MORPHOLOGICAL CONTROL IN CONJUGATED POLYMERS: SYNTHESIS AND APPLICATIONS OF POLYMER MICROSPHERES

by

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Abstract

The synthesis, characterization, and application of conjugated polymer colloidal microspheres are reported. Monodisperse mesoporous silica spheres were utilized as hard templates for the preparation of poly(3,4-ethylenedioxythiophene) (PEDOT)–silica composites, which could in turn be etched with hydrofluoric acid to yield monodisperse conjugated polymer microparticles. The synthetic procedure was generalized to include other polymers such as polythiophene and poly(N-methylpyrrole). The colloidal and electronic properties of these composites were subsequently studied, and it was found that a balance between colloidal stability and electrical conductivity could be achieved when the mesopores of the silica template were partially filled with polymer. These insights enabled the successful self-assembly of an opaline film of the PEDOT–silica composite. Bragg diffraction of visible light by the lattice planes of the opal was then demonstrated.

The silica host was subsequently explored for its ability to control the phase separation of polymer blends. It was found that depending on the order of polymer addition, phase separation could be suppressed. This resulted in an intimate mixture of the two constituent polymers, and has potential impact in the field of photovoltaics. The colloidal microspheres were also examined for their utility as electrode materials in supercapacitors. The PEDOT microspheres were found to have a mass specific capacitance higher than that of typical electropolymerized PEDOT films, indicating that the morphological control was translated into an improvement in device performance.

An ion exchange and in situ polymerization approach was developed in order to incorporate poly(p-phenylenevinylene) into the mesoporous silica template. This yielded a luminescent colloidal material that displayed enhanced optical properties relative to the unencapsulated
polymer. This is again due to the morphological constraints imposed on the polymer by the mesoporous template; polymer chains are isolated from each other, thus shutting down access to non-radiative decay pathways.

Other template approaches were explored as a way of producing conjugated polymer microspheres. Sodium dodecyl sulfate micelles were utilized as soft templates for the synthesis of carbohydrate-functionalized poly(p-phenyleneethynylene) particles. These microparticles were examined for their protein-binding ability, and were found to extract the common lectin concanavalin A from solution.
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# List of Symbols and Abbreviations

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<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>1-D</td>
<td>one-dimensional</td>
</tr>
<tr>
<td>2-D</td>
<td>two-dimensional</td>
</tr>
<tr>
<td>3-D</td>
<td>three-dimensional</td>
</tr>
<tr>
<td>δ</td>
<td>chemical shift</td>
</tr>
<tr>
<td>ΔV/Δt</td>
<td>scan rate</td>
</tr>
<tr>
<td>ε</td>
<td>electric permittivity</td>
</tr>
<tr>
<td>ζ</td>
<td>zeta potential</td>
</tr>
<tr>
<td>η</td>
<td>viscosity</td>
</tr>
<tr>
<td>θ</td>
<td>angle of incidence</td>
</tr>
<tr>
<td>κ</td>
<td>Debye-Hückel parameter</td>
</tr>
<tr>
<td>λ</td>
<td>wavelength</td>
</tr>
<tr>
<td>μ</td>
<td>electrophoretic mobility</td>
</tr>
<tr>
<td>ρ</td>
<td>resistivity</td>
</tr>
<tr>
<td>σ</td>
<td>conductivity</td>
</tr>
<tr>
<td>τ_f</td>
<td>fluorescence lifetime</td>
</tr>
<tr>
<td>Φ_f</td>
<td>fluorescence quantum yield</td>
</tr>
<tr>
<td>A</td>
<td>pre-exponential fitting factor</td>
</tr>
</tbody>
</table>
$a$ exponential fitting factor

ADIMET acyclic diyne metathesis

$B$ pre-exponential fitting factor

$b$ exponential fitting factor

bipy $2,2'$-bipyridine

ca. *circa* (approximately)

CB conduction band

$C_M$ mass specific capacitance

CN-MBE 1-cyano-*trans*-1,2-bis-(4'-methylbiphenyl)-ethylene

ConA concanavalin A

ConA–TR concanavalin A, Texas Red conjugate

CV cyclic voltammetry/voltammogram

d doublet

d $d$ particle diameter

dd doublet of doublets

DLVO Derjaguin-Landau-Verwey-Overbeek

dppp 1,3-bis(diphenylphosphino)propane

DSS 4,4-dimethyl-4-silapentane-1-sulfonic acid

EDOT 3,4-ethylenedioxythiophene
EDX: energy dispersive X-ray microanalysis

$E_g$: electronic bandgap

ESI: electrospray ionization

fcc: face centered cubic

FE-SEM: field emission scanning electron microscopy/microscope

FRET: Förster resonance energy transfer

FT-IR: Fourier transform infrared

$h$: hour(s)

HH: head-to-head

HOMO: highest occupied molecular orbital

HT: head-to-tail

$i$: current

IEP: isoelectric point

$J$: NMR coupling constant

LDA: lithium diisopropylamide

LSCM: laser scanning confocal microscopy

LUMO: lowest unoccupied molecular orbital

$M$: molarity

$m$: multiplet
m_e  electrode mass
m/z  mass-to-charge ratio
MAS  magic angle spinning
MCS  microporous carbon spheres
MEH-PPV  poly(2-methoxy-5-(2'-ethylhexyloxy)-p-phenylenevinylene
Me-LPPP  methyl-substituted ladder-type poly(p-phenylene)
min  minute(s)
MSS  mesoporous silica spheres
MSS_{xxx}  mesoporous silica spheres, of average diameter xxx nm
n  pore filling percentage
n_{eff}  effective refractive index
N/A  not applicable
N/D  not detectable
NIR  near-infrared
NMP  N-methyl-2-pyrrolidone
NMR  nuclear magnetic resonance
(O)LED  (organic) light emitting diode
p  para
P3DDUT  poly(3-(2-(N-dodecylcarbamoyloxy)ethyl)thiophene-2,5-diyl)
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI</td>
<td>polyaniline</td>
</tr>
<tr>
<td>PANI-PSA</td>
<td>polyaniline – phenol sulfonate</td>
</tr>
<tr>
<td>PAT</td>
<td>poly(3-alkylthiophene)</td>
</tr>
<tr>
<td>PBI</td>
<td>polybenzimidazole</td>
</tr>
<tr>
<td>PCBDM</td>
<td>[6,6]-phenyl-C_{61}-butyric acid methyl ester</td>
</tr>
<tr>
<td>PEDOT</td>
<td>poly(3,4-ethylenedioxythiophene)</td>
</tr>
<tr>
<td>PFA</td>
<td>poly(furfuryl alcohol)</td>
</tr>
<tr>
<td>PFO</td>
<td>poly(9,9-dihexylfluorenyle-2,7-diyl)</td>
</tr>
<tr>
<td>PFPV</td>
<td>poly((9,9-dioctyl-2,7-divinylene-fluorenylene)-alt-co-(2-methoxy-5-(2′-ethylhexyloxy)-p-phenylene))</td>
</tr>
<tr>
<td>PMePy</td>
<td>poly((N)-methylpyrrole)</td>
</tr>
<tr>
<td>PMMA</td>
<td>poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PPE</td>
<td>poly((p)-phenyleneethynylene)</td>
</tr>
<tr>
<td>pPPV</td>
<td>poly((p)-phenylenevinylene), precursor polymer</td>
</tr>
<tr>
<td>PPV</td>
<td>poly((p)-phenylenevinylene)</td>
</tr>
<tr>
<td>PPy</td>
<td>polypyrrole</td>
</tr>
<tr>
<td>PS-PVP</td>
<td>polystyrene-\textit{co}-poly(2-vinylpyridine)</td>
</tr>
<tr>
<td>PSS</td>
<td>poly(styrene sulfonate)</td>
</tr>
<tr>
<td>PT</td>
<td>polythiophene</td>
</tr>
</tbody>
</table>
PTA  poly(1,3-bis-(2-(3-alkylthienyl))azulene)
PVDF  poly(vinylidene fluoride)
PVP  poly(N-vinylpyrrolidone)
$Q^2$  Si(O–Si)$_2$(OH)$_2$$^{29}$Si NMR resonance
$Q^3$  Si(O–Si)$_3$(OH)$_1$$^{29}$Si NMR resonance
$Q^4$  Si(O–Si)$_4$$^{29}$Si NMR resonance
$R$  resistance
$r$  particle radius
$s$  singlet
SDS  sodium dodecyl sulfate
STEM  scanning transmission electron microscopy/microscope
t  triplet
TEM  transmission electron microscopy/microscope
TEMPO  2,2,6,6-tetramethylpiperidine-1-oxyl
TGA  thermogravimetric analysis
THF  tetrahydrofuran
TMS  tetramethylsilane
TT  tail-to-tail
UV-vis-NIR  ultraviolet-visible-near-infrared
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>v/v</td>
<td>volume-by-volume</td>
</tr>
<tr>
<td>$V_{\text{acc}}$</td>
<td>accelerating voltage</td>
</tr>
<tr>
<td>VB</td>
<td>valence band</td>
</tr>
<tr>
<td>w/w</td>
<td>weight-by-weight</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>Z</td>
<td>atomic number</td>
</tr>
</tbody>
</table>
Acknowledgments

There are a number of people without whom this thesis would not have been possible. Firstly, I would like to thank my research supervisor, Prof. Michael Wolf, for his invaluable support, encouragement, and career advice. I am extremely appreciative of all the members of the Wolf group, both past and present, for their company and camaraderie during the highs and lows of my time in the lab. In particular, I’d like to thank Tracey Stott and Carolyn Moorlag for showing me the ropes; Agostino Pietrangelo for his expertise and experience, both in the lab and at the pub; and Matt Roberts for his steady humour, even when climbing trips go awry. It was also my privilege to supervise three excellent undergraduate students, Michael Lam, Christian Reuter, and Sara Che.

This thesis has been influenced by any number of collaborators, technical personnel, and support staff. Special thanks are owed to Toyota Central R & D Labs, Inc., Dr. Kazuhisa Yano, and Yuri Yamada for both funding and assistance with many projects. Garnet Martens, Derrick Horne and Brad Ross at the UBC Bioimaging Facility, and Mary Fletcher of Metals and Materials Engineering have taught me everything I know about electron microscopy, and have been a genuine pleasure to work with. Dr. Saeid Kamal of the LASIR facility offered endless advice and assistance on anything related to photonics. I also thank the technicians and staff of all the UBC Chemistry Department shops and services, who provided invaluable support for my experiments. I am thankful for funding from both NSERC and UBC.

I am deeply grateful to my parents, Ian and Donna, for twenty six years of love, support and guidance. I have always appreciated the freedom you gave me to find my own way. Finally, I am, and will always be, grateful to Amy for letting me pass her notes in class; the things I learned that day had nothing to do with polymers or polarons.
Dedication

for Amy, the most important thing I learned about in school.
Co-Authorship Statement

Chapters 2 – 6 involved collaboration with the research group of Dr. Kazuhisa Yano at Toyota Central R & D Labs, Inc., in Nagakute, Japan. In all chapters Prof. Michael O. Wolf acted in a supervisory role.

Versions of Chapters 2 and 3 have been published previously. I am the principal author of these works and carried out all experiments except where noted. The MSS templates were prepared and the nitrogen adsorption isotherms acquired by Yuri Yamada and Dr. Kazuhisa Yano at Toyota Central R & D Labs, Inc. The PEDOT@MSS$_{550}$, PT-$n$@MSS, and PMePy-$n$@MSS composites were synthesized by an undergraduate student (Sara Che) while under my supervision.

A version of Chapter 4 has been published previously. I am the principal author of this work and carried out all experiments except where noted. The MSS templates were prepared and the nitrogen adsorption isotherms acquired by Dr. Kazuhisa Yano at Toyota Central R & D Labs, Inc. The XPS spectra were acquired by Dr. Ken Wong at the Interfacial Analysis & Reactivity Laboratory at UBC.

A version of Chapter 5 will be submitted for publication. I am the principal author of this work and carried out all experiments except where noted. The MSS templates were prepared and the nitrogen adsorption isotherms acquired by Dr. Kazuhisa Yano at Toyota Central R & D Labs, Inc.

A version of Chapter 6 has been submitted for publication. I am the principal author of this work and carried out all experiments except where noted. The MSS templates were prepared and the nitrogen adsorption isotherms acquired by Yuri Yamada and Dr. Kazuhisa Yano at Toyota Central R & D Labs, Inc.
Central R & D Labs, Inc. The MAS-NMR spectra were acquired by Dr. Celine Schneider at Memorial University.

A version of Chapter 7 has been published previously. I am the principal author of this work and carried out all experiments except where noted. The three compounds β-Glc(OAc)$_4$-M, β-Glc(OAc)$_4$-PPE, and β-Glc-PPE were prepared by an undergraduate student (Michael Lam) while under my supervision. ESI mass spectra were acquired by staff at the UBC chemistry mass spectrometry facility.
CHAPTER 1

INTRODUCTION

1.1 OVERVIEW

The manipulation of matter into useful forms and shapes has been one of the defining goals of humanity for millennia. As technology and scientific knowledge advanced through the period of the industrial revolution, tools and components were machined on ever smaller length scales. Concomitantly, the burgeoning discipline of chemistry gave rise to the ability to control the transformation of matter at the molecular level.\(^1\) Both of these abilities were extensively developed during the 20\(^{th}\) century. Photolithographic techniques enabled the fabrication of sub-micron devices from bulk material,\(^2\) while the field of macromolecular science gave rise to the ability to synthesize extremely large molecules such as polymers.\(^3\) These two methodologies have come to be known as the “top-down” and “bottom-up” approaches to the fabrication of micro- and nanostructures. They are extensively exploited in the growing field of electronic device fabrication.

This thesis straddles the boundary between the two approaches. It deals with the control of shape and structure in \(\pi\)-conjugated polymers at the \(10^0 - 10^6\) nm length scale; as such, both physical and chemical methods of morphological control are employed. This chapter aims to develop the concepts, theory, and techniques used in the discipline of colloid science, as well as applications thereof. An introduction to the important electronic properties of \(\pi\)-conjugated polymers will be given. Finally, literature pertinent to the morphological control of conjugated polymers, especially that at the interface of colloid, polymer, and materials science, will be reviewed.
1.2 COLLOIDS

1.2.1 Definition

In the 19\textsuperscript{th} century, Thomas Graham divided matter into two categories: crystalloids, substances that dissolve in solvent to form homogeneous solutions, and colloids, which form heterogeneous dispersions. Since then, the definition of a colloid has been refined; the modern definition of a colloid is a multi-phase system whereby a discrete, or dispersed, phase is suspended in a continuous matrix (the dispersant).\textsuperscript{4} Practically, the dispersed phase is defined as having at least one dimension in the size range of 1 nm – 1 µm,\textsuperscript{5} although assigning an upper limit to the size regime can be done only tentatively at best. For reference, the typical sizes of a number of colloidal and non-colloidal materials are shown in Figure 1-1.\textsuperscript{6}

\begin{figure}[h]
\centering
\includegraphics[width=0.6\textwidth]{colloidal_size_regime.png}
\caption{Typical sizes of a number of colloidal and non-colloidal materials. Adapted from reference 6.}
\end{figure}

Colloids can be broken down into classifications based on the phases of the discrete and continuous media. Sols are fluid colloidal systems, such as solid-in-liquid, liquid-in-liquid, or
liquid-in-gas dispersions. Emulsions, aerosols, and latexes are particular types of sols. Emulsions are liquid-in-liquid mixtures of two immiscible phases, such as milk (an oil-in-water emulsion). Aerosols are either solid-in-gas or liquid-in-gas dispersions, such as smoke, mist, or fog. Latexes are sols in which the individual colloidal particle is composed of multiple macromolecules. While a number of other colloidal classifications are possible (e.g., foams, which are gas-in-liquid dispersions) the only examples discussed further in this thesis will be solid-in-liquid colloids such as inorganic sols and polymer latexes. Some examples of colloidal systems are tabulated in Table 1-1.  

<table>
<thead>
<tr>
<th>Examples</th>
<th>Class</th>
<th>Dispersed Phase</th>
<th>Continuous Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fog, mist</td>
<td>Liquid Aerosols</td>
<td>Liquid</td>
<td>Gas</td>
</tr>
<tr>
<td>Smoke</td>
<td>Solid Aerosols</td>
<td>Solid</td>
<td>Gas</td>
</tr>
<tr>
<td>Milk, butter, mayonnaise</td>
<td>Emulsions</td>
<td>Liquid</td>
<td>Liquid</td>
</tr>
<tr>
<td>Gold nanoparticles, metal hydroxides, colloidal silica, colloidal sulfur, etc.</td>
<td>Sols</td>
<td>Solid</td>
<td>Liquid</td>
</tr>
<tr>
<td>Froth, foam</td>
<td>Foam</td>
<td>Gas</td>
<td>Liquid</td>
</tr>
<tr>
<td>Expanded plastics</td>
<td>Solid Foam</td>
<td>Gas</td>
<td>Solid</td>
</tr>
</tbody>
</table>

1.2.2 Synthesis

Broadly speaking, the synthesis of colloidal systems such as sols and latexes can be classified into dispersion and condensation methods. The first approach involves fragmentation of bulk material into ever finer particulate; eventually the size of this particulate reaches the colloidal
regime. In the second approach, molecular starting materials are added together (either by physical aggregation or a chemical reaction) to form colloidal particles.

Typical physical methods of dispersing bulk material into colloidal particles are crushing in a mortar and pestle or grinding in a ball mill.\textsuperscript{6} These methods will produce particles with diameters in the range of 1 – 5 $\mu$m, which is at the extreme upper limit of the colloidal size regime. Additionally, these techniques offer little in the way of control over the particle morphology or size; a variety of particle shapes and sizes are produced. While smaller particles can be produced by the addition of a low surface tension liquid or surfactant to the grinding medium, these wet-milling techniques still typically produce particulate with a lower size limit of 0.1 $\mu$m. While some exceptions to this rule do exist,\textsuperscript{8} the technique will not be discussed further.

In the preparation of colloidal systems, condensation methods offer the most control over the size and shape of the colloidal particles. Typically, a chemical reaction or supersaturated solution is used to produce an insoluble precipitate. If nucleation occurs in a single, rapid burst, then particle growth occurs only on the surfaces of the initial nuclei and the colloid will be monodisperse; otherwise, nucleation occurs throughout the course of the reaction and the particles will be of various diameters.\textsuperscript{9,10} A suitable surface stabilizer must also typically be used in order to prevent coagulation. This allows the particles to remain within the colloidal size regime rather than forming bulk material. Three examples of common condensation methods for producing colloids are discussed below: the Brust–Schiffrin method of synthesizing gold nanoparticles,\textsuperscript{11,12} the Stöber–Fink–Bohn method of preparing monodisperse silica spheres,\textsuperscript{13} and the emulsion polymerization technique for producing polystyrene and polyacrylate latexes.
The Brust–Schiffrin synthesis of gold nanoparticles\textsuperscript{11, 12} is an excellent example of a condensation approach to colloidal particles. Aqueous sodium borohydride is added to a two-phase mixture of tetrachloroaurate, tetroctylammonium bromide, and dodecanethiol in toluene and water. The tetroctylammonium bromide acts as a phase-transfer catalyst, drawing the tetrachloroaurate into the organic layer. There it is reduced to gold(0) by the sodium borohydride. The gold(0) thus formed is insoluble, and begins to form small nuclei. These are then capped by the dodecanethiol, which prevents further agglomeration of the gold nanoparticles. This illustrates two important components of condensation syntheses, namely the sudden nucleation of an insoluble precipitate due to a chemical reaction, and the use of a surfactant or capping group to prevent particle coalescence.

This same trend is also demonstrated in the Stöber–Fink–Bohn synthesis of monodisperse silica spheres.\textsuperscript{13} In this case, a silicon precursor (such as tetramethyorthosilicate, tetraethylorthosilicate, or tetra(\textit{n}-butyl)orthosilicate) is hydrolyzed in the presence of ammonia. The hydrolysis is followed by condensation to form Si–O–Si bridged dimers; the hydrolysis and condensation process continues until the silicon alkoxide starting material is fully depleted and silica formation is complete. The ammonia serves both to catalyze the hydrolysis of the silicon precursors and to direct the spherical morphology of the resultant nanoparticles. The diameter of the silica spheres produced by this process can be tailored by careful control over the amount of water, alcohol, silicon alkoxide, and ammonia added to the reaction mixture.

Emulsion polymerization is an extremely versatile technique in polymer chemistry for the production of monodisperse polymer latexes.\textsuperscript{14-17} It is commonly used in the polymerization of acrylates, styrene, vinyl chloride, and many other monomers. The reaction medium consists of a continuous aqueous phase to which a suitable surfactant (such as sodium dodecyl sulfate (SDS), which has a negatively charged hydrophilic head and a long, hydrophobic tail) and monomer are
added. The surfactant forms hydrophobic micelles, which are swollen by a small amount of monomer. The residual monomer resides in micrometer size droplets throughout the mixture. A water soluble initiator (such as sodium persulfate) is added to the mixture, and the radical initiator diffuses into the micelles, where polymerization begins. As the monomer concentration in the micelles drops, it is replenished by diffusion from the monomer droplets; this continues until the monomer has been depleted. The process is schematically illustrated in Figure 1-2. Importantly, because the polymerization occurs only within the interior of the micelles, the particles produced are both highly spherical and extremely monodisperse.

![Schematic of the emulsion polymerization process](image)

**Figure 1-2.** Schematic of the emulsion polymerization process, showing diffusion of the initiator (SO$_4$–$^\cdot$) into the hydrophobic micelles, replenishment of monomer inside the micelles by diffusion, and the eventual production of polymer particles.

1.2.3 **Properties**

Due to the extremely small size of colloidal particles, they possess a very high surface area to volume ratio; thus, interfacial properties begin to dominate the properties of colloidal
dispersions. Two of the most important of these are van der Waals interactions and electrostatic attraction or repulsion. As will be shown briefly here, it is the combination of these attractive and repulsive forces that dictate whether a colloidal material will remain stable in solution, loosely aggregate, or coalesce into bulk material.\textsuperscript{4, 6}

As colloidal particles undergo Brownian motion in solution, occasionally two particles will collide. If there is nothing to prevent the two surfaces from making intimate contact, attractive van der Waals forces will cause the two particles to associate. If this aggregation process results in permanent fusion of the two particles, it is known as coagulation; otherwise, the reversible aggregation process is known as flocculation. In order to prevent excessive aggregation and subsequent sedimentation of the colloidal material, the two particles must be kept from coming into close contact. This can be accomplished by one of two means: electrostatic or steric stabilization.

Since the early days of colloid science, it has been known that colloidal particles in solution tend to accumulate charge on their surface; thus, the presence of an applied electric field causes the particles to undergo migration. The molecular phenomena responsible for this electrical charge are varied, but include acid-base equilibria, ion dissociation, crystal lattice defects, and surfactant adsorption, among others.\textsuperscript{6, 18} Two examples are shown in Scheme 1-1. In Scheme 1-1a, the material possesses sulfonic acid groups; these will dissociate in aqueous solution, leaving behind a negatively charged surface. In Scheme 1-1b, a colloidal particle of silver iodide is placed in aqueous solution. The iodide is preferentially solubilised by the solvent, leaving behind an excess of positive charge on the surface of the colloidal particle. Due to these effects, individual colloidal particles are charged, and the charges of the individual particles are necessarily the same sign. This creates an electrostatic barrier to particle-particle contact and reduces the rate of particle aggregation.
The charging of the colloidal surface creates an electrical double layer at the particle surface, as described by Guoy and Chapman in the early part of the 20th century.\textsuperscript{6, 18, 19} The model was subsequently modified by Stern to include the effects of finite ion size.\textsuperscript{20} Under this model, the layer of counter-ions immediately adjacent to the particle surface is considered fixed and immobile (the Stern layer). When the particle migrates in the presence of an applied electric field, the ions within the shear plane of the particle (located just beyond the Stern layer) move with the particle, while ions outside of the shear plane move independently. The electrostatic potential at this no-slip boundary is referred to as the electrokinetic, or zeta potential ($\zeta$, Figure 1-3). It is this potential that can be experimentally determined through electrophoretic experiments and that is most relevant in determining the stability of a colloidal dispersion.
Figure 1-3. (a) The electric potential due to the surface of a charged colloidal particle. The dashed line denotes the shear plane, and the potential at the shear plane is defined as the zeta potential (ζ). (b) A model of the electrical double layer adjacent to a charged surface, showing the Stern and shear planes.

If the attractive van der Waals and repulsive electrostatic forces are the dominant factors in a colloidal system (which is often the case), the stability of a colloidal dispersion will be governed by DLVO theory. This theory was independently developed by Derjaguin and Landau, Verwey and Overbeek. Due to differences in how the two different interactions scale with interparticle distance, at short distances the attractive forces will dominate, at intermediate distances the electrostatic forces may dominate the interaction, while at long distances both forces decay to zero. This is illustrated in Figure 1-4. The van der Waals forces create a potential well that leads to particle flocculation, whereas the electrostatic forces create a kinetic barrier that acts to slow the rate of aggregation. Therefore, in order to create a stable colloidal dispersion the surfaces of the colloidal particles must be highly charged in order to create an effective electrostatic barrier to flocculation.
One other method of stabilizing a colloidal dispersion is known as steric stabilization, and it is not accounted for by DLVO theory. Polymer chains are attached to the surface of the colloidal particle either through chemical grafting or adsorption, as shown in Figure 1-5. The steric interactions between the polymer chains on adjacent particles prevent the colloidal particles from coming into close enough contact for flocculation to occur. Importantly, the polymer must be well solvated by the solvent; otherwise the polymer chains will lie flat on the particle surface and provide no steric barrier to flocculation. Additionally, this provides a method for the precipitation of sterically-stabilized colloids. A non-solvent for the polymer stabilizer is added to solution, which causes desolvation of the stabilizer and leads to flocculation and sedimentation.

**Figure 1-4.** Total interaction energy obtained using DLVO theory for particles with a large, moderate, and zero zeta potential.
1.2.4 Photonic Crystals and Opals

While colloids have a number of extremely important technological applications in the areas of paint and ink formulation, drug delivery, cosmetics, and electronics, one of the emerging applications of colloidal materials is in the fabrication of photonic crystals. Photonic crystals are dielectric materials that possess periodically modulated refractive indices that vary on the length scale of visible light. In a manner analogous to electronic semiconductors, this periodicity gives rise to a range of wavelengths for which propagation within the crystal is forbidden; this wavelength range is known as the photonic bandgap (Figure 1-6). Light with wavelengths within the photonic bandgap that is incident upon the photonic crystal will be diffracted from the surface rather than transmitted through the material.
Opals are naturally occurring examples of photonic crystals, and are composed of highly ordered arrays of silica microspheres. Typically, the spheres adopt a face centered cubic (fcc) structure; it is Bragg diffraction from the lattice planes of the crystal that gives rise to the brilliant iridescent colouration of the gemstone. Synthetically, opals can be made by the self-assembly of monodisperse, spherical, colloidal particles, such as Stöber silica or polymer latexes. A variety of methods have been developed to carry out this self-assembly process, however, the end result is typically either a monolithic opal fragment or an opaline thin film. Field emission scanning electron microscopy (FE-SEM) was used to image the surface of an opaline thin film produced in this way (Figure 1-7a).
Figure 1-7. (a) FE-SEM micrograph of the (111) face of an fcc silica opal, showing crystalline domains (white arrow), stacking faults (black arrow), and disordered defects (black arrow with white dot). $V_{\text{acc}} = 3.0$ kV; (b) Fourier transform of (a), showing both the hexagonal periodicity and the polycrystalline nature of the film in (a).

The novel optical properties of photonic crystals have been utilized effectively in a number of applications. Due to the inhibition of spontaneous emission within the photonic bandgap, photonic crystals have been exploited as a laser gain medium. A luminescent material such as a small molecule organic fluorophore, luminescent polymer, or inorganic quantum dot is incorporated into a photonic crystal such that the emission band of the fluorophore overlaps with the photonic bandgap. This has been shown to lead to extremely low threshold lasing. By engineering defects into photonic crystal architectures, the flow of light can be precisely directed; since propagation through the crystal is forbidden, propagation necessarily occurs through the defect. This phenomenon has been used in the preparation of low-loss waveguides and interferometers. By incorporating magnetic materials such as yttrium iron garnet into opal structures, enhanced nonlinear magneto-optical Kerr effects are observed at the edges of the photonic bandgap. This is due to the coupling of the magnetic and optical properties of these
magneto-photonic crystals. The synthesis of opals and photonic crystals composed of new, functional materials can therefore be expected to yield a variety of new optical properties.

1.3 CONJUGATED POLYMERS

1.3.1 \( \pi \)-Conjugation and Band Structure

The discovery of the metallic character of doped polyacetylene\(^{50}\) ushered in an era of research into the synthesis, properties, and applications of \( \pi \)-conjugated polymers. This led to the award of a Nobel prize in 2001 to Shirakawa, MacDiarmid and Heeger for “the discovery and development of conductive polymers”.\(^{51}\) The properties of these materials can best be understood by considering the simplest possible case, that of polyacetylene (Figure 1-8). In polyacetylene and its oligomers, each carbon atom contributes one \( p_z \) orbital to the \( \pi \)-electron system. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of polyacetylene oligomers are \( \pi \) and \( \pi^* \) orbitals, respectively. With an increasing number of repeat units, the number of \( \pi \) orbitals increases accordingly, and the HOMO-LUMO gap is reduced. Since each \( -(CH) \)- repeat unit contributes one \( \pi \) electron, the \( \pi \) orbitals are completely filled, and the \( \pi^* \) orbitals are completely empty. In the extreme limit of polyacetylene, the orbitals are so closely spaced that the system is best described by a band diagram; due to the mixture of occupied \( \pi \) and unoccupied \( \pi^* \) orbitals, the band is half occupied. However, due to the degenerate electronic ground state of polyacetylene, the polymer undergoes a structural distortion (Peierls distortion) in order to lift the degeneracy. The Peierls distortion is manifested as an alternation of localized single and double bonds along the length of the polymer chain. This leads to a separation of the filled and empty bands, and a band structure similar to that of conventional inorganic semiconductors such as silicon. The filled \( \pi \) orbitals overlap to form a filled valence band (VB), while the empty \( \pi^* \) orbitals overlap to form an empty
conduction band (CB). Between the two bands the density of states is zero, and if the bandgap ($E_g$) is small (as is the case for polyacetylene, and for conjugated polymers in general), then the polymer can be expected to behave as an organic semiconductor.

![Diagram of HOMO and LUMO progression into band structure](image)

**Figure 1-8.** Progression of the HOMO and LUMO of polyacetylene oligomers into the band structure of polyacetylene with increasing number of repeat units. The valence band (VB) and conduction band (CB) become split with the lifting of the ground state degeneracy by the Peierls distortion.

Since the discovery of the semiconducting behavior of polyacetylene, a number of other $\pi$-conjugated, semiconducting polymers have been prepared. Several examples of these are shown in Chart 1-1. The electronic structure of each of these polymers can be described using semiconductor band theory, similar to that shown in Figure 1-8. Of the polymers shown in Chart 1-1, polythiophene (PT), poly($p$-phenylenevinylene) (PPV), and poly($p$-phenyleneethynylene) (PPE) have the most relevance to this thesis and will be discussed in more detail; the interested reader can obtain more information regarding other conjugated polymers in *The Handbook of Conducting Polymers* and references therein.
The band structure shown in Figure 1-8 predicts that conjugated polymers should display semiconducting behavior; it does not explain the observation that the exposure of polyacetylene to halogens results in a metallic material. While the charge carriers in doped polyacetylene have been shown to consist of charged solitons, the charge carriers for polymers with non-degenerate ground states (such as polythiophene) are typically polarons or bipolarons (Figure 1-9). A one-electron oxidation of the polymer results in the formation of an inter-band state near the valence and conduction bands; the state just above the VB in energy is populated by a single electron. A second oxidation leaves this inter-band state empty. Importantly, thermal population of the lower inter-band state from the valence band is possible; this leads to a partially filled valence band and the observed metallic behavior. These two charge carriers are referred to as polarons and bipolarons, respectively. Oxidation to form these charge carriers is known as p-doping, in analogy with conventional inorganic semiconductors.
Figure 1-9. Oxidation of polythiophene by halogens to form polaron or bipolaron charge carriers, as illustrated by short segments of polythiophene.

Polythiophenes are a broad class of conjugated polymers that have been extensively exploited for their high stability and excellent electronic properties.\textsuperscript{53} The properties of polythiophenes are extremely sensitive to subtle changes in the polymer structure. While the polythiophene shown in Chart 1-1 consists of thiophene rings connected by $\alpha,\alpha'$-linkages, $\alpha,\beta'$ and $\beta,\beta'$-linkages are also possible (Figure 1-10). The $\alpha,\alpha'$-connected polythiophenes typically have more planar conformations, leading to enhanced $\pi$-orbital overlap and extended conjugation. This in turn leads to enhanced electronic properties (e.g., conductivity).\textsuperscript{53}

Figure 1-10. The $\alpha$ and $\beta$ positions of thiophene and the three regioisomers of bithiophene.

Despite its promising electronic properties, unsubstituted polythiophene has proved to be a particularly troublesome material to prepare and process. Polythiophene of molecular weight greater than 3000 is not soluble in hot chloroform,\textsuperscript{54} and it is the inherent insolubility of the
polymer backbone that led to the development of poly(3-alkylthiophene)s (PATs). The addition of solubilising functional groups such as hexyl chains led to materials that could be processed from solution using techniques such as drop casting or spin coating. The functionalization of the β position of the thiophene ring adds an additional complication to the polymer; different regioisomers are possible, depending on how the substituents on adjacent thiophene rings are situated with respect to one another (Figure 1-11). Extensive work has shown that regioregular head-to-tail (HT) poly(3-alkylthiophene)s have dramatically improved properties compared to non-regioregular analogues. This is due to the steric hindrance caused by the alkyl chains on adjacent thiophene rings in the head-to-head linkages; it forces the thiophene rings to adopt a non-planar conformation, and destroys the π-orbital overlap necessary for extensive π-conjugation to occur. The regioregular HT-PATs possess a low energy planar conformation, and therefore exhibit smaller bandgaps and improved conductivities.

![Figure 1-11. Regioisomers of poly(3-alkylthiophenes): head-to-tail (HT), head-to-head (HH), and tail-to-tail (TT) couplings.](image)

Two related types of conjugated polymers are poly(p-phenylenevinylene) and poly(p-phenyleneethynylene). While polythiophenes are best known for their high conductivity when p-doped, these two polymers have been much studied for their photoluminescent and electroluminescent properties. It is possible to p-dope PPV and PPE; however, the doped materials are unstable and prone to decomposition. Despite this, the bright luminescence observed in both polymers has led to the extensive use of PPVs in organic light emitting diodes.
Due to the rigid rod-like structure of both polymers, unsubstituted PPV and PPE are extremely insoluble and intractable materials. Extensive research has gone into the synthesis of soluble versions of the polymers; prototypical examples of soluble PPVs and PPEs are shown in Chart 1-2. The installation of long alkoxy chains on PPV to form poly(2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylenevinylene) (MEH-PPV) provided a material that could be dissolved in common organic solvents and both processed and characterized by standard techniques such as spin coating and gel permeation chromatography. Similarly, Giesa and Schultz added long alkoxy chains to the PPE backbone to provide a material that is amenable to solution processing techniques.

![Chart 1-2](image)

### 1.3.2 Synthesis of Conjugated Polymers

A number of well-developed synthetic procedures exist for the preparation of polythiophene and its derivatives, although they differ in terms of the molecular weight, polydispersity, and regioregularity produced. While a comprehensive review of the synthesis of polythiophenes is beyond the scope of this chapter and can be found in the *Handbook of Oligo- and
Polythiophenes, three key examples will be presented: metal-catalyzed cross-couplings, such as the Kumada coupling; chemical oxidation using iron (III) chloride; and, electrochemical polymerization.

One of the first reported procedures for the polymerization of thiophene was based on the Kumada coupling of Grignard reagents with aryl halides. Yamamoto et al. added a stoichiometric amount of metallic magnesium to 2,5-dibromothiophene in order to form 2-bromo-5-magnesiobromothiophene; addition of a (2,2’-bipyridine)dichloronickel(II) catalyst (Ni(bipy)Cl$_2$) then initiated the metal-catalyzed self-condensation, producing polymer (Scheme 1-2). Lin and Dudek published a similar route to unsubstituted polythiophene in the same year. Due to the insolubility of the growing polymer chain in THF, this synthetic route was only capable of producing low molecular weight polymer. Despite a number of improvements to these initial procedures, the most significant advancement was made by McCullough and coworkers (Scheme 1-2). The addition of an alkyl chain (e.g., hexyl) ensures good solubility of the growing polymer chain so that high molecular weight polymer can be obtained. The sequential addition of lithium diisopropylamide (LDA) and magnesium bromide specifically produces the 2-bromo-3-alkyl-5-(bromomagnesio)thiophene regioisomer; this can then be treated with (1,3-bisdiphenylphosphinopropane)dichloronickel(II) (Ni(dppp)Cl$_2$) to yield regioregular head-to-tail poly(3-alkylthiophene).
The iron(III) chloride and electrochemical routes to polythiophene are very similar to each other; they proceed via a similar oxidative mechanism, although the source of the oxidant is different (Scheme 1-3). The first step consists of a one electron oxidation of thiophene – this is accomplished by either a one electron oxidizing agent, such as iron(III) chloride, or the application of an anodic potential. This forms a thiophene radical cation; two such radicals couple together and are subsequently deprotonated to give bithiophene. Since the oxidation potential of bithiophene is lower than that of thiophene, the product is subsequently oxidized to again form a radical cation. This process repeats itself until eventually polythiophene is produced.
The synthetic protocols for the preparation of poly(p-phenylenevinylene)s are similarly well established, and a thorough review can be found in Chapter 13 of *The Handbook of Conjugated Polymers*. In short, the major difficulty in preparing PPV arises from its insolubility. The polymer can either be solubilised by the addition of long alkoxy chains (Chart 1-2), or a precursor polymer can be prepared, characterized, and processed, with a subsequent conversion step to produce PPV. While methods such as the Gilch polymerization work particularly well with solubilised monomers, the Wessling sulfonium route is of the most relevance to this thesis and will be discussed below (Scheme 1-4).

![Scheme 1-3](image)

The Wessling route uses a bis(sulfonium) monomer which can easily be prepared by nucleophilic substitution of α,α'-dichloro-p-xylene with tetrahydrothiophene. The first step of the synthesis is the deprotonation of the monomer by the addition of base. This initiates the polymerization reaction, which produces a non-conjugated tetrahydrothiophenium
polyelectrolyte. The reaction is carried out at 0 °C in order to limit the base-catalyzed elimination of the final tetrahydrothiophenium group and to halt the reaction at the precursor polymer stage. The non-conjugated polyelectrolyte is water soluble, can be readily purified by dialysis, and can be processed from solution using techniques such as spin coating. Once any desired characterization and processing is complete, the polymer is thermally treated in vacuo to eliminate the residual tetrahydrothiophenium functionality and produce the fully conjugated PPV. Despite the fact that the synthetic methodology was originally developed by Wessling nearly 40 years ago, the mechanism of the reaction was extremely controversial until very recently. The two possibilities, anionic nucleophilic attack and radical coupling, are shown in Scheme 1-5.
Wessling’s original hypothesis was that the polymerization proceeded via a free radical process. This was later challenged by Lahti,\textsuperscript{74} who proposed a carbanion-mediated process. The authors observed no decrease in electron paramagnetic resonance signal intensity when carrying out the polymerization in the presence of 0.1 – 1.0 equivalents of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO). Additionally, no evidence of polystyrene formation was found when styrene was added as a comonomer to the reaction mixture. Later work provided more conclusive evidence for Wessling’s proposed free radical mechanism;\textsuperscript{75-77} it was demonstrated that the rate of reaction was attenuated by the addition of radical scavengers such as TEMPO and enhanced by radical initiators such as persulfate. The addition of large quantities of TEMPO was observed
to completely halt the formation of polymer. This provided conclusive evidence of the involvement of a free radical intermediate, and the Wessling polymerization is now considered to proceed via a free radical chain growth mechanism.

The synthesis of poly(\(p\)-phenyleneethynylene)s can be broken down into two major categories: metal-catalyzed coupling reactions, such as the Sonogashira reaction, and alkyne metathesis.\(^6^3\) Of these, the usage of Sonogashira conditions was the first to be developed. The coupling of an appropriately substituted diethynylbenzene and dihalo arene using copper(I) and palladium(0) catalysts yields PPE (Scheme 1-6); however, the molecular weight of polymer obtained in this manner is typically low. Additionally, the presence of oxygen may lead to defects in the polymer backbone due to the oxidative homocoupling of two ethynyl groups. Despite these drawbacks, the reaction conditions are mild, general, and water-tolerant.
More recently, Bunz and coworkers have developed a metathesis approach to the synthesis of PPEs known as acyclic diyne metathesis (ADIMET).\textsuperscript{78} This approach was envisioned as a means of eliminating undesirable oxidative alkyne homocoupling and end-group defects while still obtaining high molecular weight polymer. The combination of Mo(CO)$_6$ and 4-chlorophenol was determined to be an effective catalyst for the ADIMET reaction. With the judicious choice of solubilising groups, PPEs containing up to 2000 repeat units can be successfully prepared.\textsuperscript{79}
1.4 MORPHOLOGICAL CONTROL IN CONJUGATED MATERIALS

1.4.1 Overview

Despite the successful synthesis of a number of soluble, processable conjugated polymers, controlling the microstructure and morphology of these materials poses considerable challenges. The majority of $\pi$-conjugated polymers are still prone to aggregation, both in solution and in the solid state. There is a large body of evidence that suggests that in order to achieve optimal performance in many electronic devices, both the size and shape of the phase domains must be carefully controlled.\textsuperscript{80} Thus, the overall morphology of the polymer is critical in device performance. There are two main approaches that have been adopted for the preparation of conjugated polymer micro- and nanostructures. These are referred to as soft and hard template approaches. In both of these methods, the polymer is incorporated into or around the template, and when the template is removed the polymer retains the negative imprint. Soft templates develop a particular shape that is easily deformed and often persists only in solution (e.g., surfactant or polymer micelles). Hard templates retain their structure both in and out of solution. Colloidal silica particles, porous alumina, and mesoporous silica are examples of hard templates. Both types of templates are used throughout this thesis, and are discussed in more detail below.

1.4.2 Soft Templates

One of the simplest techniques for preparing nanoparticles of $\pi$-conjugated materials is reprecipitation. A solution of the $\pi$-conjugated compound (either a small molecule or polymer) in an organic solvent is added to a large volume of water, typically under conditions of ultrasonication or vigorous stirring. The organic material rapidly aggregates into small nanoparticles, and the organic solvent is driven off by evaporation. This technique was used to prepare organic nanocrystals of perylene by redispersing ethanolic solutions of perylene in
water. These nanocrystals displayed important size-dependent emission properties not observed in either solution or the bulk material, highlighting the importance of controlling the microstructure and morphology of π-conjugated systems.

The reprecipitation technique has since been shown to be successful with a number of other systems (Chart 1-3). By reprecipitating THF solutions of 1-cyano-trans-1,2-bis-(4′-methylbiphenyl)-ethylene (CN-MBE) in water, CN-MBE nanoparticles were prepared. Notably, CN-MBE is essentially non-emissive in dilute solution, whereas a 700-fold enhancement in the emission intensity was observed in the nanoparticles. Polymeric nanoparticles have also been prepared by the reprecipitation method. Poly(9,9-dihexylfluorenlyl-2,7-diyl) (PFO), poly((9,9-dioctyl-2,7-divinylene-fluorenylene)-alt-co-(2-methoxy-5-(2′-ethylhexyloxy)-p-phenylene)) (PFPV), and MEH-PPV have all been reprecipitated from THF solution to form small (d ~ 10 nm) nanoparticles. Size-dependent emission properties have also been observed in poly(1,3-bis-(2-(3-alkylthienyl))azulene) (PTA) nanoparticles precipitated from mixed chloroform/methanol solutions. Similarly, Kurokawa et al. observed size-dependent absorption, emission, and thermochromic characteristics in poly(3-(2-(N-dodecylcarbamoyloxy)ethyl)thiophene-2,5-diyl) (P3DDUT) nanoparticles. The size-dependent optical properties of this series of π-conjugated organic nanoparticles are thought to derive from aggregation-induced changes in the electronic states of the conjugated materials.
A more advanced version of the reprecipitation technique has been developed that makes use of surfactants to control the particle size. Soluble polymers (e.g., methyl-substituted ladder-type poly(\(p\)-phenylene) (Me-LPPP)) are dissolved in a suitable solvent, and emulsified in an aqueous solution of sodium dodecyl sulfate. Evaporation of the organic solvent leaves behind a surfactant-stabilized aqueous dispersion of polymer nanoparticles (Figure 1-12).\(^8^7\) This methodology has not only been used to produce aqueous dispersions of conjugated polymers, but also to control Förster resonance energy transfer (FRET),\(^8^8\) produce blended polymer nanoparticles,\(^8^9\) and fabricate organic electronic devices with improved performance.\(^9^0\)
Figure 1-12. Preparation method for producing conjugated polymer nanoparticles from an organic emulsion.

Alternatively, rather than using an aqueous surfactant as the soft template, the surfactant can be incorporated directly into the conjugated polymer or oligomer of interest. The addition of penta(ethylene glycol) chains to the $\alpha$ and $\omega$ positions of a sexithiophene oligomer yields a bolaamphiphilic compound that has been shown to self-assemble in polar solvents such as water or $n$-butanol. These hollow vesicles can be deformed into ellipsoids by the application of a strong, uniaxial magnetic field.

Soft templates need not yield only spherical particles. It was found that both polyaniline (PANI) and polypyrrole (PPy) could be polymerized in aqueous solution in the presence of an anionic dopant (e.g., $\beta$-naphthalene sulfonic acid) to yield both nanotubes and hollow microspheres. In this case, the acid acts as a charge-balancing anion for the p-doped conjugated polymer, as well as a structure-directing template. This self-assembly process is enabled, in part, due to the good solubility of aniline and pyrrole in water.

Emulsion polymerization techniques have also been used to prepare conjugated polymer nanoparticles, in direct analogy to polystyrene and polyacrylate latexes. The water-tolerance of the Sonogashira cross-coupling was exploited in the preparation of poly($p$-phenyleneethynylene) micro- and nanoparticles. By dispersing the appropriate monomers, co-monomers, solvent, base, and catalysts in an aqueous medium, the cross-coupling reaction could be carried out.
exclusively within the hydrophobic interior of sodium dodecyl sulfate micelles. The addition of 1,2,4-tribromobenzene as a co-monomer produced cross-linked polymer chains which could be subsequently redispersed in organic solvents without dissolution.

Emulsion polymerization techniques for the polymerization of pyrrole, acetylene, and 3,4-ethylenedioxythiophene (EDOT) have also been developed. Generally, the monomer is dispersed in an aqueous medium by the use of a surfactant. A water-soluble oxidant such as ammonium persulfate or iron(III) chloride is added to the mixture, which then produces the conjugated polymer nanoparticles. This approach has had only limited success. The use of dodecylbenzene sulfonic acid as a surfactant and doping agent for PEDOT yielded amorphous and polydisperse microparticles.\(^97\) Short chain alcohol ethoxylate surfactants yielded more spherical particles, but a significant amount of surfactant residue was trapped in the PEDOT latex, and secondary nucleation could not be controlled.\(^98\) Some of the best success has been in preparing small \((d < 50 \text{ nm})\) nanoparticles of polypyrrole and PEDOT. By carrying out the oxidative polymerization of pyrrole using iron(III) chloride under microemulsion conditions (using decyltrimethylammonium bromide as a surfactant), fairly monodisperse polypyrrole nanoparticles could be prepared.\(^99\) The non-aqueous reverse emulsion system of acetonitrile-in-cyclohexane has been used to prepare nanoparticles of both polyacetylene and PEDOT using a polyisoprene-\textit{block}-poly(methyl methacrylate) copolymer emulsifier.\(^100\)

These examples illustrate that while the soft template approach has been a versatile method for preparing conjugated polymer micro- and nanoparticles, it suffers from several drawbacks. The types of morphologies that are accessible by this approach are fairly limited; despite some examples of self-assembled nanotubes, the methodology typically produces particles displaying spherical symmetry. Additionally, control over such important parameters as particle diameter
and polydispersity is often not as tight as it is in the case of other polymers (e.g., polystyrene latexes). Many of these issues can be addressed by the use of a hard template.

### 1.4.3 Hard Templates

Due to the shape persistence of hard templates, they typically offer a more reliable way of directing the shape of conjugated polymer micro- and nanostructures. A variety of approaches have been developed for the hard templating of organic materials, and in particular conjugated polymers. These include vapor-phase conformal coverage, solution coating of pre-formed nanowires, coating of colloidal particles (e.g., Stöber silica and polymer latexes), infiltration of opaline structures, and encapsulation within the pores of zeolites, anodized alumina, mesoporous carbons, and mesoporous silicas. Broadly speaking, these approaches can be further divided into endotemplating and exotemplating approaches. In the case of an endotemplate, the polymer coats the surface of an object forming a hollow replica. Exotemplates possess a high degree of porosity, and the polymer is encapsulated within the empty pore volume of the template. This is illustrated in Figure 1-13.
The vapor-phase polymerization of 3,4-ethylenedioxythiophene has been used successfully as a means of preparing PEDOT-coated microstructures. It is perhaps one of the most versatile endotemplating techniques in that it can accommodate a wide variety of template shapes and geometries; paper towel fibres, silicon microtrenches, and Gore-Tex® membranes have all been coated with PEDOT in this way. The conformal coverage provided by this oxidative chemical vapor deposition technique allowed for the use of a Gore-Tex® membrane as an endotemplate, which in turn led to the construction of a high surface area air-PEDOT-electrolyte interface. This enabled the material to be used as an effective catalyst for the reduction of oxygen.

While the exotemplate approach shown in Figure 1-13 may seem like a natural method for producing one-dimensional PEDOT wires, PEDOT micro- and nanotubes can be also prepared by an endotemplating approach. By adding a sulfonic acid functional group to the PEDOT backbone, a self-doped, water-soluble polymer is produced. This polymer can be self-assembled onto amyloid fibrils, leading to the formation of micron-sized conductive nanowire networks. These networks can then be utilized in electrochemical transistors. Electrospun biodegradable...
polymer fibres have also been coated with PEDOT by electropolymerization,\textsuperscript{107} and have been utilized as drug-release agents. Meanwhile, polyaniline nanowires can be synthesized by a self-assembly procedure described previously, and subsequently used as an endotemplate for the formation of co-axial PEDOT–PANI nanofibres.\textsuperscript{108}

Conjugated polymer micro- and nanoparticles have been the subject of intensive research due to the insoluble and intractable nature of most conjugated polymers; the processability of colloidal dispersions has made an attractive target. Recent developments in the field of opals and photonic crystals have ignited further interest in processable, monodisperse microspheres. Thus, much effort has been expended on using microspheres (either polymer latexes or Stöber silica) as endotemplates for conjugated polymers.

The first examples of a conjugated polymer being grown on a microsphere template were reported in the late 1980s and early 1990s when polypyrrole and polyaniline were coated onto polymer latexes.\textsuperscript{109, 110} Unfortunately, the colloidal stability of these particles was limited. This issue was eventually resolved by growing polypyrrole and polyaniline films on the surfaces of sterically stabilized polyurethane latexes.\textsuperscript{111, 112} The core-shell particles produced in this manner were found to have good film-forming properties, as well as excellent conductivities and stabilities. Other approaches have since been developed, such as the use of ultra-fine silica sols as stabilizers in the chemical polymerization of EDOT; however, the particles produced by this method were both relatively amorphous and polydisperse.\textsuperscript{113} As such, much of the work to date has followed on the original premise of coating either polymer latexes or silica microspheres with conjugated polymers.

Armes and coworkers extended this methodology to produce a series of polypyrrole,\textsuperscript{114, 115} polyaniline,\textsuperscript{116} and PEDOT-coated\textsuperscript{117} polystyrene latexes (Figure 1-14). A poly(N-
vinylpyrrolidone) (PVP) stabilized polystyrene latex was first prepared by dispersion polymerization. Either pyrrole, aniline, or EDOT was then polymerized in the presence of the PVP-stabilized latex; the conjugated polymer deposited on the colloidal support as it grew. It was found that these core-shell colloids would form stable dispersions as long as the thickness of the conjugated polymer layer was not greater than that of the PVP stabilizer.

**Figure 1-14.** Method of coating a PVP-stabilized polystyrene latex with conjugated polymer layers.

Han and Foulger adopted a similar approach in preparing PEDOT-coated silica\(^{118}\) and PEDOT-coated polystyrene\(^{119}\) microspheres. By adding EDOT to an aqueous dispersion of colloidal silica, the monomer became adsorbed to the surface of the silica microspheres. The addition of ammonium persulfate then polymerized the monomer on the surface of the silica, forming core-shell silica-PEDOT composites. A similar approach was carried out using a polystyrene latex; however, in this case the surfactant dodecylbenzene sulfonic acid had to be added to the reaction mixture in order to stabilize the resultant colloidal dispersion.

A series of PANI-coated latexes has been developed using very similar methodology, although the exact mechanism by which the conjugated polymer was trapped on the particle surface differed. The layer-by-layer deposition technique was used to prepare polyelectrolyte-coated melamine formaldehyde particles. These were then infiltrated with aniline and subsequently polymerized. The melamine formaldehyde could then be removed to yield polyelectrolyte–
Similarly, polystyrene latexes were sulfonated by treatment with concentrated sulfuric acid to form a template for aniline polymerization. Polymerization of PANI took place preferentially at the sulfonic acid sites, localized on the particle surface. The PANI-coated polystyrene latex could then be etched to yield hollow PANI particles. Mezzenga et al. demonstrated that by casting a mixture of polyaniline-phenolsulfonate (PANI-PSA), polystyrene-co-poly(2-vinylpyridine) (PS-PVP) and polystyrene latex, followed by annealing, a cellular morphology resulted that contained a finely dispersed PANI-PSA/PS-PVP continuous phase. In comparison to traditional polymer blends, this reduced the percolation threshold for charge transfer dramatically, while simultaneously increasing the conductivity and thermal stability of the film.

While early work focused on preparing highly conductive core-shell particles using conjugated polymers such as PPy, PANI, and PEDOT, highly fluorescent polymers such as PPE have also been attached to the surface of colloidal microparticles. Layer-by-layer deposition of alternating layers of a cationic polyelectrolyte and an anionic poly(p-phenyleneethynylene) on silica microspheres has led to enhanced sensory amplification in the fluorescence detection of nitroaromatic compounds. Ogawa et al. also prepared anionic poly(p-phenyleneethynylene)s which were grafted to the surface of silica microparticles, although this was accomplished by a dramatically different mechanism (Scheme 1-7). In this instance, the silanol groups of a silica microsphere were modified using 4-iodo-N-(3-(trimethoxysilyl)propyl)benzamide, such that the particle displayed reactive aryl iodide groups. These were then incorporated as co-monomers in the polymerization of a dihalo arene and diethynylbenzene under Sonogashira conditions to afford PPE grafted to the surface of the silica microspheres.
A number of specific applications are made possible due to the monodisperse, spherical morphology of the conjugated polymer-coated microspheres. Opals can be self-assembled from many of the materials, which then possess both the optoelectronic properties of the conjugated polymer and the interesting photonic behavior of the opal.\textsuperscript{118, 119, 125-127} Additionally, opal templates can first be fabricated by self-assembly of a polystyrene latex, and the interstitial voids filled with a polymer such as PPV\textsuperscript{128} or PEDOT\textsuperscript{129} (Figure 1-15). This template approach yields an inverted opal of the conjugated polymer. The materials have also been exploited for increased sensitivity in fluorescence assays,\textsuperscript{123} as inks in the inkjet printing of electrochromic devices,\textsuperscript{130} and even as projectiles in hypervelocity impact experiments.\textsuperscript{131}
Figure 1-15. Electropolymerization of PEDOT around a polystyrene opal to form a PEDOT inverted opal.

Exotemplates have also been extensively exploited in the control of conjugated polymer morphologies. Pioneering work by Martin and coworkers demonstrated that hollow nanotubes and solid nano-fibrils of polypyrrole, polyaniline and polythiophene could be prepared by either electrochemical or chemical synthesis in the pores of both polycarbonate and alumina membranes.\textsuperscript{132-135} This work has been carried forward by a number of other groups. Han and Foulger reported the synthesis of 1-D PEDOT nanostructures in an alumina membrane by chemical oxidation,\textsuperscript{136} while electrochemical polymerization has also been used to synthesize PEDOT inside the pores of porous alumina.\textsuperscript{137} Importantly, conjugated polymers prepared inside such confined spaces have shown enhanced conductivities relative to bulk material.\textsuperscript{133, 134} Soluble polymers such as MEH-PPV can also be drawn into the pores of porous alumina membranes by an infiltration process.\textsuperscript{138}

Another prominent class of exotemplates is zeolites. These inorganic aluminosilicates have small pore diameters (< 2 nm), and can act as hosts for a variety of conjugated polymers. These include polypyrrole,\textsuperscript{139} polyaniline,\textsuperscript{140} and poly(p-phenylenevinylene).\textsuperscript{141, 142} Due to the large loss of entropy involved in threading a soluble conjugated polymer into the pores of such a confined
system, the zeolite composites must typically be prepared by the infiltration of the monomer, followed by a discrete polymerization step. The extreme confinement of the zeolite micropores implies that the polymer fibrils must be confined to molecular dimensions. This has a number of important consequences for the guest polymer; for example, zeolite encapsulated poly(p-phenylenevinylene) displays improved properties, such as enhanced resistance to photobleaching.\textsuperscript{142}

Since its discovery in the early 1990s,\textsuperscript{143, 144} MCM-41 and other related mesoporous silicas have rapidly become one of the most common inorganic hosts for conjugated polymers and other functional organic materials. MCM-41 possesses hexagonal-close-packed mesopores. These are templated by surfactant micelles during the synthesis; tetraethylorthosilicate or another silicate precursor is hydrolyzed and condensed around the surfactant template. Depending on the surfactant used, the pore diameter can be tuned between 1.5 and 10 nm.\textsuperscript{145} The uniformity of pore sizes obtained using this approach, coupled with their variety and tunability, has led to the preparation of a huge variety of mesoporous silica encapsulated organic materials. While the full breadth of work in this area is beyond the scope of this thesis, key examples related to conjugated polymers will be presented.

Due to the larger pore sizes of mesoporous silicas (1.5 – 10 nm) compared to zeolites (< 2 nm), infiltration approaches towards conjugated polymer composites are more effective. This has been extensively exploited in the preparation and study of MEH-PPV–mesoporous silica composites. Nguyen et al. demonstrated in 2000 that after encapsulating MEH-PPV inside oriented mesoporous silica, energy transfer occurred unidirectionally from aggregated polymer outside of the pores towards the isolated, aligned polymer chains within the pores.\textsuperscript{146} This work enabled the measurement and comparison of the intra- and inter-chain energy transfer rate. It was important in our understanding of exciton diffusion dynamics in conjugated polymers and
has a number of implications for the construction of light emitting diodes or photovoltaic cells based on MEH-PPV. Further work in this area\textsuperscript{147, 148} highlighted this engineered control over energy transfer, while adjusting the pore diameter of the mesoporous host was shown to alter the aggregation state of the polymer chains and therefore the optoelectronic properties.\textsuperscript{149} These results were utilized in the fabrication of an aligned MEH-PPV–mesoporous silica composite which demonstrated enhanced optical gain and low threshold amplified spontaneous emission.\textsuperscript{150}

Related work has investigated the role of solvent on the infiltration of MEH-PPV into MCM-41 silica;\textsuperscript{151} however, previous work in the Wolf group demonstrated an entirely different synthetic approach.\textsuperscript{152} The interior silanol groups of the MCM-41 silica were deprotonated using a non-aqueous solution of tetrabutylammonium hydroxide. The exposed siloxide sites were then used as the base initiator for the Wessling synthesis\textsuperscript{71} of PPV (Scheme 1-8). This led to a material where the PPV selectively polymerized inside the pores of the mesoporous template, as demonstrated by energy filtered transmission electron microscopy (TEM) and nitrogen adsorption studies.
Other conjugated polymers have been encapsulated in a mesoporous silica matrix. Driving pyrrole vapor into an MCM-41 host by capillary condensation, followed by oxidative polymerization using iron(III) chloride has been shown to be a route to polypyrrole–MCM-41 composites. By sequentially coating the pore walls of SBA-15 mesoporous silica with poly(methyl methacrylate) (PMMA) and polypyrrole, coaxial nanocables of PMMA and PPy were synthesized. Using a dramatically different approach, Li et al. demonstrated the encapsulation of polythiophene within the pores of a mesoporous silica. A quaternary ammonium salt was first tethered to a thiophene ring by a long alkyl chain (Chart 1-4), effectively forming a surfactant. This surfactant was then used as the structure-directing agent in the synthesis of a mesoporous silica, effectively building the silica host around the monomer. After the silica host was established, the monomer could be polymerized using iron(III) chloride. A similar approach was adopted by Yang et al. in the preparation of silica microspheres. While the actual structure-directing step of these two reports involves a soft template (the
thiophene-based surfactant), the final structure is that of polythiophene encapsulated inside a hard template (the silica).

**Chart 1-4**

![Chart 1-4](image)

The general theme of monomer infiltration followed by polymerization has been carried over into other mesoporous templates, such as carbon. By filling the silica mesopores with carbon and etching the silica with hydrofluoric acid, a mesoporous carbon can be produced. The pores of this mesoporous carbon can then be filled with monomers such as EDOT, which can then be polymerized by treatment with ammonium persulfate.\(^{157}\)

These examples illustrate several key points about exotemplating: the procedure often involves monomer infiltration followed by polymerization; the composites often display new or different properties compared to bulk material; and, the polymer takes on the shape (e.g., nanotubes or nanowires) of the empty pore volume of the inorganic host.

### 1.4.4 Mesoporous Silica Spheres (MSS)

An emerging class of mesoporous silica hosts are mesoporous silica spheres (MSS). These resemble Stöber silica microspheres in terms of their size and shape, but possess radially-oriented, hexagonal-close-packed mesopores similar to MCM-41. Additionally, if the synthetic conditions are carefully controlled, these materials can be prepared with a high degree of monodispersity. In terms of their synthesis, the Stöber process is modified such that ammonia is replaced by the combination of a cationic alkylammonium surfactant and sodium hydroxide (Scheme 1-9).\(^{158, 159}\) The surfactant templates the formation of the mesopores and directs the
overall spherical morphology, while the sodium hydroxide catalyzes the hydrolysis of the silica precursor.

Through variation of the synthetic conditions, a variety of MSS hosts with different pore sizes and properties can be obtained. A two-step growth process utilizing different silicate precursors can be used to produce core-shell particles with a hydrophilic core and a hydrophobic shell.\textsuperscript{160} Alternatively, a surfactant exchange method can be used to expand the pores of pre-existing MSS hosts while retaining the hexagonal-close-packed nature of the mesopores.\textsuperscript{161}

Applications of the mesoporous silica spheres have just begun to be explored. Due to their monodispersity, they have been utilized as building blocks in the fabrication of opaline films; due to the porosity of the individual spheres, the adsorption or desorption of various gases changes the effective refractive index of the film and therefore the position of the Bragg diffraction peak.\textsuperscript{162} Additionally, the host–guest chemistry of these materials is beginning to be elucidated. Inorganic precursors can be incorporated into various MSS hosts, and due to the extreme thermal stability of the silica, they can be transformed into functional materials such as ferromagnetic iron–platinum alloys.\textsuperscript{163} Organic chromophores such as chlorophyll a have also been incorporated into the MSS hosts and the energy transfer, charge separation, and photoreduction processes of the composites studied.\textsuperscript{164, 165} However, prior to this thesis, no examples of conjugated polymer–MSS composites have been reported.
1.5 GOALS AND SCOPE

The overarching aim of the work described in this thesis is to examine the morphological control of conjugated polymers through the use of structure-directing templates. This theme will be developed by first attempting to prepare conjugated polymer micro- and nanoparticles. Secondly, the colloidal and optoelectronic properties of these new colloidal materials will be studied. Thirdly, the suitability of these new materials for emerging applications in photonics, energy storage, and biology will be evaluated.

These three aspects — synthesis, characterization, and application — are explored throughout the thesis. Chapter 2 describes the synthesis of a PEDOT@MSS composite material and demonstrates its self-assembly into an opaline film. The synthetic methodology for the preparation of polymer–silica composites is further developed in Chapter 3, and is extended to include other examples of conjugated polymers. The colloidal and optoelectronic properties of the composites are studied in more detail. The MSS hosts are also evaluated for their ability to confine multiple materials in close proximity; this provides a route to polymer blends in which phase separation can be controlled in a systematic way (Chapter 4).

The application of these morphologies to energy storage is discussed in Chapter 5. A series of conjugated polymer–microporous carbon composites are synthesized, characterized, and evaluated for their capacitive capability. Highly luminescent PPV@MSS composites are described in Chapter 6, and the impact of the silica template on the photophysical properties of the polymer is studied. Finally, colloidal preparations of PPEs with biological significance are discussed in Chapter 7. These carbohydrate-functionalized PPE microparticles are evaluated for their affinity to proteins of biological significance.
1.6 REFERENCES


CHAPTER 2

MONODISPERSE POLY(3,4-ETHYLENEDIOXYTHIOPHENE)-SILICA MICROSPHERES: SYNTHESIS AND ASSEMBLY INTO CRYSTALLINE COLLOIDAL ARRAYS

2.1 INTRODUCTION

In the years following the pioneering work by Yablonovich\textsuperscript{1} and John,\textsuperscript{2} the field of study of photonic crystals has grown dramatically. These dielectric materials have a periodically modulated refractive index that varies on the length scale of visible light. This modulation gives rise to a photonic bandgap, or range of wavelengths for which propagation within the crystal is forbidden. This bandgap is due to Bragg diffraction from the lattice planes of the crystal, and the phenomenon has been exploited in the development of new ways to harness and control the flow of light. These include optical filters,\textsuperscript{3,4} waveguides,\textsuperscript{5} and lasers.\textsuperscript{6,7}

While 1-D (Bragg mirrors)\textsuperscript{8-10} and 2-D\textsuperscript{11,12} photonic crystals have been extensively explored in the literature, perhaps the most interesting optical effects can be observed when the periodicity is extended to three dimensions. These 3-D photonic crystals can be prepared by a number of techniques, including laser holography, but perhaps the simplest and most straightforward method is by the self-assembly of monodisperse colloidal spheres to form opals.\textsuperscript{13} The self-assembly process can be accomplished by a variety of fabrication techniques, including sedimentation,\textsuperscript{14,15} spin-coating,\textsuperscript{16,17} ink-jet printing,\textsuperscript{18,19} capillary flow,\textsuperscript{20,21} and assisted vertical deposition.\textsuperscript{22-24}

The general approach of colloidal self-assembly has a number of advantages over other fabrication methods due to its low cost and simplicity. Unfortunately, the requirements imposed by the self-assembly process are particularly demanding of the colloidal material. The particles must be spherical; they must be monodisperse; and they must be mutually repulsive (i.e., form a stable colloidal dispersion). If the particles possess defects in shape or size, this will introduce defects in the crystal lattice of the opal such as point defects and stacking faults. In order to form high quality opals, the standard deviation of the particle diameter must typically be $\leq 5\%$.\textsuperscript{13} Additionally, if the particles are prone to aggregation, the rate of sedimentation will be competitive with the rate of self-assembly. This also leads to errors in particle stacking; in the limit of extremely fast aggregation, only disordered flocs can be obtained from the material. As such, the number of materials that can be self-assembled in this way is quite limited.

In the pursuit of new, high quality colloidal materials, the preparation of conjugated polymer microspheres makes an attractive target. Conjugated polymers have been extensively exploited in materials research for their light weight, conductive and luminescent characteristics, and their chemical tunability.\textsuperscript{25} In particular, poly(3,4-ethylenedioxythiophene) (Chart 2-1) is one of the most commercially successful examples of a conjugated polymer to date. This is due to its high stability, conductivity, and transparency in the doped state.\textsuperscript{26} Early studies on PEDOT were hampered, however, by the insolubility of the polymer. This obstacle was eventually overcome by the use of poly(styrene sulfonate) (PSS) as a charge-balancing dopant in the oxidative polymerization process.\textsuperscript{27} The PEDOT:PSS material (known under the trade name Baytron-P, Chart 2-1) can be processed from aqueous solution and is now produced by Bayer on a multi-ton scale annually.\textsuperscript{26} Recent reports have also highlighted the potential of PEDOT-based photonic crystals,\textsuperscript{28,29} including the electrochemical modulation of the photonic bandgap.\textsuperscript{30}
Early attempts to prepare well-defined colloidal PEDOT materials were met with limited success. One approach has been to prepare core–shell particles. These derive their spherical structure and monodispersity from a polystyrene or silica core, and active optoelectronic properties from a thin polymer shell. Khan and Armes\(^{31}\) prepared a series of PEDOT-coated polystyrene latexes; however, for PEDOT loadings \(\geq 6.5\% \text{ (w/w)}\) the particles displayed a less well-defined morphology and a propensity for aggregation. Additionally, the spherical morphology of the composite was lost after removal of the polystyrene template. Foulger adopted a similar approach in the preparation of PEDOT coated polystyrene\(^{29}\) and silica\(^{32}\) microspheres. While these materials could be self-assembled into colloidal crystals, the PEDOT loadings were again low and etching of the template resulted in particle collapse.

Emulsion or dispersion polymerization is another technique commonly employed in the preparation of polymer colloids. Choi et al. prepared PEDOT nanoparticles by the polymerization of 3,4-ethylenedioxythiophene in aqueous dodecylbenzene sulfonic acid micelles,\(^{33}\) but the approach offered only poor control over the particle size and morphology. Novel emulsion systems, such as an acetonitrile-in-cyclohexane reverse emulsion\(^{34}\) or an emulsion stabilized by short chain alcohol ethoxylate surfactants,\(^{35}\) were required in order to give well-defined PEDOT colloids. While these approaches yielded spherical particles, the reverse emulsion system was found to produce only PEDOT nanoparticles \((d < 100 \text{ nm})\), and secondary
nucleation could not be avoided when using the ethoxylate surfactants. Recently, the use of end-functionalized reactive surfactants enabled the synthesis of PEDOT latexes with a smaller size distribution.\textsuperscript{36}

In this chapter, a novel in situ polymerization technique for the template formation of PEDOT particles in the 0.1 – 1 µm size regime is described. Composite PEDOT–silica particles are first prepared. The silica template can then be removed by etching with hydrofluoric acid, leaving behind an intact PEDOT microparticle. The composition, morphology, optoelectronic properties, and colloidal stability of both the PEDOT–silica composite and pure PEDOT particles are evaluated. Additionally, the preparation of an opaline film of a PEDOT–silica composite is described.

\section*{2.2 EXPERIMENTAL}

2.2.1 General

\textbf{Materials and Equipment.} EDOT and PEDOT:PSS were donated by Bayer under the trade names Baytron-M and Baytron-P, respectively. The EDOT was vacuum distilled prior to use, and stored at 4 °C under nitrogen. Sodium persulfate was purchased from Sigma-Aldrich and used as received. The mesoporous silica spheres were prepared according to an established procedure by Toyota Central R & D Labs, Inc.,\textsuperscript{37} and were dried in vacuo at 120 °C prior to use. Hydrofluoric acid (49\%) was purchased from Fisher Scientific and used as received. FT-IR spectra were recorded as KBr pellets on a Nicolet 4700 spectrometer (Thermo Electron Corporation). UV-vis-NIR spectra were recorded as ethanolic dispersions in a 1 cm quartz cuvette on a Varian Cary 5000 spectrophotometer. Pore volumes were measured on a Quantachrome Autosorb-1 analyzer at 77 K using nitrogen gas. Thermogravimetric analysis (TGA) was performed on a Pyris 6 analyzer. Powder X-ray diffraction data were recorded on a
Bruker D8 Advance X-ray diffractometer in the Bragg-Brentano configuration, using copper Kα radiation at 40 kV, 40 mA. Resistivity measurements were made using the four-point probe technique on pressed pellets. Pellet thicknesses were measured by cross-sectional analysis in the field-emission scanning electron microscope. Reflectivity spectra were obtained using a tunable (750 – 1000 nm) titanium:sapphire laser operating in continuous wave mode as the light source (Mira 900, Coherent Inc.) and Nova II power meters (Ophir Optronics) to measure both incident and reflected beam intensities.

**Scanning Electron Microscopy.** Dilute suspensions of colloidal material (ca. 1 mg mL⁻¹) were prepared in ethanol by ultrasonication. An aliquot (100 µL) of this suspension was drop-cast on an aluminum stub and allowed to dry. Microscopy was carried out on a Hitachi S4700 scanning electron microscope equipped with a cold field-emission electron gun and pinhole objective lens. Accelerating voltages of 1.5 kV were chosen in order to provide a balance between image resolution, charging effects, and surface penetration. Particle diameters were determined by measuring the diameter of a minimum of 200 particles in the FE-SEM. Energy dispersive X-ray microanalysis (EDX) was carried out on a Hitachi S3000-N scanning electron microscope operating at 20.0 kV.

**Electrokinetic Measurements.** Measurements of electrophoretic mobilities were made on a Beckman-Coulter Delsa 440SX instrument. Samples were measured at a particle concentration of 0.1% (w/w) in 0.010 M aqueous sodium chloride matrix. The pH was adjusted to 6.7 prior to measurement by addition of either HCl(aq) or NaOH(aq) as required. All measurements were taken at 25.0 ± 0.1 ºC. The Smoluchowski equation was used to relate the experimentally determined electrophoretic mobilities to the zeta potential.
2.2.2 Synthesis

**Preparation of PEDOT@MSS.** A sample of MSS (0.100 g) was dried in a Schlenk tube and placed under a nitrogen atmosphere. Enough EDOT to completely fill the mesopores of the silica (88 µL, 0.117 g, 0.823 mmol) was added by micropipette, and the mixture agitated with a spatula for 6 – 7 min. The powder was transferred to a clean vial and dried at 60 ºC for 1 hour, after which a solution of sodium persulfate (0.15 g, 0.63 mmol) in water (3.00 mL) was added. The mixture was stirred overnight, and the solid isolated by centrifugation. The solid was washed with distilled water (3 × 15 mL) and ethanol (1 × 15 mL) by redispersion/centrifugation cycles, and dried at 60 ºC overnight to yield the product as a midnight-blue powder (0.20 g).

**Etching of the Silica Template.** A sample of the PEDOT@MSS composite (0.100 g) was placed in a 50 mL Teflon beaker and dispersed in ethanol (10 mL) by sonication. Aqueous hydrofluoric acid (49%, 10 mL) was then added, and the mixture stirred for 45 minutes. The mixture was centrifuged and the midnight-blue residue washed with distilled water (3 × 15 mL) and ethanol (1 × 15 mL) by redispersion/centrifugation cycles. It was dried at 60 ºC overnight, yielding the solid PEDOT particles as a dark blue powder.

**Preparation of a PEDOT@MSS Colloidal Crystal.** A sample of PEDOT@MSS_{550} (0.170 g, 30% pore filling) was ground with a mortar and pestle and sonicated for four hours in ethanol (15 mL). The colloid was further purified by redispersion/centrifugation cycles with ethanol (3 × 15 mL) in order to remove particle fragments and small particulate, and finally redispersed in ethanol (15 mL). A glass slide was soaked in piranha solution (3:1 concentrated sulphuric acid : 30% hydrogen peroxide), rinsed with copious quantities of distilled water, and dried using a heat gun. The slide was then partially vertically immersed in the colloidal dispersion. The bottom of the vial was heated to 60 ºC and the setup covered with a 600 mL beaker to block drafts. After
two days an opaline film had formed on the slide. It was removed from the suspension and air dried.

### 2.3 RESULTS AND DISCUSSION

#### 2.3.1 Preparation of PEDOT@MSS Composites

The first step in the synthetic procedure is the preparation of the mesoporous silica spheres. Yano and Fukushima have shown that these can be prepared via the hydrolysis of organic silicon precursors (such as tetramethylorthosilicate) in the presence of alkylammonium surfactants.\(^{37}\) After synthesis, the particles are calcined in order to remove the residual surfactant template. The preparation of the silica particles was carried out by Toyota Central R & D Labs, Inc. and the isolated MSS hosts shipped to UBC.

In order to vary the diameter of the composite particles, three different batches of mesoporous silica spheres were produced. These had diameters of \((670 \pm 35)\) nm, \((550 \pm 29)\) nm, and \((330 \pm 30)\) nm, and are abbreviated MSS\(_{670}\), MSS\(_{550}\), and MSS\(_{330}\), respectively. The spheres possess a high degree of porosity as determined by nitrogen adsorption (typically ca. 0.8 g cm\(^{-3}\)). Once the mesoporous host is received, it is first dried at 120 °C in vacuo in order to remove adsorbed water. After drying, a volume of 3,4-ethylenedioxythiophene equal to the total pore volume of the silica is added by micropipette. The mixture is agitated by stirring with a spatula, and the liquid monomer is drawn into the pores of the silica by capillary action. A chemical oxidant (sodium persulfate) in a small amount of water is then added to induce oxidative coupling of the monomer. Both the capillary forces of the mesopores and the poor solubility of EDOT in water ensure that the monomer stays isolated within the mesopores during the polymerization process. After isolating the particles by centrifugation and washing by a series of redispersion/centrifugation steps, the particles are dried at 60 °C overnight. This yields the
PEDOT@MSS composites with virtually quantitative conversion (Scheme 2-1). It should be noted that this in situ polymerization technique is required in order to prepare the PEDOT–silica composite materials. Attempts at directly incorporating PEDOT:PSS (Baytron-P) into the mesopores of the silica failed, yielding only silica suspended in a PEDOT matrix.

**Scheme 2-1**

![Scheme 2-1](image)

**2.3.2 Characterization of PEDOT@MSS Composites**

After the PEDOT@MSS\textsubscript{670}, PEDOT@MSS\textsubscript{550} and PEDOT@MSS\textsubscript{330} materials had been prepared, the filling of the mesopores was confirmed by nitrogen adsorption and powder X-ray diffraction studies. Figure 2-1 shows the nitrogen adsorption isotherm of the empty MSS\textsubscript{670} host, as well as the three PEDOT@MSS composites.
As can be seen in Figure 2-1, the MSS\textsubscript{670} host (which is representative of the MSS hosts in general) displays a type IV adsorption isotherm typical of mesoporous materials. After filling of the mesopores with polymer, the PEDOT@MSS composites no longer adsorb any significant quantity of nitrogen. This suggests that the polymer has completely filled the pores of the silica. This is reinforced by powder X-ray diffraction studies. The diffraction patterns of the MSS\textsubscript{550} host, the PEDOT@MSS\textsubscript{550} composite, and a physical blend of 50:50 (w/w) Baytron-P:MSS\textsubscript{550} are shown in Figure 2-2.
Figure 2-2. Powder X-ray diffraction patterns for the MSS\textsubscript{550} host (solid line), the PEDOT@MSS\textsubscript{550} material (dashed line), and a physical blend of 50:50 (w/w) Baytron-P:MSS\textsubscript{550} (dashed-dotted line).

The MSS hosts exhibit strong diffraction peaks in the region of 2 – 8° (2θ) due to the highly ordered nature of the mesopores. Once the pores have been filled with polymer the electron density contrast between the pore wall and the interior is greatly diminished. This leads to a dramatic reduction in peak intensity. The peak intensity of the PEDOT@MSS\textsubscript{550} sample is an order of magnitude less intense than that of a physical mixture of PEDOT (in the form of Baytron-P) and the silica host, indicating that the diminished intensity is due to the filling of the mesopores and not simply dilution of the diffracting material.

FE-SEM images of the composite materials are shown in Figure 2-3. A cursory evaluation reveals the overall spherical geometry of the mesoporous silica host is retained after the incorporation of PEDOT. Additionally, the surface of the particles is not smooth; there is a fuzzy texture on the surface that is most clearly visible in the higher magnification micrograph (Figure 2-3c).
A more detailed analysis of the particle diameters shows that in all cases, there is a slight increase (2% – 9%) in particle diameter compared to the pure silica host (Table 2-1). This is due to some polymer growth on the surface of the spheres in addition to inside the mesopores. The monodispersity of the particle diameter is not affected by this surface growth, and does not fundamentally differ from that of the silica host. It is thought the surface polymer growth may occur via dissolution of small amounts of monomer during the polymerization process. The dissolved monomer is free to migrate from the mesopores, and is oxidatively coupled to form oligomers. The oligomer then likely becomes adsorbed to the silica particle surface, where the polymer chain continues to grow. Importantly, these results demonstrate that the diameter of the
spheres can be tuned by judicious choice of the template; a variety of template sizes have already been synthesized, rendering control of the particle diameter facile.

**Table 2-1.** Diameters and standard deviations of the PEDOT@MSS composites.

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<tr>
<td>PEDOT@MSS\textsubscript{670}</td>
<td>730</td>
<td>35</td>
<td>670</td>
<td>35</td>
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<tr>
<td>PEDOT@MSS\textsubscript{550}</td>
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<tr>
<td>PEDOT@MSS\textsubscript{330}</td>
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Thermogravimetric analysis of the PEDOT composites reveals materials with similar thermal stabilities and polymer loadings (Figure 2-4). All samples show a slight mass loss between 60 and 120 °C; this is likely due to residual solvent trapped in, or adsorbed on, the spheres. If not rigorously dried, the mesoporous silica hosts show a similar mass loss due to adsorbed water. The onset of polymer decomposition occurs at ca. 280 °C, followed immediately by a precipitous mass loss between 300 and 350 °C. The decomposition of PEDOT is complete by 600 °C. The polymer loadings are typically ca. 50% (w/w) for all samples.
Figure 2-4. Thermogravimetric analysis of PEDOT@MSS$_{670}$ (solid line), PEDOT@MSS$_{550}$ (dashed line), and PEDOT@MSS$_{330}$ (dashed-dotted line).

Energy dispersive X-ray microanalysis and combustion analysis were also carried out on the PEDOT composites in order to determine elemental composition. The results are tabulated in Table 2-2. The results are qualitatively similar for each of the composites, despite the variation of particle diameter. Both EDX and combustion analyses are in agreement that the materials are ca. 20% (w/w) carbon; based on this value and the empirical formula of PEDOT, the elemental analysis indicates that the composites are approximately 40% PEDOT by mass. This is slightly lower than the value determined by TGA (ca. 45 – 50%). This can be explained by the doping level of the polymer. The as-prepared PEDOT@MSS materials are p-doped (vide infra), meaning that the polymer chains are partially oxidized. Anions must therefore be present in order to balance the charge. These will take the form of sulfate (the byproduct of persulfate oxidation), and their additional mass accounts for the additional decomposition observed in the TGA. They are also indicated by the < 6:1 carbon:sulfur ratio (on an atomic basis) observed by EDX.
Table 2-2. Elemental analysis of the PEDOT@MSS composites.

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<th>Energy Dispersive X-ray Microanalysis</th>
<th>Combustion Analysis</th>
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<tr>
<td></td>
<td>% C [w/w]</td>
<td>% Si [w/w]</td>
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<tr>
<td>PEDOT@MSS&lt;sub&gt;670&lt;/sub&gt;</td>
<td>20</td>
<td>19</td>
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<td>PEDOT@MSS&lt;sub&gt;550&lt;/sub&gt;</td>
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<td>18</td>
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<tr>
<td>PEDOT@MSS&lt;sub&gt;330&lt;/sub&gt;</td>
<td>18</td>
<td>22</td>
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Despite the encapsulation of PEDOT by the silica host, the redox state and doping level of the polymer can be easily tuned by chemical means. In the as-prepared composite materials, the PEDOT is highly doped, as indicated by the presence of a polaron/bi-polaron peak in the NIR region of the absorption spectrum (Figure 2-5). This peak largely disappears upon heating the material to reflux in a solution of anhydrous hydrazine in methanol. A new peak at 600 nm can be observed, and is assigned to the $\pi \rightarrow \pi^*$ transition of the de-doped PEDOT polymer. There is a slight remnant of the polaron absorption in the de-doped sample, possibly due to polymer buried deeply in the core of the particle that is inaccessible to the chemical reductant.
Figure 2-5. UV-vis-NIR spectra of PEDOT@MSS$_{550}$ (solid line) and PEDOT@MSS$_{550}$ after treatment with anhydrous hydrazine in methanol (dashed line).

The presence or absence of the polaron absorption can be readily correlated to the conductivity of the materials. In the PEDOT@MSS$_{550}$ sample, which exhibits a polaron absorption, the conductivity of a pressed pellet was measured to be $\sigma = 0.062 \pm 0.008$ S cm$^{-1}$. The conductivity is lower than that observed for typical PEDOT films, which display conductivities as high as 300 S cm$^{-1}$. One explanation for this behavior is the limited cross-sectional area available for hole transfer between particles. Close-packed spheres are in contact only in a small, finite region, which may act as a bottleneck for hole transfer; in contrast, for a monolithic film of PEDOT, holes are relatively free to migrate in all directions. As expected, after de-doping the resistivity increases by over three orders of magnitude, to $\sigma = (1.5 \pm 0.4) \times 10^{-5}$ S cm$^{-1}$.

The doping of the PEDOT composite material was also evaluated by measurement of the zeta potential. A sample of PEDOT@MSS$_{550}$ was found to have $\zeta = 35$ mV, when measured at pH = 6.7 in 0.010 M NaCl$_{(aq)}$. The polaron absorption observed in the spectrum of the PEDOT sample indicates that positive charges are located on the polymer chains. Since some polymer is present
on the surface of the colloidal particle (as shown in Table 2-1), this positive surface charge creates a positive zeta potential. The absolute value of $\zeta$ is slightly less than that of a standard polystyrene latex ($\zeta = -50 \text{ mV}$). According to DLVO theory, the PEDOT@MSS colloidal should therefore be slightly more prone to aggregation than standard latexes; however, the 35 mV potential still provides an effective electrostatic barrier to particle flocculation, leading to a stable colloidal dispersion.

### 2.3.3 Preparación de PEDOT Colloidal Spheres by HF Etching

One key test of the PEDOT@MSS materials is their stability with respect to template removal. The PEDOT-coated silica spheres prepared by Han and Foulger\textsuperscript{32} suffered from the fact that etching of the silica core led to a collapse of the PEDOT shell. As such, pure PEDOT microparticles could not be prepared by their approach. With this in mind, a sample of each of the PEDOT@MSS materials was subjected to a brief (45 min) etch using 25% HF\textsubscript{(aq)}.

FE-SEM micrographs show the morphology of the materials is retained after etching (Figure 2-6). The samples clearly retain the overall spherical geometry of the polymer–silica precursor, although there is a reduction in particle diameter (Table 2-3). This reduction in particle diameter can be attributed to the removal of the silica pore walls and subsequent bead collapse due to strong polymer van der Waals interactions. For all HF-etched samples, however, the overall particle size distribution remains narrow ($\leq 9\%$ standard deviation in particle diameter).
Figure 2-6. FE-SEM micrographs of (a) PEDOT@MSS$_{670}$, (b) PEDOT@MSS$_{550}$, and (c) PEDOT@MSS$_{330}$ materials after etching with HF$_{(aq)}$. $V_{\text{acc}} = 1.5$ kV.

Table 2-3. Diameters and standard deviations of the PEDOT@MSS composites before and after etching with hydrofluoric acid.

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<td>PEDOT@MSS$_{670}$</td>
<td>605</td>
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<td>PEDOT@MSS$_{550}$</td>
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<td>PEDOT@MSS$_{330}$</td>
<td>270</td>
<td>23</td>
<td>335</td>
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</table>

It is important to note that the HF treatment does not degrade the polymer backbone, as evidenced by infrared and UV-vis-NIR spectroscopy (Figure 2-7). In the FT-IR spectrum, the
majority of peaks are present in both the etched and unetched samples, while those that are
absent in the etched sample are typical of the silica host. In the UV-vis-NIR spectrum, the
copolaron/bi-polaron bands in the NIR region do not change in intensity. The only change in the
spectrum is at higher energies, where the decrease in intensity is most likely due to a decrease in
Rayleigh scattering in the etched sample. The conductivity of the etched samples is also only
very slightly different than that of the un-etched material ($\sigma = 0.018 \pm 0.004$ S cm$^{-1}$).

**Figure 2-7.** (a) FT-IR spectra of the PEDOT@MSS$_{670}$ material before (top) and after (bottom)
etching with 25% HF$_{\text{(aq)}}$. The spectra have been vertically offset for clarity. (b) Normalized UV-
vis-NIR spectra of PEDOT@MSS$_{670}$ material before (solid line) and after (dashed line) etching
with 25% HF$_{\text{(aq)}}$

The complete removal of the silica host is verified by both TGA and EDX analyses. TGA
shows complete decomposition ($\geq 99\%$ mass loss) for all samples (Figure 2-8), while the
elemental composition ascertained by EDX reveals that less than 1% (w/w) Si remains (Table
2-4). The polymer particles can be redispersed in alcohols such as methanol and ethanol without
noticeable loss of integrity of the sphere. The morphology can therefore be retained, even after
multiple redispersion/centrifugation cycles, drying at elevated temperatures (60 °C) and
placement in the ultra-high-vacuum environment of the SEM.
Table 2-4. Elemental analysis of the PEDOT@MSS composites after etching with hydrofluoric acid.

<table>
<thead>
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<th>Energy Dispersive X-ray Microanalysis</th>
<th>Combustion Analysis</th>
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</table>

Figure 2-8. Thermogravimetric analysis for PEDOT@MSS$_{670}$ (solid line), PEDOT@MSS$_{550}$ (dashed line), and PEDOT@MSS$_{330}$ (dashed-dotted line) after etching with 25% HF$_{(aq)}$.

2.3.4 Fabrication and Characterization of a PEDOT@MSS Opal Film

In order to demonstrate the utility of these materials for potential optoelectronic applications, a colloidal crystal was fabricated. It was found that due to surface roughness and some particle aggregation, the PEDOT@MSS$_{550}$ material yielded only poor quality photonic crystals. The quality of crystalline material could be vastly improved by using a 30% (v/v) solution of EDOT
in toluene to initially fill the pores of the MSS$_{550}$ silica. This leaves the pores 30% filled with EDOT, and 70% filled with toluene. The toluene can be preferentially removed by evaporation at 60 °C, and the EDOT polymerized by treatment with sodium persulfate, yielding spheres with approximately a 30% pore filling fraction.

The colloidal crystal was deposited as an opaline film on a glass substrate using the assisted vertical deposition technique.$^{22-24}$ This technique is known to produce good quality opals of uniform thickness, and is illustrated in Figure 2-9. In summary, a clean glass slide is immersed vertically in an ethanolic colloidal dispersion of the material to be deposited. The ethanol wets the glass substrate, forming a meniscus. Due to the increased surface area, evaporation is fastest at the meniscus; however, this necessitates that there be a continual upwards flow of material to replenish the meniscus and prevent it from completely disappearing. This upward flow brings colloidal material with it, which then self-assembles at the ethanol–glass interface. As the level of solution drops, the self-assembled opal film is left behind on the glass substrate. In order to successfully form an opal film on the glass slide, the colloidal dispersion must be stable over the course of days or weeks; if the colloidal particles are too large, sedimentation begins to compete with self-assembly, leading to thin or patchy films. In order to use the vertical deposition technique with particles of diameter > 500 nm, the bottom of the dispersion is heated gently. This induces convection currents in the solution, which help keep the colloid suspended, while leaving the surface of the dispersion quiescent so that self-assembly can occur.
Figure 2-9. Schematic of the assisted vertical deposition setup (left); cartoon diagram showing the evaporation of the solvent from the meniscus and upwards flow of colloidal particles (right).

FE-SEM images of the film (Figure 2-10) clearly reveal the ordered nature of the colloidal crystal. For typical Stöber processed silica spheres, the vertical deposition technique produces crystals adopting the face centered cubic lattice where the (111) face is parallel to the substrate surface. The packing observed in the FE-SEM image is consistent with this arrangement; however, it is impossible to definitively assign the lattice without the observation of three perpendicular crystal faces which converge on a single sphere. The film thickness was determined to be 15 µm by analyzing a cross-section in the FE-SEM (Figure 2-10).
Figure 2-10. FE-SEM images of a PEDOT@MSS\textsubscript{550} colloidal crystal with a 30\% pore filling fraction; (a) view normal to the crystal surface, (b) cross-section of the crystal viewed at a 45° angle. V\textsubscript{acc} = 1.5 kV.

Figure 2-11. UV-vis-NIR spectrum of the PEDOT@MSS\textsubscript{550} colloidal crystal with a 30\% pore filling fraction.

The optical properties of the crystalline film were investigated by UV-vis-NIR spectroscopy (Figure 2-11). There is a broad peak in the NIR region of the spectrum (ca. 1100 – 2000 nm) for the PEDOT@MSS\textsubscript{550} colloidal crystal; this is due to PEDOT absorption and is also present in
disordered films of the same material. The photonic bandgap for this crystal is predicted by Equation 2-1 to be in the range of 1000 – 1200 nm, and is therefore obscured by the PEDOT NIR absorption band.

**Equation 2-1**

\[ \lambda = 2\sqrt[3]{\frac{2}{3}d \left(n_{eff}^2 \sin^2(\theta) \right)} \]

**Figure 2-12.** Schematic of the laser reflectance experiment.

Attempts to deconvolute the two peaks proved unsuccessful; however, evidence for the presence of a photonic bandgap can be obtained by measurement of the reflectance of the film (Figure 2-12). These spectra were obtained using a tunable Ti:sapphire laser as the source, and the angles of incidence were chosen such that the photonic bandgap coincides with the tunable range of the laser. A fibre optic probe coupled to a spectrometer was used to measure the incident wavelength, and the reflectance was obtained by simultaneously measuring the ratio of the incident and reflected beam intensities.
The observed peak is angle dependent, as expected for a Bragg diffraction peak (Figure 2-13). The position of the peak ($\lambda$) is also in good agreement with Equation 2-1, which describes the bandgap position for light incident on the (111) face of an fcc opal film. The peak wavelengths are consistent with a particle diameter ($d$) of 550 nm (determined from analysis in the FE-SEM), and an effective index of refraction ($n_{eff}$) of 1.21 (which can then be extracted from Equation 2-1).

![Normalized reflectance spectra for the PEDOT@MSS\textsubscript{550} colloidal crystal with a 30\% pore filling fraction at 40° (solid line), 45° (dashed line), and 50° (dashed-dotted line) angles of incidence.](image)

**Figure 2-13.** Normalized reflectance spectra for the PEDOT@MSS\textsubscript{550} colloidal crystal with a 30\% pore filling fraction at 40° (solid line), 45° (dashed line), and 50° (dashed-dotted line) angles of incidence.

### 2.4 CONCLUSIONS

In summary, PEDOT has been encapsulated in mesoporous silica spheres by a templated synthesis approach. This approach offers a number of important advantages in the preparation of conjugated polymer colloidal materials: the materials are monodisperse, with a complete suppression of secondary nucleation; they retain many of the advantageous properties of the silica host, including colloidal stability and self-assembly; at the same time, they also exhibit the
optoelectronic properties of the conjugated polymer (e.g., conductivity). Etching of the silica host with hydrofluoric acid offers an excellent route to pure PEDOT particles in the 0.1 – 1.0 µm size regime; the polymer spheres retain the spherical morphology and monodisperse character of the precursor material, unlike any other reports to date. The combination of these useful properties with self-assembly into opaline arrays is expected to allow for the construction of novel photonic crystal architectures based on electrochemically tunable opals.
2.5 REFERENCES


CHAPTER 3

INFLUENCE OF SURFACE MORPHOLOGY ON THE COLLOIDAL AND ELECTRONIC BEHAVIOR OF CONJUGATED POLYMER-SILICA MICROSPHERES

3.1 INTRODUCTION

The physical behavior of colloids is of importance to a wide variety of industries, including mineral processing, food technology, and cosmetics. Selective flocculation can be used to extract valuable minerals from waste effluent,\(^1\) while emulsifiers are often used in food and cosmetics in order to stabilize oil-in-water mixtures.\(^2\) With the recent emergence of opals and colloidal crystals as important materials in photonics,\(^3\) the study of colloidal microspheres has become increasingly important. In particular, developing methods for the synthesis and stabilization of these particles has taken on a renewed importance due to the stringent monodispersity and stability requirements that must be met in order for self-assembly to occur.

The most common methods of preparing colloidal particles that meet these requirements have been the Stöber-Fink-Bohn\(^4\) method of synthesizing monodisperse silica spheres and the emulsion polymerization technique\(^5,6\) for preparing polystyrene or polyacrylate latexes. Both of these methods produce particles that are spherical, monodisperse, and stable in dispersion. Few other materials possess these characteristics. Therefore, the assembly of colloidal crystals has been almost exclusively accomplished by first preparing a silica or polystyrene opal as a template.\(^7,8\) Direct assembly of colloidal crystals from other colloidal particles would be of great

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interest due to the sheer simplicity of the methodology; however, relatively few examples have been reported. The majority of these are high refractive index inorganic semiconductors such as TiO$_2$, ZnS, ZnSe, and CdS. Core-shell Se@$\text{Ag}_2\text{Se}$ particles were recently prepared by Jeong and Xia, and these particles exhibit a thermally switchable photonic band gap. Clusters of magnetite nanoparticles have also been assembled into a photonic band gap structure in the presence of an applied magnetic field. These examples illustrate the intriguing new properties that can result from expanding the range of colloidal materials to include a wider diversity of function.

In the previous chapter, the synthesis of a new PEDOT–mesoporous silica composite was described. The composite particles are spherical, monodisperse, and have a moderately large zeta potential; however, it was observed that well-formed colloidal crystals could only be prepared from composites with a lower PEDOT loading. The goal of the present study was to generalize the synthesis by determining what factors are integral to the synthesis of the conjugated polymer–silica composites. This should allow for the preparation of an even wider variety of colloidal materials – an important goal for the preparation of photonic crystals with novel properties. Even more important is the discovery of which factors govern the colloidal and electronic behavior of the composite particles. A thorough understanding of the factors that influence the colloidal behavior of such hybrid materials has to date been lacking and is investigated in this chapter by physical and electrophoretic measurements on a series of hybrid colloidal materials.
3.2 EXPERIMENTAL

3.2.1 General

Materials and Equipment. EDOT was donated by Bayer under the trade name Baytron-M. The EDOT was vacuum distilled prior to use, and stored at 4 °C under nitrogen. N-Methylpyrrole was similarly purified after purchase from Sigma-Aldrich. 2-Bromothiophene, magnesium powder, and sodium persulfate were also purchased from Sigma-Aldrich and used as received. 1,3-Bis(diphenylphosphino)propane nickel(II) chloride was purchased from Strem Chemicals and used as received. 2,2’-Bithiophene was synthesized from 2-bromothiophene by a modified Kumada coupling using 1,3-bis(diphenylphosphino)propane nickel(II) chloride catalyst. The mesoporous silica spheres were prepared according to an established procedure by Toyota Central R & D Labs, Inc., and were dried under vacuum at 120 °C prior to use. UV-vis-NIR spectra were recorded as ethanolic dispersions in a 1 cm quartz cuvette on a Varian Cary 5000 spectrophotometer. Pore volumes were measured on a Quantachrome Autosorb-1 analyzer at 77 K using nitrogen gas. Thermogravimetric analysis was performed on a Pyris 6 analyzer. Powder X-ray diffraction data were recorded on a Bruker D8 Advance X-ray diffractometer in the Bragg-Brentano configuration, using copper Kα radiation at 40 kV, 40 mA. Drop-cast films on glass microscope slides were prepared and resistivity measurements were made using the four-point probe technique. The film thicknesses were determined by cross-sectional analysis in the FE-SEM.

Scanning Electron Microscopy. Dilute suspensions of colloidal material (ca. 1 mg mL⁻¹) were prepared in ethanol by ultrasonication. An aliquot (100 µL) of this suspension was drop-cast on an aluminum stub and allowed to dry. Microscopy was carried out on a Hitachi S4700 scanning electron microscope equipped with a cold field-emission electron gun and pinhole objective lens. Accelerating voltages of 1.5 – 5.0 kV were chosen in order to provide a balance
between image resolution, charging effects, and surface penetration. Sputter coating was carried out using a Cressington 208HR sputter coater. Particle diameters were determined by measuring the diameter of a minimum of 200 particles in the FE-SEM. Energy dispersive X-ray microanalysis was carried out on a Hitachi S3000-N scanning electron microscope operating at 20.0 kV.

**Electrokinetic Measurements.** Measurements of electrophoretic mobilities were made on a Beckman-Coulter Delsa 440SX instrument. Samples were measured at a particle concentration of 0.01% (w/w) in 0.010 M aqueous sodium chloride matrix. The pH was adjusted prior to measurement by addition of either HCl\(_{(aq)}\) or NaOH\(_{(aq)}\) as required. All measurements were taken at 25.0 ± 0.1 °C. The Smoluchowski equation was used to relate the experimentally determined electrophoretic mobilities to the zeta potential.

### 3.2.2 Synthesis

**Preparation of PEDOT-\(n\)@MSS.** A sample of MSS (0.100 g) was dried in a Schlenk tube and placed under a nitrogen atmosphere. A solution of \(n\)% (v/v) EDOT in toluene was prepared \((n = 10 – 100)\). Enough of the solution to completely fill the mesopores of the silica (88 µL, 0.117 g, 0.823 mmol) was added by micropipette, and the mixture agitated with a spatula for 6 – 7 min. The powder was transferred to a clean vial and dried at 60 °C for 1 hour, after which a solution of sodium persulfate (0.15 g, 0.63 mmol) in water (3.00 mL) was added. The mixture was stirred overnight, and the solid isolated by centrifugation. The solid was washed with distilled water (3 × 15 mL) and ethanol (1 × 15 mL) by redispersion/centrifugation cycles, and dried at 60 °C overnight to yield the product as a midnight-blue powder.

**Preparation of PT-\(n\)@MSS.** A sample of MSS (0.100 g) was dried as described previously. A solution of \(n\)% (v/v) 2,2’-bithiophene in toluene was prepared \((n = 10 – 100)\). The solution
addition, drying, oxidation, isolation and purification steps were the same as for the PEDOT materials, except for the amount of oxidant added (0.30 g). Also, for higher volume percentages of bithiophene (> 50%), the sample was first melted at 100 °C prior to transfer.

**Preparation of PMePy-n@MSS and PPy-100@MSS.** These materials were prepared, isolated, and purified in the same way as the PEDOT samples, except that methanol was used as the solvent for the N-methylpyrrole solutions and the samples were dried at 45 °C instead of 60 °C.

### 3.3 RESULTS AND DISCUSSION

#### 3.3.1 Preparation of PEDOT, PT, PPy, and PMePy@MSS Composites

The mechanism by which PEDOT remained isolated within the pores of the MSS host during the polymerization process was unknown up to this point. One possibility was the insolubility of the organic monomer in the aqueous reaction medium. Other possibilities included the capillary forces of the mesoporous silica, which trap the monomer inside the host, or a high rate constant for polymerization, whereby the rate of polymerization is more rapid than the rate of monomer diffusion. Understanding why the monomer polymerizes inside the pores, rather than diffusing into the bulk solution, is important in the design of other host–guest colloidal materials. In order to probe the role of the monomer in the preparation of the polymer@MSS composites, four different composites were prepared with various guest polymers. Poly(3,4-ethylenedioxythiophene), poly(thiophene), poly(pyrrrole), and poly(N-methylpyrrole) (PMePy) (Chart 3-1) were all encapsulated within the mesopores of the MSS host by an in situ polymerization procedure similar to that described in the previous chapter.
The PEDOT@MSS composite was prepared as a reference. Unsubstituted polythiophene was also chosen as a guest polymer; this was due to the higher oxidation potential and insolubility in water (< 0.02 g L\(^{-1}\)) of the 2,2'-bithiophene monomer. Both pyrrole and N-methylpyrrole were studied as monomers. They not only have much lower oxidation potentials than those of EDOT, but also much higher solubilities in water (60 and 13 g L\(^{-1}\), respectively, compared to 2.1 g L\(^{-1}\) for EDOT).
The MSS hosts used in this work had a mean diameter of 746 ± 30 nm (Figure 3-1). The synthesis of the composites, briefly described, involves drawing the appropriate monomer (EDOT, 2,2'-bithiophene, pyrrole, or N-methylpyrrole) into the pores of the mesoporous silica host by capillary action. The monomer is then polymerized by the addition of an aqueous oxidant (sodium persulfate). This is illustrated in Scheme 3-1. In order to prepare the unsubstituted thiophene analogue, the use of 2,2'-bithiophene was necessary; attempts to polymerize thiophene within the pores of the MSS host were unsuccessful.
Figure 3-1. FE-SEM micrograph of the MSS host. The sample was sputter coated with a 5 nm thick layer of gold prior to imaging. \( V_{acc} = 5.0 \) kV.

Field-emission scanning electron microscopy yields important information about the surface morphology of the composite particles. Low accelerating voltages (1.5 kV) were used in acquiring the micrographs in order to reveal as much surface texture as possible, and the micrographs are shown in Figure 3-2. Clearly visible in the PPy@MSS sample are globular polymer clumps that are unattached to any silica particle. Since the diameter of this particulate is much greater than that of the silica mesopores (ca. 300 nm compared to ca. 3 nm), this can only be the result of monomer that polymerized either in bulk solution or on the surface of the silica spheres, as opposed to inside the pores. In contrast, no unattached polymer is observed in the PMePy@MSS sample. This can perhaps best be explained in terms of the solubility of the monomer. As mentioned previously, the solubility of pyrrole in water is moderate (60 g L\(^{-1}\)), while methylation of the heterocyclic nitrogen results in a compound that is much less water soluble. Thus, it is believed that a significant amount of pyrrole originally localized within the mesopores of the silica rapidly diffuses into the aqueous polymerization medium. This diffusion must be much more rapid than the rate of polymerization, since the final product resembles silica particles embedded in a polypyrrole matrix. In the case of PMePy, because the solubility of the
monomer is several times lower, it is believed that much less of the monomer diffuses into solution. This explains the lack of unattached polymer in the FE-SEM micrograph. There are, however, surface defects which are visible; large, aspherical bumps appear on the surface of some particles but not others. These are thought to be caused by either the limited amount of monomer diffusion which does occur or the surface polymerization of adsorbed monomer. The surfaces of the PEDOT and PT analogues are much more homogeneous in comparison, as the monomers for these materials have extremely poor solubility in water. The surfaces of the PEDOT and PT composite particles do exhibit some surface roughness on the nanometer length scale, as seen from the higher magnification micrographs. This is due to the presence of a polymer surface layer and may be caused by the polymerization of surface adsorbed monomer. The PEDOT@MSS surface appears to consist of nanometer scale fibers, whereas the PT@MSS surface appears bumpy due to the presence of a more globular polymer layer. These more subtle differences may be due to either the slight differences in solubility or the small differences in capillary forces and surface tension caused by the ethylenedioxy functional group. Clearly, however, the most critical factor in preparing spherical, monodisperse colloidal materials by this template approach appears to be the insolubility of the monomer in water.
Figure 3-2. FE-SEM micrographs of (a) PPy@MSS, (b) PMePy@MSS, (c) PEDOT@MSS, and (d) PT@MSS. White arrows indicate (a) unattached polypyrrole and (b) poly(N-methylpyrrole) present as an inhomogeneous surface defect. $V_{\text{acc}} = 1.5$ kV.

3.3.2 Variation of Pore Filling

To understand the behavior of these composite materials, it is clearly important to gain knowledge of how the polymer loading affects both the optoelectronic and colloidal properties. In order to address this question, varying amounts of monomer were used in the pore filling mixture. This resulted in composite particles where the pores range from completely empty to completely full. Since well defined PPy@MSS composites could not be successfully prepared, these studies were not carried out using pyrrole. The synthesis of these partially filled composites was accomplished by diluting the appropriate monomer with either toluene (for
EDOT and 2,2′-bithiophene) or methanol (for N-methylpyrrole). The monomer was diluted, rather than simply added to the silica, in order to obtain homogeneous composites; Figure 3-3 illustrates how the addition of undiluted monomer could lead to inhomogeneities in the final material. The partially-filled composites are denoted as PEDOT-$n$@MSS, PT-$n$@MSS and PMePy-$n$@MSS, where $n$ is the percentage of monomer (v/v) in the filling mixture.

**Figure 3-3.** (a) Addition of a small amount of pure monomer (yellow) may lead to a mixture of completely full and completely empty mesopores; (b) addition of monomer diluted with solvent (blue) leads to homogeneous pore filling.

The filling of the mesopores with the guest polymers was confirmed by both powder X-ray diffraction and nitrogen adsorption studies. In the small angle region of the powder X-ray diffraction pattern, the mesoporous silica hosts exhibit a prominent diffraction peak due to the highly ordered nature of the hexagonal mesopores. The high electron density contrast between the pore walls and the pore interior is responsible for the clear visibility of the peak; thus, by filling the pores with organic material, the peak intensity is expected to decrease. This is the observed behavior for the PEDOT, PT, and PMePy samples, as shown in Figure 3-4. The intensity of the peaks clearly decreases with increased pore loading for both the PEDOT-
n@MSS and PT-n@MSS materials, indicating filling of the mesopores. In the case of the PMePy-n@MSS samples, the peak intensity decreases sharply for the first 10% – 30% pore filling, but rapidly reaches a constant intensity for the samples with higher polymer loading. This would seem to indicate that initially the N-methylpyrrole polymerizes inside the mesopores but that additional polymer simply accumulates on the surfaces of the particles. This is in keeping with the surface polymer defects observed in the FE-SEM (Figure 3-2b).

Figure 3-4. Powder X-ray diffraction patterns for (a) PEDOT-n@MSS, (b) PT-n@MSS, and (c) PMePy-n@MSS materials. n = 0 (purple line), 10 (dark blue line), 30 (blue line), 50 (green line), 70 (yellow line), 90 (orange line), and 100 (red line).

The nitrogen adsorption isotherms for PEDOT-n@MSS, PT-n@MSS, and PMePy-n@MSS samples (Figure 3-5) are in qualitative agreement with the results obtained from powder X-ray
diffraction. The total volume of adsorbed nitrogen decreases steadily for both the PEDOT-
$n$@MSS and PT-$n$@MSS samples. This trend continues until the pores have been completely
filled and the amount of adsorbed nitrogen is essentially zero. In the case of the PMePy-$n$@MSS
samples, the same trend as that in the powder X-ray diffraction data is observed, namely that the
actual filling of the pores rapidly reaches a limiting value. From (Figure 3-5c) this limiting value
is approximately 50% filling of the total pore volume and is first observed for the PMePy-
50@MSS sample.
Figure 3-5. Nitrogen adsorption isotherms for (a) PEDOT-$n$@MSS, (b) PT-$n$@MSS, and (c) PMePy-$n$@MSS materials. $n = 0$ (purple line), 10 (dark blue line), 30 (blue line), 50 (green line), 70 (yellow line), 90 (orange line), and 100 (red line).

The polymer loading in the composite materials is closely correlated to the amount of monomer introduced in the filling mixture, as revealed by TGA. Figure 3-6a shows the amount of polymer present (as determined by TGA) as a function of percent monomer in the filling mixture. The individual TGA curves are shown in Figure 3-6b-d. While all polymers exhibit a similar temperature for the onset of decomposition (ca. 250 – 300 °C), and subsequently completion of decomposition (ca. 600 – 700 °C), the amount of polymer ultimately incorporated in the composite varies with the polymer type. For each data point, the amount of polythiophene incorporated is similar to, but greater than, the amount of poly(3,4-ethylenedioxythiophene)
incorporated, while the amount of poly(N-methylpyrrole) incorporated is about half that of the polythiophene analogue. These trends closely mirror those of the monomer solubility, with 2,2'-bithiophene being least soluble in water, EDOT being very sparingly soluble, and N-methylpyrrole having moderate solubility. One plausible explanation for this behavior is that during the polymerization process, monomer dissolves and diffuses from the mesopores. It can then either polymerize in the bulk (seen in the polypyrrole composite), polymerize at the particle surface to form a surface layer, or remain as either monomer or low molecular weight oligomers. These oligomers are then likely washed away during the workup process, resulting in the lower polymer mass percentage observed for the PEDOT and PMePy composites. For a given polymer, the polymer loading in the composite increases monotonically up to approximately 50% pore filling; thereafter, the composite’s polymer loading reaches a limiting value corresponding to complete filling of the mesopores.
Figure 3-6. (a) Mass percentage of polymer in the composite materials (as determined by TGA) as a function of the amount of monomer in the filling mixture (pore filling percentage, n). Data for PEDOT-\(n\)@MSS are shown as circles, PT-\(n\)@MSS as squares, and PMePy-\(n\)@MSS as triangles. TGA curves for the (b) PEDOT-\(n\)@MSS, (c) PT-\(n\)@MSS, and (d) PMePy-\(n\)@MSS composites.

The polymer loadings measured by TGA are confirmed by elemental analysis. This was accomplished by both EDX and combustion analysis, and the results for the PEDOT-\(n\)@MSS, PT-\(n\)@MSS, and PMePy-\(n\)@MSS materials are tabulated in Table 3-1, Table 3-2, and Table 3-3, respectively. These data are in agreement with the analysis by TGA, and the trend towards decreasing polymer content with decreased monomer loading is evident from the decrease in the carbon, sulfur, and nitrogen content with decreasing values of \(n\). Due to the poor sensitivity of
the EDX technique to low-Z elements such as carbon and nitrogen, and the absorption of carbon and nitrogen characteristic X-rays by higher Z components of the matrix (e.g., silicon), no carbon and nitrogen could be detected for several of the samples. This occurred when the element was present in low abundance (< 5%), as determined by combustion analysis.

**Table 3-1.** Elemental analysis of the PEDOT-$n$@MSS composite materials.

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<tr>
<th>$n$</th>
<th>%C [w/w]</th>
<th>%S [w/w]</th>
<th>%Si [w/w]</th>
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**Table 3-2.** Elemental analysis of the PT-$n$@MSS composite materials.

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<td>43</td>
<td>12.90</td>
<td>1.90</td>
</tr>
<tr>
<td>30</td>
<td>21</td>
<td>4</td>
<td>18</td>
<td>57</td>
<td>13.03</td>
<td>1.93</td>
</tr>
<tr>
<td>10</td>
<td>N/D</td>
<td>3</td>
<td>40</td>
<td>57</td>
<td>3.92</td>
<td>1.64</td>
</tr>
</tbody>
</table>

N/D: Not Detectable.
Table 3-3. Elemental analysis of the PMePy-\(n\)@MSS composite materials.

<table>
<thead>
<tr>
<th>(n)</th>
<th>(% C\ [w/w])</th>
<th>(% N\ [w/w])</th>
<th>(% Si\ [w/w])</th>
<th>(% O\ [w/w])</th>
<th>(% C\ [w/w])</th>
<th>(% H\ [w/w])</th>
<th>(% N\ [w/w])</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>10</td>
<td>N/D</td>
<td>35</td>
<td>54</td>
<td>10.51</td>
<td>2.46</td>
<td>2.34</td>
</tr>
<tr>
<td>90</td>
<td>12</td>
<td>N/D</td>
<td>27</td>
<td>61</td>
<td>11.94</td>
<td>2.66</td>
<td>2.69</td>
</tr>
<tr>
<td>70</td>
<td>10</td>
<td>N/D</td>
<td>35</td>
<td>55</td>
<td>9.05</td>
<td>3.09</td>
<td>1.99</td>
</tr>
<tr>
<td>50</td>
<td>10</td>
<td>N/D</td>
<td>33</td>
<td>58</td>
<td>9.21</td>
<td>1.90</td>
<td>1.98</td>
</tr>
<tr>
<td>30</td>
<td>N/D</td>
<td>N/D</td>
<td>39</td>
<td>61</td>
<td>5.04</td>
<td>1.71</td>
<td>1.05</td>
</tr>
<tr>
<td>10</td>
<td>N/D</td>
<td>N/D</td>
<td>39</td>
<td>61</td>
<td>0.56</td>
<td>2.26</td>
<td>0.05</td>
</tr>
</tbody>
</table>

N/D: Not Detectable

Investigations were also carried out to determine how the variation of the pore filling fraction affects the optoelectronic properties of the composite. The electronic structure of the composites was probed by UV-vis-NIR spectroscopy (Figure 3-7). The absorption spectra of the PEDOT composites are all quite similar; they feature a NIR absorption band centered at ca. 800 nm and a stronger absorption extending deep into the infrared. Both of these features scale with the amount of PEDOT present in the composite, and can be assigned to PEDOT polaron or bipolaron bands.\(^{19, 20}\) Notably absent (or unresolvable) is the PEDOT \(\pi - \pi^*\) band. These data suggest the PEDOT is heavily p-doped. This is in marked contrast to the polythiophene-based materials, which all display a \(\pi - \pi^*\) absorption band at ca. 500 – 600 nm; there is also no evidence of a NIR polaron absorption.\(^{20, 21}\) Additionally, the PT-\(n\)@MSS composites exhibit a sharply sloped baseline at higher energies, which is characteristic of Rayleigh scattering. This Rayleigh scattering background is the only feature observed in the spectra of the PMePy-\(n\)@MSS materials. This is likely due to the lower polymer loading in these samples; the conjugated polymer is the only chromophore in the composite, and at low loadings no peaks are discernable.
Figure 3-7. UV-vis-NIR absorbance spectra for the (a) PEDOT-$n$@MSS, (b) PT-$n$@MSS, and (c) PMePy-$n$@MSS materials. $n = 10$ (dark blue line), 30 (blue line), 50 (green line), 70 (yellow line), 90 (orange line), and 100 (red line).

One of the key electronic characteristics of $\pi$-conjugated polymers such as PEDOT, PT, and PMePy is their conductivity when p-doped. Films of each of the colloids were prepared by drop-casting suspensions onto glass microscope slides, and the sheet resistance was measured using the four-point probe technique. Unfortunately, both the polythiophene and poly($N$-methylpyrrole) samples had resistances that were too high to be measured using this technique, and the only data that could be obtained was for the PEDOT-based materials. The low conductivity for the PT samples is likely a function of the doping level of the polymer. The
electronic absorption spectrum of the PT-100@MSS material clearly indicates that the polythiophene is either undoped or has a very low doping level. The conductivities for undoped conjugated polymers are typically in the range of $10^{-8} - 10^{-12}$ S cm$^{-1}$, well below the detection level of the instrument. The lack of doping is unsurprising, given that the oxidation potential for PT is higher than that of either PEDOT or PMePy. In the case of PMePy, it is believed that the high resistance is due to the polymer being largely isolated within the mesopores of the silica. Evidence for this can be found from the particle size distributions. The average particle diameters for the PEDOT-100, PT-100, and PMePy-100@MSS samples were found to be 759 ± 24, 781 ± 24, and 744 ± 32 nm, respectively. This suggests that there is a 10 – 30 nm thick polymer shell surrounding the PEDOT-100@MSS and PT-100@MSS samples. In the case of the PMePy analogue, which has a much lower polymer loading, the particle diameter is indistinguishable from that of the silica host. With the conducting polymer isolated inside the insulating host, the overall conductivity of the material is negligible.

Reliable conductivity data could, nonetheless, be obtained for the PEDOT-$n$@MSS samples (Figure 3-8). The conductivities obtained for the PEDOT-100@MSS, PEDOT-90@MSS, and PEDOT-70@MSS samples are all very similar at approximately 0.04 S cm$^{-1}$ ($\rho = 25$ Ω cm). This is consistent with the conductivity reported in the previous chapter for the PEDOT-100@MSS material. As the filling fraction of the mesopores decreases, however, the conductivity begins to drop sharply. By the 50% pore filling level, it has decreased by one order of magnitude to 0.004 S cm$^{-1}$ ($\rho = 250$ Ω cm), and the decrease is even more pronounced for the PEDOT-30@MSS sample, where $\sigma = 0.0006$ S cm$^{-1}$ ($\rho = 1650$ Ω cm). No data could be obtained for the PEDOT-10@MSS sample, indicating a very low value for the conductivity. This behavior can be explained by a simple model whereby the conductivity is primarily due to contact between the surface polymer layers on adjacent spheres. At high polymer loadings, the surface polymer layer
is reasonably thick, which leads to relatively high values for the conductivity. At the 30% and 50% loadings, this polymer shell is greatly diminished, and interparticle contacts are poor. Presumably, the 30% loading level is the lowest at which any polymer is present on the surface; at lower loading levels, all of the polymer is buried within the core of the mesoporous sphere. This is illustrated in Figure 3-8.

**Figure 3-8.** (a) Conductivity (red squares) and resistivity (black circles) as a function of pore filling percentage for the PEDOT-\(n\)@MSS materials. (b) Model for conductivity in PEDOT-\(n\)@MSS materials; charge can move between particles when a conductive polymer layer bridges adjacent particles (top), but not when the conductive polymer is surrounded by an insulating silica shell (bottom).

In order to provide support for this proposal, the surface morphology of each of the composites was examined as a function of pore filling fraction, \(n\). Micrographs of the PEDOT-\(n\)@MSS materials are shown in Figure 3-9. The surfaces of the particles in Figure 3-9a have a rough, fuzzy texture that is resolved by the FE-SEM; this texture is absent in the MSS hosts, and is presumably due to a PEDOT surface layer. The same surface texture can be observed in Figure 3-9b,c, and d, suggesting that in all samples there is PEDOT present on the surface of the particles. By the 30% filling fraction, the rough surface texture is partially replaced by a
smoother particle surface, and the PEDOT-10@MSS material has a surface that is entirely smooth. This suggests that it is at the 30% and 10% filling fractions that the polymer begins to be completely localized within the mesopores of the MSS host; this is consistent with the conductivity data reported above, and the hypothesis illustrated in Figure 3-8.

The same trend observed for the PEDOT-\textit{n}@MSS composites is also observed in the polythiophene analogues. Figure 3-10a shows a globular surface texture that presumably arises from polythiophene present on the surface of the MSS host. By the 30% filling fraction (Figure 3-10e), the surfaces of the particles are a mixture of textured and smooth; the PT-10@MSS materials show no visible surface morphology.

The PMePy-\textit{n}@MSS composites show less of a definite trend due to the lower overall polymer loading (vide supra). The FE-SEM micrograph of the PMePy-100@MSS material (Figure 3-11a) reveals that some particles have smooth surfaces, while other particles are rough and bumpy. This same trend is observed in most of the PMePy-\textit{n}@MSS samples, and it is only the PMePy-10@MSS sample (Figure 3-11f) for which the surfaces are completely smooth.
Figure 3-9. High magnification FE-SEM micrographs of (a) PEDOT-100@MSS, (b) PEDOT-90@MSS, (c) PEDOT-70@MSS, (d) PEDOT-50@MSS, (e) PEDOT-30@MSS, and (f) PEDOT-10@MSS.
Figure 3-10. High magnification FE-SEM micrographs of (a) PT-100@MSS, (b) PT-90@MSS, (c) PT-70@MSS, (d) PT-50@MSS, (e) PT-30@MSS, and (f) PT-10@MSS.
Figure 3-11. High magnification FE-SEM micrographs of (a) PMePy-100@MSS, (b) PMePy-90@MSS, (c) PMePy-70@MSS, (d) PMePy-50@MSS, (e) PMePy-30@MSS, and (f) PMePy-10@MSS.
3.3.3 Electrophoretic Measurements

The measurement of electrophoretic mobilities is a particularly useful technique for understanding a number of important properties of colloids, including surface charge and colloidal stability. The mobilities of the PEDOT-n@MSS, PT-n@MSS, and PMePy-n@MSS materials were measured as a function of both pH and pore filling fraction; the mobilities can then be used to calculate the zeta potential ($\zeta$) of each of the samples via the Smoluchowski equation (Equation 3-1). Here, $\mu$ is the electrophoretic mobility, $\varepsilon$ is the electrical permittivity of the medium, and $\eta$ is the viscosity of the medium.

\textbf{Equation 3-1}

$$\mu = \frac{\zeta \varepsilon}{\eta}$$

The Smoluchowski equation is an approximation valid for values of $\kappa r \geq 100$, where $\kappa$ is the Debye-Hückel parameter and $r$ is the particle radius.\textsuperscript{23, 24} Under the conditions chosen for measurement (10 mM NaCl$_{\text{aq}}$) and for the particle diameters in question (ca. 750 nm), $\kappa r > 100$, and the Smoluchowski equation should yield a reasonable approximation of the zeta potential. These potentials are plotted as a function of pH in Figure 3-12a and as a function of pore filling fraction in Figure 3-12b.
Figure 3-12. Zeta potential as a function of (a) pH, and (b) pore filling percentage (n). The MSS host is shown as hollow circles, the PEDOT-\(n\)@MSS composites as solid circles, the PT-\(n\)@MSS composites as squares, and the PMePy-\(n\)@MSS composites as triangles.

As can be seen from Figure 3-12a, the zeta potential of the PEDOT-100@MSS sample is relatively pH independent. The value ranges from approximately 30 – 40 mV across the entire pH range studied. The lack of an isoelectric point (IEP) and pH independence suggests that the origin of the positive charge is not derived from acid–base equilibria, as is often the case with typical colloidal materials. A more plausible explanation of this behavior is that the surface charge originates with the positive charge present in the conjugated polymer due to the formation of polarons or bipolarons. Further evidence for this can be obtained from the variation of \(\zeta\) with pore filling fraction. As shown in Figure 3-12b, the zeta potential for the PEDOT-100@MSS material is +39 mV. The materials with 90%, 70%, and 50% pore filling fraction also display a zeta potential of the same sign and roughly the same magnitude. The zeta potential of the PEDOT-30@MSS material, however, is essentially zero. At lower loadings, the sign of the zeta potential reverses; the negative potential indicates negatively charged surface groups. These results are consistent with the conductivity measurements (vide supra). At greater than 30% pore filling fraction, films of the particles display relatively high conductivity. This indicates that a p-
doped surface polymer layer is present. The positive charges localized in the polymer (in the form of either polarons or bipolarons) give rise to the positive zeta potential. At the 30% filling level, the resistivity of the sample increases sharply; this indicates that the surface polymer layer has been greatly reduced and that the sample is at the percolation threshold. The surface of the sphere is now likely a mixture of both positively charged polymer and negatively charged silanol groups. The two charges roughly balance, leading to a zeta potential of zero. Below this threshold, the PEDOT-10@MSS material displays essentially zero conductivity and a negative zeta potential characteristic of surface silanol groups. This hypothesis is supported by both UV-vis-NIR spectroscopy and particle size analysis by FE-SEM. As discussed previously, the lack of a π – π* absorption band and the presence of pronounced bands in the near-infrared are good evidence for polaron or bipolaron formation. Also, the diameter of the PEDOT-30@MSS material was determined to be 741 ± 23 nm. The fact that the diameter of the PEDOT-30@MSS sample is essentially indistinguishable from that of the silica host (746 ± 30 nm) is good evidence that it is at the 30% pore filling level that the silanol groups of the underlying silica host begin to become exposed.

The behavior of the polythiophene analogues is markedly different from that of their PEDOT counterparts. As indicated by the negative zeta potential, nonmeasurable conductivity, and pronounced π – π* absorption band, the polymer exists in its pristine, undoped state. Since the polymer itself is electrically neutral, and contains no particularly acidic functional groups, the origin of the negative zeta potential is at first unclear. As shown in Figure 3-12a, the value of ζ is strongly negative across the pH range studied. Even if the low pH region was heavily extrapolated, it is unclear whether an IEP would ever be reached. This behavior is atypical for the MSS host, which displays an IEP at a pH of approximately 3.5, and also for other examples of colloidal silica, which display IEPs in the pH range of 1.8 – 4.0.24-26 This suggests that the
origin of the negative zeta potential is not the silanol groups of the silica host. Rather, the pH independence of $\zeta$ for this sample is similar to that observed for polystyrene latexes synthesized using an anionic initiator such as ammonium persulfate.$^{23, 27}$ In these cases, the negative surface charge is due to either sulfonic acid polymer end-groups or residual sulfate anions tightly adsorbed to the latex surface. Since a stoichiometric amount of oxidant is required to facilitate the thiophene polymerization, it is very likely a similar mechanism is operative here. Due to their nature as extremely weak bases, the sulfonic acid groups or sulfate anions remain negatively charged even at the low pH end of the region studied.

The poly($N$-methylpyrrole) samples offer another interesting contrast. The samples are still negatively charged; however, the pH dependence is more pronounced than in the case of either the PEDOT or PT materials. Also, if the low pH end of Figure 3-12a is extrapolated slightly, this material may be expected to display an IEP at a pH of approximately 2.0. Due to the low polymer content in these samples (see Figure 3-6), and the fact that there is no significant polymer surface layer observed in the FE-SEM micrographs (Figure 3-11), it seems reasonable to suggest the negative zeta potential is at least partially due to the deprotonation of surface silanol groups. Both the gradual decrease in $\zeta$ with increasing values of $n$ and the shift of the IEP to a more acidic pH compared to the silica host are likely due to a small contribution to $\zeta$ from adsorbed sulfate anions. This effect is far less pronounced than in the case of the polythiophene analogues due to the much lower surface coverage of the microspheres by poly($N$-methylpyrrole).

Also of note is that all three data sets shown in Figure 3-12b begin to converge on a zeta potential of approximately $-16$ mV for low polymer loadings. This is quite similar to the potential observed for the silica host, indicating that, at low loadings, the zeta potential is dominated by the surface silanol groups of the silica host. This may explain the previously
observed phenomenon whereby good quality colloidal crystals could be formed from PEDOT-30@MSS materials with diameters of 550 nm, but only poor ordering was observed for higher polymer loadings. Even though these samples have a relatively small zeta potential, and would therefore be expected to flocculate by conventional Derjaguin-Landay-Verwey-Overbeek (DLVO) theory, it is the anomalously high stability of relatively uncharged colloidal silica surfaces\textsuperscript{28-33} that appears to stabilize the dispersions. Some researchers initially postulated that this colloidal stability is due to a highly ordered layer of water at the particle interface,\textsuperscript{28,30} while others have more recently proposed that the presence of a “hairy” partially dissolved polysilicic acid layer gives rise to increased steric stabilization.\textsuperscript{31-33} Regardless of the exact mechanism of stability, the fact that insoluble, unprocessable materials with large Hamaker constants\textsuperscript{34} can be encapsulated by mesoporous silica spheres and subsequently processed as stable colloidal dispersions is an important advancement.

### 3.4 CONCLUSIONS

The major goals of this research were to identify key design criteria for the synthesis of polymer–mesoporous silica composites, generalize the synthesis to a range of other conjugated polymers, and subsequently understand how to balance the desirable colloidal properties of the silica host with the electronic properties of the polymer guest. Clearly, the insolubility of the monomer and polymer in the aqueous polymerization medium is important for the preparation of the polymer–silica composites. This is a particularly interesting point in that it turns a major disadvantage of organic conjugated polymers, that is, their inherent hydrophobicity and insolubility, into a decisive advantage in terms of their processing. This development could potentially lead to greener approaches for materials synthesis and the replacement of volatile organic solvents with aqueous media. Additionally, it opens up a route into colloidal
preparations of previously unprocessable materials, such as unsubstituted polythiophenes. The understanding of the factors affecting the colloidal properties for the PEDOT, PT, and PMePy composites, namely, the polymer doping, anion adsorption, and silanol deprotonation, respectively, is expected to aid in the preparation of more stable colloids. This in turn may lead to enhanced self-assembly into colloidal crystals and therefore higher quality crystalline films.
3.5 REFERENCES


CHAPTER 4

NANOSCALE CONTROL OVER PHASE SEPARATION IN CONJUGATED POLYMER BLENDS USING MESOPOROUS SILICA SPHERES

4.1 INTRODUCTION

Polymer blends and composites have found extensive use as coatings,¹, ² biomedical tissue scaffolds,³ fuel cell membranes,⁴ and conductive films.⁵ Through judicious choice of the constituent polymers and their relative mole fractions, a variety of properties can be realized in the final film.⁶ These range from desirable mechanical properties such as elasticity and toughness to optoelectronic properties such as conductivity and luminescence. This breadth of function is due to the wide range of possible polymeric components. Blending two polymers with complementary properties is one approach to ameliorating detrimental properties and enhancing the overall usability of a material. Conductive elastomers,⁷, ⁸ ferroelectric semiconductors,⁹ and mechanically stabilized dielectrics¹⁰ have all been prepared in this manner. This approach has a number of advantages over the synthesis of various copolymers or block copolymers in that no additional chemical synthesis is required. Libraries of commercially available polymers can be combined in an extremely simple and rapid fashion, leading to an extremely broad and versatile set of possible functionality.

These blends are typically prepared by casting the two polymers from a common solvent, whether by drop casting, spin coating, or some other technique. Due to the low entropy of mixing for most polymers the resultant blend may not be completely homogeneous; the drying

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process results in separation of the two polymers into distinct phase domains. This process is extraordinarily complex, and is controlled by factors such as the relative solubility of the two polymers in the common solvent, evaporation rates, annealing times, polymer miscibility, and substrate interactions. This means that control over the size and distribution of these domains is non-intuitive, and film morphologies must typically be optimized by an iterative trial and error process.

The issue of phase separation is particularly pronounced for conjugated polymer blends. These can be extremely useful in organic devices such as field effect transistors, organic light emitting diodes, memory storage elements and photovoltaic cells. In particular, photovoltaics based on polymer blends have received much attention due to the high efficiencies that can be achieved. These bulk heterojunction devices rely on the excitons generated upon irradiation being separated into electrons and holes at the interface of the two different semiconducting polymers; however, the exciton diffusion radius is quite short (on the nanometer length scale). Thus, coarse phase domains (relative to the exciton diffusion radius) will result in many excitons decaying back to the ground state before a phase boundary is reached. Similar results were obtained in the study of OLEDs based on p- and n-type semiconducting polymers arranged in a bilayer structure; the size and shape of the phase domains play a huge role in dictating device behavior. The lack of a suitable methodology for controlling this phase separation in a predetermined fashion has meant that most devices are necessarily fabricated by trial and error, and many subsequent optimization steps are necessary in order to achieve optimal device performance.

Recent work on conjugated polymer nanoparticles suggests a partial remedy to this problem. Barnes et al. prepared polymer blend microparticles by rapid evaporation of solvent from a microdroplet of dilute polymer blend solution and examined their phase separation behavior.
Homopolymer and polymer blend microparticles can also be produced in a variety of particle diameters by a miniemulsion process. The benefit of these approaches is that by blending two different polymers within an individual nanoparticle, phase separation is initially limited to the dimensions of a single particle diameter. This methodology provides good efficiencies when films based on the blended nanoparticles are incorporated into organic electronic devices. The nanoparticles can be further mixed with other colloidal dispersions, resulting in statistical mixtures of conjugated and non-conjugated beads. The approach has also recently been extended to provide insight into the early stages of phase separation in polystyrene–poly(methyl methacrylate) blends.

The goal of this chapter is to evaluate whether the MSS hosts can be used as structure-directing agents for the formation of polymer blend microparticles, and to determine the effect of this approach on the phase separation of the constituent polymers. Due to the spatial constraints imposed by the mesopore walls, phase separation can conceptually be limited to dimensions of no more than the overall pore diameter — 3 nm — which is well within the exciton diffusion radius of most semiconducting polymers.

4.2 EXPERIMENTAL

4.2.1 General

Materials and Equipment. EDOT was donated by Bayer under the trade name Baytron-M. The EDOT was vacuum distilled prior to use, and stored at 4 °C under nitrogen. Sodium persulfate and furfuryl alcohol were purchased from Sigma-Aldrich and used as received. Hydrofluoric acid (49%) was purchased from Fisher Scientific and used as received. The mesoporous silica spheres were prepared according to an established procedure by Toyota Central R & D Labs, Inc., and were dried under vacuum at 120 °C prior to use. Pore volumes
were measured on a Quantachrome Autosorb-1 analyzer at 77 K using nitrogen gas. Thermogravimetric analysis was performed on a Pyris 6 analyzer. Drop-cast films on glass microscope slides were prepared and resistivity measurements were made using the four-point probe technique. The film thicknesses were determined by cross-sectional analysis in the FE-SEM.

X-ray Photoelectron Spectroscopy (XPS). XPS analyses were carried out on a Leybold Max200 spectrometer using an aluminum $K_α$ X-ray source ($Al\,K_α = 1486.6\,eV$) and operating at a base pressure of $1\times10^{-9}\,Torr$. Initial survey scans were acquired with a pass energy of 192 eV, while higher resolution scans were acquired with a pass energy of 48 eV. Spectra were referenced to the C 1s peak at 285 eV. Peak fitting was carried out using the XPSpeak v4.1 software package; Shirley background corrections were applied and Gaussian/Lorentzian peak shapes were used. Atomic percentages were converted to weight percentages for ease of comparison with the EDX data.

Scanning Electron Microscopy. Dilute suspensions of colloidal material (ca. 1 mg mL$^{-1}$) were prepared in ethanol by ultrasonication. An aliquot (100 µL) of this suspension was drop-cast on an aluminum stub and allowed to dry. Microscopy was carried out on a Hitachi S4700 scanning electron microscope equipped with a cold field-emission electron gun and pinhole objective lens. An accelerating voltage of 1.5 kV was chosen in order to provide a balance between image resolution, charging effects, and surface penetration. Particle diameters were determined by measuring the diameter of a minimum of 200 particles in the FE-SEM. Energy dispersive X-ray microanalysis was carried out on a Hitachi S3000-N scanning electron microscope operating at 20.0 kV.
**Transmission Electron Microscopy.** Dilute suspensions of colloidal material (ca. 1 mg mL$^{-1}$) were prepared in ethanol by ultrasonication. An aliquot (2 µL) of this suspension was drop-cast on a carbon-coated 300-mesh copper TEM grid and allowed to dry. Microscopy was carried out on an FEI Tecnai G2 transmission electron microscope equipped with a field emission electron gun and a super-twin objective lens. An accelerating voltage of 200.0 kV was applied. EDX analysis was carried out in scanning TEM mode with a beam diameter of ≤ 2.0 nm.

4.2.2 **Synthesis**

**PEDOT@MSS Synthesis.** The PEDOT@MSS composite material was prepared using a 25% (v/v) solution of EDOT in toluene to fill the pores of the MSS host. The annealing, polymerization, and work-up procedures were the same as those described in the previous chapter.

**PEDOT/PFA@MSS Synthesis.** A sample of the PEDOT@MSS composite (0.239 g) was placed in a Schlenk tube and dried in vacuo at 85 °C for 2 h. The atmosphere was replaced with nitrogen gas, and enough furfuryl alcohol to completely fill the remaining pore volume of the MSS host (90 µL) was added. The mixture was agitated with a spatula for 6 min, and the monomer was polymerized by heating at 150 °C for 3.5 h. This yielded the PEDOT/PFA@MSS composite as a green-black powder (0.32 g).

**PFA@MSS Synthesis.** Mesoporous silica spheres (0.255 g) were placed in a Schlenk tube and dried in vacuo at 120 °C for 2 h. The atmosphere was replaced with nitrogen gas, and a 1:1 (v/v) mixture of furfuryl alcohol and ethanol (200 µL) was added. The mixture was agitated with a spatula for 6 min, and the monomer polymerized by heating at 150 °C for 3.5 h. This yielded the PFA@MSS composite as a red-brown powder (0.43 g).
**PFA/PEDOT@MSS Synthesis.** The PFA@MSS composite (0.250 g) was placed in a Schlenk tube and dried in vacuo at 85 °C for 2 h. The atmosphere was replaced with nitrogen gas, and enough 3,4-ethylenedioxythiophene to fill the remaining pore volume (115 µL) added. The mixture was agitated with a spatula for 6 min, and the powder annealed at 60 °C for 1 h. After cooling to room temperature a solution of sodium persulfate (0.15 g) in water (3.00 mL) was prepared and added to the sample. The mixture was stirred for 16 h at room temperature, and the solid material isolated by centrifugation. The residue was washed by redispersion/centrifugation cycles with ethanol (1 × 15 mL), water (2 × 15 mL) and ethanol (1 × 15 mL), and then dried at 60 °C for 5 h to yield the PFA/PEDOT@MSS composite as a green-black powder (0.35 g).

**HF Etching.** A sample of the material to be etched was dispersed in ethanol (10 mL) by ultrasonication and transferred to a Teflon beaker. Aqueous hydrofluoric acid (49%, 10 mL) was added to the dispersion and the mixture stirred for 45 min. The solid material was isolated by centrifugation, and washed with water (4 × 15 mL) and ethanol (2 × 15 mL) by redispersion/centrifugation cycles. Drying at 60 °C for 5 h yielded the etched microparticles as a dry powder.

### 4.3 RESULTS AND DISCUSSION

#### 4.3.1 Synthesis of PEDOT/PFA@MSS and PEDOT/PFA Composites

The preparation of the polymer blend–silica composites was carried out by the sequential incorporation of the two individual polymers, PEDOT and poly(furfuryl alcohol) (PFA), into the mesoporous silica sphere templates (Scheme 4-1). Adsorbed moisture was first removed from the empty MSS host by drying at 120 °C in vacuo. The mesopores were then filled with a solution of EDOT in toluene (25% v/v). Annealing and polymerization were carried out as
described in Chapter 3. Once the partially filled PEDOT@MSS composite had been prepared and dried, the empty pore volume was measured (vide infra) and filled with furfuryl alcohol. The furfuryl alcohol was then polymerized by heating at 150 °C for 3.5 h to yield the PEDOT–PFA blend. Previous reports have demonstrated the polymerization of furfuryl alcohol within the mesopores of both zeolite Y\textsuperscript{24} and the MSS hosts,\textsuperscript{25} and shown that heating at 150 °C is sufficient to form polymeric chains, but low enough to avoid carbonization. The acidic silanol functionality of the MSS host may act as the acidic catalyst implicated in the polymerization process.\textsuperscript{26} Blended polymer microparticles were then prepared from the silica composites by removing the silica template using 25% hydrofluoric acid. These etching conditions were described in Chapter 2 and have been shown to etch only the silica host while leaving the conjugated polymer guest intact.

**Scheme 4-1**

The sequential incorporation of PEDOT and PFA into the mesopores was followed by measurement of the nitrogen adsorption isotherms at the end of each step (Figure 4-1). Initially,
the mesopores of the silica host are empty, and the MSS template displays a Type IV isotherm with a total pore volume of ca. 0.8 cm$^3$ g$^{-1}$. Partial filling of the pores with PEDOT reduces the total available pore volume by 50%, although the same Type IV isotherm is observed, indicating that the overall pore structure remains intact. Filling the remaining pore volume with PFA reduces the amount of adsorbed nitrogen to essentially zero, and the type III isotherm observed is typical of a macroporous or non-porous material. Notably, removal of the silica template only marginally increases the amount of nitrogen adsorbed, and the shape is still consistent with a type III isotherm. This suggests that some structural rearrangement occurs during the etching process; otherwise, removal of the silica support has been shown to produce a microporous starburst-like morphology.\textsuperscript{27}

\textbf{Figure 4-1.} Nitrogen adsorption isotherms for the empty MSS host (black circles), PEDOT@MSS composite (blue circles), PEDOT/PFA@MSS composite (red circles) and etched PEDOT/PFA microparticles (green circles).

The compositions of the polymer–silica and polymer blend microparticles were evaluated by thermogravimetric analysis. The TGA curves for the PEDOT@MSS, PEDOT/PFA@MSS and
PEDOT/PFA materials are shown in Figure 4-2. All three curves follow the same general trend of a small mass loss at 100 °C due to adsorbed moisture, followed by polymer decomposition between 250 and 650 °C. By measuring the mass loss between 200 and 700 °C, it can be determined that the PEDOT@MSS sample is approximately 22% PEDOT by mass; in comparison, the PEDOT/PFA@MSS sample is composed of 45% polymer. This suggests that the PEDOT/PFA@MSS blend contains PEDOT and PFA in a roughly 1:1 (w/w) ratio. Importantly, after etching with HF(aq), greater than 99% of the total mass of the polymer blend is lost by 900 °C, indicating complete combustion and the absence of any residual silica.

![Thermogravimetric analysis](image)

**Figure 4-2.** Thermogravimetric analysis of the PEDOT@MSS (blue line), PEDOT/PFA@MSS (red line) and PEDOT/PFA (green line) composites.

### 4.3.2 Particle Morphology

Field emission scanning electron microscopy was carried out on the composites in order to determine the effect of polymer blending on the morphology of the binary and ternary composites. As can be observed in Figure 4-3a, the PEDOT/PFA@MSS composite displays a similar overall morphology to the mesoporous silica template – the particles are spherical, near-
monodisperse in terms of their diameter, and no extraneous polymer is visible in the FE-SEM micrograph. The mean particle diameter is $745 \pm 22$ nm, which is essentially indistinguishable from that of the empty MSS host ($749 \pm 23$ nm); this suggests that all of the polymer is encapsulated within the mesopores of the silica. From Figure 4.3b, it can be seen that the surfaces of the PEDOT/PFA@MSS microparticles are relatively smooth, with few notable features that can be resolved by the FE-SEM (the dimple present on the left sphere is also typically found in the empty MSS host). FE-SEM and TEM micrographs of the etched particles are shown in Figure 4.3c-e. From the low-magnification micrograph shown in Figure 4.3c, it can be observed that the particles retain the overall spherical geometry of the PEDOT/PFA@MSS material. Closer examination reveals that there is a reduction in particle diameter ($d = 600 \pm 24$ nm for PEDOT/PFA as compared to $d = 745 \pm 22$ nm for PEDOT/PFA@MSS) that takes place during the etching process, although the standard deviation of the diameter does not change. This may be caused by inter-chain van der Waals interactions causing a collapse of the free volume in the body of the sphere, as was observed for pure PEDOT microparticles (Chapter 2); however, the higher magnification FE-SEM micrograph clearly reveals a macroporous structure in the PEDOT/PFA microparticles that is not present in the pure PEDOT analogues. The macroporous nature of the spheres is highlighted in the TEM micrograph in Figure 4.3e, where lighter areas represent areas of higher porosity. This porosity may explain the slight increase in the volume of adsorbed nitrogen for the etched particles when compared to the unetched material; however, this difference is extremely small, indicating that any porosity is macroscopic, rather than mesoscopic, in size.
Figure 4-3. Low (a) and high (b) magnification FE-SEM micrographs of the PEDOT/PFA@MSS composite; low (c) and high (d) magnification FE-SEM micrographs and (e) bright field TEM micrograph of the etched PEDOT/PFA composite (FE-SEM $V_{acc} = 1.5$ kV).
It is not obvious from the scanning electron micrographs which polymer or polymers (if any) are present on the particle surfaces. Thus, it is ambiguous whether the polymers are a homogeneous blend of PEDOT and PFA or whether phase separation has occurred. Various possibilities for phase separation are illustrated in Figure 4-4. One possibility is that the PEDOT first homogeneously coats the interior walls of the mesopores, with poly(furfuryl alcohol) filling the remaining pore volume. At the other extreme, complete phase separation would produce a core–shell like structure, where all of the PEDOT is localized in the core of the sphere and the PFA fills only the outermost half of the pore volume.

![Figure 4-4](image_url)

**Figure 4-4.** Model of the mesopore interior in the PEDOT/PFA@MSS composite showing various blending morphologies for the PEDOT (blue) and PFA (tan) phases. Not drawn to scale.

In order to determine whether the PEDOT/PFA@MSS blend adopts a core–shell morphology or it has radially aligned phase boundaries, the particles were subjected to energy dispersive X-ray microanalysis in a scanning transmission electron microscope (STEM). Rastering the finely focused STEM electron beam across the surface of an individual particle yields a map of the various characteristic X-ray line intensities, and therefore a map of the elemental distribution throughout a particle. Monte Carlo simulations of the electron trajectories (Figure 4-5) were carried out in order to determine the theoretical limit of resolution for the experiment. It was...
found that only 5.5% of the incident electrons were scattered by more than 1 nm. Since each image is composed of 50 sampling points (pixels) per line, and the overall image width is ca. 750 nm, the image resolution should be limited by the number of sampling points and not by scattering of the electron beam.

**Figure 4-5.** Simulated electron trajectories for a 200.0 keV, 2.0 nm diameter electron beam incident on a 750 nm thick film of silica supported on a 10 nm thick carbon film. 1000 electron trajectories are shown; approximately 55 of those (5.5%) deviate from the incident trajectory by more than 1 nm. Monte Carlo simulations were made using the CASINO (v2.42) software package.

The STEM-EDX element maps are shown in Figure 4-6. Figure 4-6a shows the secondary electron signal from the high angle annular dark field (HAADF) electron detector, and clearly shows the overall shape of the microparticle under study. This same general shape is replicated
in each of the following four element maps (Figure 4-6b-e). In each case, the intensity is greatest in the center of the particle, where the sampling volume is largest (the particle being thickest in the center). The carbon map shows some intensity outside of the particle boundary as defined by Figure 4-6a; this is due to the thin carbon support film that covers the copper mesh of the TEM grid. Both the oxygen and silicon signals are quite homogeneous throughout the particle body, and fade out towards the particle edge due to the decreasing sampling volume. Most importantly, since neither silica nor PFA contains sulfur, the intensity of the sulfur characteristic X-ray line is a measure of the PEDOT concentration at any point in the image. As can be seen in Figure 4-6d, the sulfur signal is brightest at the center of the particle, and fades to zero just past the particle edge. This behavior closely mirrors that observed in the silicon and oxygen element maps, indicating a homogeneous distribution of PEDOT throughout the body of the particle. This effectively disproves the core–shell morphology proposed on the right side of Figure 4-4, and suggests that the polymer distribution within the material lies closer to the left side of Figure 4-4 (radially aligned polymer nanowires).
Figure 4-6. STEM-EDX analysis of a single PEDOT/PFA@MSS microparticle. (a) HAADF detector image; (b) carbon K-line image; (c) oxygen K-line image; (d) sulfur K-line image; (e) silicon K-line image.

Similar element mapping experiments were carried out on the PEDOT/PFA microparticles after etching with hydrofluoric acid (Figure 4-7). The results are very similar to those for the unetched particles; namely, the brightest point in each of the element mapped images is in the center of the particle, where the sampling volume is greatest. These data suggest the nanoscale mixing of the PEDOT and PFA polymers present in the PEDOT/PFA@MSS composite is not lost upon removal of the silica template. The greater mechanical strength of PFA compared to PEDOT may then be responsible for maintaining the more porous structure of the final polymer microparticle than was the case for analogous pure PEDOT materials.
Figure 4-7. STEM-EDX analysis of a single PEDOT/PFA microparticle. (a) HAADF detector image; (b) carbon K-line image; (c) oxygen K-line image; (d) sulfur K-line image.

In order to more closely probe the surface composition of the sphere (where the sampling volume and therefore signal-to-noise ratio of the STEM-EDX experiment is low), X-ray photoelectron spectroscopy was carried out on the sample. XPS is a particularly surface sensitive technique. Due to the limited escape depth of an emitted photoelectron, only the first 10 – 15 nm of a surface is probed by XPS. This technique has been previously used in conjunction with C_{60}^+ ion sputtering to carry out a depth-profile analysis of PEDOT:PSS containing multi-layer devices; the authors clearly demonstrate that the technique is selective for only the first few nanometers of the surface layer.\textsuperscript{28} In the case of the PEDOT/PFA@MSS and PEDOT/PFA composites, if the elemental composition of sulfur in this surface layer matches the elemental composition of the bulk (which can be determined by EDX using a scanning electron microscope
operating at 20.0 kV, see Figure 4-8), then phase separation in the radial direction must necessarily be limited. The XPS spectra of the PEDOT/PFA@MSS composite are shown in Figure 4-9.

Figure 4-8. Simulated electron trajectories for a 20.0 kV, 10.0 nm diameter electron beam incident on a 5 µm thick film of silica supported on an aluminum substrate. 1000 electron trajectories are shown; the interaction volume is approximately 6500 nm wide at its widest point, indicating that the SEM-EDX experiment yields an analysis of the bulk elemental composition for 5 µm thick films of particles with $d \sim 750$ nm. Scattered electron trajectories are shown in blue, and backscattered electron trajectories are shown in red. Monte Carlo simulations were made using the CASINO (v2.42) software package.
Figure 4-9. X-ray photoelectron spectra of the PEDOT/PFA@MSS microparticles: (a) survey scan, showing the presence of carbon, oxygen, sulfur, and silicon; (b) carbon 1s peak; (c) oxygen 1s peak; (d) sulfur 2p peak; (e) silicon 2p peak. The experimental data is shown as a solid black line, the fitted data as a solid red line, the individual peaks as dashed black lines, and the Shirley background as a dotted black line.
Figure 1: X-ray photoelectron spectroscopy (XPS) spectra for various elements.

(a) O KLL and O 1s peaks.
(b) C 1s peak.
(c) O 1s peak.
(d) S 2p peak.
(e) Si 2p peak.

The x-axis represents binding energy in eV, and the y-axis represents counts in $10^6$ s$^{-1}$. Each peak corresponds to a different element, indicating the presence and concentration of these elements in the sample.
The XPS survey scan (Figure 4-9a) clearly shows the presence of a number of characteristic peaks, including those of the carbon 1s, oxygen 1s, sulfur 2s and 2p, and silicon 2s and 2p transitions. A higher resolution scan of the carbon 1s peak is shown in Figure 4-9b. The binding energies of the four fitted peaks (284.5, 285.6, 286.8, and 288.3 eV) are consistent with previous reports of the carbon 1s transitions in PEDOT.\textsuperscript{29-31} Due to the similar chemical structure of PEDOT and PFA, the binding energies of the two polymers are expected to be similar. The oxygen 1s peak is fit to two peaks centered at 533.5 and 532.6 eV (Figure 4-9c). These values are typical both of SiO\textsubscript{2} and of oxygen containing organic compounds such as ethers. The two peaks used in the fitting procedure can possibly be assigned to oxygen in the form of SiO\textsubscript{2} and oxygen present due to the ethylenedioxy and furan functionality of the polymers, although with only a subtle difference in energy between the two signals, definitive assignment of the peaks is difficult. The sulfur 2p signal (Figure 4-9d) is relatively weak, but is fit to a spin-split doublet with a 2p\textsubscript{3/2} transition at 165.0 eV and a 2p\textsubscript{1/2} transition at 163.7 eV. The doublet can be assigned to the sulfur of the thiophene ring, and both the binding energies and doublet splitting (1.3 eV) are consistent with previous reports of the XPS spectra of PEDOT.\textsuperscript{29-31} Importantly, despite the low intensity of the sulfur 2p peak, it is still clearly resolvable, indicating the presence of PEDOT within 10 nm of the particle surface. The silicon 2p peak (Figure 4-9e) is also fit to a spin-split doublet, and the results are consistent with previous reports of the XPS spectra of SiO\textsubscript{2}.\textsuperscript{32}

Analysis of the etched PEDOT/PFA microparticles by XPS (Figure 4-10) yields spectra very similar to those of the PEDOT/PFA@MSS composites. The most marked difference is the absence of the silicon 2s and 2p peaks in the survey scan, which is consistent with the removal of the MSS template. The shape of the carbon 1s (Figure 4-10b) peak is very similar to that of the PEDOT/PFA@MSS sample, indicating that there was little change in the chemical environment
of the element. The oxygen 1s (Figure 4-10c) spectrum shows a new peak at 531.2 eV, while the sulfur 2p (Figure 4-10d) peak is now much more distinct than it was in the case of the unetched sample. This is due to the larger weight percentage of sulfur in the etched sample, which leads to a higher intensity of the sulfur 2p peak and a better signal-to-noise ratio. Not only can the same sulfur 2p doublet be resolved (at 163.4 and 164.5 eV), but another spin-split peak at higher binding energy (165.3 and 167.0 eV) becomes apparent. This may be due to delocalization of the sulfur lone pair into the thiophene ring.\textsuperscript{30, 31} The presence of sulfate as a dopant anion may be expected to give rise to a third peak in the S 2p region of the spectrum; however, the binding energies for sulfates are typically much higher, at approximately 169 eV.
Figure 4-10. X-ray photoelectron spectra of the etched PEDOT/PFA microparticles: (a) survey scan, showing the presence of carbon, oxygen, and sulfur; (b) carbon 1s peak; (c) oxygen 1s peak; (d) sulfur 2p peak. The experimental data is shown as a solid black line, the fitted data as a solid red line, the individual peaks as dashed black lines, and the Shirley background as a dotted black line.

Quantification of the carbon, oxygen, sulfur and silicon content of the composites was carried out by both XPS and SEM-EDX (Table 4-1). The mass percentages of carbon and sulfur for the materials are consistent with the TGA results of 22% and 45% polymer in the PEDOT@MSS and PEDOT/PFA@MSS materials, respectively. Importantly, the sulfur content of the bulk (as determined by EDX) and the surface of the particles (as determined by XPS) is the same within
error for all samples. This is indicative of a constant PEDOT concentration in the radial direction; i.e., the phase separation of the two polymers is much more consistent with the left side of Figure 4-4. This is also the case for the etched PEDOT/PFA microparticles; both EDX and XPS analyses agree on an 8% (w/w) sulfur concentration in the sample, indicating that the sulfur is homogeneously distributed throughout the particle.

Table 4-1. Elemental analysis of the PEDOT/PFA®MSS and PEDOT/PFA composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Energy Dispersive X-ray Analysis</th>
<th>X-ray Photoelectron Spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%C  [w/w]</td>
<td>%S  [w/w]</td>
</tr>
<tr>
<td>PEDOT@MSS</td>
<td>14</td>
<td>3</td>
</tr>
<tr>
<td>PEDOT/PFA@MSS</td>
<td>29</td>
<td>3</td>
</tr>
<tr>
<td>PEDOT/PFA</td>
<td>67</td>
<td>8</td>
</tr>
</tbody>
</table>

The experimental uncertainty in the analyses is estimated to be ± 2% (w/w) for both EDX and XPS.

4.3.3 Synthesis of PFA/PEDOT®MSS and PFA/PEDOT Composites

In order to further probe the phase separation behavior of encapsulated PEDOT/PFA blends, the order of addition to the mesoporous template was reversed. A solution (50% v/v) of furfuryl alcohol in ethanol was prepared, and the mesopores of the silica host filled as before. Thermally induced polymerization at 150 °C resulted in particles with mesopores that were approximately 50% full. This was followed by the addition of 3,4-ethylenedioxythiophene, annealing, and finally polymerization using aqueous sodium persulfate to yield the PFA/PEDOT@MSS composite. The procedure was again followed by nitrogen adsorption (Figure 4-11a) and thermogravimetric analysis (Figure 4-11b). Importantly, the results indicate that the amount of each polymer incorporated into the MSS template is similar both by volume (measured by
nitrogen adsorption) and by weight (measured by TGA) to the PEDOT/PFA@MSS material, although the total amount of polymer incorporated into the MSS host appears to be slightly lower. Etching of the PFA/PEDOT@MSS composites was carried out in an identical fashion to that of the PEDOT/PFA microparticles. This yielded the inverted PFA/PEDOT composite.

Figure 4-11. Nitrogen adsorption isotherms (a) and thermogravimetric analyses (b) for the empty MSS host (black), PFA@MSS composite (blue), PFA/PEDOT@MSS composite (red) and etched PFA/PEDOT microparticles (green).

4.3.4 Particle Morphology

Imaging of the inverted PFA/PEDOT@MSS and etched PFA/PEDOT microparticles in the FE-SEM revealed striking differences compared to the PEDOT/PFA analogues (Figure 4-12). While the low magnification image of the PFA/PEDOT@MSS (Figure 4-12a) appears to exhibit the same spherical, monodisperse morphology as the PEDOT/PFA@MSS analogue, at higher magnifications a fuzzy texture becomes apparent on the particle surface (Figure 4-12b). This surface texture has been observed previously in PEDOT@MSS composites with completely filled mesopores, and is due to PEDOT that is present on the surface of the particles. The differences become even more dramatic after etching with hydrofluoric acid; the PFA/PEDOT
material visible in Figure 4-12c is amorphous particulate rather than the well-defined spherical PEDOT/PFA particles observed previously. At higher magnifications (Figure 4-12d) the material appears to consist of amorphous particles of sub-micron dimension interspersed in a poorly defined matrix. This may represent an extreme case of phase separation, where the partially intact particles may be PEDOT or PFA, and the less well defined material the second polymer.

**Figure 4-12.** Low (a) and high (b) magnification FE-SEM micrographs of the PFA/PEDOT@MSS composite; low (c) and high (d) magnification FE-SEM micrographs of the etched PFA/PEDOT composite ($V_{\text{acc}} = 1.5$ kV).

To explain the FE-SEM results, both the unetched PFA/PEDOT@MSS particles and etched PFA/PEDOT material were subjected to STEM-EDX analysis. The results for the PFA/PEDOT@MSS particles are shown in Figure 4-13. The secondary electron image, as well
as the carbon, oxygen, and silicon K-line images (Figure 4-13a,b,c,e respectively) are all consistent with a spherical morphology; the results are qualitatively the same as for the PEDOT/PFA@MSS particles. The sulfur K-line image (Figure 4-13d) is markedly different, however. The image appears to have a corona or halo that is ca. 150 nm thick, suggesting that the sulfur distribution is localized towards the surface of the particle. This would be consistent with a phase separated core–shell motif, where the PFA is buried in the core of the MSS, while the PEDOT forms a second layer inside the mesopores as well as on the surface (as shown on the right side of Figure 4-14).

**Figure 4-13.** STEM-EDX analysis of a single PFA/PEDOT@MSS microparticle. (a) HAADF detector image; (b) carbon K-line image; (c) oxygen K-line image; (d) sulfur K-line image; (e) silicon K-line image.
Figure 4-14. Model of the mesopore interior in the PFA/PEDOT®MSS composite, showing various blending morphologies for the PEDOT (blue) and PFA (tan) phases. Not drawn to scale.

The STEM-EDX analysis of the PFA/PEDOT material is shown in Figure 4-15. The element maps are less well defined than in the previous cases, due to the fragmented nature of the material and the limited interaction volume. It can nonetheless be seen that certain areas enriched in carbon are depleted in sulfur, while in other regions the sulfur signal is disproportionately intense. This is indicative of phase separation between PFA-rich and PEDOT-rich particles, and appears to occur on a length scale of 50 – 300 nm; this is approximately the same dimension as the individual particle fragments, as observed in the FE-SEM micrograph.
Figure 4-15. STEM-EDX analysis of the etched PFA/PEDOT material. (a) HAADF detector image; (b) carbon K-line image; (c) oxygen K-line image; (d) sulfur K-line image.

In order to confirm that phase separation is occurring in the PFA/PEDOT@MSS and PFA/PEDOT composites, the samples were subjected to analysis by XPS (Figure 4-16 and Figure 4-17). The peak energies are very similar to those observed in the PEDOT/PFA@MSS composite; the only major difference between the two sets of spectra lies in the relative intensity of the S 2s and 2p peaks.
Figure 4-16. X-ray photoelectron spectra of the PFA/PEDOT@MSS microparticles: (a) survey scan, showing the presence of carbon, oxygen, sulfur and silicon; (b) carbon 1s peak; (c) oxygen 1s peak; (d) sulfur 2p peak; (e) silicon 2p peak. The experimental data is shown as a solid black line, the fitted data as a solid red line, the individual peaks as dashed black lines, and the Shirley background as a dotted black line.
Figure 4-17. X-ray photoelectron spectra of the PFA/PEDOT material: (a) survey scan, showing the presence of carbon, oxygen, sulfur and trace silicon; (b) carbon 1s peak; (c) oxygen 1s peak; (d) sulfur 2p peak. The experimental data is shown as a solid black line, the fitted data as a solid red line, the individual peaks as dashed black lines, and the Shirley background as a dotted black line.

Elemental analysis of the PFA/PEDOT@MSS and PFA/PEDOT composites as determined by both EDX and XPS is given in Table 4-2. When comparing the bulk (EDX) and surface (XPS) compositions of the PFA/PEDOT@MSS microspheres, it is immediately obvious that the sulfur and carbon concentrations are much higher at the surface of the particles. For sulfur, the concentration measured at the surface is three times that measured in the bulk; clearly, there is a
dramatic localization of PEDOT at the surface of the particles. The atomic carbon:sulfur ratio measured by XPS is 6:1. The carbon:sulfur ratio in the PEDOT monomer is also 6:1, suggesting that the first 10 – 15 nm of the particle surface is almost exclusively PEDOT and silica, with little PFA present. This is consistent with the observation by FE-SEM that there is a layer of PEDOT on the surface of the particle, as well as the STEM-EDX data which suggests a PEDOT shell surrounding a PFA core. Taken together, these data suggest that most of the PEDOT is present within approximately 150 nm of the particle surface, with the first 15 nm being PEDOT and silica, with no PFA present. After the removal of the silica template the two analyses are in agreement, and thus the core-shell morphology appears to be lost. This is consistent with the FE-SEM micrographs (Figure 4-12c,d), which show an amorphous collection of particulate. The surfaces of the particles must consist of a statistical mixture of PEDOT and PFA in order for the bulk and surface compositions to be identical, confirming the loss of any morphological control.

Table 4-2. Elemental analysis of the PFA/PEDOT@MSS and PFA/PEDOT composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Energy Dispersive X-ray Analysis</th>
<th>X-ray Photoelectron Spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%C [w/w]</td>
<td>%S [w/w]</td>
</tr>
<tr>
<td>PFA/PEDOT@MSS</td>
<td>16</td>
<td>5</td>
</tr>
<tr>
<td>PFA/PEDOT</td>
<td>52</td>
<td>15</td>
</tr>
</tbody>
</table>

The experimental uncertainty in the analyses is estimated to be ± 2% (w/w) for both EDX and XPS.

4.3.5 Conductivity of PEDOT/PFA@MSS and PFA/PEDOT@MSS

Another particularly sensitive probe of the PEDOT distribution within a microparticle is the conductivity. Good conductivity requires conductive material (in this case, PEDOT) to be present at the interparticle contacts, as well as to provide a continuous path between them.
contrast, if the PEDOT is sheathed in an insulating matrix, the conductivity will be low. The PEDOT/PFA@MSS material was determined to have a conductivity of \((2.8 \pm 0.4) \times 10^{-5} \text{ S cm}^{-1}\), whereas the conductivity of the PFA/PEDOT@MSS material was two orders of magnitude higher \((\sigma = (1.6 \pm 0.4) \times 10^{-3} \text{ S cm}^{-1})\). This increase is again consistent with a much higher PEDOT surface concentration in the PFA/PEDOT@MSS material compared to the PEDOT/PFA@MSS sample. Notably, the conductivity of the PEDOT/PFA@MSS composite is greater than \(10^{-5} \text{ S cm}^{-1}\), indicating that the PEDOT is not completely isolated within the core of the particle; this reinforces the theory that the PEDOT and PFA are homogeneously distributed throughout the total mesopore volume. The conductivity of the etched PEDOT/PFA microparticles was intermediate between the two MSS encapsulated materials at \((1.7 \pm 0.4) \times 10^{-4} \text{ S cm}^{-1}\), indicating that the overall phase separation is somewhere between the two samples, towards the middle of Figure 4-4. Due to the poor film forming properties of the etched PFA/PEDOT material, no conductivity data could be obtained.

Taken together, these data suggest that when the MSS template is initially loaded with PEDOT, followed by a second polymer, phase separation is limited to the dimensions of a single mesopore diameter (ca. 3 nm). This may partly be due to strong PEDOT/SiO\(_2\) physisorption, which would favour a thin coating of the mesopore walls in preference to accumulation in the center of the microsphere. Thus in both the PEDOT/PFA@MSS and PEDOT/PFA materials, the phase separation likely resembles the left-most side of Figure 4-4. When the order of polymer addition is reversed, the less favourable PFA/SiO\(_2\) interactions lead to accumulation of PFA in the center of the microsphere. Addition of a second polymer therefore forms a core–shell structure. If the adhesion between the two polymer layers is poor, then removal of the silica template will lead to particle fragmentation, as was observed in Figure 4-12c,d. Thus, the phase domains in the PFA/PEDOT@MSS material strongly resembles the right side of Figure 4-14.

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The variations may also be influenced by the change in solvent used to load the monomer into the mesoporous host (toluene for EDOT as compared to ethanol for furfuryl alcohol), or the differing solubility of PEDOT in furfuryl alcohol and PFA in EDOT.

4.4 CONCLUSIONS

Polymer blend micro- and nanoparticles have proven to be a viable means of controlling phase separation in thin films, with important ramifications for high-tech devices such as photovoltaics. Here, we have demonstrated a facile and general approach for the preparation of blended conjugated polymer microparticles by the sequential infiltration and polymerization of two different monomers into a mesoporous template. In the case of the PEDOT/PFA@MSS composite, not only did the polymer blend retain the overall shape and monodispersity of the MSS template, but phase separation appeared to be limited by the silica pore walls. Analysis by STEM-EDX and XPS revealed that the two polymers were intimately mixed within the mesopores and that phase separation was limited to a maximum of ca. 3 nm, as defined by the pore walls. This represents an important advance over alternative methods of controlling the size of polymer phase domains, in that the size of the phase domains is extremely small, providing unparalleled mixing of the two polymers. This homogeneity appears to be preserved after etching the PEDOT/PFA@MSS materials with hydrofluoric acid, and the increased mechanical strength of PFA gives rise to microparticles exhibiting a new, macroporous morphology. It was also demonstrated that the order in which the polymers are introduced into the template has a remarkable effect on the phase separation of the two materials. If PEDOT is introduced first, homogeneous polymer blends are obtained, whereas is PFA is first added to the template, a phase separated core-shell particle is obtained, which subsequently fragments into 50 – 300 nm pieces. These results are expected to provide a route towards better, more precise control of film
morphology in polymer blends. This in turn may potentially improve the charge separation efficiency of photovoltaic devices based on polymer blends.
4.5 REFERENCES


5.1 INTRODUCTION

One of the emerging applications of conjugated polymer nanostructures is as electrode materials for supercapacitors. Supercapacitors are becoming an important class of energy storage materials due to their high power density.\textsuperscript{1} As such, they have found use in situations where large energy demands are made in a short period of time, such as in electric vehicles and portable electronic devices. Materials such as porous carbon,\textsuperscript{2,3} transition metal oxides,\textsuperscript{4} and conjugated polymers\textsuperscript{5-7} are all commonly employed in the fabrication of supercapacitors. Of these, conjugated polymers have the advantage of being able to store charge not just in the electrical double layer, but also throughout the body of the polymer by rapid Faradaic charge transfer (pseudo-capacitance). While this is also true of the transition metal oxides, these materials typically suffer from poor electrical conductivity. In contrast, conjugated polymers typically have good conductivity in their doped state; they also display fast, reversible and stable electrochemical behavior. Among conjugated polymers, poly(3,4-ethylenedioxythiophene) has been extensively exploited as a charge storage material.\textsuperscript{8-10} While the mass specific capacitance ($C_M$) of PEDOT is typically lower than other conjugated polymers (e.g., polyaniline, polypyrrole), its high stability with respect to repeated cycling makes it very suitable as a potential supercapacitor material.

\textsuperscript{*} A version of this chapter will be submitted for publication. Kelly, T. L., Yano, K., and Wolf, M. O. (2009) Supercapacitors based on PEDOT and Carbon Colloidal Microspheres.
Recent research has focused on improving both the energy and power density of PEDOT-based supercapacitors. Since the charging and discharging of PEDOT involves the mass transport of counter-ions into and out of the polymer film (Scheme 5-1), the rate of ion diffusion is often one of the limiting factors in the efficiency of PEDOT-based supercapacitors. Thus, improvements in both energy and power densities have been achieved by preparing nanostructured, high surface area electrodes; this limits the distance over which ion diffusion must occur. A number of groups have prepared PEDOT electrodes in this manner. Li et al. examined the effects of ultrasonication on the chemical synthesis of PEDOT, and found a moderate increase in the specific capacitance of the polymer due to the increase in porosity.\textsuperscript{11} PEDOT–carbon nanotube composites have also been shown to possess good mass specific capacitance due to the interconnected high surface area network of carbon nanotubes.\textsuperscript{12} Jang et al. have prepared mesocellular foams based on PEDOT.\textsuperscript{13} In a similar fashion, the high interfacial surface area leads to rapid ion diffusion and a high value for the specific capacitance. Lee and coworkers have extensively developed hollow PEDOT nanotubes;\textsuperscript{14, 15} due to the extremely thin nature of the polymer tube (on the order of nanometers) ions diffuse into and out of the polymer extremely rapidly. This leads to very high energy and power densities.
Chapter 2 described the preparation of highly monodisperse PEDOT–silica and PEDOT microspheres. This morphology offers a potentially interesting platform for the study of supercapacitor behavior, in that densely packed arrays of such microspheres have a network of continuous interstitial voids that should allow for the rapid diffusion of ions. Additionally, Yano and coworkers have reported the synthesis of monodisperse, microporous carbon microspheres (MCS).\textsuperscript{16} The hierarchical combination of macro- (the interstitial voids) and microporosity (within individual microspheres) may allow for extremely fast ion transport within the electrode film. In this chapter, the synthesis and characterization of a new PEDOT–carbon composite is described. Each of these materials — the PEDOT@MSS, PEDOT, MCS, and PEDOT@MCS microspheres — is evaluated for its potential utility in a supercapacitor.
5.2 EXPERIMENTAL

5.2.1 General

Materials and Equipment. EDOT was donated by Bayer under the trade name Baytron-M. The EDOT was vacuum distilled prior to use, and stored at 4 °C under nitrogen. N-methylpyrrolidinone (NMP), poly(vinylidene fluoride) (PVDF, $M_w \sim 275000$) and sodium persulfate were purchased from Sigma-Aldrich and used as received. Concentrated sulphuric acid was purchased from Fisher Scientific and used to prepare a 1 M aqueous solution. The mesoporous silica spheres and microporous carbon spheres were prepared according to established procedures by Toyota Central R & D Labs, Inc. Pore volumes were measured on a Quantachrome Autosorb-1 analyzer at 77 K using nitrogen gas. Thermogravimetric analysis was performed on a Pyris 6 analyzer.

Scanning Electron Microscopy. Dilute suspensions of colloidal material (ca. 1 mg mL$^{-1}$) were prepared in ethanol by ultrasonication. An aliquot (100 µL) of this suspension was drop-cast on an aluminum stub and allowed to dry. Microscopy was carried out on a Hitachi S4700 scanning electron microscope equipped with a cold field-emission electron gun and pinhole objective lens. Accelerating voltages of 1.0 – 3.0 kV were chosen in order to provide a balance between image resolution, charging effects, and surface penetration. Sputter coating was carried out using a Cressington 208HR sputter coater. Particle diameters were determined by measuring the diameter of a minimum of 200 particles in the FE-SEM. Energy dispersive X-ray microanalysis was carried out on a Hitachi S3000-N scanning electron microscope operating at 20.0 kV.

Electrochemistry. Working electrodes were made by dispersing an accurately known amount (10 – 15 mg) of the colloidal microspheres in a solution (1.00 mL) of PVDF in NMP (0.0112 g
mL$^{-1}$). From this stock dispersion, a small amount (50 µL) was pipette onto the end of a stainless steel plate (1 × 3 cm) and dried at 130 °C for 16 h. Cyclic voltammetry and galvanostatic charge/discharge experiments were carried out using a three-electrode setup, which consisted of the modified stainless steel working electrode, a platinum mesh counter electrode, and a 3 M Ag/AgCl reference electrode. A 1 M solution of sulfuric acid was used as the electrolyte. Potentials/currents were applied using an Autolab potentiostat/galvanostat.

5.2.2 Synthesis

**PEDOT@MCS Synthesis.** Microporous carbon spheres (0.100 g) were placed in a Schlenk tube and dried at 120 °C under vacuum for 2 h. The atmosphere was replaced with nitrogen gas, and enough EDOT to completely fill the pore volume of the microporous carbon (105 µL) was added. The mixture was agitated with a spatula for 6 min, and then annealed at 60 °C for 1 h. The black powder was then stirred in a solution of sodium persulfate (0.15 g) in water (3.00 mL) at room temperature for 16 h. The solid material was isolated by centrifugation and washed by redispersion/centrifugation cycles using water (1 × 15 mL), ethanol (2 × 15 mL), and water (1 × 15 mL). Drying at 60 °C for 5 h yielded the PEDOT@MCS composite as a black powder (0.18 g).

5.3 RESULTS AND DISCUSSION

5.3.1 Synthesis

The syntheses of the PEDOT@MSS, PEDOT, and MCS materials were accomplished by an infiltration and in situ polymerization approach that has been previously reported.$^{16,18}$ In order to introduce PEDOT into the mesopores of the carbon template, a similar approach was adopted. The carbon microspheres were first dried at 120 °C under vacuum in order to remove adsorbed
water. The pores were then filled with EDOT by capillary action, and the EDOT polymerized by addition of sodium persulfate (an oxidizing agent). This process is shown in Scheme 5-2.

**Scheme 5-2**

![Scheme 5-2 Diagram]

The amount of redox active polymer present in each of the materials is the first important parameter to quantify for each of the samples. This was determined by a combination of TGA and EDX. The TGA curves of the MCS and PEDOT@MCS samples are shown in Figure 5-1, while those of the PEDOT@MSS and PEDOT samples have been reported previously in this thesis (Chapter 2). From Figure 5-1 it can be seen that for the microporous carbon spheres the onset of decomposition occurs at ca. 500 °C and that decomposition is complete by 750 °C. After the carbon template has been filled with PEDOT, the decomposition process occurs in a series of discrete steps. The first mass loss (8%) occurs at 100 °C. This is typical of adsorbed moisture, and has also been observed in the PEDOT@MSS and PEDOT materials (Chapter 2). A second loss of ca. 27% occurs between 200 and 450 °C with an inflection point at 350 °C. This may be due to the (partial) decomposition of PEDOT; since the decomposition of PEDOT should occur in the range of 300 to 600 °C, it is unlikely that all of the PEDOT has been lost by 450 °C in the PEDOT@MCS sample. The temperature range of 450 °C to 900 °C sees a continual, gradual loss of material from the PEDOT@MCS sample. Some of this mass loss is likely due to residual PEDOT decomposition, while the remainder is due to combustion of the carbon
template. Thermogravimetric analysis of the PEDOT@MSS and PEDOT microspheres reveals mass losses (50% for PEDOT@MSS and 100% for PEDOT) between 300 and 600 °C that are easily attributable to the decomposition of the conjugated polymer.

![Thermogravimetric analysis graph](image)

**Figure 5-1.** Thermogravimetric analysis of the microporous carbon spheres (dashed line) and the PEDOT@MCS composite (solid line).

While the PEDOT@MSS, PEDOT, and MCS materials are straightforward to analyze by TGA, the results for the PEDOT@MCS composite are more ambiguous. EDX was carried out in order to obtain more quantitative results. The EDX data are shown in Table 5-1; importantly, the analysis reveals a 12% (w/w) sulfur concentration in the sample. If it is assumed that all of the sulfur present is due to the presence of PEDOT, then this would indicate that in addition to the 12% of sulfur content, 12% of the total mass of the sample was due to the PEDOT oxygen atoms and 27% due to the PEDOT carbon atoms. The remaining oxygen is also present in the carbon template, and is likely due to alcohol, aldehyde, or carboxylic acid functionality. These data are consistent with the TGA results, which indicated that the composite was > 27% PEDOT. From both the TGA and EDX data it can be concluded that the carbon and PEDOT microspheres are
essentially pure materials, whereas the PEDOT@MCS and PEDOT@MSS samples are both approximately 50% PEDOT by mass.

**Table 5-1.** Energy dispersive X-ray microanalysis of the MCS and PEDOT@MCS samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%C [w/w]</th>
<th>%O [w/w]</th>
<th>%S [w/w]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCS</td>
<td>91</td>
<td>9</td>
<td>N/A</td>
</tr>
<tr>
<td>PEDOT@MCS</td>
<td>68</td>
<td>20</td>
<td>12</td>
</tr>
</tbody>
</table>

### 5.3.2 Particle Morphology

The suitability of each of these materials for supercapacitor applications will be dictated at least partly by their morphology; high magnification FE-SEM micrographs of each of the four colloidal materials are shown in Figure 5-2. Previous work has shown that the PEDOT@MSS composite consists of monodisperse, spherical particles with a diameter of $730 \pm 35$ nm. The surface texture visible in Figure 5-2a is likely due to a layer of PEDOT present on the surfaces of the particles. It is this surface layer that is responsible for making electrical connections between both adjacent particles and with the current collector in a working device. Figure 5-2b shows the micrograph of the PEDOT microspheres after removing the silica template with hydrofluoric acid. The diameter of these particles is $670 \pm 32$ nm; the free volume that would have been present due to the removal of the template is lost on etching due to collapse of the particle structure. The microporous carbon particles (Figure 5-2c) are also quite spherical and monodisperse in diameter ($d = 321 \pm 20$ nm). The surface texture visible on the particles is due to the presence of radially-aligned micropores that extend outwards from the center of each particle. The presence of this microporosity was confirmed by nitrogen adsorption measurements (Figure 5-3); the high surface area of the carbon microspheres ($S_{BET} = 1600 \text{ m}^2 \text{ g}^{-1}$) might
therefore be expected to lead to a large value for the specific capacitance. In the PEDOT@MCS composite, this void space has been filled with PEDOT. As such, the surface texture in Figure 5-2d is much coarser and globular in nature, since it is likely due to the presence of a layer of PEDOT at the surface of the particles, similar to what is observed in the PEDOT@MSS composite. The diameter of the PEDOT@MCS composite \( d = 326 \pm 19 \) nm is essentially the same as that of the carbon template.

**Figure 5-2.** FE-SEM micrographs of the (a) PEDOT@MSS \( (V_{\text{acc}} = 1.0 \, \text{kV}) \), (b) PEDOT \( (V_{\text{acc}} = 1.5 \, \text{kV}) \), (c) MCS \( (V_{\text{acc}} = 1.0 \, \text{kV}) \), and (d) PEDOT@MCS \( (V_{\text{acc}} = 1.5 \, \text{kV}) \) microspheres.
5.3.3 Electrochemistry

The capacitance of each of the four materials was initially evaluated by cyclic voltammetry. The cyclic voltammograms shown in Figure 5-4 display good capacitive behavior, with a sharp rise in current at low voltages followed by a sharp drop at the vertex potential. In the case of the PEDOT-containing materials, this is due to the generation and destruction of charge carriers on the polymer backbone and the concomitant in- and out-flow of anions (Scheme 5-1). For the microporous carbon spheres, the current is simply due to the charging of the electrical double layer. At fast scan rates ($> 25 \text{ mV s}^{-1}$), each of the four sets of voltammograms has a similar, distorted rectangular shape. This deviation from ideal behavior is indicative of uncompensated resistance in the system. At higher scan rates the currents are correspondingly higher, leading to a more pronounced $iR$ loss. The uncompensated resistance may be due to imperfect contact between the active electrode material and the stainless steel current collector, which is a well
known issue in electrodes of this type. The effect may be more pronounced due to the lack of any carbon black to improve the conductivity of the electrode film.

**Figure 5-4.** Cyclic voltammograms recorded at scan rates of 1, 2, 5, 10, 25, 50 and 100 mV s\(^{-1}\) for the (a) PEDOT@MSS, (b) PEDOT, (c) MCS and (d) PEDOT@MCS microspheres.

Comparing the electrochemistry of the various materials, several differences are immediately apparent. Firstly, in the case of the PEDOT@MSS composite the widths of the voltammograms (the difference between the anodic and cathodic plateau currents) are much smaller than they are in the case of the pure PEDOT analogues. The width of the voltammogram is directly related to the mass specific capacitance of the material by Equation 5-1. The currents obtained at 1 mV s\(^{-1}\)
can be directly converted into capacitance values by Equation 5-1, and the results are shown in Figure 5-5a.

**Equation 5-1**

\[
C_M = \frac{i}{(\Delta V / \Delta t) \cdot m_r}
\]

**Figure 5-5.** Cyclic voltammograms recorded at 1 mV s\(^{-1}\) for the PEDOT@MSS (solid black line), PEDOT (dashed black line), carbon (solid red line), and PEDOT@MCS (dashed red line) materials. The y-axis has been converted to specific capacitance. (b) Mass specific capacitance as a function of scan rate for the PEDOT@MSS (squares), PEDOT (triangles), MCS (circles) and PEDOT@MCS (diamonds) microspheres. The dashed connecting lines are meant to guide the eye.

At these slow scan rates additional detail in the voltammograms can be resolved. For the PEDOT@MSS material, a faint oxidation peak can be observed at 0.6 V, and the reverse reduction wave is visible at 0.25 V. These peaks may be due to the oxidation and reduction of PEDOT; similar peaks were observed by Jang et al. in their electrochemical study of PEDOT nanoparticles\(^\text{13}\). These peaks can still be observed but are no longer as prominent in the pure
PEDOT sample, which displays a more rectangular voltammogram. The carbon and PEDOT@MCS samples display similar electrochemical behavior. Both voltammograms resemble slightly distorted rectangles, indicative of capacitive behavior with a slight uncompensated resistance.

The specific capacitances of the four materials are plotted as a function of scan rate in Figure 5-5b. It can be seen that the maximum capacitance of the PEDOT microspheres is nearly twice that of the PEDOT@MSS composite (115 F g\textsuperscript{-1} as compared to 62 F g\textsuperscript{-1}). In light of the elemental analysis data presented in Figure 5-1 and Table 5-1, these values are in reasonable agreement; the PEDOT@MSS composite contains approximately 50% (w/w) of electrochemically inactive material (silica), and therefore on a mass basis the specific capacitance is expected to be roughly half that of the pure PEDOT analogue. Importantly, however, the presence of the silica template has a dramatic effect on the overall usability of the material. As the scan rate is increased, the specific capacitance of the PEDOT@MSS material drops dramatically; in contrast, the capacitance of the PEDOT microparticles shows a much more gradual decline. As the scan rate approaches 50 mV s\textsuperscript{-1}, the PEDOT microparticles retain ca. 50% of their maximum total capacitance, whereas the PEDOT@MSS microparticles have lost almost all of their capacitive ability.

This behavior is also reflected in the data for the MCS and PEDOT@MCS samples. The microporous carbon spheres have a maximum specific capacitance of 109 F g\textsuperscript{-1}, which is larger than that of commercially available high surface area carbon,\textsuperscript{6, 19} and competitive with many recent state-of-the-art examples. For example, carbon inverted opal structures have been shown to have specific capacitances in the range of 64 to 127 F g\textsuperscript{-1},\textsuperscript{3} while Largeot et al. reported capacitances of 100 to 160 F g\textsuperscript{-1} in an optimization study of microporous carbons in ionic liquid electrolyte.\textsuperscript{2} The incorporation of PEDOT into the carbon template does not dramatically
influence the capacitance of the material, and the specific capacitance \(C_M = 106 \text{ F g}^{-1}\) is very similar to that of the pure carbon microspheres. This suggests that the additional charge storage capacity provided by the addition of the redox-active polymer is offset by the elimination of microporosity in the composite (Figure 5-3). In both the MCS and PEDOT@MCS materials, the specific capacitance of the sample decreases sharply with increasing scan rate. This is especially evident when compared to the PEDOT microspheres, which have a much more constant specific capacitance.

In order to further probe the capacitive behavior of these materials, the electrode films were subjected to galvanostatic charge/discharge experiments. The data recorded at 0.1 mA are shown in Figure 5-6. As expected from the cyclic voltammetry results, the PEDOT@MSS material performed relatively poorly. The charging and discharging cycle deviated markedly from the ideal triangular shape of a capacitor, and the discharge time was short, indicating a low specific capacitance. The other three materials displayed more promising behavior. Aside from a small \(iR\) drop, the PEDOT microspheres exhibited a very triangular charge/discharge cycle, and a lengthy discharge time. The data for the microporous carbon closely mirrors that for the PEDOT spheres, and while the data for the PEDOT@MCS composite are slightly less than ideal, the total discharge time is long. The specific capacitances obtained from these data are tabulated in Table 5-2, along with the values obtained by cyclic voltammetry.
Figure 5-6. Normalized galvanostatic charge/discharge cycles recorded at 0.1 mA for the PEDOT@MSS (solid line), PEDOT (dashed line), MCS (solid red line) and PEDOT@MCS (dashed red line) microspheres.

Table 5-2. Mass specific capacitances obtained from cyclic voltammetry and galvanostatic experiments.

<table>
<thead>
<tr>
<th></th>
<th>PEDOT@MSS</th>
<th>PEDOT</th>
<th>MCS</th>
<th>PEDOT@MCS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_M$ (F g$^{-1}$) Galvanostatic</td>
<td>39</td>
<td>99</td>
<td>112</td>
<td>102</td>
</tr>
<tr>
<td>$C_M$ (F g$^{-1}$) CV</td>
<td>62</td>
<td>115</td>
<td>109</td>
<td>106</td>
</tr>
</tbody>
</table>

The specific capacitances of the PEDOT@MSS and PEDOT microspheres determined by the galvanostatic experiments are similar to, but slightly lower than, those measured by cyclic voltammetry. This observation can be explained by the fact that the value of $C_M$ measured by cyclic voltammetry is reported at one particular potential, while that obtained by galvanostatic cycling is an average capacitance for the potential range of 0 to 0.8 V. From Figure 5-5a, it can be seen that the overall width of the voltammogram is wider in the lower half of the voltage
range studied and narrower at the upper limit. Thus, averaging the capacitances over the entire voltage range leads to the observed decrease. The specific capacitances of the MCS and PEDOT@MCS microspheres, as determined galvanostatically, are the same as those determined by cyclic voltammetry (within experimental error). This finding is in agreement with the more rectangular voltammograms observed for these materials (Figure 5-5b).

5.3.4 Film Morphology

In order to explain the differences in electrochemical behavior between the four samples, the electrode films were subjected to analysis in the FE-SEM. The micrographs are shown in Figure 5-7. Figure 5-7a and Figure 5-7b show the film morphologies of the PEDOT@MSS and PEDOT-based electrodes, respectively. In Figure 5-7a there are areas of low film coverage where the steel substrate can be seen (light grey), although most of the field of view is thickly covered by the PEDOT@MSS microspheres (dark grey). The PEDOT@MSS film appears to have semi-regular pores (black areas) penetrating into the film. These are due to the disordered nature of the film; a close packed array of colloidal microspheres would be expected to possess no such porosity. The film morphology of the PEDOT microspheres is similar, with a high degree of porosity (black areas) interspersed in a PEDOT matrix (grey areas). In both cases the pore diameters are roughly 1 – 2 µm in size (approximately 1 to 3 particle diameters). Despite the similarities of the film morphology, however, the PEDOT@MSS materials exhibited a much sharper decrease in capacitance with increasing scan rate. This is likely due to restrictions on ion diffusion within the individual microparticles. The silica template provides an impermeable barrier to ions, forcing them to follow very narrow, defined pathways through the particle; once an ion has entered the body of a pore, it can diffuse only in the radial direction. In contrast, in the case of the PEDOT microspheres the ions are free to migrate throughout the bulk of the particles. This is schematically illustrated in Figure 5-8.
Figure 5-7. FE-SEM micrographs of the electrodes made of (a) PEDOT@MSS/PVDF ($V_{acc} = 2.0$ kV); (b) PEDOT/PVDF ($V_{acc} = 1.5$ kV); (c) MCS/PVDF ($V_{acc} = 3.0$ kV); and (d) PEDOT@MCS/PVDF ($V_{acc} = 3.0$ kV).

Figure 5-7c and Figure 5-7d show the film morphologies of the microporous carbon and PEDOT@MCS electrodes. The morphologies are markedly different from those of the PEDOT@MCS and PEDOT electrodes. Rather than a smooth, macroporous film, the individual particles form large aggregates that are between 10 and 50 µm in size. This aggregation is less pronounced for the PEDOT@MCS sample, but is nonetheless still present. In contrast to films composed of the PEDOT microspheres, the clustering of the particles and the lack of semi-regular porosity in the film may limit the rate of ion diffusion. In turn, this may lead to the observed drop-off in the specific capacitance of the electrode at higher scan rates. Alternatively,
it may be the ion diffusion within an individual particle that is the limiting factor in maintaining high capacitance at faster scan rates.

**Figure 5-8.** Schematic illustration of ion diffusion within (a) an individual PEDOT@MSS particle; (b) a single mesopore shown in (a); and (c) an individual PEDOT microsphere. Possible routes for ion diffusion are indicated by white arrows. Silica is shown in grey and PEDOT in blue.

### 5.4 CONCLUSIONS

In summary, the synthesis of a PEDOT@MCS composite material and an investigation into the suitability of a series of colloidal microspheres for use as supercapacitor electrode materials is described. Of the four materials under study, the PEDOT and microporous carbon materials exhibited the highest specific capacitances, and it was demonstrated that the PEDOT microparticles retained their capacitive properties at higher scan rates. FE-SEM investigations suggested that this may be due to the semi-regular, macroporous nature of the electrode film, which would allow for facile ion diffusion throughout the material. This chapter demonstrates the feasibility of using sub-micron colloidal microspheres to introduce porosity into an electrode film through an interconnected sequence of interstitial voids and micron-sized macropores. It also demonstrates the subsequent effect on the specific capacitances of the materials under study; namely, an increase in capacitance relative to the bulk materials.
5.5 REFERENCES


CHAPTER 6

ENHANCED OPTICAL PROPERTIES OF PPV
ENCAPSULATED IN MESOPOROUS SILICA SPHERES

6.1 INTRODUCTION

Poly(\(p\)-phenylenevinylene) has attracted a great deal of attention in the two decades since it was first used as the active layer in an OLED.\(^1\) The widespread use of PPV in organic devices has been hampered by a number of fundamental drawbacks in the material. PPV is insoluble and intractable, making processing difficult. To date, this problem has typically been circumvented by either processing a soluble sulfonium-salt precursor polymer (pPPV),\(^2\)-\(^5\) followed by post-processing thermal treatment, or by the installation of solubilising side-chains on the polymer backbone (i.e., MEH-PPV).\(^6\),\(^7\) Due to the high temperature required to convert pPPV to PPV, the sulfonium-salt route is not suitable for processing on thermally sensitive substrates such as paper or plastics. Meanwhile, the side chains of MEH-PPV require a multi-step synthesis to prepare the monomer, which dramatically increases the cost and effort of the overall process. Furthermore, the side chains inevitably perturb both the electronic and steric properties of the polymer, leading to red-shifts in both the absorption and emission spectra and influencing inter-chain interactions.\(^6\)

One of the other major weaknesses of PPV is its propensity to photobleach in the presence of molecular oxygen.\(^8\)-\(^12\) This is particularly problematic for high energy and high intensity applications such as LEDs and lasers. The presence of high energy excitons leads to polymer oxidation and the formation of carbonyl defects. These defects are known to act as low energy

\* A version of this chapter has been submitted for publication. Kelly, T. L., Yamada, Y., Schneider, C., Yano, K., and Wolf, M. O. (2009) Enhanced Optical Properties and Opaline Self-Assembly of PPV Encapsulated in Mesoporous Silica Spheres.
trap sites and are highly efficient fluorescence quenchers, limiting the lifetime of PPV-based
devices. Additionally, the aggregation of polymer chains has been shown to lead to a lower
fluorescence quantum yield.\textsuperscript{13, 14} This is problematic in the solid state where inter-chain effects
are particularly pronounced, and results in lower device efficiency.

One approach that has been explored in order to remedy some of these deleterious effects is to
encapsulate the polymer inside a protective matrix.\textsuperscript{15} This host matrix fulfills a number of roles.
It directs the morphology of the overall material, acts to reduce inter-chain effects by separating
polymer chains, and provides a measure of both thermal stability and photostability for the
polymer. A variety of such hosts for PPV have been explored to date. These include porous
silica\textsuperscript{16-21} and alumina,\textsuperscript{22} zeolites,\textsuperscript{23, 24} layered clays,\textsuperscript{25, 26} amylose,\textsuperscript{27, 28} poly(norbornene)\textsuperscript{29} and
vault protein cages.\textsuperscript{30} The encapsulated PPV@host materials often possess a variety of properties
lacking in the unencapsulated conjugated polymer, including an increased fluorescence quantum
yield, resistance to photobleaching, liquid crystallinity, and solubility.

In this chapter the preparation of a composite material by encapsulation of PPV inside
monodisperse mesoporous silica spheres is described. The ion-exchange and in situ
polymerization method affords a high degree of synthetic control, and the resulting colloidal
material offers some important advantages over both unencapsulated PPV and its various
functionalized derivatives. Most significantly, the composite material has a remarkably high
fluorescence quantum yield; it has improved resistance to the degradative effects of molecular
oxygen; and, it is highly processable, capable of being processed as a colloidal dispersion.
6.2 EXPERIMENTAL

6.2.1 General

Materials and Equipment. Aqueous hydrofluoric acid (49%), methanol, and ethanol were purchased from Fisher Scientific and used as received. Tetrahydrothiophene and α,α-dichloro-p-xylene were purchased from Sigma-Aldrich and used as received. p-Xylylenebis(tetrahydrothiophenium chloride) was synthesized from α,α-dichloro-p-xylene and tetrahydrothiophene according to a literature procedure. The mesoporous silica spheres were prepared according to an established procedure by Toyota Central R & D Labs, Inc. UV-vis-NIR spectra were recorded as ethanolic dispersions in a 1 cm quartz cuvette on a Varian Cary 5000 spectrophotometer. Fluorescence spectra were acquired using a Photon Technology International QuantaMaster fluorimeter equipped with an integrating sphere. Time-correlated single photon counting experiments were run on a Horiba Jobin Yvon Fluorocube fluorescence lifetime measurement system. Pore volumes were measured on a Quantachrome Autosorb-1 analyzer at 77 K using nitrogen gas. Thermogravimetric analysis was performed on a Pyris 6 analyzer. Powder X-ray diffraction data were recorded on a Bruker D8 Advance X-ray diffractometer in the Bragg-Brentano configuration, using copper Kα radiation at 40 kV, 40 mA.

Scanning Electron Microscopy. Dilute suspensions of colloidal material (ca. 1 mg mL⁻¹) were prepared in ethanol by ultrasonication. An aliquot (100 μL) of this suspension was dropcast on an aluminum stub and allowed to dry. Microscopy was carried out on a Hitachi S4700 scanning electron microscope equipped with a cold field-emission electron gun and pinhole objective lens. An accelerating voltage of 5.0 kV was chosen in order to provide a balance between image resolution, charging effects, and surface penetration. Sputter coating was carried out using a Cressington 208HR sputter coater. Particle diameters were determined by measuring the diameter of a minimum of 200 particles in the FE-SEM. Energy dispersive X-ray
microanalysis was carried out on a Hitachi S3000-N scanning electron microscope operating at 20.0 kV.

**Transmission Electron Microscopy.** Dilute suspensions of colloidal material (ca. 1 mg mL$^{-1}$) were prepared in ethanol by ultrasonication. An aliquot (2 µL) of this suspension was drop-cast on a carbon-coated 300-mesh copper TEM grid and allowed to dry. Microscopy was carried out on an FEI Tecnai G2 transmission electron microscope equipped with a field emission electron gun and a super-twin objective lens. An accelerating voltage of 200.0 kV was applied. EDX analysis was carried out in scanning TEM mode with a beam diameter of ≤ 2.0 nm.

**MAS-NMR Spectroscopy.** The spectra were obtained at 298 K using a Bruker Avance II 600 spectrometer, with a SB Bruker 4 mm MAS double-tuned probe operating at 600.33 MHz for $^1$H and 119.26 MHz for $^{29}$Si and a SB Bruker 3.2 mm MAS triple-tuned probe operating at 600.33 MHz for $^1$H and 150.97 MHz for $^{13}$C. Chemical shifts are referenced to TMS using glycine and DSS as an intermediate standard for $^{13}$C and $^{29}$Si NMR respectively. The samples were spun at 12.5 kHz for $^{29}$Si NMR spectra and 20 kHz for $^{13}$C NMR spectra. Cross-polarization spectra were collected with a Hartmann-Hahn match at 62.5 kHz and 100 kHz $^1$H decoupling. The recycle delay was 2 s. The contact time was 6000 µs for $^{13}$C NMR and 14000 µs for $^{29}$Si NMR.

6.2.2 **Synthesis**

**PPV@MSS Synthesis.** A solution of $p$-xylylenebis(tetrahydrothiophenium chloride) (0.652 g, 1.86 mmol) was prepared in methanol (50 mL), and a sample of MSS containing residual surfactant (0.503 g) added. The mixture was rapidly heated to reflux. After 5 h, the solids were isolated by centrifugation, and subsequently washed by redispersion/centrifugation cycles with methanol (3 × 50 mL). The solid was redispersed in methanol (50 mL) and isolated by suction.
filtration on a 0.22 µm cellulose acetate membrane. The pale yellow powder was dried and thermally treated at 200 °C in vacuo, yielding a bright canary yellow powder (0.25 g).

6.3 RESULTS AND DISCUSSION

6.3.1 Synthesis

Preparation of PPV@MSS. The first step in the preparation of the PPV@MSS composite is the synthesis of the mesoporous silica host. This is accomplished by an established procedure, whereby an organic silica precursor (tetramethylorthosilicate) is hydrolyzed using aqueous sodium hydroxide in the presence of an alkylammonium surfactant. The surfactant templates the formation of hexagonal-close-packed mesopores; prior to any other work-up or calcination procedure, the interior of the mesopores contains alkylammonium-siloxide ion-pairs. Next, the mesoporous silica spheres (still containing the surfactant) are heated to reflux in a methanolic solution of \( p \)-xylylenebis(tetrahydrothiophenium chloride) for five hours (Scheme 6-1). The doubly-charged monomer is exchanged for the alkylammonium surfactant inside the pores. The basic siloxide sites are then able to deprotonate the monomer and cause it to undergo polymerization. In contrast to previous reports of PPV materials prepared via ion-exchange, no preliminary calcination or deprotonation steps are required; the host can be used as-prepared with no additional treatment, simplifying the overall synthetic procedure. The pPPV@MSS material is obtained as a pale ivory solid. At this stage, the material exhibits bright blue emission when excited at 366 nm by a hand-held UV lamp. This is indicative of partial elimination of the tetrahydrothiophenium groups and the formation of a partially conjugated polymer. Subsequent heating of the pPPV@MSS intermediate at 200 °C under vacuum produces the fully conjugated PPV@MSS material as a bright yellow solid that exhibits strong green emission.
6.3.2 Characterization

The PPV@MSS material was characterized by both scanning and transmission electron microscopy. A field-emission scanning electron microscopy image is shown in Figure 6-1a. The composite particles clearly retain the overall spherical morphology of the silica template. Figure 6-1b shows a transmission electron microscopy image of the material, which emphasizes the spherical, monodisperse geometry. The average diameter of the particles was determined to be 563 ± 26 nm, which is very similar to that of the unmodified silica host (575 ± 28 nm). This suggests (at least within the limit of resolution of the TEM) that the polymer is largely encapsulated within the mesopores of the silica rather than present as a layer on the surface. Figure 6-1c shows a higher magnification TEM micrograph. At the edge of the left sphere, alternating regions of high and low electron contrast can be seen extending radially from the body of the sphere. The spacing of these lines (ca. 3 nm) is consistent with the hexagonal-close-packed arrangement of mesopores and is in agreement with the spacing calculated from powder X-ray data (vide infra).
Figure 6-1. (a) FE-SEM micrograph of the PPV@MSS composite ($V_{\text{acc}} = 5.0$ kV). The sample was sputter coated with a 5 nm thick layer of gold prior to imaging; (b) Low magnification TEM micrograph of the PPV@MSS composite; (c) High magnification TEM micrograph of the PPV@MSS composite.

The silica host and the composite material were both analyzed by $^{13}$C and $^{29}$Si magic angle spinning (MAS) NMR spectroscopy (Figure 6-2 and Figure 6-3). The $^{13}$C NMR spectrum of the MSS host shows seven signals at 63.0, 49.9, 28.3, 26.2, 22.6, 19.3, and 10.3 ppm. These are
consistent with the resonances of the cetyltrimethylammonium cation.\textsuperscript{32} The $^{29}\text{Si}$ NMR spectrum consists of two broad resonances at $-100.6$ and $-110.9$ ppm. These can be assigned as the silicon $\text{Si(O–Si)}_3\text{(OH)}$ (or $Q^3$) and $\text{Si(O–Si)}_4$ (or $Q^4$) signals, respectively. The relatively high ratio of the $Q^3$ to $Q^4$ signal is indicative of a high surface area silica material (since terminal silanol groups are predominantly present at interfacial surfaces). The $^{13}\text{C}$ NMR spectrum of the PPV@MSS composite consists of a relatively sharp signal at 45.2 ppm, and two faint, broad signals at 123.0 and 133.5 ppm. No evidence of residual surfactant is observed. The broad signals in the aromatic region of the spectrum (123.0 and 133.5 ppm) are consistent with previous reports of MAS-NMR spectra for poly($p$-phenylenevinylene).\textsuperscript{33} The origin of the resonance at 45.2 ppm is slightly less obvious. The chemical shift is similar to that of methanol (ca. 50 ppm); however, due to the thermal treatment (200 °C in vacuo) carried out after the ion-exchange process, it is unlikely that any residual methanol is left inside the mesopores. Rather, the resonance at 45 ppm may be due to silanol groups that became methylated during the first step of the synthesis. Analysis of the $^{29}\text{Si}$ NMR spectrum shows the appearance of a new resonance at $-95.0$ ppm, in addition to the $Q^3$ and $Q^4$ resonances. This is due to the formation of geminal silanol groups of the type $\text{Si(O–Si)}_2\text{(OH)}_2$ (or $Q^2$), and indicates that some degree of silica hydrolysis occurred during the synthetic procedure. Clearly, the ion-exchange conditions employed (heating the methanolic monomer solution to reflux) lead not only to polymerization of the sulfonium-based monomer, but also to partial hydrolysis and methylation of the silica surface.
Figure 6-2. (a) $^{13}$C and (b) $^{29}$Si cross-polarization MAS-NMR spectra of the MSS host.

Figure 6-3. (a) $^{13}$C and (b) $^{29}$Si cross-polarization MAS-NMR spectra of the PPV@MSS composite.

In order to quantify the amount of PPV present in the composite material, thermogravimetric analysis, combustion analysis, and energy dispersive X-ray microanalysis were carried out. The TGA curve is shown in Figure 6-4. The first mass loss (2%) occurs between 50 – 200 °C with an inflection point at 100 °C. This loss is typical of the mesoporous silica host, and is due to moisture that is adsorbed in the mesopores upon standing in air. The second major loss (14%)
occurs gradually in the temperature range of 250 – 750 °C and is consistent with previous reports of the thermal decomposition of PPV–inorganic composites.\textsuperscript{19, 26}

![Thermogravimetric analysis of the PPV@MSS composite; TGA curve (black line), and its first derivative (grey line).](image)

**Figure 6-4.** Thermogravimetric analysis of the PPV@MSS composite; TGA curve (black line), and its first derivative (grey line).

The results obtained from EDX and combustion analyses are tabulated in Table 6-1. The latter two techniques indicate that there is approximately 10% (w/w) carbon present in the sample. The EDX analysis also shows 34% (w/w) silicon and 56% (w/w) oxygen, and the combustion analysis further reveals an additional 2% (w/w) hydrogen (note that combustion analysis can only detect carbon, hydrogen, and nitrogen, while EDX cannot detect elements lighter than beryllium). These results indicate a total of ca. 12% (w/w) organic material present in the composite, and are in qualitative agreement with the TGA data.
Table 6-1. EDX and combustion analysis data.

<table>
<thead>
<tr>
<th>Energy Dispersive X-ray Microanalysis</th>
<th>Combustion Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>%C [w/w]</td>
<td>%Si [w/w]</td>
</tr>
<tr>
<td>10</td>
<td>34</td>
</tr>
</tbody>
</table>

Given the evidence for partial methylation of the silica surface (vide supra), it is not clear exactly what percentage of the organic material present is PPV. The $^{13}$C cross-polarization MAS-NMR spectrum shows that the integrated methyl signal is approximately 2.3 times more intense than the aromatic region; however, the NMR signal of the methyl group is greatly amplified by magnetization transfer from the three bound hydrogen atoms, whereas the PPV signals originate with either tertiary or quaternary carbon atoms. Taken together, these data suggest that approximately equal quantities (by mass) of PPV and methyl groups are present, and the composite material is therefore approximately 6% (w/w) PPV.

Elemental analysis and NMR spectroscopy provide evidence for the presence of PPV, but give no information with respect to how that polymer is distributed within the composite material. Both nitrogen adsorption and powder X-ray diffraction were used in order to probe for the presence of PPV within the mesopores of the host. The nitrogen adsorption isotherms and powder diffraction patterns of the PPV@MSS composite and the MSS host (with the surfactant removed by ion-exchange using methanolic hydrochloric acid) are shown in Figure 6-5a and Figure 6-5b, respectively. The nitrogen adsorption isotherm of the MSS host is a type IV isotherm typical of mesoporous silica materials. The total pore volume was determined to be 0.75 cm$^3$ g$^{-1}$. The PPV@MSS composite displays a similar type IV isotherm, indicating that the pore structure of the material is retained; however, the total pore volume is reduced to 0.38 cm$^3$ g$^{-1}$. Both the incorporation of the guest polymer and the methylation of silanol residues lead to a
reduction in the total accessible pore volume, providing evidence for the localization of PPV within the mesopores. A peak corresponding to diffraction from the highly ordered mesopores of the MSS host is found in the small angle region of the X-ray diffraction pattern in both samples. In both cases, the d-spacing of this peak is 3.5 nm, which is in qualitative agreement with the pore spacing observed in the TEM micrograph (vide supra). The intensities of the two diffraction peaks are slightly different, with the PPV@MSS composite displaying reduced diffraction intensity. This is consistent with the partial pore filling observed by nitrogen adsorption; it has been shown previously that the adsorption of organic species in the mesopores of hosts such as MCM-41 decreases the scattering contrast and therefore the intensity of the diffraction peak.34

![Figure 6-5](image)

**Figure 6-5.** (a) Nitrogen adsorption isotherms of the empty MSS host (open circles) and the PPV@MSS composite (black circles); (b) powder X-ray diffraction patterns of the empty MSS host (black line) and the PPV@MSS composite (grey fill).

In order to further probe the distribution of the polymer within the particle, an individual sphere was mapped by EDX using STEM. The element maps are shown in Figure 6-6. Monte Carlo simulations of the electron beam interaction with the sample were carried out (Figure 6-7), demonstrating that the resolution of the microanalysis is limited by the number of pixels (or sampling points) in the image, and not by the beam width. Examination of the data in Figure 6-6
shows that the distribution of each of the elements within the image closely overlaps the signal obtained from the high angle annular dark field electron detector. This suggests that the distribution of the elements is roughly homogeneous within the sphere. Since the host material is silica, the silicon and oxygen K-line signals are expected to be evenly distributed. The roughly even distribution of carbon throughout the particle supports the conclusion that the polymer is evenly distributed throughout each of the spheres. The non-zero background of the carbon element map is due to the carbon support film on the TEM grid. It should be noted that the upper-left quadrant of Figure 6-6b is slightly dimmer than the other three quadrants; this may be due to variation in the thickness of the carbon film supporting the sample. It may also be due to damage in the sample caused by exposure to the electron beam, or a slight inhomogeneity in the polymer distribution. Importantly, there is no surface layer of polymer visible in the carbon map, providing further evidence that the PPV is encapsulated within the mesopores of the silica spheres.
Figure 6-6. STEM-EDX analysis of a single PPV@MSS microparticle. (a) HAADF detector image; (b) carbon K-line image; (c) oxygen K-line image; (d) silicon K-line image.
Figure 6-7. Simulated electron trajectories for a 200 keV, 2.0 nm diameter electron beam incident on a 600 nm thick film of silica supported on a 10 nm thick carbon film. 1000 electron trajectories are shown; approximately 30 of those (3%) deviate from the incident trajectory by more than 1 nm. Monte Carlo simulations were made using the CASINO (v2.42) software package. Individual pixels in Figure 6-6 are approximately 10 – 15 nm wide.

6.3.3 Optical Properties

The absorption, emission, and excitation spectra of the PPV@MSS material (prepared as a colloidal dispersion in ethanol) are shown in Figure 6-8. The absorption spectrum features a broad band centered at approximately 360 – 370 nm, which in turn is superimposed on a sharply sloped baseline. The absorption band is assigned to the PPV $\pi$ to $\pi^*$ transition and closely mirrors the peak observed in the excitation spectrum, while the baseline (which rises exponentially at shorter wavelengths) is due to Rayleigh scattering from the sample. The
emission band displays the three vibronic peaks at 490, 520, and 575 nm typical for PPV. Both the absorption and emission spectra are blue-shifted by approximately 20 nm relative to unencapsulated PPV. While this has been observed previously in zeolite-encapsulated PPV samples, the precise origin of the blue-shift is not clear. One explanation is that the confined environment of the mesopores causes torsion in the polymer backbone, which in turn limits the effective conjugation length and results in a blue shift in both the absorption and emission spectra. Alternatively, the material may consist of shorter PPV oligomers which have spectra that are blue-shifted relative to PPV, or the thermal elimination step may have been incomplete, resulting in methylene bridges in the polymer backbone that disrupt the conjugation. Since removal of the silica template by HF etching results in no change in the emission spectrum (vide infra), the first explanation seems unlikely. Given that exposure to solvents such as tetrahydrofuran, dimethylsulfoxide and toluene fails to yield any extractable material, it also seems unlikely that the observed blue-shift is due to the presence of shorter, more soluble oligomers. Therefore, the presence of methylene bridges in the polymer backbone appears to be the most likely explanation for the observed blue-shift.
Figure 6-8. Absorption (black line), excitation (blue line, $\lambda_{em} = 492$ nm), and emission (green line, $\lambda_{ex} = 366$ nm) spectra of the PPV@MSS composite dispersed in ethanol.

The fluorescence quantum yield of PPV@MSS as both a colloidal dispersion in ethanol and as a powder was measured using an integrating sphere. The results are tabulated in Table 6-2, along with results for a variety of other PPV preparations previously reported in the literature. The value of $\Phi_f = 0.84 \pm 0.12$ obtained for the PPV@MSS material as an argon-degassed dispersion is very high, especially compared to a fluorescence quantum yield of only $\sim 0.2$ obtained for unencapsulated or otherwise unprotected PPV.\textsuperscript{14, 36-38} While the value of $\Phi_f$ decreases to $0.63 \pm 0.12$ when measured as a powder, this nonetheless represents a significant enhancement in the quantum yield of PPV relative to other measurements carried out in the solid state. Previous work by Rothberg and coworkers has suggested that the formation of inter-chain excimers has a deleterious effect on the fluorescence quantum yield of PPV and PPV derivatives.\textsuperscript{13, 14} Further evidence for this comes from near-field scanning optical microscopy studies on films of MEH-PPV which show evidence for excimer formation in aggregated sections of the film.\textsuperscript{39} Bazan et al. also demonstrated an increase in $\Phi_f$ when PPV segments were isolated within a poly(norbornene) matrix.\textsuperscript{29} This suggests that the very high quantum yield observed for the
PPV@MSS material may be due to the isolation of polymer chains within the mesopores of the silica host. By preventing the formation of inter-chain excimers, the quantum yield for formation of the fluorescent intra-chain excitons is increased. The decrease in $\Phi_f$ of the PPV@MSS composite in the solid state may be due to polymer localized on the surface of the particles. When the particles are dilutely dispersed in solvent, inter-chain excimer formation between adjacent particles is limited and the fluorescence quantum yield is high. Particle-particle contact in the powder may allow for a limited amount of excimer formation in the solid state, thus slightly decreasing the overall fluorescence quantum yield.

**Table 6-2.** Fluorescence quantum yields of various PPV preparations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Phi_f$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPV@MSS (dispersion)</td>
<td>0.84 ± 0.12</td>
<td>This work</td>
</tr>
<tr>
<td>PPV@MSS (solid state)</td>
<td>0.63 ± 0.12</td>
<td>This work</td>
</tr>
<tr>
<td>PPV (dispersion)</td>
<td>0.20</td>
<td>Sharma$^{38}$</td>
</tr>
<tr>
<td>PPV (film)</td>
<td>0.04</td>
<td>Lemmer$^{37}$</td>
</tr>
<tr>
<td>PPV (film)</td>
<td>0.07-0.15</td>
<td>Rothberg$^{14}$</td>
</tr>
<tr>
<td>PPV (film)</td>
<td>0.27</td>
<td>Greenham$^{36}$</td>
</tr>
<tr>
<td>PPV$<em>{10\text{-}block}$-PNBE$</em>{200}$</td>
<td>0.75</td>
<td>Bazan$^{29}$</td>
</tr>
</tbody>
</table>

In order to further probe the photophysics of the PPV@MSS composite, fluorescence lifetime measurements were carried out using time-correlated single photon counting, and the results are shown in Figure 6-9. The decay curve fits well to a single exponential function with a fluorescence lifetime of $\tau_f = 1.2$ ns. Notably absent is a fast decay component ($\tau_f < 1$ ns) that has been associated with exciton diffusion to carbonyl defect sites.$^{11, 37}$ The measured lifetime is
consistent with previous reports of the fluorescence lifetime in pristine PPV chains ($\tau_f = 1.1 - 1.4$ ns) that possess few (if any) defects in the polymer backbone.$^{11, 14, 37}$

![Figure 6-9. TC-SPC data (grey line) and the fit to a single exponential decay function with $\tau_f = 1.2$ ns (black line).](image)

Figures 6-9. TC-SPC data (grey line) and the fit to a single exponential decay function with $\tau_f = 1.2$ ns (black line).

An advantage of encapsulating the polymer chains inside an inorganic matrix such as mesoporous silica is the potential for protecting the guest organic material from environmental degradation. In order to determine if such an effect may be observed in the PPV@MSS material, a sample was irradiated at 366 nm using a hand-held UV lamp and the fluorescence intensity monitored as a function of time. In order to provide a sample for comparison, the silica of the PPV@MSS material was removed by etching for 45 minutes using 25% HF$_{(aq)}$. The etched PPV material does not appear to exhibit any adverse effects due to the etching. The emission spectra of the PPV@MSS and etched PPV materials decay smoothly with increased irradiation time, with a concomitant decrease in the relative intensity of the highest energy vibronic peak (see Figure 6-10). The decay of the integrated fluorescence intensities is shown in Figure 6-11. Both data sets fit to a bi-exponential decay function (Equation 6-1).
Figure 6-10. Emission spectra as a function of irradiation time for (a) the PPV@MSS composite, and (b) the etched PPV control sample. Note that the axes in (a) and (b) have identical scaling.

Figure 6-11. Integrated fluorescence intensity as a function of irradiation time for the PPV@MSS composite (black circles) and the etched PPV control sample (grey diamonds). The solid black and grey lines are bi-exponential decay functions that have been fit to the experimental data.
Equation 6-1

\[ I = Ae^{-at} + Be^{-bt} \]

The fitted parameters are tabulated in Table 6-3. In the PPV@MSS material, there is both a fast \((a = 0.06)\) and a slow \((b = 0.004)\) component to the overall photobleaching, with a weighting towards the slow component \((87\%)\). On etching of the silica host both rates of photobleaching increase, and the increase is particularly pronounced for the faster decay \((a = 0.25, b = 0.01)\). Additionally, the relative weighting of the fast component increases from \(13\%\) to \(28\%). Clearly, removal of the protective silica matrix results in an increased rate of photobleaching in the sample.

Table 6-3. Fitted parameters for decay of fluorescence intensity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(A)</th>
<th>(a)</th>
<th>(B)</th>
<th>(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPV@MSS</td>
<td>0.13</td>
<td>0.06</td>
<td>0.87</td>
<td>0.004</td>
</tr>
<tr>
<td>PPV (HF etched)</td>
<td>0.28</td>
<td>0.25</td>
<td>0.72</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The increased photostability in the PPV@MSS sample may be due to one of any number of causes. It has been shown previously that irradiating a PPV sample in the absence of oxygen results in essentially no photobleaching.\(^{11}\) The constrained environment of the mesopores may limit the rate at which oxygen can diffuse into the pores and further prevent it from reaching the correct geometry for oxidative photobleaching to occur. Additionally, the sequestration and isolation of the polymer within individual mesopores may limit the effect of the carbonyl defects which do form. It is well known that these defects act as low energy traps in PPV films, and exciton diffusion will funnel energy towards these quenching sites, resulting in an amplified quenching of the emission.\(^{11, 37}\) The silica may act to reduce the number of polymer chains
within the exciton diffusion radius of a quenching site. Thus, the silica may act to either prevent oxidation of the polymer, or limit the effect of the oxidation which does occur. In fact, both of these mechanisms may be simultaneously operative.

6.4 CONCLUSIONS

This chapter demonstrated the incorporation of PPV into monodisperse, mesoporous silica spheres by a new ion-exchange and in situ polymerization route. This synthetic route selectively incorporated the insoluble polymer into the mesopores of the spheres, as demonstrated by STEM-EDX, nitrogen adsorption, and powder X-ray diffraction. By controlling the morphology of the polymer chains in this way, the optical properties of the PPV guest are significantly improved. Inter-chain excimer formation is limited, thus improving the fluorescence quantum yield of the polymer; photodegradation of the polymer is slowed due to reduced oxygen diffusion; and the composite material is rendered processable as a stable colloidal dispersion. This combination of improved optical and physical properties is expected to make this material useful in the development of new photonic applications and devices.
6.5 REFERENCES


35. The fluorescence quantum yield of the PPV@MSS material varies according to the ion-exchange reaction time, as well as the annealing time and temperature. The value reported here reflects the average of two different batches of material, each of which was measured on two different integrating spheres.


CHAPTER 7

CARBOHYDRATE-LABELLED FLUORESCENT MICROPARTICLES AND THEIR BINDING TO LECTINS

7.1 INTRODUCTION

The binding of proteins to cell-surface carbohydrates is of critical importance in molecular biology and mediates a wide variety of responses, including inflammation,\(^1\) blood antigenicity,\(^2\) and viral attack on host cells.\(^3\) The carbohydrate-binding proteins involved in these processes are known as lectins.\(^4\) Due to the importance of the carbohydrate–lectin interaction, a great deal of work has gone into developing synthetic analogues of cell-surface carbohydrates.\(^5\) This work has typically been carried out with one of two goals in mind. First, the neoglycans can act as the recognition element of a molecular sensor for pathogenic agents. Second, by competing with host cells for binding sites on the pathogen, the neoglycans can act as high affinity inhibitors for the bacteria or virus.

The interaction of lectins with sugars is typified by a multivalent response; monomeric interactions are often weak, whereas presenting the lectin with an array of carbohydrate ligands can substantially enhance the binding affinity.\(^6,7\) Thus, the designs of potential substrates often feature multiple glycosides tethered to a common aglycone. The designs of the aglycone range from short, flexible linkers,\(^8,9\) to complex dendrimers,\(^10-12\) polymers,\(^13-15\) and proteins\(^16,17\) (Chart 7-1). Labelling colloidal particles with carbohydrates has also attracted recent attention. This geometry potentially offers an advantage over linear or dendritic structures in that it more closely mimics the cell surface that is the natural substrate for lectins. To this end, multivalent

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carbohydrate liposomes,\textsuperscript{18-21} magnetic beads,\textsuperscript{22, 23} quantum dots,\textsuperscript{23-25} and polymer beads\textsuperscript{26} have all been explored.

\textbf{Chart 7-1}

Conjugated polymers have also been exploited successfully as aglycones for neoglycopolymers.\textsuperscript{27-33} Owing to their electrical conductivity and luminescence, they can act as signal transduction elements in biological probes and sensors. Both Phillips et al.\textsuperscript{34} and Disney et al.\textsuperscript{29} have recently prepared linear sugar-functionalized poly(p-phenyleneethynylene)s (Chart 7-2). Both sets of polymers act as fluorescence-based sensors for \textit{E. coli} bacteria and mannose-
binding lectins such as concanavalin A (ConA). Similarly, Baek et al. describe polythiophene-based biosensors for both *E. coli* and influenza virus. The development of simple, cost-effective sensors for common pathogens is expected to be enormously beneficial in controlling the spread of disease. This is especially true when laboratory resources are limited.

**Chart 7-2**

\[
R = \text{CH} = \text{CH} \\
R' = \text{NHC(NH)}(\text{CH}_2)_3\text{S(\text{CH}_2)_2C(O)}\text{NH}
\]
In this chapter, the preparation of carbohydrate functionalized PPE microparticles is reported. The morphology of the particles is controlled using dispersion polymerization methodology and subsequently evaluated by scanning electron microscopy. The particles have been characterized in terms of both their colloidal and optical behavior. The importance of these materials as cellular mimetics is discussed in the context of their affinity for simple, well-known lectins such as ConA.

7.2 EXPERIMENTAL

7.2.1 General

Materials and Equipment. Diisopropylamine, boron trifluoride diethyl etherate, boron tribromide, sodium dodecyl sulfate, sodium methoxide, and copper(I) iodide were purchased from Sigma-Aldrich. 1,2,4-tribromobenzene was purchased from Alfa-Aesar. Concanavalin A, Texas Red conjugate (ConA–TR) was purchased from Invitrogen. Tetrakis(triphenylphosphino)palladium(0) was purchased from Strem Chemicals. Deuterated solvents were purchased from Cambridge Isotope Laboratories. All of the above reagents were used as received without further purification. Sugar trichloroacetimidates, 1,4-diido-2,5-hydroquinone, and 1,4-dimethoxy-2,5-diethynylbenzene were prepared according to previously published literature procedures. Anhydrous dichloromethane was obtained by passing degassed solvent through a column of activated alumina. NMR spectra were acquired on either a Bruker Avance 300 or 400 system and referenced to residual solvent (CHCl\textsubscript{3}, \(\delta = 7.27\), \(13\text{C}, \delta = 77.23\)). All reactions were carried out using standard inert atmosphere Schlenk techniques under nitrogen gas unless otherwise noted. FT-IR spectra were recorded as KBr pellets on a Bomem MB-100 spectrometer. UV-vis-NIR spectra were recorded as aqueous or methanolic dispersions in a 1 cm quartz cuvette on a Varian Cary 5000 spectrophotometer. Fluorescence
spectra were measured as aqueous or methanolic dispersions in a 1 cm quartz cuvette using a Photon Technology International QuantaMaster fluorimeter. Laser scanning confocal microscopy (LSCM) was carried out on a Zeiss 510 Meta microscope using 488 nm and 568 nm laser excitation. 96-Well plates were analyzed using a Beckman Coulter Biomek FX plate reader. Electrospray ionization (ESI) mass spectra and elemental analyses were obtained at the UBC Mass Spectrometry/Microanalysis Facility.

**Scanning Electron Microscopy.** Dilute suspensions of colloidal material (ca. 1 mg mL⁻¹) were prepared in distilled water by ultrasonication. An aliquot (100 µL) of this suspension was drop-cast on an aluminum stub and allowed to dry. Microscopy was carried out on a Hitachi S4700 scanning electron microscope equipped with a cold field-emission electron gun and pinhole objective lens. Accelerating voltages of 1.0 – 2.0 kV were chosen in order to provide a balance between image resolution, charging effects, and surface penetration. Particle diameters were determined by measuring the diameter of a minimum of 200 particles in the FE-SEM.

**Electrokinetic Measurements.** Measurements of electrophoretic mobilities were made on a Beckman-Coulter Delsa 440SX instrument. Samples were measured at a particle concentration of 0.1% (w/w) in 0.010 M aqueous sodium chloride matrix. All measurements were taken at 25.0 ± 0.1 ºC. The Smoluchowski equation was used to relate the experimentally determined electrophoretic mobilities to the zeta potential.

### 7.2.2 Synthesis

**1,4-bis(2’,3’,4’,6’-tetra-O-acetyl-β-D-galactopyranosyl)-2,5-diiodobenzene (β-Gal(OAc)₄-M).** A 250 mL round bottom Schlenk flask was charged with 2,3,4,6-tetra-O-acetyl-α-D-galactose trichloroacetimidate (2.15 g, 4.36 mmol), 1,4-diiodo-2,5-hydroquinone (0.45 g, 1.24 mmol), anhydrous dichloromethane (60 mL), and activated, crushed 4Å molecular sieves. The
flask was cooled to −30 °C and the atmosphere replaced with nitrogen. Boron trifluoride
diethyletherate (2.0 mL, 2.3 g, 16 mmol) was added. The reaction mixture was stirred for three
hours at −30 °C and then allowed to warm to room temperature overnight. It was flushed through
a plug of diatomaceous earth to remove the crushed sieves. The solution was washed with brine
(4 × 75 mL), water (1 × 100 mL), and dried over anhydrous magnesium sulfate. It was filtered
and concentrated to dryness by evaporation under reduced pressure. The crude product was
purified by column chromatography on silica gel using 40:60 ethyl acetate:hexanes as eluent,
yielding β-Gal(OAc)₄-M as a white solid (0.95 g, yield 77%). ¹H NMR (CDCl₃, 400 MHz) δ
7.49 (2H, s, aromatic CH), 5.56 (2H, dd, ³J_HH = 10.4 Hz, ³J_HH = 8.0 Hz, galactose C2H), 5.46
(2H, d, ³J_HH = 3.2 Hz, galactose C4H), 5.09 (2H, dd, ³J_HH = 10.4 Hz, ³J_HH = 3.2 Hz, galactose
C3H), 4.93 (2H, d, ³J_HH = 8.0 Hz, galactose C1H), 4.20 (4H, m, galactose C6H₂), 4.09 (2H, m,
galactose C5H), 2.19 (6H, s, CH₃COO), 2.14 (6H, s, CH₃COO), 2.10 (6H, s, CH₃COO), 2.01
(6H, s, CH₃COO). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 170.72, 170.37, 170.27, 169.33, 152.87,
126.61, 100.79, 86.63, 71.81, 70.89, 68.25, 67.19, 62.20, 21.47, 21.17, 20.83, 20.74. ESI-MS:
m/z = 1045 (M+Na⁺, 100%). Anal. Calcd. For C₃₄O₂₀H₄₀I₂: C, 39.94; H, 3.94. Found: C, 40.00;
H, 4.20.

1,4-bis(2’,3’,4’,6’-tetra-O-acetyl-β-D-glucopyranosyl)-2,5-diiodobenzene (β-Glc(OAc)₄-M). The same procedure was used as for β-Gal(OAc)₄-M, yielding β-Glc(OAc)₄-M as a white
solid (0.41 g, yield 33%). ¹H NMR (CDCl₃, 400 MHz) δ 7.41 (2H, s, aromatic CH), 5.26 (4H, m,
glucose C2H and C3H), 5.07 (2H, t, ³J_HH = 9.4 Hz, glucose C4H), 4.93 (2H, d, ³J_HH = 7.2 Hz,
glucose C1H), 4.18 (4H, m, glucose C6H₂), 3.88 (2H, m, glucose C5H), 2.11 (6H, s, CH₃COO),
2.05 (6H, s, CH₃COO), 2.01 (6H, s, CH₃COO), 1.99 (6H, s, CH₃COO). ¹³C{¹H} NMR (CDCl₃,
100 MHz) δ 170.77, 170.33, 169.53, 169.24, 152.83, 126.57, 100.19, 86.78, 72.65, 72.56, 70.84,
1,4-bis(2′,3′,4′,6′-tetra-O-acetyl-α-D-mannopyranosyl)-2,5-diiodobenzene (α-Man(OAc)₄-M). The same procedure was used as for β-Gal(OAc)₄-M, yielding α-Man(OAc)₄-M as a white solid (0.40 g, yield 56%). ¹H NMR (CDCl₃, 400 MHz) δ 7.53 (2H, s, aromatic CH), 5.63 (2H, dd, ³J_HH = 6.7 Hz, ³J_HH = 3.4 Hz, mannose C3H), 5.53 (2H, dd, ³J_HH = 1.9, ³J_HH = 1.4, mannose C2H), 5.44 (2H, d, ³J_HH = 1.7 Hz, mannose C1H), 5.38 (2H, t, ³J_HH = 10.1 Hz, mannose C4H), 4.30 (2H, m, mannose C5H), 4.13 (4H, m, mannose C6H₂), 2.21 (6H, s, CH₃COO), 2.13 (6H, s, CH₃COO), 2.08 (6H, s, CH₃COO), 2.05 (6H, s, CH₃COO). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 170.78, 170.09, 170.02, 169.93, 151.60, 125.94, 97.42, 87.29, 70.11, 69.37, 68.84, 66.01, 62.52, 21.14, 21.05, 20.92, 20.88. ESI-MS: m/z = 1045 (M+Na⁺, 100%). Anal. Calcd. for C₃₄O₂₀H₄₀I₂: C, 39.94; H, 3.94. Found: C, 40.20; H, 4.11.

2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl-PPE (β-Gal(OAc)₄-PPE). A 50 mL round bottom Schlenk flask was charged with toluene (4 mL) and diisopropylamine (2 mL). The solution was sparged with nitrogen for 15 minutes, and 1,4-dimethoxy-2,5-diethynylbenzene (75 mg, 0.40 mmol), 1,4-bis(2′,3′,4′,6′-tetra-O-acetyl-β-D-galactopyranosyl)-2,5-diiodobenzene (β-Gal(OAc)₄-M) (278 mg, 0.27 mmol), 1,2,4-tribromobenzene (20 mg, 0.06 mmol), tetrakis(triphenylphosphino)palladium(0) (16 mg, 0.01 mmol), and copper(I) iodide (3 mg, 0.02 mmol) were added. The mixture was stirred for 60 s, and a degassed solution of sodium dodecyl sulfate (0.8 g, 2.77 mmol) in distilled water (60 mL) was added. The yellow suspension was stirred at 70 ºC for 24 hours, and then heated to reflux for two hours. The mixture was centrifuged, and the residue washed by redispersion/centrifugation cycles in toluene (1 × 100 mL), 2:1 toluene:methanol (1 × 100 mL), 1:2 toluene:methanol (1 × 100 mL), and toluene (1 × 50 mL). This yielded β-Gal(OAc)₄-PPE as an orange solid (100 mg).
2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl-PPE (β-Glc(OAc)$_4$-PPE). The same procedure was used as for β-Gal(OAc)$_4$-PPE, yielding β-Glc(OAc)$_4$-PPE as an orange solid (44 mg).

2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl-PPE (α-Man(OAc)$_4$-PPE). The same procedure was used as for β-Gal(OAc)$_4$-PPE, yielding α-Man(OAc)$_4$-PPE as an orange solid (180 mg).

β-D-galactopyranosyl-PPE (β-Gal-PPE). 2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl-PPE (100 mg) was suspended in anhydrous methanol (10 mL) and a solution of sodium methoxide in methanol (10 mL, 0.2 M) was added. The mixture was stirred at room temperature for two hours. A solution of ammonium chloride (15 mL, 1.6 M) was added dropwise and the mixture was stirred for 15 minutes. The orange solid was isolated by centrifugation, yielding β-Gal-PPE (75 mg).

β-D-glucopyranosyl-PPE (β-Glc-PPE). The same procedure was used as for β-Gal-PPE, yielding β-Glc-PPE as an orange solid (30 mg).

α-D-mannopyranosyl-PPE (α-Man-PPE). The same procedure was used as for β-Gal-PPE, yielding α-Man-PPE as an orange solid (140 mg).

7.2.3 Protein-Binding Assays

All experiments were carried out in 0.1 M phosphate buffered saline (PBS) containing 0.7% (w/w) sodium chloride, 1 mM manganese(II) chloride and 1 mM calcium chloride. A stock solution of concanavalin A–Texas Red was prepared by adding 6 mg of the protein to 6 mL of buffer solution. The protein was dissolved by sonication, and the solution was centrifuged to remove any aggregated material. Dispersions of β-Gal-PPE and α-Man-PPE were prepared by adding 5 mg of the appropriate polymer to 5 mL of buffer solution and sonicking the mixture.
The dispersions were vortexed briefly prior to use. Aliquots of the glycosylated polymer beads, ConA–TR, and buffer solution were combined such that the final polymer concentration varied from 0 to 0.8 mg mL\(^{-1}\) and the final ConA–TR concentration was 0.2 mg mL\(^{-1}\). The combined samples were incubated for four hours at room temperature in the dark, with occasional (ca. every 30 minutes) vortexing of the sample tubes. Samples were then centrifuged at 7500 rpm for 5 minutes to separate the polymer beads and the supernatant. Aliquots (150 µL) of the supernatant solutions were analyzed in a 96-well plate reader by monitoring the emission at 625 nm (35 nm bandwidth) after excitation at 590 nm (20 nm bandwidth).
7.3 RESULTS AND DISCUSSION

7.3.1 Synthesis

Scheme 7-1

OCH₃

I₂, KIO₃
H₂SO₄, HOAc, H₂O reflux, 16 hrs.
78%

1. BBr₃, CH₂Cl₂
-78 °C to r.t., 48 hrs.
2. HCl, H₂O
97%

M

β-Gal(OAc)₄-M

β-Glc(OAc)₄-M

α-Man(OAc)₄-M
The synthesis of carbohydrate functionalized monomers $\beta$-Gal(OAc)$_4$-M, $\beta$-Glc(OAc)$_4$-M, and $\alpha$-Man(OAc)$_4$-M is shown in Scheme 7-1. The hydroquinone aglycone (M) is prepared by a two step literature procedure involving iodination of 1,4-dimethoxybenzene followed by boron tribromide ether cleavage. Glucose, galactose and mannose trichloroacetimidates are prepared by a literature procedure involving selective protection/deprotection of the carbohydrate hydroxyl groups followed by reaction with trichloroacetonitrile and 1,8-diazabicyclo[5.4.0]undec-7-ene. The glycosidation reaction itself is carried out using the trichloroacetimidates, 1,4-diido-2,5-hydroquinone and boron trifluoride diethyletherate as a catalyst. This yields $\beta$-Gal(OAc)$_4$-M and $\beta$-Glc(OAc)$_4$-M with complete inversion of stereochemistry; only the $\beta$ anomer is observed. Owing to the anchimeric assistance of the acetoxy group at the C2 position in mannose, $\alpha$-Man(OAc)$_4$-M exhibits exclusively $\alpha$ stereochemistry. In neither case is a mixed $\alpha$-$\beta$ diastereomer observed. The assignment of stereochemistry was made by measurement of the $^1J_{C1H1}$ and $^3J_{H1H2}$ coupling constants, which are tabulated in Table 7-1. In galactose and glucose, the relationship of H1 and H2 is axial–axial, leading to large values of the $^3J_{H1H2}$ coupling constant (8.0 and 7.2 Hz respectively) as expected from the Karplus equation. In mannose, the relationship of H1 and H2 is equatorial–equatorial, and the value of $^3J_{H1H2}$ is correspondingly small (1.7 Hz). The $^1J_{C1H1}$ coupling constants have been previously shown to correlate directly with the stereochemistry at the anomeric carbon, and the values reported in Table 7-1 are in agreement with $\beta$ stereochemistry for both galactose and glucose, and $\alpha$ stereochemistry for mannose.
Table 7-1. Coupling constants of carbohydrate functionalized monomers.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{3}J_{HH2}$ (Hz)</th>
<th>$^{1}J_{CH}$ (Hz) [a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-Gal(OAc)$_4$-M</td>
<td>8.0</td>
<td>163</td>
</tr>
<tr>
<td>$\beta$-Glc(OAc)$_4$-M</td>
<td>7.2</td>
<td>161</td>
</tr>
<tr>
<td>$\alpha$-Man(OAc)$_4$-M</td>
<td>1.7</td>
<td>176</td>
</tr>
</tbody>
</table>

[a] Measured from a $^{13}$C-gated pulse sequence (CDCl$_3$, 100 MHz).

The carbohydrate functionalized monomers were polymerized under Sonogashira conditions using 1,4-dimethoxy-2,5-diethynylbenzene and 1,2,4-tribromobenzene as co-monomers (Scheme 7-2). A large volume of aqueous SDS was added in order to carry out the reaction under dispersion polymerization conditions. This is possible due to the water tolerance of the palladium cross-coupling reaction. This in turn causes the polymerization to occur only within the hydrophobic interior of the SDS micelles, and leads to spherical PPE particles of roughly one micrometer in diameter. The tribromobenzene acts to crosslink the PPE chains, ensuring that the resultant polymers retain their morphology despite redispersion in strong solvents such as toluene. 1,2,4-Tribromobenzene was chosen as a crosslinker in preference to 1,2,4-triiodobenzene; the lower reactivity of the bromine groups ensures that the polymer chains grow primarily linearly, without premature crosslinking and subsequent precipitation.
Owing to the insolubility of the PPE microparticles, the stereochemistry of the PPE glycosides could not be evaluated directly. While the starting materials were stereochemically pure as evaluated by $^1$H and $^{13}$C NMR spectroscopy, mutarotation during the polymerization reaction is a possibility. In order to determine if this plays a significant factor in the stereochemical outcome of the polymerization, a model reaction was carried out where β-Glc(OAc)$_4$-PPE was heated to 70 ºC for 24 hours in the presence of diisopropylamine (1 mL), toluene (1 mL), and water (15 mL). No mutarotation was observed, which suggests that the stereochemistry of the polymers reflects that of the monomers.

The final step in the synthesis of the carbohydrate-labeled polymers is the removal of the acetate protecting groups. This is accomplished by treatment of the acetate protected polymers with sodium methoxide at room temperature for two hours. The deprotection step is relatively facile, and the complete removal of the acetate protecting groups can be confirmed by the lack of a carbonyl stretching frequency in the infrared spectrum of β-Gal-PPE, β-Glc-PPE, and α-Man-PPE. In the acetate protected precursors, a distinctive stretching frequency at 1751 cm$^{-1}$ can be observed.
7.3.2 Polymer Characterization

Scanning electron micrographs of the PPE microparticles are shown in Figure 7-1. The spherical morphology is clearly evident, and is caused by the polymerization occurring within the hydrophobic interior of the sodium dodecyl sulfate micelles. The mean particle diameter of each sample was found to be ca. 0.8 ± 0.4 µm. The size distribution of the particles is quite broad (50% relative standard deviation), in contrast to polystyrene or polyacrylate latexes prepared by emulsion polymerization. The differences in the polymerization mechanism (a radical initiated chain growth mechanism for the latexes, as compared to a condensation mechanism for the Sonogashira reaction), may explain the observed differences in the polydispersity of the latex diameters. Condensation polymerizations are particularly sensitive to both the stoichiometry and purity of the reagents, and the rate of the Sonogashira polymerization is also sensitive to the amount of catalyst present in the micelle. Thus, even small, local inhomogeneities in monomer, co-monomer, or catalyst concentrations may result in inhomogeneities in the final particle diameter.
As expected for polymers derived from the PPE backbone, β-Gal-PPE, β-Glc-PPE, and α-Man-PPE were found to be emissive as colloidal dispersions in both phosphate buffered saline and methanol, although only weakly so in the solid state. The emission band has its maximum at 560 nm in methanol, which is markedly red-shifted compared to linear PPEs in dilute solution (Figure 7-2). Halkyard et al. have shown that aggregation of alkyl substituted PPEs in solvent/non-solvent mixtures or in thin films results in a substantial bathochromic shift of the emission spectrum. In this case, the short methoxy substituents are not long enough to prevent interchain aggregation, and both hydrogen bonding of the carbohydrate groups and cross-linking of the polymer chains may encourage this phenomenon. While the emission spectra of the PPE
microparticles prepared by Hittinger et al. show no such shift, this is likely due to the bulkier 2-ethylhexyl and n-octyl substituents, which lead to a more porous bead structure that is readily swollen by organic solvents. The slight bathochromic shift for β-Gal-PPE as compared to β-Glc-PPE and α-Man-PPE may be explained by batch-to-batch variability in terms of the cross-linking density; increased cross-linking in β-Gal-PPE may lead to a more aggregated polymer structure and therefore a larger bathochromic shift.

Figure 7-2. Emission spectra of β-Gal-PPE (black line), β-Glc-PPE (red line), and α-Man-PPE (blue line) at an excitation wavelength of 408 nm.

The zeta potentials of β-Gal-PPE, β-Glc-PPE, and α-Man-PPE were determined to be −11, −30, and −14 mV respectively. The negative sign of the zeta potential is typical of polystyrene latexes prepared via emulsion polymerization. In the case of polystyrene, this is due to tightly adsorbed anionic surfactant that imparts the particle surface with a negative charge. Given the use of sodium dodecyl sulfate as a surfactant in the preparation of the polymers, this is a likely contributor to the observed negative surface charge. It should be noted that the magnitude of the zeta potential in all cases is low to moderate, which according to conventional DLVO theory.
implies a lack of colloidal stability. The particles do in fact aggregate; if the particle diameters are measured by LSCM, the mean diameter is found to be 4.9 µm. This is several times larger than the mean diameter obtained by SEM analysis. Part of the discrepancy is undoubtedly due to the inherent resolution limit of the optical microscope (as defined by the Rayleigh criterion). Small ($d < 1.0 \, \mu m$) particles will appear as single pixels in the final image, and thus their diameter will tend to be overestimated. Despite this, aggregation is still the most important contribution to the larger mean, given that the observed difference is quite dramatic.

7.3.3 Lectin Affinity

To probe the utility of these PPE beads for potential biosensor, biocapture, or affinity chromatography application, their binding to lectins was examined. Dispersions (1 mg mL$^{-1}$) of $\alpha$-Man-PPE and $\beta$-Gal-PPE were prepared in PBS containing Mn$^{2+}$ and Ca$^{2+}$, two cofactors required for the lectin ConA. Similarly, a stock solution of ConA–TR was prepared in the same matrix. In this experiment, the Texas Red fluorophore serves as a means of measuring the concanavalin A concentration in solution. The samples were diluted to the same final concentration of ConA–TR, incubated for four hours, and the supernatants isolated by centrifugation. The isolated supernatants were then analyzed for protein content by a fluorescence assay at 625 nm (i.e., quantifying the emission from the Texas Red fluorophore, and therefore the ConA concentration). The experiment is illustrated schematically in Figure 7-3.
Figure 7-3. Schematic illustration of the protein-binding assay. PPE microparticles are dispersed in solution and ConA–TR is added. The protein becomes bound to the microparticles, and the PPE–protein conjugates are isolated by centrifugation. The residual ConA–TR in the supernatant is quantified by a fluorescence assay using the excitation and emission wavelengths of Texas Red.

As seen in Figure 7-4, there is clearly an extraction of the protein from the solution as compared to the blank (zero added PPE). ConA should bind to α-D-mannose residues, but should display little to no affinity for β-D-galactose functionality. The amount of protein extracted is slightly greater for α-Man-PPE than for β-Gal-PPE, perhaps indicating some specificity; however, there is clearly a dominant non-specific interaction present. This is likely due to electrostatic interactions between the negatively charged PPE particles and the positively charged concanavalin A, while other possibilities include hydrophobic van der Waals interactions or non-specific hydrogen bonding.
A competition experiment was also carried out, where 100 µL of ConA–TR solution, 200 µL of polymer dispersion, and 200 µL of a 0.3 M D-mannose solution were incubated under conditions identical to those above. For both β-Gal-PPE and α-Man-PPE there was an increase in fluorescence intensity (20% and 9%, respectively) of the supernatant relative to the control, indicating a decrease in overall protein-polymer adhesion. The free sugar appears to compete with the polymer for binding sites on the protein, and concentrated sugar solutions may be able to remove bound protein from a polymer sample.

The isolated protein–polymer bioconjugates were washed twice with 200 µL aliquots of fresh PBS buffer by redispersion/centrifugation cycles, and suspended in 50 µL of PBS. Laser scanning confocal microscopy is used to confirm the binding of the protein to the polymer microparticles; it reveals colocalization of the polymer beads with the Texas Red fluorophore (Figure 7-5). Additionally, there appears to be some degree of aggregation among the individual particle beads upon lectin adhesion. This phenomenon is similar to cellular agglutination, which

Figure 7-4. Extraction of ConA–TR from solution by β-Gal-PPE (grey diamonds) and α-Man-PPE (black circles).
is mediated by the multivalent character of lectins; by binding sugar residues on more than one cell, the proteins link the cells together in large aggregates. Owing to the similar size of these microparticles (1 µm) and erythrocytes (7 µm), their highly fluorescent properties, and their surface carbohydrate residues, these beads may prove to be useful models in the study of agglutination and other important biological processes. The mannose-substituted polymer beads may also form clusters with *E. coli* bacteria in a manner analogous to the mannosylated-PPE of Swager, making them useful as fluorescent tags for pathogens.

![Figure 7-5. Laser scanning confocal micrographs: (a) 488 nm excitation, showing a cluster of mannose-substituted particles; (b) 568 nm excitation, showing the location of Texas Red tagged ConA; (c) merged image.](image)

### 7.4 CONCLUSIONS

In this chapter, the synthesis of carbohydrate functionalized PPE microparticles was described. A series of 1,4-bis(glycoside)-2,5-diiodobenzene monomers was prepared by glycosidation of 1,4-diodo-2,5-hydroquinone using sugar trichloroacetimidates under Lewis acid catalyzed conditions. Palladium catalyzed cross-coupling of the glycosylated diiodobenzenes with 1,4-dimethoxy-2,5-diethynylbenzene and 1,2,4-tribromobenzene as co-monomer afforded conjugated polymers. The morphology of the resultant polymers was successfully controlled
using dispersion polymerization conditions, and evaluated by scanning electron microscopy. It was found that the particles effectively bind to concanavalin A; however, the dominant mechanism of interaction is non-specific and likely electrostatic. Aggregates of the PPE particles and ConA–TR were visualized by laser scanning confocal microscopy, confirming colocalization of the polymer and ConA.

In order to further develop these particles as potential biological probes, tags, or sensors, a number of key points must be addressed by further research. The non-specificity of the polymer-protein interaction will obviously hamper efforts to develop sensors or labels based on these materials. One potential approach is to add a long, water-soluble linker (such as oligo(ethylene oxides)) between the PPE polymer backbone and the carbohydrate. This should allow for a greater degree of flexibility, giving the carbohydrate better access to the binding pocket on the lectin. Other factors, such as the colloidal stability, polydispersity, and biocompatibility of the polymers may also need to be addressed. Using biocompatible materials known to produce stable colloids (such as silica) for a hard template or coating may prove effective in this regard.
REFERENCES


CHAPTER 8

8.1 CONCLUSION

This thesis describes the use of structure-directing templates to control the morphology and microstructure of a wide variety of conjugated polymers. In particular, colloidal microspheres were chosen as synthetic targets due to their high degree of symmetry, ease of processability, and potential utility as inks, biological mimics and as building blocks for opals. Mesoporous silica spheres, microporous carbon spheres, and sodium dodecyl sulfate micelles were all successfully employed as templates for conjugated polymer microspheres. The goals of this chapter are to summarize the work that was accomplished, to provide an overview as to its significance, and provide possible future directions for this field of study.

While the ability to self-assemble polypyrrole and polyaniline into various nanostructured morphologies has been extensively studied,\textsuperscript{1-3} prior to this thesis little analogous work on PEDOT had been successfully carried out. Chapter 2 describes the successful templating of PEDOT microstructures using mesoporous silica spheres. Importantly, the mass loading of PEDOT in the PEDOT@MSS composites was over 50\% (w/w), which is an order of magnitude larger than any previous example of a PEDOT-containing core–shell particle.\textsuperscript{4-6} In order to obtain the best optoelectronic properties from such composites, the mass loading of the conjugated material should ideally be as high as possible, with a minimum amount of template present. Notably, the silica template can be removed by etching with hydrofluoric acid; this leaves behind a spherical microparticle composed entirely of PEDOT. This represents the first published report of a monodisperse, spherical PEDOT microparticle. Additionally, the feasibility of using the PEDOT@MSS materials as building blocks for the self-assembly of opals was demonstrated, and the resultant photonic bandgap was measured. The ability to control the
position or intensity of a photonic bandgap by electrochemical means has recently begun to be explored as a means of fabricating robust display technologies,⁷⁻⁹ and the PEDOT@MSS opals are exciting candidates for such applications.

In order for such applications to truly be realized, the interplay between the colloidal and electronic properties of the composites needed to be thoroughly evaluated. Chapter 3 describes such a study. The systematic variation of the degree of pore filling was designed to provide a wide range of samples for study. It was found that if the pores were completely filled, monomer or oligomer diffusion would result in a polymer layer on the surfaces of the microspheres. This is undesirable from the standpoint of colloidal stability, in that conjugated polymers are notoriously prone to aggregation. If the pores were drastically underfilled, then films made of the composite materials were observed to be electrically insulating. A balance between these colloidal and electronic properties was found at the 30% filling level; at this point, the PEDOT composites were found to be both stable as colloidal dispersions and electrically conductive. Chapter 3 also further generalized the synthetic procedure to include other conjugated polymers, such as polythiophene and poly(N-methylpyrrole).

In Chapters 4 and 5, different applications of the PEDOT@MSS composites were explored. Phase separation in conjugated polymer blends has proven to be one of the most important factors in determining the efficiency of bulk heterojunction photovoltaic cells,¹⁰ yet there are very few ways to control this phase separation in a predetermined, methodical fashion. Such a technique is explored in Chapter 4. By combining the two polymers PEDOT and PFA inside the MSS template, the two polymers become intimately mixed; since they are presumably trapped within the same mesopore, phase separation is limited. Chapter 5 explores the application of the PEDOT@MSS composite and the etched PEDOT microparticles to the field of supercapacitors. The chapter also describes the preparation and electrochemical characterization of a
PEDOT@MCS composite. It was found that while the PEDOT@MSS microspheres displayed a relatively modest specific capacitance of ca. 60 F g$^{-1}$, the PEDOT, MCS and PEDOT@MCS microparticles displayed dramatically improved capacitances of > 100 F g$^{-1}$. These values are greater than those typically achieved for both electropolymerized PEDOT (< 80 F g$^{-1}$)$^{11}$ and commercially available carbon (< 100 F g$^{-1}$)$^{12}$, indicating that the morphological control is influencing the material properties of the polymer. Supercapacitors made from these materials may find use in power-intensive applications such as portable electronic devices or electric vehicles where large quantities of energy are required in a short amount of time.

PPV has been extensively studied and exploited in organic devices due to its desirable luminescent properties. Unfortunately, the polymer is both insoluble and infusible; this means that processing the material is extremely difficult and must be accomplished by a somewhat circuitous route. The polymer is also prone to aggregation-induced fluorescence quenching and oxidative photobleaching.$^{13, 14}$ These factors limit both the efficiency and lifetime of devices based on the polymer. Attempts to ameliorate some of these issues by encapsulating the luminescent polymer within the mesopores of the MSS are described in Chapter 6. By shutting down access to nonradiative decay pathways (excimer formation), the fluorescence quantum yield of the polymer was dramatically enhanced. The measured value of 84% represents one of the highest ever reported in the literature for a PPV derivative. Additionally, the rate of photobleaching was attenuated in the PPV@MSS composite relative to a PPV control sample. These two factors suggest the possibility of increases in the efficiency and longevity of photonic devices based on this composite material. Additionally, the monodispersity, processability and colloidal stability of the composite have the potential to be exploited in the fabrication of opaline structures. This has been recently accomplished by Yuri Yamada at Toyota Central R & D Labs, Inc. The opaline films display a photonic bandgap that overlaps with the emission band of the
polymer. This has important ramifications for lasing. It has been shown previously that by incorporating a luminescent material into a photonic crystal such that the emission band and photonic bandgap coincide, low threshold or threshold-less lasing can be achieved.$^{12, 15}$ Thus, these materials may find future application as low threshold and high efficiency lasers that have an increased lifetime relative to other PPV-based lasing media.

Cell-surface carbohydrates are some of the most important biological mediators in the body and control such processes as the inflammatory response and blood antigenicity. Importantly, they also mediate the attack of influenza virus on host cells. Thus, there is a growing demand for cheap and simple carbohydrate-based sensors for the detection of pathogens. This is particularly important in the context of global influenza pandemics, where rapid diagnosis and quarantine is critical in halting the spread of disease. Chapter 7 discusses the synthesis of carbohydrate-functionalized PPE microparticles. The particles were prepared by dispersion polymerization and examined for their affinity to lectins. The particles were found to efficiently extract the lectin concanavalin A from solution. Importantly, the first step of influenza infection is the binding of a hemagglutinin lectin on the virus to carbohydrate residues on the surface of the host cell. These fluorescent PPE microparticles, due to their similar size to eukaryotic cells, may prove to be useful as fluorescent tags in hemagglutinin assays.

In conclusion, this thesis developed the methodology necessary to synthesize a wide variety of conjugated polymer colloidal microspheres. This has led to previously inaccessible micro- and nanostructures, such as monodisperse PEDOT microspheres. Additionally, the systematic study of the colloidal and electronic properties of these materials has led to a greater understanding of the behavior of conjugated polymer colloids. The methodology and understanding were applied in several areas, including in the systematic control of phase separation and the improvement of supercapacitor device performance. Other approaches were developed to conjugated polymer
microspheres. These included an ion-exchange methodology for synthesizing PPV composites. This work may provide a route to high efficiency, low threshold lasing by combining the unique optical properties of photonic crystals with the high quantum yield and low photobleaching of a nanostructured PPV composite. Carbohydrate-functionalized microparticles were also described in this thesis, and hold some promise for rapid assays of pathogenic agents.
8.2 REFERENCES


