Directed Self-Assembly of Block Copolymers and Nanostructures

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Abstract

Self-assembly of block copolymers (BCPs) has attracted considerable attention for decades due to its potential in novel applications. The key to achieve their function critically relies on the control of nanostructure, shape and morphology of the BCP assemblies. The aim of this thesis is to develop a toolbox to manipulate the nanostructure of BCPs in a reliable and predictable manner, and provide mechanistic insights into their self-assembly behaviour. In this work, the strategies used to control the shape and morphology of BCP assemblies lie in three areas: (a) copolymer composition; (b) control of molecular weight distribution; and (c) interfacial properties.

In this thesis, a series of BCPs have been synthesised at different compositions and their self-assembled structures have been reported. The influence of the skewed molecular weight distribution and varied dispersity on BCP self-assembly was explored in both solution and thin film systems. The interface between BCP nanoparticles and the surrounding medium was investigated and a morphological evolution from onion-like spheres to axially stacked lamellae has been observed. It is envisaged that the modification of copolymer chemistry and a combination of these addressed strategies will facilitate the synthesis of BCPs assemblies with higher structural complexity.
Declaration

This is to certify that:

i. The thesis comprises only my original work towards the MPhil except where indicated in the preface;

ii. Due acknowledgement has been made in the text to all other material used;

iii. The thesis is less than 50,000 words in length, exclusive of tables, bibliographies and appendices.

Chao Chen
Preface

Chapter 1 and a part of Chapter 6 of this thesis have been published in the following article:


Chapter 5 of this thesis has been published in the following article:


In Chapter 4, Dr. Brett Fors and Dillon Gentekos performed the synthesis of a series of polystyrene-block-polyisoprene with skewed molecular weight distribution.

In Chapter 5, Dr. Zeyun Xiao provided insightful advice regarding the synthesis of hydroxy functionalised cetyltrimethylammonium bromide and its subsequent NMR spectroscopic analysis.
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Publications

The following publications and manuscripts arose during the course of this MPhil candidature:

First author


Co-author


Presentations

The following presentations were given during the course of this MPhil candidature:


2. **Chen, C.** “Phase Separated Block Copolymer Particles with Tuneable Morphologies”, *36th Australian Polymer Symposium (APS)*, oral presentation, November 2016, Lorne, VIC Australia.
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<td>1D</td>
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<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>AIBN</td>
<td>2,2’-azobis(2-methylpropionitrile)</td>
</tr>
<tr>
<td>Au-NP</td>
<td>gold nanoparticle</td>
</tr>
<tr>
<td>BCP</td>
<td>block copolymer</td>
</tr>
<tr>
<td>s-BuLi</td>
<td>sec-butyllithium</td>
</tr>
<tr>
<td>13C</td>
<td>carbon-13</td>
</tr>
<tr>
<td>CDCl₃</td>
<td>deuterated chloroform</td>
</tr>
<tr>
<td>CDSA</td>
<td>crystallisation-driven self-assembly</td>
</tr>
<tr>
<td>CPPA</td>
<td>4-cyano-4-(phenylcarbonothioylthio)pentanoic acid</td>
</tr>
<tr>
<td>CTA</td>
<td>chain transfer agent</td>
</tr>
<tr>
<td>CTAB</td>
<td>cetyltrimethylammonium bromide</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>DLS</td>
<td>dynamic light scattering</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>DP</td>
<td>degree of polymerisation</td>
</tr>
<tr>
<td>DTMPA</td>
<td>2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid</td>
</tr>
<tr>
<td>EDDA</td>
<td>2,2’-(ethylenedioxy)diethylamine</td>
</tr>
<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
</tr>
<tr>
<td>GQD</td>
<td>graphene quantum dot</td>
</tr>
<tr>
<td>H</td>
<td>hydrophobic</td>
</tr>
<tr>
<td>¹H</td>
<td>proton (hydrogen-1)</td>
</tr>
<tr>
<td>Hₐ</td>
<td>hydrogen acceptor</td>
</tr>
<tr>
<td>H-bonding</td>
<td>hydrogen-bonding</td>
</tr>
<tr>
<td>H₉D</td>
<td>hydrogen donor</td>
</tr>
<tr>
<td>HEX</td>
<td>hexylamine</td>
</tr>
<tr>
<td>HO-CTAB</td>
<td>hydroxyl incorporated cetyltrimethylammonium bromide</td>
</tr>
<tr>
<td>HPMA</td>
<td>2-hydroxypropyl methacrylate</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
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<tr>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>hPS</td>
<td>polystyrene homopolymer</td>
</tr>
<tr>
<td>LHS</td>
<td>left hand side</td>
</tr>
<tr>
<td>m</td>
<td>mass of a component</td>
</tr>
<tr>
<td>M</td>
<td>micelle segment</td>
</tr>
<tr>
<td>MCM</td>
<td>multicompartiment micelle</td>
</tr>
<tr>
<td>MeOH-(d_4)</td>
<td>deuterated methanol</td>
</tr>
<tr>
<td>(M_n)</td>
<td>number averaged molecular weight</td>
</tr>
<tr>
<td>(M_p)</td>
<td>peak maximum molecular weight</td>
</tr>
<tr>
<td>(M_w)</td>
<td>weight averaged molecular weight</td>
</tr>
<tr>
<td>MWD</td>
<td>molecular weight distribution</td>
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<tr>
<td>n</td>
<td>normal</td>
</tr>
<tr>
<td>N</td>
<td>non-interactive block</td>
</tr>
<tr>
<td>(N_i)</td>
<td>block length of (i) segment in a block copolymer</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>iNP</td>
<td>inorganic nanoparticle</td>
</tr>
<tr>
<td>OLA</td>
<td>oleylamine</td>
</tr>
<tr>
<td>P2VN</td>
<td>poly(2-vinyl naphthalene)</td>
</tr>
<tr>
<td>P2VP</td>
<td>poly(2-vinylpyridine)</td>
</tr>
<tr>
<td>P3HT</td>
<td>poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>P4VP</td>
<td>poly(4-vinylpyridine)</td>
</tr>
<tr>
<td>P</td>
<td>polar</td>
</tr>
<tr>
<td>PAA</td>
<td>poly(acrylic acid)</td>
</tr>
<tr>
<td>PAD</td>
<td>poly(((N)-amidine)dodecyl acrylamide)</td>
</tr>
<tr>
<td>PB</td>
<td>polybutadiene</td>
</tr>
<tr>
<td>PBLG</td>
<td>poly((\gamma)-benzyl-L-glutamate)</td>
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<tr>
<td>PBMA</td>
<td>poly((n)-butyl methacrylate)</td>
</tr>
<tr>
<td>PCEMA</td>
<td>poly(2-cinnamylethyl methacrylate)</td>
</tr>
<tr>
<td>PCL</td>
<td>poly((\varepsilon)-caprolactone)</td>
</tr>
<tr>
<td>PDEAEMA</td>
<td>poly((N,N)^'-diethylaminoethyl methacrylate)</td>
</tr>
<tr>
<td>PDI</td>
<td>polydispersity index</td>
</tr>
<tr>
<td>PDMA</td>
<td>poly((N,N)^'-dimethyl acrylamide)</td>
</tr>
<tr>
<td>PDMAEMA</td>
<td>poly((N,N)^'-dimethaminoethyl methacrylate)</td>
</tr>
<tr>
<td>PDMS</td>
<td>poly(dimethylsiloxane)</td>
</tr>
</tbody>
</table>
PDP 3-n-pentadecylphenol
PEG poly(ethylene glycol)
PEO poly(ethylene oxide)
PetOx poly(2-ethyl-2-oxazoline)
PFMS poly(ferrocenylmethylsilane)
PFS poly(ferrocenyldimethylsilane)
PGMA poly-(glycerol monomethacrylate)
PHPMA poly(2-hydroxypropyl methacrylate)
PI polyisoprene
PISA polymerisation-induced self-assembly
PLA polylactide
PMA poly(methyl acrylate)
PMAA poly(methacrylic acid)
PMMA poly(methyl methacrylate)
PMVS OH hydroxyl-functionalised poly(methylvinylsiloxane)
PNIPAM poly(N-isopropylacrylamide)
PS polystyrene
PS-AuNP polystyrene coated gold nanoparticle
PSGMA sucinated poly(glyceryl monomethacrylate)
PtBA poly(tert-butyl acrylate)
PTMSS poly(trimethylsilylstyrene)
PVA poly(vinyl alcohol)
\( r \) random copolymer
RF radiofrequency
rcf relative centrifugal force
RAFT reversible addition fragmentation chain transfer
RHS right hand side
RI refractive index
SBM polystyrene-\textit{block}-polybutadiene-\textit{block}-poly(methyl methacrylate)
SDM polystyrene-\textit{block}-poly(3-butenyl(dodecyl)sulfane)-\textit{block}-poly(methyl methacrylate)
SEM scanning electron microscopy
Front Matter

TEM transmission electron microscopy
THF tetrahydrofuran
TMS tetramethylsilane
UV-Vis ultraviolet visible

Parameters

\(a\) Mark-Houwink exponent coefficient
\(A\) wavelength-dependent absorbance of light
\(A_2\) second virial coefficient
\(A_s\) asymmetric factor
\(B_0\) external magnetic field
\(B_{eff}\) effective magnetic field
\(B_0\) magnitude of magnetic field
\(d\) particle diameter
\(c\) concentration of a component
\(C\) concentration of GPC analyte
\(D\) dispersity
\(D_t\) translational diffusion coefficient
\(E\) Young’s modulus
\(\Delta E\) energy difference between the two spin states
\(f_i\) volumetric ratio of \(i\) component in block copolymer
\(\hbar\) Planck constant
\(I\) light intensity after passing through a sample
\(I\) quantum number of spin
\(I_0\) intensity of original incident light
\(k_B\) Boltzmann’s constant
\(K\) Mark-Houwink constant
\(K_{GPC}\) GPC equipment coefficient
\(l\) large section of comicelle
\(m\) medium section of comicelle
\(m\) magnetic quantum number
\(M\) molar concentration
\(P\) angular momentum
$P_z$ magnitude of angular momentum in the $z$-axis
$q$ magnitude of scattering wave vector
$q$ scattering wave vector
$R_\theta$ Rayleigh ratio
$T_c$ crystallisation temperature
$T_g$ glass transition temperature
$T_m$ melting temperature
$s$ small section of comicelle
$x$ mass fraction of cetyltrimethylammonium bromide in binary surfactant mixture

Greek Letter

$\alpha$ shielding constant
$\beta$ semi-angle of collection of the magnifying lens
$\gamma$ magnetogyric ratio of nuclei
$\Gamma$ decay rate
$\delta$ resolution
$\Delta$ resolution
$\eta$ viscosity of medium
$[\eta]$ intrinsic viscosity
$\theta$ scattering angle
$\lambda$ wavelength of the electron or light
$\nu_L$ Larmor frequency
$\nu_{L,o}$ observed Larmor frequency
$\nu_{L,r}$ reference Larmor frequency
$\mu$ refractive index of the medium
$\mathbf{\mu}$ nuclear magnetic moment vector
$\tau$ decay time
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Chapter 1 — Literature Review
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Chapter 1

1.1. Introduction

In natural nanomaterials, shape is a significant parameter as it enables highly complex functions. Achieving the same degree of control over the shape of synthetic nanostructures is an interesting challenge that requires bringing together a variety of disparate concepts from a multitude of diverse disciplines. Combining the ability to control particle shape or nanostructure morphology with the inherent functionality of (synthetic) macromolecular building blocks represents a multidisciplinary hierarchical approach toward the fabrication of highly complex materials with new functionalities. Moreover, materials with unique and complex nanostructured order possess many functional properties including targeting abilities, optical tunability, and the expansions of the structures available upon design will create even further functional materials with a range of desired proprieties.\textsuperscript{1,2} These properties are a function of their structure, size and composition. Therefore, effective tailoring of nanoparticles into desired arrangement becomes the key to realise the performance of nanomaterials.\textsuperscript{3} Soft nanomaterials offer great potential because each hierarchical level has room for innovation. The synthetic preparation and modification of functional macromolecular building blocks offers challenges and opportunities as well as the design of new physical assembly methods. However, these two areas are not independent of each other and it is the intersection of the disciplines of synthetic (polymer) chemistry, colloidal chemistry and interfacial physics that enables the development of powerful new tools for the preparation of new materials. With the increasing ability to control the introduction of chemical functionality into synthetic and natural building blocks, new methods of shape control can be envisioned.

Polymer chemists have a large and ever-expanding toolbox of materials that can be utilised and designed for controlled self-assembly. Block copolymers (BCPs) have emerged as a promising building block to access nanostructures of extreme complexity.\textsuperscript{1,2,4} Although systems of one-dimensional (1D) and two-dimensional (2D) confinement are extensively studied theoretically and experimentally, three-dimensional (3D) confinement systems with higher structural order still remain a challenge. The ability to design the chemistry of BCP building blocks is paramount to controlling their final self-assembly. Non-covalent interactions, such as metal coordination,\textsuperscript{5} host-guest interactions\textsuperscript{6,7} and hydrogen bonding\textsuperscript{8} are often utilised to guide the architecture of formed aggregates. The design of these interactions and the
strict and systematic control of self-assembly conditions and reaction conditions have spurred the development of new techniques to control the shape of soft nanostructured systems.

The collaboration of traditional disciplines such as chemistry, physics and biochemistry facilitates the design of new hierarchical materials that uniquely combine shape control with inherent chemical functionality, thereby representing highly interesting materials for a broad variety of applications such as therapeutic delivery, photonic bandgap materials and optochemical sensing. This chapter provides an overview of the varied approaches to control the shape of BCP assemblies in a predictable manner, and highlights the state-of-the-art of nanoarchitectures based on BCP building blocks. We hope that this review chapter can provide a reference for the many methods developed in shape control of nanomaterials.

1.2. BCP Micellar Assemblies

For amphiphilic BCPs, shape control of micellar assemblies can be achieved through the interaction of the BCP with the solvent, the crystallisation of the core-forming blocks or more dynamically through external stimuli. In contrast, for fully hydrophobic BCPs, the shape of solid nanoparticles is strongly correlated to their internal morphology. Therefore, shape control can be achieved by tuning the morphology of the self-assembled BCP in the colloidal confinement. There are many common methods used in both systems to manipulate BCP assemblies, such as controlling temperature, polymer block weights and solvent composition. However, the resulted shape evolution may be attributed to different mechanisms. Therefore, this section addresses the shape control strategies, which are schematically summarised in Figure 1.1, from a mechanistic viewpoint. Herein, we focus on the shape-controlled micellar assemblies from BCPs and highlight state-of-the-art techniques that go beyond traditional assemblies and into complex shape-controlled nanoconstructs.
Figure 1.1. Summary of control strategies for micellar BCP assemblies. (a) Shape-controlled micelles through polymerisation, governed by BCP packing parameter. (b) Morphology and shape of micellar assemblies governed by interactions between copolymers and surrounding medium. This is achieved through solvent quality control and introduction of external stimuli. (c) Crystallisation-driven self-assembly and its superstructure. (d) Multicompartiment micelle and its precursor. Pictures are reproduced from ref 14, ref 15, ref 16, ref 17 and ref 18.

1.2.1. Influence of BCP Geometry

Ahmed and Discher reported the well-known correlation between morphologies of amphiphilic diblock copolymer assemblies and the volumetric ratios of their different blocks ($f_A$ and $f_B$, with $f_A + f_B = 1$).\textsuperscript{19} For a symmetric diblock copolymer, where $f_A$ and $f_B$ are equal, the polymer chains prefer to aggregate into membranes or sheet/disc-like micelles.\textsuperscript{20} As the volume fraction of one block decreases, the polymer aggregates change their shape to cylinders and further into energetically favorable spheres as the system has lower interfacial area and increased configurational entropy.\textsuperscript{21} The first instance is reported by Eisenberg and Zhang in 1995. In this seminal work, they observed a morphological evolution of BCP aggregates from spheres to cylinders, to bilayers and eventually to inverted micelles when one block is decreased.\textsuperscript{22, 23} The packing parameter is another indicator to predict micellar shape. It not only takes into account the volume of the hydrophobic chain but also the cross-sectional area of the hydrophilic core and the length of the hydrophobic chain.\textsuperscript{24} These factors crucially depend on the respective molecular weights ($M_w$) as well as on the interaction between
the hydrophilic block and the surrounding aqueous phase. Therefore, controlling the shape of micellar assemblies can occur via adjusting either of the two factors. This leads to different shape control strategies for dynamic assemblies such as (a) changing $M_w$ of respective blocks during the assembly, (b) changing solvent conditions and (c) introducing external stimuli.

**Increasing BCP $M_w$ During Self-Assembly.** This concept is based on the self-assembly of BCPs during their polymerisation. Here, starting from one block and changing the molecular weight of the second block upon chain growth leads to continuous changes of the BCP symmetry (i.e., the packing parameter).\textsuperscript{14} Thus, the shape/structure of the assembly changes correspondingly. Armes and co-workers demonstrated the polymerisation-induced self-assembly (PISA) of poly(glycerol monomethacrylate)-block-poly(2-hydroxypropyl methacrylate) (PGMA-$b$-PHPMA) via aqueous dispersion polymerisation using reversible addition-fragmentation chain transfer (RAFT) chemistry.\textsuperscript{25, 26} PGMA with a fixed molecular weight is used as a chain transfer agent (CTA) for the *in situ* polymerisation of HPMA to generate a series of PGMA-$b$-PHPMA diblock copolymers. When the targeted degree of polymerisation (DP) of PHPMA block equals 90, PGMA$_{47}$-$b$-PHPMA$_{90}$ (where the subscript denotes DP) exclusively forms spherical micelles. With increasing targeted length of core-forming PHPMA block, morphology transitions from spheres through worm-like micelles (DP=130) to vesicles (DP=160) are observed.\textsuperscript{26} The *in situ* structural evolution is assessed by periodical sampling of polymer solution during the RAFT polymerisation. Significantly, the *in situ* morphologies obtained at a given time during the synthesis correspond closely to the final morphologies observed at full conversion when the *in situ* degree of polymerisation is targeted. This implies that the unreacted HPMA monomers do not affect the self-assembly process of the copolymer. PISA is a one-pot technique and a range of shapes, such as branched worms, bilayer octopi and jellyfish, can be targeted through, providing a unique mechanistic insight of the sphere-to-worm and worm-to-vesicle transitions. Also, this dynamic strategy has been facilitated by the advances in polymer synthesis which offers a wide range of controlled polymerisation techniques. Another advantage of PISA is the uniquely high solids content that can be utilised and thereby promises scale-up production of BCP assemblies.

**Changing Solvent Composition During Self-Assembly.** Similar to the Flory-Huggins parameter, which specifies the degree of incompatibility between two blocks
in bulk, the solvent quality influences the interactions between copolymers and surrounding mediums. In this process changes in solvent composition lead to different solvent-polymer interactions, thereby influencing the conformation of the individual blocks. As a result, a varied shape/structure can be observed through this process. Pioneering work by Wooley and Pochan groups demonstrated the shape transformation of BCP aggregates using a system of poly(acrylic acid)-*block*-poly(methylacrylate)-*block*-polystyrene (PAA-*b*-PMA-*b*-PS) triblock copolymer, 2,2’-(ethylenedioxy) diethylamine (EDDA) and tetrahydrofuran (THF)/water solvents. This unique BCP system with PAA-diamine complexes forms discrete spherical micelles due to phase separation of unlike blocks. When THF is introduced, the spherical micelles change their intramicellar geometry and aggregate into disk-like nanostructures. With further addition of THF, unidirectional packing of these nanostructures is observed, which is ascribed to the electrostatic interactions between PAA-diamine complexes.

In the extended work of the same BCPs system, Wooley and Pochan groups demonstrated different pathways to produce toroidal PAA-*b*-PMA-*b*-PS micelles from their lamellar precursor by adding water to the water/THF mixtures. The authors also reported the ability to induce a disk-to-cylinder change of PAA-*b*-PMA-*b*-PS by adjusting the water/THF ratio. When the water content increases from 30 to 90 vol-%, BCP assemblies transform from disks to disk-cylinder intermediates, cylinders, and eventually mixtures of cylinders and spheres. In this process, the solubility of the hydrophobic PS and PMA blocks declines, thus resulting in shrinkage of the hydrophobic core and an increase in the interfacial curvature. Reversibility of the disk-to-cylinder structure transition was investigated by adding THF back to the system. Through increasing addition of THF into the 90 vol-% water content system, disk-cylinder intermediates are observed at 70 vol-% water content and disks are observed at 45% water content, representing the reversible process of disk-to-cylinder transition.

In a similar fashion, Kempe *et al.* recently reported non-spherical faceted and cauliflower-like particles formed from PS-*block*-poly(2-ethyl-2-oxazoline) (PS-*b*-PETOx) through solvent exchange methods and choice of solvent mixtures based on THF, a good solvent for copolymers, and ethanol and water as non-solvents for the PS block. The authors also investigated the influence of block weights and assembling temperature on particle structures, demonstrating a new set of tools to prepare nonconventional shapes formed from amphiphilic copolymers (shown in Figure 1.2).
Although in this work the authors did not elaborate the mechanistic influence of temperature, we postulate that the increase in the assembling temperature increases combinatorial entropy, which is supported by the disorganised structure (i.e., homogeneous) at high temperatures (Figure 1.2d-f). The above works are of particular significance since their results indicate that a myriad of structured particles from the same BCP system can be accessed by introducing multiple variables to the system.\textsuperscript{15,27,28,30-32}

![Figure 1.2](image)

**Figure 1.2.** (Top) TEM images of PS\textsubscript{12K}-b-PEtOx\textsubscript{2K} particles with different morphologies after self-assembly from adding THF into (a) water, (b) ethanol, (c) ethanol-water mixture at 1:1 volume ratio. (Bottom) TEM images of PS\textsubscript{12K}-b-PEtOx\textsubscript{2K} particles assembled in the same fashion but THF is removed at different temperature: (d) 20 °C, (e) 40 °C and (f) 60 °C. Scale bar: (a) 500 nm, (b) 1 µm, (c) 200 nm, (d)-(f) 100 nm. Pictures are reproduced from ref 31.

**Stimuli-Responsive Shape Control.** Apart from “intrinsic” shape controlling methods, external stimuli such as light, pH, redox and temperature can be used to change dynamically the shape of the BCP assemblies. Here, changing the interaction between solvent and the respective responsive block allows tuning the BCP volumetric ratio and thereby the structure of the assembly. Recently, the introduction of tertiary amines\textsuperscript{33,34} and amidines\textsuperscript{35} into BCPs has regained interest since it was demonstrated that such polymers (e.g. poly(\textit{N},\textit{N}-dimethylaminoethyl methacrylate) (PDMAEMA)) exhibit a tunable water solubility with respect to CO\textsubscript{2} gas.\textsuperscript{34,36} Therefore the macroscopic self-assembly of BCPs containing a PDMAEMA block can be controlled
by introducing and removing CO$_2$ gas. Using the same stimulus, the Yuan group developed a strategy to produce CO$_2$-responsive BCPs based on amidine-containing poly(ethylene oxide)-block-poly((N-amidine)dodecyl acrylamide) (PEO-b-PAD). In this study, the vesicular nanostructures with a radius of approximately 60 nm expanded to 120 nm upon introducing CO$_2$ gas.$^{37}$ The Zhao group also reported a similar observation: poly($N,N'$-dimethyl acrylamide)-block-poly($N,N'$-diethylaminoethyl methacrylate) (PDMA-b-PDEAEMA) vesicles with cross-linked PDEAEMA expand and swell in the presence of CO$_2$.\textsuperscript{16} Zhou and Yan also demonstrated the CO$_2$-responsive feature using a triblock copolymer, PEO-b-PAD-b-PS. The intermediate PAD blocks become water soluble when protonated, which is controlled by the introduction of CO$_2$ gas. With increasing fraction of hydrophilic sections, the triblock copolymers undergo shape transformation from tubules through vesicles to spherical architectures,\textsuperscript{16} as schematically illustrated in Figure 1.3 with corresponding TEM images. Although solvent exchange methods modify the solution chemistry, the introduction of CO$_2$ gas changes the polymer chemistry, and both strategies rely on the change of interactions between copolymers and surrounding medium.

![Figure 1.3. CO$_2$-switchable amidine-containing triblock copolymer PEO-b-PAD-b-PS and change of (top) and CO$_2$-driven shape transformation behavior (middle). Insets (a), (b) and (c) are TEM images of PEO-b-PAD-b-PS aggregates in different levels of CO$_2$ stimulus (bottom). Scale bars: (a) is equal to 500 nm, (b) and (c) are equal to 200 nm. Pictures are reproduced from ref 16.](image-url)
1.2.2. Influence of BCP Crystallisation

Crystallisation-assisted self-assembly has become an emerging pathway to construct complex BCP assemblies with various shape and functionality. This increasing interest is facilitated by the recent development of new synthetic strategies that gives easy access to semicrystalline BCPs.\textsuperscript{38, 39} Controlling the self-assembly process of such block copolymers with one semicrystalline block is highly complex and remains a significant challenge.\textsuperscript{40-44} This is in strong contrast to non-crystalline BCPs where excellent agreement between theoretical and experimental studies has been demonstrated.\textsuperscript{2, 29, 45} This section first highlights how the combination of crystallisation and self-assembly results in entirely different mechanisms of structure formation. These can be exploited to precisely manipulate the shape of BCP micelles with crystalline cores. This section also focuses on the vast potential of these systems to generate very elaborate and unique morphologies of semicrystalline BCP micelles by utilising the “living” character of such crystallisation-driven assemblies. Of special interest is here the combination of different building blocks and their continuous or stepwise addition.

Manipulation of crystallisation conditions opens up new pathways to access a large variety of unique morphologies. For example, Mihut and co-workers presented an experimental phase map of semicrystalline polybutadiene-\textit{block}-PEO (PB-\textit{b}-PEO) copolymers in dilute \textit{n}-heptane solutions.\textsuperscript{46} Here, the thermally controlled crystallisation of the PEO block forms micelles with a PB corona. By reducing the temperature at which self-assembly occurs, the crystallinity of PEO increases correspondingly. Simultaneously, the solvent quality for PB reduces drastically which causes less steric repulsion in the PB corona thereby resulting in a shape change from spheres to worm-like structures. Schmalz and co-workers also reported worm-like micelles with tailored functionality using SEM (polystyrene-\textit{block}-polyethylene-\textit{block}-poly(methyl methacrylate)) through crystallisation-driven self-assembly (CDSA). In this work, polyethylene is a semicrystalline block placed in the middle of the triblock copolymer. Through control of solvent quality, worm-like crystalline-core micelles with a patch-like microphase separated polystyrene/poly(methyl methacrylate) (PS/PMMA) corona are obtained.\textsuperscript{47, 48} The Xu group investigated the influence of crystallisation temperature on the micellar morphologies of poly(\textit{\varepsilon}-caprolactone)-\textit{block}-PEO (PCL-\textit{b}-PEO), wherein the PCL block is a core-forming crystalline block.\textsuperscript{49} For low $M_w$ PEO blocks it is observed that a higher self-assembly temperature tends to
induce lamellar micelles whereas spherical micelles or cylindrical micelles are formed at lower temperatures. However, for PCL-\(b\)-PEO with longer PEO blocks it is found that the crystallisation temperature has opposite effects on the morphology. A mechanism of two competitive factors, namely the perfection of PCL crystals in the core and the deformation of the soluble PEO block, is proposed to elucidate the opposite observations with respect to crystallisation temperature.\(^{49, 50}\) The same authors also observed morphology transitions from spherical through rod/worm-like to lamellar architectures when the length of the PCL block increases in the PCL-\(b\)-PEO copolymer for low weight PEO blocks.\(^{51}\) Similarly, the Su group suggested that crystallisation temperatures have a strong influence on BCPs structure formation. Su and co-workers prepared lamellar structures with elongated truncated lozenge-shaped single crystals from poly(2-vinylpyridine)-\(b\)-PCL (P2VP-\(b\)-PCL) at 20 °C.\(^{52}\) When the temperature is increased to 30 °C, the crystallisation process is suppressed and only spherical structures are observed. In such amphiphilic BCPs with one crystalline block this influence of crystallisation temperature can be used to control shape by switching crystallisation on or off. If self-assembly above the crystallisation temperature gives a specific structure, cooling down the system then leads to a shape transition because crystallisation sets in.

Generally, for semi-crystalline BCPs the accessible structures vary significantly from those observed for non-crystalline BCPs. For the conventional systems, spherical micelles are the most common architecture as it is more energetically favorable. Consequently, only a narrow range of non-crystalline BCPs are able to form asymmetric architectures with extreme aspect ratios. On the contrary, BCPs with crystalline coil-forming blocks tend to form nanofiber structures under a wide range of assembly conditions.\(^{17, 53-65}\) The Manners and Winnik groups found an unexpected rod-like morphology formed by poly(ferrocenyldimethylsilane)-\(b\)-poly(dimethylsiloxane) (PFS-\(b\)-PDMS) in which PFS forms the core and PDMS forms the corona. The authors suggested that the formation of rod-like micelles is attributed to crystallisation of the core polymer.\(^{53}\) The formation of these structures was investigated through epitaxial growth of BCP seeds with crystalline cores. Patra \textit{et al.} explored this epitaxial growth using a different BCP, i.e., poly(3-hexylthiophene)-\(b\)-PDMS (P3HT-\(b\)-PDMS), to produce monodisperse nanocylinders with a P3HT core and a PDMS corona through CDSA using seed micelles as initiators.\(^{58}\) These seed micelles
are prepared by sonication. Upon adding P3HT-\(b\)-PDMS unimers, cylindrical micelles grow into long chains by continuous addition of unimers to the reactive chain ends without termination. Analogously to living polymerisations, the length of the resulted nanofibers is controlled by the ratio of added unimer to seed. Though this type of epitaxial growth is extremely desirable, the technique of unimer addition can only be extended to a few other BCPs with crystalline coil-forming blocks, such as polyisoprene-\(block\)-poly(ferrocenylmethylsilane) (PI-\(b\)-PFMS)\(^{62}\) and PFS-\(block\)-poly(\(N\)-isopropylacrylamide) (PFS-\(b\)-PNIAPAM)\(^{66}\). Although the crystalline core provides a scaffold for nanofiber growth, the functionality of corona forming blocks affords design of smart nanomaterials such as thermoresponsive nanofibrillar hydrogels when PNIPAM is involved. Because of the fact that both ends of crystallite seeds are active, the addition of BCP unimers to seeds leads to bidirectional epitaxial growth giving an A-B-A centrosymmetric cylindrical comicelle. With the aim to create A-B or A-B-C non-centrosymmetric cylindrical comicelles, Manners and Winnik groups developed a strategy by combining CDSA of crystalline BCPs in solution, selective micelle corona cross-linking and selective middle block dissolving to induce unidirectional growth.\(^{59}\) This structural hierarchies through selective immobilising and dissolution is a versatile strategy can extend to arrangement of 2D nanostructures. As an example illustrated in Figure 1.4, Qiu et al. produced hollow and patchy rectangular platelet micelles from crystallisable BCP and homopolymer blends.\(^{67}\) The 2D platelet is assembled by adding PFS-\(b\)-P2VP unimer to cylindrical micelles of PFS-\(b\)-PDMS, followed by cross-linking of P2VP, a hollow platelet is formed upon selective dissolution using THF (Figure 1.4A). The AFM image and height retrace confirmed the removal of PFS-\(b\)-PDMS cylindrical micelles. Similar to the epitaxial growth in cylindrical comicelles, the sequential addition of different polymer blends gives a platelet consisting of several rings of different materials. Through selective of immobilisation, these rings can detach upon dispersal in a good solvent, as schematically illustrated in Figure 1.4B. We postulate that the sequential growth of the 2D structures is of particular importance as this leads to encoded information with high data density. Success has already been achieved in 1D linear comicelles\(^{68}\) and this may be further applied to multidimensional structures. The example of 2D platelet micelles also demonstrates the power of blending crystallisable homopolymer and BCPs. Cambridge et al. used the same blending method to produce micelles consisting of elongated lamellae with long protruding fibers based on PFS homopolymer and PFS-
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However, in this study pure PFS platelets were used as seeds instead of a cylindrical seed. This hierarchical strategy can also be applied to form nanotubes, as first reported by the Liu group. Here, the authors produced BCP nanotubes from PI-block-poly(2-cinnamoylethyl methacrylate)-block-poly(tert-butyl acrylate) (PI-b-PCEMA-b-PtBA) through selective cross-linking and degradation.

When polymer-medium interactions are utilised in addition to living CDSA of cylindrical comicelles, this strategy opens up control of multidimensional architectures. This is achieved through manipulating solvent qualities with respect to each moiety of BCPs. In the above section, we highlight the influence of solvent composition on amphiphilic BCP assembly from the viewpoint of BCP geometry, however the mechanism of how solvent quality affects comicelle superstructures is different. In the coassembly of P-H-P and H-P-H cylindrical comicelles with hydrophobic (H) or polar (P) segments, comicelles are able to assemble either side-by-side or end-to-end depending on the solvent quality. Moreover, the supermicellar arrangement can be controlled by the length of P and H segments giving irregular network, chain networks and even 3D superlattices. On the basis of the same strategy, Li et al. produced “cross” supermicelles using amphiphilic cylindrical triblock comicelle of M(PFS-b-PtBA)-b-
M(PFS-b-PDMS)-b-M-(PFS-b-PtBA), where M denotes micelle segment. In this example, PFS-b-PtBA is the P segment and PFS-b-PDMS is the H segment. Li et al. investigated not only the influence of solvent quality on supermicellar arrangement but also the length of P segment (L₁) and degree of polymerisation of PtBA (DP₂). Under certain conditions, the cylindrical comicelle can form superstructures via side-by-side stacking; however, other interesting supermicelles such as “cross” and multiple “cross” have been found when L₁ and DP₂ are manipulated, as depicted in Figure 1.5. A mechanistic insight of the coassembly and influence of L₁ and DP₂ has been proposed and a phase diagram summarising the possible superstructures and their corresponding conditions has been produced. This allows the prediction of superstructures when the detail of cylindrical comicelle is given. The same group also explored this “cross” feature of supermicelles through a different driving force, namely hydrogen-bonding (H-bonding) interactions. In analogy to the P-H-P or H-P-H system, the use of H-bonding interactions requires design of polymeric segment with desired properties. Li et al. investigated BCP systems possessed a crystallisable, core-forming PFS block together with a corona-forming segment that was either hydroxyl-functionalised poly(methylvinylsiloxane) (PMVSOH) as H-bonding donor (H_D), P2VP as H-bonding acceptor (H_A) or PtBA as non-interactive block (N). Therefore, a cylindrical triblock comicelle consisting of a middle H-bonding acceptor segment and two non-interactive terminal segments is denoted as N-H_A-N. Not only the “cross” supermicelles can be assembled, end-to-end or side-by-side supermicelles are also possible when the position of H_A and H_D segment is controlled. The author also demonstrated a hierarchical strategy in combination of sequential addition of different unimers and selective cross-linking of segments to produce “windmill”-like supermicelles.
Figure 1.5. (A) Chemical structures of PFS-b-PDMS and PFS-b-PtBA, abbreviated as H and P, respectively. The P-H-P triblock comicelle is prepared through CDSA. $L_1$ is the length of H section and $L_2$ is the length of PtBA corona, which is directly related to its degree of polymerisation. The boxed section (middle) shows 4 scenarios of different $L_1$ and $L_2$ which provides a mechanistic insight for the formation of supermicelles. (B) Schematic representations of the supermicelles formed in methanol by the triblock comicelle P-H-P with different value of $L_1$ and $L_2$. The phase diagram (right) summarises the influences of $L_1$ and DP2 (to which $L_2$ is related) on the supermicellar structures formed by the amphiphilic triblock comicelle P-H-P. “I” denotes individual cylinders, “C” denotes “cross” micelles, “MC” denotes multiple “cross” and “B” denotes cylinder bundle. Pictures are reproduced from ref 72.

From the above examples, it is clear that living CDSA is a powerful method to manipulate the structures of BCP assemblies. In particular, the living character allows sequential coassembly which enables construction of hierarchical architectures with great complexity. With the development of polymer chemistry, living CDSA is also capable to produce stimuli-responsive intermediate structures.74 This hierarchical strategy to produce superstructures can further extend to non-crystalline systems, which are discussed in the following section.
1.2.3. Multicompartment Micelles and Superstructures

Multicompartment micelles and their superstructures further expand the structural complexity that can be engineered from BCPs. By using mixtures from two different BCPs that have the same hydrophilic corona block but two different hydrophobic blocks, multicompartment micelles can be formed with a phase separated core. This general concept can further lead to the assembly into superstructures by utilising the interactions between the same core materials in two different micelles, and thereby leading to the buildup of a longer hierarchical structure that is stabilised by the hydrophilic corona blocks. Concepts to tune the shape of mixed micelles by varying self-assembly conditions and composition are also introduced in this section.

Wooley and Pochan groups reported multicompartment and multigeometry assemblies. These were formed from simple diblock copolymers, PAA$\text{-}b$-PB and PAA$\text{-}b$-PS, and polystyrene-coated gold nanoparticles (PS-AuNPs) via kinetic control. In this study, BCPs are first dissolved in THF, a good solvent for both PS and PB blocks: this is followed by the addition of EDDA, thus forming hydrophilic EDDA-complexed PAA blocks. Owing to the incompatibility of PS and PB blocks, local phase separation is observed within the aggregate core of PS and PB blocks when water is added either quickly or slowly. Figure 1.6 shows control over shape and internal morphology of phase separated nanoparticles via the speed of water addition. In the rapid water-induced assembly pathway, BCPs are kinetically trapped resulting in a shell-core spherical shape. In contrast, PAA$\text{-}b$-PS and PAA$\text{-}b$-PB are able to adopt their preferred interfacial curvature in the slow pathway, thus forming spherical and cylindrical particles respectively, as shown in Figure 1.6d and i. The authors also demonstrated the formation of micelle-like aggregates with PS-AuNPs trapped in the PS domain of the hydrophobic cores. In further studies of this BCP blending strategy, the same authors used a similar binary system of PAA$\text{-}b$-PS and PAA$\text{-}b$-PI copolymers, and EDDA diamine to construct disk-cylinder hybrid nanoparticles. In analogy to the coassembly of PAA$\text{-}b$-PS and PAA$\text{-}b$-PB, the formation of multigeometry particles of PAA$\text{-}b$-PS and PAA$\text{-}b$-PI blends also relies on the incompatibility of the unlike hydrophobic blocks, that is, in the latter case, polystyrene and polyisoprene. When this strategy is utilised to coassemble sphere-forming PAA$\text{-}b$-PB with vesicle-forming PAA$\text{-}b$-PMA$\text{-}b$-PS tri-BCP, disk-sphere hybrid nanoparticles are obtained via a kinetically controlled pathway.
Figure 1.6. TEM images of PAA-b-PB and PAA-b-PS blend nanoparticles formed via fast water addition, (a)-(c), and slow water titration, (d)-(i). All nanoparticles are formed in a 1:4 volume ratio of THF and water mixture with an amine to acid molar ratio 1:2. The PAA-b-PB to PAA-b-PS molar ratio is: (a) 6:1; (b) 3:1; (c) 1:6; (d) 1:0; (e) 6:1; (f) 3:1; (g) 2:1; (h) 1:3; (i) 0:1. The PB phase of the nanoparticles is stained by OsO₄. The TEM image insets in (a)-(i) are high magnification of typical particles, cartoon insets in (a)-(i) represent the approximate relative proportion of each block domain within the multicompartment BCP nanoparticles. Scale bars: insert scale bars (a)-(c) are equal to 20 nm; all other scales bars are equal to 100 nm. Pictures are reproduced from ref 75.

Another approach of utilising demixing blocks to control the shape of BCP particles is to exploit the phase separation of the corona-forming block as reported by Cheng and co-workers. The authors made polymeric Janus particles from mixed-shell micelles and assembled poly(2-vinyl naphthalene)-block-PAA (P2VN-b-PAA) and PEO-b-PAA into tubular superstructures and nanosheets. The Cheng group further advanced this strategy by making more complex polymeric double helices using the same BCPs system. The structure of helices are similar to what reported by Dupont et al.; however, the latter system uses poly(n-butyl methacrylate)-block-PCEMA-block-PtBA (PBMA-b-PCEMA-b-PtBA), which relies on the control of solvent quality.
Higher-ordered complex multicompartment superstructures can be accessed by precise hierarchical assembly of preformed BCP nanoparticles with phase separated cores. The Müller and Walther groups elegantly demonstrated a general concept of directed self-assembly: stepwise reduction of the degree of conformational freedom lead to the formation of multicompartment micelles (MCMs) composed of linear ABC tri-BCPs. This construction strategy largely contrasts Wooley and Pochan groups’ kinetically controlled approaches as it aims to avoid the undesirable kinetic traps. In the hierarchical pathways, as illustrated in Figure 1.7, the ABC tri-BCP is first dissolved in a non-solvent for the middle block B, yielding a micellar subunit with B core and compartmentalised corona of A and C (Figure 1.7a). Subsequent addition of a non-solvent for block-A through dialysis triggers the collapse of block-A forming intermediate subunits (Figure 1.7b and c). Depending on the volume ratio of A and B blocks, the rearrangements and phase segregation between blocks A and C give secondary aggregation. Figure 1.7d-f shows corresponding TEM images of a PS-b-PB-b-PMMA model system. Interestingly, the football MCMs and linear MCMs in Figure 1.7 are very similar to Liu and co-workers’ patchy nanoparticles with segregated surface chains and hamburger-like micelles, respectively. The latter structures are assembled from PtBA-b-PCEMA-b-PSGMA, where PSGMA denotes succinylated poly(glyceryl monomethacrylate). In these seminal works of soft patchy nanoparticles, the authors demonstrated unprecedented diversity of well-defined morphologies and, most importantly, exhibited highly homogeneous populations that are remarkably monodisperse in size. The TEM image and its Fourier-transformed insert of “Football” MCM in Figure 1.7d are evidence of such a homogeneous structure.
Figure 1.7. Mechanism of the directed hierarchical self-assembly of well-defined MCMs. (a) ABC tri-BCP is forced into micellar subunit. (b-e) Upon dialysis, these subunits assemble via refinement of the corona structure into various micellar structures with well-defined number of patches depending on the volume ratio of A and B. (f) Worm-like aggregates may form under certain conditions. Cartoon represents generic ABC tri-BCPs whereas TEM images are PS-\(b\)-PB-\(b\)-PMMA. All scale bars are 50 nm except where otherwise stated. Pictures are reproduced from ref 18.
Groschel et al. further coassembled patchy nanoparticles into well-ordered hierarchical superstructures.\textsuperscript{79} Colloidal building blocks consisting of SBM (polystyrene-\textit{block}-polybutadiene-\textit{block}-poly(methyl methacrylate)) and SDM (polystyrene-\textit{block}-poly(3-butenyl(dodecyl)sulfane)-\textit{block}-poly(methyl methacrylate)) are prepared separately by self-assembly through solvent exchange. SBM and SDM are rearranged into monovalent \(x\text{-SB}^M\) particles (\(x\) indicates the size of particle, \(x=s\) (small), \(m\) (medium) or \(l\) (large)) and divalent \(SD^M\text{S}\) particles as monomeric units. The superscript indicates that the M corona is attached to either a B or D core, and bold letters represent assembled subunits distinguished from the free polymer chains.\textsuperscript{79} Both building units are illustrated schematically in Figure 1.8a. Upon reduction of solvent quality for S patches, the building blocks undergo self-assembly into linear superstructures to minimise energetically unfavorable interfaces of S patch and non-solvent.\textsuperscript{79} Figure 1.8b shows an example of decorated linear superstructure formed from both building units. The authors also reported that the overall size of \(x\text{-SB}^M\) noticeably affects the number of particles attached to each segment of the \(SD^M\text{S}\) superstructure chain, i.e., \(-\text{S}\) segment of \(SD^M\text{S}\) can accommodate \textit{ca.} eight \(s\text{-SB}^M\) units (Figure 1.8c) or one \(m\text{-SB}^M\) unit (Figure 1.8d). As for the \(l\text{-SB}^M\) unit, it is too large for lateral decoration and acts instead as a selective end-capping agent (Figure 1.8e). This character of \(l\text{-SB}^M\) particle can be used to tailor the length of the worm-like supracolloidal chain through manipulation of the \(l\text{-SB}^M\) to \(SD^M\text{S}\) ratio. This inspiring example shows the fantastic potential of self-assembly to give highly complex structures of well-defined shape and morphology when a synthetic chemistry approach to self-assembly is applied. In the latest work, the same authors reported a myriad of multicompartment nanostructures obtained from an ABC triblock copolymer where A/B (polystyrene/polybutadiene) are cores and C (poly(\textit{tert}-butyl methacrylate)) is the corona. When the ratio of block length \(N_c/N_A\) is controlled, the tri-BCP assembles into various morphologies such as spheres, cylinders and bilayer sheets. The insoluble blocks undergo phase separation to core A and surface patch B, where \(N_B\) controls the patch morphology. Therefore, the combination of control over these independent parameters allows constructing of extreme versatile morphology and decoration when a single BCP system is used.\textsuperscript{90}
Figure 1.8. (a) SBM and SDM building blocks. (b) Representation of linear worm-like supracolloidal chain. (c)-(e) depicts the linear chain formed from small, medium and large SBM particles, respectively. In (c) and (d), M corona is removed for clarify. Pictures are reproduced from ref 79.

Instead of using preformed micelles as building blocks, various BCP superstructures can also be accessed directly through self-assembly of copolymer mixtures. Altering the composition of the mixture then results in different shapes and morphologies. As an example, Yoshida demonstrated worm-like structures by using mixtures of different poly(methacrylic acid)-block-poly(methyl methacrylate-random-methacrylic acid) (PMAA-b-P(MMA-r-MAA)) copolymers with different compositions. Worm-like vesicles are found when the fraction of the copolymer with a long PMAA block (PMAA-L) is increased. In another example, Cai and co-workers made super-helical virus-like structures using poly(γ-benzyl-L-glutamate)-block-poly(ethylene glycol) (PBLG-b-PEG) and homo-poly(γ-benzyl-L-glutamate) (homo-PBLG). The hybrid aggregates of PBLG-b-PEG and homo-PBLG form helices including rings and rods while pure PBLG-b-PEG self-assembles into spheres. These virus mimicking structures are of particular interest due to their potential application in biomedical research. In this attempt, the Gu group made viral capsid-mimicking nanoarchitectures through cooperative electrostatic and/or hydrogen bonding between polymers.
Other interactions, such as host-guest interactions, can also be applied to manipulate nanoarchitectures. As an example, Wooley and co-workers reported a hierarchical assembly strategy of utilising PAA-\textit{b}-PS and crown ether functionalised PAA-\textit{b}-PMMA to assemble into 1D chains, 2D rings and 3D superstructure aggregates.\textsuperscript{93} Here, the crown ether grafted PAA-\textit{b}-PMMA copolymer provides interparticle interactions ascribed to its host-guest chemistry property. Zhou and co-workers also constructed large vesicle aggregates through host-guest interactions between functionalised blocks using “branched polymersomes” as subunits.\textsuperscript{94}

1.3. BCP Self-Assembly in 3D Confinements

Fully hydrophobic block copolymers have proven to self-assemble into a range of interesting nanoparticles,\textsuperscript{95-97} in which the shape of the final particle crucially depends on the phase separation of the BCP. This dictates the internal morphology that drives the evolution of the overall nanoparticle shape. Therefore, controlling the shape of a particle to deviate from the natural sphere requires the realisation of spatially anisotropic BCP morphologies in the particle interior. However due to a variety of factors, the BCP morphology in a nanoparticle is more complex than in the corresponding bulk. Much like in thin films, interfacial tensions and consummation effects in small confinements both influence the morphology and thereby the shape. It is therefore of high importance to be able to control all these factors to be able to control the shape of nanoparticles.

It has been demonstrated that the interfacial interaction between BCP and surrounding medium strongly influences the phase separation and thereby the morphology and shape of the particles. Control over the BCP morphology/orientation requires careful adjustments of interfacial tensions between the individual blocks and the aqueous medium. In this technique, BCPs are firstly dissolved into an organic solvent and then emulsified using surfactants in aqueous medium. These dispersed emulsion droplets provide the 3D confinement for BCP self-assembly. Upon removal of organic solvent, BCPs are solidified giving dispersed nanoparticles with rearranged morphologies. Carefully designed synthetic strategies to control interfacial energies through functional surfactants has been demonstrated to be a powerful route to BCP particles with unique nonconventional shapes.\textsuperscript{75} In the pioneering work of the groups of Yang and Yi, the authors demonstrated the interface-driven structure evolution of
PS-\textit{b-PB} from onion-like particles to striped ellipsoids using a mixture of two amphiphilic BCPs surfactants, PS-\textit{b-PEO} and PB-\textit{b-PEO}, functioning as domain active interface-tuning agents. In addition, the authors also added polystyrene homopolymer (hPS) in the emulsion phase to control the structure of BCP assemblies: PS-\textit{b-PB/hPS} blends were reported to give many other interesting structures. Spheres with internal helical PB domains and prolate particles with hexagonally packed PB domains could be obtained in dependence on the amount of hPS homopolymer.

Inorganic nanoparticles (iNPs) can also function as surfactants to tailor the shape and internal morphology of BCPs when the iNP location is precisely controlled at the interface between the two polymeric domains. As a recent example, the Hawker group developed a simple, yet powerful strategy to control the shape of PS-\textit{block-poly(4-vinylpyridine)} (PS-\textit{b-P4VP}) particles using gold nanoparticle (Au-NP) surfactants. A morphology transition and overall shape change from spherical, onion-like particles to stacked lamellae ellipsoids were observed upon addition of Au-NPs. In a similar manner, Kim and co-workers developed a facile strategy to produce convex lens-shaped BCP particles with highly ordered and defect-free nanoporous channels using size-controlled Au-NPs as surfactants. The authors first prepared supramolecular modified PS-\textit{b-P4VP} via hydrogen bonding with 3-n-pentadecylphenol (PDP), giving a comb-like structure of PS-\textit{b-P4VP(PDP)}. After emulsification in the presence of cetyltrimethylammonium bromide (CTAB), PS-\textit{b-P4VP(PDP)} forms spherical particles with internal cylindrical P4VP(PDP) domains. Because of the favourable interaction of the PS layer with the CTAB surfactants at the particle surface the particles exhibit an outer PS layer. On the contrary, upon addition of small amount of Au-NPs, BCP particles transform from spherical to convex lens shape with hexagonally packed dimples.

In a recent study, Kim and co-workers further investigated the shape and morphology transition of PS-\textit{b-P4VP(PDP)} using surface-engineered graphene quantum dots (GQDs). The authors first synthesised alkylamine-grafted GQDs using hexylamine (HEX) and oleylamine (OLA), which have preferential interactions with PS and P4VP block respectively. While particles stabilised by GQD-HEX assemble into spheres with PS as outmost layer, GQD-OLA induces spherical particles with P2VP(PDP) as outer layer due to the preferential wetting of respect blocks. The authors also demonstrated the morphological evolution of PS-\textit{b-P4VP(PDP)} from traditional
spheres to convex lens-shaped particles when a mixture of GQD-HEX and GQD-OLA is used as surfactant. The feasibility of using alkyl ligands to tune the surface properties of GQDs has demonstrated the potential of GQD surfactants in producing shape-controlled colloidal particles.

The use of Au-NPs and surface-engineered GQDs as surfactant for preparation of structured particles poses a significant fabrication limitation; as a result, the Zhu group introduced a facile strategy to achieve reversible transformation of PS-\(b\)-P4VP nanoparticles using poly(vinyl alcohol) (PVA) to adjust the particle/medium interfacial properties. In this work, the authors prepared the nanoparticles based on an emulsion technique pioneered by Liu and co-workers. The morphological transition from onion-like spheres to ellipsoidal stacked lamellae is achieved through solvent annealing and it is found that the concentration of PVA in aqueous solution is critical in determining the particle morphology. The Hawker group also reported similar strategy to synthesise ellipsoidal PS-\(b\)-P2VP nanoparticles and provided some mechanistic insights. In this system, the particle/medium interfacial properties are tuned using a surfactant package, namely a combination of CTAB and modified CTAB with a terminal hydroxy group (HO-CTAB). Due to the selective wetting ability of the two surfactants to different domains, the surfactants mixtures can accurately tune interfacial energies between BCP blocks and blocks with surrounding medium. For instance, HO-CTAB shows preferential interactions with P2VP whereas CTAB is selective for PS. Thus, increasing the HO-CTAB content in the surfactants mixture results in a shape transition from onion-like spherical to axially stacked lamellae structures and eventually to inverse onion-like particles, as illustrated schematically in Figure 1.9a. In addition to surfactant mixtures, Klinger et al. also demonstrated the ability to tune the aspect ratio of the ellipsoidal particles by manipulating the lamellae thickness through the molecular weight of the BCPs. In the same system, P2VP chains can be cross-linked to form hydrogel discs. The formed hydrogel layers enable a reversible anisotropic shape transformation of the whole ellipsoidal particles in response to a pH change, as shown in Figure 1.9b. Such a dynamic, stimuli-responsive material is of significant interest as it is the first example combining shape anisotropy, internal morphology and stimuli-responsive features in one single system.
Figure 1.9. (a) Schematic representation and TEM images of PS-\textit{b}-P2VP particles assembled at different conditions. (b) pH responsiveness of lamellar ellipsoids with cross-linked P2VP domains at different pH value. Pictures are reproduced from ref 108.

It becomes obvious that controlling the assembly of BCPs via the polymer-medium interface offers great potential for the fabrication of highly functional dynamic materials (e.g. shape changing particles). Therefore, it is of high interest to expand this self-assembly method to more functional BCPs. As has been demonstrated by Gallei and co-workers, this concept can also be used to generate ferrocene-containing PFS-\textit{b}-P2VP particles. In this system, the self-assembly is additionally strongly influenced by the crystallisation of the PFS block.\textsuperscript{110} Consequently, different assembly conditions/compositions lead to different structures such as ellipsoids with axially stacked lamellae or nanosheets with hexagonal PFS cylinders. Furthermore, the ferrocene-containing PFS block rendered these particles redox responsive. By adding an oxidant such as FeCl\textsubscript{3} a shape transition of the particles was observed. This can be attributed to a change of PFS polarity from hydrophobic to hydrophilic upon oxidation.\textsuperscript{111, 112} The redox-active character of PFS-based polymers therefore allows changes in the properties of these assemblies and thus expands the scope of anisotropic particles. Moreover, the combination of redox-responsive PFS with pH-responsive P2VP domains allows a multi-stimuli-responsive behavior which represents a powerful platform for a wide range of applications.\textsuperscript{110, 113-119}

From the examples above, we can see that the control of anisotropic BCP nanoparticles crucially relies on the interfacial properties. However, Higuchi and Yabu groups demonstrated that the anisotropic internal morphology of BCP assemblies can be achieved through control of solvent quality and temperature without using surfactants. Higuchi and co-workers pioneered the preparation of BCPs particles with different morphologies via self-organisation during precipitation.\textsuperscript{120} Particle formation
from BCP solutions is induced by evaporating a good solvent from a binary system of good and poor solvents. Depending on the evaporation temperature, PS-\textit{b}-PI formed ordered stacked lamellar structures or onion-like structures from THF/water mixtures.\textsuperscript{121} Disordered structures were found at low evaporation temperature (10 °C).\textsuperscript{121} This may be attributed to the low mobility of polymer chains at this temperature.

Russell and Hayward further investigated a similar system and observed that depending on the overall size of PS-\textit{b}-PI particles, the core of onion-like sphere is either PI or PS block whereas the outer layer of the particles is always PS.\textsuperscript{122} In addition to solvent evaporation, exchange of solvents can also be achieved via dialysis method.\textsuperscript{123-125} However, both methods produced particles that exhibit anisotropic morphologies (stacked stripes) but are still spherical. This can be attributed to the fact that these morphologies are kinetically trapped. Consequently, they are not able to cause a deviation from the spherical shape. In other words, the shape of such hydrophobic systems can ultimately be controlled if the particles are in thermodynamic equilibrium.

In addition to these considerations, the size of the colloidal confinement also affects the inner morphology and thereby the particle shape. The phase separated BCP structure crucially depends on the relative size of the particle in comparison to the domain size of the BCP. From the seminal work by Stucky and co-workers, new and interesting morphologies can be formed in a physically confined environment due to the fact that confinement-induced entropy loss and structural frustration play dominant roles in determining molecular arrangements.\textsuperscript{126} Therefore, the confined particle may not allow true deviations from the spherical shape. From these examples, it can be seen that all these factors have to be taken into account. To realise truly shape in anisotropic particles, the following things are required: the phase separation of BCP has to be in an equilibrium state and has to occur in confinements bigger than the domain size of the BCP so that consummation effects can be minimised.
1.4. Directed BCP Self-Assembly in Thin Films

Similar to BCP self-assembly in 3D confinement that discussed above, thin film assemblies can also be directed by the interface between BCP and substrates or between BCP and air (or other medium). The former is achieved through substrate processing to tune its surface tension. In the seminal work of the Russell group, a facile and versatile method of substrate processing to produce a solid surface with controlled wetting behaviour has been demonstrated. In this study, a series of random copolymers PS-\textit{r}-PMMA with varied composition (from 100\% to 0\% of polystyrene) were used to tune the surface properties of a solid substrate. The synthesis scheme of PS-\textit{r}-PMMA terminated with a hydroxyl group on one end is shown in Figure 1.10A. Although the use of random copolymers to manipulate the interface energy of polymers and a surface has been previously reported, Russel and co-workers significantly improved the stability of the modified surface by end-grafting the hydroxyl group functionalised polymer chains to the silicon oxide layer on the solid surface. The interfacial tension $\gamma_{jf}$ (where $j$=S or M for PS and PMMA respectively, and $f$ denotes the weight fraction of polystyrene in the random copolymer) between thin films of homopolymers (PS or PMMA) and the random copolymer layer with corresponding polystyrene content $f$ were measured and plotted in Figure 1.10B. The resulting interfacial energy difference $\Delta \gamma(f)$ of $\gamma_{MF}$ and $\gamma_{SF}$ are shown in Figure 1.10C. It is found that with increasing content of polystyrene in the random copolymer, the interfacial energy $\gamma_{SF}$ decreases while $\gamma_{MF}$ increases, and at $f=0.57$, $\gamma_{SF} = \gamma_{MF}$, indicating a neutral surface. Therefore, block copolymers of PS-\textit{b}-PMMA can potentially self-assemble on such surface to form perpendicular nano- and microdomains. This work is of significant importance as it opens up a new method to produce a neural surface that can potentially accommodate a myriad number of block copolymers.

Recently, Stein and co-workers investigated the oxidation of organo-silane coating onto a clean silicon wafer. Similar to the random copolymer brushes, hydrophobic organo-silane can assemble on the native oxide layer of a silicon substrate, and through oxidation a neutral interface can be obtained. Based on this method, the Stein group has demonstrated the perpendicular orientation of PS-\textit{b}-PMMA films in a wide range of thickness.
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Figure 1.10. (A) Scheme of PS-r-PMMA synthesis via living free-radical polymerisation. (B) Interfacial energies $\gamma_{Sf}$ (circles) and $\gamma_{Mf}$ (triangles). (C) Difference of the interfacial energies as a function of $f$. Pictures are reproduced from ref 127.

An alternative way to direct the thin film morphology is through top coating. Bates et al. introduced a more advanced technique to form lamellar features of BCP thin films based on poly(trimethylsilylstyrene)-block-polylactide (PTMSS-b-PLA) and PS-b-PTMSS-b-PS through a polarity-switching of top coats over the copolymer films. Similar to traditional surface processing of a solid substrate, the use of top coats is to render a neutral interface with non-preferential wetting to either block of BCPs. However, neutral coating materials can only be soluble in a solvent that dissolves at least one block of the BCP films. Hydrophobic BCPs such as PS-b-PTMSS-b-PS demand a top-coat out of a polar solvent, but the material can be dissolved in such solvent is too polar to have a neutral wetting to the hydrophobic blocks. To circumvent this challenge, Bates et al. developed a top-coating method that utilises a polymer with switchable polarity triggered by thermal annealing. When the coating polymer is in its polar form, it can be dissolved into aqueous ammonium hydroxide, a non-solvent for hydrophobic BCPs, permitting top-coating onto the BCPs films via spin-casting. Upon thermal annealing, the top-coats undergo a chemical decomposition giving a less polar state, as shown in Figure 1.11A. This transformation of the coating material can effectively neutralize the interface between BCP films and the top-coating polymer, enabling perpendicular features of the BCP when it is mobile (e.g. annealing above its
glass transition temperature). The top-coating layer can be stripped off, revealing amazing orientation of BCPs, as shown in the SEM images in Figure 1.11B and C.

**Figure 1.11.** (A) Polarity-switching of top-coating polymer upon thermal annealing. (B) SEM images of PTMSS-b-PLA baked at 17 °C for 20 hours with top-coating polymer. The inset shows same BCP film without top-coating. (C) SEM images of PS-b-PTMSS-b-PS baked at 210 °C for 1 min with top-coating polymer. The inset shows same BCP film without top-coating. Pictures are reproduced from ref 131.

### 1.5. Potential Application of BCP Assemblies

Biology controls shape of soft nanostructures to impart properties, hence many of the potential applications that have been developed or are in development are bioinspired. A classic example is the folding of enzymes to control a range of highly specific reactions, which has driven some of the work in protein self-assembly. Optical properties are also potentially tuned using shape, which are highlighted by the camouflage techniques of many marine and land animals. For example, the colour shift in chameleons through tuning of a lattice of guanine nanocrystals within a superficial thick layers of dermal iridophores. Inspiration from these could lead to next generation camouflage and optical derives using shape controlled nanostructures.

Nanostructures prepared from synthetic or biological building blocks have vast potential applications in drug delivery. Especially the nanoparticles assembled from BCPs where the distinctive chemistry of two sections permit controlled release of the payload. For example, Robb et al. prepared a novel drug delivery vehicles with controlled morphologies based on poly(allyl glycidyl ether)-b-poly(lactide) (PAGE-b-
PLA). As shown in Figure 1.12, the biodegradable PLA block is first functionalised with fluorescent model drug via copper catalysed azide alkyne cycloaddition “click” chemistry. Aqueous dispersion of BCP nanoparticles with phase separated interiors are obtained through solvent exchange. Upon degradation of the PLA scaffold under physiological conditions, the covalently attached model drug is released. Besides the spherical delivery vehicles, nonconventional shapes of nanoparticles have shown great promise as carrier materials especially in cancer treatments. Worm-like polymer brushes, for instance, are promising to be the next generation of delivery medium because they exhibit high tumor cell penetration in combination with long circulation times. Cylindrical micelles have also found applications in biomedicine with advantages in prolonged circulation time of their payloads. These examples also demonstrate why shape control of nanostructures is important when it comes to biomedical applications.

Figure 1.12. Example of model drug release based on PAGE-b-PLA nanoparticles. The PLA block is biodegradable. Pictures are reproduced from ref 95.
Other potential applications, along with preparation parameters and pros and cons for BCP building blocks, are tabulated in Table 1.1. We are in no doubt that with the further evolution of shape controlled soft nanoparticle even further applications will be achieved. In Table 1.1, it should be noted that the size distribution of these nanoassemblies is extremely wide, even in the same structure assembled from same materials. Moreover, the length of linear 1D assemblies formed by unimer addition often extend to micrometre. Therefore, the selected range of size of these assemblies in Table 1.1 is a representative example.

**Table 1.1.** Assembly strategies and preparation parameters in shape control for BCPs. The size of assemblies only refers to low aspect ratio structures (spheres, stars, ellipsoids). Linear 1D assemblies have extreme aspect ratio and the length of which can extend to micrometer scale.

<table>
<thead>
<tr>
<th>Assembly Strategy</th>
<th>Example of Assembled Structures</th>
<th>Range of Size (nm)</th>
<th>Representative Materials Used</th>
<th>Pros and Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>geometry-driven</td>
<td>rods,15 toroid,27 spheres,16 vesicles16</td>
<td>~80-400</td>
<td>amphiphilic copolymers, such as PAA-b-PMA-b-PS</td>
<td>Pros: large library of available BCPs, versatile chemical modification</td>
</tr>
<tr>
<td>crystallisation-driven</td>
<td>dots,56 rods,17 stars,59 irregular46</td>
<td>micrometers</td>
<td>crystalline blocks, such as PCL, PFS</td>
<td></td>
</tr>
<tr>
<td>multigeometry</td>
<td>spheres,75 worm-like18,79</td>
<td>~50-100</td>
<td>pairs of copolymers, such as PAA-b-PI+PS-b-PAA</td>
<td>Cons: deviated assemblies, inconsistent in morphologies</td>
</tr>
<tr>
<td>interfacial-driven</td>
<td>onion-like,108 stacked lamellae88</td>
<td>~100-500</td>
<td>hydrophobic copolymers, such as P2VP-b-PS</td>
<td></td>
</tr>
</tbody>
</table>
1.6. Thesis Scope

The development of nanoarchitectures and shape-controlled nanoparticles are highly promising for a variety of innovative applications in many different areas. In bulk, the nanostructures of BCP assemblies relies on the incompatibility of the two chemically distinct blocks. In comparison, self-assembly of BCPs into nanoparticles and thin films represents higher complexity. The interactions between polymer chains and the surrounding mediums provide additional room for manipulation. In this thesis, we focus on both modification of BCPs at molecular level and their supramolecular interactions at interfaces to tune the nanostructures of BCP assemblies.

Chapter 2 provides an overview of characterisation techniques that have been used in this thesis and briefly introduces the fundamental theories of these instrumentations. In Chapter 3, we describe the synthesis of a series of BCPs with targeted molecular weights and their subsequent self-assembly behaviour. This chapter also provides experimental details in copolymer synthesis and functionalisation to obtain the desired properties that can facilitate the self-assembly. An advanced control of molecular weight distribution (MWD) of BCPs through modular synthetic technique is introduced in Chapter 4. In this chapter, the parameters to describe a MWD are discussed in depth and their influences on self-assembled nanostructures are demonstrated. Chapter 5 describes a morphological evolution of BCPs nanoparticles controlled by interfacial properties. A nonconventional yet highly ordered morphology is reported in this work. Chapter 6 summarises the results and conclusions that derived from this research project. This chapter also provides an outlook and further perspectives to tuning of BCPs nanoassemblies.
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2.1. Aim

This chapter aims to provide a description of the mechanics and theoretical principles that underlying the instrumentation and techniques used in this thesis. Due to the nature of the research of polymeric nanoparticles, advanced microscopy is the most prevalent technique to reveal the nanoarrangement. Spectroscopic techniques are also crucial to understand structure property relationships. Detailed methodologies for the instruments are described in the respective sections below, and experimental protocols are described in the appropriate result chapters.

2.2. Transmission Electron Microscopy

In nanoparticle studies where the structures are too small to be well observed with an optical microscope, transmission electron microscopy (TEM) is often utilised due to its super-high resolution. Similar to visible-light microscopy, a typical TEM is composed of a source, a condenser, an objective and a projector. However, in TEM or other EM the source is an electron gun generating electrons at high voltages (above 100 kV) wherein the wavelength of electrons is governed by the acceleration voltage. Another difference when compared to a conventional optical microscope is that the lenses are electro-magnetic coils instead of glass lenses. The dispersion of the electron beam is restrained in a central column and deflected by the electro-magnetic coils. The beam is then concentrated by the condenser and subsequently focused on the object by objective lens. The transmitted electrons pass through the object and the projector visualises the object on a fluorescent screen. The column and the inner compartment of TEM are vacuumed in order to minimise the overheating from the collisions between ambient gas and electron beam. A schematic illustration of TEM layout and the comparison with conventional optical microscope and scanning electron microscope are shown in Figure 2.1.
Figure 2.1. Schematic illustration of a conventional optical microscope (left), transmission electron microscope (middle) and scanning electron microscope (right). The respective theoretical resolutions are indicated at the bottom of the diagram.

The image resolution of TEM can be described by the classic Rayleigh criterion for visible-light microscope which approximates the resolution limit, $\delta$, as shown in Equation 2.1,

$$\delta = \frac{0.61\lambda}{\mu \sin \beta}$$

where $\lambda$ is the wavelength of the electrons, $\mu$ is the refractive index of the medium, and $\beta$ is the semi-angle of collection of the magnifying lens. The wavelength of electrons is inversely proportional to the square root of electron volts, and thus electrons generated at high voltage often permit theoretical resolution in atomic size. However, there are also a number of limitations of the TEM, for instance, higher resolution often limits the sampling abilities of the device, i.e., only a small part of specimen can be observed at any one time. Therefore, in this thesis visible-light microscope is also used to provide a bigger picture of samples. Another limitation is that the TEM image presents a 2D projection of 3D specimens and thus causes difficulties in interpretation.
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To circumvent this disadvantage, one can perform cryo-TEM at tilted angle and subsequently reconstruct the 3D model of a sample.\(^3\)\(^4\)

As for the sample preparation, the object is usually casted on a specialised thin substrate (such as TEM grids). When the incident electron beam encounter atoms with a heavy atomic nucleus, electrons rebound or absorbed in these regions. On the other hand, the lighter materials allow the incident electrons to traverse and reach the scintillator plate. This provides contrast of different phases within the object when the scintillator plate converts incoming electrons to light. In the captured imaged, the brighter areas represents thinner section whereas the darker areas represent the thicker section of a sample. Because of this, sample staining with heavy metals or other materials are often necessary to enhance the contrast of the characteristic structures. In this thesis, iodine is used to stain the pyridine groups in the nanoparticle sample (Chapter 3 and 5) due to their preferential interactions. In Chapter 4, osmium tetroxide is used to stain polyisoprene through cross-linking. Detailed sample preparation protocol is described in the respective chapters.

2.3. Scanning Electron Microscopy

While TEM gives a 2D projection of specimen, scanning electron microscope (SEM) is often used to probe the surface structure of a sample. Similar to TEM, a typical SEM also consists of a source, a condenser and an objective. When SEM is in operation, primary electrons from the source bombard the object through scan coils according to certain scanning pattern and subsequently generates secondary electrons. It is the number and velocity of these secondary electrons that co-determines the height and slope of the sample surface. The energy of secondary electrons are detected and converted into photons (Figure 2.1, right) and then the luminescence signal is amplified and transduced to video signal. The final image is processed digitally by a computer giving a shadow-cast review of sample surface. Apart from secondary electrons, there are back-scatter electrons emitted from object surface that indicates the hardness of surface material. In comparison with TEM, a SEM sample often requires gold-coating to enhance the surface conductivity before imaging. To achieve this, the sample is firstly glued to a metal substrate and then mounted on a sample holder. The sample chamber, which is the heart of the microscope, is vacuumed to avoid collisions between electrons and ambient gas.
In this thesis, SEM (XL30 Philips FESEM) was applied in Chapter 5 to probe the surface and overall arrangement of polymeric nanoparticles. Detailed sample preparation is described in the Chapter 5 experimental section.

**2.4. Atomic Force Microscopy**

As a type of scanning probe microscopy, atomic force microscopy (AFM) is composed of a cantilever with an extremely sharp tip located at its free end. The mode of TEM scanning can be chosen from tapping or contact mode, and the medium of scanning is either water or air. In contact mode, the probing tip remains constant contact with the specimen surface during imaging under certain repulsive force that exerted by the piezoelectric positioning element. The deflection of cantilever is maintained constant by the z-piezo positioning device as the tip is raster scanned across sample surface. The raster scan produces the height information of each line and through the scanning in the xy-plane, an image of topography can be obtained by stacking the individual lines.

In contrast, tapping mode allows intermittent contact when the tip scans across the sample surface. During operation, the tip is oscillated by an actuator piezo at or near its resonance frequency. The feedback control loop maintains the amplitude of the tip at the desired value. Because of the interactions between the probing tip and specimen surface, the force exerted on the tip is deviated according to the surface topography. This deflection of cantilever due to the change of interactions is monitored by a laser spot, which is reflected to a position sensitive photodetector. Figure 2.2 schematically illustrates the key elements of the AFM.
Figure 2.2. Schematic diagram of the AFM using beam deflection detection. The amplitude of the cantilever-tip system is controlled at fixed value when it scans in tapping mode.

In the work of Chapter 3 and 4, tapping mode in air is applied to probe the surface morphology of polymeric thin films. In comparison to contact mode, tapping mode is advantageous as the intermittent contact may reduce the adhesion of sample materials on the tip especially when a soft material is being examined. Since the cantilever tip has a radius of curvature in the nanoscale, any adhesion between tip and sampler material would significantly reduce the resolution and causes defects and artefacts during imaging.

2.5. Dynamic Light Scattering

Dynamic light scattering (DLS), also known as photon correlation spectroscopy, is a technique that can be used to determine the size and geometrical structure of particles dispersed in suspension. Upon incident of a monochromatic light beam (such as a laser) to a solution, the dispersed spherical particles cause a time-dependent change in scattered intensity due to their Brownian motion. This change is measured by a photomultiplier to give a variation of voltage, which reflects the size distribution of particles. The scattering fluctuations are analysed by an autocorrelation function, which is described by Equation 2.2,
where $g$ is the dimensionless correlation function at a particular decay time, $\tau$, and $I$ is the intensity.\(^6\) Once the data of $g$ is generated, various numerical approaches can be employed to interpret the size information of the measured particles. As an example, the autocorrelation function can be treated as a single exponential decay with the decay rate given by:

$$\Gamma = q^2 D_t$$ \hspace{1cm} (2.3)

where $\Gamma$ is the decay rate, $D_t$ is the translational diffusion coefficient and $q$ is the magnitude of scattering wave vector, $q$, which is given by the equation below:

$$q = |\mathbf{q}| = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right)$$ \hspace{1cm} (2.4)

where $\lambda$ is the wavelength of incident laser, $n$ is the refractive index and $\theta$ is the scattering angle. For spherical particles, the diffusion coefficient is related to particle diameter, $d$, by Stoke-Einstein relation, which is shown in Equation 2.5,

$$D_t = \frac{k_B T}{3\pi \eta d}$$ \hspace{1cm} (2.5)

where $k_B$ is Boltzmann’s constant, $T$ is the temperature and $\eta$ is the viscosity of medium. From the measurement of $g$, the diffusion coefficient can be obtained and thus the corresponding radius of particles can be determined. This technique can also be applied to determine other parameters of interest, such as radius of gyration of polymer molecules or its concentration in a medium.\(^9\)

In the work of BCP self-assembly in solution, particle size or its hydrodynamic radius is an important factor that affects its functionality. Although the size of individual particle is shown in the image studies (such as TEM and SEM), DLS provides an overall of size distribution and examines a much larger population of nanoparticles at a time. In this thesis, DLS technique (Zetasizer Nano ZS, Malvern) has been utilised to determine the size profile of self-assembled BCP nanoparticles (see Chapter 5).
2.6. Ultraviolet-Visible Spectroscopy

The ultraviolet-visible (UV-Vis) spectroscopy is a widely used technique to characterise chemical compounds based on their absorption spectra. A UV-Vis spectrometer utilises light in the visible and ultraviolet region of the electromagnetic spectrum and thus it is typically equipped with double beam source: one light source provides long wavelength ranging from 800 to 400 nm and the other incident light has short wavelength (400-200 nm). The instrument is composed of a monochromator, a sample cell and a detector. The incident light beam passing through the entrance slit is collimated and directed to a moveable diffraction grating, which reflects the selected wavelength to the exit slit through its programmed movement. This monochromatic beam is then split by the half minor passing through a reference and a sample respectively. When the wavelength of the applied beam passing through the sample is varied, an absorption spectrum can be produced. The diagrammatic illustration of a typical UV-Vis spectrometer is shown in Figure 2.3.

![Diagrammatic illustration of a double beam UV-Vis spectrometer consisting of a monochromator (diffraction grating unit), a sample cell and detectors.](image)

**Figure 2.3.** Diagrammatic illustration of a double beam UV-Vis spectrometer consisting of a monochromator (diffraction grating unit), a sample cell and detectors.
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In a sample characterisation, the chemical compound absorbs photons at specific wavelength to excite the electrons from ground to excited state. Because of the absorption of the photons, the intensity of the transmitted light is reduced, which is described by Beer-Lamber Law:

\[ A(\lambda) = -\log_{10} \frac{I}{I_0} \]

where \( A \) is the wavelength-dependant absorbance of light, which measures the light intensity passing through a sample \( I \) and compares it to the intensity of original incident light before passing through a sample \( I_0 \). The ratio of which is referred the transmittance. Depending on the characterisation purpose, this instrument can also be configured to measure the reflectance of light. In this case, the intensity of light reflected from a sample is measured instead of the absorbed light. In this thesis, a UV-Vis spectrometer (Cintra 2020, GBC Scientific Equipment) is utilised to identify the removal of end group of a functionalised copolymer (see Chapter 3).

2.7. Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is facile and powerful technique to elucidate chemical structures based on the magnetic properties of certain atomic nuclei. It relies on the nuclear magnetic resonance phenomenon of the magnetically active nuclei when exposed to an external magnetic field.\(^\text{10}\) The magnetic response of distinct nuclei is measured to determine the physical or chemical properties, structure and chemical environment of molecules. In polymer chemistry, proton \((^1\text{H})\) and carbon-13 \((^{13}\text{C})\) NMR spectroscopy are the most common spectroscopic analysis due to their abundant presence in all organic chemicals. A typical NMR spectrometer consists of a radiofrequency (RF) emitter, a RF receiver and a spinning sample holder.\(^\text{11}\)

Nuclei with an uneven number of protons and neutrons, such as \(^1\text{H}, ^{13}\text{C}\) and \(^{15}\text{N}\) exhibit nuclear spin, which possess a nuclear magnetic moment vector \((\mathbf{\mu})\) and an angular momentum \((\mathbf{P})\). They related by the equation below:

\[ \mathbf{\mu} = \gamma \mathbf{P} \]

where \( \gamma \) is the magnetogyric ratio of nuclei. Because of the quantum mechanical property of the nuclear spin, the number of observable spin energy level is given by \((2I+1)\), where \( I \) is the quantum number of spin. When the nuclei are subjected to an
external magnetic field ($B_0$), the magnitude of $\mathbf{P}$ in the $z$-axis ($P_z$), which aligns with the magnetic field, is described by:

$$P_z = m \frac{\hbar}{2\pi}$$

where $m$ is magnetic quantum number and $\hbar$ is the Planck constant. In case of $^1$H NMR spectroscopy, there are two spin states, namely $m=\pm 1/2$. The energy difference ($\Delta E$) between the two spin states increases while the strength of magnetic field increases, however this difference is usually small. Its value is proportional to the Larmor frequency ($v_L$), given by:

$$v_L = \frac{\gamma B_0}{2\pi}$$

where $B_0$ is the magnitude of the external magnetic field. When the nuclei are exposed under strong magnetic field, the electrons surrounding the nuclei will respond to $B_0$ by generating an opposite magnetic field. Therefore, the effective magnetic field experienced by the nuclei is reduced to $B_{\text{eff}}$, giving an observed Larmor frequency ($v_{L,o}$) described by below equation:

$$v_{L,o} = \frac{\gamma B_0 (1 - \alpha)}{2\pi}$$

where $\alpha$ is the shielding constant dependent on the adjacent functional groups and bonding arrangement of a nucleus. Consequently, for a given atomic isotope, the nuclei under different chemical environment will exhibit different $v_L$, due to the changing of shielding constant. This can be measured by NMR spectroscopy in terms of chemical shift ($\delta$), as described by below equation:

$$\delta = 10^6 \left(\frac{v_{L,o} - v_{L,r}}{v_{L,r}}\right)$$

where $v_{L,r}$ is the Larmor frequency of a reference group with a value separated from the examined nuclei. In $^1$H NMR spectroscopy, tetramethylsilane (TMS) is usually used as the reference due to the high electron density around its protons (thus high shielding constant) and its inert chemical properties. Additionally, all protons of TMS are under the same chemical environment, and thus they exhibit a single peak on the NMR spectrum. Typically, the chemical shift values of the examined protons are in the range of 12-0 ppm while the reference is set at 0 ppm.
In this study, $^1$H NMR spectroscopy (Varian MR400) has been utilised to determine the molecular weight of the synthesised copolymers and chemical structure of other synthetic materials. It has also been used to determine the extent of reactions in a kinetic study (see Chapter 3).

### 2.8. Gel Permeation Chromatography

Gel permeation chromatography (GPC), which was invented by Moore in 1964,$^{12}$ is a technique used to determine the size of analytes based on the retention time. When a solution containing polymers passes through a packed column in GPC, the polymer molecules are separated according to their molecular weight or hydrodynamic volume. The column of GPC is packed with porous beads that allows larger analytes to elute quickly and thus results in a short retention time. On the contrary, smaller analytes can enter the pores of packing materials and hence it has more volume to traverse and takes longer time to elute.$^{13}$ This discriminative permeation process of large and small molecules is schematically illustrated in Figure 2.4.

![Figure 2.4](image)

**Figure 2.4.** GPC separation of polymers at different molecular weights. The larger polymers elute first and the smaller polymers elute last due to the porous packing material. Pictures are adapted from ref 14.

The eluted analytes can be measured by various detectors, such as UV absorption, infrared (IR) absorption and refractive index (RI) detector. These detectors are concentration sensitive and requires a calibration based on certain standards to calculate the molecular weights of analytes. There are other detectors such as light scattering and
viscosity detectors, which are molecular weight sensitive. As for the viscosity detectors, the molecular weight of analytes can be determined from Mark-Houwink function,

\[ [\eta] = KM_w^a \]  \hspace{1cm} 2.12

where \([\eta]\) is the intrinsic viscosity, \(a\) and \(K\) are Mark-Houwink parameters dependent on the polymer-solvent system. Regarding the light scattering detector, it correlates the molecular weight of analyte to its concentration, \(C\), and Rayleigh ratio, \(R_\theta\), which is described by below equation when the scattering angle and concentration are small:

\[ \frac{K_{GPC}C}{R_\theta} = \frac{1}{M_w} + 2A_2C \]  \hspace{1cm} 2.13

where \(A_2\) is the second virial coefficient and \(K_{GPC}\) is a constant coefficient depending on equipment. Various mobile phase can be applied to elute the analyte depending on the compatibility between polymers and solutions.

In this thesis, GPC chromatography is used to determine the molecular weight of synthesised polymers (sees Chapter 3 and 4) using RI detectors. The GPC is calibrated based on polystyrene standards.
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Chapter 3 — Synthesis of Block Copolymer at Targeted Molecular Weights and Its Subsequent Self-Assembly
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3.1. Aim

This chapter is focused on the synthesis of PS-\textit{b}-P2VP with desired polymer composition and their subsequent self-assembly in both solution and thin film systems. The aim of this work is to explore the morphological transition of PS-\textit{b}-P2VP assemblies with respect to the change of polymer composition. In addition, this chapter also describes the end group modification of the copolymer, and the effect this has on self-assembly can be probed.

3.2. Introduction

The self-assembly process of BCPs is driven by a small mixing entropy and an unfavorable mixing enthalpy, while the two chemically distinct blocks are connected by a covalent bond.\textsuperscript{1} In bulk, the microphase separation of BCP assemblies is dependent on parameters such as Flory-Huggins parameter (also known as $x$-parameter) and copolymer composition.\textsuperscript{2} Regarding the copolymer composition, both block ratio and total degree of polymerisation ($N$) play a role in self-assembly behaviour. The product of $N$ and $x$-parameter determines the degree of microphase separation and thus it can influence the final structure of BCP assemblies. This incompatibility between the constituent blocks also affects the self-assembly of BCPs in solution or thin film systems. In comparison to bulk systems, self-assembly in solution or thin film permits the use of interactions between copolymer and surrounding medium to control the assembled nanostructures. Thus, the synthetic chemistry, functionalisation and modification of BCPs all play a role in controlling the self-assembly of BCPs.

To access BCPs with targeted copolymer composition, it is often achieved through controlled polymerisation, such as RAFT chemistry. In comparison to other free radical polymerisation techniques, RAFT polymerisation has enjoyed a considerable popularity for the preparation of functional BCPs due the suppressed formation of dead polymers and good compatibility with a variety of monomers and reaction media.\textsuperscript{3} BCPs are synthesised in a two-step sequential polymerisation through chain extension of a macro-RAFT agent. With careful control of reaction conditions, di-BCPs can be obtained at desired molecular weight. This allows the studies to explore the morphological evolution of BCP assemblies with respect to the change of copolymer composition. Furthermore, RAFT polymerisation is regarded as the most versatile technique as the thiocarbonylthio group provides additional room for post-
polymerisation modification. The functionalisation of the RAFT end group opens up new opportunity in molecular design and thus expands the toolbox in controlling the nanostructure of BCP assemblies. For instance, the end of the copolymer chain can be functionalised through reactions with nucleophiles or removed completely through thermolysis. This functional handle can be utilised to modify the properties of copolymer, which may affect the self-assembly behaviour of BCPs. In this study, a series of PS-\textit{b}-P2VP were synthesised with controlled molecular weights through RAFT polymerisation and we investigated their morphological evolution in both solution and thin film systems.

3.3. Experimental

3.3.1. Materials

Styrene (99\%) and 2-vinylpyridine (97\%) monomers were purchased from Alfa Aesar and Sigma-Aldrich respectively. Both monomers were stabilised with 0.1wt-\% 4-\textit{tert}-butylcatechol. The inhibitor remover dedicated to 4-\textit{tert}-butylcatechol was purchased from Sigma-Aldrich. Cetyltrimethylammonium bromide (CTAB, \(\geq\)99\%), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPPA, \(\geq\)97\%), 2-(dodecyl thiocarbonothioylthio)-2-methylpropionic acid (DTMPA, 98\%), and 2,2’-azobis(2-methylpropionitrile) (AIBN, 98\%) were also purchased from Sigma-Aldrich. Propylamine (98\%) was purchased from Merck. THF (AR Grade, stabilised with butylated hydroxytoluene), dichloromethane (DCM, AR Grade) and methanol (99.8\%) were obtained from Chem-Supply. Toluene (99.9\%) and dimethylformamide (DMF, \(\geq\)99.9\%) were both purchased from VWR Chemicals. Chloroform (99.8\%), diethyl ether (99.7\%) and \textit{n}-hexane (95\%) were purchased from RCI Labscan. TEM grids (Cu, 200 mesh with formvar coating) and silicon wafers were purchased from ProSciTech and ePAK, respectively.

3.3.2. Synthesis of PS-\textit{b}-P2VP

An example of the synthesis procedure followed for the preparation of a series of PS-\textit{b}-P2VP copolymers at desired degree of polymerisation (DP) is described below. Polystyrene block was synthesised first and then followed by the chain extension with 2-vinylpyridine through sequential RAFT polymerisation. The monomer to chain transfer agent (CTA) ratio in the polymerisation was controlled to give polymers at desired DP. In an example of PS-macroRAFT CTA synthesis, styrene (21.14 g, 203
mmol), CPPA (11.3 mg, 0.04 mmol) and AIBN (2 mg, 0.01 mmol) were mixed in a 200 mL Schlenk tube reactor equipped with a magnetic stirrer. 20 mL of DMF was charged into the reactor to dilute the reactant. The solution was degassed through three cycles of freeze-pump-thaw followed by back filling of nitrogen. The reactant was subsequently immersed in an oil bath equipped with a heating plate to allow the polymerisation to take place. The temperature of oil bath was controlled at 80 °C for 20 hours to synthesise the PS-macroRAFT CTA with desired DP. At the end of polymerisation, the Schlenk tube was placed in a water bath at room temperature to quench the reaction. The viscous mixture was diluted with THF and subsequently added into excess methanol under constant stirring to separate the polymer. The precipitation process was repeated twice to ensure all unreacted monomers were removed. The collected polymer was vacuum dried for 24 hour and then stored in a refrigerator before further chain extension. The molecular weight and dispersity ($D$) of synthesised PS-macroRAFT CTA was determined by GPC chromatography (LC-20AD with RID-10A detector, Shimadzu).

In the second stage, the synthesised PS-macroRAFT CTA (2.69 g, 0.03 mol, $M_n=90.8 \text{ kg mol}^{-1}$) was first dissolved in DMF (20 mL) and the solution was charged into a 200 mL Schlenk tube reactor. 2-vinylpyridine (15.54 g, 0.147 mol) and AIBN (1.5 mg, 0.009 mmol) were subsequently added into the reactor. After sufficient mixing, the tube reactor was degassed through three cycles of freeze-pump-thaw followed by backing filling of nitrogen. The chain extension of polymer started when the reactor was immersed in an oil bath thermostated at 80 °C. Depending on the targeted molecular weight, the reaction time was prescribed for 15 to 22 hours. At the end of polymerisation, PS-$b$-P2VP was collected through precipitation by slowly adding the solution into excess n-hexane or diethyl ether under constant stirring. This process was repeated twice to ensure all monomers were filtered. The molecular weight of P2VP block was determined by NMR spectrum provided the PS block was predetermined. The synthesised copolymers were vacuum dried before further functionalisation or direct use in self-assembly. It should be noted that all monomers were processed to remove the inhibitor by passing through a packed column before use. All solvents were used as received unless otherwise stated.
Chapter 3

3.3.3. Functionalisation of PS-b-P2VP

The RAFT end group of PS-b-P2VP was removed through either hydrolysis or reaction with nucleophiles (aminolysis). As an example, 1.43 g of PS79k-b-P2VP132k (1 eqv.) was dissolved in 14.3 mL of DCM in a 5 mL round bottom flask. After dissolving the copolymer, 10 µL of propylamine (0.122 mmol, 20 eqv.) was charged into the flask. The nucleophilic reaction took place under Ar protection at room temperature for 48 hours. At the completion of reaction, the end group removed copolymers were collected through standard precipitation procedure using either n-hexane or diethyl ether as non-solvent. The GPC analysis was performed for the collected copolymers to ensure that the thiols formed were not oxidised to disulfides. The removal of RAFT end group was determined by UV-Vis spectroscopy.

3.3.4. Preparation of PS-b-P2VP Nanoparticles

The P2VP-b-P2VP nanoparticles were prepared from an emulsion. Firstly, the copolymers were dissolved in chloroform as dispersed phase at a concentration of 1 wt-%. The continuous phase is composed of CTAB aqueous solution at a concentration of 0.5 mg mL⁻¹. 1.5 g of the dispersed phase (1 wt-% of BCP in chloroform) was added into the continuous phase and warmed at 30 °C in a water bath. The two-phase mixture was emulsified by vortexing for 1 minute followed by sonication in an ultrasound bath (VWR) for 3 minutes. The above cycle was repeated twice to make sure the emulsion was stable. In the last step, nanoparticle dispersions were prepared by evaporating chloroform under constant stirring for 48 hours in open vials in a 30 °C water bath. The particle dispersions were purified through centrifugation at 3000 rcf for 50 minutes and re-dispersed in distilled water. This centrifugation/re-dispersing cycle was repeated for 3 times to ensure all impurities were removed.

3.3.5. Preparation of PS-b-P2VP Thin Films

To prepare the thin films of PS-b-P2VP, the copolymers were first dissolved in toluene at a concentration of 1 wt-%. The solution was subsequently drop-casted on a silicon substrate with a size of 1 cm² placed in a chamber under toluene atmosphere. The slow evaporation of toluene under such atmosphere permitted rearrangement of copolymer nanostructures in thin films. After the thin films became completely dry, their surface morphology was characterised using AFM (Asylum Research Cypher).
3.3.6. Sample Preparation for TEM Imaging

Once the nanoparticle suspensions were purified through centrifugation and re-dispersion, nanoparticles were drop-casted on a small copper grid with formvar films specialised for TEM imaging. The population of nanoparticles on TEM grid was directly proportional to the concentration of nanoparticles dispersed in suspensions. After the casted TEM grids became completely dry, these nanoparticles were stained in a specialised chamber with iodine atmosphere. Typically the staining process took 8 minutes to obtain satisfactory phase contrast under TEM giving a dark colour of P2VP domain.

3.4. Results and Discussion

3.4.1. Synthesis of PS-\textit{b}-P2VP with Controlled Molecular Weight

A series of PS-\textit{b}-P2VP copolymers were synthesised with targeted molecular weights through RAFT polymerisation. Two RAFT agents (DTMPA and CPPA) were used to synthesise the BCPs; however, only CPPA was used to synthesise the copolymer for end group functionalisation because it is easy to hydrolyse its thiocarbonylthio group. The two-step synthesis of PS-\textit{b}-P2VP using CPPA as RAFT agent is shown in Scheme 3.1. It has been reported that at high conversion (above 70%) of monomers, there is a prevalence of dead chain contaminants in macroRAFT agents. Although there are other reports demonstrating relatively low $D$ at high conversions, careful control to maintain monodispersity is necessary. Therefore, the monomer is added in excess and its conversion is carefully monitored. To achieve this, samples of reactant were extracted periodically for NMR spectroscopic analysis. An example of calculation to determine monomer conversion based on NMR spectrum is shown in Figure 3.1. Based on the plot of polymerisation rate, the targeted molecular weight can be achieved by terminating the reaction at an appropriate time. A linear best fit line of the rate plot has been drawn, which represents a pseudo-first-order polymerisation of PS-macroRAFT CTA. A brief induction period has been observed since the best fit line intersects with the horizontal axis at approximately 0.3 hour (inset of Figure 3.1). This induction period in RAFT polymerisation has been widely reported with different polymer systems, and it is particularly common when certain RAFT agent (such as cumyl dithiobenzoate) is employed in the synthesis.
Scheme 3.1. Sequential synthesis of PS-\textit{b}-P2VP at desired molecular weight through RAFT polymerisation. CPPA is used as an example of RAFT agent.

\[
\text{Conversion} = \frac{1}{4.66 + 1} = 17.7\%
\]

Figure 3.1. An example of NMR spectrum of PS-macroRAFT CTA for the calculation of reaction conversion. The inset shows a plot of pseudo-first-order polymerisation rate for PS-macroRAFT CTA synthesis.
Based on the sequential RAFT polymerisation, a series of PS-\textit{b}-P2VP copolymers have been synthesised. Table 3.1 shows the summary of BCPs used in self-assembly with details in molecular weights of each block. The molecular weight of PS-macroRAFT CTA was predetermined through GPC analysis before its chain extension with 2-vinylpyridine. The GPC chromatogram also gives the total molecular weight of copolymers when the synthesised copolymer is tested; however, there is a significant difference when compared to the results obtained from NMR analysis. This error in molecular weight is attributed to the calibration standards. The incorporation of P2VP block to polystyrene deviates the determined molecular weights from its true value since the GPC is calibrated based on polystyrene standards. Therefore, NMR analysis is employed to determine the molecular weight of synthesised copolymers, an example of which is shown in Figure 3.2. The NMR spectrum does not show the molecular weight of copolymers directly, but it gives the ratio of block abundance. Consequently, the block weight of P2VP can be calculated as the weight of PS block is predetermined by GPC analysis. The inset of Figure 3.2 compares the GPC chromatograms of PS-macroRAFT CTA and its subsequent copolymer after chain extension with 2-vinylpyridine. The \( D \) of each copolymer is determined by GPC analysis using DMF as the mobile phase. NMR spectra of other synthesised copolymers are shown in Appendix A.

<table>
<thead>
<tr>
<th>Entry</th>
<th>( M_n ) of PS kg mol(^{-1})</th>
<th>( M_n ) of P2VP kg mol(^{-1})</th>
<th>Total ( M_n ) kg mol(^{-1})</th>
<th>PS fraction ( f_{PS} ) (%)</th>
<th>( D )</th>
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</thead>
<tbody>
<tr>
<td>P1</td>
<td>13.5</td>
<td>47.0</td>
<td>60.5</td>
<td>22.3</td>
<td>1.12</td>
</tr>
<tr>
<td>P2</td>
<td>78.8</td>
<td>127.0</td>
<td>206.0</td>
<td>38.3</td>
<td>1.53</td>
</tr>
<tr>
<td>P3</td>
<td>27.0</td>
<td>33.8</td>
<td>60.8</td>
<td>44.4</td>
<td>1.47</td>
</tr>
<tr>
<td>P4</td>
<td>90.8</td>
<td>35.6</td>
<td>126.4</td>
<td>71.8</td>
<td>1.41</td>
</tr>
<tr>
<td>P5</td>
<td>25.0</td>
<td>25.0</td>
<td>50.0</td>
<td>50.0</td>
<td>1.44</td>
</tr>
</tbody>
</table>

Table 3.1. Summary of the synthesised PS-\textit{b}-P2VP that used in self-assembly and further modification. N.B: P1 is a commercial sample purchased from Polymer Source.
Figure 3.2. An example of NMR spectrum of PS-\(b\)-P2VP (P4) with the calculation to determine the block weight ratio of PS and P2VP, where “m” denotes the DP of P2VP block and “n” denotes the DP of PS block. An example of GPC chromatogram for PS-macroRAFT CTA and its subsequent PS-\(b\)-P2VP (P4) is shown in the inset.

3.4.2. Influence of Block Ratio on Self-Assembly

Before further modifications, these synthesised BCPs were used to self-assemble into both nanoparticles and thin films with aims to explore the influence of weight fraction of each block on final nanostructures. In amphiphilic BCPs, the correlation between morphologies and block ratio has been widely reported.\(^{14-17}\) Therefore, it is of interest to investigate the influence of weight fraction of each block on the self-assembly of fully hydrophobic BCPs. The copolymers tabulated in Table 3.1 were self-assembled into nanoparticles using emulsion techniques and subsequently taken to TEM imaging, as shown in Figure 3.3. With the smallest weight fraction of PS block (P1, \(f_{\text{PS}}=22.3\%\)), it forms a particle with PS spheres dispersed in P2VP matrix (Figure 3.3a). In direct contrast, the copolymer with largest fraction of PS block (P4, \(f_{\text{PS}}=71.8\%\)) self-assembles into nanoparticles with P2VP spheres dispersed in PS matrix (Figure 3.3d). This transition corresponding to the change of \(f_{\text{PS}}\) is expected since the dominant block typically forms the matrix. Nevertheless, the format of dispersion of
minor block in the two cases is different: PS spheres form an ordered, hexagonal-like pattern in a nanoparticle whereas in the latter case P2VP spheres are randomly dispersed in the particle. It is also noticeable that in the latter case, the nanoparticles all have a relatively large area of dark spot within the nanoconfinement. This type of defects are commonly found when the organic solvent evaporated too fast during the preparation of nanoparticles. When the weight fraction of the two blocks is relatively close to each other, the formed nanoparticles show onion-like interior. In the Figure 3.3b, the onion-like interior is skewed, which is attributed to the fact that the $f_{PS}$ is not large enough to afford a well-defined onion-like structure. At a higher fraction of PS, where $f_{PS}=44.4\%$ (Figure 3.3c), highly ordered onion-like spheres are observed.

In this work, when the influence of weight fraction of each block is explored, the overall molecular weight of each copolymer is not controlled. However, Bates and co-workers produced a phase diagram for copolymers demonstrating that the morphological evolution with respect to the change of block ratio is by and large independent on the overall molecular weight of copolymers.\textsuperscript{14} The increase in overall weight may change the cut-off value of $f_{PS}$ for structural transition, but the general trend of evolution is consistent for a wide range of molecular weight. Moreover, Hawker and co-workers also demonstrated the consistency in morphology evolution of BCP nanoparticles driven by interfacial properties when the overall molecular weight of copolymers is varied.\textsuperscript{18} Therefore, we postulate that if the molecular weight of the copolymers is controlled, a similar structural evolution (Figure 3.3) would be observed but the structural transition may take place at a different block ratio.
Figure 3.3. TEM images of nanoparticles assembled from PS-b-P2VP with varied $f_{PS}$. (a) is assembled from P1 where $f_{PS} = 22.3\%$; (b) is assembled from P2 where $f_{PS} = 38.3\%$; (c) is assembled from P3 where $f_{PS} = 44.4\%$; (d) is assembled from P4 where $f_{PS} = 71.8\%$. All nanoparticles are prepared through emulsion techniques using CTAB as sole surfactants. P2VP block is stained by iodine showing dark colour whereas PS show block shows grey colour. All scale bars are equal to 100 nm.

We also investigated the morphological transition of nanoparticles with respect to the change of interfacial properties, as demonstrated in Figure 3.4. The interface between BCP nanoparticles and surrounding mediums were tuned using two different surfactants, namely CTAB and hydroxy functionalised CTAB (HO-CTAB). When P4 is assembled into particles using different surfactants, there is no obvious structural evolution observed. On the other hand, nanoparticles of P3 demonstrate a slight change in phase separated interior when emulsified by different surfactants. At 100\% of CTAB, the nanoparticles form well-defined onion-like spheres; after introducing HO-CTAB in the surfactant mixture, the formed structures become disorganised, as shown in the inset of Figure 3.4C(ii).
Figure 3.4. TEM images of PS-\(b\)-P2VP nanoparticles produced through control of interfacial properties. (A) Nanoparticles produced through emulsification using CTAB as sole surfactant. (B) Emulsified using both CTAB and HO-CTAB at a ratio of 1:1. (C) Emulsified using HO-CTAB as sole surfactant. Top samples are prepared from high overall molecular weight (\(P_4\), \(M_n = 126.4\) kg mol\(^{-1}\), \(f_{PS} = 71.8\%\)); bottom samples are prepared from low overall molecular weight (\(P_3\), \(M_n = 60.8\) kg mol\(^{-1}\), \(f_{PS} = 44.4\%\)). Insets of A(ii) and C(ii) show the schematic morphology of the corresponding nanoparticles. P2VP block is stained by iodine showing dark colour whereas PS block shows grey colour. Scale bars: A(i) = 200 nm; B(i) = 200 nm; C(i) = 500 nm; A(ii) = 100 nm; B(ii) = 100 nm; C(ii) = 100 nm.

It is noteworthy that in both cases the observed morphological evolutions deviate from what is reported previously when same polymer chemistry and surfactants are utilised.\(^{18}\) This inconsistency may be ascribed to the RAFT end group of the synthesised copolymers as it has been proved that end group significantly influences the functionality of copolymers.\(^5\), \(^{19}\) Furthermore, the \(D\) also affects the self-assembly behaviour, which is discussed in details in Chapter 4. While the morphology of \(P_3\) shows a change with respect to interfacial properties, \(P_4\) is not perturbed to the tuning of interface. We postulate that the interior phase separation of copolymer with higher
molecular weight mainly relies on its packing parameter or polymer composition and is less sensitive to the interface between copolymer and the surrounding medium.

In thin films, the fabricated nanopattern of BCP assemblies is of particular interest due to its vast applications in emerging nanotechnologies.\textsuperscript{20-23} The control of such nanopattern effectively relies on the weight ratio of the constituent blocks.\textsuperscript{24-26} For this reason, the synthesised copolymers with varied $f_{PS}$ were self-assembled into thin films to identify the window of PS fraction for structural transition. The thin films were prepared by drop-casting of copolymer solutions and characterised using AFM in tapping mode. The thickness of thin films is measured to be ca. 20 nm using AFM to scan across the interface between empty substrate and the edge of thin films. As demonstrated in Figure 3.5, the increase in $f_{PS}$ results in a morphological evolution from long lamellae to worm-like morphology with shorter section length. Unlike traditional perpendicularly oriented structures, the worm-like morphologies obtained from this study show a relatively disorganised arrangement with short and discrete sections. Although all thin films are prepared from copolymers with similar molecular weight, \textbf{P1} is a commercial sample with much smaller $D$ in comparison to other synthesised copolymers. Therefore this transition from an ordered lamellae to disorganised worm-like morphology may be attributed to the synergy effect of increased $D$ and varied $f_{PS}$. The influence of varied $D$ on self-assembly behaviour is investigated and discussed in Chapter 4. The preparation of these thin films may result in topographical artefacts as solvent annealing with toluene favours PS block to migrate polymer-air interface. Therefore, alternative preparation process may be of interest in the future studies.

\textbf{Figure 3.5.} Phase retrace AFM images of PS-\textit{b}-P2VP thin films. (a) Prepared from \textbf{P1}, where $f_{PS} = 22.3\%$; (b) prepared from \textbf{P3}, where $f_{PS} = 44.4\%$; (c) prepared from \textbf{P5}, where $f_{PS} = 50.0\%$. All copolymers have similar overall molecular weight.
3.4.3. End Group Removal of PS-\textit{b}-P2VP

The end group of copolymer chain provides an additional functional handle for innovation.\textsuperscript{5} We demonstrate an example of reaction with nucleophiles to cleave the RAFT end forming a thiol functionalised copolymer. Although styrene and 2-vinylpyridine monomers are compatible with a variety of RAFT CTA, CPPA is selected over DTMPA because it is easy to hydrolyse. The functionalisation of end group is of particular interest as it opens up new way to modify the chemical properties of copolymers. In particular, the thiol functionalised end can be used for other chemical moiety conjugation through a variety of click chemistry. The reaction scheme for end group removal is shown in Scheme 3.2.

\textbf{Scheme 3.2.} Reaction scheme to remove the RAFT end group of PS-\textit{b}-P2VP through aminolysis at room conditions under Ar atmosphere.

One of the challenges in dealing with the thiol group is the stability, as thiol can easily be oxidised to disulfides during aminolysis. The formation of disulfides not only prohibits the subsequent functional material conjugation but also doubles the molecular weight of copolymer. This essentially converts the A-B diblock copolymer to an A-B-A triblock copolymer, and hence affects the assembled nanostructures. Consequently, the reaction conditions of aminolysis is carefully controlled under Ar protection to avoid oxidation of the thiol group. Alternatively, NaBH\textsubscript{4} can be added as a reducing agent to prohibit the formation of disulfides. However, considering the subsequent precipitation process, NaBH\textsubscript{4} is not added in practise due to the difficulty in copolymer purification. UV-Vis spectrum analysis has been performed to confirm the cleavage of RAFT end group, as shown in Figure 3.6A. The inset is a UV-Vis spectrum of CPPA showing a characteristic absorbance of the thiocarbonylthio group at a wavelength of 310 nm. Clearly, the BCP after aminolysis shows no absorbance at this wavelength, which confirms the removal of the RAFT end group. The example of GPC chromatograms a copolymer (P2) before and after aminolysis shows identical
molecular weights, which indicates that the formation of disulfides is minimal (Figure 3.6B).

![Figure 3.6](image)

**Figure 3.6.** (A) UV-Vis spectrum of a copolymer after aminolysis to confirm the removal of end group. The inset shows absorbance of the RAFT end group, of which the peak is at 300 nm. (B) GPC chromatogram of a copolymer (P2) before and after end group removal.

We also tentatively investigated the influence of end group on BCP self-assembly based on P5, wherein the block weights of PS and P2VP are equal. In the nanoparticle system, the overall shape and interior morphology remain the same when self-assembled from a copolymer with end group removed. In the direct contrast, a transition of the thin film surface from worm-like morphology to standing cylinders has been
observed when the RAFT end is removed (Figure 3.7). The inconsistency of the change in the two systems may be attributed to the different interactions between copolymers and surrounding medium. Herein, we only demonstrate an example of morphology change with respect to end group. To fully understand the influence of end group chemistry on self-assembly behaviour, further investigations are necessary.

![Figure 3.7](image)

**Figure 3.7.** Phase retrace images showing the thin film morphologies of P5 prepared before (a) and after (b) end group removal. (a) gives a worm-like morphology while (b) forms standing cylinders of one block dispersed in the matrix of the other.

### 3.5. Conclusion

To summarise this study, we have synthesised a series of PS-\textit{b}-P2VP with varied polymer composition. These materials were subsequently self-assembled into both nanoparticles and thin films. Different morphologies in nanoparticle and thin film were observed at corresponding weight fraction of PS block. A reaction with nucleophiles was demonstrated to cleave the RAFT end group of copolymers and its influence on assembled nanostructures was explored with results showing a morphology change from worm-like surface to standing cylinders in thin film system. The end group is a powerful and versatile tool that can be utilised to modify copolymer chemistry. In the demonstrated example, the thiol functionalised end could be further conjugated to various reactive molecules for controlling the self-assembly and functionality of the materials.
3.6. References


Chapter 3


Chapter 4 — Self-Assembly of Block Copolymers with Skewed Molecular Weight Distribution and Controlled Dispersity
Chapter 4

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Chapter 4

4.1. Aim

In this chapter, novel block copolymers with skewed molecular weight distribution (MWD) have been investigated. The copolymers of PS-b-PI used in this work are provided by our collaborator, the Fors group from Cornell University. These materials have three types of segmental weight distribution, namely molecular weight of PS skewed to: (i) high molecular weight; (ii) low molecular weight; and (iii) no skew (normal distribution). These samples with different skewed MWD were synthesised with varied segmental dispersity of PS ranging from 1.07 to 1.52. The aim of this study is to explore the influence of MWD composition and polydispersity on the self-assembled nanostructures and their synergy effect.

4.2. Introduction

Traditionally, the distribution of polymer molecular weight is described by dispersity ($D$), which is the ratio of the weight averaged molecular weight ($M_w$) and number averaged molecular weight ($M_n$). It is well-known that the $D$ of BCPs has a profound influence on their self-assembly behaviour and chemical/physical properties; however, this parameter is not able to describe the overall shape or composition of MWD as it only represents the breadth of MWD and the relative span of molecular weights. Therefore, it is important to introduce the asymmetry factor, $A_s$, to describe the shape of the MWD. The calculation of this factor is schematically illustrated in Figure 4.1. It has been postulated that the shape of entire MWD, and not just its $D$, has a notable influence on polymer phase behaviour. It is thus of particular interest to investigate the self-assembly behaviour of BCPs when the shape of their MWD is controlled.

The research in BCP self-assembly relies on the development of well-controlled synthetic techniques. However, the majority of these techniques, such as controlled termination processes, pulsed initiation through photolysis, controlled monomer to initiator addition ratio and varying the flowrates of monomer or initiator in a continuous flow reactor, only afford partial control over the relative breadth of MWD in living polymerisation. To realise fully the regulation of MWD shape, new strategies are needed in the synthesis processes. Recently, the Fors Group reported a modular synthetic strategy to prepare polymers with deterministic control of MWD through temporal regulation of initiation in nitroxide-mediated polymerisation or anionic
polymerisation.\textsuperscript{16} This synthetic technique largely replaces the traditional polymer blending strategy\textsuperscript{1, 17} to control the shape of MWD, which allows a continuous distribution of molecular weights and block compositions. With this technique, it becomes easier to access materials with particularly shaped MWD and thus promotes the research of their subsequent self-assembly.

\textbf{Figure 4.1.} Graphical illustration of calculation of asymmetry factor, $A_s$, where $\text{peak height}$ and $B$ are at 10% peak height. The GPC trace is partitioned at peak molecular weight ($M_p$). The example of GPC chromatogram used in the figure is from PS-$b$-PI copolymers with an overall $M_n$ of 59.7 kg mol$^{-1}$ and skewed to low molecular weight.

The study of BCP self-assembly generally requires a well-defined and narrow MWD when exploiting their nanostructures. In the polymer synthesis community, it is often believed that a monodisperse MWD is preferred compared to polydisperse when it comes to BCP self-assembly. However, in the seminal work of Hadziioannou and Skoulios, they concluded that the bimodal MWD achieved through mixing two monodisperse copolymers does not affect the sharpness and quality of the structural interface.\textsuperscript{18} This was the first demonstration that the self-assembly of polydisperse copolymers can be well-defined and draws attention to the influence of overall MWD shape on assembled nanostructures. The use of controlled MWD composition and $D$ as a tool to manipulate the morphologies of BCP assemblies in solution or in thin films remains relatively unstudied. Herein, we elected to investigate the self-assembly of BCPs with skewed MWD and the polydispersity induced structural evolution based on a model copolymer of PS-$b$-PI as this system has been widely studied in general.\textsuperscript{19} The influence of block ratio on self-assembled structures has also been explored. We
postulate that it is the interplay of MWD composition, \( D \) and block ratio that have a synergy effect on the final nanoarrangement of BCP assemblies.

### 4.3. Experimental

#### 4.3.1. Materials

Styrene (≥99%) and isoprene (≥99%) were purchased from Sigma Aldrich and filtered over a column packed with stabiliser removal before use. Sec-butyllithium (\( s \)-BuLi, 1.4 M in cyclohexane) was obtained from Sigma Aldrich and used as received. Cyclohexane (ACS Grade) were obtained from Fisher Scientific and were dried over calcium hydride before use. Isopropanol (anhydrous, 99.5%) and THF (AR Grade, stabilised with butylated hydroxytoluene) were purchased from ChemSupply. Toluene was purchased from VWR Chemicals. All solvents were used as received unless otherwise stated. TEM grids (Cu, 200 mesh with formvar coating) and silicon wafers were purchased from ProSciTech and ePAK, respectively.

#### 4.3.2. Synthesis of PS-\( b \)-PI Copolymers

Polystyrene macroinitiators were first synthesised before chain extension with isoprene monomers. The polymerisation took place in a nitrogen atmosphere in a screw vial fitted with Teflon septum. As an example of copolymer synthesis, styrene (0.8 mL, 6.98 mmol) was mixed with 6.9 mL of cyclohexane in a scintillation vial and degassed through freeze-pump-thaw for three times. The initiator, \( s \)-BuLi, was dissolved into cyclohexane giving a 0.16 M stock solution. A total volume of 360 \( \mu \)L of the stock solution was charged into a 1 mL syringe that mounted onto a syringe pump (New Era NE-4000). The pump was programmed to dispense the initiator at designed rate profiles. Depending on the rate profiles and total time of addition, polystyrene with varied \( D \) and skewed MWD can be synthesised.

As for PS-\( b \)-PI synthesis, isoprene monomers were added to the polystyryllithium intermediates and stirred for 6 hours to reach full conversion. The mixture can be extracted during the course of synthesis to obtain a copolymer sample with desired weight fraction of isoprene \( (f_{PI}) \). The copolymers were isolated by evaporating the solvent under vacuum for 24 hours. The molecular weight and dispersity of synthesised polymers were determined from chromatograms of refractive index (RI) calibrated using polystyrene standards. The GPC system (Tosoh EcoSEC HLC 8320) is equipped
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with SuperHM-M columns. The conversion of reactions were determined from NMR 
\(^1\)H spectra (Varian Mercury 300).

4.3.3. Preparation of PS-b-PI Nanoparticles

The PS-b-PI nanoparticles were prepared using both emulsion and solvent exchange 
methods. As for the solvent exchange methods, PS-b-PI was first dissolved into THF at 
a concentration of 0.1 mg mL\(^{-1}\). 1 mL of the copolymer solution was extracted into a 
20 mL open vial equipped with a magnetic stir bar. A total volume of 2 mL deionised 
water was added slowly into the copolymer solution. The mixture was left under room 
conditions and constant stirring to allow THF evaporation over a course of 48 hours. 
The remnant aqueous suspension containing self-assembled PS-b-PI nanoparticles was 
used to prepare samples for TEM imaging (Tecnai Spirit, 120 kV) by drop-casting the 
liquid on TEM grids.

The nanoparticles were prepared through emulsification in a similar fashion as 
described in Chapter 3. The copolymer was first dissolved into toluene giving a 1 wt-% 
stock solution. 1.5 g of the stock solution (dispersed phase) was charged into a 20 mL 
sцинцилляционный пробирку и смешан с 10 mL of CTAB aqueous solution (continuous phase, 
0.5 mg mL\(^{-1}\)). The mixture was emulsified through vortexing and sonication until a 
homogenous emulsion was obtained. The emulsion was left in an open vial under 
constant stirring and elevated temperature (30 °C) to evaporate the organic solvent over 
a period of 48 hours. After obtaining the suspension, it was purified to remove residual 
CTAB through centrifugation and re-dispersion for three cycles. The purified 
suspension was used to prepared samples for TEM imaging through drop-casting.

4.3.4. Preparation of PS-b-PI Thin Films

PS-b-PI thin films were prepared according to the general procedure described in 
Chapter 3. The copolymers were dissolved in toluene at a concentration of 2 wt-%. The 
solution was then drop-casted on a cut silicon substrate. The silicon substrate was 
cleaned through UV-ozone system before use. The loaded substrate was left in a 
chamber with toluene atmosphere allowing a slow evaporation of the solvent. It was 
dried completely before AFM imaging (Asylum Research Cypher AFM).
4.3.5. Sample Preparation for TEM Imaging

The sample for TEM imaging was prepared in a similar fashion as described in Chapter 3. However, OsO$_4$ in aqueous solution was used to stain the PI block of the formed nanoparticles. The suspensions were drop-casted on the TEM grid and left in a closed chamber together with OsO$_4$ solution for 12 hours. The PI block interacts with OsO$_4$ vapor and thus it shows a dark colour under TEM while PS block shows a grey colour.

4.4. Results and Discussion

4.4.1. Analysis of MWD Composition

The copolymers used in this study were synthesised by the Fors group through anionic polymerisation using $s$-BuLi as initiator. The reaction is schematically illustrated in Scheme 4.1 showing both polydisperse and monodisperse polystyryllithium obtained through controlled addition of $s$-BuLi. The chain extension of polystyrene macroinitiators takes place at different stage due to the programmed addition of initiator and thus induces the change in MWD composition. When the full amount of initiator is added at the beginning of polymerisation, the chain extension of polystyryllithium takes place simultaneously that results in monodisperse product. Nevertheless, in all scenarios the final $M_n$ is independent of the addition scheme when full conversion is achieved since the total amount of initiator and monomer is fixed. In this study, three initiator addition schemes were explored to obtain the skewed feature of MWD: (1) addition of full amount of $s$-BuLi at beginning of reaction; (2) addition of fixed amount of $s$-BuLi at a constant rate; (3) and addition of fixed amount of $s$-BuLi at an exponentially ramped rate.
Scheme 4.1. Reaction scheme of polystyryllithium synthesis based on temporal regulation of chain initiation. The MWD shape is skewed due to polymerisation initiated at different stage.

Based on the three addition schemes, we have observed that a MWD is skewed to left hand side (LHS, i.e., skewed to higher molecular weight and tailing to lower molecular weight) when initiator is added at a constant rate. In the direct contrast, when initiator is added at an exponentially ramped rate, it results in a MWD skewed to right hand side (RHS, i.e., skewed to lower molecular weight and tailing to higher molecular weight). In the latter scenario, less polystyrene macroinitiators are formed in the early stage of polymerisation due to slow addition rate of initiator at the beginning of reaction. Since all high molecular weight polystyrene can only be obtained when its chain extension is triggered at early stage, this addition scheme consequently produces a MWD skewed to RHS with tails towards high molecular weights. According to this mechanism, we postulate that for exponentially decayed addition rate, it would produce a MWD of polystyrene skewed to LHS but with a much sharper distribution. Figure 4.2A demonstrates three examples of GPC curves of polystyryllithium synthesised according to the three addition schemes. The red and green curves represent MWD skewed to either directions (LHS or RHS) when s-BuLi is added at constant rate and exponentially ramped rate, respectively. The black curve represents nonskewed MWD obtained from traditional synthesis where full amount of s-BuLi is added at the beginning of reaction. As shown in Scheme 4.1 that these polymers can be synthesised at same \( M_n \) regardless the initiator addition scheme. However, the shape of MWD and
$D$ are not independent on each other. To shift the shape of MWD will inevitably broaden the overall shape of distribution and thus increase the $D$ to certain extend depending on the control of initiator addition scheme. As an example, in Figure 4.2A the $D$ of nonskewed MWD is 1.07 whereas the $D$ of both skewed MWDs are equal to 1.18.

In the light of the correlation between $D$ and skewed MWD, polymers can be synthesised with varied $D$ using the same technique (initiator addition scheme) but with varied total time of addition. Figure 4.2B shows the GPC chromatograms of polystyrene synthesised based on the constant initiator addition scheme whereas the overall addition time is varied. In the profiles of addition scheme (inset of Figure 4.2B), the area under each profile (integration of profile) represents the total amount of initiator added in the system. Therefore, for fixed amount of s-BuLi addition, fast scheme takes less time to complete the addition process. Significantly, by controlling the overall time of addition (in the other words, the speed of addition rate), a series of polystyrene with same skewed feature can be synthesised at varied $D$. The corresponding $A_s$ are tabulated in Table 4.1. This implies that when exploring the influence of the degree of MWD skew on self-assembly, the influence of $D$ has to been taken into account as the degree of skew (directly reflected by $A_s$) is strongly correlated to $D$. 
Figure 4.2. (A) GPC chromatograms of polystyrene synthesised according to different initiator addition programs. The red curve represents addition of initiator at constant rate while green curve represents exponentially ramped addition. Black curve represents addition of full amount of initiator at the beginning of polymerisation. (B) GPC chromatograms of polystyrene synthesised at different addition rate of initiator but all cases have the same addition scheme. All samples have similar $M_n$ at approximately $20\pm1$ kg mol$^{-1}$. The initiator addition profiles are shown in the insets.
Table 4.1. Asymmetric factor of polystyrene with varied $D$. All polymers have same $M_n$ and are synthesised based on constant addition rate but the overall time of addition is varied.

<table>
<thead>
<tr>
<th>Addition Speed</th>
<th>$D$</th>
<th>$A_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>quick</td>
<td>1.18</td>
<td>2.5</td>
</tr>
<tr>
<td>medium</td>
<td>1.40</td>
<td>3.4</td>
</tr>
<tr>
<td>slow</td>
<td>1.50</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Permitted by the living nature of this technique, copolymers of PS-$b$-PI can be synthesised by adding isoprene monomers to polystyryllithium wherein the segmental features of the starting PS block are retained. However, for simplicity the molecular weight of PI block is not skewed and assumed to be monodisperse. The influence of skewed MWD on polymers or copolymers’ physical properties have been reported previously.\textsuperscript{16} Kottisch et al. measured the Young’s modulus ($E$) of the PS-$b$-PI wherein PS block has varied MWD and $D$. It has been found that for all copolymers with $A_s < 1$ (skewed to lower molecular weights), the measured $E$ is consistently higher than their counterparts with $A_s > 1$ (skewed to higher molecular weights). In both skewed features, the increase of $D$ results in a decrease of $E$, however the difference in $E$ between the two skewed features increases when $D$ increases.\textsuperscript{16} More simply, the sensitivity of the copolymers to the change of $D$ is different. Furthermore, in our groups’ unpublished results, we have found differences in the rheological behaviour when the MWD is skewed to different directions. It is therefore of particular interest to investigate the influence of MWD composition and $D$ on the nanostructures that assembled from these copolymers with such features.

4.4.2. Self-Assembly of PS-$b$-PI in Thin Films and Particles

In Chapter 3, we have demonstrated that the weight fraction of one block significantly influences the final morphologies of copolymer assemblies in solution. This is because the change in relative block weight affects the packing parameter which in turn affects the morphological evolution.\textsuperscript{20} In this particular study, the increase of the second block (PI) in the copolymer also affects the degree of skewness of the overall MWD. As an example, a series of PI-$b$-PI synthesised through the one-pot technique has demonstrated varied weight fraction of PI block (Figure 4.3) with identical PS block (same MWD composition). The corresponding $A_s$ for each copolymers is tabulated in
Table 4.2. Evidently, with increasing weight fraction of PI block, the copolymer MWD loses the skewed feature as the $A_s$ approaches unity. Because of the nonskewed segmental MWD of the PI block, the overall shape of MWD approaches normal distribution when PI becomes the dominant block in the copolymers. Therefore, in the self-assembly of PS-$b$-PI, the influence of the skewed segmental MWD from PS block has to be taken into account even though the overall MWD is symmetric. The GPC chromatograms of all other PS-$b$-PI copolymers used in this study can be found in Appendix B.

![Figure 4.3](image)

**Figure 4.3.** GPC chromatograms of an example of one-pot synthesis of PS-$b$-PI with increasing PI fraction and MWD skewed to RHS. The $D$ of the starting PS macroinitiators is 1.39.

**Table 4.2.** Asymmetric factor of a series of PS-$b$-PI with increasing weight fraction of PI block. All copolymers have same PS blocks because of the one-pot synthesis.

<table>
<thead>
<tr>
<th>Polymer or Copolymers</th>
<th>Weight Fraction of PI ($f_{PI}$)</th>
<th>$A_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS$_{19.4k}$</td>
<td>0</td>
<td>0.4</td>
</tr>
<tr>
<td>PS$<em>{19.4k}$-$b$-PI$</em>{13.2k}$</td>
<td>41%</td>
<td>0.7</td>
</tr>
<tr>
<td>PS$<em>{19.4k}$-$b$-PI$</em>{21.9k}$</td>
<td>53%</td>
<td>0.7</td>
</tr>
<tr>
<td>PS$<em>{19.4k}$-$b$-PI$</em>{28.0k}$</td>
<td>59%</td>
<td>0.8</td>
</tr>
<tr>
<td>PS$<em>{19.4k}$-$b$-PI$</em>{38.6k}$</td>
<td>67%</td>
<td>0.9</td>
</tr>
</tbody>
</table>
In order to establish the AFM conditions to measure the nanostructures, we first explored the thin film morphologies assembled from a PS-\textit{b}-PI with a normal distribution in both blocks (overall $M_n = 36.2$ kg mol$^{-1}$, $f_{\text{PI}} = 41\%$). It has been found that the copolymer self-assembles into perpendicularly oriented lamellae (Figure 4.4). In the phase retrace AFM image, the nanodomain is measured using ImageJ software showing a periodic feature size of $\sim$30 nm. Since the surface of the substrate is unprocessed, the formation of perpendicular orientation may be ascribed to the neutral interface between copolymer and toluene atmosphere.$^{21,22}$

**Figure 4.4.** Phase retrace AFM images of PS-\textit{b}-PI with normal distribution of molecular weights. Overall $M_n = 36.2$ kg mol$^{-1}$ and $f_{\text{PI}} = 41\%$.

We then wanted to establish the TEM conditions for analysis of the particle formation using the same BCP as above (overall $M_n = 36.2$ kg mol$^{-1}$, $f_{\text{PI}} = 41\%$). With this PI fraction, the BCP forms onion-like spheres; however the radially stacked materials show discontinuous sections yet highly ordered, as demonstrated in Figure 4.5. It is notable that some parts of the PI domain (dark areas as stained by OsO$_4$) are discontinuous in terms of change of contrast while some parts are completely disjointed showing individual dots arranged radially. We postulate that the individual dots are PI cylinders distributed in PS matrix in a particular order. The discontinuity of contrast may be attributed to the limitation from the 2D projection of a 3D sphere.
Figure 4.5. TEM images of nanoparticles assembled from PS$_{21.4k}$-b-PI$_{14.8k}$ where $f_{\text{PI}}$ = 41%. The BCP used in this example has nonskewed MWD in both blocks. Nanoparticles are stained by OsO$_4$ giving dark PI domain and grey PS domain. Scale bar: 100 nm.

4.4.3. Influence of $D$ and Skewed MWD on Self-Assembly

After introducing the skewed feature in MWD, the self-assembly of PS-$b$-PI in thin films reflects subtle difference in the morphologies. At low $D$ (1.18), the thin films prepared from small $f_{\text{PI}}$ with oppositely skewed MWD both show perpendicularly oriented morphologies with long-range lateral order of periodic nanodomains (Figure 4.6a and c). However, the feature size of the two thin films with opposite MWD skewness is different: when the MWD is skewed to higher molecular weight (Figure 4.6a), the periodic size is approximately 30 nm and dark to grey domain ratio is close to 1; when the MWD is skewed to lower molecular weight (Figure 4.6c), the periodic size is measured to be 32 nm with dark to grey domain ratio of 0.3. It is noticeable that although the overall feature size is similar in the two cases, the ratio of the two microphases (PS and PI phases) significantly differs from each other. The consistency in overall feature size can be attributed to the fact that both perpendicularly oriented morphologies are obtained from copolymers with similar overall $M_n$ (Figure 4.6a: feature size=30 nm while $M_n$=32.6 kg mol$^{-1}$; Figure 4.6c: feature size=32 nm while $M_n$=32.6 kg mol$^{-1}$). The difference in phase ratio is ascribed to the segmental skewed MWD of the copolymers. It should be noted that the schematic MWD shown in the
insets of Figure 4.6a and c has opposite skewness when compared to its original GPC chromatograms, i.e. the horizontal axis represents molecular weight instead of retention time and large retention time reflects smaller molecular weights.

Figure 4.6. Phase retrace AFM images of thin film morphologies assembled from a series of PS-b-PI with similar $M_n$ and $f_{PI}$ but varied MWD. (a) Assembled from PS$_{20.6k}$-b-PI$_{12.0k}$, where segmental $D$ of PS is 1.18. (b) Assembled from PS$_{20.3k}$-b-PI$_{12.0k}$, where segmental $D$ of PS is 1.40. (c) Assembled from PS$_{19.5k}$-b-PI$_{13.1k}$, where segmental $D$ of PS is 1.18. (d) Assembled from PS$_{19.4k}$-b-PI$_{13.6k}$, where segmental $D$ of PS is 1.52. The MWD and $D$ are indicated in the insets: red line indicates MWD shifted to higher $M_n$ while green line represents MWD shifted to lower $M_n$. In the insets, the breadth of MWD indicates the value of $D$ (profiles are not to scale). The insets in (a) and (c) also schematically illustrate the size of dark domain and overall periodic domain. Scale bar equals to 200 nm.

It has been reported that the broad segmental $D$ enlarges the microphase separated domains in some thin film systems. However, in the PS-b-PI thin films, the increase in segmental $D$ of PS completely changes the surface morphology. When the $D$ of PS segment is increased to 1.40 and beyond, the two thin films with oppositely skewed MWD both lose the lamellae features and standing cylinders are observed instead
(Figure 4.6b and d). As discussed above, the degree of skewness is strongly correlated to polydispersity, i.e. the $A_s$ of copolymers is skewed further away from unity when segmental $D$ is increased. Therefore, the difference of thin film morphology between the two MWD shapes is expected to be more significant when segmental $D$ is large since the difference in $A_s$ of the two MWD is more significant. It is found that with MWD skewed to lower molecular weight (Figure 4.6d), the thin film shows standing cylinders in a particular order. In comparison, its analogue with MWD skewed to higher molecular weight (Figure 4.6b) shows a relatively disorganised morphology.

In the nanoparticle self-assembles, the influence of skewed MWD is less significant compared to thin film systems. At low $D$ (1.18), both types of MWD give similar morphologies that are composed of cylinders of PI oriented in the matrix of PS spheres. In Figure 4.7a, one side of the nanoparticle edge shows individual dots of PI, and the other side of the edge shows a smooth continuous cylinder of PI. We postulate that the dots on one edge are the heads or cross-sectional areas of the PI cylinders as the body of these cylinders are observed (shown in the enlarged picture of Figure 4.7a). The diameter of the PI cylinders is measured to be 11 nm on average. As for the nanoparticles assembled from oppositely skewed MWD, the diameter of PI cylinders is measured giving an average value of 10 nm (Figure 4.7d), which is similar to the size of its counterpart (Figure 4.7a). In the two cases, the overall size of nanoparticles are similar to each other, at a diameter of approximately 500 nm. We also assembled ultra-large nanoparticles at a diameter of 1 μm with the same morphology. Interestingly, the change in confinement significantly changes the average value of the PI cylinders diameters from 10 nm to 14 nm. With increasing $D$ at 1.40 and 1.50, the assembled nanoparticles become disorganised in the interior regardless the MWD shape and demonstrate an onion-like sphere with discontinuous stacking (Figure 4.7b, c, e and f).
Figure 4.7. (a–c) TEM images of nanoparticles assembled from PS-\(b\)-PI with MWD skewed to higher \(M_n\) at (a) \(D=1.18\); (b) \(D=1.40\); (c) \(D=1.50\). (d–f) TEM images of nanoparticles assembled from PS-\(b\)-PI with MWD skewed to lower \(M_w\) at (d) \(D=1.18\); (e) \(D=1.39\); (f) \(D=1.52\). The shape of MWD and \(D\) are reflected in the insets (profiles are not to scale). All copolymers used in self-assembly have same \(f_{\text{PI}}\) at \(\sim60\%\). Nanoparticles are stained by OsO\(_4\) giving dark PI domain and grey PS domain. All scale bars are equal to 100 nm.
4.5. Conclusion and Outlook

In this study, the influence of \( D \) and skewed MWD on PS-\( b \)-PI self-assembly were investigated. As for thin films, we have found that the skewed MWD affects the size of nanostructures whereas its influence on nanoparticles is minimal. Furthermore, the increase of \( D \) dramatically influences the self-assembled structures in both thin films and nanoparticles. In thin films system, the increase in \( D \) induces a morphological evolution from perpendicular orientation of alternating PS and PI domain to standing cylinders of one block dispersed in the matrix of the other block. Although this evolution has been observed in both skewness of MWD, the copolymers with MWD skewed to lower molecular weight give better ordered cylinders in the assembled nanostructures. Regarding nanoparticle systems, the increase in \( D \) causes the disorder in the particle interior yet the radially stacked feature is retained. Though the assumption that low degree of heterogeneity is necessary for the formation of periodic structure has been questioned,\(^{24,25}\) we have found that the segmental polydispersity does play a role in the disorganised nanostructures in both thin film and nanoparticle systems.

Although the influence of \( D \) on copolymer self-assembly and phase behaviour has been widely explored, it is, to the best of our knowledge, the first report to describe the effect of skewed MWD on BCP self-assembled nanostructures. We foresee that the use of scattering techniques will better interpret the nanodomains of both nanoparticle and thin film systems. In this study, only the segmental \( D \) and MWD of PS block are varied due to the limitation in the anionic polymerisation. It might be of interest to explore the copolymers wherein both blocks have skewed MWD and controlled \( D \). This can be achieved through RAFT polymerisation to synthesise the constituent polymers separately in order to obtain controlled overall shape of MWD. After functionalisation of the end group of each polymer to form a thiol group through aminolysis (described in Chapter 3), the two blocks can be conjugated by forming disulphide bonds. This largely increase the complexity of copolymer chemistry and thus can be potentially used as a tool to manipulate the self-assembled nanostructures.
4.6. References


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Chapter 5 — Phase Separated Block Copolymer Particles with Tuneable Morphologies Controlled by Interface
Chapter 5

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Chapter 5

5.1. Aim

This chapter presents the aqueous solution self-assembly of a series of P2VP-\textit{b}-PDMS diblock copolymers. The studies herein have been conducted primarily based on emulsion technique but solvent exchange methods have also been investigated. The first section explores the influence of interfacial properties on the morphological evolution of P2VP-\textit{b}-PDMS nanoparticles. The second part of this work examines the effect of copolymer composition on the final nanoparticle structure.

5.2. Introduction

The ability to engineer and manipulate polymeric nanostructures is a blossoming field that can take inspirations from nature to create unique shapes and morphologies. BCP nanoparticles, in particular, have drawn considerable focus in both academia and industry due to its vast potential applications in biomedicine, catalysts and electronics.\textsuperscript{1-4} Recent advances in polymer chemistry\textsuperscript{5} and synthesis technologies\textsuperscript{6} have further enriched the library of BCPs with great control over their molecular weight and functionality. This allows the design of complex structures with great reproducibility. In bulk, the competitive factors of entropically driven phase separation and the chemical bond constraints between blocks lead to the formation of ordered structures.\textsuperscript{7} On the contrary, self-assembly of BCPs in solution heavily relies on the interactions between blocks and the surrounding medium. Therefore, control over interfacial properties not only can provide driving forces for self-assembly but can also tailor the nanoarchitectures of the assembled structures.

Traditionally solution self-assembly of BCPs has focused on micellar assembly;\textsuperscript{8-10} recently new methods in the synthesis of more complex solution self-assemblies have been reported.\textsuperscript{11-14} An interesting example pioneered by Jeon and co-workers reports the structural evolution of non-spherical BCP particles driven by controlling the mobile interface of copolymer confined in emulsion droplets.\textsuperscript{15} Upon evaporation of the organic solvent, nanoparticles with unique external shape and internal morphologies are formed through phase separation. The self-assembly of BCPs into phase separated nanoscopic particles provides control over particle distribution and orientation and thus enables the development of engineered nanomaterials with enhanced properties.\textsuperscript{16} The controlled internal morphologies of BCP nanoparticles create additional surface area and nanoenvironments for the incorporation of functional groups within the system.\textsuperscript{17}
By modifying the chemistry of constituent blocks, the resulted nanoparticles possess dynamic properties which hold potentials in template and stimuli-responsive materials. Although spherical nanoparticle dominates the assembled architectures, asymmetric particle afforded by BCPs is of particular academic interest as it allows fundamental insights into the shape-dependent properties and functionalities.

Herein, we report an interfacial-driven self-assembly of anisotropic nanoparticles with axially stacked lamellae morphology using a diblock copolymer of P2VP_12.5k-b-PDMS_{10k}. To this end, a binary surfactant mixture composed of CTAB and HO-CTAB with a hydroxy functionalised terminal is utilised to control the phase separation of P2VP-b-PDMS within dispersed nanoparticles (shown in Scheme 5.1). The self-assembly procedure consists of emulsification of BCPs in water and removal of chloroform in the dispersed phase. Within the confinement of dispersed droplets, phase separation occurs upon evaporating organic solvents. In analogy with the self-assembly of BCPs in thin films, a neutral interface of surrounding surfactant layer can be achieved by accurate tuning of the surface energies, which induces an axially stacked internal morphology of dispersed particles.

Scheme 5.1. Schematic representation of P2VP-b-PDMS nanoparticles. At 100% HO-CTAB, the diblock copolymer self-assembles into onion-like spheres, while it forms axially stacked lamellae structures in the presence of CTAB.
5.3. Experimental

5.3.1. Materials

Diblock copolymers, P2VP-\textit{b}-PDMS with various block ratios, were purchased from Polymer Source, Inc. The $M_n$ of P2VP block are 8500, 12500 and 17000, respectively, while the $M_n$ of PDMS is 10000 for all BCPs. Table 5.1 shows details of the three BCPs purchased from Polymer Source, Inc. including thermal analysis results and chemical structure. CTAB ($\geq 99\%$), 16-bromo-1-hexadecanol and trimethylamine (4.2 M in ethanol) were purchased from Sigma Aldrich. Chloroform, THF, DMF and ethyl acetate were obtained from Fisher Scientific. Iodine for P2VP staining was obtained from Thermo Fisher.

Table 5.1. BCPs specifications and thermal analysis results obtained from provider. $T_m$ = melting temperature, $T_c$ = crystallisation temperature, and $T_g$ = glass transition temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Block Copolymers</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P2VP$<em>{8.5k}$-\textit{b}-PDMS$</em>{10k}$</td>
<td>1.20</td>
</tr>
<tr>
<td>2</td>
<td>P2VP$<em>{12.5k}$-\textit{b}-PDMS$</em>{10k}$</td>
<td>1.28</td>
</tr>
<tr>
<td>3</td>
<td>P2VP$<em>{17k}$-\textit{b}-PDMS$</em>{10k}$</td>
<td>1.28</td>
</tr>
</tbody>
</table>

5.3.2. Synthesis of HO-CTAB

0.48 g of 16-bromo-1-hexadecanol was first dissolved in 7.5 mL of ethyl acetate in a flask followed by addition of 5.6 mL of trimethylamine (4.2 M in ethanol). The reactants were stirred in the sealed flask at 60 °C under Ar for 7 days. The synthesised HO-CTAB was filtered and rinsed by ethyl acetate and the obtained solids were purified by recrystallising from water. The yield of HO-CTAB was approximately 50% measured by weighing. $^1$H NMR (CDCl$_3$ + MeOH-$d_4$): $\delta = 3.49$ (t, 2H, $CH_2$OH), 3.12 (s, 9H, $(CH_3)_3N^+CH_2$), 1.67 (m, 2H, $N^+CH_2$), 1.46 (m, 2H, $N^+CH_2CH_2$), 1.32-1.13 (m,
26H, HOCH$_2$CH$_2$(CH$_2$)$_{11}$). The synthesised HO-CTAB is characterised using NMR spectrometer at 400 MHz (MR400, Varian) and the spectrum is shown in Appendix A.

5.3.3. Preparation of BCP Particles

*Nanoparticles Prepared by Emulsion Technique.* The preparation of copolymer nanoparticles followed the standard procedure as described in Chapter 3. However, a binary surfactant mixture consisting of HO-CTAB and CTAB was used to emulsify the system. Firstly, HO-CTAB and CTAB surfactants were separately dissolved into distilled water giving two stock aqueous solutions (both are 1 mg mL$^{-1}$). Stock polymer solutions were prepared by dissolving BCPs into chloroform at a concentration of 1 wt-%. Desired amount of each surfactant solutions were mixed in 20 mL vials and diluted to an overall mixed surfactant concentration of 0.05 wt-% as a continuous phase. The relative amounts of HO-CTAB and CTAB stock solutions were varied according to the designed mass fraction of HO-CTAB. The detailed composition of surfactant mixtures and weight of BCP solutions to prepare nanoparticles are tabulated below in appropriate result sections.

*BCP Assemblies Prepared by Solvent Exchange Methods.* As for copolymer micelles prepared via THF solvent exchange, the preparation details are described in Chapter 4. Regarding polymer micelles made via DMF dialysis, P2VP-$_b$-PDMS was firstly dissolved into DMF at a concentration of 0.1 wt-%. DMF was then exchanged by water through dialysis. The resulted polymer dispersions were then used to prepare TEM grids for morphology characterisation.

5.3.4. Sample Preparation for SEM Imaging

The suspensions containing assembled nanoparticles were first drop-casted onto a thin glass substrate and then affixed onto a sample holder specialised for SEM imaging. After the sample became completely dry, it was coated with a thin layer of gold through sputter deposition. The coated sample can be used directly for SEM imaging (XL30 Philips FESEM).
5.4. Results and Discussion

5.4.1. Morphological Evolution Controlled by Interface

When the emulsifying surfactant used was 100% HO-CTAB, onion-like spheres were observed with P2VP as the outermost layer, as shown in Figure 5.1a. Images were taken by transmission electron microscopy (TEM) at 120 kV (Spirit, Tecnai). This expected structure is attributed to the preferential interactions between the hydroxy group of HO-CTAB and the pyridine group of P2VP block, as previously reported by the Hawker group.26 The particles were observed to be slightly deformed, which may be ascribed to the extremely low glass transition temperature ($T_g$) of the PDMS block (thermal analysis results are shown in Table 5.1). A series of nanoparticles were prepared with increasing amount of CTAB in the surfactant mixtures. Detailed compositions are available in Table 5.2 where the first column indicates the content of CTAB in binary surfactant mixture. Significantly, the introduction of CTAB induces a clear morphology transition from onion-like spheres to axially stacked lamellae with particles observed to have one tapered head (Figure 5.1). It is noted that while most well-defined particles have a tapered head at one end, a certain fraction of assembled particles vary in overall shape displaying prolate spheroids. When 10% of CTAB ($x=0.1$, where $x$ denotes the mass fraction of CTAB in the binary surfactant mixtures) is used in the emulsification process, stacked strips are observed but onion-like sphere is still the dominant structure, as shown in Figure 5.1b. Further increasing of the mass fraction of CTAB leads to the prosperity to form lamellar structure (Figure 5.1c). It is believed that the formation of axially stacked lamellae is induced by the neutral interface where it has no preferential interactions to either block. The nanoparticles shown in Figure 5.1b and c are in transient structures between onion-like spheres and lamellae, and thus the boundaries of individual particle become vague and ill-formed. It is interesting to see that at 100% of CTAB (i.e., $x=1$, shown in Figure 5.1d), the nanoparticles remain in perfect lamellar structure instead of forming reverse onion-like spheres. These results show that the stacked lamellae structures can be prepared using CTAB as a sole surfactant. The preparation of axially stacked lamella structures from BCPs using a commercially available and inexpensive surfactant (CTAB) is significant as this removes the requirement for engineering surfactant/emulsion system,15, 19, 22, 26, 27 and to the best of our knowledge it has not been reported in other systems.
Figure 5.1. TEM images of P2VP$_{12.5k}$-$b$-PDMS$_{10k}$ nanoparticles obtained from chloroform droplets emulsified with surfactant mixtures at different ratio of HO-CTAB/CTAB: (a) $x=0$, (b) $x=0.1$, (c) $x=0.7$, (d) $x=1$. Nanoparticles are stained by iodine giving dark P2VP domain and grey PDMS domain. Scale bars are 500 nm; inset scale bars are 100 nm. These results show that stacked lamellae structures can be prepared using CTAB as a sole surfactant.

Table 5.2. Composition of continuous phases for different values of mass fraction of CTAB in the respective sample.

<table>
<thead>
<tr>
<th>mass fraction of CTAB ($x$)</th>
<th>CONTINUOUS PHASE</th>
<th>DISPERSED PHASE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>stock solution CTAB (1 mg mL$^{-1}$)</td>
<td>stock solution HO-CTAB (1 mg mL$^{-1}$)</td>
</tr>
<tr>
<td>0.0</td>
<td>0.0 mL</td>
<td>5.0 mL</td>
</tr>
<tr>
<td>0.1</td>
<td>0.5 mL</td>
<td>4.5 mL</td>
</tr>
<tr>
<td>0.7</td>
<td>3.5 mL</td>
<td>1.5 mL</td>
</tr>
<tr>
<td>0.8</td>
<td>4.0 mL</td>
<td>1.0 mL</td>
</tr>
<tr>
<td>1.0</td>
<td>5.0 mL</td>
<td>0.0 mL</td>
</tr>
</tbody>
</table>
5.4.2. Control of Overall Nanoparticle Size

It is well-known that the size of emulsion droplet can be controlled by surfactant concentration and emulsification energy input. Here we developed size control techniques for these BCP emulsions by varying surfactant concentration while keeping the emulsification intensity (time and power) constant. The concentration of surfactant is varied in two ways, namely changing the weight of dispersed phase (Table 5.3) or changing surfactant concentration in the continuous phase (Table 5.4). In both cases, we have found a general trend that at higher surfactant concentrations, nanoparticles tend to form smaller size, whereas lower surfactant concentrations induce larger particles, as shown in the size distribution profiles by number (Figure 5.2a and d). The size of nanoparticles was characterised using dynamic light scattering (DLS, Zetasizer Nano ZS, Malvern). The increasing weight of BCP solutions (denoted by “m”) corresponds to decreasing relative surfactant concentration. Although the size of nanoparticles is generally inversely proportional to the surfactant concentration, there is a number of samples deviate the trend (such as when m=1.75). The deviation in nanoparticles size may be attributed to the non-linear correlation and change in sensitivities of size to surfactant concentration. Figure 5.2b and c demonstrate the size distribution by volume and intensity, respectively. As shown in Figure 5.2, particles can be prepared from 70 nm to 400 nm using this technique.

Table 5.3. Composition of continuous and dispersed phases for different surfactant concentration in the respective sample. The concentration of surfactant is controlled by changing the weight of dispersed phase.

<table>
<thead>
<tr>
<th>mass fraction of CTAB (x)</th>
<th>CONTINUOUS PHASE</th>
<th>DISPERSED PHASE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>stock solution</td>
<td>stock solution</td>
</tr>
<tr>
<td></td>
<td>CTAB (1 mg mL⁻¹)</td>
<td>HO-CTAB (1 mg mL⁻¹)</td>
</tr>
<tr>
<td>1.0</td>
<td>5.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1.0</td>
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<td>1.0</td>
<td>5.0</td>
<td>0.0</td>
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</tbody>
</table>
Table 5.4. Composition of continuous and dispersed phases for different surfactant concentration in the respective sample (surfactant concentrations varied in the continuous phase).

<table>
<thead>
<tr>
<th>surfactant concentration (%)</th>
<th>stock solution CTAB (1 mg mL(^{-1})) mL</th>
<th>stock solution HO-CTAB (1 mg mL(^{-1})) mL</th>
<th>deionised water mL</th>
<th>stock solution PS-(b)-P2VP (1 wt-%) g</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>4.0</td>
<td>0.0</td>
<td>6.0</td>
<td>1.0</td>
</tr>
<tr>
<td>0.05</td>
<td>5.0</td>
<td>0.0</td>
<td>5.0</td>
<td>1.0</td>
</tr>
<tr>
<td>0.06</td>
<td>6.0</td>
<td>0.0</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>0.07</td>
<td>7.0</td>
<td>0.0</td>
<td>3.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Figure 5.2. Size distribution (a) by number, (b) by volume, (c) by intensity of nanoparticles prepared by different weight of dispersed phase, where “m” denotes the weight of BCP solution in gram. (d) Size distribution by number of nanoparticles prepared by different surfactant concentration in the continuous phase, where “c” denotes surfactant concentration in continuous phase.
Because of the sampling ability of TEM imaging (see discussion in Chapter 2), we elected to use SEM (XL30 Philips) and optical microscope (Eclipse Ci, Nikon) to probe the dispersed nanoparticles in large fields of view, as illustrated in Figure 5.3. Although this technique is out of the resolution of the BCP dimensions, they provide a visual illustration of size distribution in conjunction with DLS data.

Figure 5.3. Example of SEM (a) and optical images (b-c) of nanoparticles prepared by different mass fraction of HO-CTAB in CTAB/HO-CTAB surfactant mixtures (a) 100% of HO-CTAB; (b) 90% of HO-CTAB; (c) 70% of HO-CTAB; (d) 0% of HO-CTAB. Scale bar: 1 μm.

5.4.3. Solvent Exchange Methods to Prepare Nanoparticles

We were interested in how the self-assembly conditions can control the final nanoparticle size and shape. To investigate this further we examined non-emulsion techniques, i.e., assembly pathways via solvent exchange, that is, evaporation of THF from THF/water mixture and DMF dialysis against water based on the same BCP system. In the former pathway, P2VP-b-PDMS copolymers are firstly dissolved into THF. Following addition of water, a bad solvent for copolymers, P2VP-b-PDMS self-assembles into micelles with P2VP core encapsulated by spread PDMS corona upon evaporating THF. Although the P2VP blocks have more favourable interactions with the surrounding aqueous medium, PDMS blocks form the corona of the micelles. This may be attributed to the fluidity of PDMS blocks or reorganisation of micelles when deposited for TEM observation. The size of the micellar core is approximately 20 nm consisting of only P2VP block and thereby no phase separated interior is observed. As
for nanoparticles prepared via DMF dialysis, it also forms a similar micelle without interior phase separation (see Figure 5.4). These results demonstrate the power of controlling the interface in an emulsion system to prepare complex nanoparticles as presented in Figure 5.1. It should be pointed out that though solvent exchange methods failed to produce self-assembled nanoparticles in this particular system, this procedure has demonstrated its applicability in a wide variety of copolymers and solvents.28

![Figure 5.4](image)

Figure 5.4. TEM images of P2VP_{12.5k}-b-PDMS_{10k} assemblies obtained from (a) THF evaporation from THF/water mixture and (b) DMF dialysis against water. P2VP block is stained by iodine giving dark domain. All scale bars are 200 nm.

5.4.4. Kinetic Studies of Assembled Nanoparticles

There are a number of ill-defined particles observed in some samples especially the ones emulsified by higher mass fraction of HO-CTAB in the surfactant mixtures. It is believed that the defects in nanoparticles are resulted from the defects in emulsion droplets as the stability of HO-CTAB in water is low.

Another attribution of the ill-formed nanoparticles may be from kinetic influence. In this work, all nanoparticles prepared from emulsion were examined immediately after self-assembly. However, an important feature of BCP assemblies is the propensity to form kinetically trapped structures in non-equilibrium states.29, 30 To realise truly shape anisotropic particles, the phase separation of BCP has to be in an equilibrium state and has to occur in confinements bigger than the domain size of the copolymer. Although the absence of polymer chain exchange due to energy penalty has been demonstrated,31, 32 local rearrangement of the assemblies may still occur within the particle confinement. Therefore, a kinetic study has been carried out over a time scale of weeks (see Figure 5.5). Since both blocks are non-crystalline, the static structures
over the time of studies suggest that the nanoparticles are in thermodynamic equilibriums after their self-assembly in solution.

Figure 5.5. TEM images of nanoparticles prepared by P2VP\textsubscript{12.5k-}b-PDMS\textsubscript{10k} at 100\% of HO-CTAB. (a) Image taken right after self-assembly. (b) Sample aged for 2-week before imaging. P2VP domain is stained by iodine. Scale bars: 500 nm; inset scale bars: 100 nm.

5.4.5. Influence of Block Ratio on Self-Assembly

To elucidate the influence of block ratio on morphology of self-assembled nanoparticles, P2VP-b-PDMS copolymers with fixed PDMS block ($M_n=10k$) and either smaller ($M_n=8.5k$) or larger P2VP block ($M_n=17k$) were investigated using CTAB as a sole surfactant. When P2VP\textsubscript{8.5k-}b-PDMS\textsubscript{10k} were assembled under these conditions, well-defined particles were not isolated, but the polymer self-assembles into a maze-like aggregated structure with P2VP walls and PDMS channels, shown in Figure 5.6a. The inset shows an individual particle prepared from a low particle concentration suspension. The black arrows point out possible boundaries of aggregated particles where the confined area has a similar scale as the individual particle in the inset. The propensity to form a continuous film upon TEM sample preparation may be ascribed to the fluidity of PDMS, which is the dominant block in this case. Using BCPs with different composition is a facile way to access new morphologies, as demonstrated by the self-assembly of BCPs with medium ($M_n=12.5k$) and large ($M_n=17k$) P2VP blocks. Significantly, the copolymer with increased P2VP composition (P2VP\textsubscript{12.5k-}b-PDMS\textsubscript{10k}) assembles into axially stacked lamella particles (Figure 5.6) while further increasing the P2VP length (P2VP\textsubscript{17k-}b-PDMS\textsubscript{10k}) forms well-defined prolate spheroids with
phase separated morphology consisting of onion-like spheres on one pole and patchy decorations in all other areas (Figure 5.6c). These results suggest that increasing the mass fraction of the P2VP phase is important in forming stable particles and can be easily used to engineer the final shape and morphology of the particles. The patch decorated structure in Figure 5.6c resembles the soft patchy nanoparticles reported by Muller et al., who utilised an A-B-C triblock copolymer. In contrast, this system uses a much simpler chemistry to form patchy structures yet with extreme complexity.

**Figure 5.6.** TEM images showing the tuneable morphologies obtained by varying block ratio of P2VP-\(b\)-PDMS. (a) Aggregated film formed from P2VP=8.5k, the inset shows a non-aggregated individual particle; (b) axially stacked strips formed from P2VP=12.5k; (c) prolate particles with radially stacked spheres on one pole and patchy decoration formed from P2VP=17k. All samples are emulsified by CTAB as sole surfactant. P2VP domains are stained by iodine. Scale bars are 500 nm; inset scale bars are 100 nm.
5.5. Conclusion

In summary, we have demonstrated a simple method to prepare a range of shape controlled phase separated BCP nanoparticles. The tuneable morphologies that can be engineered are diverse; from onion-like sphere to axially stacked lamellae through the use of functional surfactants to tune the interfacial energies. Furthermore, we have also demonstrated that a myriad of nanostructures can be accessed based on the same copolymer chemistry. For high fraction of PDMS block, it is found that the copolymers have a propensity to coalesce and form a film upon evaporation of the particle solution. In this work, a nonconventional and unprecedented structure of prolate particles with patchy decoration formed from a P2VP-\textit{b}-PDMS copolymer has been revealed. To the best of our knowledge, it is the first time to discover such complex yet highly ordered architecture formed from a simple diblock copolymer with commercially available surfactants. The patchy structures of the particles may be further extended to hierarchical co-assembly of pre-formed nanoparticles, offering great promise to the construction of novel superstructures. This and other features hold significant potential in particle-based technologies.
5.6. References


Chapter 5


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Chapter 6 — Thesis Summary
Chapter 6

The control of BCP self-assembly and their nanostructures is an important goal toward achieving their functional properties. In both solution and thin film systems, tailoring the overall properties such as shape, morphology and functionalities of the final architectures represents the key challenge. In a synthetic approach, these requirements are addressed by programming the BCPs accordingly on a molecular level. From this viewpoint, the nanoassemblies of BCPs can be controlled by parameters such as polymer chemistry, copolymers architecture and solvent quality. Furthermore, the process to prepare the assembled nanostructures is also important from the viewpoint of kinetics. Therefore, this thesis addresses the strategies to control shape and morphology of BCP assemblies from these areas.

The influence of copolymer composition on BCP self-assembly has been investigated for various systems. To access BCPs with desired composition and chemical properties, we have explored the synthetic technique to generate and modify copolymers. As outlined in Chapter 3, a series of PS-\textit{b}-P2VP has been synthesised through RAFT polymerisation and subsequently self-assembled into both nanoparticles and thin films. The morphological transition of nanoparticles with respect to the change of polymer composition has been reported. The end group chemistry of BCPs has been modified through a nucleophilic reaction giving a thiol group at one end of the copolymer chain, which provides a functional handle for innovation. In Chapter 5, the copolymer of P2VP-\textit{b}-PDMS has also been investigated demonstrating different morphology of nanoassemblies at different block ratio, and a nonconventional patchy nanoparticles has been observed when P2VP block is significantly large.

With the development in synthetic approaches, the segmental MWD of one block can be controlled in depth with novel features. In Chapter 4, these properties of MWD have been utilised to tune the nanostructures of BCPs assemblies. In thin films, a change in the nanodomain size has been reported when BCPs with oppositely skewed MWD are used. The controlled $D$ is utilised to achieve a thin film morphological transition from perpendicularly oriented lamellae to a structure with standing cylinders. In nanoparticles, the two copolymers with oppositely skewed MWD both assemble into a phase separated interior with PI cylinders dispersed in PS shell. In both cases, the increase in $D$ induces a disorganised interior in the particles. In Chapter 5, the interactions between BCPs and the surrounding medium, which are controlled by the interface, have been tuned to achieve a morphological evolution of P2VP-\textit{b}-PDMS
nanoparticles. The interfacial properties of the dispersion system are tuned using a mixture of surfactants with preferential wetting to respective blocks. Other preparation process, such as solvent exchange methods, are explored to assemble P2VP-b-PDMS into micelles.

Although this work has presented a variety of BCP architectures that can be accessed, the current level of complexity is still insignificant when compared to natural systems. Future ways to slowly approach nature’s complexity require a better and profound understanding of the respective self-assembly mechanisms. As described in Chapter 3, the fluorophore conjugation at copolymer end permits the use of fluorescent microscopy to probe the nanoarrangement of the individual copolymer chian and thus provides a mechanistic insights of BCP self-assembly. Additionally, kinetic studies via \textit{in situ} microscopy may play a crucial role to investigate the time-dependent mechanism and dynamic behaviours of these systems. In particular, the availability and tools developed by ultra-high resolution optical microscopy techniques will play a role here. In BCP self-assembly, it is often the complex interplay of various interactions that governs the self-assembly process, and therefore the understanding of the synergy of all these interactions is another challenge. The development in these areas will enable the design and the interaction of complex building blocks of differing shapes. By utilising these tools and engineering complex designs we may start to realise truly some of nature’s function.
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Appendix A: NMR Spectra of Synthetic Products

Figure A.1. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of P2. Example of calculation to determine block ratio is shown in Chapter 3.

Figure A.2. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of P3.
Appendix

Figure A.3. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of P5.

Figure A.4. $^1$H NMR (400 MHz, CDCl$_3$ + MeOH-$d_4$) spectrum of synthesised hydroxyl incorporated cetyltrimethylammonium bromide. $\delta = 3.49$ (t, 2H, CH$_2$OH), 3.12 (s, 9H, (CH$_3$)$_3$N$^+$CH$_2$), 1.67 (m, 2H, N$^+$CH$_2$), 1.46 (m, 2H, N$^+$CH$_2$CH$_2$), 1.32-1-13 (m, 26H, HOCH$_2$CH$_2$(CH$_2$)$_{11}$)
Appendix B: GPC Chromatograms

Figure B.1. GPC results of PS-\textit{b-PI} with normal MWD. The $D$ of starting PS is 1.07.

Figure B.2. GPC results of PS-\textit{b-PI} with MWD skewed to LHS. The $D$ of starting PS is 1.18.
Appendix

Figure B.3. GPC results of PS-b-PI with MWD skewed to RHS. The \(D\) of starting PS is 1.18.

Figure B.4. GPC results of PS-b-PI with MWD skewed to LHS. The \(D\) of starting PS is 1.4.
Figure B.5. GPC results of PS-b-PI with MWD skewed to LHS. The $D$ of starting PS is 1.5.

Figure B.6. GPC results of PS-b-PI with MWD skewed to RHS. The $D$ of starting PS is 1.52.