy of BCP chains and NPs play a significant role in determining the NP spatial distribution within BCP microdomains, with small NPs uniformly distributing within the microdomains and larger NPs sequestering to the center of the microdomains. However, these studies are limited to NPs that are significantly smaller than the radius of gyration of the BCP. In this chapter, assembly of NPs with sizes approaching the BCP radius of gyration are investigated, as the effect of entropic perturbation of large NP incorporation on the overall nanocomposite morphology is previously unknown. Thermodynamically, it is hypothesized that the energy landscape changes significantly since the entropy associated with the polymer chain increases with NP size, the inter-particle interactions increases and the geometric packing also varies. The experimental results outlined in this chapter suggest that for sufficiently large NPs, the NP assemblies can no longer be guided by the supramolecular framework. The large NP can readily change the morphology of the supramolecule and new assemblies, such as a double-row lamellae and square lattices, emerge. The observed NP size-dependent morphological transitions are explained as a balance among NP translational entropy, BCP chain conformational entropy, and BCP geometric packing entropy. The results of this investigation illustrate the importance of entropic modulation in stabilizing morphologies unique from bulk BCP and BCP-based supramolecules, and provide valuable knowledge for the rational design of nano-materials for applications as photonic crystals and plasmonic waveguides.

§ 2.1 Introduction

Nanoparticles (NPs) are often regarded as “artificial atoms” because of their unique optical, electronic and magnetic properties due to quantum confinement effects. These nanoscopic effects can potentially be translated into desired macroscopic properties by precisely controlling the NP spatial arrangement, rendering these assemblies useful in applications such as energy transport, sensing, and memory storage. While precise control over spatial distribution can be readily achieved with top down fabrication techniques, the control over spatial distribution of NPs has been a major impediment in bottom-up fabrication of functional materials. Achieving a high degree of NP spatial control with bottom-up fabrication approaches can enable low cost, high throughput production of functional NP-based composite materials.
Traditionally, DNA templating techniques can create NP assemblies with precisely defined and tunable nanostructures. However, these approaches are limited by high cost, low yield, are only applicable in aqueous environments, and rely on chemical compatibility between DNA and NP surface chemistry. Thus, these approaches are not ideal for the large scale fabrication of functional NP-based nanocomposite materials. Block copolymer (BCP) templating approaches, on the other hand, are able to generate complex NP nanostructures, such as body centered cubic NP spherical clusters, hexagonally packed NP arrays, and NP lamellae, that are low cost and can readily be scaled up. However, the NP spatial precision is generally lower than DNA-based approaches, and BCP-based approaches are also limited by chemical compatibility between BCP and NP surface chemistry.

To address the remaining challenges in BCP templated NP assembly, Xu et al. devised a BCP-based supramolecular approach to template NP assembly (Figure 2.1). The BCP-based supramolecules, comprised of \text{poly(styrene-block-4-vinylpyridine)} (PS-b-P4VP) with 3-n-pentadecylphenol (PDP) small molecules hydrogen bonded to the 4VP moieties, provide a versatile materials platform for NP assembly that has several advantages over simple BCPs. Firstly, the alkyl tails of the PDP small molecule side chains interact favorably with alkyl ligands of NPs \textit{via} attractive van der Waals interaction. Since many types of organic soluble NPs are synthesized with alkyl-based stabilizing ligands, such as alkyl-thiols, alkyl-amines, alkyl-acids \textit{etc}, the supramolecule templating approach has been demonstrated to be viable for a wide variety of NPs regardless of NP chemistry. For NPs with non-alkyl ligands, the non-covalently bound side chains can readily be exchanged with other types of small molecule side chains to introduce chemically compatible moieties. Secondly, the rigid coil-comb structure of the supramolecules incur high entropic penalty during NP incorporation, thus NPs tend to readily segregate to the center of the P4VP(PDP) microdomains. In effect, this high conformational entropic penalty increases the precision of NP spatial distribution within the supramolecule template.
A remaining challenge in supramolecule templated NP assembly is the precise assembly of large NPs (i.e. NPs approaching the radius of gyration of the supramolecules), as larger NPs tend to possess stronger interparticle coupling of certain plasmonic and magnetic properties. However, the effect of larger NPs on the entropic landscape and overall assembly of BCPs and supramolecules is not well investigated. Previous theoretical\textsuperscript{28-32} and experimental\textsuperscript{33-35} studies on simple BCP/NP nanocomposites revealed that while small NPs distribute uniformly within the BCP microdomain to maximize favorable enthalpic interactions and NP translational entropy, larger NPs tend to segregate to the center of the microdomains to minimize the polymer chain conformational entropic penalty. While these studies provide valuable insight to the importance of entropy in dictating NP spatial distribution in these systems, they are limited to NPs with diameters below 30\% of the BCP radius of gyration ($R_g$). For larger NPs, the conformational entropic penalty significantly increases, and is even more pronounced for supramolecule systems relative to coil-coil BCPs due to the comb block rigidity. The larger NPs may simply be completely expelled from the bulk supramolecule, forming a new macrophase, or the large entropic penalty may force the supramolecule
chains to rearrange, potentially leading to new nanocomposite morphologies not accessible in previous BCP/NP and supramolecule/NP bulk systems.

In this chapter, the effect of NP size on the resulting nanostructures of supramolecule/NP nanocomposites is systematically investigated for NPs with diameters ranging from 10% to over 100% of supramolecule $R_g$. Morphologies unique from BCP/NP and supramolecule/NP bulk systems are indeed observed, and the trend in morphological evolution are explained in terms of the changing nanocomposite entropic landscape as a function of increasing NP size. These studies demonstrate the important role of entropic modulation in stabilizing unique bulk morphologies in supramolecular nanocomposite systems, and provide valuable insight for the rational design of functional materials with precise control over NP spatial distribution.

§ 2.2 Size-dependent assembly of nanoparticles in bulk supramolecular nanocomposites

Two supramolecules, PS(40 $kdal$)-b-P4VP(5.6 $kdal$)(PDP)$_1$ and PS(33 $kdal$)-b-P4VP(8 $kdal$)(PDP)$_2$, are used in the size-dependent NP assembly studies. The PS(40 $kdal$)-b-P4VP(5.6 $kdal$)(PDP)$_1$ supramolecule, with a P4VP(PDP) comb-block volume fraction $f_{P4VP(PDP)} = 0.42$, lies in the lamellar regime of a typical BCP phase diagram. On the other hand, the PS(33 $kdal$)-b-P4VP(8 $kdal$)(PDP)$_2$ supramolecule, with $f_{P4VP(PDP)} = 0.63$, lies close to the lamellar/cylinder phase boundary. FTIR of the supramolecules clearly show peak shifts characteristic of pyridine/phenol hydrogen bond formation (Appendix 1.1), indicating that the PDP small molecules are indeed attached to the P4VP block via hydrogen bonding. TEM images of the supramolecules (Figure 2.2a-b) show that both supramolecules form lamellar morphology without the addition of any NPs (samples are stained with I$_2$ to highlight the P4VP domain as darker regions. Small angle X-ray scattering (SAXS) profiles of both supramolecules (Figure 2.2c-d) agree with the TEM observation, with structure factors of 1:2:3 indicating lamellar morphology of the supramolecules. For the PS(40 $kdal$)-b-P4VP(5.6 $kdal$)(PDP)$_1$ supramolecule, the first order scattering peak at $q = 0.0194$ Å$^{-1}$ indicates a lamellar periodicity of 32.5 nm. The PS(33 $kdal$)-b-P4VP(8 $kdal$)(PDP)$_2$ supramolecule, the first order scattering peak at $q = 0.0200$ Å$^{-1}$ indicates a lamellar periodicity of 31.4 nm.
Figure 2.2. TEM images of a) PS(40 kdal)-b-P4VP(5.6 kdal)(PDP)$_1$ and b) PS(33 kdal)-b-P4VP(8 kdal)(PDP)$_2$ supramolecules, both showing lamellar morphologies in bulk. Their respective SAXS profiles (c-d) show structure factors in agreement with the formation of lamellar morphologies.

2.2.1 Size-dependent assembly of nanoparticles in lamellar supramolecular nanocomposites

The PS(40 kdal)-b-P4VP(5.6 kdal)(PDP)$_1$ supramolecule is then loaded with dodecanethiol capped Au NPs ~ 3.5 nm in diameter to generate supramolecular nanocomposites (Appendix 1.6). At 1 vol% loading, NPs only partially fill the
P4VP(PDP) microdomains, forming very short lamellae primarily at defect sites where there is a change in supramolecule lamellae orientation. At 3 vol% loading, more NPs localize to the P4VP(PDP) microdomains, and the outline of the lamellar morphology becomes more pronounced. At 6 vol% loading, the NPs completely fill the P4VP(PDP) microdomains, forming lamellae ~ 13 nm in thickness, corresponding to 3-4 NPs in width (Figure 2.3a).

The nanostructure and assembly kinetics of the supramolecular nanocomposite is probed further using in situ SAXS carried out during heating of the sample from room temperature to 100 °C in 10 °C increments (Figure 2.3b). It can be observed that at 30 °C, the nanocomposite already possesses short range lamellar ordering, as revealed by the first and second order scattering peaks with a structure factor of 1:2. The first order peak position of \( q = 0.0182 \text{ Å}^{-1} \) indicates a periodicity of 34.4 nm, which is slightly larger than the supramolecule periodicity. As the annealing temperature increases, the first order scattering peak shifts to lower values and the full width half max (FWHM) of the peak increases, indicating an increase in both the periodicity and grain size of the lamellar morphology. At 80 °C, a third order peak emerges, and a fourth peak emerges at 100 °C with a structure factor of 1:2:3:4, indicative of long range lamellar ordering. The first order scattering peak at 100 °C at \( q = 0.0157 \text{ Å}^{-1} \) represents a significantly increased lamella periodicity of 40 nm. The increase in periodicity during thermal annealing is likely caused by the continued diffusion of NPs into the P4VP(PDP) microdomain. From the TEM and SAXS observations, it can be concluded that the morphology of this nanocomposite is a lamellar structure with a periodicity of ~ 40 nm with 3-4 layers of NPs within each lamella (Figure 2.3c). The in situ SAXS studies also suggest that the assembly kinetics of supramolecular nanocomposites is very rapid in comparison to BCP/NP nanocomposites, likely owing to the plasticizing effect of the PDP small molecules. In addition, the onset of disorder-to-order transition occurs at low temperatures of < 60 °C, in agreement with the low \( T_g \) of PS-\( b \)-P4VP(PDP) supramolecules reported by previous literature\(^{36, 37}\). Thermal annealing of subsequent samples are carried out at 60 °C for 12 hours.
Figure 2.3. a) TEM, b) in situ SAXS scattering profile and c) schematic of a PS(40 kdal)-b-P4VP(5.6 kdal)(PDP)₁ supramolecule with 6 vol% of ~ 3.5 nm Au NPs, forming a lamellar nanostructure with 3-4 layers of NPs sequestered in each P4VP(PDP) microdomain. Scale bar is 100 nm for the TEM image.

Oleic acid capped Fe₂O₃ NPs ~ 10 nm in diameter are incorporated into PS(40 kdal)-b-P4VP(5.6 kdal)(PDP)₁ supramolecules to investigate the effect of increasing NP size on the self-assembled nanocomposite morphology (Figure 2.4). TEM of the nanocomposite (Figure 2.4a) shows a lamellar morphology with a single layer of NPs occupying the center of each P4VP(PDP) microdomain. SAXS profile of the nanocomposite sample supports the TEM observation (Figure 2.4b). The structure factor of 1:2 indicates lamellar morphology. However, only up to second order scattering peak is observed, suggesting that the long range order is poor compared with nanocomposites containing ~ 3 nm Au NPs. The first order scattering peak value of \( q = 0.0153 \text{ Å}^{-1} \) corresponds to a lamellar periodicity of 41 nm, a slight increase compared to nanocomposites containing ~ 3 nm Au NPs. The broader peaks beyond the second order scattering peak represent the form factor of the spherical Fe₂O₃ NPs. From these observations, it can be concluded that ~ 10 nm Fe₂O₃ NPs are sequestered to the center of the P4VP(PDP) microdomain, forming lamellae 1 NP in width and 41 nm in periodicity (Figure 2.4c).
Further increasing the NP size, ~20 nm oleic acid capped Fe$_3$O$_4$ NPs are incorporated into the PS(40 kdal)-b-P4VP(5.6 kdal)(PDP)$_1$ supramolecule and the resulting nanostructures are characterized using TEM and SAXS (Figure 2.5). Surprisingly, the NPs are again observed to form lamellae one NP in width within the supramolecule (Figure 2.5a), despite the diameter of the NPs exceeding 0.6R$_g$. SAXS profile of the nanocomposite shows a scattering peak at $q = 0.0127$ Å$^{-1}$, corresponding to a lamellar periodicity of 50 nm, a significant increase from previous nanocomposite samples incorporating smaller NPs (Figure 2.5b). Only the first scattering peak is visible and is quite broad, in agreement with TEM observation that the grain size is further reduced. As a result, the structure factor cannot be determined from the SAXS data. The higher order broad scattering peaks represent the form factor of the NPs. These results suggest that ~20 nm Fe$_3$O$_4$ NPs are indeed sequestered within the P4VP(PDP) microdomains, forming lamellae 50 nm in periodicity, albeit with smaller grain sizes (Figure 2.4c). This is a remarkable result, because the NPs incur significant chain conformational entropic penalty on the supramolecule matrix by remaining within the lamellar microdomains instead of being expelled into a separate macrophase. Further increasing the NP size to 25 nm and 30 nm oleic acid capped Fe$_3$O$_4$ NPs resulted in random spatial distribution within the supramolecule (Appendix 1.7).
Figure 2.4. a) TEM, b) in situ SAXS scattering profile and c) schematic of a PS(40 kdal)-b-P4VP(5.6 kdal)(PDP) supramolecule with 6 vol% of ~ 20 nm Fe$_2$O$_3$ NPs, forming a lamellar nanostructure 1 layer of NPs sequestered in the center of each P4VP(PDP) microdomain. Scale bar is 100 nm for the TEM image.

To understand the NP size-dependent assembly in bulk lamellar supramolecular nanocomposites, it is necessary to revisit the thermodynamics of bulk supramolecular nanocomposite systems as discussed in Chapter 1. The thermodynamics is governed by the total free energy of the system, $\Delta G_{SM/NP}$, given by

$$\Delta G_{SM/NP} = \Delta H_{SM/NP} - T(\Delta S_{trans} + \Delta S_{con} + \Delta S_{geo})$$

where $\Delta H_{SM/NP}$ represents the attractive van der Waals’ enthalpic interaction between supramolecule and NPs, and the three entropic terms are the NP translational entropy, supramolecule chain conformational entropy, and chain geometric packing entropy, respectively.

In the case of the ~ 3.5 nm Au NPs, the diameter of the NPs is roughly equal to 0.11$R_g$. The NPs are significantly smaller than the P4VP(PDP) microdomain size, and thus do not incur appreciable conformational entropic penalty upon incorporation into the P4VP(PDP) microdomain. Instead, the NPs distribute uniformly throughout the P4VP(PDP) microdomain to maximize $\Delta S_{trans}$, forming multiple layers of NPs within each lamella. Another interesting observation in this system is that the microdomain spacing increased by 23% upon NP incorporation, which would allow the supramolecule chains to further relax and maximize their conformational entropy.

For the larger 10 nm Fe$_2$O$_3$ and 20 nm Fe$_3$O$_4$ NPs, the conformational entropic penalty upon NP incorporation is much higher. Therefore, for the 10 nm NPs, only one layer of NPs is sequestered to the center of each P4VP(PDP) lamellar microdomain to minimize the chain conformational entropic penalty. The observed trend in self-assembly
behavior for both the 3.5 nm and 10 nm NPs are similar to BCP/NP composite systems, in which an increase in NP size leads to sequestration of the NPs to the center of BCP microdomains. The self-assembly of the ~ 20 nm NPs is more interesting, as self-assembly of NPs in this size range (NP diameter > 0.6Rg) have not been previously studied. Remarkably, the lamellar microdomains are able to expand in periodicity by up to 54% to accommodate the large NPs without incurring significant entropic penalty. However, the ability of the supramolecule microdomains to expand apparently has an upper limit, as 25 nm and 30 nm Fe3O4 NPs are observed to randomly distribute within the supramolecule, likely due to their expulsion out of the supramolecule matrix.

2.2.2 Size-dependent assembly of nanoparticles in cylindrical supramolecular nanocomposites

Cylindrical supramolecular nanocomposites can be achieved by loading NPs into the PS(33 kdal)-b-P4VP(8 kdal)(PDP)2 supramolecule. Although this supramolecule was shown to self-assemble into a lamellar morphology without NP loading, its high fP4VP(PDP) suggests that the addition of NPs that preferentially localize to and swell the P4VP(PDP) comb block will increase the fP4VP(PDP) into the cylindrical regime. To initialize the investigation of NP size-dependent self-assembly in bulk cylindrical supramolecular nanocomposites, the PS(33 kdal)-b-P4VP(8 kdal)(PDP)2 supramolecule is loaded with 6 vol% of ~ 6 nm dodacanethiol capped Au NPs. The resulting morphology and self-assembly kinetics are studied using TEM and in situ SAXS during temperature ramp from room temperature to 100 ºC (Figure 2.5).

The TEM image of the supramolecular nanocomposite (Figure 2.5a) clearly shows the NPs neatly sequestered into the P4VP(PDP) microdomains, forming hexagonally arranged network structures surrounding the bright PS blocks. These nanostructures are consistent with those observed by Xu et al in PS-b-P4VP(PDP) supramolecules containing 2-5 nm CdSe NPs 27. The concentration of NPs is slightly higher in the interstitial sites at the intersection of three PS blocks, likely due to a larger amount of free volume within these interstitial sites.

In situ SAXS is conducted on this sample during a temperature ramp from 30 ºC to 100 ºC in 10 ºC increments to further probe its self-assembly kinetics (Figure 2.5b). At 30 ºC, the SAXS profile reveals a largely disordered morphology, with a broad scattering peak at approximately q = 0.010 Å⁻¹. This peak represents a real space characteristic spacing of 63 nm, and may signify the formation of polydisperse NP clusters fairly uniformly dispersed within the supramolecule matrix. Upon increasing the annealing temperature to 50 ºC, a first order peak at q = 0.016 Å⁻¹ and a second order scattering peak at q = 0.031 Å⁻¹ begin to appear as the nanocomposite gains sufficient thermal energy to undergo long range diffusion. The first order peak signifies a periodicity of 39
nm, while the structure factor of 1:2 signify the formation of lamellar morphology. The first and second order peaks increase in intensity and decrease in FWHM as annealing temperature further increases. Starting from 60 °C, another scattering peak emerges at \( q = 0.05 \text{ Å}^{-1} \), until 100 °C, when up to 4 scattering peaks are clearly visible, with a structure factor of \( 1: \sqrt{3}: \sqrt{4}: \sqrt{7} \), indicative of hexagonal morphology. The first order scattering peak at \( q = 0.0171 \text{ Å}^{-1} \) suggests a periodicity of 37 nm. From these observations, it can be concluded that nanocomposites comprised of PS(33 kdal)-b-P4VP(8 kdal)(PDP)\(_2\) supramolecule with 6 nm NPs form cylindrical morphology, with the NPs dispersed in the P4VP(PDP) microdomains, forming hexagonal grids (Figure 2.5c). Subsequent samples are annealed at 60 °C for 12 hours to maintain consistency with the previous thermal annealing conditions.

Figure 2.5. a) TEM, b) in situ SAXS scattering profile and c) schematic of a PS(33 kdal)-b-P4VP(8 kdal)(PDP)\(_2\) supramolecule with 6 vol% of ~ 6 nm Au NPs, forming a hexagonal grid nanostructure ~ 37 nm in periodicity, with NPs dispersed in the P4VP(PDP) microdomains. Scale bar is 100 nm for the TEM image.

The NP size is subsequently increased to investigate the effect of increasing NP size on overall supramolecular nanocomposite morphology. 6 vol% of Fe\(_3\)O\(_4\) NPs ~ 15 nm in diameter are incorporated into PS(33 kdal)-b-P4VP(8 kdal)(PDP)\(_2\) supramolecule and the resulting morphology is characterized by TEM and SAXS (Figure 2.6). The TEM image (Figure 2.6a) displays a double row morphology with one line of NPs occupying each row. This morphology is unique from any bulk BCP and BCP-based supramolecule templated morphology, and has not been predicted by existing theories of BCP/NP nanocomposites. In order to shed light on the underlying supramolecule morphology, the nanocomposite sample is stained using I\(_2\) vapor to increase the contrast between PS and P4VP microdomains under TEM (Figure 2.6b). The staining reveals that the NPs are still localized to the dark P4VP(PDP) microdomains, although the NP size now exceeds the thickness of one P4PV(PDP) microdomain, and NPs of two adjacent microdomains face
inwards towards each other, creating an intriguing asymmetry within the nanocomposite. Upon closer inspection of the stained TEM image, it appears that some regions still retain the hexagonal morphology, with one NP occupying each vertex of the hexagon. These observations suggest that the observed double row morphology may be a derivative of the hexagonal network morphology. The SAXS profile (Figure 2.6c) also indicates the onset of morphological transition. Three scattering peaks are visible in the scattering profile, with a structure factor of 1:√2:√5, indicating a morphology with square or cubic geometry. The first order scattering peak at $q = 0.0157 \text{ Å}^{-1}$ suggests a periodicity of 40 nm, a significant increase from supramolecules containing ~ 6 nm Au NPs. The higher order peaks in the high $q$ region originate from the spherical NP form factor.

**Figure 2.6.** TEM images of PS(33 kdal)-b-P4VP(8 kdal)(PDP)$_2$ supramolecules loaded with 6 vol% of ~ 15 nm Fe$_3$O$_4$ NPs a) without and b) with I$_2$ vapor staining, revealing an asymmetric double row NP nanostructure. c) The corresponding SAXS profile suggests a nanostructure with square or cubic symmetry, with a periodicity of 40 nm. Scale bars are 100 nm for all TEM images.

To further elucidate the self-assembled nanostructure, TEM tomography is used to obtain a 3-D rendering of the nanocomposite sample (Figure 2.7). Figure 2.7a shows the 3-D tomography reconstruction of the nanocomposite viewed at 0° to the sample’s normal axis (i.e. the same viewing angle as TEM). The NPs appear as gold colored dots and form the double row morphology as observed under TEM. Upon rotating the sample by 10° (Figure 2.7b), it is evident that there exists another layer of NPs beneath the double row morphology, forming NP quadruplets spaced 33 nm apart. The double rows are spaced 41 nm apart from adjacent double rows, which explains the origin of the first order scattering peak in the SAXS profile. Although TEM tomography does not provide a full explanation of the self-assembled morphology, it does reveal that the morphology indeed possess square symmetry and is periodic in all three dimensions, which is
uniquely distinct from lamellar or cylindrical morphologies that can possibly be formed by the underlying supramolecule.

![Figure 2.7. TEM tomography reconstruction of the supramolecular nanocomposite comprised of PS(33 kdal)-b-P4VP(8 kdal)(PDP)$_2$ supramolecules loaded with 6 vol% of ~ 15 nm Fe$_3$O$_4$ NPs, viewed from a) 0º and b) 10º with respect to the sample normal, revealing a morphology that is periodic in three dimensions.]

The NP size is increased further by incorporating 6 vol% of ~ 20 nm Fe$_3$O$_4$ NPs into the PS(33 kdal)-b-P4VP(8 kdal)(PDP)$_2$ supramolecule (Figure 2.8). TEM of the nanocomposite sample reveals a morphology with distinctly square symmetry (Figure 2.8a). Grains oriented at a different angle relative to the square lattices (see top left region of Figure 2.8a) show NP arrays with very small interparticle spacing, suggesting that the observed morphology may be defined as 1-D NP arrays arranged into 2-D square lattices. The TEM data is corroborated with SAXS data (Figure 2.8b), in which first order and second order scattering peaks are visible with a structure factor of 1:$\sqrt{2}$, again indicating square lattice geometry. The first order peak at $q = 0.0120$ Å$^{-1}$ indicates a periodicity of 52 nm, a further increase in comparison to cylindrical supramolecular nanocomposites containing NPs with smaller diameters.
Figure 2.8. a) TEM and b) SAXS profile of the supramolecular nanocomposite comprised of PS(33 kdal)-b-P4VP(8 kdal)(PDP)$_2$ supramolecules loaded with 6 vol% of ~20 nm Fe$_3$O$_4$ NPs, revealing a nanostructure with square symmetry.

The morphology of the supramolecular nanocomposite is further probed using TEM tomography (Figure 2.9). The top view of the 3-D tomography reconstruction (Figure 2.9a) shows NPs arranged into square lattices, similar to the TEM observation. Rotating the reconstruction by 90º (Figure 2.9b) reveals that the interparticle distance is indeed much smaller, suggesting that the NPs are arranging into 1-D arrays. These observations, combined with TEM and SAXS data, demonstrate that the morphology of a PS(33 kdal)-b-P4VP(8 kdal)(PDP)$_2$ cylindrical supramolecule containing ~20 nm NPs self-assembly into a morphology in which 1-D NP arrays arrange into square lattices in the orthogonal direction (Figure 2.9c). This morphology is also unique from BCP/NP and supramolecular nanocomposites containing smaller NPs, as morphologies with square symmetry are not predicted to exist in pure BCPs and supramolecules.
Figure 2.9. TEM tomography reconstruction of the supramolecular nanocomposite comprised of PS(33 kdal)-b-P4VP(8 kdal)(PDP)_2 supramolecules loaded with 6 vol% of ~ 20 nm Fe₃O₄ NPs, viewed a) parallel and b) perpendicular to the sample normal axis, revealing a morphology in which 1-D NP arrays are arranged into square lattices oriented orthogonally to the arrays, as schematically illustrated in c).

The observed trend in NP size-dependent morphological transition in bulk cylindrical supramolecular nanocomposites can again be explained by changes in the entropic landscape and overall thermodynamic balance of the composite system. Without the addition of NPs, the PS(33 kdal)-b-P4VP(8 kdal)(PDP)_2 supramolecule self-assembles into a lamellar morphology, as its composition of \( f_{P4VP(PDP)} = 0.63 \) lies close to both the lamellar and P4VP(PDP) majority cylindrical morphologies. Upon addition of 6 vol% ~ 6 nm Au NPs, the NPs diffuse into the P4VP(PDP) microdomains during thermal annealing to maximize \( \Delta H_{SM/NP} \), while at the same time increasing \( f_{P4VP(PDP)} \) further into the P4VP(PDP) majority cylindrical morphology regime. Due to the small size of the NPs, NP incorporation does not incur significant conformational entropic penalty to the P4VP(PDP) supramolecule chains, and therefore the NPs uniformly disperse within the P4VP(PDP) microdomain to maximize \( \Delta S_{trans} \), forming the hexagonal network nanostructure.

As the NP size increases, the conformational entropic penalty incurred in accommodating the NPs increases dramatically. Similar to the lamellar supramolecular nanocomposites, the cylindrical nanocomposites experience an increase in microdomain size as the polymer chains stretch to create larger interstitial sites to accommodate the larger NPs. However, in addition to increasing in periodicity, cylindrical supramolecular nanocomposites possess an additional degree of freedom to rearrange the packing geometry of the cylindrical microdomains in order to create larger interstitial sites. This
morphological transition brings about the concept of $\Delta S_{geo}$, the polymer chain conformational entropy due to microdomain geometry.

In a regular hexagonally packed P4VP(PDP) majority cylindrical morphology (Figure 2.10), the interstitial site exists at the intersection of three adjacent cylinders. The radius of the interstitial site, $r$, is related to the radius of the supramolecule cylinder, $R$, by

$$r = \left(\frac{2}{\sqrt{3}} - 1\right) R$$

In the case of the cylindrical supramolecular nanocomposite with ~ 6 nm NPs, $2R = 37$ nm, giving the interstitial diameter $2r = 5.7$ nm. Without NP loading, the P4VP(PDP) chains in the proximity of the interstitial site must stretch beyond their equilibrium conformation to fill the interstitial site, thereby creating inherent entropic penalty attributed to $\Delta S_{geo}$. The presence of the ~ 6 nm NPs serve to fill these interstitial sites and relieve supramolecule chain stretching, which leads to a decrease in entropic penalty and stability of the hexagonally packed cylindrical nanostructure. However, as NP size increases further, the size of the interstitial sites cannot increase sufficiently to accommodate the NPs without incurring significant entropic penalty associated with $\Delta S_{con}$. For example, assuming a hexagonal cylinder packing geometry, the cylindrical supramolecular nanocomposite containing ~ 20 nm NPs, which has a periodicity $2R = 52$ nm, would only have an interstitial size $2r = 8.0$ nm, not nearly large enough to accommodate the 20 nm NPs without incurring extremely large entropic penalties.
Figure 2.10. Schematic representation of a cylindrical supramolecule morphology with hexagonally arranged cylinders.

On the other hand, if the cylinders are instead arranged in a square lattice (Figure 2.11), the radius of the interstitial site becomes

\[ r = (\sqrt{2} - 1)R \]

Under this assumption, the cylindrical supramolecular nanocomposite containing ~ 20 nm NPs, which has a periodicity of \( 2R = 52 \text{ nm} \), would have interstitial sites with diameters \( 2r = 21.5 \text{ nm} \), a significant increase from the hexagonally packed cylindrical geometry. Without NP loading, the square packing geometry of the supramolecule cylinders is not thermodynamically stable, as significant entropic penalty associated with \( \Delta S_{\text{geo}} \) must be incurred to fill the interstitial sites. However, the presence of ~ 20 nm NPs in the interstitial sites may serve to relieve the polymer chain stretching and favor the stability of the square packing geometry over the hexagonal packing geometry. Therefore, it is plausible that the large NP diameter has induced a hexagonal to square packing cylinder morphology transition within the supramolecular nanocomposite. The observed double row morphology of the cylindrical supramolecular nanocomposites containing the ~ 15 nm NPs may be a transitional state between the hexagonal and square lattice morphologies.
The investigation and observation of NP size-dependent self-assembly in supramolecular nanocomposites is significant for several reasons. Firstly, previous theoretical studies of BCP/NP self-assembly \(^{28-32}\), were limited to NPs with diameters less than \(0.3R_g\), and it was assumed that the overall microdomain spacing remains constant regardless of NP size. The experimental results described in this chapter demonstrate that the supramolecule microdomain spacing is able to expand by over 60% to accommodate NPs with diameters larger than \(0.6R_g\). Secondly, previous simulations and experiments focused on assembly within lamellar nanocomposites, and this study provides insight on the effect of NP size in self-assembly within cylindrical nanocomposites. Remarkably, NPs of sufficient diameters are shown to not only increase the cylindrical microdomain spacing, but also alter the packing geometry of the cylinders from hexagonal packing to square packing. At these size regimes, the self-assembly mechanism can no longer be considered as supramolecule templated NP assembly. Rather, the NPs also play a structure-directing role in the self-assembly process, leading to a previously unobserved co-assembly mechanism.

\section*{Conclusion}

In this chapter, the effect of NP size on the entropic landscape and overall self-assembly within lamellar and cylindrical supramolecular nanocomposites is systematically explored. In lamellar nanocomposites, increasing the NP size causes nanostructural changes from lamellae containing multiple layers of small NPs to lamellae containing a single layer of large NPs. The microdomain spacing increased by over 60% to accommodate the larger NPs without incurring significant conformational entropic penalty. In cylindrical nanocomposites, a significant increase in microdomain spacing is also observed as the NP size increases beyond the size of the interstitial sites. Furthermore, the increase in NP size induced a morphological transition from hexagonal network morphology to a unique asymmetric double row morphology, and eventually to a square lattice morphology. These morphological transitions are attributed to changes in the packing geometry of the supramolecule template from hexagonally packed cylinders to square packing to reduce the supramolecule chain conformational entropic penalty associated with geometric packing of the microdomains.

The conclusions gained from these studies demonstrate the important role of entropy in altering the morphology in supramolecular nanocomposites, and expand the existing knowledge of self-assembly in bulk BCP/NP and supramolecule/NP systems.
While the assembly of smaller NPs are templated by the underlying supramolecule morphology, sufficiently large NPs significantly perturb the entropic balance within the nanocomposite, resulting in the formation of co-assembled nanostructures that are not accessible in composites containing smaller NPs. The insights gained from these observations provide valuable knowledge for the rational design of nano-materials for applications as photonic crystals and plasmonic waveguides.

§ 2.4 Methods

Nanoparticle Synthesis

Gold (III) chloride trihydrate (HAuCl₄•3H₂O), oleylamine (technical grade, 70%), 1,2,3,4-tetrahydronaphthalene (tetralin), tert-butylamine-borane complex (TBAB, 97%), were all purchased from Sigma Aldrich and used as received. Iron oxide NPs are purchased from Ocean Nanotech and dissolved in chloroform to the desired concentration.

Au NPs were synthesized as described by Sun et al²⁸. For a typical synthesis, 200 mg of HAuCl₄•3H₂O was dissolved in a mixture of 20 mL oleylamine and 20 mL tetralin solution and stirred for 30 min under N₂ gas. Then, 86 mg of TBAB dissolved in 2mL of oleylamine and 2 mL of tetralin was added to the solution to reduce the gold salt. The reaction was stirred for a further 1 hour and the NPs are purified by washing with acetone and chloroform. The NP size is tunable by adjusting reaction temperature, with 3 nm NPs produced at room temperature, and 6 nm NPs produced at -10°C. All NP size distributions were obtained using Igor Pro and ImageJ.

Supramolecular nanocomposite preparation

P4VP and PS-b-P4VP were first dissolved in chloroform to form 1–2% (wt/v) stock solutions. The desired amount of PDP small molecules were dissolved in chloroform. The PS-b-P4VP solution was then added drop-wise to the PDP solution, followed by stirring overnight. The desired amount of NP solution in chloroform was added to the resulting PS-b-P4VP(PDP) supramolecule solution and the mixture was casted and dried in a Teflon beaker at room temperature in a chloroform atmosphere, allowing the solvent to slowly evaporate over 12 hours. The blend was then annealed at 60°C under vacuum for overnight to completely remove the solvent.

Transmission electron microscope

For TEM observations, samples were embedded in resin (Araldite 502, Electron Microscopy Sciences) and cured at 60°C for overnight. Thin sections about 50 nm in thickness were microtomed using an RMC MT-X Ultramicrotome (Boeckler Instruments)
and picked up on carbon coated Cu grids on top of water. The thin sections were exposed to iodine vapor for 1h to stain the P4VP domain selectively and imaged using a FEI Tecnai 12 TEM operating at 120kV accelerating voltage or a JEOL 2100 TEM operating at 200kV.

**TEM tomography**

TEM tomography was collected using an FEI ultratwin Tecnai F20 operated at 200 kV and a Hummingbird Scientific high-tilt tomography holder. The tilt series were acquired from -70° to 70° with 1° tilt step increments and pixel resolution of 0.43 nm. Post-processing alignment and tomographic reconstruction of the tilt images were processed using the eTomo software package. IMOD and the Avizo 7.0 software packages were used for 3-D visualization.

**Small-angle X-ray scattering**

SAXS studies were carried out at the Advanced Light Source beamline 7.3.3. X-rays with a wavelength of 1.240 Å (10 keV) were used. Spectra were collected on an ADSC Quantum 4u CCD detector with an area of 188 mm × 188 mm (2,304 pixels × 2,304 pixels) or a Pilatus 1M detector with an area of 169 mm × 179 mm (981 px × 1043 px). The 1D SAXS profiles were obtained by circularly averaging the 2D data. Prior to SAXS experiment, samples were mounted in standard differential scanning calorimetry pans, which were used as a heating stage during scanning. All SAXS profiles were measured after keeping the samples at each temperature for 10 min.
Chapter 3

Entropy Modulation in Supramolecular Nanocomposite Thin Films

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Self-assembly of nanoparticles (NPs) in block copolymer (BCP) based templates opens many pathways towards generation of functional nanostructured materials with desirable optical, mechanical and electrical properties. A great challenge in this field is the effective control of NP spatial distribution within the BCP matrix. In the previous chapter, it was demonstrated that NP spatial distribution can be precisely controlled in bulk BCP-based supramolecular nanocomposites by modulating the entropic balance within the self-assembled system. This chapter extends this discussion with a description of systematic investigation of the effect of NP size on the spatial distribution of NPs upon blending with a BCP-based supramolecule, PS-\textit{b}-P4VP(PDP), in thin film. The spatial distribution of NPs in thin film was observed to be strongly dependent on NP size. Increasing NP size drives the localization of NPs from the P4VP(PDP) matrix to the hexagonal interstitial sites, and eventually to the film surface. This observation can be explained by the increase in entropic penalty of incorporating larger NPs associated with the deformation of the P4VP(PDP) block to accommodate the NPs. This effect is observed for NPs with different chemistries and the thin film assemblies are viable on Si substrates as well as low surface energy substrates such as graphene, thereby serving as a promising route to creating multifunctional thin film nanocomposites.

§ 3.1 Introduction

The self-assembly of nanoparticles (NPs) into ordered nanostructured thin films is a promising route towards the bottom up generation of functional materials with unique optical, mechanical and electrical properties, with potential applications ranging from energy harvesting to memory storage. A wide variety of techniques have been discovered to direct the self-assembly of NPs into desired nanostructures. A promising materials platform towards the precise self-assembly of NPs is the BCP-based supramolecule, which is constructed via the bonding of small molecules to a block copolymer by non-covalent interactions, such as hydrogen bonding, ionic bonding, or metal coordination. The BCP-based supramolecule combines the processibility and rich morphology variation of the BCP with the functionalities of the small molecules to create functional and stimuli-responsive scaffolds without any synthetic modifications to the BCP. By carefully choosing the small molecules, one can construct BCP supramolecules that are proven to assemble NPs into various morphologies without chemical modification of the NP ligand, thus opening many pathways towards the design and construction of multifunctional nanomaterials. In addition, as demonstrated in Chapter 2, entropic penalty induced by NP incorporation within bulk supramolecules has a significant effect on the NP spatial distribution within the supramolecular nanocomposite.

A major challenge and key bottleneck of NP self-assembly in BCP supramolecules is the precise control of NP spatial distribution in thin film, which affects
the tunability of many macroscopic properties. In addition, the translation of bulk self-assembled nanostructures into thin films is requisite for many types of thin film device applications. Previous studies of NP spatial distribution in BCP bulk\textsuperscript{13-19} and thin film\textsuperscript{20-23} have shown that the final distribution of NPs is determined by both enthalpic and entropic interactions between the BCP and NP. On one hand, localization of NPs to the BCP block with preferential chemical affinity to the NP ligands lowers the enthalpy and thus free energy of the composite system. On the other hand, since NPs are very rigid relative to the polymer matrix, the polymer chains must stretch around the NPs, thus incurring a loss in conformational entropy and increase in free energy of the system that increases with NP size. The resulting morphology of the BCP/NP composite is determined by a balance between the gain in enthalpy and loss in entropy during NP incorporation into the BCP. Balazs et al have shown that with increasing NP size, the NP spatial distribution in a BCP transitions from uniform dispersion within one microdomain to localization at the center of the microdomain, and eventually macrophase separation from the BCP bulk for larger NPs\textsuperscript{13}.

Previous studies by Xu \textit{et al} have demonstrated that the bulk morphologies in BCP-based supramolecules can be translated into thin film analogs by spin casting and solvent annealing on Si substrates\textsuperscript{24}. However, in a supramolecular thin film, the self-assembly and energetic contributions from different components in the system are more complicated. First, the surface energies of the film/substrate and film/air interfaces introduce additional considerations in the total free energy of the system. Second, the addition of small molecules also alters the thermodynamics of the system. The coupling of small molecules to one block of the BCP changes the block from a coil like structure to a more rigid comb like structure. The increase in rigidity means that the comb block would incur a higher entropic penalty upon deformation to accommodate NP addition. The effect of this enhanced entropic effect is not well understood and thus requires further investigation.

This chapter presents a systematic investigation of the effect of NP size on NP spatial distribution in a thin film of the supramolecule, PS-\textit{b}-P4VP(PDP), comprised of the BCP poly(styrene-block-4-vinylpyridine) (PS-\textit{b}-P4VP) with hydrogen bonded 3-pentadecylphenol (PDP) small molecule side chains. The alkyl groups of the PDP side chains interact favorably with native alkyl ligands of different NPs \textit{via} van der Waal’s forces. This decouples the chemistries of the BCP and NP, thus rendering the supramolecule useful in assembling a wide variety of NPs\textsuperscript{12}. Understanding the NP spatial distribution in this system as a function of NP size and entropic penalty would address a significant issue in NP self-assembly in supramolecular thin films. Furthermore, it is demonstrated that the supramolecule and supramolecular nanocomposite thin film nanostructures are viable on both high surface energy substrates such as Si and low energy substrates such as graphene, thereby opening more possibilities in the generation of functional organic/inorganic nanocomposite thin films.
§ 3.2 Effect of Nanoparticle Size on Nanoparticle Spatial Distribution in Supramolecular Nanocomposite Thin Films

Three batches of PbS NPs with different mean core diameters of (I) 3.5 nm, (II) 5.5 nm, and (III) 7.0 nm, as well as two batches of Au NPs with mean core diameters of (IV) 3.5 nm and (V) 5.0 nm, are synthesized to observe the effect of NP diameter on their spatial distribution in PS(19 kdal)-b-P4VP(5.2 kdal)(PDP)1.7 thin films. The NP ligands also add to the overall NP size. Since PbS NPs are stabilized with oleylamine (2.0 nm) ligands and Au NPs are stabilized with dodecanethiol (1.8 nm) ligands, the overall NP sizes are increased by 4.0 nm for PbS NPs and 3.6 nm for Au NPs, bringing the overall size for each NP batch to (I) 7.5 nm, (II) 9.5 nm, (III) 11.0 nm, (IV) 7.1 nm and (V) 8.5 nm. The TEM images of the NPs and their size distributions are shown in Appendix 2 (Figure A2.1). The NPs are incorporated into the supramolecular thin film by mixing the NP and supramolecule solutions and spin casting the mixture onto Si wafers to fabricate thin films ~180 nm in thickness. The as cast thin films contain NPs randomly distributed throughout the supramolecule matrix (Figure A2.2), regardless of NP size, as the nanocomposite is kinetically trapped after spin casting due to the rapid rate of solvent removal. The thin film samples are subsequently solvent annealed in a chloroform solvent vapor to obtain ordered nanostructures (see Section 3.5 for detailed sample preparation procedures).

The thin film sample loaded with batch I NPs is shown in Figure 3.1. Atomic force microscopy (AFM) image of the thin film shows formation of fingerprint-like patterns with alternating PS (light region) and P4VP(PDP) (dark region) domains (Figure 3.1a). The NPs are too small to appear visible under AFM. However, the top view transmission electron microscopy (TEM) image in Figure 3.1b more clearly reveals that the PbS NPs form vaguely defined, ordered arrays that conform to the contours of the fingerprint-like patterns. NPs also can be observed in the regions between the arrays, although the NP density is somewhat sparser in these regions. Tilting the thin film sample by 60° under TEM (Figure 3.1c), it is observed that the ordered arrays appear much denser and well ordered, while there still appear to be NPs localized between the arrays. A cross-sectional TEM image of the thin film sample (Figure 3.1d) provides an ends-on view of the self-assembled nanostructure, showing that the NPs are evenly distributed within the P4VP(PDP) matrix, forming networked structures that are oriented at approximately 60° relative to the substrate. This also explains why the top view TEM appears more ordered when the TEM holder is tilted by 60°, as this registers with the alignment of the NP network arrays.

Although TEM provides a clear picture of the self-assembled structure, the technique can be complimented by grazing incidence small angle X-ray scattering...
(GISAXS), which is the thin film analog to SAXS and provides structural information throughout a much larger (1 mm by 2 cm) area of the film. In GISAXS, the X-ray beam is incident on the sample at a very small grazing angle, between the critical angles of the supramolecule thin film and the underlying Si substrate. The beam thus penetrates the thin film yet reflects from the Si substrate, thereby maximizing the scattering within the thin film. The scattered beam exits the film and is projected onto a CCD detector, forming a 2-D GISAXS pattern that provides information about the internal nanostructure of the thin film. The GISAXS pattern (Figure 3.1e) and a 1-D Q_y linecut taken at Q_x = 0 Å^{-1} (Figure 3.1f) show a strong first order peak in the Q_y direction at q = 0.0184 Å^{-1}, indicating an inter-array spacing of 2\pi/q = 34.1 nm. The second order scattering peak is located at q = 0.0365 Å^{-1}, giving a structure factor of 1:2, consistent with a parallel cylindrical morphology. The peak at q = 0.0797 Å^{-1} indicates a characteristic distance of 7.9 nm, which represents the average interparticle distance within the thin film. The overall TEM and GISAXS analysis suggests that batch I PbS NPs distribute throughout the P4VP(PDP) microdomain, forming network structures within the thin film.
Figure 3.1. Self-assembly of small (batch I) PbS NPs in PS(19 kdal)-b-P4VP(5.2 kdal)(PDP)_{1.7} supramolecular nanocomposite thin films. a) AFM image (inset: magnified view), b) top view TEM, c) 60° tilt TEM (inset: magnified view), and d) cross-sectional TEM images show NPs uniformly distributed throughout the P4VP(PDP) microdomains, forming networked structures. e) 2-D GISAXS and f) q_y linecut data show scattering profiles consistent with parallel cylindrical thin film morphology, consistent with AFM and TEM data. Scale bars are 100 nm for all images.
The spatial distribution of the larger batch II PbS NPs in the thin film was found to be drastically different from that of batch I (Figure 3.2). The AFM image shows formation of the similar fingerprint-like pattern (Figure 3.2a). The NPs are slightly visible in this case due to the larger NP size, appearing as faint white dots sequestered within the dark P4VP(PDP) microdomains. The top view TEM (Figure 3.2b) appears similar to the thin film samples containing batch I NPs. Tilting the sample by 60° (Figure 3.2c) shows that the NPs localize into layers that are oriented approximately 60° relative to the substrate, as demonstrated by the reappearance of the well-defined NP lines with almost no NP between the lines, in contrast to thin films containing the smaller batch I PbS NPs. The cross-sectional view of the thin film (Figure 3.2d) further reveals that the NPs are no longer distributed uniformly throughout the P4VP(PDP) microdomain, instead self-assembling into well-ordered parallel cylinders in a distorted hexagonal lattice that is compressed in the z-direction. The GISAXS pattern (Figure 3.2e) shows stronger scattering peaks due to increased NP long range order, both in the Q_y and Q_z directions. A Q_y linecut (Figure 3.2f) shows first order peak at q = 0.180 Å⁻¹, corresponding to inter-array spacing of 34.9 nm, a slight increase from the thin film samples containing batch I NPs. The structure factor in the Q_y direction is also 1:2, suggesting the overall morphology to be parallel cylinders. A Q_z linecut shows first order peak at q = 0.0252, corresponding to inter-layer spacing of 24.9 nm in the z-direction. Thus, it can be concluded that 5.5 nm batch II PbS NPs assemble within the interstitial sites at the intersection of four adjacent cylinders, forming well ordered 3-D parallel NP arrays.
Figure 3.2. Self-assembly of medium (batch II) PbS NPs in PS(19 kdal)-b-P4VP(5.2 kdal)(PDP)\textsubscript{1.7} supramolecular nanocomposite thin films. a) AFM image (inset: magnified view), b) top view TEM, c) 60° tilt TEM (inset: magnified view), and d) cross-sectional TEM images show NPs sequestered within the interstitial sites at the intersection of four adjacent cylinders, forming well ordered NP arrays arranged in a distorted hexagonal lattice. e) 2-D GISAXS and f) q\textsubscript{y} linecut data show scattering profiles consistent with
parallel cylindrical thin film morphology, consistent with AFM and TEM data. Scale bars are 100 nm for all images.

Upon further increasing PbS NP size (batch III), the resulting self-assembled nanostructures are shown in Figure 3.3. AFM of the thin film (Figure 3.3a) shows formation of fingerprint-like patterns with NPs clearly visible and localized within the dark P4VP(PDP) microdomains. Top view TEM (Figure 3.3b) reveals that the PbS NPs form ordered arrays of 1 NP width that conform to the contours of the fingerprint-like pattern, with no NPs in between the arrays. The NP lines are also found to have a height of 1 NP and are localized on the air/film interface of the thin film, as evidenced by the 60° tilted (Figure 3.3c) and cross-sectional TEM views (3.3d), respectively. The cross-sectional TEM clearly shows that the majority of the NPs remain on the film/air interface of the thin film. The GISAXS pattern (Figure 3.3e) and its associated Q_y linecut (Figure 3.3f) show a strong first order peak in the Q_y direction at q = 0.190 Å\(^{-1}\), indicating an inter-array spacing of 2π/q = 33.1 nm, an actual decrease in periodicity compared to thin films containing batch I and II NPs. Furthermore, only the first order peak is observed with decreased scattering intensity. Upon increasing the NP loading to 20v% and 30v%, the NPs are observed to remain segregated to the surface, stacking into square lattices (Figure 3.4). Therefore, for larger NP sizes (batch III), NPs remain segregated to the film/air interface despite increased NP loading.
Figure 3.3. Self-assembly of large (batch III) PbS NPs in PS(19 kdal)-b-P4VP(5.2 kdal)(PDP)$_{1.7}$ supramolecular nanocomposite thin films. a) AFM image (inset: magnified view), b) top view TEM, c) 60° tilt TEM (inset: magnified view), and d) cross-sectional TEM images show NPs expelled to the film/air interface, forming 1-D NP arrays that are one NP in width. e) 2-D GISAXS and f) q$_y$ linecut data show scattering profiles consistent with parallel cylindrical thin film morphology, consistent with AFM and TEM data. Scale bars are 100 nm for all images.
Figure 3.4. TEM images of PS(19 \text{ kdal})-b-P4VP(5.2 \text{ kdal})(PDP)_{1.7} supramolecular nanocomposite thin films loaded with a) 20 v\% and b) 30 v\% 7.0 nm PbS NPs, showing that additional NPs all segregate to the film/air interface, forming square NP lattices. Scale bars are 200 nm for (a) and 100 nm for (b).

In order to illustrate that the observed changes in NP spatial distribution are due to NP size rather than NP chemistry, two batches of Au NPs (batch IV and V) were incorporated into the supramolecule thin film with a NP loading of 3v\% and thickness of \sim 180 nm. The top view TEM images (Figure 3.5a) of thin film samples loaded with batch IV Au NPs shows self-assembly of Au NPs into parallel cylinders, while the cross-sectional TEM (Figure 3.5b) clearly shows the formation of network nanostructures as Au NPs uniformly distribute throughout the P4VP(PDP) microdomain, similar to batch I PbS NPs. In contrast, the thin film sample loaded with batch V Au NPs form neat NP arrays hexagonally packed within the interstitial sites of the supramolecule, as revealed by top view and cross-sectional TEM (Figure 3.5c and d), similar to batch II PbS NPs. The above observations clearly suggest that NP distribution in a supramolecular thin film is critically dependent on NP size and is independent of NP chemistry. The size dependent NP assemblies within supramolecular nanocomposite thin films is summarized in Table 3.1.
Figure 3.5. a) 60° tilted and b) cross-sectional TEM images of 3.5 nm Au NPs in PS(19 kdal)-b-P4VP(5.2 kdal)(PDP)\textsubscript{1.7} supramolecular nanocomposite thin films, showing uniform distribution of NPs within the P4VP(PDP) microdomain. c) 60° tilted and b) cross-sectional TEM images of 5.5 nm Au NPs with the supramolecular nanocomposite thin films, showing the NPs sequestered within the interstitial sites.

Table 3.1. A summary of the spatial distribution for each batch of NPs incorporated into PS(19 kdal)-b-P4VP(5.2 kdal)(PDP)\textsubscript{1.7} supramolecular nanocomposite thin films.

<table>
<thead>
<tr>
<th>NP Batch #</th>
<th>Overall NP Size</th>
<th>NP Chemistry</th>
<th>NP Spatial Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>7.5 nm</td>
<td>PbS</td>
<td>Throughout P4VP(PDP) matrix</td>
</tr>
<tr>
<td>II</td>
<td>9.5 nm</td>
<td>PbS</td>
<td>Within P4VP(PDP) interstitial sites</td>
</tr>
<tr>
<td>III</td>
<td>11.0 nm</td>
<td>PbS</td>
<td>Sequestered to film/air interface</td>
</tr>
<tr>
<td>IV</td>
<td>7.1 nm</td>
<td>Au</td>
<td>Throughout P4VP(PDP) matrix</td>
</tr>
<tr>
<td>V</td>
<td>8.5 nm</td>
<td>Au</td>
<td>Within P4VP(PDP) interstitial sites</td>
</tr>
</tbody>
</table>

It is obvious that NP size has a strong influence on NP spatial distribution within the supramolecular nanocomposite thin film. Small NPs uniformly distribute throughout
the P4VP(PDP) microdomains. As NP size increases, NPs are sequestered within the interstitial sites of the supramolecule, and finally expelled to the film/air interface for large NPs (Figure 3.6). The different NP spatial distributions observed in the supramolecule thin film as a function of NP size can be explained by a combination of entropic and enthalpic interactions between the NPs and the BCP supramolecule.

![Figure 3.6. Schematic showing the effect of NP size on NP spatial distribution within cylinder forming supramolecular nanocomposite thin films.](image)

As discussed in Chapter 1, the overall Gibb’s free energy governing BCP/NP composite thin films, $\Delta G_{BCP/NP}$, is given by

$$\Delta G_{BCP/NP} = \Delta H_{BCP/NP} + \Delta H_{NP/\text{Air}} + \Delta H_{NP/Sub} - T(\Delta S_{\text{trans}} + \Delta S_{\text{con}} + \Delta S_{\text{geo}})$$

The PS(19 kdal)-b-P4VP(5.2 kdal)(PDP)$_{1.7}$ supramolecule has a semiflexible, coil-like PS block and a rigid, comb-like P4VP(PDP) block, where the volume fraction of the comb-block is approximately $f_{\text{comb}} = 0.62$. At this volume fraction, the supramolecule assumes a hexagonally packed cylindrical morphology that is oriented parallel to the substrate. The PDP of the P4VP(PDP) comb block interacts favorably with the alkyl ligands of the NPs due to van der Waals forces between alkyl chains. Therefore, NPs are enthalpically driven to localize in the P4VP(PDP) block instead of the PS block. However, the P4VP(PDP) chains must stretch to accommodate the extra volume occupied by the NPs. Since the P4VP(PDP) block is rigid, its deformation incurs a high polymer chain conformational entropic penalty, $\Delta S_{\text{con}}$, that increases rapidly with NP size. Above a certain critical NP diameter, conformational entropy of the comb block dominates the self-assembly process and expels the NPs from the interior of the thin film. This critical diameter is related to the size of interstitial sites in the cylindrical morphology that are high in free volume.

During solvent annealing, the thin film is swollen to 150% of its original thickness by the chloroform vapor, and the supramolecule forms a P4VP(PDP)-majority
hexagonally packed cylinders with a periodicity of ~33 nm (Figure 3.7a). The size of the interstitial sites in this system is about 5.1 nm. Upon solvent removal, the film collapses to its original thickness. The hexagonally packed cylinders correspondingly collapse to a thickness that is roughly 70% of the fully relaxed film, with dimensions $a = 33$ nm and $c = 44$ nm, as confirmed by Xu et al in a previous study\textsuperscript{24}. The collapsed film forms a distorted cylindrical morphology with interstitial sites of diameter ~11 nm (Figure 3.7b). NPs with diameters below the size of these interstitial sites (batches I and IV) would cause little deformation of the P4VP(PDP) block upon incorporation into the thin film. The NPs are distributed uniformly throughout the P4VP(PDP) microdomain to maximize the enthalpic interaction between NPs and BCPs, $\Delta H_{\text{BCP/NP}}$, and the NP translational entropy, $\Delta S_{\text{trans}}$. This self-assembly behavior is similar to what is typically observed for simple BCP/NP composite thin film systems.

As NP size slightly increases (batches II and V), the $\Delta S_{\text{con}}$ associated with comb block deformation during NP incorporation is similarly increased. As a result, it is less entropically favorable for the NPs to distribute throughout the P4VP(PDP) matrix. However, the interstitial sites contain a larger amount of free volume than within the matrix of the comb block. If no NPs are present, the P4VP(PDP) chains must stretch beyond their equilibrium conformations to fill the interstitial sites, which results in entropic penalty that is inherent in the supramolecular thin film system. The incorporation of NPs into the interstitial sites actually serves to relax the chain stretching and decrease the entropic penalty. This chain relaxation in turn stabilizes the precise 3-D arranged parallel NP arrays within the supramolecular nanocomposite system, forming a morphology that was not previously observed in simple BCP/NP systems. In addition, the

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**Figure 3.7.** Schematic showing the difference in the size of interstitial sites under a) close packed hexagonal (interstitial size = 5.1 nm) and b) collapsed hexagonal cylinder (interstitial size = 11.0 nm) packing schemes.
interstitial sites likely contain high mobility free PDP small molecules that can easily redistribute to accommodate the NPs. As a result, the NPs localize within the interstitial sites to maximize the favorable enthalpic interactions and minimize unfavorable entropic penalties.

For larger NPs with sizes that approach or exceed the size of the interstitial sites (batch III), the $\Delta S_{\text{con}}$ associated with NPs incorporating within the P4VP(PDP) matrix or the interstitial sites dominates the free energy balance and destabilizes such packing arrangements. As a result, the larger NPs are expelled to the film/air interface, where there exists a large amount of free volume to accommodate the NPs without incurring significant entropic penalties. In addition, the lower surface energy of the film/air interface also likely increases favorable enthalpic interactions between the NP ligands and air.

§ 3.3 Transfer of supramolecular nanocomposite thin film assemblies to graphene substrates

The previous section demonstrated that by modulating the entropy within supramolecular nanocomposite thin films, a variety of nanostructures such as NP 1-D and 3-D arrays, as well as NP networks, can be accessed. All of these nanostructures are realized on Si substrates. To demonstrate the universality of the supramolecular nanocomposite thin film construct, this section describes experiments that successfully transfers the hierarchically structured thin films to graphene substrates.

Graphene, a single layer of sp$^2$ bonded, hexagonally packed carbon atoms, has become a promising material for applications in electronics$^{27}$, sensing$^{28}$, catalysis$^{29,30}$, photovoltaics$^{31,32}$ and nanocomposites$^{33}$ due to its unique electrical$^{34,35}$ and mechanical properties$^{36}$. Graphene can be nanostructured or decorated with small molecules or nanoparticles (NPs) to tune its properties or introduce new functionalities$^{37}$. Graphene nanodots$^{38}$, nano-ribbon$^{39}$ and nanomesh$^{40,41}$ have been shown to have semiconducting properties not observed in unpatterned graphene sheets. Typically, the patterning process requires an additional step of depositing a grafting layer, such as polydopamine$^{42}$ or SiO$_2$ $^{40}$, on top of graphene or a chemical modification step$^{43}$ to increase its surface energy and prevent the dewetting of the sacrificial layer. Furthermore, the graphene surface energy must be precisely tailored to balance the polymer/surface interfacial interactions to control the macroscopic orientation of BCP microdomains. Graphene surfaces decorated with metal or semiconducting NPs act as efficient sensing, catalytic or photovoltaic device components in which the graphene acts as a conductive layer to deliver electrical charges across the device$^{29,44-48}$ $^{31}$. The NPs can be placed onto the graphene surface via in-situ reduction of precursors, which requires different synthetic
chemistries for different types of NPs\textsuperscript{49, 50, 51, 52}, or via adsorption of preformed NPs to the graphene surface, which requires chemical modification of the graphene or NP surface\textsuperscript{53, 54}. These modifications may affect the physical properties of the graphene and NPs. In addition, these approaches often cannot guarantee a desired spatial distribution of NPs on the graphene, which is important to generate reliable devices. Therefore, the successful transfer of hierarchically structured supramolecular nanocomposite thin films to graphene substrates not only demonstrate the universality of the self-assembled NP nanostructures, but also greatly simplifies the patterning and functionalization of graphene, and opens opportunities to explore the structure-property correlations of graphene/NP composite materials.

Supramolecular nanocomposite thin films (~ 120 nm thick) containing batch V Au NPs are spun cast onto graphene covered Si substrates (with a 200 nm SiO\textsubscript{2} top coating) and solvent annealed as previously described. Figure 3.8 shows the AFM and optical microscopy of the substrates before and after spin casting. Before spin casting, the AFM image shows creases on the surface characteristic of the wrinkles of graphene sheets deposited on flat substrates (Figure 3.8a). After spin casting, the AFM image shows the typical fingerprint patterns of the parallel cylindrical supramolecule thin film morphology, while the optical microscope image shows a change in color due to optical interference effects caused by the presence of the thin film (Figure 3.8b). No indication of dewetting is observed, thus demonstrating a successful transfer of supramolecular nanocomposite thin films onto the low surface energy graphene substrates.

**Figure 3.8.** AFM and optical microscope (inset) images showing graphene covered Si substrates a) before and b) after deposition of supramolecular nanocomposite thin film \textit{via} spin casting. Scale bars are 100 nm for all images.
The thin films are analyzed further to determine their internal nanostructure. Figure 3.9 shows the AFM and GISAXS images of a PS(19 kdal)-b-P4VP(5.6 kdal)(PDP)\textsubscript{1.7} supramolecule loaded with 6 v% of batch V Au NPs. A smooth film with parallel cylinders is observed in the AFM phase image (Figure 3.9a). A higher magnification view of the image in the inset shows NPs assembled into the darker P4VP(PDP) microdomains. A GISAXS pattern of the film (Figure 3.9b) shows a highly ordered morphology with up to third order scattering peaks clearly visible along the \( q_y \) direction. The strong scattering peaks in the \( q_y \) and \( q_x \) directions form a pattern characteristic of a distorted hexagonal lattice of parallel oriented NP arrays\textsuperscript{24}. A \( q_y \) linecut of the GISAXS pattern shows a first order scattering peak at \( q = 0.0238 \text{ Å}^{-1} \), which corresponds to a supramolecule nanocomposite periodicity of 26.4 nm (Figure 3.9c). The spatial distribution of NPs is further elucidated via transmission electron microscopy (TEM), as shown in Figure 3.9. An in-plane TEM view of the thin film (Figure 3.9d) clearly shows the NPs assembled into arrays with an inter-array spacing of ~25 nm. The cross-sectional TEM (Figure 3.9e) shows the NP arrays organized into hexagonal lattices on graphene, as predicted by GISAXS. These observations confirm that the 3-D ordered NP array morphology can be transferred from Si to graphene substrate (Figure 3.9f).
assembly is confirmed using d) GISAXS and e) its associated \( q_y \) linecut. f) schematic of the assembly on graphene (yellow layer) coated SiO\(_2\)/Si substrate. Scale bars are 200 nm for all images.

Upon decreasing the film thickness to \( \sim 30 \) nm, a single layer of 1-D NP chains can be assembled on the graphene substrate, as confirmed by AFM and GISAXS (Figure 3.10). The AFM image (Figure 3.10a) clearly shows the Au NPs to be precisely assembled within the P4VP(PDP), forming 1-D NP arrays. The GISAXS scan taken at a glancing angle of \( \alpha = 0.10^\circ \) (Figure 3.10b), below the thin film critical angle, shows periodic structures in the \( q_y \) direction only. GISAXS scans taken at \( \alpha = 0.15^\circ \) (Figure 3.10c) and \( \alpha = 0.15^\circ \) (Figure 3.10c), both above the thin film critical angle, also show periodicity in the \( q_y \) direction but an absence of scattering peaks in the \( q_z \) direction. This suggests there is indeed only one layer of ordered Au NP arrays in the thin film. Besides Au NPs, previous studies have demonstrated the PS-\( b\)-P4VP(PDP)-directed assembly of PbS, PbSe NPs\(^{55}\) and CdSe nanorods\(^{56}\) due to the common alkyl native ligands shared by these nanocrystals. These assemblies can be readily adapted to a graphene substrate, thus establishing the versatility of this supramolecule to decorate graphene with ordered assemblies of functional NPs.

**Figure 3.10.** a) AFM image (left) and schematic (right) of a \( \sim 30 \) nm supramolecular nanocomposite thin film spun cast on graphene. The inset to the AFM clearly shows NPs ordered within the P4VP(PDP) microdomain, forming 1-D arrays. GISAXS of the sample taken at incidence angles of b) \( \alpha = 0.10^\circ \), c) \( \alpha = 0.15^\circ \), and d) \( \alpha = 0.20^\circ \) confirm that only 1 layer of NPs is present in the thin film.
§ 3.4 Conclusion

Self-assembly of NPs in thin films of supramolecular nanocomposites have been investigated using a combination of AFM, TEM, and GISAXS techniques, and the spatial distribution of NPs within the thin films are shown to be highly dependent on NP size. NPs significantly smaller than the interstitial sites between the cylindrical supramolecule domains uniformly distribute throughout the P4VP(PDP) microdomain, forming 3-D NP networks, while NPs with increasing sizes localize strictly into the interstitial sites, forming 3-D NP arrays, and are eventually expelled to the film/air interface for NPs with sizes approaching or exceeding the interstitial size, forming 1-D NP arrays. The transitions in NP spatial distribution as a function of NP size is mainly attributed to the increasing polymer chain conformational entropic penalty as larger NP sizes are incorporated within the thin film. While smaller NPs tend to adopt spatial distributions that maximize their NP translational entropy, conformational entropic penalty dominates for larger NPs and eventually cause the NPs to localize to the film/air interface to relax chain stretching. These results differ from the trend observed in bulk supramolecular nanocomposites as discussed in Chapter 2, as the existence of the film/air interface provides ample free volume to accommodate larger NPs without inducing excessive conformational entropic penalty.

Although the overall trend of NP spatial distribution transitions is similar to simple BCP/NP systems, the 3-D NP array morphology is unique to the supramolecular nanocomposite thin film system, and is attributed to relaxation of the P4VP(PDP) chains at the interstitial sites as NPs of suitable sizes fill in the free volume within the interstitial sites. These studies again demonstrate the importance of entropy as a means to access certain self-assembled nanostructures without resorting to altering the BCP chemistry or composition. In addition, the 1-D and 3-D NP array nanostructures are readily transferrable from high surface energy Si substrates to low energy graphene substrates, thus highlighting the versatility of the supramolecular nanocomposite thin film materials system and opening opportunities to explore the structure-property correlations of polymer/NP/graphene composite thin film materials.

§ 3.5 Methods

Nanoparticle Synthesis

Gold (III) chloride trihydrate (HAuCl₄•3H₂O), oleylamine (technical grade, 70%), 1,2,3,4-tetrahydronaphthalene (tetralin), tert-butylamine-borane complex (TBAB, 97%), lead (II) oxide (PbO) (99.999%), lead (II) chloride (PbCl₂), sulfur, 1-octadecene (ODE)
Small and medium PbS NPs (batches I and II) were synthesized using methods developed by Tao et al.\textsuperscript{57}. Briefly, 223 mg of PbO is dissolved in 3.39 g of oleic acid and 25 mL of ODE, and heated under vacuum to 100 °C. The PbO was reduced by adding 105 μL of (TMS)₂S dissolved in 2.5 mL ODE. Subsequent reaction at 90 °C yielded batch I NPs, while reaction at 130 °C yielded batch II NPs. Large PbS NPs were synthesized as described by Ozin et al.\textsuperscript{58}. Briefly, 5 g PbCl₂ was dissolved in 9.65 g oleylamine and heated under vacuum at 100 °C for 30 min. The lead salt is then reduced by adding 57.5 mg of sulfur dissolved in 1 g oleylamine into the reaction mixture, and allowed to react for 5 min to yield ~7 nm PbS NPs. All PbS NPs are washed with isopropyl alcohol before use.

Au NPs (NP batches IV and V) were synthesized as described by Sun et al.\textsuperscript{59}. For a typical synthesis, 200 mg of HAuCl₄•3H₂O was dissolved in a mixture of 20 mL oleylamine and 20 mL tetralin solution and stirred for 30 min under N₂ gas. Then, 86 mg of TBAB dissolved in 2 mL of oleylamine and 2 mL of tetralin was added to the solution to reduce the gold salt. The reaction was stirred for a further 1 hour and the NPs are purified by washing with acetone and chloroform. The NP size is tunable by adjusting reaction temperature, with batch IV NPs produced at room temperature, and batch V NPs produced at -10°C. All NP size distributions were obtained using Igor Pro and ImageJ.

**Thin film sample preparation**

Block copolymers (PS-b-P4VP) were purchased from Polymer Source. 3-pentadecylphenol (PDP) (95%) was purchased from Acros. Chloroform (pentene stabilized) was purchased from Fisher. All chemicals were used as received. Graphene is obtained by chemical vapor deposition (CVD) on polycrystalline copper (99.8 % Alfa Aesar, Ward Hill, MA) with a growth temperature of 1035 °C.\textsuperscript{60} After synthesis, the one side of the graphene-on-copper sample is coated with polymethyl methacrylate (PMMA). The copper foil is then etched away by soaking the sample in an aqueous solution of 100 mg/mL sodium persulfate (Na2S2O8) for approximately three hours. The resulting graphene, supported by PMMA, is then transferred to a silicon substrate with a 300 nm SiO2 dielectric layer. The PMMA is subsequently removed by soaking in hot acetone. The experiments were also reproduced on CVD-grown graphene deposited on Si wafers (with 285 nm SiO2 layer) purchased from Graphene Laboratories Inc. The BCP supramolecule is prepared by separately dissolving PS-b-P4VP and PDP in CHCl₃ at 15 mg/mL concentration. The PDP solution is then added dropwise to the PS-b-P4VP solution while stirring to achieve the desired P4VP:PDP molar ratio. The mixture is stirred for a further 12 hours to allow for the formation of P4VP-PDP hydrogen bonds. The supramolecule solution is mixed with a 20 mg/mL NP solution in CHCl₃ to form the nanocomposite solution. The nanocomposite solution is spuncast onto the graphene-
coated substrate at a spinning rate of ~3,000 rpm for 10 s to form a BCP/NP nanocomposite thin film on graphene. The thickness of the film is measured using a Filmetrics F20 interferometer.

**Solvent annealing**

For solvent annealing, nanocomposite thin film samples are suspended in a 250mL top-capped jar at room temperature. 200-300uL of CHCl₃ is injected into the jar, which is immediately sealed for 12-15 minutes to allow CHCl₃ to vaporize and swell the thin film. The cap is then opened to allow the CHCl₃ to freely evaporate. The PDP small molecules are removed by depositing 50uL of isopropyl alcohol onto the film, followed by spinning at 3,000 rpm for 10 s.

**Atomic force microscopy**

Atomic Force Microscopy (AFM) was performed on a Molecular Imaging PicoSPM II with a PicoScan 2500. The cantilevers used are composed of antimony-coated silicon have spring constants of 20-80 N/m and resonant frequencies ranging from 204-497kHz.

**Transmission electron microscopy**

Transmission Electron Microscopy (TEM) images are taken on a FEI Tecnai 12 TEM at an accelerating voltage of 120 kV, or a JEOL 2100 TEM at an accelerating voltage of 80 kV. The thin film TEM samples are prepared by cutting the spuncast wafers into ~2mm by 2mm pieces and floating the pieces on top of a 5v% aqueous solution of hydrofluoric acid (HF) solution. The HF etches away the SiO₂ within minutes, thereby detaching the nanocomposite and graphene layers from the underlying Si substrate. The detached films are collected onto carbon-coated 200 mesh copper grids from Ted Pella Inc. for top view TEM and onto epoxy resin (Araldite 502, Electron Microscopy Sciences) for cross-sectional TEM. For cross-sectional TEM samples, the epoxy with the thin film sample are cured at 60°C for 12 hours to ensure good contact between the epoxy and the nanocomposite thin film. The sample is then cut into ~60 nm thin sections using an RMC MT-X Ultramicrotome (Boeckler Instruments) and collected on copper grids. TEM samples containing supramolecule alone are stained using iodine vapor for 30 min to highlight the P4VP(PDP) microdomain as darker regions.

**Grazing incidence small angle X-ray scattering**

Grazing incidence small angle X-ray scattering (GISAXS) experiments were performed on beamline 7.3.3 in ALS at Lawrence Berkeley National Laboratory (beam energy = 10 keV) and on beamline G1 in CHESS at Cornell University (beam energy = 9.8 keV). The scattering intensity distribution was captured by a Pilatus 1MF detector at ALS and a Finger Lakes CCD detector at CHESS. The intensities (I) are plotted with
respect to q, where \( q = \frac{4\pi}{\lambda} \sin(\theta/2) \), \( \lambda \) is the wavelength of the incident X-ray beam, and \( \theta \) is the scattering angle.
Chapter 4

Self-Assembly of Supramolecules and Supramolecular Nanocomposites under Cylindrical Confinement

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BCP-based supramolecules represent a versatile materials platform to direct the self-assembly of NPs into nanostructures with tunable morphology and functionality. The work described in Chapters 2 and 3 demonstrated that a wide variety of NP nanostructures can be accessed in supramolecular nanocomposites by tuning the entropic balance within the materials system, either by tuning the NP size or by subjecting the nanocomposite under thin film (1-D) geometric confinement. This chapter expands the discussion on the effect of entropic modulation with an investigation of supramolecules and supramolecular nanocomposites under 2-D cylindrical confinement. Supramolecules confined within cylindrical anodic aluminum oxide (AAO) membrane pores exhibited morphologies distinct from pure BCPs with similar composition, as the small molecules within the supramolecules mediates the interfacial interactions between supramolecule and pore wall, and alters the supramolecule composition. The increasing entropic frustration as a function of decreasing pore size leads to the appearance of morphologies that are distinct from bulk BCP or bulk supramolecule morphologies. Upon introduction of NPs, a variety of unique NP nanostructures can be accessed, such as NP chains, stacked rings, and single/double helices. This study represents the first experimental realization of such complex 3-D NP nanostructures via cylindrically confined supramolecules, and demonstrates the significance of entropic modulation in greatly expanding the library of nanostructures accessible from supramolecular nanocomposites. Finally, the single Au NP helical nanostructures are observed to be plasmonically and chiro-optically active via single molecule circular dichroism (CD) measurements, thus opening opportunities to utilize cylindrically confined supramolecular nanocomposites as optical metamaterials.

§ 4.1 Introduction

Nanoparticles (NPs) exhibit optical, electrical and magnetic properties that are unique from their bulk material due to quantum confinement effects. These nanoscale building blocks are often regarded as “artificial atoms” that can be used to construct artificial materials with interesting physical properties due to interparticle coupling effects in multiple dimensions. Metallic NPs closely arranged in 1-D linear arrays can facilitate the transport of surface plasmons along the array due to strong coupling of plasmon modes between adjacent NPs. Specifically arranged 2-D NP assemblies can be used to generate plasmonic “hot spots” and applied towards surface-enhanced Raman scattering (SERS). 3-D NP assemblies arranged in specific chiral conformations, such as non-symmetric multi-mers and single or double helices, have demonstrated strong optical coupling to circularly polarized light. Due to this wide range of unique collective properties, NP assemblies have potential applications in a vast array of
emerging technologies, such as plasmonic waveguides, chemical and mechanical sensors, photovoltaics, memory storage devices, and chiral optics.

The control and optimization of these collective properties require precise control over the structure and spatial distribution of NPs. Therefore, to further enable the integration of NP assemblies into next-generation devices, a versatile and cost effective platform to template NP assembly over multiple length scales is requisite. Currently, “top-down” lithographic approaches (i.e. physical \textsuperscript{24-26} and chemical patterning\textsuperscript{27, 28}) and “bottom-up” self-assembly approaches (i.e. controlled drying \textsuperscript{29-31}, DNA linkers \textsuperscript{32, 33}, DNA origami \textsuperscript{22, 34} and block copolymers (BCPs) \textsuperscript{35-39}) are used to template NP assembly. For practical applications, the ideal assembly technique should address several key challenges: 1) versatility in assembling different types of NPs, 2) precise control of NP spatial distribution over multiple length scales, 3) ease of scaling up, and 4) accessibility to a wide range of nanostructures.

Previous chapters have demonstrated that a BCP-based supramolecular approach to NP assembly addresses most of the above mentioned challenges. The PS-\textit{b}-P4VP(PDP) supramolecules, comprised of a block copolymer, polystyrene-\textit{block}-poly(4-vinylpyridine) (PS-\textit{b}-P4VP) hydrogen bonded to the small molecule 3-pentadecylphenol (PDP), achieves NP assembly within the P4VP(PDP) microdomain due to the favorable interaction between alkyl chains on the PDP molecules and NP native ligands. Due to the non-specific linking chemistry, this technique is effective in assembling NPs regardless of NP chemistry or geometry. The stiffness of the P4VP(PDP) microdomain results in high conformational entropic penalty upon NP incorporation into the supramolecule, which results in the precise spatial confinement of the NPs to the center of the microdomain. The supramolecule-directed NP assemblies can be easily and cost effectively scaled up in bulk and thin film geometries\textsuperscript{40-44}. Furthermore, several NP nanostructures, such as 1-D arrays, 2-D sheets and 3-D networks, hexagonal lattices, square lattices, and ladder-like structures can be generated by tuning the supramolecule morphology and NP size\textsuperscript{41, 43}.

In this study, we demonstrate that the NP nanostructures accessible \textit{via} the supramolecular assembly approach can be greatly extended by subjecting the supramolecule/NP composite material to a 2-D geometric confinement within cylindrical anodized aluminum oxide (AAO) membrane pores (Figure 4.1). While it is well known from theoretical\textsuperscript{45-53} and experimental\textsuperscript{54-58} evidence that 2-D geometric confinement induce formation of BCP morphologies unique to bulk BCP, such as toroids and helices, due to polymer chain frustration and symmetry breaking, the extrapolation of these concepts to supramolecule nanocomposite self-assembly under cylindrical confinement is not trivial, as the entropic landscape within supramolecular nanocomposites is more complex. The NP incorporation affects the polymer matrix chain conformation depending on the particle size. The interfacial activity of NPs and rheological properties of the nanocomposite under nanoscopic confinement further complicate the molding process.
needed to achieve geometric confinement. The presence of small molecules non-covalently attached to the BCP side chain changes the chain architecture and rigidity, and consequently the confinement induced entropic contribution. The presence of unbounded small molecules further complicates incommensurability between the geometric confinement and periodicity of supramolecular system. To date, there is no report on how to fabricate complex 3-D NP assemblies based on BCP and supramolecular nanocomposites.

**Figure 4.1.** PS-b-P4VP(PDP)/NP nanocomposites are drawn into AAO membrane pores by thermal annealing, removing residue nanocomposite material on the membrane surface, and dissolving the AAO template to yield supramolecule/Au NP nanotubes with cylindrically confined nanostructures.

The work described in this chapter is the first experimental demonstration of such effect on the nanostructure of BCP-based supramolecules and supramolecule/NP composites. Characterization of the cylindrically confined nanotubes using a combination of transmission electron microscopy (TEM) and TEM tomography reveal a variety of unique supramolecule morphologies as well as precisely-defined NP nanostructures, such as clusters, arrays, stacked rings, single helices and double helices, which are tunable as a function of NP loading. These nanostructures are unique to the supramolecular nanocomposite system and demonstrate 2-D confinement to be an effective means to tailor NP self-assembly. The resulting structures are shown to exhibit strong chiral plasmonic activity, thus opening opportunities for large scale manufacturing and application as metamaterials and optoelectronic devices.
§ 4.2 Self-assembly of cylindrically confined supramolecules

The self-assembled of supramolecules under cylindrical confinement is more complicated than simple BCPs due to the presence of PDP small molecules. The small molecules may potentially impact the cylindrically confined supramolecule self-assembly in several ways. Firstly, the small molecules can increase the rigidity of the P4VP(PDP) block, thus resulting in increased conformational entropic penalty under increasing degrees of cylindrical confinement, thus potentially resulting in morphologies unique from the BCP system. Secondly, the small molecules may detach from the 4VP units due to the non-covalent P4VP/PDP bonding, thus changing the overall volume fraction and morphology of the supramolecule. Thirdly, detached small molecules may change the supramolecule/AAO interfacial interaction, which may also impact the resulting morphologies. This section explores the role of PDP small molecule and effect of the degree of confinement on the resulting morphology of supramolecules cylindrically confined within AAO pores.

4.2.1 Role of small molecules

A series of supramolecules based on PS(19 kdal)-b-P4VP(5.2 kdal) with various small molecule loading are used to initiate the investigation on the role of PDP small molecules on the self-assembly of supramolecules under cylindrical confinement (Table 4.1). All of the supramolecules have the same volume fraction of P4VP ($f_{P4VP}$), but varying volume fraction of the P4VP(PDP) comb block ($f_{comb}$) due to increasing PDP loading from batch I to batch IV.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>BCP</th>
<th>PDP:4VP Ratio</th>
<th>$f_{P4VP}$</th>
<th>$f_{comb}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>PS(19 kdal)-b-P4VP(5.2 kdal)</td>
<td>0</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>II</td>
<td>PS(19 kdal)-b-P4VP(5.2 kdal)</td>
<td>0.7</td>
<td>0.22</td>
<td>0.45</td>
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<tr>
<td>III</td>
<td>PS(19 kdal)-b-P4VP(5.2 kdal)</td>
<td>1.7</td>
<td>0.22</td>
<td>0.62</td>
</tr>
<tr>
<td>IV</td>
<td>PS(19 kdal)-b-P4VP(5.2 kdal)</td>
<td>3</td>
<td>0.22</td>
<td>0.73</td>
</tr>
</tbody>
</table>

Table 4.1. Supramolecules based on PS(19 kdal)-b-P4VP(5.2 kdal) used to investigate the effect of PDP small molecule loading on the resulting supramolecule morphology under cylindrical confinement.

The supramolecule samples are drawn into AAO membranes with average pore sizes of 35 ± 3 nm (Appendix 3.1) by drop casting a supramolecule film on top of an AAO membrane and subsequently annealing the film at 110°C for 24 hours under vacuum. The strong capillary forces induce the supramolecule to flow into the nanoscopic AAO pores, resulting in the formation of supramolecule nanofibers about 35 nm in width and tens of microns in length, corresponding to the AAO membrane pore dimensions. The TEM images of the nanofibers, which are stained with I$_2$ vapor to darken the P4VP(PDP) microdomains, are shown in Figure 4.1. Nanowires of
supramolecule I exhibits a single row of P4VP(PDP) spheres in the center of the nanowires (Figure 4.1a). This morphology is consistent with its $f_{P4VP}$, which lies in the spherical regime of the BCP morphology space. For supramolecule II nanowires, a slightly different double row spherical morphology is observed (Figure 4.1b). This morphology is consistent with the $f_{P4VP}$ of this supramolecule, but not its $f_{comb}$, which lies in the lamellar regime. Interestingly, TEM images of supramolecule III (Figure 4.1c) and IV (Figure 4.1d) nanofibers also show double or triple row spherical morphology, despite the $f_{comb}$ of supramolecule IV being as high as 0.73, which forms P4VP(PDP) majority cylindrical morphology in bulk. In addition, the periodicity of the 4 nanofiber samples are all ~24 nm. From these observations, it is apparent that the cylindrically confined supramolecule morphologies are a function of $f_{P4VP}$ rather than $f_{comb}$.
Figure 4.1. Effect of PDP small molecule loading on cylindrically confined supramolecules. TEM images of cylindrically confined supramolecules a) I, b) II, c) III, and d) IV stained with I\textsubscript{2} vapor. Scale bars are 50 nm for all images.

To confirm the observation that cylindrically confined supramolecule morphologies are a function of $f_{P4VP}$ rather than $f_{comb}$, another series of supramolecule samples with the same $f_{comb}$ and varying $f_{P4VP}$ (Table 4.2) are cylindrically confined within the 35 nm AAO membrane pores in the same manner. As a reference, supramolecules with $f_{comb}$ of 0.62 are known to form lamellar or P4VP(PDP) majority cylindrical morphologies in bulk.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>BCP</th>
<th>PDP:4VP Ratio</th>
<th>$f_{P4VP}$</th>
<th>$f_{comb}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>PS(19 kdal)-b-P4VP(5.2 kdal)</td>
<td>1.7</td>
<td>0.22</td>
<td>0.62</td>
</tr>
<tr>
<td>VI</td>
<td>PS(32.1 kdal)-b-P4VP(13.2 kdal)</td>
<td>1.3</td>
<td>0.29</td>
<td>0.62</td>
</tr>
<tr>
<td>VII</td>
<td>PS(20 kdal)-b-P4VP(19 kdal)</td>
<td>0.8</td>
<td>0.49</td>
<td>0.62</td>
</tr>
<tr>
<td>VIII</td>
<td>PS(11.8 kdal)-b-P4VP(15 kdal)</td>
<td>0.7</td>
<td>0.56</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Table 4.2. Supramolecules used to investigate the effect of $f_{P4VP}$ on the resulting supramolecule morphology under cylindrical confinement.

The I\textsubscript{2} stained TEM images of the resulting cylindrically confined supramolecule nanofibers are shown in Figure 4.2. Nanofibers of supramolecule V exhibit the double row P4VP sphere morphology that is similar to the previous supramolecule series and consistent with $f_{P4VP} = 0.22$ (Figure 4.2a). Nanofibers of supramolecule VI demonstrate a mixture morphology of a dark P4VP cylinder parallel to the nanofiber axis surrounded by P4VP spheres. This morphology is somewhat consistent with $f_{P4VP} = 0.29$, which lies in the P4VP minority cylindrical morphology domain and is close to the sphere/cylinder morphology boundary (Figure 4.2b). Further increasing $f_{P4VP}$ to 0.49, supramolecule VII nanofibers display morphologies that appear to be either elongated P4VP spheres or distorted P4VP disks that are oriented perpendicular to the nanofiber axis. This morphology resembles the stacked disk morphology of a lamellar BCP under cylindrical confinement (Figure 4.2c). Finally, supramolecule VIII nanofibers clearly demonstrate a stacked disk morphology (4.2d), consistent with $f_{P4VP} = 0.56$, which forms lamellar morphology in bulk. This series of experiments further support the observation that morphologies of cylindrically confined supramolecular nanocomposites are more strongly dependent on $f_{P4VP}$ rather than $f_{comb}$. 

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Figure 4.2. Effect of $f_{P4VP}$ on cylindrically confined supramolecules. TEM images of cylindrically confined supramolecules a) V, b) VI, c) VII, and d) VIII stained with I$_2$ vapor. Scale bars are 200 nm for all images.

The dependence of the cylindrically confined supramolecule morphology to $f_{P4VP}$ rather than $f_{comb}$ suggests that the PDP small molecules may have diffused out of the P4VP microdomain during processing of the nanofibers, which leads to a decrease in $f_{comb}$ that approaches $f_{P4VP}$. This diffusion is possible due to the non-covalent nature of the 4VP/PDP hydrogen bond. In fact, it is known from previous studies by Ikkala et al on bulk PS-$b$-P4VP(PDP) supramolecules that the hydrogen bonds destabilize at elevated temperatures, causing the PDP to diffuse out of the P4VP microdomain and resulting in order-order transitions towards PS majority morphologies$^{59}$. When the supramolecule
samples are subsequently cooled back down to room temperature, the order-order transitions reverse towards PS minority morphologies as the PDP small molecules diffuse back into the P4VP microdomains and the P4VP/PDP hydrogen bonds re-stabilize.

To test the hypothesis of PDP diffusion during thermal annealing, a PS(19 kdal)-b-P4VP(5.2 kdal)(PDP)$_{1.7}$ supramolecule confined within 35 nm AAO pores was thermally annealed at 110 °C for 12 hours, then cooled back down to room temperature at different rates (Figure 4.3). When the supramolecules are cooled rapidly, double row spherical morphologies are observed under TEM (Figure 4.3a). However, when the supramolecules are cooled slowly down to room temperature over a period of 4 hours, a majority of parallel cylindrical morphologies are observed (Figure 4.3b). This discrepancy is possibly due to the PDP small molecules diffusing back into the P4VP microdomain during the slow cooling process, thereby increasing $f_{comb}$.

Figure 4.3. TEM images of cylindrically confined PS(19 kdal)-b-P4VP(5.2 kdal)(PDP)$_{1.7}$ supramolecules cooled a) rapidly and b) slowly over 4 hours from 110 °C to room temperature, exhibiting a clear difference in morphology. Scale bars are 200 nm for both images.

Another observation in support of the PDP diffusion hypothesis stems from the difference in microdomain orientation between supramolecules and their corresponding pure BCPs. This evidence is most apparent in the lamellar forming PS(11.8 kdal)-b-P4VP(15 kdal)(PDP)$_{0.8}$ supramolecules in comparison to pure PS(11.8 kdal)-b-P4VP(15 kdal) BCPs (Figure 4.4). The supramolecules form lamellae that are oriented perpendicular to the AAO pore axis (Figure 4.4a), while the pure BCPs form a cylindrical morphology oriented parallel to the AAO pore axis (Figure 4.4b). This difference in orientation suggests a difference in the supramolecule/AAO pore wall interfacial
interaction. The AAO pore walls are hydrophilic and selective to the P4VP microdomains, which may induce the formation of parallel morphologies in the cylindrically confined supramolecule. However, PDP small molecules that diffuse out of the P4VP microdomain during thermal annealing may also diffuse to the AAO pore wall, which mediates the supramolecule/AAO interaction, and in turn results in the formation of perpendicular supramolecule morphologies. The tendency of PDP small molecules to mediate supramolecule/substrate interfacial interactions have been previously observed by Xu et al in PS-b-P4VP(PDP) thin films on top of Si/SiO$_2$ substrates $^{60}$.

![Figure 4.4](image.png)

**Figure 4.4.** TEM images of a) PS(11.8 kdal)-b-P4VP(15 kdal)(PDP)$_{0.8}$ supramolecules and b) PS(11.8 kdal)-b-P4VP(15 kdal) BCPs under cylindrical confinement in 35 nm AAO pores, exhibiting a clear difference in microdomain orientation. Scale bars are 50 nm for both images.

From these observations, the role of PDP small molecules in the self-assembly of cylindrically confined PS-b-P4VP(PDP) supramolecules is more clear. During the thermal annealing process, the 4VP/PDP hydrogen bonds destabilize at elevated temperatures, and the PDP small molecules diffuse out of the P4VP microdomain. This diffusion has two main effects on the supramolecule morphology. Firstly, the diffusion of PDP small molecules decreases $f_{comb}$, which leads to an order-order transition towards equilibrium morphologies resembling those of the corresponding pure BCPs. Secondly, the PDP small molecules possibly diffuse to the relatively hydrophilic AAO pore wall and mediates the supramolecule/AAO interfacial interaction, leading to the formation of morphologies oriented perpendicular to the pore axis (Figure 4.5).
4.2.2 Effect of commensurability

The effect of commensurability on the morphology of cylindrically confined supramolecules is another important factor in achieving structural control in these materials. To investigate these effects, three supramolecules (Table 4.3) are each subjected to cylindrical confinement within AAO membranes with pore sizes of 35 nm, 55 nm, and 100 nm, and their resulting morphologies are investigated using TEM (Figure 4.6).

<table>
<thead>
<tr>
<th>Sample #</th>
<th>BCP</th>
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<tbody>
<tr>
<td>IX</td>
<td>PS(19 kdal)-b-P4VP(5.2 kdal)</td>
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<td>0.62</td>
</tr>
<tr>
<td>X</td>
<td>PS(20 kdal)-b-P4VP(19 kdal)</td>
<td>0.8</td>
<td>0.49</td>
<td>0.62</td>
</tr>
<tr>
<td>XI</td>
<td>PS(11.8 kdal)-b-P4VP(15 kdal)</td>
<td>0.7</td>
<td>0.56</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Table 4.3. Supramolecules used to investigate the effect of commensurability on the resulting supramolecule morphology under cylindrical confinement.

For supramolecule IX, confinement under 35 nm AAO pores yielded mostly double row spherical morphologies as observed previously (Figure 4.6a). Upon confinement to 55 nm pores, spherical morphology is still observed, although the spheres...
are often arranged into triple rows owing to the wider pore diameter (Figure 4.6b). Under confinement within 100 nm AAO pores, the supramolecules are observed to undergo a morphological transition, forming parallel cylinders and double helix-like morphologies (Figure 4.6c). In the case of supramolecule X, a similar trend in morphology is observed. Confinement under 35 nm AAO pores resulted in spherical and ellipsoidal P4VP(PDP) microdomains embedded in PS matrix (Figure 4.6d), while increasing AAO pore diameter to 55 nm resulted in an increase in the proportion of ellipsoidal P4VP(PDP) microdomains relative to spherical ones (Figure 4.6e), while further increasing AAO pore size to 100 nm yielded mostly lamellar morphology, consistent with the $f_{P4VP}$ of supramolecule X (Figure 4.6f). Finally, for supramolecule XI, increases in AAO pore size from 35 nm to 100 nm all yielded lamellae oriented perpendicular to the pore axis, although for wider pore sizes, the widths of the lamellae in the perpendicular direction to the AAO pore axis also increase to accommodate for the increase in pore diameter (Figure 4.6g-i).

The observed trends in morphological transitions of supramolecules under cylindrical confinement as a function of pore diameter are similar to those of simple BCPs. Under a high degree of confinement (i.e. small pore diameters), the formation of lamellar or cylindrical morphologies require high degrees of conformational entropic penalty. To compensate, the supramolecule adopts spherical morphologies to relax the polymer chains. As pore diameter increases, the entropic effect becomes less dominant and the supramolecules adopt morphologies closer to their bulk morphologies. In addition, larger pores have relatively lower ratios of pore surface area to supramolecule volume, which means more PDP may remain within the supramolecule during thermal annealing. This may explain the formation of cylindrical morphology within supramolecule IX in 100 nm AAO pores. Supramolecule XI has a somewhat anomalous trend, forming lamellar morphology for all three pore diameters. This may be due to the relatively higher $f_{P4VP}$ of the supramolecule, which increases the entropic penalty of forming P4VP spheres. In addition, the relatively smaller molecular weight of supramolecule XI may mean that smaller pores are necessary to induce enough entropic penalty to result in the formation of spherical morphologies.
**Figure 4.6.** Effect of commensurability on the morphologies of cylindrically confined PS-\(b\)-P4VP(PDP) supramolecules. TEM images of supramolecule IX confined under a) 35 nm, b) 55 nm, and c) 100 nm AAO pores; supramolecule X confined under d) 35 nm, e) 55 nm, and f) 100 nm AAO pores; supramolecule XI confined under g) 35 nm, h) 55 nm, and i) 100 nm AAO pores. Scale bars are 200 nm for all images.
§ 4.3 Self-assembly of cylindrically confined supramolecular nanocomposites

The stabilization of morphologies within cylindrically confined supramolecules that are unique from bulk supramolecule morphologies is an intriguing result, as it opens opportunities to use the morphologies to template NP assembly. The incorporation of NPs within cylindrically confined supramolecules also increases the complexity in the entropic landscape of the material system, and the effect of NP incorporation on the nanocomposite morphology has never been previously explored. This section will investigate the assembly of NPs in cylindrically confined supramolecules forming lamellar and spherical morphologies.

4.3.1 Nanoparticle assembly in lamellar supramolecules under cylindrical confinement

From Section 4.2, it is known that the supramolecule PS(11.8 \textit{kda})-b-P4VP(15 \textit{kda})(PDP)\textsubscript{0.7} forms perpendicular lamellae under cylindrical confinement within AAO pores. To assess the effect of NP incorporation, supramolecules with different volume fractions of ~4 nm Au NPs capped with dodecanethiol ligands (Appendix 3.2) are drop cast onto AAO membranes with 35 nm pores and annealed at 110 °C for 12 hours, and the resulting nanocomposite nanofibers are isolated by dissolving the AAO template and characterized using TEM (Figure 4.7). Nanofibers with 3 v% Au NP loading shows clusters of NPs distributed somewhat randomly throughout the nanofiber (Figure 4.7a). Upon increase in NP loading to 6 v% (Figure 4.7b) and 9 v% (Figure 4.7c), the outline of the NP clusters become more apparent, and the clusters appear to form disk-like structures oriented perpendicular to the AAO pore axis, similar to the supramolecule morphology.

To characterize the morphology of the underlying supramolecule, the nanofibers are stained with I\textsubscript{2} vapor to highlight the P4VP(PDP) microdomain as darker regions. After staining, it becomes clear that the NPs are sequestered in the dark lamellar P4VP(PDP) microdomains, and increasing the NP loading leads to an increase in the density of NPs localized within the P4VP(PDP) microdomains (Figure 4.7d-f). These observations demonstrate that cylindrically confined supramolecules are viable in templating the assembly of NPs into nanostructures unique from BCP or bulk/thin film supramolecule morphologies. In addition, for the lamellar forming supramolecule, it appears that the NPs simply conform to the underlying supramolecule morphology, and play a passive role in the self-assembly process.
Figure 4.7. TEM images of PS(11.8 kdal)-b-P4VP(15 kdal)(PDP)_{0.7} supramolecules loaded with a) 3 v%, b) 6 v%, and c) 9 v% of ~4 nm Au NPs under cylindrical confinement. c-e) The three nanocomposite samples are stained with I\textsubscript{2} vapor to highlight the P4VP(PDP) microdomains as dark regions.

4.3.2 Nanoparticle assembly in spherical supramolecules under cylindrical confinement

Similar experiments were performed using blends of ~4 nm Au NPs capped with dodecanethiol ligand and PS(19 kdal)-b-P4VP(5.2 kdal)(PDP)_{1.7}. Figure 4.8 shows the resulting nanostructures as a function of NP loading. At 3 vol% loading of NPs, three NP nanostructures are predominant: double row spherical NP clusters (Figure 4.8a), single NP arrays oriented parallel to the AAO pore axis (Figure 4.8b) and NP “disks” oriented perpendicular to the AAO pore axis (Figure 4.8c). At 6 vol% NP loading, the NP “disk” morphology becomes more predominant and a single helix morphology begins to appear (Figure 4.8d). At 9 vol% NP loading, the disk and single helical NP morphologies represent the most predominant morphologies, and a small number of nanotubes with a double helical morphology are observed (Figure 4.8e). At 12 vol% NP loading, the NP nanostructures become largely disordered (Appendix 3.3). In addition to Au NPs, ~ 4 nm Ag NPs have also been successfully incorporated into cylindrically confined supramolecular nanocomposites, forming morphologies such as 1-D NP arrays and single
helices as a function of increasing NP loading, thus demonstrating the versatility of the supramolecular approach for a variety of NP chemistries (Appendix 3.4).

**Figure 4.8.** Different NP structures are predominant as a function of increasing NP loading in the PS(19 kdal)-b-P4VP(5.2 kdal)(PDP)_{1.7} supramolecule/Au NP nanocomposite system under cylindrical confinement, as revealed by TEM: a) spherical clusters, b) NP arrays parallel to pore axis, c) stacked disks perpendicular to pore axis, d) single helices, and e) double helices.

TEM tomography is employed to provide further characterization of the 3-D morphology of the NP nanostructures (Figure 4.9). Figure 4.9a shows a snapshot of the 3-D rendering of the perpendicular stacked disk morphology at 0°, 45° and 90° to the AAO pore axis. It is clear that the “disks” observed in the in-plane TEM images are actually hollow rings, suggesting the NPs reside at the surface of the nanowires. Figure 4.9b shows the 3-D reconstruction of the single helical nanostructure at 0°, 45° and 90° to the AAO pore axis, which clearly demonstrate that the helical morphology observed under TEM is a true representation of the 3-D nanostructure. It is important to point out that the supramolecule architecture is necessary to induce the observed 3-D ordering, as similar nanocomposite systems with little or no PDP addition do not result in ordered NP structures (Appendix 3.5).
Figure 4.9. TEM tomography 3-D reconstruction of PS(19 kdal)-b-P4VP(5.2 kdal)(PDP)$_{1.7}$ supramolecules with a) 3 v% Au NP loading, forming stacked ring nanostructures, and b) 6 v% Au NP loading, forming single helical nanostructures.

Although the observed morphologies in the cylindrically confined supramolecule and supramolecular nanocomposites have been predicted and experimentally demonstrated in pure BCP systems, the formation of the corresponding NP structures is remarkable for two reasons: 1) this is the first time that directed assemblies of NPs into disks and helices have been generated upon blending with polymeric matrix, and 2) the NP nanostructures bear very little resemblance to the spherical supramolecule morphology, suggesting that at high NP loadings the self-assembly mechanism may be quite complex.

At low NP loadings (3 vol %), the NP cluster morphology closely resembles the supramolecule morphology without NP loading, thus in this case the supramolecule may serve as a structural scaffold to guide the NP assembly. In the case of parallel NP array morphology, the NPs may increase the volume fraction of the P4VP(PDP) microdomain such that it assembles into a cylindrical morphology with the axis of the cylinder directed parallel to the pore axis, such that the BCP chain stretching is azimuthally uniform. At higher NP loading (6-9 vol%), the stacked rings and helical NP structures no longer correspond to the supramolecule structure. One possible explanation for this deviation is that the observed morphologies are simply the result of frustrated NP packing due to high NP loading, and are independent of supramolecule morphology. However, NP structures in P4VP(36.3 kdal)(PDP)$_1$ homopolymer-based supramolecules with 6 vol% and 9 vol%
Au NP loadings show no ordered structures under cylindrical confinement (Appendix 3.6).

Thus, the BCP-based supramolecule must still play a structure-directing role in the self-assembly process. The stacked ring and helical morphologies have been observed in BCP systems as manifestations of the cylindrical morphology under 2-D confinement\(^{45-58}\). Thus, it is possible that these structures are also the result of additional NP loading increasing the P4VP(PDP) volume fraction of the supramolecule into the cylindrical morphology regime. The parallel to perpendicular transition in the morphology is favorable because the system has more freedom to relieve BCP chain stretching and accommodate any changes in the periodicity of the nanostructures along the pore axis. The co-occurrence of these three structures suggests that they are similar in energy. At even higher NP loading (12 vol%), ordered morphologies within the nanotubes largely disappear, as the presence of high numbers of NPs likely acts as a kinetic barrier to slow the self-assembly process. The NP nanostructure distribution is counted from over 100 TEM images and plotted as a function of NP loading (Appendix 3.7). The polydispersity in the nanostructures formed may be due to the slight deviations in pore shape and diameter, which perturb the confinement conditions and overall entropic landscape of the nanocomposite system.

§ 4.4 Chiral optical properties of helical nanoparticle assemblies

In the cylindrical confinement-induced single NP helices, the geometry of the NP assembly is intrinsically asymmetric and thus should give rise to rich optical behavior. In fact, the optical and chiral plasmonic properties of a single helical NP chain were verified by dark field single-particle scattering spectroscopy. Scattered light from an individual Au NP helix is selected on a TEM grid by placing a pinhole at a reimaged focal plane and allowing light from only the structure of interest to enter the spectrometer (Figure 4.10).

![Figure 4.10. Schematic of the dark field single-particle scattering spectroscopy experimental setup.](image-url)
Figure 4.11a shows a vertically mirrored, bisignate dip-peak signal of the circular dichroism (CD) spectra which is characteristic of right-handed helical arrangements of plasmonic particles. The strong CD signal is a result of the helical arrangement of the NP nanostructure, which is confirmed by TEM (inset). Unlike optically active molecules such as DNA, the chiral plasmonic response is determined by the phase lag of electromagnetic wave propagation due to cross coupling of plasmonic dipoles (Figure 4.11b). More specifically, due to the phase lag along the propagation direction of the excitation light beam, a time-domain right-handed polarization rotating light will build “left-handed” polarization rotating light along this propagation direction in space. Therefore, coulomb repulsion of the induced charges for a right-handed plasmonics NP chain under right-handed light excitation is higher than the case when it is excited by left-handed light. As a result, a right-handed plasmonics NP chain is expected to have resonance wavelength split with a lower energy (higher wavelength) resonance preference for left-handed light excitation.

![Figure 4.11.](image)

**Figure 4.11.** a) dark field scattering spectrum of a right handed Au NP single helix (inset: TEM image, scale bar is 50 nm), showing a bisignate peak indicative of chiral optical activity. b) schematic showing the phase lag of electromagnetic wave propagation due to cross coupling of plasmonic dipoles for right handed gold helices in left handed and right handed circularly polarized electromagnetic fields.

The CD responses of chiral plasmonic nanoparticle assemblies were also simulated by using commercial software package CST Microwave Studio, which applies a finite integration technique (FIT). The FIT is an approach based on the integral formulation of the Maxwell’s equations written for a chiral medium,

\[ D\omega = \varepsilon E\omega + i\xi B\omega \]
\[ H_\omega = \frac{B_\omega}{\mu} + i\xi E_\omega \]

where \( \varepsilon \) and \( \mu \) are the effective permittivity and permeability of the medium, and \( \xi \) describe the excitation of electric (magnetic) dipoles by the magnetic (electric) field which is a key parameter describing the chiral property.

This method is distinct from finite difference time domain methods. The polymer index of 1.6 in which the nanoparticle are embedded was used as medium index and the radius (20 nm) and pitch (18 nm) of helix was employed for simulation according to TEM image. The chiral structure was excited by left-handed and right-handed circular polarized plane wave respectively. Then the CD signal was collected by calculating the difference between scattering signal in farfield of left- and right-handed excitation in frequency domain (Figure 4.12a-b). The simulated spectrum also shows a bisignate peak in the 800-1000 nm range, which corresponds reasonably well to the experimental results (Figure 4.12c).
Figure 4.12. Simulated scattering signal in farfield of a) left- and b) right-handed excitation in frequency domain, and c) the resulting simulated CD spectrum of a Au single helix nanostructure.
§ 4.5 Conclusion

Entropic modulation of BCP-based supramolecules and supramolecular nanocomposites via 2-D cylindrical confinement has led to the generation of morphologies that are unique from unconstrained BCP and BCP/NP systems. In cylindrically confined supramolecules, the non-covalently bound small molecules play a significant role in the self-assembly process, serving to mediate the supramolecule/AAO pore wall interfacial interaction and simultaneously decrease the comb block volume fraction. These effects, combined with the entropic constraints induced by the geometric confinement, resulted in the formation of a variety of morphologies, such as double/triple row spheres, parallel cylinders, and stacked disks, some of which are unique from bulk supramolecule morphologies.

Cylindrically confining supramolecule/NP nanocomposites have generated nanofibers with NPs ordered into spherical clusters, linear arrays, stacked rings, and single and double helical nanostructures, as confirmed by TEM and TEM tomography. These results represent the first experimental demonstration of using confined BCP-based materials systems to generate these 3-D ordered NP nanostructures, thus proving entropic modulation to be a powerful tool in expanding the library of nanostructures accessible in BCP-based supramolecular nanocomposites.

Furthermore, this NP assembly strategy has several advantages compared to other top-down and bottom-up techniques. All of the NP structures generated via cylindrical confinement of supramolecular nanocomposites have sub-10 nm feature sizes, which is beyond the capability of conventional lithographic techniques. The patterning of NPs relies on van der Waal’s attraction between the alkyl tails of the PDP small molecules and the alkyl NP ligands, which are common for a wide variety of NP chemistries. This decouples the template chemistry from the NP chemistry, which renders the strategy applicable to a wide variety of NPs without the need for additional ligand modifications. In this Chapter, Au and Ag NPs have been successfully self-assembled under cylindrical confinement without the need for any chemical modification of the NP ligands or supramolecules. This strategy is also very simple and scalable, requiring only thermal annealing and tuning of the NP loading to obtain the desired NP nanostructures. Finally, the demonstration of chiral plasmonic properties of these NP assemblies via dark field circular dichroism paves the way for this assembly approach to be applied towards next generation chiral metamaterials and optoelectronic devices.
§ 4.6 Methods

Nanoparticle synthesis

Gold (III) chloride trihydrate (HAuCl₄•3H₂O), oleylamine (technical grade, 70%), 1,2,3,4-tetrahydronaphthalene (tetralin), and tert-butylamine-borane complex (TBAB, 97%) were all purchased from Sigma Aldrich and used as received. Ag NPs were purchased from Nanocomposix and used as received. Au NPs were synthesized as described by Sun et al.⁶² For a typical synthesis, 200 mg of HAuCl₄•3H₂O was dissolved in a mixture of 20 mL oleylamine and 20 mL tetralin solution and stirred for 30 min under N₂ gas. Then, 86 mg of TBAB dissolved in 2mL of oleylamine and 2 mL of tetralin was added to the solution to reduce the gold salt. The reaction was stirred for a further 1 hour and the NPs are purified by washing with acetone and chloroform. The NP size is tunable by adjusting reaction temperature, with batch IV NPs produced at room temperature, and batch V NPs produced at -10°C. All NP size distributions were obtained using Igor Pro and ImageJ.

Nanowire preparation

Block copolymers (PS-b-P4VP) were purchased from Polymer Source. 3-pentadecylphenol (PDP) (95%) was purchased from Acros. Chloroform (pentene stabilized) was purchased from Fisher. All chemicals were used as received. The BCP supramolecule is prepared by separately dissolving PS-b-P4VP and PDP in CHCl₃ at 15 mg/mL concentration. The PDP solution is then added dropwise to the PS-b-P4VP solution while stirring to achieve the desired P4VP:PDP molar ratio. The mixture is stirred for a further 12 hours to allow for the formation of P4VP-PDP hydrogen bonds. Supramolecule solution or supramolecule/NP mixture solution is drop cast on top of an AAO membrane and allowed to dry. The dried supramolecule or supramolecule/Au NP nanocomposite is then thermal annealed in a vacuum oven at 150°C for 24 hours under vacuum. The nanocomposite is drawn into the AAO pores during thermal annealing due to strong capillary forces within the pores. The AAO membrane is subsequently dissolved using a 5 wt% NaOH (aq) solution to release the composite nanotubes for further characterization.

Scanning electron microscopy (SEM)

Nanotube samples were deposited on a Si substrate and coated with 2 nm of gold in a Denton Vacuum thin film sputter station. SEM images are taken using a JEOL field emission SEM operating at 5.0 kV accelerating voltage and a working distance of 6.0 mm.
Transmission electron microscopy (TEM)

Nanotube samples were deposited on carbon coated Cu grids and allowed to dry. Supramolecule nanotubes were exposed to iodine vapor for 4 hours to selectively stain the P4VP microdomain. The samples are imaged using a FEI Tecnai 12 TEM operating at 120 kV accelerating voltage or a JEOL 1200EX TEM operating at 80 kV.

TEM tomography

TEM tomography was collected using an FEI ultratwin Tecnai F20 operated at 200 kV and a Hummingbird Scientific high-tilt tomography holder. The tilt series were acquired from -70° to 70° with 1° tilt step increments and pixel resolution of 0.43 nm. Post-processing alignment and tomographic reconstruction of the tilt images were processed using the eTomo software package. IMOD and the Avizo 7.0 software packages were used for 3-D visualization.

Single molecule circular dichroism

The circular dichroism (CD) signal of single Au NP helix was recorded using a home built inverted optical microscope (Axiovert 200, Carl Zeiss MicroImaging Inc., Thornwood, NY) equipped with a dark-field objective (100x, NA = 0.9). The sample was prepared by dropcasting nano-helix on TEM grid. The white light from a halogen lamp passes through a polarizer followed by a quarter waveplate which converts linear polarization to circular polarization. By rotating the fast axis of the quarter wave-plate set to -45 deg and 45 deg with respect to the axis of the polarizer, left-handed and right-handed circular polarization was generated respectively and coupled into a dark-field reflector and objective to excite the structure. Then the CD spectrum was recorded by subtracting the spectrum for right-handed circular polarization from that taken with left-handed circular polarization and normalized to the intensity of light source. All data analysis was original without smoothing.
Chapter 5

Supramolecules Containing Liquid Crystalline Side Chains

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Chapters 2 to 4 focused on the effect of nanoparticle size and external geometric confinement on the entropic landscape of supramolecular nanocomposites and the resulting nanostructures. Besides these factors, polymer chain rigidity may also significantly alter the conformational entropy of the supramolecule. In BCP-based supramolecules, chain rigidity can be readily tuned by exchanging the non-covalently bound small molecule side chains with more crystalline small molecules. This chapter explores the effect of exchanging alkylphenol small molecules with more rigid liquid crystalline small molecule side chains, and their impact on the morphological behavior of the supramolecule and supramolecular nanocomposite systems. The liquid crystalline supramolecule was observed to hierarchically assemble into highly ordered lamellar-within-lamellar morphologies. Furthermore, the supramolecules undergo a distinctive, non-reversible order-to-order transition upon thermal annealing due to the diffusion and crystallization of the liquid crystalline small molecules. Finally, the supramolecules are demonstrated to template nanoparticle assembly, and the supramolecular nanocomposite system also undergoes non-reversible order-order transitions as a function of increasing temperature. Thus, liquid crystalline supramolecules and supramolecular nanocomposites represent new classes of stimuli responsive nanomaterials.

§ 5.1 Introduction

Block copolymers with one block containing liquid crystalline side chains have been extensively studied because of their structural complexity \(^1\)\(^-\)\(^6\) and stimuli responsiveness \(^7\)\(^-\)\(^{10}\). This special class of block copolymers self-assembles simultaneously on multiple length scales. The block copolymer microphase separates into spherical, lamellar and networked microdomains with periodicities of tens to hundreds of nanometers \(^11\). The liquid crystalline side chains typically self-organize on a smaller length scale, assembling into smectic, nematic and cholesteric liquid crystalline phases with characteristic lengths of several nm, while the side chains themselves pack on the several Angstrom scale \(^2\)\(^,\)\(^{12-16}\). In addition, the liquid crystalline side chains can be tailored to be responsive to external stimuli, such as electric \(^{17}\), magnetic \(^9\), \(^{18},\)\(^{19}\), and optical fields \(^{20},\)\(^{21}\). The structural complexity and stimuli responsiveness of the liquid crystalline side chains introduce additional versatility and functionality into the traditional block copolymer, making it potentially applicable in existing and emerging technologies such as photonics \(^{22}\), photolithography \(^{23},\)\(^{24}\) and holographic memory storage \(^{25},\)\(^{26}\).

Traditionally, the liquid crystalline side chains are attached to the block copolymer backbone via covalent bonding. The liquid crystalline side chain is motionally decoupled from the backbone by an alkyl spacer to enable partial conformational freedom.
of the side chains and thus formation of liquid crystalline mesophases. Due to the rigidity of the side chains, the liquid crystalline block forms a comb like molecular structure, in contrast to the coil-like structure of the other block. Smectic A and C* phase have been observed in the liquid crystalline microdomains, forming lamellae-within-lamellae morphologies. The smectic ordering of the mesophases can be readily and reversibly transformed to nematic and isotropic phases by tuning the sample temperature beyond the liquid crystalline phase transition temperatures. Thermodynamically, these coil-comb structured block copolymers have phase behaviors slightly different from symmetric coil-coil block copolymers. Most notably, the lamellar phase has been observed at a wider range of liquid crystalline block volume fractions because the high bending modulus of the liquid crystalline block strongly favors a microphase with low curvature. Liquid crystalline side groups possessing strong electric or magnetic dipoles have been shown to induce responsiveness to external electric or magnetic fields, while side groups containing the light-responsive azobenzene group align under polarized light due to Weigert’s effect. These mechanisms have been exploited extensively to produce long range ordering and orientational switching in BCPs.

The entropic landscape in liquid crystalline BCPs are also significantly different from simple coil-coil BCPs. As discussed in Chapter 1, the rigid liquid crystalline block does not have the same conformational entropy as the coil block, which restricts its ability to pack within self-assembled microdomains, resulting in zig-zag and nematic morphologies not observed in coil-coil BCPs. In addition, the effect of NP incorporation into liquid crystalline BCP systems remain an interesting topic due to the increased conformational entropy to accommodate the NPs.

Although these liquid crystalline block copolymers have demonstrated considerable potential in producing novel structural and functional materials, their versatility is limited due to the complexity involved during synthesis. One approach to circumvent this issue is to attach the liquid crystalline moieties to the polymer backbone via non-covalent bonds, such as hydrogen bonds, ionic bonds, metal coordination, \( \pi-\pi \) stacking, or combinations of multiple bonding mechanisms to form supramolecular assemblies. This approach significantly simplifies polymer synthesis, thus enabling a larger variety of liquid crystalline small molecules to be attached to the block copolymer while maintaining motional decoupling and liquid crystalline behavior of the side chains. Hydrogen bonding is a particularly attractive strategy because it occurs in many biological and natural systems. Supramolecular systems containing hydrogen bonded liquid crystals and block copolymers have shown many similar thermodynamic and functional behaviors as covalently bonded systems. Hierarchical assemblies of lamellar-within-lamellar, lamellar-within-spherical, lamellar-within-cylindrical, lamellar-within-perforated lamellar, spherical-within-lamellar, cylindrical-within-lamellar, and gyroid-within-lamellar morphologies have been observed. In addition,
responsiveness to externally applied electric, magnetic and optical fields could be introduced into the supramolecular system via hydrogen bonding of specifically designed small molecules to the block copolymer backbone.

In hydrogen bonded supramolecules, additional energetic contributions influence the final morphology. The relative interaction strengths between small molecule and small molecule, and between small molecule and polymer backbone, play an important role in the self-assembly process. Ruokolainen et al. have shown that microphase-separated, mesomorphous morphologies can only be achieved if the hydrogen bonding force between small molecule and polymer backbone is significantly stronger than the repulsive force. More recently, Rancatore et al. demonstrated that strong interactions between small molecules can facilitate microphase separation, such that small molecules confined in one microdomain can attract unconfined, macrophase separated small molecules into the microdomain during heating via strong intermolecular interaction between small molecules.

This chapter explores the self-assembly of BCP-based supramolecules containing liquid crystalline side chains, and their associated supramolecular nanocomposites. In this study, a supramolecular system with a weaker intermolecular interaction between small molecules is investigated. This system, comprised of a block copolymer, polystyrene-block-poly-4-vinylpyridine (PS-b-P4VP) hydrogen bonded to the cholesteric small molecule 3-hydroxyphenyl cholesteryl succinate (ChHP), is systematically studied for its thermal driven self-assembly behavior. This system underwent a series of permanent block copolymer phase transitions and decrease in block copolymer periodicity upon thermal annealing at increasing temperatures, which is in stark contrast from a supramolecular system with strong small molecule-small molecule interactions. A model based on the competition between small molecule-backbone interaction and small molecule-small molecule interaction forces is proposed to explain the observed thermally driven phase transitions, and highlight the importance role that small molecule-small molecule interactions play in the self-assembly of supramolecular liquid crystalline block copolymers. Furthermore, the supramolecules are demonstrated to template nanoparticle assembly, and the supramolecular nanocomposite system also undergoes non-reversible order-order transitions as a function of increasing temperature. Thus, liquid crystalline supramolecules and supramolecular nanocomposites represent new classes of stimuli responsive nanomaterials.

§ 5.2 Liquid crystalline supramolecule phase behavior

The ChHP small molecules are synthesized via 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) mediated coupling between cholesteryl
hemisuccinate (ChHS) and phenol. The synthesis procedures are described in detail in Appendix 4.1. While ChHS small molecules are capable of forming hydrogen bonds with pyridine as well, the carboxylic groups are also known to induce dimer formation. The addition of the phenol group thus prevents dimer formation and increases the efficiency for hydrogen bonding between phenol and pyridine on the P4VP. DSC is performed on the ChHP small molecule to characterize its thermotropic phase behavior (Appendix 4.2). The heating scan of ChHP contained two endotherms at 122.1°C and 137.6°C, corresponding to the melting point and clearing point of ChHP, respectively. From the peak of the cooling curve, the enthalpy of crystallization for ChHP is calculated to be 11.6 kJ/mol. POM was conducted on ChHP to confirm the phase transitions in ChHP (Appendix 4.3). From 30°C to 125°C, the ChHP sample shows distinct birefringent crystallites. At about 140°C, the crystallites disappear and the POM image shows birefringent oily streaks, indicating a phase transition from crystalline to liquid crystalline. Upon heating to 150°C, all birefringence disappear as the ChHP small molecules transition from liquid crystalline phase to isotropic phase.

Figure 5.1. Reaction schematic for the synthesis of ChHP small molecule. ChHS small molecules (1) are functionalized with resorcinol (2) via EDC coupling, yielding ChHP small molecules (3).
Small angle X-ray scattering (SAXS) was performed on ChHP insitu during heating from 30°C to 150°C to analyze its structural variations during thermal transition (Appendix 4.4). The ChHP sample has a characteristic scattering peak at q = 0.14 Å⁻¹, corresponding to a crystal structure with a periodicity of 4.5 nm. Upon heating to above 120°C, the periodicity of the crystal structure begins to decrease, reaching 3.8 nm at 130°C. Above 140°C, the characteristic scattering peak disappears as the ChHP becomes isotropic. The transitions in characteristic peak spacings corroborate with the DSC and POM data, suggesting crystalline/liquid crystalline/isotropic phase transitions. As the sample is gradually cooled back to room temperature, the 4.5 nm peak reappears around 120°C, indicating recrysallization of the small molecules.

FTIR was performed on P4VP(46.7 k dal)(ChHP)₁ supramolecules, and compared with the FTIR spectrum of P4VP(46.7k) homopolymer to confirm the formation of hydrogen bonding between the phenol group of ChHP and the pyridine group of P4VP (numbers in brackets denote molecular weight and subscripts denote molar ratio). From previous research on hydrogen bonded complexes of P4VP and the small molecule 3-pentadecylphenol (PDP) by Ruokolainen et al, the absorption peaks of importance in the FTIR spectrum are 1597 and 993 cm⁻¹, which correspond to stretching modes of P4VP. These peaks shift to higher wavenumbers upon hydrogen bonding formation with the small molecule due to changes in the electronic distribution in the pyridine ring as bonds in the pyridine ring strengthen. This wavenumber shift increases in magnitude with the strength of the non-covalent bonding. For phenolic hydrogen bonding, the shift is typically about 6 cm⁻¹. The FTIR spectra of the homopolymer and block copolymer are shown in Figure 5.2. Both spectra have an absorption peak at 1597 cm⁻¹. This absorption peak shifts to 1603 cm⁻¹ for the two corresponding supramolecules, indicating phenolic hydrogen bonding between ChHP and 4VP. The FTIR spectra of the polymers also show a pyridine ring absorption peak at 993 cm⁻¹, which shifts to 1011 cm⁻¹ for the supramolecules. This peak shift is also consistent with previously reported FTIR data from P4VP hydrogen bonded complexes with PDP and another carboxylated cholesteric small molecule, cholesteryl hemissucinate (CholHS). These data suggest that the ChHP small molecules indeed hydrogen bond with the 4VP group to form a stable supramolecule at room temperature.
Figure 5.2. FTIR spectra of ChHP, P4VP, and P4VP₁(ChHP)₁ supramolecule. The supramolecule had two absorbance peak shifts relative to the P4VP homopolymer, a 993 cm⁻¹ to 1011 cm⁻¹ and a 1597 cm⁻¹ to 1603 cm⁻¹ shift, indicative of hydrogen bonding between P4VP and ChHP.

The concept of supramolecular formation between P4VP and ChHP is then extended to a diblock copolymer system by blending ChHP with PS-b-P4VP. The effect of temperature on the phase behavior of the supramolecule is investigated in more detail using in situ SAXS and TEM. In situ SAXS measurements are conducted on a PS(24 kdal)-b-P4VP(9.5 kdal)₁(ChHP)₁ supramolecule during heating from room temperature to 150°C at a heating rate of 20°C/min (Figure 5.3, left panel). SAXS data is collected at every 10°C interval. At room temperature, the supramolecule has a scattering peak at q = 0.017 Å⁻¹, corresponding to a periodicity of 37 nm characteristic of the block copolymer microdomain size. In addition, there is a peak at q = 0.104 Å⁻¹ and a second order peak at q = 0.208 Å⁻¹, corresponding to a periodicity of 6.18 nm. This periodicity is slightly larger than the closely packed ChHP small molecules in crystalline form determined by SAXS, and we interpret this peak as the periodicity of smectically packed ChHP layers in the P4VP microdomain. Upon heating to 120°C, the second order small molecule peak
disappears and the first order small molecule peak shifts to a lower q value, suggesting that the ChHP molecules are no longer closely packed inside the P4VP microdomain. This observation is consistent with the insitu FTIR result that the hydrogen bonding begins to destabilize and ChHP also begins to melt at around 120°C. Furthermore, there is a gradual decrease in the periodicity of the block copolymer with further increase in temperature, indicating that the P4VP chains are no longer stretched into a comb block but is gradually relaxing into a coil block. At 130°C, the ChHP peaks completely disappear, and at this temperature the domain size begins to decrease sharply. At 150°C the periodicity of the block copolymer has decreased from 37 nm to 27.2 nm. Upon cooling the supramolecule from 150°C, the periodicity of the block copolymer microdomains increases slightly, suggesting that the P4VP block again regains some rigidity from reformation of hydrogen bonding between P4VP and ChHP. When cooling the sample to 110°C, a q = 0.14 Å⁻¹ scattering peak appears. This peak corresponds to a periodicity of 4.5 nm, which is approximately equal to the periodicity of the crystallized ChHP. This result, combined with the observation that the block polymer periodicity only slightly increased, indicates that most of the ChHP small molecules crystallized into a separate phase rather than reincorporating into the P4VP(ChHP) microdomain.

The same family of supramolecules with different compositions was also studied. Similar trends of decrease in BCP periodicity during heating and appearance of the ChHP crystallization peak during cooling are observed for PS(19 kdal)-b-P4VP(5.2 kdal)₁(ChHP)₁ supramolecule (Figure 5.3, middle panel) and PS(40 kdal)-b-P4VP(5.6 kdal)₁(ChHP)₁ supramolecule (Figure 5.3, right panel). The in-situ SAXS studies suggest that the supramolecule undergoes thermoresponsive, non-reversible changes such as decrease in periodicity of BCP and ChHP packing. These drastic changes lead to a range of morphological transitions, such as cylinder-lamellae-to-inverse cylinder and lamellae-to-cylinder, in the supramolecule.
Figure 5.3. *In situ* SAXS plots of PS(24k)-b-P4VP(9.5k)(ChHP) (left panel), PS(19k)-b-P4VP(5.2k)(ChHP) (middle panel), and PS(40k)-b-P4VP(5.6k)(ChHP) (right panel) supramolecules heated from 30°C (bottom) to 150°C and subsequently cooled back to 30°C (top). All three supramolecules undergo a decrease in microdomain size upon heating, a small increase in microdomain size upon cooling, and a shift in the ChHP scattering peak to higher $q$.

Transmission electron microscopy (TEM) was used to characterize the morphology of the supramolecules (Figure 5.4). For the PS(24 kdal)-b-P4VP(9.5 kdal)(ChHP) (Figure 5.4a), the unannealed sample forms a morphology with hexagonally packed PS cylinders embedded in the P4VP(ChHP) matrix, consistent with the volume fraction of the P4VP(ChHP) block, $f_{P4VP(ChHP)} = 0.721$. After being annealed at 130°C, there is a clear morphological transition from cylinder to lamellar. When the annealing temperature is increased further to 150°C, inverse cylinder was seen, in which the majority block is now the unstained polystyrene block, appearing as the lighter phase.

TEM studies were carried out for the two other supramolecules, PS(19 kdal)-b-P4VP(5.2 kdal)(ChHP) ($f_{P4VP(ChHP)} = 0.64$) (Figure 5.4b) and PS(40 kdal)-b-P4VP(5.6 kdal)(ChHP) ($f_{P4VP(ChHP)} = 0.48$) (Figure 5.4c) to determine whether such temperature driven OOTs are universal for this supramolecular system. For the PS(19 kdal)-b-P4VP(5.2 kdal)(ChHP), TEM (Figure 5.4b) shows that the unannealed sample has a mixture of P4VP(ChHP) majority cylindrical morphology and lamellar morphology. This
is consistent with the comb block volume fraction for this supramolecule, which lies at the boundary of lamellar and cylindrical morphology. At higher annealing temperatures, the morphology transitions to a lamellar morphology at 130°C and then an inverse cylindrical morphology at 150°C. Similar thermally induced morphological transitions were observed for the PS\((40k)\)-b-P4VP\((5.6k)\)\(_1\)(ChHP)\(_1\), i.e. from lamellar (<130°C) to inverse cylindrical microdomains (150°C) (Figure 5.4c). TEM suggests that the morphological transitions during thermal annealing are universal for this supramolecular system. The morphologies after cooling are stable at room temperature and precisely tunable by annealing temperature.

Figure 5.4. TEM images of a) PS\((24k)\)-b-P4VP\((9.5k)\)\(_1\)(ChHP)\(_1\), b) PS\((19k)\)-b-P4VP\((5.2k)\)\(_1\)(ChHP)\(_1\), and c) PS\((40k)\)-b-P4VP\((5.6k)\)\(_1\)(ChHP)\(_1\) in their as cast state and after thermal annealing at 110°C, 130°C and 150°C in vacuum for 12 hours. The samples are stained with I\(_2\) to enhance the contrast between PS (bright) and P4VP(ChHP) (dark) microdomains. Transitions from a P4VP(ChHP) comb block (dark) majority microphase to a comb block minority microphase are clearly seen in all three supramolecules. Scale bars are 100nm for all images.

The macrophase separation of the ChHP molecules is visible from TEM images taken at lower magnification (Figure 5.5). For all three supramolecules, the unannealed
sample has a uniform composition. At higher annealing temperatures, a second brighter phase begins to appear, and the sizes of the second phase increase as the annealing temperature increases. A zoomed-in view of the interface between the bright and dark phases show that the dark phase is the microphase separated PS-\(b\)-P4VP(ChHP) supramolecule, while the bright phase should be ChHP-rich. The interface between PS-\(b\)-P4VP(ChHP) and macrophase separated ChHP is very sharply defined, and that both PS and P4VP(ChHP) microdomains reside at the interface (Figure 5.6). This suggests that the “free” ChHP molecules that have diffused out of the P4VP microdomain during thermal annealing do not diffuse back to either the PS or P4VP(ChHP) microdomains and the free ChHP forms into a macrophase separated crystalline phase.

**Figure 5.5.** Low magnification TEM images of a PS(24k)-\(b\)-P4VP(9.5k)\(_1\)(ChHP)\(_1\) a) as cast, b) annealed at 110°C for 12 hours, c) annealed at 130°C for 12 hours, and d)
annealed at 150°C for 12 hours. The appearance of phase separated ChHP are observed in samples annealed at temperatures higher than 110°C as brighter regions. Scale bars are 1μm for all images.

Figure 5.6. TEM images (left) showing the sharp interface between the a) lamellar and b) cylindrical microdomains in PS-b-P4VP(ChHP) phase and the crystalline ChHP phase. The schematic (right) shows a structural view of the interface.

These observations, coupled with the in-situ SAXS and TEM data, provide a more detailed picture for the observed morphological transitions in this supramolecular system (Figure 5.7). At room temperature, the solvent-cast supramolecule adopts a morphology that is expected from the calculated volume fraction of the supramolecule assuming complete incorporation of ChHP into the P4VP microdomain. Upon heating of the supramolecule, several morphological transitions take place on the length scales of both the BCP and ChHP. The comb structure of P4VP(ChHP) disintegrates above 120°C as ChHP molecules diffuse out of the P4VP microdomain and the supramolecule periodicity decreases (Figure 5.7b). The overall supramolecular morphology undergoes multiple OOTs spanning a wide range of \(f_{\text{P4VP(ChHP)}}\), from P4VP(ChHP)-majority cylinders to P4VP(ChHP)-minority inverse cylinders (Figure 5.7c). Upon cooling below 130°C, only a small fraction of ChHP molecules diffuse back into the P4VP microdomain (Figure
5.7d), while the remaining ChHP molecules crystallize in separate, sharply defined macrophase that help preserve the high temperature supramolecule morphologies (Figure 5.7e). The sharp interface between the two macrophases further ensures the uniformity of obtained nanostructures as a function of temperature.

![Figure 5.7](image.png)

**Figure 5.7.** Schematic showing the mechanism of the observed phase transitions of PS-b-P4VP(ChHP) during heating and cooling. (a) Below 120°C, all ChHP molecules are confined in P4VP microdomain. (b) as temperature reaches 120°C, unbonded ChHP molecules start to diffuse out of P4VP microdomain. (c) Further diffusion of ChHP molecules out of P4VP microdomain cause OOTs to P4VP(ChHP) minority phase. (d) Cooling below 130°C causes some ChHP to reform hydrogen bond with P4VP. (e) Further cooling below T_m of ChHP causes crystallization of unbounded ChHP in a separate phase.

There are several possible mechanisms to explain the observed non-reversible OOTs. The hydrogen bonding between 4VP and ChHP is the main driving force to sequester ChHP within P4VP(ChHP) microdomains. Upon heating, the H-bonds start to break. In-situ FTIR measurements were carried out using a P4VP(46.7 kdal/(ChHP) supramolecule during heating from room temperature to 150°C (Figure 5.8). At room temperature, the FTIR spectrum of the supramolecule has absorption peaks at 1011 cm^{-1} and 1602 cm^{-1}, characteristic of a stretched pyridine ring and indicating the formation of hydrogen bonds between 4VP and ChHP. As the temperature increases, the intensity of the 1011 cm^{-1} peak decreases slightly, accompanied by the appearance of a peak at 993 cm^{-1} around 120°C, corresponding to free 4VP. In addition, the 1602 cm^{-1} peak
shifts to 1597 cm\(^{-1}\). This indicates the destabilization of the phenol-pyridine hydrogen bonding at T>120°C. Upon cooling, the 993 cm\(^{-1}\) peak disappears and the 1011 cm\(^{-1}\) peak reappears, while the 1597 cm\(^{-1}\) peak shifts back to 1602 cm\(^{-1}\), suggesting that the hydrogen bonded complex between P4VP and ChHP is thermally reversible, similar to that seen in the supramolecular systems based on alkylphenol\(^{52}\). Thus, hydrogen bond breaking cannot be the sole explanation for non-reversible OOTs observed in this supramolecular system.

**Figure 5.8.** In situ FTIR spectra of P4VP\(_1\)(ChHP)\(_1\) heated from 30°C (bottom) to 150°C and subsequently cooled back to 30°C (top). Absorption peaks corresponding to unstretched 4VP units (993 cm\(^{-1}\) and 1597 cm\(^{-1}\)) appear above 120°C during both heating and cooling cycles, signifying destabilization of hydrogen bonding at higher temperatures.

A change in \(\chi\) is known to induce OOTs in BCP systems because the phase boundaries in a BCP system are curved with respect to \(\chi\) and volume fraction \(f\) of each block \(^{54}\). It is reasonable to believe the Flory-Huggins interaction parameter \(\chi\) between the PS and P4VP(ChHP) blocks decreases with increasing temperature. However, such morphological transitions were typically observed over a narrow range of volume
fraction of one component and are typically thermally reversible. Therefore, this cannot explain the non-reversible OOTs that occur over a wide range of volume fractions observed here.

Rather, the observed OOTs may be due to a combination of three factors, i.e. increased miscibility between PS and ChHP at high temperatures, slow diffusion of ChHP back into the P4VP(ChHP) microdomain during cooling due to steric repulsion between ChHP small molecules, and reduced mobility of ChHP due to crystallization upon cooling. The increased PS/ChHP miscibility at high temperatures would result in the diffusion of ChHP from the P4VP to the PS microdomain during thermal annealing, thereby resulting in a significant decrease in $f_{P4VP(ChHP)}$ and inducing OOTs over a wide morphology range. This is similar to the mechanism proposed by Ikkala et al in their investigation of the supramolecule comprising of PS-$b$-P4VP and 3-pentadecylphenol (PDP)\textsuperscript{52}. The miscibility of ChHP in PS is evident from differential scanning calorimetry (DSC), showing a depression in the $T_g$ of PS from 104°C to 91°C (Appendix 4.5). The extent of PS/ChHP miscibility is further confirmed via polarized optical microscopy (POM) studies (Appendix 4.6). PS and ChHP have low miscibility (~10wt% ChHP in PS) at room temperature. At higher ChHP loadings (30-50wt%), ChHP molecules crystallize to form a separate birefringent macrophase. As the temperature increases to above 135°C, the birefringent crystalline phase disappears instantaneously, suggesting high solubility of ChHP in PS. Upon cooling of the mixture to below 135°C, the birefringent phase reappears, suggesting that PS and ChHP are no longer miscible and ChHP crystallizes. From these observations, it is evident that at high annealing temperatures, there is a strong driving force for ChHP to diffuse into the PS microdomain. This phase behavior is in contrast with the supramolecular system based on oligothiophene (4T), PS-$b$-P4VP(4T) system reported by Rancatore et al\textsuperscript{49}. 4T has an even higher crystallization temperature than ChHP, but has a linear molecular shape that is more conducive to close packing and is immiscible with PS, so that crystallization occurs within the P4VP microdomain rather than within a separate macrophase. In addition, another key difference between the PS-$b$-P4VP(ChHP) system and the PS-$b$-P4VP(PDP) system is that upon cooling the PDP becomes immiscible with the PS microdomain and the small molecules reincorporate into the P4VP microdomain, resulting in a thermoreversibility in the OOTs. For the PS-$b$-P4VP(ChHP) supramolecule, however, during cooling there is a competition between diffusion of ChHP back into the P4VP microdomain and crystallization of ChHP into a separate macrophase. Clearly, crystallization of ChHP dominates, although a small fraction of ChHP does diffuse back into the P4VP microdomain, resulting in a small increase in the domain spacing during cooling.

The dominance of ChHP crystallization over reversible diffusion is possibly due to two factors. One is that ChHP has a higher crystallization temperature (~135°C) than PDP (~55°C)\textsuperscript{45, 52}, such that upon cooling, ChHP crystallizes while still being highly miscible within PS. On the other hand, PDP’s crystallization temperature may be below
the PDP/PS miscibility gap (Figure 5.9), thus PDP small molecules tend to diffuse back into the P4VP microdomain upon cooling. Additionally, we hypothesize that there are additional driving forces, specific to the ChHP molecule, that prevent the reincorporation of ChHP into the P4VP microdomain. The ChHP molecule contains a bulky cholesteric group, which may affect its molecular packing and introduces intermolecular steric repulsion that may further slow the diffusion of ChHP back into the P4VP microdomain. This slowed diffusion can be seen in PS-b-P4VP(ChHP) samples that are cooled on a longer timescale, with temperatures decreasing from 150 °C to 100°C over 4 hours (Appendix 4.7). The resulting morphologies are similar to the samples cooled within 1 hour, suggesting no significant changes in the diffusion of ChHP back into P4VP due to the slower cooling rate.

**Figure 5.9.** Plot demonstrating the crystallization temperature of ChHP and PDP relative to the miscibility in PS microdomain.
§ 5.3 Liquid crystalline supramolecular nanocomposites

The previous section demonstrates that liquid crystalline supramolecules can be created by hydrogen bonding the cholesteric ChHP small molecules to PS-\(b\)-P4VP, and the liquid crystalline supramolecules undergo non-reversible OOTs during thermal annealing due to the diffusion of ChHP small molecules. This supramolecule provides a materials platform to investigate the entropic effect of NP loading on the NP spatial distribution within the supramolecule. Theoretically, the high rigidity of the liquid crystalline P4VP(ChHP) block would incur high entropic penalty in accommodating NPs, thus leading to NP expulsion to defect sites or morphological distortion at lower NP loadings and/or smaller NP sizes in comparison to PS-\(b\)-P4VP(PDP) supramolecules. In addition, it would be interesting to investigate whether the supramolecule OOTs are transferable to supramolecular nanocomposites, which could lead to the generation of stimuli responsive NP assemblies.

To investigate the effect of NP incorporation in PS-\(b\)-P4VP(ChHP) supramolecules, a PS(40 kdal)-\(b\)-P4VP(5.6 kdal)\(_1\)(ChHP)\(_1\) supramolecule and a PS(24 kdal)-\(b\)-P4VP(9.5 kdal)\(_1\)(ChHP)\(_1\) supramolecule are loaded with different amounts of \(\sim 3\) nm CdSe NPs and \(\sim 8\) nm PbS NPs capped with oleic acid (Appendix 4.8). The TEM images of the resulting supramolecular nanocomposites are shown in Figure 5.10. For PS(40 kdal)-\(b\)-P4VP(5.6 kdal)\(_1\)(ChHP)\(_1\) supramolecules loaded with 2 vol% (Figure 5.10a) and 5 vol% (Figure 5.10b) \(\sim 3\) nm CdSe NPs, lamellar morphologies are formed with the NPs distributed uniformly throughout the P4VP(ChHP) microdomain. Lamellar morphologies are consistent with \(f_{P4VP(ChHP)} = 0.48\) for this supramolecule. Upon loading with 2 vol% of \(\sim 8\) nm PbS NPs, lamellar structures are still observed, although the NPs appear to be more closely sequestered to the center of the P4VP(ChHP) microdomain, forming thinner NP arrays (Figure 5.10c). Increasing the NP loading to 5 vol% resulted in the disruption of the lamellar morphology, as some NPs appear to be no longer sequestered to the P4VP(ChHP) lamellae (Figure 5.10d). In PS(24 kdal)-\(b\)-P4VP(9.5 kdal)\(_1\)(ChHP)\(_1\) supramolecules loaded with 2 vol% (Figure 5.10e) and 5 vol% (Figure 5.10f) of \(\sim 3\) nm CdSe NPs, NPs appear to be randomly distributed within the supramolecular framework.

These observations do not fully support the hypothesized entropic effect of increased chain rigidity. One possible explanation is that the diffusion of ChHP small molecules out of the P4VP(ChHP) microdomain during thermal annealing may decrease the chain rigidity, thus leading to NP spatial distributions similar to that observed for PS-\(b\)-P4VP(PDP) supramolecules. These observations highlight the importance of strengthening the BCP/small molecule bond for future studies of increasing chain rigidity.
Figure 5.10. TEM images of PS(40 kdal)-b-P4VP(5.6 kdal)(ChHP) supramolecules loaded with a) 2 vol% and b) 5 vol% ~3 nm CdSe NPs; c) 2 vol% and d) 5 vol% of ~8 nm PbS NPs; and PS(24 kdal)-b-P4VP(9.5 kdal)(ChHP) supramolecules loaded with e) 2 vol% and f) 5 vol% ~3 nm CdSe NPs. Scale bars are 100 nm for all images.
The thermal responsive properties of PS-\textit{b}-P4VP(ChHP)-based liquid crystalline supramolecular nanocomposites are also investigated to determine whether these materials also undergo thermally induced OOTs similar to pure supramolecules. Nanocomposites comprised of PS(24\textit{k dal})-\textit{b}-P4VP(9.5\textit{k dal})(ChHP)\textsubscript{1} supramolecules and 2 vol\% of ~3 nm CdSe NPs are thermally annealed at 110 °C, 130 °C, and 150 °C under vacuum for 12 hours and their resulting morphologies are studied using TEM (Figure 5.11). At 110 °C, the NPs are loosely organized into hexagonal grid patterns (Figure 5.11a), which conform to the P4VP(ChHP) majority hexagonaly packed cylindrical morphology as revealed by I\textsubscript{2} staining (Figure 5.11b). This morphology is in agreement with the morphology of pure PS(24\textit{k dal})-\textit{b}-P4VP(9.5\textit{k dal})(ChHP)\textsubscript{1} supramolecule thermally annealed at 110 °C. Upon annealing to 130 °C, an OOT is apparent in which the NPs appear to arrange into lamellae nanostructures (Figure 5.11c). I\textsubscript{2} staining of the sample further reveals that the underlying supramolecule has also undergone an OOT from P4VP(ChHP) majority cylindrical morphology to a mixture of lamellar and P4VP(ChHP) minority morphology (Figure 5.11d). Finally, upon annealing at 150 °C for 12 hours, the NPs are clearly observed to assemble into hexagonally packed arrays (Figure 5.11e), which is consistent with the P4VP(ChHP) minority cylindrical morphology as revealed by I\textsubscript{2} staining (Figure 5.11f).

Similar observations are made in PS(24\textit{k dal})-\textit{b}-P4VP(9.5\textit{k dal})(ChHP)\textsubscript{1} supramolecules containing 5 vol\% of ~3 nm CdSe NPs (Figure 5.12). Samples annealed at 110 °C showed a nanostructure in which the CdSe NPs are loosely hexagonal grid pattern as template by the underlying supramolecule (Figure 5.12a-b), which annealing at 130 °C (Figure 5.12c-d) and 150 °C (Figure 5.12e-f) for 12 hours resulted in OOTs to lamellar and P4VP(ChHP) minority cylindrical morphologies, respectively. The observed NP nanostructures and morphologies for both supramolecular nanocomposite samples are consistent with pure PS(24\textit{k dal})-\textit{b}-P4VP(9.5\textit{k dal})(ChHP)\textsubscript{1} liquid crystalline supramolecule samples, thus demonstrating the ability to harness the thermal responsive properties of liquid crystalline supramolecules to template the assembly of NPs (Figure 5.13). The macroscopic properties of the NP assemblies may potentially be correlated with their nanostructures, thus leading to stimuli responsive nanocomposite materials with thermally tunable properties.
Figure 5.11. TEM images of PS(24 kdal)-b-P4VP(9.5 kdal)(ChHP)$_1$ supramolecules containing 2 vol% of ~3 nm CdSe NPs at 110 °C a) without and b) with I$_2$ staining; at 130 °C c) without and d) with I$_2$ staining; and 150 °C e) without and f) with I$_2$ staining. Scale bars are 100 nm for all images.
Figure 5.12. TEM images of PS(24 kdal)-b-P4VP(9.5 kdal)(ChHP)₁ supramolecules containing 5 vol% of ~3 nm CdSe NPs at 110 °C a) without and b) with I₂ staining; at 130 °C c) without and d) with I₂ staining; and 150 °C e) without and f) with I₂ staining. Scale bars are 100 nm for all images.
Figure 5.13. Schematic of the observed OOTs from P4VP(ChHP) majority cylinder morphology to P4VP(ChHP) minority morphology in PS$(24$ $kdal)$-$b$-P4VP$(9.5$ $kdal)_1$(ChHP)$_1$ supramolecule/CdSe NP nanocomposites as a function of increasing annealing temperature. The PS microdomains are colored red and P4VP(ChHP) microdomains are colored blue.

§ 5.4 Conclusion

In this chapter, we investigated the thermoresponsive phase behavior of a block copolymer-based supramolecule containing a liquid crystal small molecule, PS-$b$-P4VP(ChHP), using DSC, POM, TEM, SAXS, and FTIR. Upon thermal annealing, the supramolecule underwent a series of non-reversible OOTs from a P4VP(ChHP) block majority phase to a P4VP(ChHP) block minority phase, which is explained by the diffusion of ChHP out of the P4VP(ChHP) block during heating, and subsequent crystallization of free ChHP into a separate phase during cooling due to the high $T_m$ of ChHP and the steric repulsion between bonded and free ChHP. The OOTs are non-reversible upon cooling, therefore the morphologies generated during thermal annealing are stable at room temperature and tunable by adjusting the thermal annealing temperature. This study highlights the important role of small molecule phase behavior, miscibility and intermolecular interactions on the overall thermal phase behavior of BCP-based supramolecules containing these small molecules, and provides a robust platform to generate multiple morphologies from a single starting material. In addition, the supramolecule may be used to produce arbitrary patterns via local heating. These unique properties may find potential applications that require locally defined periodic nanostructures.

Furthermore, the liquid crystalline supramolecules are demonstrated to template the assembly of NPs, and the resulting nanocomposite system also undergoes thermally
induced OOTs. These properties can potentially be harnessed to create stimuli responsive composite materials, as a thermally induced structural change can lead to changes in the mechanical, electronic or optical properties of the material. Although the entropic effect in liquid crystalline supramolecules and supramolecular nanocomposites cannot be thoroughly studied due to small molecule diffusion upon thermal annealing, these studies shed light on the importance of BCP/small molecule and small molecule/small molecule interactions on the construction of thermally stable liquid crystalline supramolecules to enable future studies on the entropic effect in these materials systems.

§ 5.5 Methods

Materials

P4VP (46.7 Da) and PS-\textit{b}-P4VP block copolymers were purchased from Polymer Source, Inc. Chloroform was purchased from Fisher and used without any purification. Synthetic procedure of ChHP is described in detail in Appendix 4.1.

Supramolecule preparation

P4VP and PS-\textit{b}-P4VP were first dissolved in chloroform to form 1–2\% (wt/v) stock solutions. The desired amount of ChHP was dissolved in chloroform. The PS-\textit{b}-P4VP solution was then added drop-wise to the ChHP solution, followed by stirring overnight. The resulting PS-\textit{b}-P4VP and ChHP blend was casted and dried in a Teflon beaker at room temperature in a chloroform atmosphere, allowing the solvent to slowly evaporate over 48 hours. The blend was then annealed at 60°C under vacuum for overnight to completely remove the solvent. The molar ratio of ChHP to 4VP units is 1 for all samples. Supramolecular nanocomposite samples are fabricated by mixing supramolecule solutions and the desired amount of NP solutions and drop casting the samples into Teflon beakers.

\textit{Fourier-transform infrared spectroscopy}

Samples were cast between two NaCl pellets and the absorption spectra were collected using a \textit{NICOLET 6700 FT-IR Spectrometer}. For in-situ FT-IR, samples on NaCl pellets were heated from room temperature to 150°C at heating rate of 20 °C/min under nitrogen gas. Each spectrum was collected 10 minutes after reaching the targeted temperature.

\textit{Differential scanning calorimetry}

Differential scanning calorimetry measurements were performed on a TA instrument DSC Q200. The samples (~2 mg) were heated from 0 °C to 200 °C at a heating rate of 10 °C/min under nitrogen gas. Three heating and cooling cycles are performed to
eliminate the thermal history of the samples. The transitions of ChHP were collected from the third heating and cooling cycle.

**Polarized Optical Microscope**

Birefringence in the supramolecule samples was observed using Olympus BX 51 with crossed polarizers in reflection mode. Samples were cast from chloroform solution onto a silicon wafer and covered with cover glass. Samples were put on the heating stage (Linkam TP 94) with a Linkam LTS 350 temperature controller. Samples were heated from room temperature to 150°C at heating rate of 30 °C/min under nitrogen gas and cooled from 150°C to room temperature at cooling rate of 6 °C/min. Each image was taken 5 minutes after reaching the targeted temperature.

**Small-Angle X-ray Scattering**

SAXS studies were carried out at the Advanced Light Source beamline 7.3.3. X-rays with a wavelength of 1.240 Å (10 keV) were used. Spectra were collected on an ADSC Quantum 4u CCD detector with an area of 188 mm × 188 mm (2,304 pixels × 2,304 pixels) or a Pilatus 1M detector with an area of 169 mm × 179 mm (981 px × 1043 px). The 1D SAXS profiles were obtained by circularly averaging the 2D data. Prior to SAXS experiment, samples were mounted in standard differential scanning calorimetry pans, which were used as a heating stage during scanning. All SAXS profiles were measured after keeping the samples at each temperature for 10 min.

**Transmission Electron Microscope**

For TEM observations, samples mounted in the DSC pan were annealed at 130°C and 150°C for 12 hours under vacuum and then slowly cooled to room temperature. Samples were embedded in resin (Araldite 502, Electron Microscopy Sciences) and cured at 60°C for overnight. Thin sections about 50 nm in thickness were microtomed using an RMC MT-X Ultramicrotome (Boeckler Instruments) and picked up on carbon coated Cu grids on top of water. The thin sections were exposed to iodine vapor for 1h to stain the P4VP domain selectively and imaged using a FEI Tecnai 12 TEM operating at 120kV accelerating voltage or a JEOL 2100 TEM operating at 200kV.
The work described in this dissertation demonstrated that entropic modulation is a powerful tool to control the self-assembly of supramolecular nanocomposites. By shifting the delicate balance between nanoparticle translational entropy and supramolecule chain conformational entropy, a wide variety of nanostructures can be generated in bulk, thin film, and cylindrically confined supramolecular nanocomposites that are not accessible in simple block copolymer/nanoparticle composites, thus greatly expanding the structural diversity of this class of nanocomposite materials.

Furthermore, it was discovered that under high degrees of entropic perturbation, the self-assembly mechanism can no longer be considered supramolecule directed nanoparticle assembly. Rather, the nanoparticles play a significant structure directing role, leading to co-assembled nanostructures. This co-assembly phenomenon is seldom explored and holds great promise in expanding the library of accessible nanostructures in block copolymer/nanoparticle and supramolecule/nanoparticle composite systems. The importance of nanostructure control was clearly demonstrated by the strong structure/property correlation within the nanocomposite material, as chirally arranged nanoparticles were shown to exhibit strong chiral optical properties due to the interparticle plasmonic coupling.

These research findings also present exciting opportunities to develop further understanding and structure/property control over supramolecular nanocomposites. It is important to develop a theoretical framework to model and predict thermodynamically stable nanostructures in supramolecule nanocomposites as a function of nanoparticle shape and size, supramolecule composition, and different confining boundary conditions. A thorough theoretical understanding of the self-assembly and co-assembly mechanisms would allow for the rational design of nanocomposite materials with precisely targeted nanostructures and functionalities.

In the case of chiral nanostructures obtained under cylindrical confinement, control over the handedness of the chiral nanomaterials is requisite to translate the nanoscopic chiral optical properties into macroscopic properties. One potential means to achieve chiral selectivity is by introducing chiral small molecules or chiral polymers into the supramolecular nanocomposite. In addition, beyond 2-D confinement, 3-D confinement in droplets presents ample research opportunities to further expand the morphological diversity in supramolecular nanocomposite materials.

Investigation on the liquid crystalline supramolecular nanocomposites revealed that stronger bonds between block copolymer and small molecule side chains may be necessary to
incorporate highly crystalline side chains to modulate the comb block rigidity. To this end, stronger bonding interactions, such as ionic bonding, should be explored to improve the versatility of the supramolecular construct and enable future studies on entropic effects in highly rigid supramolecules and supramolecular nanocomposites.

These studies, combined with comprehensive exploration and understanding of the structure/property correlations, as well as the development of scaled up material processing techniques that can be readily implemented into existing manufacturing infrastructure, will further increase the viability of supramolecule nanocomposites as next generation advanced functional materials.
Appendix

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Appendix 1. FTIR spectrum of PS(33 kdal)-b-P4VP(8 kdal)(PDP)$_2$ supramolecule (blue) and PS(33 kdal)-b-P4VP(8 kdal) block copolymer (yellow), demonstrating absorption peak shift due to 4VP/PDP hydrogen bond formation. In the left graph, the absorption peak at 993 cm$^{-1}$, characteristic of the C—N bond in the unstretched pyridine ring, is shifted to 1011 cm$^{-1}$ in the supramolecule, due to stretching of the C—N bond upon hydrogen bonding. In the right graph, the absorption peak at 1600 cm$^{-1}$, characteristic of the unstretched pyridine ring resonance mode, shifts to 1607 cm$^{-1}$ in the supramolecule.
Appendix 1.2. a) TEM image and b) size distribution of ~ 3 nm Au NPs.

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Appendix 3.1. SEM images of AAO membranes with a) 35 nm, b) 55 nm, and c) 100 nm diameter pores. Scale bars are 400 nm for all images.

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Appendix 3.4. a) TEM image of ~4 nm Ag NPs. Nanocomposites of PS(19 $kdal$)-b-P4VP(5.2 $kdal$)(PDP)$_{1.7}$ supramolecules loaded with b) 3 v%, c) 6v% and d) 9 v% Ag NPs exhibit cylindrical, ring-like, and helical morphologies, respectively, demonstrating the versatility of cylindrically confined supramolecular nanocomposites for NPs with different chemistries.
Appendix 3.5. TEM images of cylindrically confined supramolecular nanocomposites comprising a) PS(19 kdal)-b-P4VP(5.2 kdal) BCPs, b) PS(19 kdal)-b-P4VP(5.2 kdal)(PDP)_{0.5} supramolecules, c) PS(19 kdal)-b-P4VP(5.2 kdal)(PDP)_{1} supramolecules, and d) PS(19 kdal)-b-P4VP(5.2 kdal)(PDP)_{1.5} supramolecules, with 6 v% Au NP (~4 nm) loading each.
Appendix 3.6. TEM images of P4VP(36.3 kdal)(PDP)$_1$ homopolymer-based supramolecules with a) 3 v% and b) 6 v% of ~4 nm Au NP loading, exhibiting disordered morphologies under cylindrical confinement within 35 nm AAO membrane pores.
Appendix 3.7. The frequency of nanostructures observed in PS(19 kdal)-b-P4VP(5.2 kdal)(PDP)_{1.7} supramolecule/Au NP nanocomposites under cylindrical confinement within AAO membrane pores is plotted below as a function of NP loading. The statistics are obtained from analysis of 100 TEM images.
Appendix 4: Supporting Information for Chapter 5

Appendix 4.1. Synthesis of ChHP small molecules

All chemicals were purchased from Aldrich and used without further purification unless otherwise noted. All reactions were performed under dry N₂ unless otherwise noted. All extracts were dried over MgSO₄ and solvents were removed by rotary evaporation with aspirator pressure. Flash chromatography was performed using Merck Kieselgel 60 (230-400 mesh) silica. DMF was purchased from Fisher and vigorously purged with nitrogen for 1 h. The solvent was further purified by passing it under nitrogen pressure through two packed columns (Glass Contour) of activated molecular sieves. ¹H and ¹³C NMR spectra were recorded with a Bruker AV-600 instrument using CDCl₃ as the solvent. High Resolution Mass Spectometry (HRMS) using Fast Atom Bombardment (FAB) was done with a Micromass ZAB2-EZ double focusing mass spectrometer (BE geometry). Elemental analyses were performed at the UC Berkeley Microanalysis Laboratory.

A flask was charged with 3.45 g (7.1 mmol) cholesteryl hemisuccinate, 7.8 g (71 mmol) resorcinol, 43 mg (5%) DMAP, and 60 mL DMF. The mixture was cooled to 0 °C and 1.36 g (7.1) EDC was added. The mixture was allowed to warm to room temperature and was stirred for 6 h. The mixture was then poured into 300 mL water and the product was then extracted 3x with 100 mL DCM. The organic fractions were combined and dried with MgSO₄. The solvent was evaporated and the crude product was purified via flash chromatography, eluting with 30% ethyl acetate in hexanes to yield 2.75 g (67%) of a white solid. ¹H NMR (600 MHz): δ 0.67 (s, 3H), 0.85-0.87 (m, 6H), 0.91-1.63 (m, 28H), 1.83-1.87 (m, 3H), 1.95-2.01 (m, 2H), 2.32-2.35 (m, 2H), 2.71 (t, J = 6.6 Hz, 2H), 2.86 (t, J = 6.6 Hz, 2H) 4.63-4.68 (m, 1H), 5.37 (d, J = 4.8 Hz, 1H), 6.59-6.60 (m, 1H), 6.65-6.70 (m, 2H), 7.20-7.22 (m, 1H). ¹³C NMR (150 MHz): δ 11.84, 18.72, 19.27, 21.02, 22.56, 22.81, 23.85, 24.27, 27.69, 27.98, 28.22, 29.35, 29.44, 31.82, 31.87, 35.78, 36.18, 36.53, 36.90, 38.00, 39.51, 39.71, 42.29, 49.97, 56.15, 56.66, 74.87, 76.84, 77.06, 77.27, 109.06, 113.09, 113.09, 113.31, 122.81, 129.95, 139.38, 151.31, 157.10, 171.44, 172.01. HRMS (FAB) m/z calc for (C₃₇H₅₄O₅, M-1) 577.3898; found 577.3884. Anal. Calcd for C₃₇H₅₄O₅: C, 76.78; H, 9.40. Found C, 76.73; H, 9.56.
Appendix 4.2. DSC was performed to characterize the thermal phase transitions of ChHP. The temperature was ramped from 0°C to 200°C at a rate of 10°C/min and subsequently cooled to 0°C for three cycles to eliminate the thermal history of the ChHP sample. The DSC scan of the third heating and cooling cycles is shown below. The heating scan of ChHP shows two prominent endotherms at 122.1°C and 137.6°C, corresponding to the melting point and clearing point of ChHP, respectively. The enthalpy of crystallization for ChHP is calculated to be 11.6 kJ/mol.
Appendix 4.3. POM was conducted on the ChHP during heating from room temperature to 150°C under a heating rate of 10°C/min to confirm the phase transitions in ChHP. From 30°C to 125°C, the ChHP sample shows distinct birefringent crystallites. At about 140°C, the crystallites disappear and the POM image shows birefringent oily streaks, indicating a phase transition from crystalline to liquid crystalline. Upon heating to 150°C, all birefringence disappears as the ChHP small molecules transition from liquid crystalline phase to isotropic phase. Upon cooling, some crystallinity is recovered, although the crystallites are smaller in size.
Appendix 4.4. Small angle X-ray scattering (SAXS) was performed on ChHP insitu during heating at a rate of 10°C/min from 30°C to 150°C to analyze its crystal structure. The ChHP sample has a characteristic scattering peak at \( q = 0.14 \text{ Å}^{-1} \), corresponding to a crystal structure with a periodicity of 4.5 nm. Upon heating to above 120°C, the periodicity of the crystal structure begins to decrease, reaching 3.8 nm at 130°C. Above 140°C, the characteristic scattering peak disappears as the ChHP becomes isotropic. The transitions in characteristic peak spacings corroborate with the DSC and POM data, suggesting crystalline/liquid crystalline/isotropic phase transitions. As the sample is gradually cooled back to room temperature, the 4.5 nm peak reappears around 120°C, indicating recrystallization of the small molecules.
Appendix 4.5. Differential scanning calorimetry (DSC) was performed on a pure 22 kdal PS sample and a 30 wt% ChHP in 22k PS mixture to characterize the miscibility of ChHP in PS. The temperature was ramped from 0°C to 200°C at a rate of 10°C/min and subsequently cooled to 0°C for three cycles to eliminate the thermal history of the ChHP sample. The DSC scan of the third heating cycle is shown below. The scan of pure PS shows a $T_g$ of 104°C, while the $T_g$ of the PS/ChHP mixture decreases to 91°C, suggesting miscibility of ChHP in PS.
Appendix 4.6. Polarized optical microscopy (POM) was conducted on PS(22 kdal)/ChHP mixtures with a) 10wt%, b) 30wt% and c) 50wt% ChHP loading during heating from room temperature to 150°C under a heating rate of 10°C/min and subsequent cooling to room temperature to confirm miscibility of ChHP in PS. At 10wt% ChHP loading, no birefringence is detected at any temperature, suggesting miscibility of ChHP in PS at small loadings. For 30wt% and 50wt% ChHP loaded samples, birefringent ChHP crystals are visible from 30°C to 135°C. Between 135°C and 140°C, the crystallites promptly disappear, indicating that ChHP has become miscible and all anisotropy has been lost. During cooling to 130°C, birefringence reappears, suggesting crystallization of ChHP at temperatures below 130°C. Scale bars are 2mm.
Appendix 4.7. TEM of PS-\textit{b}-P4VP(ChHP) Supramolecule with Slow Cooling Rate. a) high magnification and b) low magnification images of PS(19k)-\textit{b}-P4VP(5.2k)\textsubscript{1}(ChHP)\textsubscript{1}, PS(24k)-\textit{b}-P4VP(9.5k)\textsubscript{1}(ChHP)\textsubscript{1}, and PS(40k)-\textit{b}-P4VP(5.6k)\textsubscript{1}(ChHP)\textsubscript{1} supramolecule samples annealed at 150°C for 12 hours and subsequently cooled slowly from 150°C to 100°C over 4 hours. The resulting morphologies are cylindrical with P4VP(ChHP) as the minority microdomain, similar to samples cooled over 1 hour.
Chapter 1


Chapter 2

Chapter 3


Chapter 4

Chapter 5