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SYNTHESIS OF NANOCAGES FOR APPLICATION AS NANO-SIZE REACTORS/CONTAINERS

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**A thesis submitted to the Nanyang Technological
University in fulfilment of the requirement for the
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List of Abbreviations

ABC	amphiphilic block copolymer
AFM	atomic force microscopy
BCP	block copolymer
CMC	critical micelle concentration
CMT	critical micelle temperature
D	polydispersity ($= M_w / M_n$)
DLS	dynamic light scattering
DN/DC	differential refractive index increment
DP	degree of polymerization
DSC	differential scanning calorimetry
FTIR	Fourier transform infrared spectroscopy
GPC	gel permeation chromatograph
HABA	2-(4'-hydroxybenzeneazo) benzoic acid
M_n	number average molecular weight
M_w	weight average molecular weight
NP	nanoparticles
NMR	nuclear magnetic resonance
PCS	photon correlation spectroscopy
PDS	parenteral depot system
PEG	poly (ethylene glycol)
PEO	poly (ethylene oxide)
ppm	parts per million
PS	polystyrene
P4VP	poly(4-vinylpyridine)
PS-P4VP	polystyrene-block-poly(4-vinylpyridine)
R_h	hydrodynamic radius
R_g	radius of gyration
SEC	size exclusion chromatograph
SLS	static light scattering
SEM	scanning electron microscopy
SMA	supramolecular assembly

T_c	crystalline temperature
T_g	glass transition temperature
T_m	melting temperature
TEM	transmission electron microscopy
THF	tetra hydro furan
4VP	4-vinylpyridine
XPS	X-ray photo electron spectroscopy

Abstract

Self-assembly of block copolymers (BCPs) have recently received much attention because of its ability to form microdomains that are tens of nanometers. Modified block copolymer has proved to be a promising way of preparing nanoparticles, as the chemistry of the various blocks can be made use to form domains of a variety of shape and size.

In this study block copolymer polystyrene-*b*-poly(4-vinylpyridine) (PS-P4VP) were synthesized by anionic polymerization and characterized using DSC, FTIR, NMR, SEC. Its self-assembled morphology was investigated using TEM and AFM.

We have for the first time synthesized polystyrene-*b*-poly(4-vinylpyridine) (PS-P4VP) betaine copolymers using PS-P4VP copolymer as a precursor. Solution properties studies and morphology investigations confirmed that the sultone-induced micellization led to the formation of ribbon shape nanostructures. It was also found that a core-corona inversion can be induced in-situ with water for PS-P4VP-sultone. The morphology of the micellar film can be tuned from hexagonal array of dots to ribbon-like by annealing or solvent treatment. Both annealing and solvent treatment add a facile yet effective tool for controlling pattern formation.

Gold nanoparticles, titania nanoparticles and Au-Ag alloy nanoparticles were synthesized in PS-P4VP micelle or PS-P4VP-sultone micelle by in-situ reduction. This procedure gives rise to monodisperse nanoparticles. The use of gold-polymer film as a memory device is also illustrated.

As a part of research, the use of nanoreactor for loading of catalyst for polymerization functional monomer was illustrated. Iron chloride, the catalyst for pyrrole polymerization, was successfully loaded into micellar core of PS-P4VP-sultone and a conducting polymer polypyrrole was polymerized in-situ in the iron chloride incorporated film. Spherical to

ribbon-like transition was also observed when loading metal precursor into micellar core. The particles showed high selectivity of polymer domain. Thus it exhibits great advantages over controlling pattern formation of polymer-metal composite.

1. Introduction

1.1 Background

To enable a variety of nanotechnologies, nanometer scale patterns formed by self-assembly have been considered as alternatives to replace or augment high resolution lithographic technologies such as X-ray, electron beam and interface lithography. In particular, block copolymers (BCPs) have recently received much attention. Thanks to the scale of the microdomains (tens of nanometers), their various chemical and physical properties (e.g. differential etching rates) and also to the convenient size and shape tenability of microdomains afforded by simply changing their molecular weights and compositions, block copolymers nanoscale patterns are ideal reactors for synthesizing nanoparticles.

The classical method to prepare nanoparticles using BCPs is to trap metal salts in amphiphilic block copolymer micelles formed in selective solvents. The core is able to entrap particles by complexation or association, and the shell provides the stabilization as shown in *Figure 1.1*. These micellar structures can be considered as very small reactors in which minute metal particles are formed by chemical transformation. However, the block copolymer must be selected in such a way that one block has affinity with the metal or metal salt, and the other block with the liquid medium.

Figure 1.1 Steps involved in the preparation of a metal nanoparticle.

1.2 Motivation

In principle, many potential uses of BCPs for different nanotechnologies have been proposed based on their ability to form interesting pattern. However, the main challenge of using BCPs lies in the control of nanostructure. Achievement of precise microdomain location, orientation, and elimination of various defects require introduction of external fields during the processing step. A variety of mechanical, electrical, magnetic biases and surface interactions have been proposed to manipulate and guide the microstructures of BCPs.

Therefore, in terms of practical applications of the block copolymer thin films, the following three points need to be considered.

- Thin films of BC have to be well-ordered to provide the highest density of the domains and an equal distance between them. The widely used approach to improve the order in BC is annealing at temperature above the glass-transition [1].
- A desired alignment of the domains (the typical example is represented by cylindrical or lamellar domains oriented perpendicular to the substrate surface) is required for practical application. However, the perpendicular orientation is in contradiction with the tendency of the domains to align parallel to the confining surface due by preferential wetting of the interface with one of the block.
- Some applications required that the minor component forming nanodomains to be eliminated in order to transform the BC film into a membrane/template.

It is a challenging task to develop an appropriate material and technology which will take into account the above-mentioned three points and allow fast fabrication of well-ordered nanomembranes/nanotemplates from block copolymer films deposited on solid substrate. In this work, two methods based on the idea of adjusting properties of a block copolymer supramolecular assembly with low molar mass additive are developed.

One of the methods is the use of selective solvents. This method involves the addition of formic acid to polystyrene-poly(4-vinylpyridine) (PS-P4VP) chloroform system to form hydrogen-bonded PS-P4VP. Chloroform is a common solvent for PS and P4VP but the complex formed will not dissolve in chloroform, hence inducing micellization. The other method is the use of chemical modification to change the properties of one of the block. This involves grafting of 1,3-propane-sultone to 4VP block of PS-P4VP in toluene. The introduction of the third component may strongly modify interactions at interfaces and change surface reconstruction.

1.3 Thesis scope and organization

In chapter 2, the synthesis of amphiphilic block copolymers (ABCs) via a variety of synthetic routes, the aggregation behavior of ABCs and the rules underlying the solubilization and adhesion of ABCs and also different ways of forming nanoparticles in ordered ABC assemblies from solubilized precursor states are extensively reviewed. Chapter 3 covers the synthesis procedures of block copolymer, betainization of poly(styrene)-block-poly(4-vinylpyridine) (PS-P4VP), and nanoparticles, and their characterization techniques. In chapter 4, we discussed the results of anionic polymerization of styrene and 4-vinylpyridine, the characterization of PS-P4VP results are outlined and discussed. Chapter 5 focused on two micellar systems. The first is the micellization behavior of PS-P4VP/formic acid complex in chloroform, and the second is the aggregation behavior of modified PS-P4VP with 1, 3-propanesultone in toluene. The superstructures formed such as spherical micelles, and other morphology in film upon changing temperature and solvent are presented. Chapter 6 discusses the synthesis of nanoparticles such as gold, gold-silver alloy and titania using PS-P4VP or PS-P4VP-

sultone as nano-reactor. Conclusions and future research directions are presented in chapter 7.

2 Literature Review

The increasing importance and interest in amphiphilic block copolymers (ABCs) arises mainly from their unique properties in solution and in solid state which are a consequence of their molecular structure. In particular, copolymer sequences made up of different and usually incompatible chemical composition give rise to a tendency to segregate in space. Amphiphilic properties in solution and microdomain formation in the solid state are directly related to specific molecular architecture, which can be designed by using monomers or polymers.

This review begins by reporting the synthesis of ABCs via a variety of synthetic routes and comparing the advantages of the different methods. Following that, the aggregation behavior of ABCs and the ability to form superstructures such as micelles, lyotropic phases, and mesophases in the solid state are presented. The rules underlying the solubilization and adhesion of ABCs and also different ways of forming nanoparticles in ordered ABC assemblies from solubilized precursor states are also discussed. In this work, the focus is the size and structure control of the particles and reporting the existing experiments dealing with the special catalytic properties, magnetism, and optical properties of such hybrids. The potential applications of such particles are discussed at the end.

2.1 Synthesis of amphiphilic or functional block copolymers

In the last decade, there has been considerable progress in the development of synthetic strategies to prepare block copolymers of various architectures, solubility and functionality. Architectures consist of di-block, tri-block, and multiblock copolymers arranged linearly or as grafts, star, or H-shaped blocks. The solubilities vary from

solvents with high cohesive- energy densities such as water, to media with very low cohesion energies, such as silicon oil or fluorinated solvents. Also, the control of functionality has become an important issue, motivated by the necessity to stabilize metallic, semiconductor, ceramic, or biological interfaces.

Many of the classical synthetic routes for block copolymers, for example, living anionic polymerization, have long been known and are summarized in an excellent review by Riess et al.[2] In recent years, new methods such as living cationic and living radical polymerization have become available, allowing the preparation of new classes of amphiphilic or functional block copolymers. Living polymerization techniques have the advantage of yielding narrow molecular weight distributions with predetermined degrees of polymerization, N , that depend only on the molar ratio of monomer $[m]$ to initiator $[i]$ concentration, $N = [m]/[i]$.

One of the important goals in block copolymer synthesis has always been the simplification of reaction conditions so that efficient production on larger scales becomes possible. Besides the well-known Pluronic (BASF Wyandotte) and Kraton (Shell) block copolymers, which are already used as emulsifiers and thermoplastic elastomers, new amphiphilic block copolymers based on polystyrene (PS), poly(ethylene oxide) (PEO), or poly(methylmethacrylate) (PMMA) have also become commercially available.

2.1.1 Living Polymerization

In the following section, the systems that are synthesized using sequential block growth [3] by living polymerization are presented. Living polymerization comprised of living anionic,[4] group-transfer,[5] ring opening metathesis,[6] cationic,[7] and free-radical polymerization.[8]

Amongst the living polymerization techniques, anionic polymerization is the oldest one used for a number of vinyl and cyclic monomers. Group-transfer polymerization is especially suited to acrylates and methacrylates. Living ring-opening metathesis polymerization, first described by Grubbs and Tumas [9], can be used with norbornene derivatives, initiated by special group VI-B transition-metal complexes. Living cationic polymerization is now well established for vinyl ethers and isobutylenes. Conditions for living radical polymerization have recently been optimized to prepare well-defined block copolymers. Since the radical intermediates are much less sensitive to impurities compared to anions or cations, this technique is becoming more widely used to synthesize amphiphilic block copolymers.

Anionic polymerization.

The block copolymers that have been prepared by anionic polymerization are the classic PS, polybutadiene (PB), polyisoprene (PI), PMMA, poly(methylacrylate) (PMA), PEO, poly(propylene oxide) (PPO), and poly(dimethylsiloxane) (PDMS) block copolymers. Some of the block copolymers are commercially available.

PS-PB-PS tri-block copolymers (Kraton) are used as thermoplastic elastomers, and PEO-PPO-PEO (Pluronics) as surfactants and steric stabilizers. PEO has an unusually wide range of solubility from water to toluene. This is due to specific interactions of the polyether leading to, for instance, the formation of hydrogen bonds to water molecules. Thus, it can serve as the hydrophilic block, which in combination with some of the other hydrophobic blocks forms amphiphilic block copolymers, e.g. PS-PEO and PS-P2VP-PEO (P2VP = poly(2-vinylpyridine)) and PEP-PEO (PEP = poly(ethylenepropylene)).[10]

Group-Transfer Polymerization.

Group-transfer polymerization (GTP) has become a valuable method for the preparation of methacrylate and acrylate polymers. An interesting polymer prepared by GTP is poly(2-(dimethylamino)ethylmethacrylate), a polymer that is directly soluble in water. Billingham and coworkers combined the polymer with hydrophobic methacrylate polymers. They synthesized poly((dimethylamino)ethylmethacrylate-b-methacrylate) [11], poly(2-(dimethylamino) ethylmethacrylate-b-n-butylmethacrylate)[12] and copolymers with other methacrylates [13].

Micellization of copolymers synthesized using GTP in aqueous media as well as the use of such copolymers as stabilizers for the dispersion polymerization of styrene in alcoholic media[14] has been investigated. GTP is not only useful for preparing block copolymers that stabilized hydrophilic/ hydrophobic interfaces, but also for biological interfaces. Okano et al.[15] created a highly blood-compatible polymer surface with a poly(styrene-b-2-(hydroxyethyl)methacrylate) (PS-PHEMA) block copolymer. If such blood compatibility can be introduced into a polymer with high gas permeability, a new high-performance artificial lung could be constructed. The work by Ito et al.[16] describes the synthesis of poly(4-(bis(trimethylsilyl)methyl)styrene-b-HEMA) (PBMS-PHEMA) via anionic polymerization technique. PBMS shows high oxygen permeability owing to its high mobility and low cohesion-energy density.

Ring-Opening Metathesis Polymerization.

Cohen and coworkers used living ring-opening metathesis polymerization (ROMP) techniques to synthesize block copolymers that contained functional groups [17]. Monomers such as norbornene and methyltetracyclodecene (MTD) together with tungsten initiators are commonly used. The functional groups included amino and cyclopentadiene, which form stable coordination complexes with a variety of metals. It is also possible to

obtain -COOH groups after hydrolysis of block copolymers containing trimethylsilyl groups.

Cationic polymerization.

Two classes of monomer polymerize cationically via a living polymerization mechanism: isobutylene[18] and vinyl ethers [7]. The latter has been used to synthesize a number of new amphiphilic block copolymers, but only a minority of these have been characterized in detail in terms of their aqueous solution properties. Armes and coworkers[19,20] investigated the synthesis by living cationic polymerization of amphiphilic water-soluble di-block copolymers of methyl tri(ethylene glycol) vinyl ether and isobutyl vinyl ether and their aqueous solution behavior, including a systematic variation of block lengths. It is also possible to prepare amphiphilic vinyl ether block copolymers with glycosidic moieties.

Living Radical Polymerization

Living radical polymerization is currently a very rapidly developing method in polymer chemistry [21]. It has been successfully used to prepare block and graft copolymers of styrenes, (meth)acrylates, (meth)acrylonitrile and dienes at temperatures ranging from 80 to 130 °C in the presence of catalytic amounts of transition-metal compounds (Cu, Fe, Ni, Pd). Molecular weights are controlled in the range $200 < M_n < 200\,000$ g/mol with polydispersities of $1.01 < M_w/M_n < 1.4$. Synthesis of block copolymers can be accomplished either by addition of the second monomer after the first one is already consumed, or by isolating the halogen-terminated polymer and dissolving it in the second monomer, in the presence of a transition-metal catalyst. Although the number of monomers that can be polymerized by living polymerization techniques is still growing, alternative routes have been investigated to increase the variety of available solubilities

and functionalities. Among these are active-center transformations and polymer-analogue reactions.

2.1.2 Polymer-Analogue Reactions

In all previous cases, according to a living mechanism, polymerizability and copolymerizability restrict the number of monomers. In addition, high purity of monomers during the reactions and/or the use of protecting-group chemistry is required. As living polymerization occurs only for a limited number of monomer, strategies for using monomers with protected functional groups and polymer analogue reactions have been exploited to provide a larger variety of block copolymers.

Polymer-analogue reactions broaden the diversity of block copolymer systems [22,23]. The reaction should start preferably from a well-defined and readily available block copolymer, e.g., polystyrene-block-polybutadiene, which is accessible, on an industrial scale, in a variety of compositions and molecular weights with a narrow molecular weight distribution. With the choice of the polymer and the polymer architecture, its absolute length and the relative block lengths are predetermined. Subsequent chemical reactions only change the chemistry of the two blocks, and not the molecular architecture (decoupling of structure and functionality control). An important goal is the development of mild and at the same time, effective conditions to transform the precursor block into a block of desired functionality or solubility. The reaction should not lead to any degradation or cross-linking of the polymer.

A commonly used polymer-analogue reaction is the hydrolysis of poly(methacrylic ester)s to obtain poly (methacrylic acid). Especially the tert-butyl esters are easily hydrolyzed with concomitant elimination of iso-butylene [24]. Poly(methacrylic acid)

may be prepared via polymerization of the protected monomer benzyl methacrylate and subsequent catalytic hydrogenolysis of the poly(benzyl methacrylate). More recently, Forder et al.[20] extended this benzyl protecting group approach to include poly(vinyl ether)s, and so developed routes to near-monodisperse poly(vinyl alcohol). Hydrogenation of polydienes has become a standard technique that is used commercially in the preparation of thermoplastic elastomers (Kraton). Quantitative hydrogenation can be accomplished by homogeneous catalysis using Wilkinson's catalyst [25], or by heterogeneous catalysis using Pd/CaCO₃ [26]. Block copolymers with a methacrylic acid block have been prepared from a trimethylsilyl methacrylate block by hydrolysis at room temperature with aqueous methanol.[27] Partially sulfonated polystyrenes are preferably synthesized via acyl sulfates [28]. An interesting route to convert polyisoprenes into a biocompatible Heparin analogue uses N-chlorosulfonyl isocyanate (CSI) [29]. This reactive isocyanate adds to the double bond of the polyisoprene forming a β -lactam that can be subsequently hydrolyzed to obtain a polymer containing sulfonic and carboxylic acid groups.

In many polymer-analogue reactions the precursor blocks are transformed into a reactive intermediate, which can subsequently be reacted with a wide variety of functionalized low molecular weight components, resulting in different amphiphilic block copolymers. An example of a transformation into a reactive intermediate is the epoxidation reaction of the double bonds of the polybutadiene, where epoxidation agents that effect complete conversion with only a minimal amount of side reaction are known [30]. Following the epoxidation, a variety of oxirane ring opening reactions, such as nucleophilic (Nu = nucleophile) ring opening[31] and reaction with acid chlorides [32], are applied to introduce different functional side groups. Another possibility of functionalization via reactive precursors is the hydroxylation via hydroboration with 9-BBN(9-

borabicyclo[3,3,1]nonane), followed by oxidation with $\text{H}_2\text{O}_2/\text{NaOH}$. [33, 34] The hydroxy derivative can simply be esterified with a functional acid chloride or acid anhydride, resulting in the target structure [35,36]. The polymer-analogue reactions are not restricted solely to one block, but can be performed on both blocks in a different, but selective, manner. This was performed during the synthesis of poly(ethylethylene)-block-poly(styrene sulfonate) block copolymers, a very powerful electrosteric stabilizer for emulsion and suspension polymerization [37].

2.2 Micellization of hydrophobic–hydrophilic block copolymers

It is now well established that micellization occurs in dilute solutions of block copolymers that has both hydrophobic and hydrophilic parts chemically bonded together. In a selective solvent, micellization occurs if the solution is either above a specific temperature at constant concentration (CMC) or above a specific concentration at constant temperature (CMT). The micellization of block copolymers often occurs via a closed association process, leading to a dynamic equilibrium between micelles with a narrow molar mass and size distribution and dispersed copolymer molecules. The micelles structure depends on the length of block forming the micelle core with respect to the block forming corona[38]. Above CMC, multimolecular micelles are in equilibrium with the unimers. This situation, analogous to classical low molecular weight surfactants is schematically represented in *Figure 2.1* for a A–B di-block copolymer in a selective solvent for the A block.

Figure 2.1. Schematic representation of di-block copolymer micelles in a selective solvent of the A block. (a) hairy micelle $L \gg R_c$, (b) crew-cut micelle $L < R_c$. (R_c : core radius; L : shell (corona) thickness.)

2.2.1 Preparation techniques

Block copolymer micellar systems are generally produced by using a common solvent or using a selective solvent.

In the first technique, the copolymer is dissolved molecularly in a common solvent, i.e., a solvent that is ‘good’ for both blocks, and then the conditions, such as temperature or composition of the solvent, are changed in the way that result in the formation of micelles. In this case, micellar system can also be achieved by gradually adding a selective precipitant of one of the blocks and eventually followed by stripping of the common solvent. The recommended technique for such a procedure is the dialysis technique where the common solvent is gradually replaced by the selective solvent.

In the second technique, a solid sample of the copolymer is directly dissolved in a selective solvent. The micellar solution is then allowed to equilibrate by standing in a particular condition and/or the solution will undergo a thermal treatment, followed by ultrasonic agitation.

However, depending on the block copolymer system, both these techniques, may not result in an equilibrium condition. This is especially so if the core-forming polymer has a high glass transition temperature (T_g). Two such examples are PS-PEO and PEO-PS-PEO di- and tri-block copolymers where the so-called *frozen micelles* are formed. Hurtrez [39] has shown that ultrasonic treatment is not recommended as demonstrated for this type of micelles. Also by size exclusion chromatography (SEC), Hurtrez shows that chain degradation of the PEO fringe occurs. This is especially true for high molecular weight blocks.

According to Munk [40], micelle formation by direct dissolution in a selective solvent is in general not a good method to prepare micellar solution. The resulting micelles depend on the two-phase morphology of the bulk sample as well as on the interactive properties of the selective solvent with respect to the presence of the polymer microphases. In order to reach an equilibrium within a reasonable time, it is necessary for the selective solvent to swell the insoluble block quite extensively.

The step-wise dialysis technique, pioneered by Tuzar and Kratochvil [41], is the preferred preparation technique for micellar systems, mainly in aqueous medium. The usefulness of this technique was demonstrated by Munk [40] for PS-PMAA block copolymers and by Hurtrez group for various micellar systems [39]. The formation of large aggregates can be suppressed by this technique but however it does not avoid the *freezing-in* of a given unimer-micelle equilibrium, e.g., by the formation of a *glassy* micellar core at a given temperature and/or at a specific solvent/non-solvent composition. Moreover, stepwise

dialysis of a copolymer sample which has a poly-disperse composition and/or molecular weight, can generate a poly-dispersity in the resulting micellar characteristics, such as in size, in composition, and in aggregation number.

2.2.2 Aggregation behavior of amphiphilic block copolymer micelles

Since the structure and dynamics of the block copolymer aggregates/micelles, play a predominant role in the size and morphology control of the metal colloids when formed inside, a better understanding of the underlying mechanisms of micelle formation is required. This understanding will give rise to an advanced morphology control. This is especially important in the application of the aggregates core as *nanoreactors*.

Micelle formation is generally obtained in selective solvents and these solvents are good for one of the polymer blocks. Depending on the polarity of the solvent, most of the block copolymers described above form micelles either with the more polar or with the more non-polar block forming the corona or shell of the micelles. They are known as regular micelles and inverse micelles respectively. This research focuses on making use of the stable assemblies formed by block copolymers. Therefore, a micelle morphology with the functional groups located in the micelle core is preferred.

Block copolymer micelles are much stable than surfactant assemblies and hence it is possible to visualize the micelle morphology by using transmission electron microscope. Micelles of amphiphilic block copolymers usually have hydrodynamic diameters, which is between 50 nm and 200 nm, with polydispersity between 5% and 30% Gaussian width. For more quantitative studies, static light scattering (SLS) can be employed. Studies done using SLS reveal that the size of the micelles is perfectly controlled by the length of the outer, dissolved block (N_A) and of the core-forming block (N_B) as well as the interface energy between core and solvent. For large interfaces, the relation between aggregation

number, Z , and the two blocks, N_A and N_B , was found experimentally to be [22,42] : $Z = Z_0 N_A^2 N_B^{-0.8}$, $Z_0 = 36\pi V_M^2 / A_M^3$

The quantity Z_0 contains all the geometric characteristics (the monomer volume, V_M , and the stabilized interface area per molecule, A_M). It is shown [] that these relation can be applied to chemically very different systems, such as nonionic surfactants and charged block copolymers.

2.3 Patterning with block copolymer films

The nanometer-scale architectures of self-assembling block copolymers in thin films have inspired a variety of new applications. For example, the uniform sized and shaped nanodomains formed in the films have been used for nanolithography, nanoparticle synthesis, and high-density information storage media. Imperative to all of these applications, however, is a high degree of control over the orientation of the nanodomains relative to the surface of the film as well as the control over order in the plane of the film. Induced fields such as electric, shear, and surface fields have been demonstrated to influence orientation [43 , 44]. Both heteroepitaxy and graphoepitaxy can induce positional order on the nanodomains in the plane of film. In this section, methods used to control the ordering of the block copolymer and the applications of these materials are presented. Particular attention is paid to the potential of perfecting long-range two-dimensional order over a broader range of length scales and the extension of these concepts to functional materials and more complex architectures.

The first obstacle to the study and reproduction of order within a self-assembling thin film is in casting a film of constant thickness and smooth over a large area. A few of the

common casting techniques and a discussion of how thermal equilibrium in the films can be achieved is also presented in the subsequent sections.

2.3.1 Inducing order during film formation

The long-range order of the nanoscale features is essential to most polymer thin film applications. In principle, the self-assembly process will lead to a regular and stable organization because the structure is close to thermodynamic equilibrium. Both dip coating and solution casting are slow processes which allow the copolymer to self-assemble during the casting process. Actually, the non-equilibrium effects of solvent evaporation lend an orientational field leading to interesting morphologies. For instance, the orientation of block copolymer cylinders changes with the evaporation rate of the solvent [45].

More commonly, block copolymer thin films are prepared by spin-coating. In this process, a drop of dilute polymer solution (about 1% by weight) is dropped on a spinning solid substrate. As the substrate spins, all but a boundary layer of the solution is spun off. The thickness of the boundary layer depends on the concentration and spin speed. These variables can therefore control the thickness of the final film.

The surface roughness of both spun-cast and solvent-cast films can be controlled by varying the evaporation rate of the solvent. When the solvent is too volatile, the surface is roughened by flow instabilities [46]. As is discussed later, the physical behavior of the solvent can also influence the order of the block copolymer. In particular, when the solvent is crystallizable, directional crystallization of the solvent can influence the orientation of the block copolymer self-assembly. Since the solvent is frequently chosen to maximize film uniformity, the use of truly nonselective solvents is rare. Furthermore, the solvent flashes off so quickly that equilibrium structures are not usually observed.

Self-assembly is frequently allowed to occur during a long anneal at elevated temperatures under vacuum. This technique not only removes solvents and minimizes surface-induced non-equilibrium effects, but also increases the chances of a polymer reaching its thermodynamic equilibrium morphology.

2.3.2 Film thickness

A difference in block interfacial energies attracts one of the blocks to the substrate, inducing a layering effect on the remainder of the film [47,48]. Lamellar films possess a natural repeat spacing of the domain structure, L_0 , and pay a free energy penalty due to chain stretching or compression when the film thickness is not commensurate with this spacing. This results in the generation of islands and holes (surface structures) at the polymer/air interface. Smooth films are observed after annealing above the glass transition only when the original, spun-cast film thickness matches a natural thickness (h). When both surfaces attract the same block, h equals to nL_0 . When the two interfaces attract different blocks, flat films only occur when the initial film thickness equals $(n + 1/2)L_0$. In sphere- and cylinder-forming block copolymers, islands and holes form when the film thickness does not closely match a natural thickness given approximately by $h = \alpha n + \beta$, where α is the sphere (or cylinder) layer-to-layer distance and β is the thickness of the brush adsorbed on the surfaces.

In very thin films, these surface effects can cause significant deviations from the predicted bulk structure. As shown in *Figure 2.2*, surface reconstructions of a cylindrical block copolymer including reorientation of nanodomains, wetting layers, and perforated lamellae have been observed due to the interplay between surface fields and confinement effects.

Figure 2.2 The self-assembly of block copolymers. (a) (b) phase SPM images of thin poly(styrene-*b*-butadiene-*b*-styrene) tri-block copolymer. (c) schematic height profile of the phase images. (d) a simulation of the same block copolymer.

2.3.3 Evolution of order

For all the applications mentioned previously, block copolymers are being utilized in part for their ability to form regularly sized and regularly spaced nanodomains. Even though a large number of different morphologies are expected, it may take a long time to reach the equilibrium structure. During this process, one may track several events: (1) the formation of equilibrium nanodomains; (2) the arrangement of these nanodomains into crystalline arrays of increasing size (grain boundary annihilation); and (3) the removal of defects such as disclinations and dislocations. In this section, the evolution of structures in both thick films (bulk) evolution and thin film (two dimensional) evolution will be presented.

2.3.3.1 Thicker films and bulk order evolution

Ordering kinetics have been examined in bulk samples but a mechanistic understanding of coarsening dynamics has failed to emerge due to the complexities of defect motions

that cannot be easily discerned in bulk samples. In bulk systems coarsening kinetics via depolarized light scattering [49,50] in polystyrene-polyisoprene bulk systems have been studied by Balsara and coworkers. They found that grain growth slowed down with time and suggested that grain boundaries gradually became pinned. It is necessary, however, to balance the kinetics of pattern formation with the thermodynamics of block copolymer segregation in order to achieve even higher degrees of order. For instance, Kim et al. [51] demonstrated that grain growth rates can be optimized by correctly tuning the quench depth of a bulk sample from the order-disorder temperature due again to an interplay between thermodynamic driving forces and viscous resistance. Recently, Hashimoto et al. [52] have shown that a single grain lamellar microdomain orientation can be achieved using an applied temperature gradient. Also in this case, the process is very slow (about 2 mm/day). Yokoyama et al. showed [53] that in the three-dimensional case of very thick films of block copolymer spheres, the interplay between kinetics and thermodynamics controls the extent to which layers of spheres stack with registry to the surface. The degree to which the two blocks will segregate is thermodynamically proportional to χN . The lower the temperature, the stronger is the driving force causing the two blocks to segregate and order. Diffusion of chains depends strongly on the geometry of the nanodomains. In the case of lamellar, cylindrical, and gyroid domains, diffusion along an interface occurs by a different mechanism. In the perpendicular diffusion case as well as in diffusion between spherical nanodomains, the diffusion coefficient [54] is given by, $D = D_0 \exp(-\alpha \chi N_{\min})$ where $N_{\min}$ is the shorter of the two blocks. At lower temperatures, the polymer may not diffuse fast enough to allow rearrangement of domains into a structure with long-range order. The interplay between these opposite dependences on temperature results in an optimum annealing condition for thick films of sphere-forming block

copolymers [53]. This concept should extend to other block copolymer geometries, though it has not yet been tested.

In the special case of very thin films, local defects may affect the reorganization process substantially. Usually the growth of such structures is an Ostwald ripening process where the structures are developed through coalescence. The Ostwald ripening of islands and holes can be easily followed and has provided significant insight into the motion of block copolymers in and out of these structures. Initially, islands and holes are formed randomly over the sample surface by a process analogous to spinodal decomposition [55]. Typically, the average size of the islands increases through coalescence of smaller domains and the growth of larger domains at the expense of smaller ones through an Ostwald ripening process [56,57]. This coarsening is driven by the line tension of the edges of the two-dimensional islands, so that, over time, there is a decrease in the total length of island edges. By watching the disappearance of isolated islands near an absorbing boundary, they concluded that the primary mechanism of island shrinkage is the viscous flow of chains along a continuous path created by a defect in the lamellar structure within the islands as was originally proposed by Grim et al. [58].

Islands and holes of a sphere-forming block copolymer formed on a topographically patterned substrate cannot disappear via a similar mechanism, since there is no route for viscous flow of chains even in defect structures. If the island near the absorbing boundary exists only on the top of a brush layer, the shrinkage appears to be limited by the detachment kinetics of a chain from the island. If the island is on the top of another layer of spheres, the shrinkage of the islands is much faster than would be expected if it were controlled by the diffusion of chains through the underlying nanodomain structure. This indicates the insertion of all the spheres from the island into the layer below, probably through a defect in the underlying film [59]. This is in contrast to the bulk case in which

diffusion does not appear to occur through the diffusion of entire spherical domains and instead occurs through the hopping diffusion of individual chains [60].

2.3.3.2 Two-dimensional ordering

The two-dimensional nature of a single layer of nanodomains on a surface also simplifies the task of identifying and observing individual defects. The confinement to two dimensions also fundamentally changes the nature of the organization. For instance, in the two-dimensional hexagonal crystal formed from a layer of spheres, dislocations are point defects and exist in equilibrium. As a result, it is not physically possible to have perfect order even with optimal annealing conditions at long times. Order evolution in two-dimensional systems is historically an area of interest, but true two-dimensional systems can be realized in only a limited set of experimental arrangements such as bubble rafts, magnetic bubbles, and colloids trapped between substrates or on fluid surfaces. A single layer of block copolymer nanodomains on a substrate is a new addition to this class of systems in which ordering occurs on an observable size scale over an accessible length of time within a wide range of temperatures.

As mentioned earlier, in the case of a single layer of block copolymer spheres, dislocations are point defects and exist in equilibrium. *Figure 2.3* demonstrates a number of the defects observed in two-dimensional hexagonal systems. Dislocations can be created and annihilated pairwise in equilibrium, leading to defect mediated melting similar to that seen in magnetic bubble and colloidal systems [61]. At sufficiently high $\chi N_{\min}$, where $N_{\min}$ is the degree of polymerization of the minority block, the kinetic barriers are too great to allow large grain growth and hence, a polycrystalline array with small grain size is seen. At moderate temperatures, large hexagonal grains with a finite number of dislocations were observed. As temperature is raised, the two-dimensional block copolymer crystal melts through the generation and unbinding of dislocation pairs

to a hexatic phase followed by the unbinding of the dislocations into their constituent disclinations at higher temperatures resulting in a majority block matrix with randomly arranged spheres [61]. The transition from a disordered array to a hexatic was observed to be first order [62].

Figure 2.3 Defects in hexagonally packed block copolymer spheres. Also shown are corresponding SPM images.

Figure 2.3 (a) shows the individual dislocation: a paired pentagon and heptagon (5–7 pair) occurs when two extra half rows of spheres (shown as red lines in the Voronoi diagram) intersect at the core of the dislocation. This defect has a Burgers vector in the direction of the indicating arrow. *Figure 2.3* (b) shows dislocation pair: in the Voronoi construction, this is seen as a quadrupole of two pentagons and two heptagons (two 5's and two 7's).

Figure 2.3 (c) shows that the 7–4–7 groupings are interstitial spheres (squares are colored yellow). Vacancies are frequently observed as 5–8–5 groupings (octagons are colored green) as shown in *Figure 2.3* (d). A grain boundary is seen as a string of dislocations as shown in *Figure 2.3* (e). A dislocation pair may be formed in equilibrium as shown in *Figure 2.3* (f), by the conversion of four hexagons (6's) into a pair of dislocations (two 5's and two 7's) with little mass movement of material and zero net Burgers vector (step 1). These dislocations (5–7 pairs) may then climb and glide away from each other in step 2. Finally, each dislocation may unbind into disclinations (individual 5's and 7's) in step 3.

2.4 Macromolecular Nanoreactors

Technologies that use components that are as small as several nanometers continue to be developed. Size reduction of the constituent components plays an important role in the development of these *nanotechnologies*. From a technological point of view, wide applications for many types of materials are found, including information storage, magnetic fluids, medical diagnostics, ceramics, and pigments in paints and cosmetics. The production of particles in the nanometer range is one of the most important challenges of modern materials science for following reasons:

- Owing to the fact that in nanoparticles, the surface/volume ratio can reach very high values, new applications associated with the inner surface have appeared; for example, the development of new catalysts. Optical, magnetic, electric, adsorptive, catalytic, and other characteristics of a given material can strongly vary with the size and shape of the particles, even though they may have the same composition or molecular structure. In

many cases, these properties change in an abrupt manner below a certain particle size, for example, the electrical conductivity or the type of magnetism. Ferromagnetic specimens are built up from many magnetic domains, and there is a critical size for each material below which the particles are single domain. Small, single-domain particles exhibit an exotic magnetic behavior that allows them to reach a limiting magnetism, i.e., the disappearance of the coercivity and remanence at a very high level of magnetization (superparamagnetism).

- Ultrafine particle properties are normally very different to those of the bulk materials and, at the same time, also different to those of isolated atoms. As improved syntheses lead to highly characterized samples with narrow size distributions and regular shapes, the behavior of single nanocrystals is being examined with increasing rigor and detail. Quantum-size effects were first recognized in relatively crude 2-4 nm colloidal II-VI semiconductor particles [63]. Weller reviewed a number of experiments dealing with these quantum-size effects, where optical transitions and spectral characteristics are linked to the particle size of metal and semiconductor colloids [64]. Such new properties can be continuously tuned-in and allow the exploration of mesoscopic effects ranging from the limits of quantum mechanics to classical phenomena.

2.4.1 Introduction to Preparation of Nanoparticles

The production of particles that is uniform in size and shape is still a very much studied area, both for academic and application reasons. The history of monodisperse systems is more than a century old, possibly starting with Michael Faraday's gold sols, but systematic studies of the methods to prepare and characterize such dispersions were initiated only about two decades ago. In general, these new synthetic methods can be divided into physical (molecular beam epitaxy, sputter deposition, electron beam lithography, etc.) and chemical methods. Chemical methods include a large variety of

different chemical techniques with a common property of using reactions in solutions to produce particles of different materials. In order to control the size and shape of the particles, the synthesis is based on the appropriate control of the parameters that influence nucleation and growth. The use of ligands (stabilizing agents) such as surfactants and polymers is very common in the specific control of growth and in the prevention of agglomeration of the particles once they are synthesized. These classical approaches to nanoparticle dispersions were recently reviewed in a number of recommendable contributions and include the discussion of new applications of nanostructured materials constructed from these nanoparticles [65,66,67].

The disadvantages of the traditional routes to fabrication of nanoparticles are obvious: the large interface area costs a lot of energy and requires large amounts of stabilizer or embedded surface units. The simple nucleation-and-growth route demands very low in-situ concentrations of the formed colloids, i.e., the mass output is rather low. Concentrating the products or harsh reaction conditions usually leads to the failure of stabilization and the formation of larger aggregates. For those reasons, some modern techniques developed to control the uniformity in size and shape make use of synthesis in mesoscopically confined geometries, such as in vesicles [68], reverse micelles [69], sol-gel processing [70], zeolites [71] or Langmuir-Blodgett (LB) films [72].

Nanoparticles formation in block-copolymers aggregates can be considered to be a further advancement of the techniques discussed previously. Nowadays, polymers can be tailor-made from a large choice of monomers, allowing the fine-tuning of their properties. This makes them attractive compounds for numerous applications [73,74,75]. The application of polymers as micro or nanoreactors, either as single macromolecules possessing hollow

interiors, or as self-assembled structures having one or more cavities, is a new, emerging field. Amphiphilic block copolymers, constructed from at least two blocks with different properties, tend to aggregate in solvents selective for one of the constituent blocks, thus resembling traditional surfactants. Analogous to surfactants, a range of morphologies can be observed when dispersions of amphiphilic copolymers are prepared, that is, micellar, [76] bilayer, [77] chiral, [78] and other architectures [79]. The driving force for the self-assembly is generally considered to be microphase separation of the insoluble blocks. [77]

2.4.2 Polymersomes as Nanoreactors

Vesicles can be prepared from macromolecular amphiphiles, that is, block copolymers. They are referred to as polymersomes. Since the first reports by Hest et. al, [80,81] a large number of examples describing the formation of polymersomes have been published. [82,83,84,85] The structure of vesicle-forming block copolymers can vary from a simple coil-coil di-block copolymers to rod-coil di-block copolymers to coil-coil and rod-coil multiblock copolymers with and without additional cross-linkable groups (*Figure 2.4*).

Figure 2.4 Structure formulas of various polymersome-forming block copolymers.

The advantage of polymersomes over liposomes is in their increased stability and the rigidity of their membrane system, which contribute to their increased lifetime. The vast amount of available monomers and the ability to vary the ratio of the two blocks make it possible to tune the properties of the resulting vesicles, for example, vesicle size, polarity, stability, toxicity, etc. in general. However, the permeability of the membranes of block

copolymer vesicles is reduced because their thicknesses are higher and their membranes have less fluidic character as compared to liposomes [83].

In Discher's group, much effort has been put into establishing the physicochemical properties of polymersomes based on poly(ethylene oxide)-*b*-polybutadiene (PEO-PBD) and poly(ethylene oxide)-*b*-polyethylethylene (PEO-PEE).[86, 87,88] As a first step toward in-vivo applications, encapsulation experiments were performed with the proteins myoglobin, hemoglobin, and albumin.

An interesting example of the application of capsules filled with reactive compounds was presented by White et al.[89]. They developed a polymer with self-healing capacity by incorporating microcapsules containing dicyclopentadiene monomers and a polymerization catalyst within an epoxy matrix. When the matrix was placed under stress, cracks were formed, which ruptured the embedded microcapsules, thereby releasing the monomers into the crack through capillary forces. Polymerization was initiated by contact with the catalyst, resulting in bonding of the crack faces. Fracture experiments yielded 75% recovery in toughness as compared to the virgin material.

A different approach toward the preparation of catalytically active polymersomes is the use of *giant* amphiphiles, in which proteins or enzymes act as the polar headgroup of the amphiphile and a synthetic polymer as the apolar tail. Boerakker et al. have developed such a biohybrid amphiphile by reconstituting apo-horseradish peroxidase (apo-HRP) with its cofactor, ferriprotoporphyrin IX, carrying a polystyrene tail [90]. In water, the enzyme-polymer hybrid formed vesicular aggregates with diameters of 80-400 nm. Catalytic activity measurements showed that the HRP-polystyrene aggregates were still active; however, the residual activity, however, was much lower than that of the native HRP. This approach is promising, because other ferriprotoporphyrin IX containing enzymes could also be used to construct giant amphiphiles. The resulting different

hybrids can be combined within one aggregate to give a catalytic system that is capable of performing cascade reactions.

2.4.3 Polymer Micelles as Nanoreactors

Nanoparticles are of increasing interest because of their large surface area ($100\text{--}3,000\text{ m}^2\text{g}^{-1}$) which makes them very useful in a wide range of chemical and physical applications. Various nanoparticles are produced in the presence of block copolymers in selective solvents, where they form micelles and encapsulate particles such as metal salts. These are then reduced or chemically converted to finely distributed colloidal metal particles with interesting catalytic, non-linear optic, semiconductor and magnetic properties[91].

The classical method to prepare such nanoparticles is to trap metal salts in amphiphilic block copolymer micelles formed in selective solvents. The core is able to entrap particles by complexation or association, and the shell provides the stabilization. These micellar structures can be considered as very small reactors in which minute metal particles are formed by chemical transformation. However, the block copolymer must be selected in such a way that one block has affinity with the metal or metal salt, and the other block with the liquid medium.

The use of micelle-forming amphiphilic block copolymers in the stabilization of metal nanoparticles has been intensively studied, especially by the groups of Antonietti, Moller, and Cohen.[73,92,93,94]. Not only does the presence of the polymeric shell around the metal particles aid in the prevention of agglomeration and precipitation, it also improves their processability. Since metal nanoparticles are synthesized inside their interior, the block copolymer micelles can indeed be regarded as nanoreactors. Homopolymers have also been frequently employed for the stabilization of metal colloids, mainly poly(*N*-

vinyl-2-pyrrolidone) (PVP). Although the resulting homopolymer- metal particle hybrids are not micelles, the systems are discussed in this section, since their dimensions and behavior are comparable to the micellar systems.

The nano-size dimensions of the metal particles give rise to a number of intriguing electronic, magnetic, optical, and catalytic properties, which is the result of size quantization effects and the high number of surface atoms as compared to the number of atoms in the bulk of the particle.[75, 92] The steps involved in the formation of such metal particles are depicted in *Figure 1.1*.

Figure 1.1 showed only one approach that used metal salts for the formation of polymer-metal hybrids. Other approaches have been developed as well. It is also possible to first attach the metal ions to the monomers, then polymerize the monomers, and, finally, induce aggregation of the resulting metal polymer hybrids. To obtain stable hybrid materials of polymers and inorganic material, there has to be sufficient adhesion between the polymer chains and the metal particles. For that purpose, homopolymers and block copolymers have been synthesized with functional blocks, i.e. acidic, basic, or neutral coordinating blocks. The formation of the metal colloids inside the loaded micelles occurs by performing a chemical reaction, typically a reduction reaction. For this purpose, H_2 , $NaBH_4$, $LiAlH_4$, $LiBEt_3H$ and hydrazine are commonly used to reduce the metal salt to form nanoparticles of Ag, Au, Co, Cu, Ni, Pb, Pd, Pt, Rh, and Zn [93]. The formed metal particles subsequently aggregate to yield larger particles by nucleation and growth processes.

Depending on the degree of supersaturation with the metal particle-forming salt, the interfacial tension of the block copolymer/metal particle interface and the diffusivity of the metal ions, one or more metal nanoclusters are formed within a micelle. The effect of

supersaturation with the salt $\text{Pd}(\text{OAc})_2$ inside di-block copolymer micelles of polystyrene-*b*-poly(4-vinylpyridine) (PS-P4VP) is studied by Klingehlf et. al.[95]. When the solubilized $\text{Pd}(\text{OAc})_2$ was rapidly reduced (high supersaturation), numerous small metal particles were formed within the micellar core, also referred to as the “raspberry” morphology. Slow reduction (low supersaturation), however, led to on average one large particle per micelle, which is called the “cherry” morphology as shown in *Figure 2.5*.

Figure 2.5 Formation of metal nanoparticles inside block copolymer micelles. (a) fast reduction (raspberry morphology), (b) slow reduction (cherry morphology).

Not only metal colloids have been produced using block copolymers, metal oxides such as Fe_2O_3 , TiO_2 , and ZnO and metal sulfides, such as CdS , CoS , CuS , FeS , PbS , and ZnS , have also been formed within micellar structures [75,96]. The metal sulfide nanoparticles are mostly formed by addition of H_2S to the metal precursors inside the nanoreactors, while the former nanoparticles are prepared by oxidation reactions. The optical properties of the metal sulfide semiconducting nanocrystals are very size-dependent, and the size

control can be obtained by varying the size of the polymer domains. In smaller domains, nanoparticles of lower dimensions are formed. These particles have absorption edges at smaller wavelengths due to the size quantization effect. Furthermore, reducing the dimensions of semiconductor nanoparticles results in photo-generated electrons that have higher energies, which can be utilized in photovoltaic devices, and have increased optical absorption coefficients. The latter is useful in applications where UV protection is an issue. Micellar fibers of di-block copolymers of carbosilane dendrimers and polyisocyanopeptides have been applied to prepare silver arrays by clustering Ag^+ ions inside these fibers [97].

The polymer micelle-metal hybrid itself can also be considered to be a nanoreactor, because the catalytically active metal colloid is buried inside the micelle core and the reactants have to pass through the micellar shell to reach the interior of the micelle. These hybrid particles combine the advantages of homogeneous and heterogeneous catalysis, since they can be dissolved in organic solvents, due to their polymeric shell; while catalyst recovery is carried out by performing ultrafiltration or precipitation in poor solvents for the polymer.

So far, polymer micelle-metal hybrids have mainly been applied in the hydrogenation of olefins and acetylenes, where advances have been made in chemo-selective, stereo-selective, and regio-selective hydrogenations of various substrates [92, 98]. A nice example of chemo-selective hydrogenation was presented by Yu et al. who used Pt nanoparticles stabilized by PVP to reduce the carbonyl group in cinnamaldehyde to cinnamic alcohol, while leaving the double bond intact [99]. Ethyl pyruvate was reduced enantioselectively to (*R*)-ethyl lactate in 95-98% enantiomeric excess by Pt colloids stabilized by PVP with cinchonidine as chiral modifier [100]. Colloidal dispersions of PVP-stabilized Au/Pd bimetallic clusters, prepared by successive reduction, were

employed by Harada et al. for partial selective reduction of cycloocta-1,3-diene to cyclooctene [101].

Polymer-stabilized metal colloids have also been used in oxidation reactions. The catalytic oxidation of ethylene to ethylene oxide by colloidal Ag catalysts, which were protected by PVP or sodium polyacrylate, was studied by Toshima et. al.[102,103]. Both systems had higher catalytic activities than commercial Ag powder, while the sodium polyacrylate-stabilized Ag particles gave the best results due to a higher thermal stability.

Another field of catalysis in which polymer-metal hybrid nanoreactors have been explored is C-C coupling reactions. Wang et al. [104] presented the first example of methanol carbonylation, which is one of the most important industrial processes, by using PVP-stabilized Rh colloids. The catalysts were used under harsh conditions of 140 °C and 54 bar, but could still be recycled six times, resulting in an overall turnover number of 19 700/atom Rh. Pd colloids stabilized by either PS-P4VP or PVP have proven to be useful in Heck reactions (*Figure 2.6*)[95,105].

Figure 2.6 Heck reaction catalyzed by Pd-polymer hybrids.

The polymer-stabilized Pd nanoparticles displayed activities comparable to those of low molecular weight Pd complexes traditionally used in Heck reactions, while having much higher stabilities; turnover numbers (moles of substrate/mole of Pd) as high as 100 000 have been reported [105]. The higher stability of the polymer-metal hybrid is also reflected in the high temperature (140 °C) at which these reactions were carried out.

El-Sayed and co-workers have used the Suzuki coupling as a test reaction to investigate the effect of the polymeric stabilizers on both the catalytic activity and the stability of Pd colloids (Figure 2.7) [106].

Figure 2.7 Suzuki coupling reaction catalyzed by polymer-stabilized Pd nanoreactors.

They prepared encapsulated Pd nanoparticles with the help of three different polymers: a PAMAM dendrimer, polystyrene-*b*-poly(sodium acrylate), and PVP. All three nanoreactor systems were efficient catalysts for the Suzuki reaction between aryl boronic acids and aryl halides. It was found that a strong interaction between the metal particle and the polymer resulted in a loss of catalytic activity. Lee et al. [107] investigated the same type of reaction in water using aggregates of rod-coil tri-block copolymers as micellar nanoreactors. At ambient temperatures, the Suzuki cross-coupling reaction of aryl halides and aryl boronic acids was performed in the absence of organic solvents, resulting in a potentially environmentally friendly reaction process.

Micelle-forming polymers have been employed to encapsulate enzymes. Micelle-like aggregates built up from di-block copolymers of (*N*-acetylimino)ethylene and (*N*-pentanoylimino)ethylene were capable of encapsulating horseradish peroxidase, lipase OF, and lipase P. Interestingly, the hydrolytic activities of the lipases in aqueous solutions increased by ca. 30% as compared to the free enzyme [108]. Even in watersaturated organic solvents, the enzymes showed enhanced activities. Harada and Kataoka have reported on supramolecular assemblies of micelle-forming poly(ethylene glycol)-poly(aspartic acid) block copolymers and chicken egg white lysozyme [109,110]. The

polyion complex (PIC) micelles could be reversibly formed and dissociated by changes in the ionic strength, simply by varying the NaCl concentration [111].

Lysozyme entrapped within the core of the micelles showed no enzymatic activity, but upon an increase in the ionic strength, the micelles dissociated, thus releasing the enzymes. A reduction of the ionic strength resulted in complete inhibition of the enzymatic activity. The dissociation of the PIC micelles to obtain enzyme activity is not a nanoreactor behavior, but Harada and Kataoka [112] also performed experiments using the substrate *p*-nitrophenyl-penta-*N*-acetyl- α -chitopentaoside, and they observed conversion within the core of the micelles. The apparent enzymatic activity of the entrapped enzymes was higher than that of the free enzymes, which was attributed to accumulation of substrate in the corona of the micelles. Applying a pulsed electric field to the polymerenzyme hybrids above a critical potential reduced the enzymatic activity to that of the free enzyme, presumably due to a minute change in the local microenvironment in the core of the micelles [113]. The enzymatic activity was fully restored when the electric field was shut-off.

As described previously, giant amphiphiles of polymers and enzymes can be prepared by reconstituting apoenzymes with its cofactor carrying a polymer tail. Velonia et al. have constructed another type of biohybrid amphiphile by specific attachment of a polystyrene block to a reduced disulfide bridge of CALB, which exposed on the outer surface of the enzyme [114]. TEM studies of aqueous dispersions of PS-CALB giant amphiphiles revealed the presence of micrometer long fibers that were built up from bundles of micellar rods. Catalysis experiments on these enzyme-polymer hybrids revealed that the enzymes retained activity, but it was notably reduced when compared to the native enzyme. Although this is not a nanoreactor, this approach of making catalytically active giant amphiphiles is a promising strategy in the preparation of ensembles of different

enzymes and has potential for the construction of multicomponent nanoreactors in which substrates are converted in several cascade-like steps into the desired products.

Micelles in which emulsion polymerizations are carried out can also be considered as nanoreactors. Apart from low molecular weight surfactants [115], micelle-forming block copolymers have been applied for this purpose. Jang and Ha have used poly-(oxyethylene)-*b*-poly(oxypropylene)-*b*-poly(oxyethylene) to make hollow polystyrene nanospheres [116]. Mini-emulsion polymerization has also proven to be a valuable tool for the fabrication of polymeric capsules [117]. Mini-emulsions are stable emulsions consisting of droplets of 50-500 nm in diameter created by shearing a mixture of oil, water, surfactant, and a highly hydrophobic compound. The hydrophobic compound prevents Ostwald ripening, while the surfactant stabilizes the droplets against collisions [118]. This process allows the preparation of latex particles having cavities with control of the particle size, cavity volume fraction, and structure [119]. The differences in the hydrophilicity of the oil and the polymer proved to be the driving force for capsule formation. Although mini-emulsion polymerizations do not involve the formation of micelles, it is an interesting technique to prepare hollow polymeric capsules with broad applicability.

2.4.4 Metal nanoparticle produced using copolymer

Block copolymers have been employed to synthesize various metal nanoparticles. In this section, a brief history survey is presented.

One of the first examples of metal ions complexed in micellar structures is demonstrated by Ossenbach-sauter [120]. He complexed Cu^{2+} with P2VP-PEO di-block copolymers in benzene, which is a selective solvent of PEO. Also a large variety of metal nanoparticles, mainly Au, Pd, Rc, Rh, Co, etc. have been prepared in organic medium using micelles,

such as those based on P2VP or P4VP[121,122,123,124], PEO[125,126], epoxidized polybutadiene[127], amide modified PS-PtBMA [128], PS-PMMA, PS-PB di- or tri-blocks[129], amphiphilic poly(oxazoline)[130], PS-poly(vinyltriphenylphosphine)[131].

Recently, new methods of synthesizing nanoclusters in microphase-separated di-block copolymers have been reported that provide greater control over cluster formation. Spatz et al.[132] used di-block copolymer micelles formed polymer films to contain well-ordered arrays of gold nanoclusters with a narrow size distribution. Polystyrene-*b*-poly(ethylene oxide) was first dissolved in toluene, forming a di-block copolymer micellar solution. When LiAuCl₄ is added to the solution, Li⁺ ions form complexes with PEO repeat units, thus binding the [AuCl₄]⁻ ions within the core of the micelles. Polymer thin films were formed by placing a small drop of the micellar solution on a TEM grid. Transmission electron microscopy revealed that the micelles had organized into a near-perfect hexagonal array. Annealing the sample resulted in formation of a single gold nanocluster within each di-block copolymer micelle. Kinetic control over the polymer film morphology proved an effective means of arranging the nanoparticles in an ordered array. Furthermore, the size of the nanoclusters could be controlled by varying the volume fraction of each block or the ratio, LiAlCl₄: EO

The synthesis of the zero-valent metal clusters was gaining more attention. The technique to synthesize such particles capitalizes on the formation of self-assembled microdomains within di-block copolymers. Organo-metallic repeat units comprising of one of the blocks are reduced by chemical treatment, leading to the formation of metal nanoclusters predominantly within the original organometallic domains [133,134]. The polymer morphology (lamellar, cylindrical or spherical) and domain size are determined by the volume fraction of each block and the total molecular weight of the block copolymer.

Optimum control over cluster formation is achieved by using a film with a spherical morphology.

Hiroki et.al. [135] have synthesized Co metal nanoparticles by a reverse micelle method. In this method, metal chloride is reduced in a nanoscale water pool surrounded by surfactants to form metal nanoparticles stabilized by the surfactants. They employed dodecyldimethylammonium bromide(DDAB) and sodium borohydride (NaBH_4) as the cationic surfactant and reducing agent respectively. TEM image revealed an average diameter of 4 nm. These nanoparticles can be dispersed in organic solvent and their size is tunable by the water concentration of NaBH_4 aqueous solution, which promises processibility and wide variation of the nanoparticles made by the reverse micelle method.

Chatterjee and Patra [136] synthesized cadmium sulfide aggregates through reverse micelles. The system cyclohexane–sorbitan monooleate(Span 80) provides a relatively suitable combination for the determination of cmc of the surfactant, as the properties, such as surface tension and UV absorption, show a discernible break below and above this concentration. TEM and XRD confirm the presence of primary nanocrystalline particles in the aggregates of CdS under the conditions. The primary particle size and aggregate size increase with an increase in aging time and concentration of Cd^{2+} in the solution. An increase in aggregate size accompanied by an increase in Cd^{2+} concentrations show a minor decrease in the intensity of emission at 520 nm.

A general method has been developed for the synthesis of transition metal nanoclusters (specifically Ag, Au, Cu, Ni, Pb, Pd and Pt) using a single block copolymer[59]. In this strategy, metal ions or complexes are coordinated to carboxylic acid groups within hydrophilic polyNORCOOH (NORCOOH: 2-norbornene-5,6-dicarboxylic acid) domains of an $[\text{MTD}]_{400}[\text{NORCOOH}]_{50}$ (MDT: methyl-tetracyclododecene) di-block copolymer

film. The ion sequestering is accomplished by immersing the film in an aqueous metal salt solution. Subsequent reduction of the metal ions by exposure to hydrogen at elevated temperatures, or immersion in an aqueous sodium borohydride solution, results in formation of nanoclusters with a narrow size distribution, uniformly distributed within the polyNORCOOH domains. (See *Figure 2.8*)

Figure 2.8 Block copolymer nanoreactor scheme for metal nanocluster synthesis.

This *universal* cluster synthesis technique uses the microphase-separated morphology of the di-block copolymer as a kinetic barrier to restrict cluster aggregation and migration out of the polyNORCOOH domains into the glassy polyMTD matrix (T_g ca. 210 °C). The technique allows for the simple, in situ synthesis of several types of nanoclusters within a di-block copolymer matrix. Furthermore, the technique allows for the possibility of increasing cluster size and producing core-shell clusters through multiple loading and reduction cycles.

2.5 Cross-linked micellar structures

Although micelles are stable in time at fixed conditions, their characteristics for a given system depend on the thermodynamic quality of the solvent and on temperature. For this reason, it is impossible to study that system under different conditions, e.g. in a different solvent, at a different temperature or at various concentrations. The idea of Prochaska and Baloch [137] and of Tuzar [138] to circumvent this problem was to stabilize a particular micellar structure such as block copolymers with a PB block by cross-linking of the micellar core, either by UV or fast electron irradiation.

A similar approach was made by Wilson and Riess[139], who studied the UV photocross-linking of a range of SB di-block copolymers differing in structure, molecular weight and composition. It was shown that cross-linking induces a reduction of the hydrodynamic radius of the micelle and that the cross-linking efficiency, typically between 65 and 85% and it depends on the molecular weight of the PB block. The unimers remaining in the system, after cross-linking, can easily be removed by fractional precipitation or dialysis.

Systematic studies on photocross-linking of block copolymer micelles, with a core of poly(cinnamoyl ethyl methacrylate) (PCEMA) were published more recently by Liu et al[140]. By changing the shell-forming block, e.g. PS, PAA, these authors could demonstrate by SLS, DLS, TEM and SEC, the photocross-linking of PCEMA locked in the initial structure of the micelles, without any significant change in their aggregation number and size distribution.

The other possibility, at first examined by Wooley et. al [141,142] is to cross-link the corona of the micelles, as indicated schematically in Figure 2.9. These kinds of nanoparticles are designated as shell cross-linked micelles by these authors. They applied this concept to a large variety of block copolymers, mainly hydrophobic-hydrophilic copolymers with PAA or quaternized PVP as the water soluble block, which can be

chemically cross-linked in their micellar forms. A similar approach has been described by Armes et.al [143] for the synthesis of shell cross-linked micelles where core and shell are both hydrophilic.

An alternative to form core cross-linked nanoparticles was reported by Ishizu[144]. He started with a PS–P4VP di-block copolymer having a spherical microphase separated mesomorphic structure in the solid state. A film of this material, having P4VP spherical microdomains dispersed in the PS matrix, is treated with 1,4-dibromobutane in order to cross-link the P4VP domains. The core–shell microspheres obtained by dissolution in benzene were characterized by SAXS.

Figure 2.9 Schematic drawing of Cross-linked micellar structures.

3 Experimental Procedures

This chapter covers the synthesis procedures of block copolymer and characterization techniques of polymer and its solution properties. The synthesis procedures include living anionic polymerization of poly(styrene)-block-poly(4-vinylpyridine) (PS-P4VP), the betainization of this block copolymer and synthesis of metal nanoparticles.

Solution properties can be studied using light scattering, nuclear magnetic resonance, small-angle X-ray scattering. The morphology of copolymer film can be studied using atomic force microscopy, transmission electron microscopy, scanning electron microscopy. This chapter provides an overview of these techniques.

3.1 Materials

4-vinylpyridine (4VP) and styrene were obtained from Aldrich company. They were first vacuum distilled over CaH_2 and then stored under a nitrogen atmosphere at -10°C . Prior to the polymerization, the 4VP was stirred over sodium until a light yellow color developed. It was then redistilled under reduced pressure just before the polymerization. Tetrahydrofuran (THF) was purified by refluxing over a fresh sodium-benzophenone complex. n-butyllithium (1.6M in hexane), 1,1-diphenylethylene were obtained from Aldrich without further treatment.

3.2 Polymerization

Block copolymers of poly(styrene)-block-poly(4-vinylpyridine) (PS-P4VP) with different molecular weights were synthesized by means of living, anionic polymerization. The molecular structure of PS-P4VP is shown in *Figure 3.1*.

Figure 3.1. Chemical structure of styrene, 4-vinylpyridine and PS-P4VP.

The purification of all reagents and solvents and the polymerizations were done on a double manifold connected to a high vacuum line (10⁻⁶ mmHg) and argon (99.9995%). The solvent was refluxed over sodium-potassium alloy at least for 24 hours to remove traces of water. Benzophenone was added before reflux. A deep purple indicates an oxygen- and moisture-free solvent. The reflux system for solvent is shown in *Figure 3.2*. The solvent was first put inside the polymerization flask, a few drops of styrene were added and the solution was subsequently titrated using the initiator. The color of solution changes into characteristic orange-yellow, indicating the presence of the living polystyryl anions. Styrene was freshly distilled over sodium mirrors, de-gassed and added to the initiator solution. Styrene in THF was initiated with the addition of n-butyllithium via syringe at -78°C under Ar environment. During the polymerization, the living polystyrene was capped with 1 equiv of 1,1-diphenylethylene after approximate 20 minutes of polymerization. In all cases, a small portion of the living PS was removed and quenched in de-gassed methanol. The molecular weight of the PS block was determined by size exclusion chromatography (SEC). Afterwards, 4-vinylpyridine (twice distilled over calcium hydride) was transferred via syringe into the polymerization mixture and the mixture was stirred for 1.5 h. The living block copolymer was then quenched with de-gassed methanol. Removal of approximate half of the THF was performed in vacuo, followed by precipitation of polymer into at least a 10 fold excess of hexane. Subsequent

filtering and drying yielded a white powder. Since approximated amounts of monomers were used, the percent yields of polymers were not calculated. The M_n , M_w , and M_w/M_n values of PS were determined from SEC based upon calibration with PS standards. The M_n values of P4VP and PS-P4VP were determined by comparison of unique aromatic proton resonances of pyridyl (8.1-8.5 ppm) and styrenyl (6.2-6.7 ppm) repeat units.

Figure 3.2 Solvent distill system.

3.3 Synthesis of Copolymer Polysulfobetaines.

Polystyrene-block-poly(4-vinylpyridine) (PS-P4VP, $M_n^{\text{PS}} = 11800$ kg/mol, $M_n^{\text{P4VP}} = 15000$ kg/mol, $M_w/M_n = 1.04$) were obtained from Polymer Source, Inc. The betainization of PS-P4VP di-block copolymer was carried out in chloroform at 60 °C by using 1, 3-propane sultone. The copolymer concentration was fixed at 4 mg/mL, while 1, 3-propane sultone was added in different amounts to achieve the desired ratio. The betainization of copolymer was also carried out in toluene at 60 °C for 24 hours. The resulting turbid solution was dropped into methanol to precipitate, and dried under

vacuum. The reaction scheme is as shown in *Figure 3.3*. The betainized copolymer was dissolved again in toluene at different concentrations to form micellar solutions. At high concentrations, the solution remained turbid after long hours of sonification.

Figure 3.3 Synthesis of PS-P4VP-Sultone and micellization.

3.4 Characterization of block copolymer

The as-synthesized block polymer was characterized using fourier transform infrared spectroscopy, differentials scanning calorimetry, nuclear magnetic resonance and size exclusion chromatography. In this section, a introduction of these techniques is presented.

3.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared (IR) spectroscopy is used for the detection of transitions between energy levels in molecules that result from stretching and bending vibrations of the inter-atomic bonds. The vibrational frequencies are known to be characteristic of particular functional groups in molecules. They are sensitive to the molecular environment, chain conformations and morphology and hence provide a useful method for polymer analysis. When used either alone or in combination with other physicochemical techniques, IR spectroscopy is capable of providing detailed information on polymer structure. When molecular vibrations result in the change in the bond dipole moment, as a consequence of change in the electron distribution in the bond, it is possible to stimulate transitions between energy

levels by interaction with electromagnetic radiation of an appropriate frequency. When the vibrating dipole is in phase with the electric vector of the incident radiation, the vibrations are enhanced and there is transfer of energy from the incident radiation to the molecule.

Interferometry was first used to investigate the otherwise inaccessible far-infrared region of the spectrum. Developments in Fourier Transform Spectroscopy (FTIR), made possible by the wide availability of powerful computers, have extended applications of interferometry to the whole infrared region. FTIR instrument has the much higher signal-to-noise ratio than a traditional double beam instrument.

In the present research, the Perkin Elmer system 2000 Fourier Transform Infrared Spectrometer was used to characterize the polymer. First, a background spectrum was run with KBr pellet. The copolymer sample was then thoroughly mixed with ground KBr powder and then the mixture was pressed into pellets. The spectrum of the mixed pellet was collected against the spectrum of air as the background. A total of ten scans at a resolution of 4 cm^{-1} (in the Mid IR region of $4000\text{--}400\text{ cm}^{-1}$) were taken to achieve a good signal-to-noise ratio.

3.4.2 Differential Scanning Calorimetry (DSC)

This experimental technique measures precisely the heat of reaction and the temperature rise of a sample under shielded conditions. One of the requirements of doing such measurements using DSC is that the difference in temperature between the sample and the reference should be sufficient for calibration. The difference is given by $\Delta T = K\Delta(mc_p)R$, where ΔT is the temperature difference between the sample and the reference, $\Delta(mc_p)$ is the difference in total heat capacity between the sample and the reference, R is the heating rate in $^{\circ}\text{Cmin}^{-1}$.

Thermal studies were performed using a DSC (DSC 2920, TA Instruments, USA), equipped with refrigerated cooling system (RCS), under a constant flow of nitrogen (50ml/min). Schematic of a DSC apparatus is shown in *Figure 3.4*. In order to prepare the sample to maximize effective heat transfer and to minimize thermal gradients, the weights of sample and reference pans must match as closely as possible. In order to obtain a reliable DSC curve, the sample must be in good contact with the base of the sample vessel. In order to obtain a good thermal contact for a solid sample, the sample may be brought to a temperature higher than the melting or glass transition temperature. The second heating curve obtained after the sample has been cooled at a programmed rate, has a lower noise level than the first heating curve. This procedure is not recommended for materials which provide important information in the first heating curve. The procedure is also not necessary for liquid samples that have good contact with the base of the sample vessel.

Figure 3.4 Schematic of a DSC apparatus: R is reference; S is specimen.

3.4.3 Nuclear Magnetic Resonance (NMR)

NMR spectroscopy is a very powerful technique for polymer characterization that has been developed in the past fifty years. NMR basically makes use of the nuclear spin (I) of the atomic nucleus which has a value of $0, \frac{1}{2}, 1, 1\frac{1}{2}$, etc, and has a unit of $\frac{h}{2\pi}$.

3.4.3.1 Chemical bonding-chemical shifts

Chemical shift is the result of nuclear shielding by the electron cloud surrounding the positive nucleus. When an atom/molecule is placed in a magnetic field, the induced motion of the electrons around the nucleus sets up a secondary, opposing magnetic field and shields it from the full impact of the magnetic field. The magnetic field experienced by the nucleus is therefore different from the applied magnetic field. The resonant frequency for given type of nucleus is directly proportional to the magnetic field felt at the nucleus. The shielding is dependent on the type of nucleus and the chemical bonding of the nucleus.

The result of the shielding is that the applied magnetic field has to be increased to compensate for the reduction due to this effect. The chemical shift is measured in the dimensionless δ scale (in parts per million, ppm, from the frequency of a reference compound). The applied field and the resonant frequency are related by a shielding

constant, σ , $\nu_{sample} = \frac{\gamma B_0}{2\pi}(1 - \sigma)$ and the chemical shift is given by

$$\delta = \frac{(\nu_{reference} - \nu_{sample})}{\nu_{spectrometer}} * 10^6 \text{ ppm}$$

If the proton is bonded to a carbon atom with a substituent atom, X, more electronegative than carbon, then the proton will be more shielded, resulting in a decrease in chemical shift, hence an upfield shift. The electron withdrawing inductive effect affects

predominantly the nearest proton and is known as the geminal effect ($:\text{CHX}$) and electron-donating conjugative effect, which affects mainly the vicinal protons, is known as vicinal effect ($\text{CH}:\text{CC}$). One important implication of these shifts is in the case of the presence of hydrogen bonding X and another H-atom. When a H-bond is formed, the hydrogen becomes more positive and the proton becomes deshielded and moves to a lower field, hence higher δ .

The NMR studies were carried out on a Bruker 400 MHz instrument, operating at 400 MHz (^1H) and 100 MHz (^{13}C). CDCl_3 was used as solvent. Tetramethylsilane (TMS) was used as an internal reference.

3.4.4 Size Exclusion Chromotography (SEC)

Molecular weight and molecular weight distribution (MWD) of the polymers were determined using an Agilent series 1100 gel permeation chromatograph. A mixed bed column ((PLGel Mixed Bed C, 5μ , 300×7.5 mm, Polymer Laboratories), along with a guard column (50×7.5 mm, Polymer Laboratories), were employed. The mobile phase was chloroform. Molecular weights of samples were obtained relative to polystyrene standards. The flow rate was 1 mL/min and the temperature for both the column compartment and the flow cell of the refractive index detector was maintained at $35 \pm 0.1^\circ\text{C}$.

3.5 Solution behavior of the block copolymers

The solution behavior of the block copolymer is of great interest to the present study. The reason is the preparation of nanoparticles usually involves some solvent environment which the block copolymer will experience. In this section, methods used for the study is presented.

3.5.1 Sample Preparation

In this section, the preparations of micellar solution of both original copolymer, PS-P4VP, and the betainized copolymer, PS-P4VP-Sultone, in selective solvents are presented.

3.5.1.1 Micellization of PS-P4VP/FA

For micellization of PS-P4VP/formic acid system in chloroform, copolymer solution in chloroform was allowed to equilibrate for 2 days, after which FA/ CHCl_3 solution was added dropwise into each of the copolymer solutions until the designed molar ratio was reached. The concentrations of block copolymer in the final solutions were 1mg/mL, and molar ratio of FA/pyridine units in the final solutions were 1/6, 1/3, $\frac{1}{2}$ and 1/1 respectively.

3.5.1.2 Micellization of PS-P4VP-Sultone

For micellization of PS-P4VP-Sultone system in chloroform, PS-P4VP copolymer solution in d-chloroform was allowed to equilibrate for 2 days, after which sultone/ CDCl_3 solution was added drop wise into each of the copolymer solutions until the designated molar ratio was reached. The solution was kept at 60 °C for 24 hours. The concentration of block copolymer in the final solutions was 1mg/mL, while the molar ratios of pyridine units/sultone in the final solutions were 1.0/0.1, 1.0/0.2, 1.0/0.5, 1.0/1.0 respectively.

3.5.1.3 Casting of sample from organic solvent

Polystyrene-block-poly(4-vinylpyridine) (PS-P4VP, $M_n^{\text{PS}} = 11800$ kg/mol, $M_n^{\text{P4VP}} = 15000$ kg/mol, $M_w/M_n = 1.04$) was dissolved in toluene at different concentrations; 2 mg/mL, 8 mg/mL and 13 mg/mL. The silicon wafer substrates were cleaned with piranha solution (3:1 concentrated H_2SO_4 /30% H_2O_2), and the substrates were rinsed with

deionized water, acetone, and methanol under sonication. Droplets of 13 mg/mL solution were cast onto two pretreated silicon wafer and allowed to dry in constant nitrogen flow and air flow respectively. They were stored in a dessicator for future AFM observation. Droplets of solutions at various concentrations was also dropped onto copper grid with holey carbon film and dried in vacuum. They were then stained with iodine at 80°C for half an hour.

3.5.2 Characterization of Solution Properties

The solution properties were carried out using ^1H -NMR, light scattering, atomic force microscopy and electron microscopy.

3.5.2.1 Laser Light Scattering.

Static Light Scattering (SLS). Static light scattering provides information on the time-averaged properties of the system, the weight-averaged molecular weight (M_w), the second virial coefficient (A_2). The z-averaged radius of gyration (R_g) could be obtained based on the relationship [145].

$$\frac{KC}{R_\theta} = \frac{1}{M_w} \left(1 + \frac{q^2 R_g^2}{3} \right) + 2A_2 C$$

where $K (= 4\pi^2 n^2 (dn/dC)^2 / N_A \lambda^4)$ is an optical constant with N_A , n , and λ (the Avogadro's number, the solvent refractive index, and the wavelength of incident light in vacuum respectively). C is the polymer concentration in g/ml, and R_θ the excess Rayleigh ratio at scattering angle θ . The scattering vector, $q (= 4\pi n \sin(\theta/2) / \lambda)$, is defined as the wave vector difference of the scattered and the incident beams. The refractive index increment of the polymer solutions, dn/dC , was measured using a differential refractometer.

R_g^2 is the mean square radius of gyration, defined as

$$R_g^2 = \frac{1}{m} \int_0^\infty r^2 dm = \frac{1}{m} \int_0^\infty \left(\frac{m}{V} \right) r^2 dV$$

with m the mass, V the volume of the particle, and r the distance from the center of mass within a particle.

Dynamic Light Scattering (DLS). Dynamic light laser scattering measures the temporal fluctuations of the scattered light produced by Brownian movement of the scattering particles. This temporal variation of scattered radiation yields the Doppler shift, and the broadening of the central Rayleigh line could be used to determine the dynamic properties of the system. The intensity of the scattered light can be analyzed by photon correlation spectroscopy (PCS) [146,147].

The intensity-intensity autocorrelation function is expressed as

$$g_2(t) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t)^2 \rangle}$$

where $I(t)$ is an average value of the products of the scattered intensity at an arbitrary time, t , and $I(t+\tau)$ is the intensity registered at delay time τ . The above expression can be simplified using the Siegert relations

$$g_2(t) = 1 + \beta |g_1(t)|^2$$

where β is the coherence factor and $g_1(t)$ is the field autocorrelation function. The normalized field autocorrelation function is described by the expression

$$g_1(t) = \int w(\Gamma) \exp(-\Gamma t) d\Gamma$$

where $w(\Gamma)$ is a continuous distribution function of decay rate Γ , which is the inverse of the decay time τ . If the inverse Laplace transform (ILT) is used to analyze the autocorrelation function, the decay time distribution function $w(\Gamma)$ can be obtained. For the translational diffusion mode, when the measurement angle θ is close to 0, the translational diffusion coefficient D is related to the decay rate by the expression:

$$D = \frac{\Gamma}{q^2}$$

The decay rates and the square of the scattering vector q exhibit a linear relationship, indicating that the decay is due to the translational diffusion of the aggregates in solution. For the translational diffusion mode of large aggregates, the hydrodynamic radius can be determined from the Stokes-Einstein equation:

$$R_h = \frac{kT}{6\pi\eta_0 D_0}$$

where η_0 is the viscosity of the solvent, T the absolute temperature, D_0 the translational diffusion coefficient at infinite dilution, and k the Boltzmann constant. If the diffusion coefficient in a dilute solution D is used instead of D_0 , the apparent hydrodynamic radius is obtained.

A Brookhaven BIS200SM laser scattering system equipped with a 522-channel Brookhaven BI9000 digital multiple τ correlator was used to perform both the static and the dynamic light scattering experiments. The light source is a power adjustable vertically polarized 35 mW argon ion laser with a wavelength of 632.8 nm. The inverse Laplace transform of REPES [148] supplied with a GENDIST software package was used to analyze the time correlation function (TCF), and the probability of rejection was set to 0.5.

3.5.2.2 Atomic force microscopy (AFM).

AFM images were taken with a Digital Instrument Dimension 3100 atomic force microscope under ambient conditions. The atomic force microscope was operated in the tapping mode with an optical readout using Si cantilevers.

3.5.2.3 Transmission electron microscopy (TEM).

The basic steps involved in all electron microscopy:

1. A stream of electrons is formed (by the electron source) and accelerated toward the specimen using a positive electrical potential
2. This stream is confined and focused using metal aperture and magnetic lenses into a thin, focused, monochromatic beam.
3. This beam is focused onto the sample using a magnetic lens
4. Interactions occur inside the irradiated sample, affecting the electron beam

Transmission electron microscopy (TEM) was performed on a JEOL 2010 operating at a magnification of 30,000x. The microscope is fitted with a LaB₆ filament and an acceleration voltage of 200kV was used.

Electron microscopes are based on the fact that the wavelength of an electron is inversely proportional to the velocity of the electrons, as was discovered by de Broglie in 1924, and the electron beam can be focused by passing it through a magnetic field, which was discovered by Busch in 1926. According to de Broglie, the wavelength of the electron is given by $\lambda = h/mv$. Since $V \times e = \frac{1}{2} mv^2$, the relationship between voltage and wavelength, λ ,

is given by $\lambda = \sqrt{\frac{1.5}{V}} \text{ nm}$

3.5.2.4 XPS Characterization.

The XPS measurements were made using a Physical Electronics Quantum 2000 ESCA scanning microprobe. This system uses a focused monochromatic Mg K α X-ray (1486.7 eV) source for excitation and it has a spherical section analyzer. The instrument has a 16-element multichannel detection system. The X-ray beam used had power of 300 W. The X-ray beam is incident normal to the sample and the X-ray detector is at 45° away from

the normal. The collected data were referenced to an energy scale with binding energies for Au (4f) at 84.0 (0.05 eV).

3.5.2.5 X-Ray Diffraction.

X-ray diffraction patterns were recorded with a Bruker GADDS X-ray diffractometer equipped with a two-dimensional area detector using $\text{CuK}\alpha$ radiation. A data acquisition time of 300 seconds was employed. The two-dimensional scattering patterns were integrated radially to obtain intensity against 2θ plots using GADDS software package.

3.5.2.6 UV-Vis Characterization.

UV-vis spectra were acquired with a UV-2501PC spectrophotometer. Nanoparticles of AgAu solutions were in toluene. The substrate of PS-P4VP/polypyrrole film was mica. The spectra were collected over the range 200-800 nm.

4 Synthesis and Characterization of PS-P4VP

Pyridine-containing polymers have attracted interests in recent years because they can be used in various applications. Living anionic polymerizations provide the most versatile methodologies for the preparation of macromolecules with well-defined structures and low degrees of compositional heterogeneity. In this chapter, synthesis of the block copolymer polystyrene-poly(4-vinylpyridine) (PS-P4VP) using anionic polymerization is described. The results of copolymerization of styrene and 4-vinylpyridine and the morphology of PS-P4VP on substrate are also discussed

4.1 Synthesis of PS-P4VP by anionic polymerization, and its characterization

Living polymerization is a chain polymerization process that occurred in the absence of the kinetic steps of *termination* or *chain transfer*. One of the unique aspects of living polymerizations is the fact that all of the chains retain their active centers when all of the monomer has been consumed [149].

4.1.1 General aspects

For living polymerization, if additional monomer is introduced into the system, the molecular weight will increase by an amount that can be calculated using following relation.

$$M_n = \text{weight of monomer consumed/moles of initiator}$$

Furthermore, if a different monomer is added, a di-block copolymer will be formed. Sequential addition of monomer charges can generate di-blocks (A-B), tri-blocks (such as

A-B-A, A-B-C), and even more complex multiblock structures. It is important to note that, in principle, each of the blocks in these polymers can be prepared with controlled molecular weight and narrow molecular weight distribution.

Monomers in two broad classifications are amenable to anionic polymerization: vinyl, diene, and carbonyl-type monomers with di-functionality provided by one or more double bonds; and cyclic monomers with di-functionality provided by a ring that can open by reaction with nucleophiles. The polymerizability of vinyl monomers cannot be deduced from the thermodynamics of polymerization. In general, most vinyl monomers exhibit negative free energies of polymerization, i.e., if a suitable pathway exists, the polymerization will proceed spontaneously to form the polymer from the monomer. The requirement that there exists a suitable pathway provides a major limitation on the polymerizability of monomers. Thus, for anionic polymerizability it is generally considered that there must be substituents on the double bond that can stabilize the negative charge that developed in the transition state for the monomer addition step as shown by the following reaction.

These substituents must also be stable to reactive anionic chain ends; thus, relatively acidic, proton-donating groups (e.g. amino, hydroxyl, carbonyl, acetylene functional groups) or strongly electrophilic functional groups that react with bases and nucleophiles must not be present or must be protected by conversion to a suitable derivative. In general, substituents that stabilize negative charge by anionic charge delocalization are the substituents that render vinyl monomers polymerizable by an anionic mechanism.

An important aspect of monomer reactivity in anionic polymerization is the relationship between monomer reactivity, the stability of the corresponding propagating carbanionic species and the appropriate initiating species. There also appears to be a general relationship between monomer reactivity in anionic polymerization and the stability of the anions formed by nucleophilic addition or ring opening as deduced from the pKa values for the conjugate acids of these anions. Similar considerations should be kept in mind for block copolymer synthesis with regard to the reactivity of the polymeric anionic initiator with a second block-forming monomer. Block copolymers by sequential monomer addition anionic polymerization proves to be the best technique for preparation of well-defined block copolymers. The ability to prepare block copolymers is a direct consequence of the stability of the carbanionic chain ends on the laboratory time scale. Since a living polymerization and the ability to prepare block copolymers requires the absence of chain termination and chain transfer reactions, monomer purity and the absence of side reactions with the monomer are important requirements.

4.1.2 Anionic polymerization of PS-P4VP and characterization

Pyridine-containing polymers have attracted interests in recent years because they can be used in various applications. Unlike with 2-vinylpyridine(2-VP), despite its more interesting properties, the living polymerization of 4-vinylpyridine(4-VP) has not been well studied until recently [150, 151]. Its interesting properties arise from the higher accessibility of nitrogen atom, that is easier to be quaternized to afford polyelectrolytes [152] and hydrogen bonding for constructing hierarchical supermolecular structures[153]. The possibility of using 4-vinylpyridine offers further options that ionomeric segments can be produced by quaternization of the pyridyl nitrogen with a variety of alkyl halides or inorganic acids. For steric reasons, the quantitative quaternization of the nitrogen on aromatic rings is more easily performed for 4-

vinylpyridine than for 2-vinylpyridine. While anionic polymerization of 2-vinylpyridine is relatively straightforward and is accompanied by only limited secondary reaction [154], considerable complications arise with 4-vinylpyridine [155, 156, 157]. These complications include the presence of enhanced secondary reaction involving a $-N=CH-$ unit of the aromatic ring in the para-position with the growing active center, which can result in either covalent or ionic structures. These newly generated active centers are also capable of initiating polymerization, which means that the polymers produced in this way can be a mixture of linear as well as branched material. Another complication is that solvents which are commonly suitable for the anionic polymerization, for instance, THF or diglyme, are nonsolvents for P4VP above a certain molecular weight, which results in a heterogeneous polymerization. As a consequence of these complications only a few studies have been devoted to the homopolymerization and copolymerization of 4VP. Another reason for lack of studies is the fact that homo-P4VP or its copolymers cannot be eluted or are only partially eluted through SEC columns using most common eluents such as THF, $CHCl_3$ or DMF. Hence, this most powerful tool for the study of the polymerization products can not be applied in this particular case.

4.1.2.1 Polymerization and Characterization

In this study, well-defined block copolymer polystyrene-*b*-poly(4-vinylpyridine) (PS-P4VP) was prepared using anionic polymerization by sequential addition of monomers using *n*-butyl lithium as the initiator. The well-defined PS, P4VP, PS-P4VP polymers were synthesized by anionic polymerization in a controlled manner.

High purity of monomers, solvents and initiators is required for the polymerization process. The polymerization process is described chapter 3. During polymerization, the following four points should be noted.

- The order of monomer addition is important. In general, a carbanionic chain end formed from one monomer will cross-over to form the chain end of a second monomer. This initiates the polymerization of the second monomer, provided that the resulting carbanion is either of comparable stability or more stable than the original carbanion. To prepare a block copolymer of styrene and 4-vinylpyridine, it is necessary first to polymerize styrene and then add 4-vinylpyridine to form the second block. This is because the newly formed carbanionic chain ends with 4-vinylpyridine after cross-over is more stable than the original carbanion formed from styrene.
- It is necessary to add 1,1-diphenylethylene to end-cap poly(styryl)lithium prior to reaction with 4-vinylpyridine. This is to increase the steric congestion around the carbanion and to decrease the basicity by conversion to a more stable, delocalized anion.
- The purity of 4-vinylpyridine is important. The 4-vinylpyridine was distilled two times because the second step in the synthesis of the di-block copolymer by sequential monomer addition requires that the carbanionic chain end of the first block initiates polymerization of the second monomer. The monomer added at this step must be very pure to prevent significant termination of the active poly(styl)lithium chain ends. If such termination occurs, the final product will be contaminated with polystyrene homopolymer and the molecular weight of the second block will be increased because of a decrease in chain end concentration.
- 4-vinyl pyridine should be added to the polymerization medium as a dilute solution (50% in THF v/v) rather than as the pure monomer; otherwise, the monomer could polymerize locally. This will give rise to various secondary reactions before being dispersed in the reaction medium. The polymerization of 4-vinyl pyridine is an exothermic reaction. The monomer conversion is quantitative in all cases. The

polymerization medium has been found to be clear and of a yellow color at preliminary stage. However, as P4VP grows to a longer chain, the polymerization solution becomes opaque. After the termination of the reaction with a few drops of methanol, the light yellow changed to white milky emulsion. This is due to the insolubility of long chain P4VP in THF [155].

Kinetics

To study the kinetics of the reaction, the percentage of conversion over time was determined. At a particular time, the reaction is stopped by adding a drop of methanol into the reaction mixture. The percentage of conversion can then be determined as the weight of polymer obtained divided by the weight of monomer originally added into the system.

The kinetics of the initiation reaction of n-butyllithium with styrene in cyclohexane is shown in *Figure 4.1*. From the figure, it can be seen that the conversion rate exhibits almost linear relationship with time. With the progress of the polymerization, the monomer concentration diminishes, resulting in a decrease of polymerization. About 18 minutes after the start of the reaction, the conversion of polymerization reaches 98%. The curve was fitted polynomial using origin software. A plateau is formed at about 20 mins. So when it is copolymerized with 4-vinyl pyridine, it is safe to add the second monomer at 30 minutes because the conversion of the first monomer is complete.

Figure 4.1 Rate of polymerization of styrene with n-BuLi (2×10^{-3} M) in cyclohexane at 30 °C.

Characterization of copolymer

Thermal characteristic of PS-P4VP was investigated using DSC. Two representative thermograms are shown in *Figure 4.2*. Polymer $S_{50}VP_{100}$ contains 50 styrene units and 100 4-vinylpyridine units ($S_{50}VP_{100}$) while polymer $S_{100}VP_{100}$ contains 100 styrene units and 100 4-vinylpyridine units ($S_{100}VP_{100}$). They both show two glass transition temperatures (T_g) which correspond to T_g of PS block and P4VP block. T_g s of $S_{50}VP_{100}$ are 85 °C for PS block and 144 °C for P4VP block, and T_g s of $S_{100}VP_{100}$ are 87 °C and 144 °C respectively. The slightly higher T_g of PS block in $S_{100}VP_{100}$ is due to the longer chains of polystyrene. The presence of the two T_g s indicates that the block copolymer was successfully synthesized.

Figure 4.2. DSC thermographs of copolymers PS-P4VP.

Infrared spectra of block copolymer were recorded on Perkin-Elmer Spectrum One FTIR instruments using KBr tablets. The spectra were obtained over a frequency range of 4000-400 cm^{-1} at a resolution of 4 cm^{-1} as shown in *Figure 4.3*. As compared to the PS spectra, a strong absorption at 1413 cm^{-1} , corresponding to the pyridine, and at 820 cm^{-1} that corresponds to the single-substituted pyridine ring appeared in the spectra of PS-P4VP. Similarly, in contrast to the P4VP spectra, the absorption peaks at 1493 cm^{-1} and 1452 cm^{-1} which were characteristic of phenyl ring, became stronger, and the peak at 700 cm^{-1} , corresponding to signals of single-substituted phenyl ring, appeared in the spectra of PS-P4VP.

Figure 4.3 IR spectrum of PS, P4VP and PS-P4VP.

The ^1H -NMR spectra and chemical structure of copolymer are shown in *Figure 4.4*. Peaks a, b, and c at 8.38 ppm, 6.5 ppm and 7.2 ppm represent the hydrogen under different chemical environment in this structure. The molar ratio of PS block to P4VP block were obtained by comparing the area of peak b and peak a.

Figure 4.4 ^1H NMR spectrum of PS-P4VP in CDCl_3 .

Molecular weights and molecular weight distributions were determined using size exclusion chromatography (SEC). The SEC (also known as size exclusion chromatography (SEC)) is one of the most useful methods for routine determination of average molecular masses and molecular mass distributions of polymers. Separation of the molecules occurs by preferential penetration of the different sized molecules into the pores; small molecules are able to permeate more easily through the pores compared to the larger sized molecules, so that their rate of passage through the column is slower. However, there is also a drawback of the SEC test, especially for the block or graft polymer. It was calibrated with linear polystyrene standards. The three-dimensional architecture of star-shaped copolymer can yield smaller hydrodynamic volumes in solution and caused an underestimation of absolute molecular weights. For this study, this drawback is not present.

Figure 4.5 SEC trace of (a) precursor PS and (b) di-block copolymer PS-P4VP.

Figure 4.5 shows the chromatograms of PS precursor and a typical PS-P4VP block copolymer synthesized in cyclohexane at -78°C . The SEC analysis shows that the number average molecular weight of homopolymer (PS), M_n , is 5000 and its distribution

(M_w/M_n) is 1.12. A broadening of the molecular weight distribution was noticed when it was copolymerized with P4VP. The distribution becomes about 1.2-1.3. In the *Table 4.1*, the experimental M_n values are compared to those calculated from the monomer/initiator molar ratio and conversion assuming a living process. The calculated molecular weight, $[M](cal)$ is given by

$$[M](cal) = 104.5 \times [M]_{10}/[I]_0 + 105.4 \times [M]_{20}/[I]_0$$

where $[M]_{10}$, $[M]_{20}$ and $[I]_0$ are the initial concentrations of the first monomer, second monomer and initiator. Both molecular weight values are close. The experimental molecular weight obtained from SEC is in general a little higher than the calculated one. This indicates that a fraction of the initiator was lost. This most likely occurs during the initiation step, because of the reactions with impurities in the monomer. It is also noted that when there is an increase in the fraction of P4VP block, molecular weight distribution becomes wider. It may be due to the fact that the level of impurities that can be tolerated decreases with increasing molecular weight of the desired polymer, since decreasing amounts of initiator is required.

Table 4.1 Block copolymer molecular characteristics

polymer	Concentration of LiBu (mol/L)	Yield(%)	$M_n(Cal)$	$M_n(SEC)$	M_w/M_n
S ₅₀	0.02	100	5200	5400	1.12
S ₅₀ V ₂₀	0.02	100	7300	7500	1.23
S ₅₀ V ₄₀	0.02	100	9416	9200	1.24
S ₅₀ V ₆₀	0.02	100	11500	12000	1.22
S ₅₀ V ₁₀₀	0.02	100	15740	15200	1.25
S ₁₀₀ V ₁₀₀	0.02	100	21000	21000	1.29

Effect of THF

The Lewis base THF has been used as an additive to modify the initiation reaction of alkyllithium compounds. *Figure 4.6* shows the chromatograms of a typical PS-P4VP block copolymer synthesized in cyclohexane at $-78\text{ }^{\circ}\text{C}$ with and without addition of THF. It was found that molecular weight distribution dropped from 1.42 to 1.23 when THF was added during polymerization. It was also found that for styrene polymerization in cyclohexane with *n*-butyllithium as initiator in the presence of THF, the initiation step is completed instantaneously on mixing of the reagents. Using small amounts of THF ($[\text{THF}]/[\text{LiBu}] = 30$), narrow molecular weight distribution polystyrenes ($M_w/M_n = 1.12$) were prepared with *n*-butyllithium in cyclohexane. The normal molecular weight distribution range of *n*-butyl lithium initialized anionic polymerization is found to be in the range 1.2 to 1.4.

Figure 4.6 SEC trace of di-block copolymer PS-P4VP (a) addition of THF, (b) without addition of THF.

Since *n*-butyllithium is aggregated predominantly into hexamers in hydrocarbon solution, the fractional kinetic order dependency of the initiation process on the total concentration of initiator was rationalized on the basis that the species that reacts with styrene monomer

must be the un-associated form of the initiator. Also, this un-associated species is formed by the equilibrium dissociation of the hexamer, and can be written as:

It is known that Lewis base decrease the average degree of association of organolithium aggregates. Thus it can be assumed that the initial additions of ether to hydrocarbon solutions of polymeric organolithiums promote dissociation of these aggregates. This can lead to an increase in propagation rate compared to the initiation rate, and thus narrower distribution of polymer can be obtained.

4.2 Self assembly of thin film

Above a certain critical micelle concentration, amphiphilic block copolymer molecules can aggregate to form micelles in selective solvents. In particular, block copolymer are known to assemble into spherical reverse micelles in organic solvents, with the insoluble polar blocks collapsing together to form the core and the soluble non-polar blocks forming the corona which extends into the solvent environment. Spherical aggregates are generally very mono-dispersed. It is commonly believed that they are formed via closed association of a fixed number of macromolecules per micelle [158]. Since the dimensions of block copolymer micelles fall between 10-100 nm range, the self-assembly of micelles into ordered patterns has many applications in nanotechnology. One example of such application is that, the polar cores of laterally ordered micelles were employed as templates in which 2D arrays of inorganic nanoclusters were created [159,160].

In this section, the self-assembly of asymmetric di-block copolymers into surface micelles, which occurs during the adsorption of copolymers onto a solid surface from solution is presented. These 2D structures are shown to be the equilibrium configuration

of the di-block copolymer in the presence of selective solvent, toluene. The films were deposited on solid surfaces by passive dipping technique which forms chemically inhomogeneous patterning masks with structure length or pattern distances in the nanometer range. Hence, the understanding of the physical principles governing the pattern formation enables one to control the scale, the morphology and the chemical composition of polymer aggregates. The morphology evolution of di-block copolymer polystyrene-block-poly(4-vinylpyridine)(PS-P4VP) thin film in the presence of different solvents was also investigated. It was also found that the pattern formed when the film is dried in air is different from when dried in nitrogen.

4.2.1 Concentration dependence of PS-P4VP micelles morphology

PS and P4VP are highly incompatible [161] due to the high interaction energy between them ($\chi = 0.1$). The phase separation takes place immediately at the air-film interface when the solvent concentration reaches the critical value due to the solvent evaporation. The P4VP phase will solidify and deplete from the solvent prior to PS phase because of its lower solubility [162]. Therefore, it is reasonable to expect the P4VP phase to protrude from the film surface, forming isolated islands.

Cooling of the top surface due to the solvent removal is similar to heating of a fluid film from the bottom surface. Both ways generate temperature gradient in the liquid layer. The temperature gradient in the fluid results in a local surface tension variation produced by the upward flow of warmer liquid from the bulk. Because of this surface tension variation, convection cells with a honeycomb pattern are produced. The unfavorable phase domains, which are made up of the less soluble phase, are at the centers of the convection cells, and in steady state due to a low surface tension force. Therefore, the domains are isolated and arranged in an ordered hexagonal pattern during the circulation of liquid. The patterns are retained in the solid film after complete solvent evaporation.

Three different concentrations, 2, 8 and 13 mg/mL, of PS-P4VP in toluene were cast. The concentrations are significantly above the critical concentration for phase separation to occur. In general, the cmc of PS-P4VP in toluene is 0.065 mg/mL [163]. Hence, the formation of reverse micelles is expected in all the three cases.

Figure 4.7 TEM images of films cast from different concentration of di-block copolymer/toluene solution: (a) 2, (b) 8, (c) 13 mg/mL.

Morphologies of thin film cast on copper grids are shown in *Figure 4.7*. Since toluene is a good solvent for PS and is a poor solvent for P4VP, the P4VP block collapses to minimize the unfavorable interaction with toluene. The dark areas in the image are the core of the micelles, which is made up of iodine vapor stained P4VP. The spaces between cores, which appear light in the TEM image, are made up of PS block. The morphology

was found to depend strongly on the solution concentration. At low concentrations, spherical micelles with fairly long-range order are observed as shown in *Figure 4.7(a)*. The unfavorable interaction between PS and P4VP limits the amount of PS/P4VP interfacial area and determines the minimum spherical micelle size and micelle-micelle distance [164]. With an increase in concentration, the micelles become bigger such that it might exceed the thickness of the film. In that case, the micelles will transform to cylindrical form that extend from one side of the film to the other. Although ribbon or cylindrical micelle configuration energy is normally higher than spherical micelle, with a further increase in concentration, this configuration becomes the ground state of the system since it can accommodate more material while keeping both the micelle core and corona dimensions constant as shown in *Figure 4.7(b)*. The micelles appear to be cylindrical as seen in the transition regions between the thinner film and the thicker film. The orientation of the cylinders is tilted due the surface tension effect. In the regions where the film is thicker, because of surface energy generated in the case of having a rod extending from one side of the film to the other is high, the rods transform into double layer of micelles which has lower surface energy. With further increase in concentration and increase in film thickness, the film now shows a uniform double layer of spherical micelles lying above the first layer as shown in *Figure 4.7(c)*. The different shades of gray are due to the formation of stable multilayers. The diameter of the I₂-stained P4VP domains (cores) of the micellar aggregates is 33 nm. The spacing between adjacent stained P4VP cores is approximately 29 nm.

TEM samples sometimes contain some artifacts introduced due to the thickness or rather the thinness of the film. To confirm the ground state structures at a particular polymer concentration, the structure is studied using AFM. AFM provides the measurement of size and size distribution. On top of that, AFM also allows the visualization of three-

dimensional shape and measurement of sizes in the solid state which eliminates the perturbations due to solvent swelling.

Figure 4.8 AFM images of copolymer solution (2 mg/mL) cast on carbon-coated mica: (a) planar view, (b) three-dimensional view, (c) profile analysis.

An AFM picture of copolymer solution cast on silicon wafer without iodine stain is shown in *Figure 4.8*. The aggregates are clearly seen on the surface. Looking at both the planar image (*Figure 4.8(a)*) and the three-dimensional image (*Figure 4.8(b)*), the micelles appear spherical with a rather narrow size distribution. The size of micelles obtained is about 40 nm, in agreement with size obtained from TEM. It was obtained by measuring the distance between of two protruding peaks as shown in the *Figure 4.8(c)*.

4.2.2 Solvent treatment of micellar film

A 13 mg/mL copolymer solution was cast on highly polished silicon wafer for AFM observation. The solution was dropped onto silicon wafer under a constant dried nitrogen flow. The film was then allowed to dry. *Figure 4.9 (a)* shows the AFM image obtained for this sample. *Figure 4.9 (b)* shows the magnified image of the morphology. The ribbon shape micelles with narrow size distribution can be seen. The diameter of the ribbon is found to be 40 nm. There is a discrepancy in the structures observed using TEM and AFM. The reason for this discrepancy is that for the thin film sample (TEM), there is moisture present in the environment and hence in the absence of surface effect and at high concentration, spherical micelles are obtained. Spherical micelles are the stable ground state because water can occupy the space in core made up of bulky P4VP chains. In the case of drying in nitrogen, water was excluded in the system. In order to pack the bulky chains efficiently (without empty space between them) they are stacked next to each other to form cylindrical micelles.

Figure 4.9 Morphology evolution of micelle film: (a) copolymer film dried in N_2 , (b) enlargement of (a), (c) after ethanol treatment, (d) after water treatment, (e) after toluene treatment.

The stability of the ribbon-like micelles in the solvent environment is also investigated. Ethanol treatment was selected because it is a good solvent for P4VP. A drop of ethanol

was dropped onto the film while it was still on the AFM testing panel. It was done to ensure that the position of the film remains unmoved and also the same area is detected when tip approaches the surface again. The image obtained is shown in *Figure 4.9 (c)*. The morphology remained largely unchanged except that holes were formed and there were more protruding regions. The surface became more uneven as compared with *Figure 4.9 (a)*. This sample was further treated with water. *Figure 4.9 (d)* shows an obvious transformation of micelles from ribbon to spherical after water treatment. The dimension of spherical micelles was larger than the original ones. This proves that in the presence of water, water will occupy the core of the micelles, and the micelles are able to achieve a lower energy state by forming spherical instead of cylindrical micelles. Toluene was added in an attempt to recover the original morphology. Instead of recovering the original ribbon structures, the micelles remained spherical. On top of that, they also become smaller and closer packed as shown in *Figure 4.9 (e)*.

The reasons behind the effect of various solvent treatments can be explained as follows: Originally, ribbon-like micelles were formed in solution. When cast on to the substrate, it retained its original shape. The drying was carried out in dried nitrogen atmosphere to exclude water in the air. Whether or not the solvent segregates into the P4VP cores is highly dependent on the solvent polarity. As ethanol is less polar than water, it did not preferentially segregate into P4VP core, but instead, remained in both regions. In the case of water, as the polarity is higher, its interacting energy with PS is higher. It resulted in a preferential segregation into the P4VP cores and in the swelling of P4VP core. Hence the mobility of the P4VP polymer chains increased and they could organize into a micelle structure that minimizes the total surface energy. The transition from small ribbon to large sphere occurred. Once the solvent has completely evaporated, the polymer chains mobility decreased and the micelle structures were frozen. The ribbon-spherical

transition, upon selectively swelling one of the blocks with selective solvent, was also explained by Hashimoto et al. [165] in terms of balancing the gain in conformational free energy with the bending of the interface. Further treatment with toluene disrupted the large micelles because of the solubilisation and new micelles form by reorganization. As there was trace amount of water, the micelles became spherical and smaller, similar to the size of micelles obtained from TEM.

Compared to the micellar film dried in nitrogen flow, the evolution of the film morphology dried in air gave a different result. The morphology obtained from 13 mg/mL sample is shown in the *Figure 4.10* (a) and *Figure 4.10* (b). Hexagonal shape holes of more than 2 μm in size formed. Interestingly, there are a large numbers of small micelles aggregating on the surface between the holes as shown in the *Figure 4.10* (c). The micellar size was about 50 nm. The hexagonal shape holes can be explained in terms of the packing of water molecules. The high vapor pressure of toluene and the velocity of air across the surface encouraged solvent evaporation, therefore, rapidly cooling the surface. This cooling leads to the nucleation and growth of water droplets as a function of time[166]. Airflow across the surface, coupled with convection currents on the solution surface due to evaporation, drove the ordering of the water droplets into hexagonally packed arrays. By the time the surface was covered by water droplets, the temperature difference between the surface and the droplets was no longer present. The droplets, which were denser than the solvent, sank into the solution. Hence, the hexagonally ordered holes were formed.

Figure 4.10 Morphology of film formed in air: (a) planar view, (b) three-dimensional view, (c) enlargement of the surface shown in (a).

In summary, successful synthesis of PS-P4VP by anionic polymerization was confirmed using DSC, FTIR, NMR and SEC. Addition of small amount of THF leads to narrower molecular weight distribution of copolymer. Also, purity of monomer, solvent, and order of addition of monomer played an important role in synthesis process.

Morphology of surface micelles of di-block copolymer polystyrene-block-poly(4-vinylpyridine) (PS-P4VP) at different concentrations was investigated using TEM. The

highly-ordered pattern of surface micelles was found to depend strongly on the solution concentration.

The spherical-to-ribbon transformation and formation of multilayers of micelles were observed at higher polymer concentration. The evolution of morphology of surface micelle on Si substrate in the presence of different solvent environment was investigated using AFM. Ribbon-to-sphere transformation was observed for the film prepared under nitrogen atmosphere when treated with water. Hexagonal shape holes were detected by AFM for the film prepared under air flow. The moisture in the air may played an important role in the formation of this structure. This work has helped to understand the physical principles governing the pattern formation, thus enabling one to control the morphology and its dimensions.

5 Solution Behavior and Film Morphology of Copolymer Derivative

Block copolymers (BC) can form micelles in selective solvents and they can self-assemble in the films of block copolymers. They are the focus of intensive investigations due to their ability to self-assemble into well-ordered periodic structures. However, in the films of practical interest (thickness in the range of several bulk periods), the surface phenomena dominate over the morphology of the film, hampering the fabrication of the ordered material with the desired orientation of nanoscopic domains. In terms of practical applications of the block copolymer thin films, the following key points need to be considered.

As mentioned earlier, the first point is that, thin films of BC have to be well-ordered to provide the highest density of the domains and an equal distance between them. The widely used approach to improve the order in BC is annealing at temperature above the glass-transition [167]. The second point is that a desired alignment of the domains (the typical example is represented by cylindrical or lamellar domains oriented perpendicular to the substrate surface) is required for practical application. However, the perpendicular orientation is in contradiction with the tendency of the domains to align parallel to the confining surface due by preferential wetting of the interface with one of the block [168]. Lastly, some applications require that the minor component forming nanodomains to be eliminated in order to transform the BC film into a membrane/template.

It is a challenging task to develop an appropriate material and technology that is simple and takes into account above-mentioned points and allows fast fabrication of well-ordered nanomembranes/nanotemplates from block copolymer films deposited on solid substrate.

In this work, two methods based on the idea of adjusting properties of a block copolymer supramolecular assembly with low molar mass additive are developed.

One of the methods is the use of selective solvents. This method involves the addition of formic acid to the PS-P4VP chloroform system. Chloroform is a common solvent for PS and P4VP, and the addition of formic acid results in formation of P4VP-acid complex which is insoluble in chloroform, inducing the micellization. The other method is the use of chemical modification to change the properties of one of the block. This involves the grafting of 1,3-propane-sultone to 4VP block of PS-P4VP in toluene. The introduction of the third component may strongly modify interactions at interfaces and change surface reconstruction.

In this chapter, the micellization behavior of PS-P4VP/formic acid complex in chloroform is presented. The solution properties was studied using ^1H -NMR, ^{13}C -NMR, light scattering, and its film morphology was investigated using TEM and AFM. The aggregation behavior of modified PS-P4VP with 1, 3-propanesultone in toluene and the self-assembly behavior that give rise to superstructures such as spherical micelles, and other morphologies in film upon changing temperature and solvent are also presented.

5.1 Micellization of PS-P4VP/FA in chloroform

Pyridine ring is an H-bond acceptor. The H-bonding between pyridine and carboxylic acid had been previously used to construct small molecular liquid crystalline complexes, side chain and main chain liquid crystalline polymers, ladder-like and cross-linked network systems. The application of the commercial poly(4-vinyl pyridine) relies on the ability of pendent pyridine rings to form H-bonds with 4-docecylbenzenesulfonic acid (DBSA).

Chloroform is a common solvent for the both blocks in the PS-P4VP copolymer, as well as a solvent for formic acid (FA). The 1.0 mg/mL solution of block copolymer in chloroform was mixed with FA at different molar ratios of FA to the pyridine rings in the block copolymer. When the block copolymer was mixed with FA at different molar ratios, blue opalescence appeared immediately. The complexes of formic acid/PS-P4VP in deuterated chloroform at different molar ratios were characterized by ^1H NMR. The spectra of the complexes with molar ratio of 1/6, 1/3, 1/2, 1/1 are shown in the *Figure 5.1*.

Figure 5.1 ^1H NMR spectra of FA/PS-P4VP in CDCl_3 at different molar ratio values: A=1/1, B=1/2, C=1/3, D=1/6.

In chloroform, the block copolymer formed complex with formic acid by hydrogen bonding. Interpolymer complexation due to hydrogen bonding can lead to micellization [169]. In this case, the driving force for the micellization is more complicated. Firstly, taking an individual repeat unit into account, after formation of H-bond with formic acid,

the P4VP block may become insoluble on complexation. Secondly, the interpolymer complexation may lead to physical cross-linking of the polymer chains due to the Coulombic interaction.. In this case, the complexed unit is insoluble and associates to form the core of aggregates, driving the micellization. These aggregated pyridine units lose their mobility as well as their signals in the spectra [170]. However, all the PS block chains, as the shell of the aggregates, should remain in a soluble state and their signals' intensities do not change with molar ratio. From the spectra, with the addition of formic acid, the relative intensity of peak b assigned to the hydrogen atoms H_b in the benzene rings only does not change while those of peak a and peak c, which are associated to H_a in the pyridine rings and H_c in both the pyridine and benzene rings, decrease. It is noted that when the molar ratio is low, the pyridine signals is fairly strong, indicating the presence of many movable pyridine units. Therefore, a large part of the pyridine units remains soluble. When the molar ratio is high, peak a disappears indicating that most of pyridine units are seriously restricted and lose their signal. It is interesting to note that the intensity ratio of b to c becomes close to $3/2$, which is the number of the H_b to H_c in the benzene ring. It is possible to conclude that the aggregates at high molar ratio are in fact the conventional micelles. It is noted that peak a in spectra D at 8.10 ppm, and peak a in spectra of copolymer (*Figure 4.4*) at 8.38 ppm, shows a high field shift. It maybe due to the fact that the detectable pyridine rings are in fact closely surrounded by aggregated ones, which partially shield the outer magnetic field for those detectable pyridine rings. A similar high-field shift (0.2 ppm) of the methyl group signal due to the shielding was found for the methyl red encapsulated in a dendrimer [171].

Figure 5.2 ^{13}C -NMR spectra of (a) PS-P4VP in CDCl_3 (b) FA / 4VP at molar ratio 1/1.

Figure 5.2 shows ^{13}C -NMR spectra of PS-P4VP/FA in deuterated chloroform at molar ratio 1/1. It can be seen that the peak associated with the carbon atoms in pyridine at 152.4 ppm disappears and the peak associated with CH-CH_2 at 40.6 ppm diminishes, indicating the formation of micelles with P4VP/FA in the core as their signals are shielded. The peak associated with the carbon atoms in the carboxyl of the acids is at 166 ppm. The lack of the hydrocarbon tails and higher acidity of FA make the complexed units of pyridine/FA insoluble in the low-polarity medium, resulting in micellization.

The resultant aggregates were characterized by static light scattering (SLS) and dynamic light scattering (DLS). The average hydrodynamic radius (R_h), the average radius of gyration (R_g), and the values of R_g/R_h of the resultant aggregates at different molar ratio are presented in Table 5.1.

Chapter 5 Solution Behavior and Film Morphology of Copolymer Derivative

Table 5.1 DLS data of PS-P4VP/FA at different ratios at concentration of 5 mg/mL

FA/4VP	R_h (nm)	Polydispersity	R_g (nm)	R_g/R_h
0.1	47.2	0.253	60.1	1.27
0.3	66.8	0.271	63.5	0.95
0.5	34.7	0.199	30.5	0.87
0.7	33.9	0.060	32.5	0.95
1.0	36.2	0.039	29.2	0.81
1.5	36.6	0.039	29.1	0.79
2.0	36.7	0.040	27.3	0.74
2.5	37.2	0.029	28.7	0.77
3.0	37.3	0.026	27.6	0.74

Figure 5.3 R_h and R_g values of PS-P4VP / FA in chloroform at different molar ratio (FA: VP) values at 5 mg/mL, at 298 K.

Figure 5.3 shows the R_h of the micelles of FA/PS-P4VP in a 5 mg/mL chloroform solution at different molar ratios. After addition of a small amount of formic acid (FA : 4VP = 1 : 10), R_h measured was 47.2 nm. The association takes place when molar ratio of FA/4VP is 1:10, since there is a marked increase of R_h compared to that of an individual copolymer chain (R_h of the pure copolymer in chloroform was measured to be approximately 12 nm). An even more remarkable increase of R_h to 66 nm was observed when molar ratio is increased to 3:10. However, an immediate decrease of R_h was recorded when molar ratio is increased to 5:10. At ratios greater than 5:10, the R_h value was kept at about 36 nm.

The increase of R_h can be explained hydrogen bond formation of formic acid with pyridine ring as shown in Figure 5.4. The bonding of formic acid to pyridine unit results in the pyridine block becoming insoluble in chloroform, causing the aggregation of polymer chains in chloroform. Small amount of formic acid is enough to induce the aggregation. When only 10% of 4VP was H-bonded with formic acid, most of pyridine units are not bonded to FA molecules and these units are soluble. Therefore, the core may be to some degree like a *soluble network* and the chain density is low. Increase of molar ratio to 3:10 makes the soluble network expands to its extreme, with R_h reaching 66.8 nm. When more FA was H-bonded with pyridine at molar ratio of 5:10, half of pyridine rings are insoluble and the P4VP block chains tend to aggregate together in a much more compact manner than the soluble network, so a smaller R_h of 37 nm was detected. It is possible that, similar to the case reported by Kabanov and Eisenberg [172], due to the binding with small molecules, the rigidity of P4VP chains increases and their conformation does not change considerably with the variation of molar ratio. Therefore, no further formic acid can be bonded to pyridine when the molar ratio was more than 5/10, and the R_h value remains constant.

The values of R_g/R_h (R_g is the average radius of gyration obtained from SLS) is an important parameter that indicate the internal feature of the aggregates. Theoretically, for a uniform non-draining solid sphere, a non-draining thin shell vesicle, a hyper-branched cluster and a random coil, the ratios of R_g/R_h are about 0.77, 1.0, 1.0 to 1.3 and 1.5 to 1.8 respectively [169]. In our case, the R_g/R_h value changes from 1.27, in the range of hyperbranched cluster, to 0.74, which is a feature of a conventional micelle.

Figure 5.4 Micellization of FA/PS-P4VP in chloroform.

Figure 5.5 Decay time distribution function of chloroform solution of PS-P4VP/FA at different molar ratio (FA:VP) values: A = 30/10, B = 10/10, C = 5/10, D = 3/10, E = 1/10 at 5 mg/mL, at 298 K.

The decay time distribution functions of FA/PS-P4VP in chloroform at 5 mg/mL at 298 K, are shown in *Figure 5.5*. $A(\tau)$ is the distribution of relaxation time in GEX(General EXponential) model [173]. In *Figure 5.5*, the peak becomes sharper with decreasing 4VP to formic acid ratio. At high molar ratio of 4VP to formic acid, one broad peak is observed, indicating the formation of large aggregates. At the higher molar ratio, the peak becomes sharper, indicating that smaller aggregates with a narrower size distribution were formed.

TEM observations, as shown in *Figure 5.6*, proved that the nanosized aggregates were formed at molar ratio FA: 4VP of 3:10 and 10:10. The dark area is the P4VP/FA stained with I_2 vapor. However, the TEM images of aggregates obtained at molar ratio of 3:10 and 10:10 are different. *Figure 5.6 (a)* shows large aggregates and small aggregates coexist in the film with high polydispersity. Some aggregates are spherical and some are elongated. The DLS polydispersity of 0.271 also indicates broad distribution of particle size. *Figure 5.6 (b)* shows relatively monodisperse spherical aggregates though there are a few large aggregates due to the aggregation of small aggregates. The diameter of the core is measured to be about 35 nm, larger than the PS-P4VP core in toluene as shown in *Figure 4.7 (a)*. This may be due to the swelling effect of formic acid on P4VP core. One distinct feature of these two images compared to the PS-P4VP is that there is no ordered array of micelles.

(a)

(b)

Figure 5.6 TEM images of (a) FA / VP = 3/10, (b) FA / VP = 10/10.

The work discussed so far focused on the changing the solution properties by physical interaction of the copolymer with third component. In the following section, chemical modification of the block copolymer is explored, trying to achieve a better control of film morphology.

5.2 Morphology control by betainization of PS-P4VP

Since addition of formic acid leads to irregular shape of micelles, it was decided to modify the copolymer using chemical reaction, i.e. to graft 1,3-propanesultone to the pyridine.

5.2.1 Introduction

Making use of the interactions between the copolymers and solvent provide a neat way of controlling the structures. Considerable interest in polybetaines arises because of their technological applications. One very interesting property of polymeric betaine is bio- and haemo-compatibility, which is a direct result of their highly hygroscopic nature. Polybetaines, which have both negative and positive charge on every monomer residue,

have been used in areas such as production of fungicides, synthesis of fire-resistant polymers, lubricating oil additives and emulsifying agents. The introduction of the ionic groups onto the polymer chain results in marked changes in its dilute solution properties. The specific behavior of the modified polymers is due in part to interactions among the ionic groups. Short-range interactions sometimes inhibit high conversion in the modification reaction.

Vinylpyridine copolymers with ionomeric properties have been studied by Gauthier and Eisenberg [174]. In their study, polystyrene-*b*-poly(4-vinylpyridine)-*b*-polystyrene triblock copolymer was quaternized by methyl iodide. The thermal and dynamic mechanical behavior of styrene-4-vinylpyridinium ABA block ionomers was investigated as a function of ion content and method of preparation. Aggregation was observed in dilute solution and it was related to the presence of the ionic groups [175]. Galin and Monroy-Soto have synthesized many polysulfobetaines by either polymerizing various betainized monomers or betainizing precursor tertiary amine polymers via free radical polymerization [176]. The relatively low solubility of these betaine monomers in organic solvents and the broad molar mass distributions of the resulting polymers are severe limitations if controlled structure polybetaines are required [177]. An alternative route to synthesize polybetaines involves the synthesis of precursor aminopolymers, followed by betainization using either 1, 4 butane sultone or 1, 3-propane sultone. Poly(vinylpyridine sulfopropyl betaines) have been synthesized by reacting precursor polymers with 1, 3-propane sultone by Cardoso and Manero [178].

The solution behavior of polybetaines is often opposite that of polyelectrolytes, exhibiting the so-called antipolyelectrolyte effect [179]. Chain expansions occur upon the addition of low molecular weight electrolyte, although it is very much dependent on chemical structure, composition, and solution conditions. Perhaps the most interesting feature is the

lack of solubility in pure water. However, the solubility of polybetaines in organic solvents is relatively less studied.

In this section, for the first time polystyrene-*b*-poly(4-vinylpyridine) (PS-P4VP) betaine copolymers using PS-P4VP copolymer as a precursor was synthesized as a part of present research. The selective betainization of the pyridine unit of this di-block copolymer was carried out in chloroform and toluene by using 1, 3-propanesultone (*Figure 3.3*). The solution properties in toluene were studied using dynamic light scattering, static light scattering and ^1H -NMR spectroscopy. The morphology of the resulting micellar film was investigated using transmission electron microscopy (TEM). These studies confirmed that the sultone-induced micellization led to the formation of ribbon shape nanostructures.

PS-P4VP-sultone system is different from the previous PS-P4VP (formic acid) in following aspects:

- The covalent bond between sultone with pyridine ring is much stronger than H-bonding interaction between acid and pyridine.
- The strong interaction should be persistent at elevated temperatures when annealing the film.
- The stability of PS-P4VP-sultone might enhance our investigation on the phase behavior upon annealing at high temperatures.

5.2.2 Chemical Analysis

The ^1H NMR spectrum of PS-P4VP-Sultone(4VP : sultone = 1.0 : 0.1) in CDCl_3 is shown in *Figure 5.7*. The peaks A, B and C at δ (chemical shift) at 8.35, 7.10 and 6.50 represent the styrene and pyridine ring hydrogens. The peaks D, E and F represent the protons from 1, 3-propane sultone. It can be seen that the peak associated with proton D in the sultone,

used to be at δ 4.40 before being attached to a pyridine ring [180], is now at δ =3.75. This indicates the presence of a chemical bond between these two species.

Figure 5.7 ^1H NMR spectrum of PS-P4VP-Sultone(4VP : sultone = 1 : 0.1) in CDCl_3 .

5.2.3 Solution Behavior

The PS-P4VP-sultone at different 4VP: sultone molar ratios (1.0/0.1, 1.0/0.2, 1.0/0.5, 1.0/1.0) in deuterated chloroform were characterized by ^1H NMR as shown in *Figure 5.8*. Looking at the spectra, one can observe that the signal associated with the pyridine ring hydrogen (H_a) disappears as the molar ratios of 4VP : sultone decreased. This is related to its micellization behavior. In this system, the driving force for the micellization is more complicated compared to without modification.

Figure 5.8 ^1H NMR spectra of PS-P4VP-Sultone in CDCl_3 at different molar ratio (4VP : sultone) values: A = 1/0.1, B = 1/0.2, C = 1/0.5, D = 1/1.

There are two possibilities. Firstly, after grafting of sultone to pyridine, the P4VP block may become insoluble and associates to form the core of the aggregates. Secondly, the interpolymer complexation may lead to physical cross-linking of the polymer chains due to the coulombic interaction. In this case, the newly formed complex is insoluble and associate to form the core of the aggregates, driving the micellization. These aggregated pyridine units will lose their mobility and therefore the signals associated with the ring hydrogens disappear in the spectra [170]. As the shell of the aggregates is made up of PS chains, their hydrogen signals' intensities should not change with molar ratio (4VP : sultone). With the addition of 1,3-propanesultone, the relative intensity of peak b assigned to the hydrogen atoms H_b in the benzene rings only does not change but those of peaks a and c, which are associated to H_a in the pyridine rings and H_c in both the pyridine and benzene rings, decrease. It is noted that when the molar ratio is high, the pyridine signals is fairly strong, indicating the presence of mobile pyridine units. Therefore, the P4VP

block remains soluble. When the molar ratio is low, peak a disappears, indicating that the mobility of most pyridine units is severely restricted. It is interesting to note that the intensity ratio of peaks b to c becomes close to 3/2, which is the number of the H_b to H_c in the benzene ring. It may be possible that the aggregates formed at low molar ratio are in fact micelles. A further proof may be derived from light scattering data.

In this study, SLS measurements were performed at different measurement angles. A typical Zimm plot was used to analyze the SLS data as shown in *Figure 5.9*. From the plot, the apparent M_w and R_g were calculated. The average aggregation number of PS-P4VP-sultone in the solution was calculated from the following equation.

$$N_{agg} = \frac{M_w(aggregate)}{M_w(unimer)}$$

The results obtained were listed in *Table 5.3*.

Figure 5.9 Zimm plot of PS-P4VP-Sultone in toluene (4VP / sultone = 1 : 1, T = 298K) for polymer concentrations ranging from 0.1032 to 1.032 mg/mL.

It is obvious that the measured M_w value is much larger than the molecular weight of individual chain, indicating the existence of larger aggregates in the solutions. The relatively large radii of gyration of PS-P4VP-sultone also suggest the presence of large aggregates or polymer clusters in solution.

Dynamic light scattering measurements were carried out at different angles and different concentrations. At high concentrations, the polymer solutions become cloudy, and no light scattering experiment was performed in this region. At lower concentrations, using Stokes-Einstein relationship, the hydrodynamic radii were calculated. The apparent hydrodynamic radius (R_h) of PS-P4VP-sultone (4VP: sultone = 1:1) were obtained for various concentrations as shown in *Figure 5.10* (a) and *Table 5.2*. Two representative relationship of relaxation rates Γ and q^2 for PS-P4VP-Sultone at concentration of (a) 1mg/mL, (b) 0.1mg/mL in toluene at molar ratio (4VP: sultone = 1:1) were shown in *Figure 5.10* (b). They exhibit a linear relationship going approximately through the origin, which confirms that the main peak is due to the translational diffusion. It is obvious that the R_h values do not change significantly with concentrations.

Figure 5.10 (a) Plot of the hydrodynamic radius R_h vs the concentration for PS-P4VP-Sultone (4VP:sultone = 1:1) in toluene. (b) Two representative relationship of relaxation rates Γ and q^2 for PS-P4VP-Sultone at concentration of (A) 1mg/mL, (B) 0.1mg/mL in toluene at molar ratio (4VP : sultone = 1:1) at 298 K.

Table 5.2 DLS data of PS-P4VP-Sultone(4VP:sultone = 1:1) at different concentrations

Concentrations(mg/mL)	R_h (nm)	Polydispersity
0.1	84.2	0.169
0.2	83.0	0.173
0.32	82.2	0.169
1.0	82.1	0.172
2.0	81.7	0.203

The decay time distribution functions of PS-P4VP-sultone in toluene at 2 mg/mL at 298 K, are shown in *Figure 5.11(a)*. Looking at *Figure 5.11(a)*, two main relaxation peaks in the time distribution plot were observed. The two main peaks shift to the left when the measurement angles are increased. The peaks are assigned as the fast and the slow decay mode respectively, and they can be represented by two characteristic relaxation times, τ_f and τ_s (where $\tau_f < \tau_s$). τ_f represents the relaxation time of the fast decay mode (the left peak). τ_s represents the relaxation time of the slow decay mode (the right peak). Meanwhile, the ratio of the two peaks, A_f/A_s decreases as the measurement angle decreases. A_f/A_s represents the relative contribution to the intensity from these two components. From the static light scattering results, the large apparent radius of gyration in the solution implies that large clusters exist in the polymer solution. For the large cluster, A_f/A_s is angle dependent because the smaller measurement angle is sensitive to large particles. The relaxation process caused by the translational diffusion movement of molecules exhibit the following relationship between relaxation time and the scattering vector [181], $\tau \propto 1/\sin^2(\theta/2)$. This relation can be used to interpret the shifting of the peaks to the left when the measurement angle is increased. We define $\Delta\tau$ as the distance of relaxation time between two peaks at a given measurement angle, i.e., $\Delta\tau = \tau_s - \tau_f$.

Since $\Delta\tau \propto 1/\sin^2(\theta/2)$ for $0 < \theta < 180^\circ$, $1/\sin^2(\theta/2)$ would decrease with increasing angle θ .

Figure 5.11 (a) Decay time distribution function at different angles and (b) Relationship of relaxation rates Γ and q^2 for 2 mg/mL PS-P4VP-Sultone in toluene at molar ratio (4VP : sultone = 1:1) at 298 K.

The decay time distribution functions of PS-P4VP in toluene at 2 mg/mL at 298 K, are shown in *Figure 5.12* as a comparison. It shows a peak with a shift to the left when angles increase. The relaxation rates Γ and q^2 for 2 mg/mL PS-P4VP in toluene show a good linear relationship and the line pass right to the origin, indicating a translational diffusion mode. On the basis of the diffusion coefficients, the apparent hydrodynamic radius was determined from the Stokes-Einstein equation. R_h of PS-P4VP in toluene was measured to be about 22.7 nm

Figure 5.12 (a) Decay time distribution function at different angles and (b) Relationship of relaxation rates Γ and q^2 for 2 mg/mL PS-P4VP in toluene at molar ratio at 298 K.

The q^2 dependence of Γ (Figure 5.11 (b)) of slow mode exhibits a linear relationship and goes through the origin, which confirms that the main peak is due to the translational diffusion. On the basis of the diffusion coefficients, the apparent hydrodynamic radii of slow modes were also determined from the Stokes-Einstein equation. The size distribution consists of a large peak with an average R_h of about 97.9 nm, accompanied by a small narrow peak. Although the q^2 dependence of Γ (Figure 5.11 (b)) of fast mode also exhibits a linear relationship, it does not go through the origin. No aggregates size was calculated for this mode. The two decay modes in the relaxation time distribution are attributed to inter-chain associative aggregates (97.9 nm) and other aggregates [182]. Combined with the result of $^1\text{H-NMR}$, it is reasonable to conclude that the aggregates at molar ratio of 4VP/ sultone = 1:1 are in fact micelles with P4VP in the core and PS in the corona. Increase of the amount of sultone facilitates the association of large aggregates.

However, when sultone is in small amount (4VP/ sultone = 1:0.1) in the system, only one peak was observed in the decay time distribution function, and relationship of relaxation rates Γ and q^2 exhibits a good linear line as shown in *Figure 5.13*, similar to PS-P4VP. Compared with the two peaks observed in low molar ratio (4VP/ sultone = 1: 1), it is possible to conclude that the fast mode aggregates can only be formed in low molar ratio. The implication is that in low molar ratio not all of sultone was grafted to PS-P4VP chain, some are coordinated to the pyridine which can not be removed by wash. These sultone, coordinating to pyridine ring of PS-P4VP, are responsible for the fast peak in the decay time distribution.

Figure 5.13 Relationship of relaxation rates Γ and q^2 for 2 mg/mL PS-P4VP-Sultone in toluene at molar ratio (4VP : sultone = 1:0.1) at 298 K.

The autocorrelation functions and their respective decay time distribution functions for 0.1 wt% PS-P4VP-sultone at different molar ratio at a measurement angle of 90° are shown in *Figure 5.14* (a) and *Figure 5.14* (b). *Figure 5.14* (a) shows that the correlation curve shifted to the right with decreasing 4VP to sultone ratio. This means that longer decay time are needed at lower 4VP to sultone ratio, indicating the presence of large aggregates. This also can be seen from *Figure 5.14* (b). The peak shifted to the right and become broader with decreasing 4VP to sultone ratio. At high molar ratio of 4VP to

sultone, only one peak was observed, indicating one relaxation time of a species. At lower molar ratio, the peak becomes wider and shifts to the right, indicating larger aggregates were formed. However, at even lower molar ratio, two main peaks were recorded, indicating two modes of relaxations. A small fastest peak was also observed in the distribution function, and the origin of this peak is still unclear. However, there is possibility that this small fastest peak is attributed to the internal mode [183]. Based on the above analysis, it is evident that at low molar ratio, large clusters exist in the polymer solution, hence giving rise to a large R_h value.

Figure 5.14 (a) Field autocorrelation function and (b) Decay time distribution function of toluene solution of PS-P4VP-Sultone at different molar ratio (4VP : sultone) values: A = 1/0.1, B = 1/0.2, C = 1/0.5, D = 1/1, at 1 mg/mL, at 298 K.

In general, the two radii R_g and R_h differ in value. The prefactor $\rho = R_g/R_h$ varies for different particle architectures or geometries and is a valuable parameter for structure estimation. The ρ parameter was calculated for various macromolecular architectures and tabulated in *Table 5.3*. In general, the ρ value gets larger when the particles become less compact and more anisometric.

Table 5.3 The characteristics of micelles derived from PS-P4VP-Sultone in toluene

4VP/sultone	$\langle R_g \rangle$ (nm)	$\langle R_h \rangle$ (nm)	$\rho = \langle R_g \rangle / \langle R_h \rangle$	$M_w (*10^6)$	M_w^*	$N_{\text{aggregation}}$
1 : 0	12.5	22.5	0.56	6.807	26800	254
1 : 0.1	19.1	24.8	0.77	7.684	28538	269
1 : 0.2	42.8	41.7	1.02	17.36	30276	573
1 : 0.5	54.4	50.3	1.08	25.8	35490	727
1 : 1	166	84.5	1.96	457	44182	10343

M_w , Weight average molecular weight of aggregate (g/mol).

M_w^* , Weight average molecular weight of unimer, calculated from $(M_n + \text{sultone}) * \text{polydispersity}$ (g/mol).

The main characteristics of the micelles are listed in *Table 5.3*. It shows the R_h of the micelles of PS-P4VP-sultone at different molar ratios at 1 mg/mL in toluene. The R_h of PS-P4VP precursor copolymer is also listed for comparison. The hydrodynamic radius of the PS-P4VP was observed to be 22.5 nm. After loading of a small amount of 1,3-propane sultone (4VP : sultone = 1 : 0.1), R_h was measured to be 24.8 nm. Further increase in the amount of sultone to 1 : 0.2, 1 : 0.5 and 1 : 1, R_h increased to about 41.7 nm, 50.3 nm and 84.5 nm respectively. The increase of R_h is explained by incorporation of sultone in the micellar core. There are two possible explanations to account for this phenomenon. The grafting of sultone to pyridine unit may expand the micellar core, thus increasing the micellar size. The other possible explanation is that the newly formed copolymer may result in aggregation of more polymer chains in toluene. This can be confirmed making contrast match Small Angle Neutron Scattering (SANS). Also, this can be confirmed by the increase of ρ value. The ρ value of the unmodified PS-P4VP in toluene was calculated to be 0.56, consistent with a globular structure of the micelles as shown in *Figure 5.15(a)*.

Upon addition of sultone at molar ratio of 10:1, ρ increases to 0.77, still consistent with a spherical structure. Upon further increasing the amount of sultone, the ρ value increases to 1.02. Such a ρ value is typical for a much less dense particle structure like a star molecule or a random coil conformation [184, 185]. When the molar ratio was increased further to 1:1, the ρ value increased sharply. A value of about 2 was observed. This is typical for non-spherical scattering objects such as rods or elongated species.^{186, 187} However, the ρ value of elongated structures strongly depends on polydispersity.

Figure 5.15 TEM image of copolymer film of (a) PS-P4VP and (b) PS-P4VP-sultone (4VP : sultone = 1 : 1).

Looking at transmission electron micrograph as shown in *Figure 5.15* (b), the structures formed showed high polydispersity. The unexpected increase in the ρ values can be explained by a loss of control on the particle formation. Agglomerates which are non-spherical in shape are observed. The question is how the incorporation of sultone into micellar core can lead to regular ribbon shape nanostructures.

It is well-known that there are two mechanisms governing the aggregation between particles, namely, diffusion-limited aggregation (DLA) and reaction-limited aggregation (RLA) [188]. Loosely connected cluster with a typical fractal dimension of 1.7-1.8 is

obtained for DLA and a denser cluster with a fractal dimension of 2.0-2.2 is obtained for RLA. Recently, Li et al. [189] reported segmented wormlike aggregates resulting from the aggregation between individual micelles formed by ABC miktoarm stars. It was stated that in forming a string, the different cores are able to share their coronas, thus protecting them from the highly unfavorable exposure to water. In addition, it was stated by Ma et al. [190] that the sphere- to- rod transition requires sphere (micelle) collisions followed by reorganization into smooth cylindrical rods.

Figure 5.16 Formation of ribbon shape micelles.

As indicated in *Figure 5.16*, when a small amount of 4VP is betainized, the PS shell is thick enough and the density of the shells is high, the contact and the subsequent fusion between the cores can be prohibited. Whereas in cases that more 4VP is grafted with sultone, the cores expand, resulting in a relatively low density of shells on the cores surface. This fluctuation in density may lead to the exposure and the coupling of the cores when two core-shell nanospheres approach one another. After a fusion of a core with other cores to become a section of a cylinder, the surface area of the core is considerably decreased. The density of shells on the core significantly increases the densification process. Upon formation of the ribbon-shape object as shown in *Figure 5.15 (b)*, the densification is enough to protect further coupling of the core with another core. It is difficult to differentiate whether the sphere-to-rod morphological transition is caused by

alteration in the local coulombic interactions within the nanostructures, a change in solvation or hydrophilicity of the core layer, or a combination of these factors.

5.3 Nanopatterns with in situ Core-Corona Inversion and Solvent Induced Sphere to Cylinder Transition

Block copolymer thin films have attracted significant interest in nanofabrication as self-assembled templates [191,192]. Because of their regular nanostructured nature, block copolymer thin films have been recognized as ideal templates for synthesizing a range of nanostructures including metal nanowires, quantum dots, and photonic waveguides [193,194]. Reconstruction of block copolymer film morphology by vapor or thermal annealing is reported in the literature [167, 195, 196]. However, this process is typically slow and usually results in morphologies indicating the coexistence of different alignments of nanodomains. Reorientation requires a combination of thermal annealing and a strong electric field and occurs even more slowly than the above process [197].

5.3.1 Introduction

Recently, it has been demonstrated that well-ordered nanostructures may be fabricated in bulk not only from block copolymers but also from supramolecular assemblies(SMA) of low molar mass additives and block copolymers [198, 199]. The ordered thin films were obtained via spin or dip coating without additional annealing for PS-P4VP and 2-(4'-hydroxybenzeneazo) benzoic acid (HABA) system[200]. Swelling of SMA in vapors of corresponding solvent leads to sufficient improvement of the ordering. Fast switching between two different alignments of the cylindrical domains and the indifference of alignment to the substrate surface were observed.

In this section, the newly-formed copolymer (PS-P4VP-sultone) micellar film maintains the hexagonal packed order which is similar to the copolymer film prior to modification. Furthermore, an interesting core-corona inversion was induced in-situ with water, a selective solvent for P4VP, due to the increased water sensitivity. Annealing effect on PS-P4VP-Sultone micellar film was investigated both without and with solvent environment. The former gives rise to a reduction in the dimension of nanodots while the latter leads to the formation of smooth cylinder-like morphology. This procedure thus adds a facile yet effective tool for controlling pattern formation.

5.3.2 Effect of water treatment

Since toluene is a selective solvent for the PS block, spherical micelles of a PS corona and P4VP core were formed at the concentration studied (2mg/mL), which were well above the critical micelle concentration (*Figure 5.17 (a)*) [201]. Similarly, similar pattern was formed for PS-P4VP-sultone as shown in *Figure 5.17 (b)*. Looking at *Figure 5.17 (b)*, it can be seen that the film is made up of a complete monolayer of PS-P4VP-sultone micelles. When a 2 mg/mL solution at 2000 rpm, is cast onto carbon-coated mica, the P4VP cores appeared as dark spheres in the image and were arranged in a short range hexagonal packing, confirmed by the Fourier transformed pattern in the inset of *Figure 5.17 (b)*. A similar result was reported in dip coating on substrate with a high pulling rate of a substrate [202]. During spin coating, solvent evaporates at a much faster rate than dip-coating and hence give rise to a two-dimensionally more compact and uniform monolayer of micelles. This compact monolayer of micelles has made it possible for the film to be transferred to other substrates. The film thickness measured by AFM on the substrate was almost identical to the micelle size, implying a monolayer of micelles is present in the film. The spin-coating procedure produces a kinetically frozen phase by very rapid solvent evaporation.

Figure 5.17 TEM images of (a) PS-P4VP, (b) PS-P4VP-Sultone(4VP/sultone = 1/0.1), (c) The inversion of (b) by floating on water for 20 seconds(minor morphology), (d) The inversion of (b) by floating on water for 20 seconds(dominant morphology).

The surface of the PS-P4VP-sultone film at the air interface measured using AFM also shows micellar patterns as shown in *Figure 5.18*. The diameter of the protruding P4VP domains (cores) of the micellar aggregates is about 28 nm which is almost consistent with the TEM analysis.

Figure 5.18 AFM phase image of PS-P4VP-Sultone micellar film.

Interestingly, the core-corona inversion was induced in-situ, without ruining the film, by simply floating the micellar film of PS-P4VP-Sultone on water, which is a selective solvent for the P4VP core. *Figure 5.17(d)* shows an inverted nanopattern of micelles consisting of bright isolated PS cores and dark continuous P4VP coronas. The transition between the two patterns can be observed in *Figure 5.17 (c)*. The long-range hexagonal packing is still maintained after inversion. The intercore spacing is slightly larger than that before inversion, although there is some uncertainty because there maybe some swelling of P4VP blocks due to I_2 staining. A short floating time is enough to induce the core-corona inversion. The diameter of the I_2 -stained P4VP-sultone domains (cores) of the micellar aggregates is 27 nm. The spacing between adjacent stained P4VP-sutone cores is approximately 8 nm. After transition, the diameter of the PS (cores) of the micellar aggregates is 15 nm. The spacing between adjacent stained PS cores is approximately 18 nm. The micelles in solid film could be considered as kinetically frozen structures by rapid solvent evaporation. Thus, the core and the corona of micelles could

be effectively reorganized by selective solvent in a short period without long-range diffusion of copolymer. It is noted that in the boundary of two areas as shown in *Figure 5.17 (c)*, the ribbon-like of P4VP is formed. It is due to the merging of the spherical P4VP domains, as the width of the ribbon formed is the same as the size of the spherical P4VP. As more and more P4VP domains merged together, they became the matrix of the film, leaving PS domain isolated. The reason behind this may be due to water penetration into P4VP-sultone domain resulting in merging of these domains.

This is the first time that water-induced core-corona morphological transition has been reported for PS-P4VP-Sultone system. Sohn et al. [203] reported the ethanol induced core-corona transition for PS-P4VP block copolymer film. In their case, even when the film was floated on water during TEM sample preparation, no morphological transition was observed. The implication is that this block copolymer film is not sensitive to water in short period of time. Only with the use of more favorable solvent for P4VP block, such as ethanol, it was possible to induce the inversion. In our results, short floating time on water was enough to induce the core-corona inversion. The fast switching between core and corona provides evidence for the very strong modification of the PS-P4VP-sultone film behavior as compared to that of PS-P4VP film. Sultone is believed to be a key factor in controlling the water sensitivity of P4VP nano-domain. Such an increased water sensitivity may be reasonably expected with only minor modification of P4VP to poly(vinylpyridine sulfopropyl betaine) which showed improved solubility in aqueous solution[176, 178]. The introduction of small amount of sultone not only results in changes to the solution behavior of the copolymer as indicated in an earlier paper [204], but also the sensitivity of the film to water.

5.3.3 Effect of temperature and solvent treatment time

To further study the temperature effect on micellar film, annealing was carried out without solvent environment and in solvent environment, respectively. The annealing temperature was set to 120 °C, which is higher than the T_g of PS block but lower than P4VP block. The micellar film was annealed at 120 °C for different time without solvent environment. The micellar structure in film is the kinetically frozen structure of micellar solution. As shown in *Figure 5.19* (a), the micellar core of original micellar film was measured to be 27 nm. However, after annealing for 10 min, the core size decreased to 20 nm (*Figure 5.19* (b)). Further increase the annealing time to 2 hours resulted in the decrease of the core size to 13 nm as shown in the *Figure 5.19* (c). This phenomenon indicates that the micellar film is in a kinetically frozen structure and will change with the change of conditions. In case of spin-coating, the fast solvent evaporation may prevent the formation of equilibrated structure in film, thereby freezing in a highly non-equilibrium surface morphology [205]. The preferred motion of block molecules within the film was allowed upon increasing temperature which acts as the driving force of reorganization. The annealing temperature, 120 °C, is between T_g of PS (104 °C) and P4VP (140 °C) which allows for limited movement of PS chain segment while P4VP movement was severely restricted. Researchers [197] reported that annealing procedure will result in increased film thickness as evidenced by the increased height difference in the block copolymer PS-PMMA film. This means in certain area, the film thickness is increased. In our case, similarly, only the PS block is mobile to redistribute, thus contributing to the increase of thickness. However, the P4VP domains remain immobile at this temperature, but they may be pushed or dragged up by PS around them to become slightly elongated cylinder perpendicular to the substrate. In that case, the regions will still appear spherical. The schematic illustration of the process is shown in *Figure 5.20*. On

top of that, the presence of small amount of sultone may increase the mobility of P4VP due to internal plasticization effect. Thus both the dots size and intercore spacing is decreased. The hexagonal morphology was also maintained so that the free energy of the system could be kept low. The annealing temperature is well below order-disorder transition temperature which is measured to be 375 °C for PS-P4VP.

Figure 5.19 TEM images of PS-P4VP-Sultone at different annealing time (a) 0 min, (b) 20 min, (c) 120 min.

Figure 5.20 Schematic illustration of PS-P4VP-sultone micellar film in response to annealing.

For the system investigated, the conventional annealing leads to one type of predominant surface morphology (nanodots), whereas annealing in solvent environment consistently produces a completely different surface morphology. This morphology is essentially cylindrical, with extensive interconnectivity and flexibility of the cylindrical segments or strands, as illustrated in *Figure 5.21*. At short annealing time, spherical micelles with fairly short-range order (*Figure 5.19 (a)*) were destroyed as shown in *Figure 5.21 (a)*. The deformation of the micellar core from spherical to irregular shape due to fusion of two or three cores can be observed on the micrographs. With an increase in annealing time of 50 minutes, the cores of the micelles fused into ribbons with the same minimum separation distance as spherical micelles. The morphology was dominated by mainly rigid short nanostrand of P4VP. However, at this time, the ribbons were separated and there were still lots of P4VP dots in the film. The ribbon or cylindrical micelle configuration energy was normally higher than spherical micelle [164]. Hence, in this case this configuration becomes the ground state of the system since it can accommodate more material while keeping both the micelle core and corona dimensions constant. A further increase in annealing time to 90 minutes led some of the P4VP ribbons to connect with each other as shown in *Figure 5.21 (c)*. And the PS domain was also forced into ribbon-like. The ends of the PS strands were capped by a sphere that appears slightly larger in diameter and much brighter in the image. The contour of nanostrand, however, appeared to be rigid for sharp angles were noted for the strands network, indicating it was still not the equilibrium

morphology. With the further increase of annealing time to 360 minutes, the P4VP part became the matrix of the film as indicated in *Figure 5.21* (d). The narrow PS ribbon was formed and sparsely distributed in the P4VP matrix. Though toluene is a poor solvent for P4VP, it may confer P4VP sufficient mobility to move around. In addition, P4VP domain had a good affinity to the carbon-coated substrate due to its polar nature and may spread to be the matrix of the film. Devereaux [206] reported this pattern as one of several features in LB monolayers of a highly asymmetric poly(styrene)-b-poly(ethylene oxide) (PS-b-PEO, 7 wt % PEO) copolymer.

Short annealing time is not sufficient to generate dominant strand morphology (although it may be present to a small extent), whereas more mixed morphologies are obtained for short annealing time. When exposed to the solvent for longer time (*Figure 5.21* (d)), the surface morphology was dominated by a dense network of interconnected, flexible strands. These strands show smooth contours and are remarkably uniform in width (about 18 nm). Other morphologies may also be present to a minor extent (*Figure 5.21* (e)). This figure showed a less tightly packed network. It was also verified that the block copolymer by itself does not give rise to this morphology. The presence of sultone is, however, essential to obtaining the nanostrand network. For the pure PS-P4VP system, nanostrand network is not obtained by annealing procedures either under solvent environment or without solvent, at least at the copolymer composition investigated.

Figure 5.21 TEM images of PS-P4VP-Sultone at different annealing time under toluene vapor (a) 20 min, (b) 50 min, (c) 90 min, (d) 360 min(dorminant morphology), (e)360 min.

A comparison of our results with recent studies of the effect of solvent-assisted formation of nanostrand networks [207], reveals that our results to some extent resemble solvent

effect on formation of LB membrane under sufficient compression, where depending on compression and solvent presence, a dominant nanostrand network can be induced. The difference is that their stimulus is surface compression applied on the spreading film and ours is the annealing effect under solvent environment. A plasticizing effect of the surfactant 3-pentadecylphenol (PDP) and fusion of spherical micelles mechanism was suggested for their case. We are aware of the differences between the compression performed on the copolymer film and temperature effect on copolymer film at the presence of solvent. However, the obvious fusion of spherical micelles and transformation of rigid non-equilibrium strands to smooth strand which indicate the presence of force field, leads us to conclude that similar underlying processes may be responsible.

The above observations suggest that the equilibrium morphology of the system studied is dot-and-planar at non-solvent annealing environment, whereas it is cylinder-like at solvent annealing environment. Seo et al. [208] reported a similar transformation in morphology from predominantly spherical to a dense network of strands upon increasing the surface pressure for a blend of poly(styrene-*b*-ferrocenyl silane) and poly(styrene-*b*-2-vinyl pyridine) spread at the air/water interface. In their case, the plasticizing effect of the low- T_g poly(styrene-*b*-ferrocenyl silane) was believed to improve the mobility allowing the transformation to take place. The implication is that, if the system is not sufficiently mobile during annealing to respond to new thermodynamic conditions, the original dot-and-planar morphology is essentially kinetically frozen in [209]. However, without the presence of the solvent to facilitate mobility, the reorganization to strand network upon changing the annealing time does not take place. At the presence of solvent, both PS and P4VP are mobile to form cylinder-like morphology. This may be attributed to a combination of two factors, one being sultone's role in providing the appropriate weight

fraction of the P4VP block with which it is associated, such that a cylindrical morphology is favored, and the second by its contribution to mobility in the system by (internal) plasticization of the P4VP block.

5.3.4 Effect of cross-linking

Cross-linking is known to be important to the preservation of mesostructural ordering during swelling and incorporation of inorganic precursors [210]. Without cross-links, the block copolymer template rearranges extensively upon swelling, destroying the spatial patterning imposed by preprocessing. By introducing cross-linkers, however, it is possible to restrict re-arrangement of block copolymer during swelling and thereby producing inorganic oxide films with mesostructures that closely mimic those of the template films. In this section, the cross-linking effect on the block copolymer film during heat and solvent treatment is investigated. It was found that heat treatment does not affect the morphology of the cross-linked film, while the solvent treatment makes the contour of PS ribbon smoother, the size cross-linked P4VP domain remains constant.

Figure 5.22 shows the decay time distribution function at different angles and relationship of relaxation rates Γ and q^2 for 2 mg/mL PS-P4VP-sultone/dibromobutane in toluene at molar ratio at 298 K obtained from dynamic light scattering. *Figure 5.22(a)*, shows only a sharp peak shifting to the left when the scattering angle was increased, indicating that the addition of cross-linker dibromobutane did not change the structure of micelles. Relaxation rates Γ and q^2 shown in *Figure 5.22(b)*, exhibits a good linear relationship and the line passes through the origin. This is an indication of the translational diffusion of micelles. R_h value was calculated to be 23.6 nm, almost the same as PS-P4VP-sultone.

Figure 5.22 (a) Decay time distribution function at different angles and (b) Relationship of relaxation rates Γ and q^2 for 2 mg/mL PS-P4VP-sultone/dibromobutane in toluene at molar ratio at 298 K.

The TEM image of cross-linked micelles is shown in *Figure 5.23* (a). Although the light scattering data shows almost no change in the hydrodynamic dimension of the micelles, the TEM images shows the internal features has greatly changed. The dimension of the core measured in TEM image is about 27 nm, similar to the size of the micelle formed by PS-P4VP-sultone (4VP/sultone = 1/0.1), but the hexagonal order array of micelles is partly lost. The ordered array is believed to be formed during solvent evaporation when preparing the film, so the sufficient mobility of polymer chains is necessary at this stage. Once the P4VP is partly cross-linked, its mobility is seriously restricted. This will hamper the chain arrangement during solvent evaporation, thus the favored hexagonal pack is restricted.

Heat treatment of the formed film at 150 °C does not affect the morphology as shown in *Figure 5.23*(b). Since the P4VP is cross-linked, the original morphology of the film remains. The size of the core is about 26 nm. PS segment is mobile at this temperature. However, it also can not move too much because of its chemical bond with P4VP and the

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spatial confinement. The movement of PS segment and PS chain is different. The former allows for limited movement, while the latter facilitate freely movement of the PS domain. So in this case the original morphology was maintained.

However, the solvent treatment of the film in toluene environment at 150 °C makes the PS contour smoother and more interconnected, because toluene has greatly facilitated the movement of PS. The size of the core (P4VP) measured is about 29 nm, larger than the one untreated with solvent. This may be due to the swelling of the cross-linked core due to the solvent.

Figure 5.23 TEM images of (a) PS-P4VP-sultone (4VP/sultone = 1/0.1) /dibromobutane (4VP/sultone = 1/0.1), (b) heat treatment of (a) film at 150 °C for 2 hours, (c) toluene treatment of (a) film at 150 °C for 2 hours.

5.3.5 Summary

The micellization of PS-P4VP in chloroform in the presence of FA was studied using NMR, Light Scattering and TEM techniques. The disappearance of the carbon signal associated with the pyridine ring in ^{13}C spectra and the disappearance of hydrogen signal in ^1H spectra indicated the micellization of PS-P4VP occurred in chloroform in the presence of enough formic acid. The variation of the hydrodynamic radius and polydispersity of the aggregates with changes in molar ratio of 4VP to FA was used as an important clue to understand the changes in the morphologies.

Polystyrene-*b*-poly(4-vinylpyridine) (PS-P4VP) betaine copolymers at different betainization degrees were synthesized. Disappearance of pyridine ring hydrogen signal in ^1H -NMR spectra indicated the sultone-induced micellization in chloroform. The laser light scattering study and TEM show the morphology evolution process of the micelle in toluene, from spherical structure to elongated species and increasing micellar size upon increasing amount of sultone grafted. Additional studies are required to understand the effects of the introduction of sultone to polymer assemblies. Controlling the size and shape of micelles can be achieved by simply adjusting the amount of sultone grafted. This system is believed to have potential as vehicles for nanoreactor applications.

The modification of polystyrene-*block*-poly(4-vinylpyridine) by introduction of 1, 3-propane sultone resulted in hexagonal packed micellar film similar to the copolymer film prior to modification. In addition, by introducing the sultone to the copolymer also result in increased water sensitivity. A core-corona inversion can be induced in-situ with water. The technological implication of this approach is that the fine control of structure of dimensions afforded by self-assembling block copolymer materials may be harnessed for applications such as the production of nanoelectronic devices where nano-pattern switch between positive and negative tones are required.

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The equilibrium morphology of the system studied was dot-and-planar at non-solvent annealing environment, whereas it is cylinder-like at solvent annealing environment. The cylinder-like morphology is attributed to the presence of the solvent that confers sufficient mobility to the system to enable reorganization in response to increased temperature. This procedure thus adds a facile yet effective tool for controlling pattern formation.

The cross-linking confers sufficient restriction to the polymer film to withstand the temperature and solvent. This can be essential in fabrication of inorganic nanoparticles using block copolymer template where solvent is used and high temperature is required.

6 Synthesis of Nanoparticles from Di-block Copolymer Solution

The synthesis of nanoparticles is an emerging area in the field of colloid science. A number of applications with an enormous impact on modern technology are expected in this area. Amphiphilic block copolymers can act as a stabilization system. They are good systems for nanoparticles synthesis because of a number of reasons:

- Micelles of block copolymers represent a nanostructured environment with adjustable structural relaxation times, i.e. they can be long compared to the growth process.
- Polymers as colloidal stabilizers are very effective steric stabilizers (organic phase) or electrostatic stabilizers (water phase).
- Corrosion of the metal particles or metal can be avoided by tying the metal salts or oxidation products to the polymeric microenvironment. Due to the variability of the block copolymer chemistry, it is possible to modify the binding block for each stabilization problem.

Since P4VP is a metal-chelating agent, it can fix a large number of metal ions in the micelle core, the size of which depends only on the aggregation number. Such a micelle core may be regarded as a long-living, nanosized reaction vessel, and the growth of colloidal particles might be limited by the micelle core. In particular, it is possible to perform a reduction in concentrated solution still ending with well defined metal particles.

This chapter describes the synthesis of several types of metal nanoparticles(single metal, alloy and oxide) using PS-P4VP or PS-P4VP-sultone as the nano-reactor. Device application of gold nanoparticles in polymer film is also briefly illustrated in this chapter.

For the purpose of metal binding, polystyrene-poly(4-vinylpyridine)-sulfone copolymers was used to synthesize nanoparticle. It also illustrates that iron chloride can be loaded into micellar core to induce polymerization of pyrrole vapors.

6.1 Pure nanoparticles – Gold nanoparticles

Gold nanoparticles present fascinating aspects in many applications. Inverse micelles are formed from PS-P4VP di-block copolymers in toluene, i.e., a shell of PS and a polar core of P4VP chains. The incompatibility between the core and the solvent/shell phase ($\chi_{\text{core-solvent}}$; $\chi_{\text{core-shell}}$) can be enhanced by partially neutralizing the 4VP monomer units of the core-forming block by tetrachloroauric acid [211]. To minimize the unfavorable contacts, the core chains stretch and the number of associated chains per micelle is increased, which minimizes the overall enthalpic interaction.

6.1.1 Synthesis of Gold nanoparticles in PS-P4VP

PS-P4VP di-block copolymer was dissolved in toluene. A stoichiometric equivalent of tetrachloroauric acid (HAuCl_4) was added to the micellar solution, i.e., $\text{HAuCl}_4/4\text{VP} = 0.5$. Protonation of the 4-VP units resulted in the formation of a polyionic block. The solution was then treated with excess hydrazine monohydrate. Because of its polar character, hydrazine is taken up preferentially in the core of the micelles where it reduces Au^{3+} to Au^0 . The originally pale yellow solution turned deep purple within a few seconds. The excess of hydrazine was removed directly after reduction by adding aqueous hydrochloric acid (HCl). Neutralization of the excess hydrazine and precipitation of $\text{N}_2\text{H}_5\text{Cl}$ is essential for long-term stability of the colloidal dispersion. The precipitated hydrazinium chloride was finally removed by centrifugation. The reaction is shown in

Figure 6.1.

Figure 6.1 Scheme of synthesis of PS-P4VP-Au and micellization

Figure 6.2 UV-vis absorbance spectra of a solution of PS-P[4VP(HAuCl₄)0.5]:

(a) Before addition of reducing agent; (b) After reduction

After addition of the reducing agent, the originally yellowish colored solution spectrum a, changed immediately to a deep purple-red color, spectrum b. While the absorbance of the $\text{PyH}^+\text{AuCl}_4^-$ ions vanished almost instantaneously as shown in Figure 6.2. The absorption band at 525 nm is characteristic for the surface plasmon resonance of small Au nanocrystals.

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Dynamic light scattering (DLS) was applied to determine the hydrodynamic radius R_h of the micelles in the different solutions. Prior to loading the micelles with the precursor, the hydrodynamic radius (R_h) of the micelles was 22.5 nm. The R_h of the micelles loaded with HAuCl_4 was observed to be 74 nm. After the reduction R_h was measured to be 52 nm. The increase of R_h of PS-P4VP from 22.5 nm to 74 nm is due to the incorporation of HAuCl_4 in the micellar core. The micelles swell upon incorporation of HAuCl_4 . The decrease of R_h to 52 nm after reduction is probably due to the disappearance of swelling effect of HAuCl_4 , as it is reduced to small gold metal crystal. The R_g/R_h value is characteristic for the particle shape in solution. A value of 0.5-0.7 is typical for spherical micelles. From *Table 6.1*, after reduction an increase of R_g/R_h value to 1.12 is seen. Such a value is typical for a much less dense particle structure.

Table 6.1 Light Scattering Data of PS-P4VP and PS-P4VP/ HAuCl_4

	$R_g(\text{nm})$	$R_h(\text{nm})$	R_g/R_h
PS-P4VP	12.5	22.5	0.56
PS-P4VPAu1	55	74	0.743
PS-P4VPAu2	58	52	1.12

PS-P4VPAu1: Before reduction, PS-P4VPAu2: After reduction

* R_h : 1mg/mL, 4VP: HAuCl_4 = 1 : 0.5

A closed monofilm of the micelles was prepared by putting a drop of the dilute solution onto the copper grid. *Figure 6.3* shows TEM micrographs of such monofilm. The core of each micelle is marked by many ultra-small Au particles. The presence of Au crystals was confirmed by the diffraction pattern of the inset of *Figure 6.3*. The diffraction pattern is typical of a face-centered cubic gold crystal.

Figure 6.3 Transmission electron micrograph of a monofilm PS-P[4VP (HAuCl₄)_{0.5}].

6.1.2 Synthesis of Gold nanoparticles in PS-P4VP-sultone

As a comparison, PS-P4VP-sultone (4VP:sultone = 1:0.1) was also employed to synthesize gold nanoparticles using the same procedures as mentioned above. It is reasonable to expect the P4VP-sultone part can have a stronger metal coordination effect due to its ionic properties, so that the nanoparticles could be strictly restricted into P4VP domain. As mentioned in chapter 5, another difference between PS-P4VP and PS-P4VP-sultone is that when annealed under solvent environment at proper temperature, PS-P4VP-sultone gives rise to ribbon-like micelles on carbon-coated mica.

The AFM height image of PS-P[4VP-sultone(HAuCl₄)_{0.5}] and TEM image of a monofilm PS-P[4VP-sultone (HAuCl₄)_{0.5}] are shown in *Figure 6.4*. It can be seen that ribbon-like micelle dominate the morphology in both AFM and TEM images. Small gold nanocrystals were found to distribute strictly in the P4VP ribbon, exhibiting high selectivity. Compared the image shown in *Figure 6.3*, more elongated micelles and larger size of gold particles were observed. This may be due to the stronger interaction of sultone with gold precursor compared to unmodified pyridine which affects the shape of micelle. The

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change in the shape of the micelle can be deduced by an increase of poly-dispersity as shown in *Table 6.2*. The prefactor $\rho (=R_g/R_h)$ is different for different particle architectures or geometries and is a valuable parameter for structure estimation. In general, the ρ value gets larger when the particles become less compact and more anisometric. The ρ value of PS-P4VP-sultone in toluene was calculated to be 0.77, consistent with a globular structure of the micelles. Upon loading of HAuCl_4 at molar ratio of 1:0.5, ρ increase to 1.24. Such a ρ value is typical for non-spherical scattering objects such as rods or elongated species [184].

Figure 6.4 (a)Height image of PS-P[4VP-sultone(HAuCl_4)_{0.5}], (b)TEM image of a monofilm PS-P[4VP-sultone (HAuCl_4)_{0.5}]

Table 6.2 Light Scattering Data of PS-P4VP-sultone and PS-P4VP-sultone/ HAuCl_4

	$R_g(\text{nm})$	$R_h(\text{nm})$	R_g/R_h	polydispersity
PS-P4VP-sultone(4VP:sultone=1:0.1)	19.1	24.8	0.77	0.172
PS-P4VP-sultone/ HAuCl_4	67.5	54.3	1.24	0.547

6.1.3 Application of gold nanoparticles in self-assembled PS-P4VP film

The in-situ method of synthesis of gold nanoparticles in self-assembled thin film can be used to design and fabricate an organic memory active layer. The thin film of self-assembling block copolymers with the nanoparticles is deposited as a thin film in a memory device. Annealing of the copolymer thin film with Au nanoparticles at a temperature above the glass transition of P4VP resulted in a thin film that has charge storage capability. This implies that the film can in turn be used as the active layer of a memory device.

Various concentrations of the gold nanoparticles in PS-P4VP were cast into films and made into the devices. Solutions of concentrations of gold nanoparticles 1×10^{-5} mol/ml and 2.12×10^{-5} mol/ml were prepared. The metal-insulator-semiconductor (MIS) structure used in this study has a metal (Au) gate electrode and a p-type Si substrate. The test structure for such an application is shown in *Figure 6.5*.

Figure 6.5 Schematic of a typical metal-insulator-semiconductor (MIS) structure with the active layer made up of Au nanoparticles embedded in PS-P4VP.

Their Current-Voltage (I-V) hysteresis of the device made using the two different concentration is shown in *Figure 6.6*. Current-Voltage (I-V) hysteresis can be observed for a MIS structure indicating a charge storage effect in the copolymer film containing Au nanoparticles.

Figure 6.6. I-V Characteristic of a Metal-Insulator-Semiconductor (MIS) structure with the nanoparticles embedded PS-P4VP copolymer film. (Data from W. L. Leong, MSE, NTU)

A higher concentration of Au nanoparticles in the self-assembled copolymer film results in a better charge storage capability. Therefore the concentration of noble particles controls the charge storage ability of the organic memory. Capacitance-Voltage (C-V) hysteresis for the MIS structure is shown in *Figure 6.7*. The C-V curve shows an anticlockwise hysteresis of the copolymer film with Au nanoparticles indicating that the memory effect of this film is due to an electron trapping mechanism in the copolymer film.

Figure 6.7 C-V characteristics of the MIS structure. Sample with Au nanoparticles trapped in thin film - anticlockwise hysteresis implies electron trapping. (Data from W. L. Leong, MSE, NTU)

Under a positive gate voltage with a magnitude sufficiently larger than the value of the flat-band voltage, the surface region of the p-type Si substrate gets inverted into n-type. In this case, under the influence of the positive gate voltage, electrons can be injected into the polymer film from the substrate inversion layer. Most of the electrons that are injected into the conduction band of the PS-P4VP-Au film, are collected by the gate or the substrate, leading to a gate current or a substrate current, respectively. Upon applying a negative gate voltage, the stored electrons in the Au nanoparticles is flushed out, resulting in lower capacitance.

In summary, the fabrication of an organic memory active layer using in-situ synthesis of nanoparticles in a self-assembled copolymer thin film is possible. This synthesis route opens up the possibility of other applications such as synthesis of hybrid structures for transistors and optical devices such as photovoltaic and light sensing.

6.2 Oxide Nanoparticles – Titania nanoparticles

Considerable attention has been paid to titanium dioxide (TiO_2) due to its extensive applications in chemical sensors, as catalyst, and as optical devices [212, 213, 214]. Also, TiO_2 is chemically stable and biologically inert, making it environment friendly. The advantages mentioned above call for finding ways of synthesizing and incorporation of TiO_2 nanoparticles in appropriate hosts depending on the nature of applications [215]. Researchers have developed various routes to synthesize nanostructured TiO_2 . Steunou et al. [216] fabricated polymer titania composites using the sol-gel process. Weng et al. [217] synthesized needle-like TiO_2 nanostructures via a polystyrene-block-poly(4-vinylpyridine) di-block copolymer template. Li et al. [218] synthesized arrays of titania nanoparticles using monolayer films of di-block copolymer templates. However, the amount of titania loaded onto their film is not controllable using the template method.

In this section, a solution method to get highly ordered arrays of titanium dioxide nanoparticles using a coordination reaction of titanium isopropoxide within the P4VP domains in the micellar solution is reported. The study of the solution behavior of the mixture can shed more light on how the nanoparticles are formed.

Titania precursor – titanium isopropoxide ($\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$) was loaded into the core of PS-P4VP in toluene solution. Different amounts of $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ were loaded into the micellar core, then they are reduced by addition of HCl aqueous solution into the toluene solution. The reaction is shown in *Figure 6.8*. Titanium isopropoxide has good solubility in the micellar solution and the strong interaction of pyridine and $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ is expected. Coordination occurred between the titanium isopropoxide and the nitrogen in the pyridine ring.

Figure 6.8 Loading of Titanium precursor into PS-P4VP micellar core.

The micelles were characterized using DLS. Measurements were carried out at different angles. Using the Stokes-Einstein relationship as discussed in section 5.2.3, the hydrodynamic radii were calculated. The relationship of relaxation rates (Γ) and the square of the scattering vector (q^2) for PS-P4VP/Titanium at concentration of 2 mg/mL in toluene at molar ratio 4VP/titanium = 1:0.5 is shown in *Figure 6.9*. A linear relationship was observed between Γ and q^2 , and the line passes through the origin, indicating that the peak is due to the translational diffusion. The R_h was calculated to be 24.6 nm, a little bit larger than PS-P4VP. It can be seen that loading of titanium precursor to the micellar core at molar ratio of 0.5 have little effect on the size and structure of PS-P4VP micelle. This can be visualized using AFM measurements as shown in *Figure 6.10*.

Figure 6.9 Relationship of relaxation rates Γ and q^2 for 2mg/mL PS-P4VP/titanium in toluene at molar ratio 4VP/Titanium = 1/0.5 at 298K.

Height contrast images of the surface of a PS-P4VP/titanium micellar film are shown in *Figure 6.10*. The brighter and darker areas in the images correspond to the P4VP microdomains and the PS matrix, respectively. The interaction between the AFM tip and P4VP domains is larger than that between the tip and PS [219] and that the hardness of the P4VP domains increases after incorporation of inorganic moieties. [220] The inset is the enlargement of the micellar film. Well-ordered array of micelles with uniform size was clearly observed from image. The average diameter of P4VP domains in the original PS-P4VP film and that after reaction with $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$, determined by the particle analysis program of Nanoscope software, is estimated to be about 28 nm, indicating that there is little change to the size of P4VP domain size. As observed from large scale scanning image, there are large holes among the film which allow us to measure the thickness of the film. The thickness of film is about 28 nm, indicating a monolayer of spherical micelles on the substrate. From *Figure 6.10* (b), it can be seen that there is a network sub-structure in the holes where the film is much thinner, indicating that the spherical particle formation depends on the film thickness.

(a)

(b)

Figure 6.10 (a) Height contrast images of the surface of a PS-P4VP/titanium micellar film, 4VP/Ti = 1/0.5, (b) enlargement of (a).

However, when the molar ratio of 4VP/Titanium reaches 1/1, the unexpected emergence of ribbon-like micelles is observed as shown in *Figure 6.11* (a). The three-dimensional image and cross-sectional analysis are also shown in the figure. The size of spherical micelles remain the same as the previous one ($4VP/Ti = 1/0.5$), but the micelles are arranged in a ribbon-like manner extending to several micrometers in length with a width of 28 nm. The width of the ribbons is exactly the same as diameter of the spherical domain at $4VP/Ti = 1/0.5$. Moreover, the ends of the P4VP strands are capped by a sphere that appears slightly larger in diameter and much brighter in the image. When the molar ratio of 4VP/Titanium reaches 1/2, the morphology, as shown in *Figure 6.11* (b), shows little difference compared with *Figure 6.11* (a). The decay time distribution function at angle of 90 degree at different molar ratio of 4VP/titanium in toluene at 1/0.5 and 1/1 are shown in *Figure 6.12*. At molar ratio of 1/0.5, a single peak was observed, indicating monodisperse particles. However, at molar ratio of 1/1 a broad peak with a small shoulder peak was observed at longer relaxation time, indicating presence of larger particles with larger poly-dispersity. Taking into account both the DLS and AFM results, one can speculate that the ribbon-like micelles come from the fusion of several spherical micelles just as as assumed for PS-P4VP-sultone system at high molar ratio in chapter 5. A similar densification process may be involved during formation of ribbon like micelles as discussed in section 5.2.3.

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(a)

(b)

Figure 6.11 Height contrast images of the surface of a PS-P4VP/titanium micellar film at different molar ratio (a) 4VP/Ti = 1/1, (b) 4VP/Ti = 1/2.

Figure 6.12 Decay time distribution function at angle of 90 degree at different molar ratio of 4VP/Ti for 2mg/mL PS-P4VP/titanium in toluene at molar ratio 4VP/Titanium (a) 1/0.5, (b) 1/1 at 298K.

The TEM images of PS-P4VP/titanium isopropoxide film at molar ratio of 4VP/titanium isopropoxide = 1/1 before reduction and after reduction are shown in *Figure 6.13*. The films were stained with I_2 vapor. Looking at the image, there is no particle deposited on the PS-P4VP before reduction. The images resemble the AFM images (*Figure 6.11(a)*) which show coexistence of spherical and ribbon-like micelles. After reduction, as shown in *Figure 6.13 (b)*, the TiO_2 particles were found to concentrate mostly in the P4VP domains, though they are not strictly confined to P4VP domain. The inset of *Figure 6.13 (b)* is the diffraction pattern of film. The bright field image and dark field image of same area in the film are shown in *Figure 6.13 (c)* and (d) respectively. They confirmed the presence of crystalline titanium dioxide. There are two important and competing issues, high density and selectivity [221], for the assembly of inorganic materials on organic scaffolds. In the case of scaffolds formed by copolymer domains, preferential wetting of one of the copolymer blocks by metal selectively aggregates the metal inside the corresponding domain. However, simple coalescence of dense metal nanoparticle aggregates into the overall shape given by the boundaries of the selected copolymer domain has not been achieved so far. This is because of the large surface energies of

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metals, exceeding those of copolymers by orders of magnitude. Consequently, metal-metal bonds will overwhelm metal-polymer bonds and, except for very small metal concentrations, the final configuration will be a large, spherical metal aggregate that completely ignores the polymer scaffold and mitigates selectivity. Thus, under equilibrium conditions, even highly elongated, anisotropic polymer scaffolds may not be able to guide self-assembling metal particles into wire-like nanostructures. However, under non-equilibrium conditions, we achieved to induce, and stabilize, recognition of complex patterns provided by a nanoscale scaffold as shown in the image.

Figure 6.13 TEM image of (a) PS-P4VP/Ti precursor (b) PS-P4VP/TiO₂, (c) bright field image (d) dark field.

In summary, Titania nanoparticles were also synthesized using similar method in PS-P4VP micelle. Loading amount of precursor was found to play important role in controlling the film morphology. Spherical to ribbon-like transition was observed when increasing molar ratio of titanium to 4VP. The particles aligned in the domain of P4VP were found.

6.3 FeCl₃ loading in PS-P4VP-sultone

The simplicity of the approach to trigger the core-corona transition of PS-P4VP-sultone as mentioned in chapter 5 suggests that this methodology can be used for the encapsulation of water soluble molecules of interest in either the core or corona. In this respect, the loading of iron chloride (FeCl₃) into the micelles, for FeCl₃ is a widely used catalyst, in the polymerization of pyrrole was studied. The FeCl₃ solid was dissolved in the copolymer micellar toluene solution under sonification. The molar ratio of 4-vinylpyridine to FeCl₃ were controlled to be 10 : 1. The resulting solution as well as the starting materials was first investigated by DLS. The decay time distribution function at different angles and relationship of relaxation rates Γ and q^2 in toluene at molar ratio (4VP/FeCl₃ = 10:1) are shown in *Figure 6.14* (a) and (b) respectively. There are two peaks in the decay time distribution function at different angles, and the relationship of relaxation rates Γ and q^2 of both these two peak shows linear correlation and passes through the origin, indicating that both these two peak are due to translational diffusion mode. This implies that there are two species in the system. The calculated R_h of these two species are 38.7 nm and 19.8 nm, respectively. They may correspond to the size of the FeCl₃ loaded micelle and PS-P4VP-sultone micelle.

Figure 6.14 (a) Decay time distribution function at different angles and (b) Relationship of relaxation rates Γ and q^2 for 2 mg/mL PS-P4VP-sultone-FeCl₃ in toluene at molar ratio (4VP/FeCl₃ = 10:1) at 298 K.

The intensity auto-correlation function was analyzed by a cumulant expansion leading to the average hydrodynamic diameter (D_h) and the polydispersity index (PDI) of the aggregates, as defined elsewhere [222]. A typical D_h distribution histogram obtained by a CONTIN transformation of the DLS data before and after FeCl₃ loading is shown in Figure 6.15. For PS-P4VP-sultone, aggregates with a D_h of 43 nm and a PDI of 0.03 were detected. Loading of FeCl₃ has an obvious effect on the D_h and on the PDI of the aggregates, which increased to 63 nm and 0.33, respectively.

Figure 6.15 CONTIN size distribution histograms obtained for (a) PS-P4VP-sultone aggregates and (b) PS-P4VP-sultone/FeCl₃.

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To obtain more information about the structural features of these aggregates, morphological investigations by TEM were performed. As shown in the inset of *Figure 6.16*, both spherical and ribbon-like micelles were found in the image, indicating that FeCl_3 has a profound effect on the shape of micelles and order in micellar film. To investigate the water effect on these aggregates, FeCl_3 containing micellar solution was spin-cast onto carbon-covered mica and then the film was floated on water for 20 seconds before it was picked up using copper grid. This procedure resulted in the inversion of core-corona and disorder of the pattern as shown in *Figure 6.16*. Water penetration into the micellar core leads to the core-corona inversion. However, the shape of the micelles becomes ribbon-like. This may be due to strong interaction of FeCl_3 containing P4VP cores.

Figure 6.16 Plan-view TEM images of films of PS-P4VP-Sultone micelles containing FeCl_3 after water treatment. (The inset is before water treatment.)

The film shown in *Figure 6.16* was exposed to pyrrole vapor and polypyrrole was synthesized selectively in nanometer-sized domains by the oxidative catalyst. TEM images after exposure for various periods of time are shown in *Figure 6.17*.

Figure 6.17 Plan-view image of PS-P4VP-sultone micelles containing FeCl_3 after exposure to Pyrrole for (a) 20, (b) 40, (c) 180 minutes.

The dark areas in the images are the P4VP domains containing polypyrrole molecules and FeCl_3 catalyst. After exposing the hexagonal micellar film to pyrrole vapor for 10 min (*Figure 6.17(a)*), a ribbon-like morphology formed by fusion between nearby spherical domains was observed. This is due to the inclusion of synthesized polypyrrole in the spherical domains. Geren et.al [223] reported the deposition of polypyrrole in the hydrophobic polystyrene surface in an aqueous polymerization condition with surface micelles of polystyrene-poly(2-vinylpyridine) fabricated by the LB method. In the present case, however, pyrrole monomer in vapor could be selectively incorporated into the P4VP domain, presumably by the polar affinity of monomer to the domain [224,225]. The

alteration of morphology may be due to the heat vapor of pyrrole treatment. Thus, polypyrrole was localized in nanometer-sized domains using the template of a single-layered film of the copolymer micelles. After further exposure of the micellar film to pyrrole vapor (*Figure 6.17(b)*), the dark domain become the dominant morphology. A smooth contour of domain boundary was observed, this is due to inclusion of more polypyrrole molecules. Eventually, the boundary became vague and a thicker layer was observed to cover the micellar film as shown in (*Figure 6.17(c)*). Although, the small ribbon-like micelles are still discernible in some areas.

The UV spectrum of film shown in *Figure 6.17 (c)* was shown in *Figure 6.18*. A broad peak centered at 558 nm was observed, which indicated the presence of polypyrrole[226].

Figure 6.18 UV-vis spectra for PS-P4VP-sultone/polypyrrole film.

In summary, iron chloride was successfully loaded into micellar core of PS-P4VP-sultone and a conducting polymer polypyrrole was polymerized in-situ in the iron chloride incorporated film.

6.4 Gold silver alloy nanoparticles prepared in PS-P4VP-sultone

Alloy nanocrystals are known to exhibit unique electronic, optical and catalytic properties, different from those of mono-metallic nanocrystals [227]. Au-Ag alloy particles that possessed interesting optical properties have been produced by the reduction of the corresponding salts using sodium borohydride, citrate or hydrazine as well as by laser irradiation of mono-metallic solutions or by the irradiation of an alloy target. In this section, the synthesis of Au-Ag alloy using block copolymer (PS-P4VP-sultone) micelle as the nano-reactor in solution is presented. The solution properties were studied using dynamic light scattering, static light scattering, and UV-visible spectroscopy. The morphology and internal structure have been examined by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS).

Two phase reduction of AuCl_4^- — AgBr_2^- (in toluene). The synthesis was carried out by separately transferring of AgBr_2^- solution and AuCl_4^- from the aqueous phase to the organic phase using tetraoctylammonium bromide (TOABr) as the phase transfer agent. For the preparation of gold-silver (1:4 molar ratio) nanoparticles, 0.064 g (1.63×10^{-4} mol) of HAuCl_4 was dissolved in 25 ml of water followed by phase transfer using 0.490 g (8.96×10^{-4} mol) of TOABr in PS-P4VP-sultone (4VP/sultone = 1:0.1) toluene solution (50 ml). AgNO_3 (0.116 g, 6.83×10^{-4} mol) was dissolved in 50 ml of water and added (dropwise) to an aqueous solution (50 ml) of KBr [0.884 g, 7.43×10^{-3} mol (10 times molar ratio)] under vigorous stirring, followed by phase transfer using 0.496 g (9.07×10^{-4} mol) of TOABr in PS-P4VP-sultone toluene solution (50 ml). The above two toluene phases, containing AgBr_2^- solution and AuCl_4^- , respectively, were then combined and stirred for 30 minute. Decanethiol (115 μL , 0.55 μmol) was added as capping agent, and

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0.246 g (6.50×10^{-3} mol) of NaBH_4 (in 12 ml water) was added (dropwise) as a reducing agent. The reaction was stirred for 4 hours, yielding decanethiolate-encapsulated AuAg (1:4 mole ratio) alloy nanoparticles in the toluene phase.

The reason for the addition of KBr is that it can convert Ag^+ into AgBr_2^- , because the formation of AgBr_2^- requires excess of Br^- . Thus, Ag^+ was transferred to the organic phase. The limited quantity of Br^- as a result of the exchange of TOA^+Br^- with HAuCl_4 (3.1 mM) is capable of forming AgBr but is not sufficient to form AgBr_2^- . An excess of Br^- in the aqueous phase is required to form a stable negatively charged AgBr_2^- first, which was then transferred into the organic phase.

DLS measurements were carried out for PS-P4VP-sultone/AuAg at different angles. Using the Stokes-Einstein relationship, the hydrodynamic radii were calculated. Decay time distribution function at different angles and the relationship of relaxation rates (Γ) and q^2 for PS-P4VP-sultone/AuAg at concentration of 2 mg/mL in toluene at molar ratio $4\text{VP}/\text{AuAg} = 1/0.5$ are shown in *Figure 6.19*. At small angles of 45, 60, 75, except the main translational peak, a broad peak of large aggregates was recorded as shown in *Figure 6.19* (a), indicating that AuAg particles were not only dispersed in the micellar core, but also in toluene solution. As the angle increased, the broad peak disappeared, indicating this peak is not due to translational diffusion. *Figure 6.19* (b) shows linear relationship between Γ and q^2 for the main peak, indicating that this peak is due to the translational diffusion. The R_h was calculated to be 24.6 nm, a little bit larger than PS-P4VP-sultone. It can be seen that loading of AuAg to the micellar core at molar ratio of 0.5 have little effect on the size and structure of PS-P4VP-sultone micelle.

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Figure 6.19 (a) Decay time distribution function at different angles and (b) relationship of relaxation rates Γ and q^2 for 2mg/mL PS-P4VP-sultone/Au-Ag in toluene at molar ratio 4VP/Au-Ag = 1/0.5 at 298K.

In this study, SLS measurements were performed at different measurement angles. A typical Zimm plot, as shown in Figure 6.20, was used to analyze the SLS data. From the plot, the apparent M_w and R_g were calculated. The R_g value is measured to be 13.9 nm. The R_g/R_h is calculated to be 0.58, typical for spherical micelles.

Figure 6.20 Zimm plot of PS-P4VP-sultone/Au-Ag in toluene (4VP / Au-Ag = 1 : 0.5, T = 298K) for polymer concentrations ranging from 0.1850 to 1.850 mg/mL.

Optically, small size particles display surface plasmon (SP) resonance bands with intensity and energy strongly dependent on size and composition. We examined the SP properties for our AuAg nanoparticles. *Figure 6.21* shows a representative set of UV-visible spectra characterizing the SP band for AuAg nanoparticles of different molar ratio (4VP/AuAg) in toluene solution. The formation of the bi-metallic nanoparticles is indicated by the presence of a single SP band. The absence of two or more bands rules out the possibility for a mixture of gold and silver nanoparticles. The spectra of AuAg nanoparticles display the SP band between 450 and 500 nm. The SP bands for the monometallic Ag and Au nanoparticles are observed at 436 nm and 520 nm, respectively [228]. A noticeable shift of SP band to the shorter wavelength (from 460.5 nm to 447.5 nm) is evident with the increase of 4VP/AuAg molar ratio as shown in *Figure 6.21*. This is characteristic of changes in interparticle spacing and properties of the dielectric medium [229]. This can be translated to a temporarily decreasing particle size or alternatively, to a decrease of intercolloidal interactions, both indications for thermodynamically stable systems. Such shifts might also be explained by slow changes in dielectric environment of the micelle core during ageing of metal colloids.

Figure 6.21 UV-vis spectra for PS-P4VP-sultone/Au-Ag solution in toluene at different molar ratio (4VP/Au-Ag): (a) PS-P4VP-sultone, (b) 1/0.1, (c) 1/0.5, (d) 1/1, (e) 1/2, (f) 0.

TEM images of AuAg nanoparticles in toluene without PS-P4VP-sultone and with PS-P4VP-sultone are shown in *Figure 6.22*. For Au-Ag in toluene, the individual nanoparticles appear to be well-isolated as shown in *Figure 6.22* (a), which is consistent with intershell interdigitation between decanethiol molecules capped on the nanoparticles [230]. The average size is about 5 nm. However, the Au-Ag nanoparticles stabilized by PS-P4VP-sultone toluene solution shows an ordered array of particles (*Figure 6.22* (b)). They are more packed and are in a hexagonal shape with short period of order. As shown in light scattering results, though AuAg nanoparticles were not well incorporated in the PS-P4VP-sultone micelles, the presence of the polymer micelles may act as better surfactant to the nanoparticles than decanethiol. This route thus shows major improvements on size and shape control of nanoparticles.

Figure 6.22 TEM images for (a) Au-Ag 1:4 in toluene and (b) Au-Ag 1:4 in PS-P4VP-sultone toluene solution.

The electron dispersive X-ray (EDX) pattern of PS-P4VP-sultone/AuAg film is shown in *Figure 6.23*. The EDX results of 9.7 keV (Au L α), 11.4 keV (Au L β) confirmed the location of gold atoms. Silver signals were not observed due to its small amount.

Figure 6.23 Electron dispersive X-ray (EDX) pattern of PS-P4VP-sultone/AuAg film

Figure 6.24 presents the XRD analysis of the synthesized AuAg nanoparticles. In the pattern, five diffraction peaks were observed at $2\theta = 38.4^\circ$, 44.6° , 64.8° , 77.8° , and 82.0° . They correspond to the Au(111)-Ag(111), Au(200), Au(220), Au(311), and Au(222)

reflections, respectively. The presence of Ag can not be conclusively determined because Ag(111) overlaps with Au(111)

Figure 6.24 XRD pattern of PS-P4VP-sultone/AuAg.

Figure 6.25 XPS spectra of PS-P4VP-sultone/AuAg film (A) Au 4f, (B) Ag 3d.

Table 6.3 XPS Peak Positions (BE/eV) for PS-P4VP-sultone/AuAg.

Sample	Au		Ag	
	4f _{7/2}	4f _{5/2}	3d _{5/2}	3d _{3/2}
PS-P4VP-sultone/AuAg	83.7	87.4	368.0	373.9

To identify the chemical nature of the silver-gold alloy particles, X-ray photoelectron spectroscopy (XPS) measurements were carried out on the PS-P4VP-sultone/AuAg film. XPS spectra of the film are shown in *Figure 6.25*. The binding energy for these peaks are listed in *Table 6.3*. The fact that both Au (4f_{7/2} and 4f_{5/2}) and Ag (3d_{5/2} and 3d_{3/2}) bands were identified [231] in the thin film, supports the presence of AuAg alloy.

In summary, XPS, and UV analysis confirmed the successful synthesis of gold-silver alloy nanoparticles in PS-P4VP-sultone solution. This method shows a better control of particle size and order.

6.5 Summary

Gold nanoparticles of 3-5 nm were synthesized in PS-P4VP micelle by in-situ reduction. Gold nanoparticles were also synthesized in ribbon-like PS-P4VP-sultone micelle, and a good selectivity in P4VP domain was observed. The gold-polymer film used as a memory device was illustrated.

Titania nanoparticles were also synthesized by in-situ reduction in PS-P4VP micelle. Loading amount of precursor was found to play important role in controlling the film morphology. Spherical to ribbon-like transition was observed when increasing molar ratio of titanium to 4VP. The particles alignment in the domain of P4VP was observed.

Chapter 6 Synthesis of Nanoparticles from Di-block Copolymer Solution

Iron chloride was successfully loaded into micellar core of PS-P4VP-sultone and a conducting polymer polypyrrole was polymerized in-situ in the iron chloride incorporated film.

Au-Ag alloy nanoparticle of about 5 nm was synthesized in PS-P4VP-sultone toluene solution using two-phase reduction method. A hexagonal array of these nanoparticles was found in the TEM observation. This new method showed a better control of particle size and order.

7 Conclusions and Future Directions

7.1 Conclusions

Successful synthesis of PS-P4VP by anionic polymerization was confirmed using DSC, FTIR, NMR and SEC. The addition of a small amount of THF led to narrower molecular weight distribution of copolymer. Also, purity of monomer, solvent, and order of addition of monomer played an important role in synthesis process. It is necessary that monomer and solvent are free of water moisture and oxygen, and styrene must be polymerized first and then followed by addition of the second monomer.

The highly-ordered pattern of surface micelles of PS-P4VP was found to depend strongly on the solution concentration. At concentration of 13 mg/mL, ribbon-to-sphere transformation was observed for the film prepared under nitrogen atmosphere using AFM when treated with water. Water may swell the P4VP due to its high polarity, leading to reorganization.

The modification of polystyrene-*b*-poly(4-vinylpyridine) was carried by introduction of 1,3-propane sultone. Polystyrene-*b*-poly(4-vinylpyridine) (PS-P4VP) betaine copolymers at different betainization degree were synthesized. Sultone-induced micellization in chloroform was observed by disappearance of pyridine ring hydrogen signal in ¹H-NMR spectra. The laser light scattering study and TEM showed the morphology evolution process of the micelle in toluene, from spherical structure to elongated species and increasing micellar size upon increasing amount of sultone grafted. Controlling the size and shape of micelles was achieved by simply adjusting the amount of sultone grafted.

The hexagonal order has been maintained at the ratio of 4VP/sultone = 1/0.1. This system is believed to have potential as vehicles for nanoreactor applications.

Polystyrene-*b*-poly(4-vinylpyridine) (PS-P4VP) betaine copolymers (4VP/sultone = 1/0.1) when cast from solvent gave rise to hexagonal packed micellar film similar to the copolymer film prior to modification. In addition, by introducing the sultone to the copolymer also resulted in increased water sensitivity. A core-corona inversion was induced in-situ using water. The technological implication of this approach is that the fine control of structure of dimensions afforded by self-assembling block copolymer materials may be harnessed for applications such as the production of nanoelectronic devices where nanopatterns switch between positive and negative tones are required.

The equilibrium morphology of the system studied is the dot-and-planar morphology at non-solvent annealing environment, whereas it is cylinder-like morphology at solvent annealing environment. The cylinder-like morphology was attributed to the presence of the solvent that confers sufficient mobility to the system to enable reorganization in response to increased temperature. This procedure thus adds a facile yet effective tool for controlling pattern formation.

The cross-linking conferred sufficient restriction to the polymer film to withstand the temperature and solvent. This is essential in fabrication of inorganic nanoparticles using block copolymer template where solvent is used and high temperature is required.

Several type of nanoparticles were synthesized using the PS-P4VP and PS-P4VP-sultone film. Gold nanoparticles of 3-5 nm were synthesized in PS-P4VP micelle by in-situ

reduction. Gold nanoparticles were also synthesized in ribbon-like PS-P4VP-sultone micelle, and a good selectivity in P4VP domain was observed. The gold-polymer film used as a memory device was illustrated.

Titania nanoparticles were also synthesized in PS-P4VP micelle. Loading amount of precursor was found to play important role in controlling the film morphology. Spherical to ribbon-like transition was observed when increasing molar ratio of titanium to 4VP. Particles alignment in the domain of P4VP was observed.

Iron chloride was successfully loaded into micellar core of PS-P4VP-sultone and a conducting polymer polypyrrole was polymerized in-situ in the iron chloride incorporated film.

Au-Ag alloy nanoparticle of 5 nm was synthesized in PS-P4VP-sultone toluene solution using two-phase reduction method. A hexagonal array of these nanoparticles was found in the TEM observation. This new method showed a better control of particle size and order.

In summary, in this research work, PS-P4VP was synthesized by anionic polymerization and betainized using 1,3-propaesultone. Their micellization behavior and film morphology evolution of betainized copolymer were studied. Metal, metal alloy and metal oxide nanoparticles were synthesized in-situ using block copolymer as nanoreactors. This route proves to be a facile yet effective way to synthesize patterned nanoparticles.

7.2 Future directions

This study has shown that the nanopattern formed by block copolymers can be successfully used as nanoreactor for the synthesis of nanoparticles. Modification of block copolymers provides a new route to control the nanopattern formation. Nevertheless, further work is needed in several areas to corroborate as well as extend this study. Some suggestions of future work are as follows:

1. The degree of betainization of a block copolymer greatly affects the morphology of the film. In this work, PS-P4VP with only one fixed block length was betainized. The effect of betainization on different PS-P4VP ratio should be studied to gain better understanding of the interactions between the various components in the system. Therefore, PS-P4VP with different block length as well as different molar ratio of block can be betainized to study solution property and morphology evolution.
2. As mentioned in chapter 6, loading amount of metal precursor leads to transformation of micelle shape and change of size. The spherical to ribbon transition and different selectivity of nanoparticles to P4VP domain was noted. The critical point where the transition takes place should be determined to further understand the mechanism. In addition, the effect of concentration and size of metal nanoparticles on the selectivity of nanodomains can also be investigated.
3. For better control the final metal morphology, it might be useful to tune the morphology of micellar film after loading of metal precursor, by solvent treatment or annealing temperature for PS-P4VP-sultone system, before reduction. It can

then be reduced in solid film. These studies will help to control the final metal morphology.

4. Whether PS-P4VP-sultone has a stronger coordination with metal salt than PS-P4VP could also be studied by measuring the amount of metal precursor loading in the core. This may indicate the undergoing interaction mechanism of PS-P4VP-sultone to metal salt which may involve the ionic strength by sultone and coordination effect by pyridine ring.
5. For some applications such as templating for deposition, it is necessary to remove the polymer template. This can be done by burning the copolymer off, O₂ plasma treatment or dissolving the template using common solvent for both blocks. The effect of removal of template to the morphology of metal particles can be investigated to achieve a precise control over the nanopattern.

List of Publications

- Song, L. X.; Lam, Y. M. Selective Betainization of PS-P4VP and Solution Properties. *Langmuir* **2006**, *22*, 319-324.
- Morphology Evolution in Diblock Copolymer Film. *Journal of nanoscience and nanotechnology*. **2006**, *6*, 1-6.
- Song, L. X.; Lam, Y. M. Nanopatterns by Monolayer Films of Diblock Copolymer Micelles with in situ Core-Corona Inversion and Solvent Induced Sphere to Cylinder Transition. (**Submitted**)
- Song L. X.; Lam, Y. M.; Teo P. W. Highly Ordered Arrays of Titania Nanoparticles From Diblock Copolymer Solution. (**Submitted**)

References

- ¹ Kim, H.C.; Russell, T. P. Ordering in thin films of asymmetric di-block copolymers. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, 39, 663-668.
- ² Riess, G.; Hurtrez, G.; Bahadur, P. in Encyclopedia of Polymer Science and Engineering (Eds: Mark H. F., Bikales N. M., Overberger C. G., Menges G.), Wiley, New York **1985**.
- ³ Rempp, P.; Merrill, E. W.; Polymer Synthesis, Hüthig & Wepf, Heidelberg **1986**.
- ⁴ Szwarc, M.; Levy, M.; Milkovich, R. A stable equimolar copper(II)-albumin. *J. Am. Chem. Soc.* **1957**, 78, 2656-2657.
- ⁵ Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. Group-transfer polymerization. 1. A new concept for addition polymerization with organosilicon initiators. *J. Am. Chem. Soc.* **1983**, 105, 5706-5707.
- ⁶ Schrock, R. R. Living ring-opening metathesis polymerization catalyzed by well-characterized transition-metal alkylidene complexes. *Acc. Chem. Res.* **1990**, 23, 158-165.
- ⁷ Miyamoto, M.; Sawamoto, M.; Higashimura, T. Living polymerization of isobutyl vinyl ether with hydrogen iodide/iodine initiating system. *Macromolecules* **1984**, 17, 265-268.
- ⁸ Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. Breathing new life into the free-radical polymerization process. *Macromolecular Symposia* **1994**, 88, 89-103
- ⁹ Grubbs, R. H.; Tumas, W. Polymer Synthesis and Organotransition Metal Chemistry. *Science* **1989**, 243, 907-915.
- ¹⁰ Hillmyer, M. A.; Bates, F. S. Synthesis and Characterization of Model Polyalkane-Poly(ethylene oxide) Block Copolymers. *Macromolecules* **1996**, 29, 6994-7002.
- ¹¹ Baines, F. L.; Armes, S. P.; Billingham, N. C.; Tuzar, T.; Micellization of Poly(2-(dimethylamino)ethyl methacrylate-*block*-methyl methacrylate) Copolymers in Aqueous Solution. *Macromolecules* **1996**, 29, 8151-8159.
- ¹² Su, T. J.; Styrkas, D. A.; Thomas, R. K.; Baines, F. L.; Billingham, N. C.; Armes, S. P. Neutron and X-ray Reflectivity Studies of Water-Soluble Block and Statistical Copolymers Adsorbed at the Air-Water Interface. *Macromolecules* **1996**, 29, 6892-6900.
- ¹³ Baines, F. L.; Billingham, N. C.; Armes, S. P. Synthesis and Solution Properties of Water-Soluble Hydrophilic-Hydrophobic Block Copolymers. *Macromolecules* **1996**, 29, 3416-3420.

-
- ¹⁴ Baines, F. L.; Dionisio, S.; Billingham, N. C.; Armes, S. P. Use of Block Copolymer Stabilizers for the Dispersion Polymerization of Styrene in Alcoholic Media. *Macromolecules* **1996**, 29, 3096-3102.
- ¹⁵ Okano, T.; Nishiyama, S.; Shinohara, I.; Akaike, T.; Sakurai, Y.; Kataoka, K.; Tsuruta, T. Effect of hydrophilic and hydrophobic microdomains on mode of interaction between block polymer and blood platelets. *J. Biomed. Mater. Res.* **1981**, 15, 393-402.
- ¹⁶ Ito, H.; Taenaka, A.; Nagasaki, Y.; Kataoka, K.; Kato, M. Silicon-containing block copolymer membranes. *Polymer* **1996**, 37, 633-637.
- ¹⁷ Clay, R. T.; Cohen, R.E. Synthesis of metal nanoclusters within microphase-separated di-block copolymers: a 'universal' approach. *Supramolecular. Science* **1995**, 2, 183-191.
- ¹⁸ Faust, R.; Kennedy, J. P. Living carbocationic polymerization. IV. Living polymerization of isobutylene. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, 25, 1847-1869.
- ¹⁹ Patrickios, C. S.; Forder, C.; Armes, S. P.; Billingham, N. C. Synthesis and characterization of amphiphilic di-block copolymers of methyl Tri(ethylene glycol) vinyl ether and isobutyl vinyl ether. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, 34, 1529-1541.
- ²⁰ Forder, C.; Armes, S. P.; Billingham, N. C. Synthesis of poly(vinyl alcohols)s with narrow molecular-weight distribution from poly(benzyl vinyl ether) precursors. *Polym. Bull.* **1995**, 35, 291-297.
- ²¹ Matyjaszewski, K. Effect of initiators, Lewis acids, deactivators, additives and medium on controlled/"living" carbocationic systems. *Macromol. Symp.* **1996**, 107, 53-63.
- ²² Antonietti, M.; Förster, S.; Hartmann, J.; Oestreich, S. Novel Amphiphilic Block Copolymers by Polymer Reactions and Their Use for Solubilization of Metal Salts and Metal Colloids. *Macromolecules* **1996**, 29, 3800-3806.
- ²³ Invengar, D. R.; Perutz, S. M.; Dai, C. A.; Ober, C. K.; Kramer, E. J. Surface Segregation Studies of Fluorine-Containing Di-block Copolymers. *Macromolecules* **1996**, 29, 1229-1234.
- ²⁴ Ramireddy, C.; Tuzar, Z.; Prochazka, K.; Webber, S. E.; Munk, P. Styrene-tert-butyl methacrylate and styrene-methacrylic acid block copolymers: synthesis and characterization. *Macromolecules* **1992**, 25, 2541-2545.
- ²⁵ Mohammadi, N. A.; Rempel, G. L. Homogeneous selective catalytic hydrogenation of C=C in acrylonitrile-butadiene copolymer. *Macromolecules* **1987**, 20, 2362-2368.
- ²⁶ Rosedale, J. H.; Bates, F. S. Heterogeneous catalytic hydrogenation of poly(vinylethylene). *J. Am. Chem. Soc.* **1988**, 110, 3542-3545.

-
- ²⁷ Morishima, Y.; Hashimoto, T.; Itoh, Y.; Kamachi, M.; Nozakura, S. Syntheses of amphiphilic block copolymers. Block copolymers of methacrylic acid and *p*-*N,N*-dimethylaminostyrene. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, 20, 299-310.
- ²⁸ Thaler, W. A. Hydrocarbon-soluble sulfonating reagents. Sulfonation of aromatic polymers in hydrocarbon solution using soluble acyl sulfates. *Macromolecules* **1983**, 16, 623-628.
- ²⁹ Gebelein, C. G.; Murphy, D. in *Advances in Biomedical Polymers* (Ed: C. G. Gebelein), Plenum, New York **1987**.
- ³⁰ Iraqi, A.; Cole-Hamilton, D. J. Preparation and reactivity of polyepoxides and polyketones: catalytic oxidation of polybutadienes. *J. Mater. Chem.* **1992**, 2, 183-190.
- ³¹ Chini, M.; Crotti, P.; Macchia, F. Metal salts as new catalysts for mild and efficient aminolysis of oxiranes. *Tetrahedron Letters* **1990**, 31, 4661-4664.
- ³² Nishikubo, T.; Kameyama, A. Addition reactions of cyclic ethers with various carbonyl compounds and their application for polymer synthesis. *Prog. Polym. Sci.* **1993**, 18, 963-995.
- ³³ Ramakrishnan, S. Well-defined ethylene-vinyl alcohol copolymers via hydroboration: control of composition and distribution of the hydroxyl groups on the polymer backbone. *Macromolecules* **1991**, 24, 3753-3759.
- ³⁴ Gronski, W.; Sanger, J.; Side-chain liquid crystalline copolymers with nonmesogenic comonomers - Influence of comonomer content on the nature of the mesophase *Macromol. Rapid Commun.* **1997**, 18, 59-64.
- ³⁵ Gimenez, V.; Mantecon, M.; Cadiz, V. Modification of poly(vinyl alcohol) with acid chlorides and cross-linking with difunctional hardeners *J. Polym. Sci., Part A: Polym. Chem.* **1996**, 34, 925-934.
- ³⁶ Frey, W.; Dederichs, B.; Klesper, E. Esterification reactions on syndiotactic poly(methallyl alcohol)—III. Esterification with cyclic carboxylic acid anhydrides. *Eur. Polym. J.* **1986**, 22, 745-753.
- ³⁷ Müller, H.; Leube, W.; Tauer, K.; Förster, S.; Antonietti, M. Polyelectrolyte Block Copolymers as Effective Stabilizers in Emulsion Polymerization. *Macromolecules* **1997**, 30, 2288-2293.
- ³⁸ Linse, P.; Malmsten, M. Temperature dependent micellization in aqueous block copolymer solutions. *Macromolecules* **1992**, 25, 5434-5439.

-
- ³⁹ Hurtrez, G. Study of PS-PEO and PEO-PS-PEO block copolymers (in French). PhD Thesis. University Haute Alsace, France; 1992
- ⁴⁰ Munk, P. Equilibrium and nonequilibrium polymer micelles. In: Webber SE, Munk P, Tuzar Z, editors. Solvents and selforganization of polymer. NATO ASI series, serie E: applied sciences, vol. 327. Dordrecht: Kluwer Academic Publisher; **1996**. 19–32.
- ⁴¹ Tuzar, Z.; Kratochvil, P. Micelles of block and graft copolymers in solution. In: Matijevic E, editor. Surface and colloid science, vol. 15. New York: Plenum Press; **1993**. p. 1–83. chapter 1.
- ⁴² Antonietti, M.; Forster, S.; Oestreich, S.; Hartmann, J.; Wenz, E. Precious metal and semiconductor colloids in polymer composites. *Nachr. Chem. Chem.Lab.Tech.* **1996**, 44, 579-586.
- ⁴³ Thurn-Albrecht, T.; Schotter, J.; Kästle G.A.; Emley, N.; Shibauchi, T.; Krusin-Elbaum, L.; Guarini, K.; Black, C.T.; Tuominen, M.T.; Russell, T.P. Ultrahigh-density nanowire arrays grown in self-assembled di-block copolymer templates. *Science* **2000**, 290, 2126-2129.
- ⁴⁴ Villar, M. A.; Rueda, D. R.; Ania, F.; Thomas, E. L. Study of oriented block copolymers films obtained by roll[hyphen]casting. *Polymer* **2002**, 43, 5139-5145.
- ⁴⁵ Kim, G.; Libera, M. Morphological Development in Solvent-Cast Polystyrene-Polybutadiene-Polystyrene (SBS) Tri-block Copolymer Thin Films. *Macromolecules* **1998**, 31, 2569–2577.
- ⁴⁶ Strawhecker, K. E.; Kumar, S. K.; Douglas, J. F.; Karim, A. The Critical Role of Solvent Evaporation on the Roughness of Spin-Cast Polymer Films *Macromolecules* **2001**, 34 4669–4672.
- ⁴⁷ Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. Neutron reflectivity studies of the surface-induced ordering of di-block copolymer films. *Phys. Rev. Lett.* **1989**, 62, 1852–1855.
- ⁴⁸ Foster, M. D.; Sikka, M.; Singh, N.; Bates, F.S.; Satija, S.K.; Majkrzak, C.F. Structure of symmetric polyolefin block copolymer thin films. *J. Chem. Phys.* **1992**, 96, 8605–8615.
- ⁴⁹ Dai, H. J.; Balsara, N. P.; Garetz, B.A.; Newstein, M. C. Grain Growth and Defect Annihilation in Block Copolymers. *Phys. Rev. Lett.* **1996**, 77, 3677–3680.
- ⁵⁰ Newstein, M. C.; Garetz, B.A.; Balsara, N. P.; Chang, M. Y.; Dai, H. J. Growth of Grains and Correlated Grain Clusters in a Block Copolymer Melt. *Macromolecules* **1998**, 31, 64–76.

-
- ⁵¹ Kim, W.G.; Garetz, B.A.; Newstein, M.C.; Balsara, N.P. Maximizing the grain growth rate during the disorder-to-order transition in block copolymer melts. *J. Polym. Sci. B: Polym. Phys.* **2001**, 39, 2231–2242.
- ⁵² Hashimoto, T.; Bodycomb, J.; Funaki, Y.; Kimishima, K. The Effect of Temperature Gradient on the Microdomain Orientation of Di-block Copolymers Undergoing an Order-Disorder Transition. *Macromolecules* **1999**, 32, 952–954.
- ⁵³ Yokoyama, H.; Mates, T.E.; Kramer, E.J. Structure of Asymmetric Di-block Copolymers in Thin Films. *Macromolecules* **2000**, 33, 1888–1898.
- ⁵⁴ Hamersky, M. W.; Hillmyer, M. A.; Tirrell, M.; Bates, F. S.; Lodge, T. P. Meierwall E.D., Block Copolymer Self-Diffusion in the Gyroid and Cylinder Morphologies *Macromolecules* **1998**, 31, 5363–5370.
- ⁵⁵ Joly, S.; Raquois, A.; Paris, F.; Hamdoun, B.; Auvray, L.; Ausserre, D.; Gallot, Y. Early Stage of Spinodal Decomposition in 2D. *Phys. Rev. Lett.* **1996**, 77, 4394–4397.
- ⁵⁶ Bassereau, P.; Brodbeck, D.; Russell, T.P.; Brown, H.R.; Shull, K.R. 2-Dimensional ostwald ripening in symmetrical di-block copolymer films – reply. *Phys. Rev. Lett.* **1995**, 74, 4961–4961.
- ⁵⁷ Collin, B.; Chatenay, D.; Coulon, G.; Ausserre, D.; Gallot, Y.; Ordering of copolymer thin films as revealed by atomic force microscopy. *Macromolecules* **1992**, 25, 1621–1622.
- ⁵⁸ Grim, P. C. M.; Nyrkova, I. A.; Semenov, A. N.; Tenbrinke, G.; Hadziioannou, G. The Free Surface of Thin Di-block Copolymer Films: Experimental and Theoretical Investigations on the Formation and Growth of Surface Relief Structures. *Macromolecules* **1995**, 28, 7501–7513.
- ⁵⁹ Segalman, R.A.; Schaefer, K.E.; Fredrickson, G.H.; Kramer, E.J.; Magonov, S. Topographic Templating of Islands and Holes in Highly Asymmetric Block Copolymer Films. *Macromolecules* **2003**, 36, 4498–4506.
- ⁶⁰ Yokoyama, H.; Kramer, E.J.; Hajduk, D.A.; Bates, F.S. Diffusion in Mixtures of Asymmetric Di-block Copolymers with Homopolymers. *Macromolecules* **1999**, 32, 3353–3359.
- ⁶¹ Segalman, R. A.; Hexemer, A.; Hayward, R.C.; Kramer, E.J. Ordering and Melting of Block Copolymer Spherical Domains in 2 and 3 Dimensions. *Macromolecules* **2003**, 36, 3272–3288.
- ⁶² Angelescu, D.; Harrison, C.; Trawick, M.; Sebastian, J.; Chaikin, P. M.; Register, R. A.; Adamson, D. H. Melting microdomain patterns in a di-block copolymer thin film, in:

Bulletin of the American Physical Society March Meeting, vol. 47, part II, Indianapolis, Indiana, 2002, p. 900.

⁶³ Brus, L. Semiconductor colloids: Individual nanocrystals, opals and porous silicon. *Curr. Opin. Colloid Interface Sci.* **1996**, 1, 197-201.

⁶⁴ Weller, H. Colloidal semiconductor q-particles-chemistry in the transition region between solid-state and molecules. *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 41-53.

⁶⁵ Fendler, J. H.; Meldrum, F. C. The colloid-chemical approach to nanostructured materials. *Adv. Mater.* **1995**, 7, 607-632.

⁶⁶ Matijevic, E. in *Controlled Particle, Droplet and Bubble Formation* (Ed: Wedlock, D. J.), Butterworth-Heinemann, Oxford **1994**, p. 39.

⁶⁷ Matijevic, E., Uniform inorganic colloid dispersions – achievements and challenges. *Langmuir* **1994**, 10, 8-16.

⁶⁸ Watzke, H. J.; Fendler, J. H. Quantum size effects of in situ generated colloidal cadmium sulfide particles in dioctadecyldimethylammonium chloride surfactant vesicles. *J. Phys. Chem.* **1987**, 91, 854-861.

⁶⁹ Pileni, M. P.; Motte, L.; Petit, C. Synthesis of cadmium-sulfide insitu in reverse micelles – influence of the preparation modes on size, polydispersity, and photochemical reactions. *Chem. Mater.* **1992**, 4, 338-345.

⁷⁰ Breitscheidel, B.; Zieder, J.; Schubert, U. Metal-complexes in inorganic matrices. 7. nanometer-sized, uniform metal particles in a SiO₂ matrix by sol-gel processing of metal-complexes. *Chem. Mater.* **1991**, 3, 559-566.

⁷¹ Wang, Y.; Herron, N.; Optical properties of cadmium sulfide and lead(II) sulfide clusters encapsulated in zeolites. *J. Phys. Chem.* **1987**, 91, 257-260.

⁷² Zhao, X. K.; McCormick, L.; Fendler, J. H. Electrical and photoelectrochemical characterization of cadmium sulfide particulate films by scanning electrochemical microscopy, scanning tunneling microscopy, and scanning tunneling spectroscopy. *Chem. Mater.* **1991**, 3, 922-935.

⁷³ Forster, S.; Antonietti, M. Amphiphilic block copolymers in structure-controlled nanomaterial hybrids. *Adv. Mater.* **1998**, 10, 195-217.

⁷⁴ Park, C.; Yoon, J.; Thomas, E. L. Enabling nanotechnology with self assembled block copolymer patterns. *Polymer* **2003**, 44, 6725-6760.

⁷⁵ Forster, S.; Konrad, M. From self-organizing polymers to nano- and biomaterials *J. Mater. Chem.* **2003**, 13, 2671-2688.

- ⁷⁶ Cameron, N. S.; Corbierre, M. K.; Eisenberg, A. 1998 E.W.R. Steacie Award Lecture Asymmetric amphiphilic block copolymers in solution: a morphological wonderland *Can. J. Chem.* **1999**, *77*, 1311-1326.
- ⁷⁷ Discher, B. M.; Won, Y.-Y.; Ege, D. S.; Lee, J. C.-M.; Bates, F. S.; Discher, D. E.; Hammer, D. A. Polymersomes: Tough Vesicles Made from Di-block Copolymers *Science* **1999**, *284*, 1143-1146.
- ⁷⁸ Cornelissen, J. J. L. M.; Fischer, M.; Sommerdijk, N. A. J. M.; Nolte, R. J. M. Helical Superstructures from Charged Poly(styrene)-Poly(isocyanodipeptide) Block Copolymers *Science* **1998**, *280*, 1427-1430.
- ⁷⁹ Jain, S.; Bates, F. S. On the Origins of Morphological Complexity in Block Copolymer Surfactants. *Science* **2003**, *300*, 460-464.
- ⁸⁰ van Hest, J. C. M.; Delnoye, D. A. P.; Baars, M. W. P. L.; van Genderen, M. H. P.; Meijer, E. W. Polystyrene-Dendrimer Amphiphilic Block Copolymers with a Generation-Dependent Aggregation. *Science* **1995**, *268*, 1592-1595.
- ⁸¹ Zhang, L.; Eisenberg, A. Multiple Morphologies of "Crew-Cut" Aggregates of Polystyrene-*b*-poly(acrylic acid) Block Copolymers. *Science* **1995**, *268*, 1728-1731.
- ⁸² Discher, B. M.; Hammer, D. A.; Bates, F. S.; Discher, D. E. Polymer vesicles in various media. *Curr. Opin. Colloid Interface Sci.* **2000**, *5*, 125-131.
- ⁸³ Discher, D. E.; Eisenberg, A. Polymer Vesicles *Science* **2002**, *297*, 967-973.
- ⁸⁴ Antonietti, M.; Forster, S. Vesicles and Liposomes: A Self-Assembly Principle Beyond Lipids. *Adv. Mater.* **2003**, *15*, 1323-1333.
- ⁸⁵ Soo, P. L.; Eisenberg, A. Preparation of block copolymer vesicles in solution *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 923-938.
- ⁸⁶ Aranda-Espinoza, H.; Bermudez, H.; Bates, F. S.; Discher, D. E. Electromechanical limits of polymersomes. *Phys. Rev. Lett.* **2001**, *87*, 208301-1.
- ⁸⁷ Bermudez, H.; Brannan, A. K.; Hammer, D. A.; Bates, F. S.; Discher, D. E. Molecular Weight Dependence of Polymersome Membrane Structure, Elasticity, and Stability. *Macromolecules* **2002**, *35*, 8203-8208.
- ⁸⁸ Discher, B. M.; Bermudez, H.; Hammer, D. A.; Discher, D. E.; Won, Y.-Y.; Bates, F. S. Cross-linked polymersome membranes: Vesicles with broadly adjustable properties *J. Phys. Chem. B* **2002**, *106*, 2848-2854.

-
- ⁸⁹ White, S. R.; Sottos, N. R.; Geubelle, P. H.; Moore, J. S.; Kessler, M. R.; Sriram, S. R.; Brown, E. N.; Viswanathan, S. Autonomic healing of polymer composites. *Nature* **2001**, *409*, 794-797.
- ⁹⁰ Boerakker, M. J.; Hannink, J. M.; Bomans, P. H. H.; Frederik, P. M.; Nolte, R. J. M.; Meijer, E. M.; Sommerdijk, N. A. J. M. Giant amphiphiles by cofactor reconstitution *Angew. Chem., Int. Ed.* **2002**, *41*, 4239-4241.
- ⁹¹ Bradley J. S. In: Schmid G, editor. Cluster and colloids. from theory to application. Weinheim: Wiley/VCH; **1994**
- ⁹² Mayer, A. B. R. Colloidal metal nanoparticles dispersed in amphiphilic polymers. *Polym. Adv. Technol.* **2001**, *12*, 96-106.
- ⁹³ Hamley, I. W. Nanostructure fabrication using block copolymers. *Nanotechnology* **2003**, *14*, 39-54.
- ⁹⁴ Kastle, G.; Boyen, H. G.; Weigl, F.; Lengel, G.; Herzog, T.; Ziemann, P.; Riethmuller, S.; Mayer, O.; Hartmann, C.; Spatz, J. P.; Moller, M.; Ozawa, M.; Banhart, F.; Garnier, M. G.; Oelhafen, P. Micellar nanoreactors - Preparation and characterization of hexagonally ordered arrays of metallic nanodots *Adv. Funct. Mater.* **2003**, *13*, 853-861.
- ⁹⁵ Klingelhofer, S.; Heitz, W.; Greiner, A.; Oestreich, S.; Forster, S.; Antonietti, M. Preparation of palladium colloids in block copolymer micelles and their use for the catalysis of the Heck reaction. *J. Am. Chem. Soc.* **1997**, *119*, 10116-10120.
- ⁹⁶ Moffitt, M.; McMahon, L.; Pessel, V.; Eisenberg, A. Size control of nanoparticles in semiconductor-polymer composites. 2. control via sizes of spherical ionic microdomains in styrene-based di-block ionomers. *Chem. Mater.* **1995**, *7*, 1185-1192.
- ⁹⁷ Cornelissen, J. J. L. M.; van Heerbeek, R.; Kamer, P. C. J.; Reek, J. N. H.; Sommerdijk, N. A. J. M.; Nolte, R. J. M. Silver nanoarrays templated by block copolymers of carbosilane dendrimers and polyisocyanopeptides *Adv. Mater.* **2002**, *14*, 489-493.
- ⁹⁸ Roucoux, A.; Schulz, J.; Patin, H. Reduced transition metal colloids: A novel family of reusable catalysts? *Chemical Review* **2002**, *102*, 3757-3778.
- ⁹⁹ Yu, W. Y.; Liu, H. F.; Tao, Q. Modification of metal cations to metal clusters in liquid medium. *Chemical Communications.* **1996**, 1773-1774.
- ¹⁰⁰ Zuo, X.; Liu, H.; Liu, M. Asymmetric hydrogenation of α -ketoesters over finely dispersed polymer-stabilized platinum clusters. *Tetrahedron Letters.* **1998**, *39*, 1941-1944.

-
- ¹⁰¹ Harada, M.; Asakura, K.; Toshima, N. Catalytic activity and structural- analysis of polymer-protected Au/Pd bimetallic clusters prepared by the successive reduction of HAuCl₄ and PdCl₂. *J. Phys. Chem.* **1993**, *97*, 5103-5114.
- ¹⁰² Shiraishi, Y.; Toshima, N. Colloidal silver catalysts for oxidation of ethylene *J. Mol. Catal. A: Chem.* **1999**, *141*, 187-192.
- ¹⁰³ Shiraishi, Y.; Toshima, N. Oxidation of ethylene catalyzed by colloidal dispersions of poly(sodium acrylate)-protected silver nanoclusters *Colloids Surf., A* **2000**, *169*, 59-66.
- ¹⁰⁴ Wang, Q.; Liu, H.; Han, M.; Li, X.; Jiang, D. Carbonylation of methanol catalyzed by polymer-protected rhodium colloid. *J. Mol. Catal. A: Chem.* **1997**, *118*, 145-151.
- ¹⁰⁵ Le Bars, J.; Specht, U.; Bradley, J. S.; Blackmond, D. G. A catalytic probe of the surface of colloidal palladium particles using Heck coupling reactions. *Langmuir* **1999**, *15*, 7621-7625.
- ¹⁰⁶ Li, Y.; El-Sayed, M. A. The effect of stabilizers on the catalytic activity and stability of Pd colloidal nanoparticles in the Suzuki reactions in aqueous solution. *J. Phys. Chem. B* **2001**, *105*, 8938-8943.
- ¹⁰⁷ Lee, M.; Jang, C.-J.; Ryu, J.-H. Supramolecular Reactor from Self-Assembly of Rod-Coil Molecule in Aqueous Environment. *J. Am. Chem. Soc.* **2004**, *126*, 8082-8083.
- ¹⁰⁸ Naka, K.; Kubo, Y.; Ohki, A.; Maeda, S. Aggregat of amphiphilic block-copolymer derived from poly[(N-acylimino)ethylene]s and guest-binding properties for 8-anilino-1-naphthalenesulfonic acid, pyrene, and enzymes. *Polym. J.* **1994**, *26*, 243-249.
- ¹⁰⁹ Harada, A.; Kataoka, K. Novel Polyion Complex Micelles Entrapping Enzyme Molecules in the Core: Preparation of Narrowly-Distributed Micelles from Lysozyme and Poly(ethylene glycol)-Poly(aspartic acid) Block Copolymer in Aqueous Medium. *Macromolecules* **1998**, *31*, 288-294.
- ¹¹⁰ Harada, A.; Kataoka, K. Novel Polyion Complex Micelles Entrapping Enzyme Molecules in the Core. 2. Characterization of the Micelles Prepared at Nonstoichiometric Mixing Ratios. *Langmuir* **1999**, *15*, 4208-4212.
- ¹¹¹ Harada, A.; Kataoka, K. On-Off Control of Enzymatic Activity Synchronizing with Reversible Formation of Supramolecular Assembly from Enzyme and Charged Block Copolymers *J. Am. Chem. Soc.* **1999**, *121*, 9241-9242.
- ¹¹² Harada, A.; Kataoka, K. Pronounced activity of enzymes through the incorporation into the core of polyion complex micelles made from charged block copolymers. *J. Controlled Release* **2001**, *72*, 85-91.

- ¹¹³ Harada, A.; Kataoka, K. Switching by Pulse Electric Field of the Elevated Enzymatic Reaction in the Core of Polyion Complex Micelles *J. Am. Chem. Soc.* **2003**, *125*, 15306-15307.
- ¹¹⁴ Velonia, K.; Rowan, A. E.; Nolte, R. J. M. Lipase Polystyrene Giant Amphiphiles. *J. Am. Chem. Soc.* **2002**, *124*, 4224-4225.
- ¹¹⁵ Hager, M.; Currie, F.; Holmberg, K. Organic reactions in microemulsions *Top. Curr. Chem.* **2003**, *227*, 53-74.
- ¹¹⁶ Jang, J.; Ha, H. Fabrication of Hollow Polystyrene Nanospheres in Microemulsion Polymerization Using Tri-block Copolymers. *Langmuir* **2002**, *18*, 5613-5618.
- ¹¹⁷ Landfester, K. *Colloid Chemistry II*; Springer-Verlag: Berlin, **2003**.
- ¹¹⁸ Landfester, K.; Montenegro, R.; Scherf, U.; Guntner, R.; Asawapirom, U.; Patil, S.; Neher, D.; Kietzke, T. Semiconducting Polymer Nanospheres in Aqueous Dispersion Prepared by a Miniemulsion Process. *Adv. Mater.* **2002**, *14*, 651-655.
- ¹¹⁹ Tiarks, F.; Landfester, K.; Antonietti, M. Preparation of Polymeric Nanocapsules by Miniemulsion Polymerization. *Langmuir* **2001**, *17*, 908-918.
- ¹²⁰ Ossenbach-sauter, M. Emulsifying properties of block copolymers water in water polymeric emulsions. PHD thesis. University of Haute Alsace, France; **1981**.
- ¹²¹ Antonietti, M.; Wenz, E.; Bronstein, L.; Seregina, M. Synthesis and characterization of noble metal colloids in block copolymer micelles. *Adv. Mater.* **1995**, *7*(12), 1000-1005.
- ¹²² Sulman E., Bodrova Y., Matveeva V., Semagina N., Cervený L., Kurtc V., Bronstein L., Platonava, O.; Valetsky, P. Hydrogenation of dehydrolinalool with novel catalyst derived from Pd colloids stabilized in Michelle cores of polustyrene-poly-4-vinylpyridine block copolymers. *Appl Catal A:Gen* **1999**, *176*(1), 75-81.
- ¹²³ Youk, J. H.; Locklin, J.; Park, M. K.; Yang, J.; Mays, J.; Advincula, R. controlled preparation of gold nanoparticles using well defined block copolymers. *ACS Polym Prepr (Div Polym Chem)* **2001**, *42*(2), 358-359.
- ¹²⁴ Hou, S.; Chan, W. K.; Polymer aggregates formed by polystyrene-poly(4-vinylpyridine) functionalized with rhenium 2,2'-bipyridyl complexes. *Macromol. Rapid. Commun.* **1999**, *20*, 440-443.
- ¹²⁵ Mayer, A. B. R.; Mark, J. E.; Transition metal nanoparticles protected by amphiphilic block copolymer as tailored catalyst systems. *Colloid Polym Sci* **1997**, *275*(4), 333-340.

- ¹²⁶ Esswein, B.; Spatz, J. P.; Moller, M. Application of phosphoranimine bases for the prepatation amphiphilic block copolymers. *ACS Polym Prepr (Div Polym Chem)* **1996**, 37(2), 647-648.
- ¹²⁷ Antonietti, M.; Forster, S.; Hartmann, J.; Oestreich, S. Novel amphiphilic block copolymers by polymer reactions and their use for solubilization of metal salts and metal colloids. *Mcromolecules* **1996**, 29, 3800-3806.
- ¹²⁸ Roescher A, Hempenius M, Klok HA, Moller M. Stabilization of colloidal palladium particles by a block copolymer of polystyrene and a block containing amide sedegroups. *Acta Polym* **1996**, 47, 481-484.
- ¹²⁹ Bronstein, L. M.; Seregina, M. V.; PLatanova, O. A.; Kabachii, Y. A.; Chernyshov, D. M.; Ezerniskaya, M. G.; Dubrovina, L.V.; Bragina, T. P.; Valetzky, P.M. Synthesis of Pd, Pt and Rh-containing polymers derived from polystyrene-polybutadiene block copolymers: micellization of di-block copolymer due to complexation. *Macromol Chem Phys* **1998**, 199, 1357-1363.
- ¹³⁰ Nuyken, O.; Persigehl, P.; Weberskirch, R. Amphiphilic poly(oxazoline)s-synthesis and application for micellar catalysis. *Macromol Symp* **2002**, 17(synthesis of defined Polymer Architectures):163-173.
- ¹³¹ Chernyshov, D. M.; Bronstein, L. M.; Beerner, H.; Berton, B.; Antonietti, M. Sythesis and induced micellization Pd-containing polystyrene-block-poly-m—vinyltriphenyl phosphine di-block copolymers. *Chem. Mater.* **2000**,12(1),114-121.
- ¹³² Spatz, J. P.; Roescher, A.; Moller, M. Gold nanoparticles in micellar poly(styrene)-b-poly(ethylene oxide) films-size and interparticle distance control in monoparticulate films. *Adv. Mater.* **1996**, 37, 337-340.
- ¹³³ Chan, Y. N. C.; Schrock, R. R.; Cohen, R. E. Synthesis of silver and gold nanoclusters within microphase-separated di-block copolymers. *Chem. Mater.* **1992**, 4, 24-27.
- ¹³⁴ Moffitt, M. and Eisenberg, A., Scaling Relations and Size Control of Block Ionomer Microreactors Containing Different Metal Ions. *Macromolecules*, **1997**, 30, 4363-4373.
- ¹³⁵ Ago, H.; Komatsu, T.; Ohshima, S.; Kuriki, Y.; Yunmura, Motoo. Dispersion of metal nanoparticles for aligned carbon nanotube arrays, *Applied Physics Letters*, **2000**, 77, 79-81.
- ¹³⁶ Chatterjee, M.; Patra, A. Cadmium sulfide aggregates though reverse micelles, *J. Am. Ceram. Soc.* **2001**, 84, 1439-1444.

-
- ¹³⁷ Prochaska, K., Baloch, M. K. Photochemical stabilization of block copolymer micelles. *Makromol. Chem.* **1979**, 180, 2521–2523.
- ¹³⁸ Tuzar, Z.; Bednar, B.; Konak, C.; Kubin, M.; Svobodova, S.; Prochaska, K. Stabilization of block copolymer micelles by UV and fast electron radiation. *Makromol. Chem.* **1982**, 183, 399–408.
- ¹³⁹ Wilson, D.J.; Riess, G.; Photochemical stabilization of block copolymer micelles. *Eur. Polym. J.* **1988**, 24(7), 617–621.
- ¹⁴⁰ Guo, A.; Liu, G.; Tao, J. Star polymers and nanospheres from cross-linkable di-block copolymers. *Macromolecules* **1996**, 29, 2487–2493.
- ¹⁴¹ Thurmond, K. B.; Kowalewski, T.; Wooley, K. L. The study of shell cross-linked knedels (SCK). Formation and applications. *ACS Polym Prepr (Div Polym Chem)* **1997**, 38(1), 62–63.
- ¹⁴² Ma, Q.; Remsen, E. E.; Kowalewski, T.; Wooley, K.L. Entirely hydrophilic shell cross-linkable knedel-like (SCK) nanoparticles. *ACS Polym Prepr (Div Polym Chem)* **2000**, 41(2), 1571–1572.
- ¹⁴³ Buřtuřn, V.; Billingham, N.C.; Armes, S.P. Synthesis of novel shell cross-linked micelles with hydrophilic cores. *ACS Polym Prepr (Div Polym Chem)* **1999**, 40(2), 236–237.
- ¹⁴⁴ Ishizu, K. Structural ordering of core cross-linked nanoparticles and architecture of polymeric superstructures. *ACS Polym Prepr (Div Polym Chem)* **1999**, 40(1), 456–457.
- ¹⁴⁵ Flory, P. J. In *Principles of Polymer Chemistry*; Cornell University Press: London, **1953**.
- ¹⁴⁶ Brown, W. *Dynamic Light Scattering- the Method and Some Applications*; Clarendon press: Boston, **1993**.
- ¹⁴⁷ Brown, W. *Light Scattering-Principles and Development*; University Press: Oxford, **1996**.
- ¹⁴⁸ Jakes, J.; Czech. *J. Phys. B* **1988**, 38, 1305.
- ¹⁴⁹ Penczek, S.; Kubisa, P. in *Encyclopedia of polymer science and engineering*, J.I. Kroschwitz, Ed., Wiley-Interscience, New York, **1989**, Supplemental Volume, p.380.
- ¹⁵⁰ Varshney, S. K.; Zhong, X. F.; Eisenberg, A. Anionic homopolymerization and block copolymerization of 4-vinylpyridine and its investigation by high-temperature size-

exclusion chromatography in N-methyl-2-pyrrolidinone. *Macromolecules* **1993**, 26, 701-706.

¹⁵¹ Creutz, S.; Teyssie, P.; Jerome, R. Anionic Block Copolymerization of 4-Vinylpyridine and *tert*-Butyl Methacrylate at "Elevated" Temperatures: Influence of Various Additives on the Molecular Parameters. *Macromolecules* **1997**, 30, 5596-5601.

¹⁵² Frere, Y.; Gramain, P. Reaction kinetics of polymer substituents: macromolecular steric hindrance effect in quaternization of poly(vinylpyridines). *Macromolecules* **1992**, 25, 3184-3189.

¹⁵³ Ruokolainen, J.; Ten Brinke, G.; Ikkala, O. Supramolecular Polymeric Materials with Hierarchical Structure-Within-Structure Morphologies. *Adv. Mater.* **1999**, 11, 777-780.

¹⁵⁴ Hogen-Esch, T. E.; Jenkins, W.L. NMR and conductometric studies of 2-pyridyl-substituted carbanions. 2. Effects of cation size and coordination. *J. Am. Chem. Soc.* **1981**, 103, 3666-3672.

¹⁵⁵ Tardi, M.; Sigwalt, P. Etude de la nature des especes ioniques intervenant au cours de la polymerisation anionique de la vinyl-4 pyridine. *Eur. Polym. J.* **1973**, 9, 1369-1379.

¹⁵⁶ Luxton, A. R.; Quig, A.; Delvaux, M. J.; Fetters, L. J. Star-branched polymers: 2. Linking reaction involving 2- and 4-vinyl pyridine and dienyland styryllithium chain ends. *Polymer* **1978**, 19, 1320-1324.

¹⁵⁷ Selb, J.; Gallot, Y. Graft copolymers: 3. Synthesis and characterization of poly (styrene-g-4 vinylpyridine). *Polymer* **1979**, 20, 1273-1280.

¹⁵⁸ Moffitt, M.; Khougaz, K.; Eisenberg, A. Micellization of ionic block copolymers. *Acc. Chem. Res.* **1996**, 29, 95-102.

¹⁵⁹ Spatz, J. P.; Roescher, D.; Moller, M. Gold nanoparticles in micellar poly(styrene)-b-poly(ethylene oxide) films - size and interparticle distance control in monoparticulate films. *Adv. Mater.* **1996**, 8, 337-340.

¹⁶⁰ Spatz, J. P.; Mossmer, S.; Hartermann, C.; Moller, M.; Herzog, T.; Krieger, M.; Boyen, H. G.; Ziemann, P.; Kabius, B. Ordered Deposition of Inorganic Clusters from Micellar Block Copolymer Films. *Langmuir* **2000**, 16, 407-415.

¹⁶¹ Walheim, S.; Ramstein, M.; Steiner, U. Morphologies in Ternary Polymer Blends after Spin-Coating. *Langmuir* **1999**, 15, 4828-4836.

¹⁶² Elbs, H.; Fukunaga, K.; Stadler, R.; Sauer, G.; Magerle, R.; Krausch, G. Microdomain Morphology of Thin ABC Tri-block Copolymer Films. *Macromolecules* **1999**, 32, 1204-1211.

-
- ¹⁶³ Tassin, J. F.; Siemens, R. L.; Tang, W. T.; Hadziioannou, G.; Swalen J. D.; Smith, B. A. *J. Phys. Chem.* **1989**, 93, 2106-2111.
- ¹⁶⁴ Shull, K. R. Interfacial phase transitions in block copolymer/homopolymer blends. *Macromolecules* **1993**, 26, 2346-2360.
- ¹⁶⁵ Hashimoto, T.; Tanaka, H.; Hasegawa, H. Ordered structure in mixtures of a block copolymer and homopolymers. 1. Solubilization of low molecular weight homopolymers. *Macromolecules* **1991**, 24, 240-251.
- ¹⁶⁶ Beysens, D.; Knobler, C. M. Growth of breath figures. *Phys. Rev. Lett.* **1986**, 57, 1433-1436.
- ¹⁶⁷ Kim, H. C.; Russell, T. P. Ordering in thin films of asymmetric di-block copolymers *J. Polym. Sci., Part B: Polym. Phys.* **2001**, 39, 663-668.
- ¹⁶⁸ Schwark, D.; Vezie, D.; Reffner, J.; Annis, B.; Thomas, E. *J. Mater. Sci. Lett.* **1992**, 11, 352-355.
- ¹⁶⁹ Duan, H. W.; Chen, D. Y.; Jiang, M.; Gan, W. J.; Li, S. J.; Wang, M.; Gong, J. Self-Assembly of Unlike Homopolymers into Hollow Spheres in Nonselective Solvent. *J. Am. Chem. Soc.* **2001**, 123, 12097-12098.
- ¹⁷⁰ Chen, D.Y.; Peng, H. S.; Jiang, M. A Novel One-Step Approach to Core-Stabilized Nanoparticles at High Solid Contents. *Macromolecules* **2003**, 36, 2576-2578.
- ¹⁷¹ Krämer, M.; Stumbè, J. F.; Türk, H.; Krause, S.; Komp, A.; Delineau, I.; Prokhorova, S.; Kautz, H.; Haag, R. PH-responsive molecular nanocarriers based on dendritic core-shell architectures. *Angew. Chem., Int. Ed.* **2002**, 41, 4252-4256.
- ¹⁷² (a) Bakeev, K. N.; Lysenko, E. A.; MacKnight, W. J.; Zezin, A. B.; Kabanov, V. A. Complexes of oil-soluble amphiphilic copolymers and low-molecular mass surfactants. *Colloids Surf., A: Physicochemical and Engineering Aspects* **1999**, 147, 263-270; (b) Lysenko, E. A.; Bronich, T. K.; Slonkina, E. V.; Eisenberg, A.; Kabanov, V. A. Block ionomer complexes with polystyrene core-forming block in selective solvents of various polarities. 2. Solution behavior and self-assembly in nonpolar solvents. *Macromolecules* **2002**, 35, 6344-6350.
- ¹⁷³ (16) <http://www.fki.uu.se/robert.johnsen/gendist.htm>.
- ¹⁷⁴ Gauthier, S.; Eisenberg, A. Vinylpyridinium ionomers. 2. Styrene-based ABA block copolymers. *Macromolecules* **1987**, 20, 760-767.
- ¹⁷⁵ Salamone, J. C.; Volksen, W.; Olson, A. P.; Israel, S. C. Aqueous solution properties of a poly(vinyl imidazolium sulphobetaine). *Polymer* **1978**, 19, 1157-1162.

- ¹⁷⁶ Monroy-Soto, V. M.; Galin, J. C. Poly(sulphopropylbetaines): 1. Synthesis and characterization. *Polymer* **1984**, 25, 121-128.
- ¹⁷⁷ Laschewsky, A.; Zerbe, I. Polymerizable and polymeric zwitterionic surfactants: 1. Synthesis and bulk properties. *Polymer* **1991**, 32, 2070-2080.
- ¹⁷⁸ Cardoso, J.; Manero, O.; Thermal and dilute-solution properties of zwitterionic copolymers. *J Polym Sci Part B Polym Phys* **1991**, 29, 639-647.
- ¹⁷⁹ Lowe, A. B.; McCormick, C. L. Synthesis and solution properties of zwitterionic polymers *Chem. Rev.* **2002**, 102, 4177-4189.
- ¹⁸⁰ Butun, V. Selective betainization of 2-(dimethylamino)ethyl methacrylate residues in tertiary amine methacrylate di-block copolymers and their aqueous solution properties. *Polymer* **2003**, 44, 7321-7334.
- ¹⁸¹ Dai, S.; Tam, K. C.; Jenkins, R. D. Microstructure of dilute hydrophobically modified alkali soluble emulsion in aqueous salt solution. *Macromolecules* **2000**, 33, 404-411.
- ¹⁸² Wang, X. H.; Goh, S. H.; Lu, Z. H.; Lee, S. Y.; Wu, C. Light-Scattering characterization of fullerene-containing poly(alkyl methacrylate)s in THF. *Macromolecules* **1999**, 32, 2786-2788.
- ¹⁸³ Dai, S.; Tam, K. C. Light scattering of dilute hydrophobically modified alkali-soluble emulsion solutions: effects of hydrophobicity and spacer length of macromonomer. *Macromolecules* **2000**, 33, 7021-7028.
- ¹⁸⁴ Huber, K.; Burchard, W.; Fetters, L. J. Electronic excited-state transport and trapping on polymer chains. *Macromolecules* **1984**, 17, 54-59.
- ¹⁸⁵ Burchard, W. Solution properties of branched macromolecules *Adv. Polym. Sci.* **1999**, 143, 113-194.
- ¹⁸⁶ Schmidt, M. Combined integrated and dynamic light scattering by poly(γ -benzyl glutamate) in a helocogenic solvent. *Macromolecules* **1984**, 17, 553.
- ¹⁸⁷ Muller, A.; Burchard, W. Structure formation of surfactants in concentrated sulfuric-acid – A tight scattering study. *Colloid Polym. Sci.* **1995**, 273, 866-875.
- ¹⁸⁸ Cheng, H.; Wu, C.; Winnik, M. A. Kinetics of Reversible Aggregation of Soft Polymeric Particles in Dilute Dispersion. *Macromolecules* **2004**, 37, 5127.
- ¹⁸⁹ Li, Z. B.; Kesselman, E.; Talmon, Y.; Hillmyer, M.; Lodge, T. P. Multicompartment micelles from ABC miktoarm stars in water. *Science* **2004**, 306, 98-101.
- ¹⁹⁰ Ma, Q. G.; Remsen, E. E.; Clark, C. G.; Kowalewski, T.; Wooley, K. L. Chemically induced supramolecular reorganization of tri-block copolymer assemblies: Trapping of

intermediate states via a shell-cross-linking methodology *Proc. Natl. Acad. Sci. U. S. A.* **2002**, 99, 5058-5063.

¹⁹¹ (a) Hamley, I. W. Nanostructure fabrication using block copolymers. *Nanotechnology* **2003**, 14, R39. (b) Park, C.; Yoon, J.; Thomas, E. L. Enabling nanotechnology with self assembled block copolymer patterns. *Polymer* **2003**, 44, 6725-6760.

¹⁹² Developments in Block Copolymer Science and Technology; Hamley, I. W., Ed.; Wiley: Chichester, **2004**.

¹⁹³ Park, M.; Harrison, C.; Chaikin, P. M.; Register, R. A.; Adamson, D. H. Block copolymer lithography: Periodic arrays of similar to 10(11) holes in 1 square centimeter. *Science* **1997**, 276, 1401-1404.

¹⁹⁴ Cheng, J. Y.; Mayes, A. M.; Ross, C. A. Nanostructure engineering by templated self-assembly of block copolymers. *Nature Material* **2004**, 3, 823-825.

¹⁹⁵ Fukunaga, K.; Elbs, H.; Magerle, R.; Krausch, G. Large-Scale Alignment of ABC Block Copolymer Microdomains via Solvent Vapor Treatment. *Macromolecules* **2000**, 33, 947-953.

¹⁹⁶ Elbs, H.; Drummer, C.; Abetz, V.; Krausch, G. Thin Film Morphologies of ABC Triblock Copolymers Prepared from Solution. *Macromolecules* **2002**, 35, 5570-5577.

¹⁹⁷ Morkved, T. L.; Lu, m.; Urbas, A. M.; Elrich, E. E.; Jaeger, H. M.; Mansky, P.; Russell, T. P. Local control of microdomain orientation in di-block copolymer thin films with electric fields. *Science* **1996**, 273, 931-933.

¹⁹⁸ Ruokolainen, J.; Mäkinen, R.; Torkkeli, M.; Mäkelä, T.; Serimaa, R. ten Birke, G.; Ikkala, O. Switching supramolecular polymeric materials with multiple length scales. *Science* **1998**, 280, 557-560.

¹⁹⁹ Mäki-Ontto, R.; de Moel, K.; de Odorico, W.; Ruokolainen, J.; Stamm, M.; ten Brinke, G.; Ikkala, O. "Hairy Tubes": Mesoporous Materials Containing Hollow Self-Organized Cylinders with Polymer Brushes at the Walls. *Adv. Mater.* **2001**, 13, 117-121.

²⁰⁰ Tokarev, I.; Krenek, R.; Burkov, Y.; Schmeisser, D.; Sidorenko, A.; Minko, S.; Stamm, M. Microphase Separation in Thin Films of Poly(styrene-*block*-4-vinylpyridine) Copolymer-2-(4'-Hydroxybenzeneazo)benzoic Acid Assembly. *Macromolecules* **2005**, 38, 507-516.

²⁰¹ Meriner, J. C.; Quintel-Ritzi, A.; Mlynek, J.; Elbs, H.; Krausch, G. Adsorption of Block-Copolymer Micelles from a Selective Solvent. *Macromolecules* **1997**, 30, 4945.

- ²⁰² Meiners, J. C.; Elbs, H.; Ritzi, A.; Mlynek, J.; Krausch, G. Chemically functionalized surfaces from ultrathin block-copolymer films. *Journal of Applied Physics*. **1996**, 80, 2224-2227.
- ²⁰³ Sohn, B. H.; Yoo, S. I.; Seo, B. W.; Yun, S. H.; Park S. M. Nanopatterns by free-standing monolayer films of di-block copolymer micelles with in situ core-corona inversion . *J. Am. Chem. Soc.* **2001**, 123, 12734-12375.
- ²⁰⁴ Song, L. X.; Lam, Y. M. Selective betainization of PS-P4VP and solution properties. *Langmuir* **2006**, 22, 319-324.
- ²⁰⁵ Turturro, A.; Gattiflia, E.; Vacca, P.; viola, G. T. Free surface morphology of block copolymers: 1. Styrene-butadiene di-block copolymers. *Polymer* **1995**, 36, 3987-3996.
- ²⁰⁶ Devereaux, C. A.; Baker, S. M. Surface Features in Langmuir-Blodgett Monolayers of Predominantly Hydrophobic Poly(styrene)-Poly(ethylene oxide) Di-block Copolymer. *Macromolecules* **2002**, 35, 1921-1927.
- ²⁰⁷ Lu, Q.; Bazuin, C. G. Solvent-Assisted Formation of Nanostrand Networks from Supramolecular Di-block Copolymer/Surfactant Complexes at the Air/Water Interface. *Nano Letters* **2005**, 5(7),1309-1314.
- ²⁰⁸ Seo, Y. S.; Kim, K. S.; Gallambos, A.; Lammertink, R. G. H.; vancso, G. J.; Sokolov, J.; Rafailovich, M. Nanowire and mesh conformations of di-block copolymer blends at the air/water interface. *Nano Letters* **2004**, 4, 483-486.
- ²⁰⁹ Baker, S. M.; Leach, K. A.; Devereaux, C. E.; Gragson, D. E. Controlled Patterning of Di-block Copolymers by Monolayer Langmuir-Blodgett Deposition. *Macromolecules* **2000**, 33, 5432-5436.
- ²¹⁰ Hayward, R.C.; Chmelka, B. F.; Kramer, E. J. Template cross-linking effects on morphologies of swellable block copolymer and mesostructured silica thin films. *Macromolecules* **2005**, 38 (18), 7768-7783.
- ²¹¹ Spatz, J. P.; Sheiko, S.; Möller, M. Ion-stabilized block copolymer micelles: Film formation and intermicellar interaction. *Macromolecules* **1996**, 29, 3220-3226.
- ²¹² Diebold, U. The surface science of titanium dioxide. *Surface Science Reports* **2003**, 48, 53-229.
- ²¹³ Linsebigler, A. L.; Lu, G. Q.; Yates, J. T. Photocatalysis on TiO₂ surfaces – principles, mechanisms, and selected results. *Chem. Rev.* **1995**, 95, 735-758.
- ²¹⁴ Hoffmann, M. R.; Martin, S. T. Choi, W. Y.; Bahnemann, D.W. Environmental applications of semiconductor photocatalysis. *Chem. Rev.* **1995**, 95, 69-96.

-
- ²¹⁵ Zhang, L. J.; Wan, M. X. Polyaniline/TiO₂ Composite Nanotubes. *J. Phys. Chem. B* **2003**, 107, 6748-6753.
- ²¹⁶ Steunou, N.; Forster, S.; Florian, P.; Sanchez, C.; Antonietti, M. Synthesis of nanostructured polymer-titanium oxide composites through the assembly of titanium-oxo clusters and amphiphilic block copolymers micelles. *J Mater. Chem.* **2002**, 12, 3426-3430.
- ²¹⁷ Weng, C.-C.; Hsu, K.-F.; Wei, K.-H. Synthesis of arrayed, TiO₂ needlelike nanostructures via a polystyrene-block-poly(4-vinylpyridine) di-block copolymer template. *Chem. Mater.* **2004**, 16, 4080-4086.
- ²¹⁸ Li, X.; Lau K. H. A.; Kim, D. H.; Knoll W. High-density arrays of titania nanoparticles using monolayer micellar films of di-block copolymers as templates. *Langmuir* **2005**, 21, 5212-5217.
- ²¹⁹ Bar, G.; Thomann, Y.; Whangbo, M. H. Characterization of the morphologies and nanostructures of blends of poly(styrene) block-poly(ethene-co-but-1-ene)-block-poly(styrene) with isotactic and atactic polypropylenes by tapping-mode atomic force microscopy. *Langmuir* **1998**, 14, 1219-1226.
- ²²⁰ Kim, D.H.; Jia, X.; Lin, Z.; Guarini, K.W.; Russell, T.P. Inorganic Nanodots from Thin Films of Block Copolymers. *Nano Letters* **2004**, 4, 1841-1844.
- ²²¹ Lopes, W. A.; Jaeger, H. M. Hierarchical self-assembly of metal nanostructures on diblock copolymer scaffolds. *Nature* **2001**, 735-738.
- ²²² Dynamic light scattering; Berne, B. J., Pecora, R. J., Eds.; Wiley: Toronto, **1976**.
- ²²³ Goren, M.; Lennox, R.B. Nanoscale polypyrrole patterns using block copolymer surface micelles as templates. *Nano Lett.* **2001**, 735-738.
- ²²⁴ de Jesus, M. C.; Weiss, R.A.; Hahn, S. F. Synthesis of conductive nanocomposites by selective in situ polymerization of pyrrole within the lamellar microdomains of a block copolymer. *Macromolecules* **1998**, 31, 2230-2235.
- ²²⁵ Selvan, S.T.; Spatz, J. P.; Klok, H. A. Möller, M. Gold-polypyrrole core-shell particles in di-block copolymer micelles. *Adv. Mater.* **1998**, 10, 132-134.
- ²²⁶ Chen, D. M.; Xia H. B.; Chan, H. S. O. Facile fabrication of AgCl@polypyrrole-chitosan core-shell nanoparticles and polymeric hollow nanospheres. *Langmuir*, **2004**, 29, 9909-9912.
- ²²⁷ Liu, J.-H.; Esng, S.-Q.; Chi, Y.-S.; Lin, H.-P.; Mou, C.-Y. Synergistic effect in an Au-Ag alloy nanocatalyst: CO oxidation. *J. Phys. Chem. B* **2005**, 109, 40-43.

-
- ²²⁸ Kariuki, N. N.; Luo, J.; Maye, M.M.; Hassan, S. A.; Menard, T.; Naslund, H. R.; Lin, Y.; Wang, C.; Engelhard, M. H.; Zhong, C. J. Composition-controlled synthesis of bimetallic gold-silver nanoparticles. *Langmuir* **2004**, 20, 11240-11260.
- ²²⁹ Han, L.; Maye, M. M.; Leibowitz, F. L.; Ly, N. k.; Zhong C. J. Quartz-crystal microbalance and spectrophotometric assessments of inter-core and inter-shell reactivities in nanoparticle thin film formation and growth. *J. Mater. Chem.* **2001**, 11, 1258-1264.
- ²³⁰ Han, L.; Luo, J.; Kariuki, N. N.; Maye, M. M.; Jones, V. W.; Zhong, C. J. Novel interparticle spatial properties of hydrogen-bonding mediated nanoparticle assembly. *Chem. Mater.* **2003**, 15, 29-37.
- ²³¹ Castner, D. G.; Hinds, K.; Grainger, D.W. X-ray photoelectron spectroscopy sulfur 2p study of organic thiol and disulfide binding interactions with gold surfaces. *Langmuir* **1996**, 12, 5083-5086.