

Microphase Separated Block Copolymers as Templates for the Directed Cross-Phase Alignment of Segmented Nanorods

A Thesis for the Degree of Doctor of Philosophy

By

Lucas Paul Johnson
B.Sc. (hons) in Nanotechnology

At

Flinders University
Faculty of Science and Engineering
School of Chemistry and Physics



Flinders University
Adelaide · Australia

Sept 2010

TABLE OF CONTENTS

Title Page	I
Table of Contents	II
Scope of this Thesis	V
Declaration	VIII
List of Figures	IX
List of Tables	XVII
Acknowledgements	XVIII
1. Literature Review and Aims	1
1.1. Metallic Nanoparticles	1
1.1.1. Basic Principles.....	1
1.1.2. Synthesis.....	17
1.1.3. Functionalisation.....	26
1.2. Nanoparticle Assemblies	28
1.2.1. Properties.....	28
1.2.2. Methods of Assembly.....	35
1.2.3. Template Formation.....	45
1.3. Block Copolymers	48
1.3.1. Definition.....	48
1.3.2. Microphase Separation.....	49
1.3.3. Synthesis.....	59
1.3.4. Template Directed Assembly.....	71
1.4. Multisegment Nanorods	85
1.4.1. Introduction.....	85
1.4.2. Synthesis.....	86
1.4.3. Selective Functionalisation.....	99
1.5. Research Aim	100
1.6. References	103

2. Block Copolymer Synthesis and Microphase Separation.....	137
2.1. Introduction	137
2.2. Experimental Method and Materials	148
2.2.1. Synthesis of PS-b-P2VP.....	148
2.2.2. Synthesis of PMMA-b-PBMA.....	148
2.2.3. Polymer Characterisation.....	153
2.2.4. Microphase Separation.....	155
2.2.5. Microphase Characterisation.....	157
2.3. Results and Discussion	159
2.3.1. PMMA Macroinitiator Synthesis.....	159
2.3.2. Microphase Separation.....	174
2.4. Conclusions	182
2.5. References	183
3. Single Segment Nanorods.....	188
3.1. Introduction	188
3.2. Experimental Method and Materials	202
3.2.1. Membrane Preparation.....	202
3.2.2. Nanorod Synthesis.....	203
3.2.3. Nanorod Characterisation.....	206
3.2.4. Other Sample Characterisation.....	207
3.3. Results and Discussion	208
3.3.1. Initial Experiments.....	208
3.3.2. Optimisation Experiments.....	232
3.3.2.1. Composition.....	232
3.3.2.2. Nanorod Length Distribution.....	240
3.3.3. Nanorod Collection.....	256
3.4. Conclusions	271
3.5. References	272

4. Multi-Segment Nanorods.....	276
4.1. Introduction	276
4.2. Experimental Methods and Materials	277
4.2.1. Membrane Preparation.....	277
4.2.2. Nanorod Synthesis.....	277
4.2.3. Nanorod Characterisation.....	278
4.3. Results and Discussion	279
4.3.1. Synthesis: Literature Conditions.....	279
4.3.2. Synthesis Optimised Conditions.....	282
4.3.2.1. Nitric Acid.....	286
4.3.2.2. Sonication.....	288
4.3.3. Nanorod Length vs. Charge.....	292
4.3.4. Final Synthesis Conditions.....	296
4.4. Conclusions	314
4.5. References	316
5. Cross-Phase Alignment of Segmented Nanorods.....	318
5.1. Introduction	318
5.2. Experimental Methods and Materials	324
5.2.1. Nanorod Functionalisation.....	324
5.2.2. Solution Preparation.....	325
5.2.3. Microphase Separation.....	325
5.2.4. Sample Characterisation.....	325
5.3. Results and Discussion	326
5.3.1. Proof of Principle Experiment.....	326
5.3.2. Influence of Experimental Conditions.....	332
5.3.3. Influence of Morphology.....	338
5.4. Conclusions	342
5.5. References	344
6. Conclusions.....	345

SCOPE OF THIS THESIS

Nanotechnology, the study of the control of matter on an atomic and molecular scale, is a field of scientific endeavour that deals with materials or devices with structure on the scale of 100nm in size or less. Nanotechnology has garnered considerable interest in recent years as the ability to manipulate matter on this scale promises to enable considerable advancements in a wide range of diverse areas such as materials, medicine, electronics, computation and energy technology, potentially providing solutions to many problems currently faced by humankind.

One area of nanotechnology which has been the subject of much investigation is the nanoparticle, which is defined as a small object that behaves as a whole unit in terms of its transport and properties, with one or more dimensions that are constricted to length scales ranging from 1 – 100 nm. [1-2] Nanoparticles, particularly those comprised of metals, are of great scientific and technological interest as they bridge the realms of atoms and molecules with that of bulk materials, and consequently exhibit a wide variety of unique properties that typically do not exist in the bulk. [3]

Much of the initial work on nanoparticles concerned the development of synthetic methods so that control over nanoparticle size, morphology and composition could be achieved, in addition to the characterisation of these particle's properties. More recently however, there has been a greater focus on the use of nanoparticles as building blocks to form nanoparticle assemblies. [4-8] This trend is driven by the desire for complex 3D devices at this scale, the formation of such structures being rather difficult to achieve using traditional 'top-down' approaches to structure formation (where small devices and structures are created at the direction of larger structures) such as lithography. [9]

One of the most versatile processes by which nanoparticles may be directed to form well controlled structures with high throughput is self assembly, a 'bottom-up' process which involves the use of interactions between structural

components to facilitate spontaneous arrangement of the particles into ordered structures. [10-11] Among the self assembly methods that have been developed to date, template assisted assembly (which involves the use of highly selective interactions between a patterned substrate and the nanoparticles to direct the nanoparticle assembly) stands out as one of the most promising, as it combines aspects of top-down and bottom-up structural arrangement approaches, thereby allowing for the rapid formation of a wide range of complex 3D structures with structural order extending over macroscopic volumes. [12-15]

There exists a wide range of suitable templates that may be applied to the template assisted assembly of nanoparticles. One particularly useful template is microphase separated block copolymers, which consist of periodic, chemically distinct domains within which appropriately functionalised nanoparticles may be selectively incorporated. Unlike most other suitable templates, block copolymers are able to form a wide range of nanoscale patterns with a high degree of control over pattern size and morphology. [9, 16-17] However, block copolymers have one disadvantage, in that the vast majority of the possible pattern morphologies are composed of isolated regions (cermet topology), while for many applications, the arrangement of nanoparticles into network type structures is desirable.

In an effort to extend the application of the otherwise advantageous block copolymers to the template directed assembly of nanoparticles into network structures, we developed an alternative methodology for nanoparticle assembly using this form of template called *cross-phase* alignment, which involves the alignment of segmented nanorods, rod shaped nanoparticles with varying composition along the long axis of the rod, across the domain interfaces in the block copolymer matrix. In this thesis, we report the results of this investigation.

1. Nam, P.H., P. Maiti, M. Okamoto, T. Kotaka, N. Hasegawa, and A. Usuki, *Polymer*, **2001**. 42: p. 9633.
2. Holister, P., Weener, J-W., Vas, C. R., Harper, T., *Nanoparticles*, in *Technology White Papers*. **2003**, Cientifica. p. 1.
3. Klabunde, K.J., Schmid, G., Pileni, M. P., Khaleel, A., Richards, R. M., Mulvaney, P., Sorensen, C. M., Mulukutla, R. S., Koper, O., Winecki, S., Parker, J., *Nanoscale Materials in Chemistry*, ed. K.J. Klabunde. **2001**, New York: John Wiley and Sons, inc. 292.
4. Lazzari, M., Lopez-Quintela, M. A., *Advanced Materials*, **2003**. 15(19): p. 1583.
5. Shouheng, S., Murray, C. B., Weller, D., Folks, L., Moser, A., *Science*, **2000**. 287: p. 1989.
6. Reiss, G., Hutten, A., *Nature Materials*, **2005**. 4: p. 725.
7. Gates, B.D., Xu, Q., Stewart, M., Ryan, D., Willson, C. G., Whitesides, G. M., *Chemical Reviews*, **2005**. 105: p. 1171.
8. Jeong, M., Doris, B., Kedzierski, J., Rim, K., Yang, M., *Science*, **2004**. 306(5704): p. 2057.
9. Park, C., Yoon, J., Thomas, E. L., *Polymer*, **2003**. 44: p. 6725.
10. Kotov, N.A., *Nanoparticles Assemblies and Superstructures*. **2006**: CRC Press.
11. Parviz, B.A., Ryan, D., Whitesides, G. M., *IEEE Transactions on Advanced Packaging*, **2003**. 26(3): p. 233.
12. Davis, S.A., Breulmann, M., Rhodes, K. H., Baojian, Z., Mann, S., *Chemistry of Materials*, **2001**. 13(10): p. 3218.
13. Maury, P.A., Reinhoudt, D. N., Huskens, J., *Current Opinion in Colloid and Interface Science*, **2008**. 13(1-2): p. 74.
14. Wang, D., Mohwald, H., *Journal of Materials Chemistry*, **2004**. 14: p. 459.
15. Wilde, G., *Nanostructured Materials*. Frontiers of Nanoscience, ed. G. Wilde. Vol. 1. **2008**: Elsevier.
16. Haryono, A., Binder, W. H., *Small*, **2006**. 2(5): p. 600.
17. Krishnamoorthy, S., Hinderling, C., Heinzlmann, H., *Materials Today*, **2006**. 9(9): p. 40.

DECLARATION

I certify that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due and direct reference has been made in the text.

Lucas Paul Johnson, B.Sc. (hons) in Nanotechnology

/ /

LIST OF FIGURES

Fig 1.1: Diagram showing the electronic structure of (a) diatomic lithium (b) a cluster of 6 lithium atoms and (c) bulk lithium.....	2
Fig 1.2: Diagram showing the density of states for a metal with (a) no spatial confinement (b) confinement in one dimension (c) confinement in two dimensions and (d) confinement in all three dimensions.....	4
Fig 1.3: Current vs. applied potential for (a) a metal nanoparticle exhibiting a coulomb blockade and (b) bulk metal.....	6
Fig 1.4: Depiction of a magnetic dipole moment arising from a “current loop”.....	7
Fig 1.5: Ferromagnetic domain structure in (a) zero field and (b) in an applied magnetic field.....	10
Fig 1.6: Diagram showing the increase in surface area when a bulk solid is divided into an equal volume of smaller particles.....	14
Fig 1.7: Diagram showing the use of grooves as a template in vapour synthesis of nanoparticles (a) direct replication of the grooves by directing the vapour at the substrate through the use a gas stream (b) utilising the groove shape and angle of vapour approach to form particles outside the “shadow” created by the grooves.....	21
Fig 1.8: Depiction of an assembly of spherical nanoparticles on a surface (top), ground state wavefunctions for charge carriers localised in two adjacent nanoparticles i.e. finite potential wells (middle) and graphs of current due to an applied voltage (bottom) where (a) the interparticle spacing is “large” such that no charge transport by tunnelling occurs (b) the interparticle spacing is “moderate” such that tunnelling can occur but is inhibited by the coulomb blockade (c) the interparticle spacing is “small” such that exchange coupling is strong enough to delocalise the charge carriers over the whole assembly.....	30
Fig 1.9: Depiction of the electric field strength and extent of the nanoparticle wavefunction away from the surface of two identical spherical nanoparticles or radius r together with the corresponding light absorption spectrum due to localised surface plasmon resonance in the case of (a) interparticle spacing $\gg 5r$ (no electromagnetic coupling) (b) interparticle spacing $= 5r$ (weak electromagnetic coupling) (c) interparticle spacing $< 5r$ (strong electromagnetic coupling) and (d) interparticle spacing $\ll 5r$ (strong electromagnetic and exchange coupling).....	32
Fig 1.10: A suspension of spherical nanoparticles on a solid substrate (a) immediately after deposition (b) after most solvent has been evaporated (c) after all solvent has evaporated....	36
Fig 1.11: A suspension of spherical nanoparticles between a patterned substrate electrode and counter electrode (a) before the electric field is applied and (b) when the electric field is applied. (c) shows an example top-down view of the deposition of nanowires onto a patterned	

electrode substrate. (d) depicts alignment of nanowires in solution by an electric field prior to deposition onto a substrate by solvent evaporation.....	38
Fig 1.12: (a) functionalised nanoparticles at the liquid-air interface (b) close packed nanoparticles when the interfacial area is compressed.....	39
Fig 1.13: Examples of block copolymer chain architectures.....	48
Fig 1.14: Composition profile for the cross section of a diblock in the weak segregation and strong segregation regime.....	51
Fig 1.15: Phase diagram depicting the morphology of a diblock copolymer at thermodynamic equilibrium as a function of volume fraction of one of the blocks (f) and the strength of inter-block repulsion (χN).....	53
Fig 1.16: Microphase separated morphologies for a triblock copolymer containing three chemically distinct blocks of varying volume fraction at thermodynamic equilibrium.....	54
Fig 1.17: An example of the short range ordering of block copolymers as seen in a lamellar microphase morphology.....	56
Fig 1.18: A depiction of the progress of a step growth polymerisation.....	60
Fig 1.19: Example of step growth polymerisation applied to the extension of a single block to form a block copolymer.....	63
Fig 1.20: A depiction of (a) a homopolymer and (b) a diblock copolymer that result from variation in chain length.....	63
Fig 1.21: Reaction mechanism for a living radical polymerisation showing the equilibrium between an active polymer radical that can undergo propagation (right) and a dormant polymer chain that cannot undergo propagation (left). Note that the equilibrium favours the formation of the dormant species.....	64
Fig 1.22: Reaction mechanism for ATRP.....	66
Fig 1.23: Reaction mechanism for ARGET ATRP.....	67
Fig 1.24: Reaction mechanism for NMRP.....	68
Fig 1.25: Reaction mechanism for RAFT.....	69
Fig 1.26: Reaction mechanism for ionic polymerisation (in this case anionic polymerisation).....	70
Fig 1.27: Computed phase diagram (as a function of volume fraction of block A (f) and nanoparticle volume fraction (Φ)) for a strongly segregated AB diblock copolymer containing nanoparticles with an enthalpically preferential interaction with the A block and diameter smaller than the A blocks radius of gyration. Regions S, C, L, DIS and 2Φ correspond to the spherical, cylindrical, lamellar, disordered and a 2 phase morphology region where both disordered and microphase separated regions are present in the polymer respectively at equilibrium.....	76
Fig 1.28: Computed phase diagram (as a function of volume fraction of block A (f) and nanoparticle volume fraction (Φ)) for a strongly segregated AB diblock copolymer containing nanoparticles with an enthalpically preferential interaction with the A block and diameter comparable to the A blocks radius of gyration. Regions S, C, L, DIS, SAC, SAL and 2Φ	

correspond to the spherical, cylindrical, lamellar, disordered, cylindrical core-shell, lamellar core-shell and a 2 phase morphology region where both disordered and microphase separated regions are present in the polymer respectively at equilibrium.....77

Fig 1.29: Depiction of a nanorod with discrete surface regions that are each compatible with different microphases of a block copolymer.....85

Fig 1.30: Example of a possible network type assemblies of anisotropic nanoparticles in a BCC microphase separated block copolymer.....85

Fig 1.31: A typical template electrodeposition process, which involves a nanochannel template (A) being coated on one side with a layer of conductive material (B). This coating serves as a cathode during the application of a potential across the channels when a metal plating solution is introduced (C). This results in electrodeposition of material within the template pores (D). The plating solution is removed and electrodeposition repeated with a different plating solution to obtain segmented nanorods.(E). The conductive coating and template are then removed, yielding free nanorods (F).....87

Fig 1.32: The diffuse double layer that forms at a metallic cathode. This consists of the inner Helmholtz plane (IHP), which is made up of specifically adsorbed ions, the outer hemlholtz plane (OHP), which is made up of solvated ions with charge opposing that of the electrode and the diffuse layer, which contains a mixture of ions/counter ions.....92

Fig 1.33: Graph showing the external potential required to obtain a specific current flow during an electrodeposition at a cathode. Several different system behaviours are shown; region I (Tafel region) exhibits kinetically controlled deposition characterised by an activation polarisation (P_o), region II exhibits kinetically controlled deposition characterised by a concentration polarisation (P_c), region III shows mass transport controlled deposition characterised by a limiting current, while region IV shows mass transport controlled depositions characterised by hydrogen evolution. The precise relationship between V and I will vary depending upon factors such as the plating solution used and the electrode area.....94

Fig 1.34: Graph of metal growth species concentration (C) as a function of distance from the cathode surface at high overpotentials. Bulk solution concentration (C_∞) decreases as one approaches the cathode surface (C_o), the distance over which this occurs being referred to as the diffusion layer (δ).....95

Fig 2.1: Depiction of a functionalised bi-segmented nanorod sequestered at the interface between two lamellar microphases with (left) a thin interface and (right) a thick interface..141

Fig 2.2: Vacuum distillation apparatus setup during nitrogen purging149

Fig 2.3: Vacuum distillation apparatus setup during addition of monomer via elution through an activated alumina column.....150

Fig 2.4: Depiction of an epoxy substrate coated with a diblock copolymer film that has been shaped to provide a suitable face for ultramicrotomy.....157

Fig 2.5: Kinetic data for the ATRP of PMMA macroinitiator using the CuBr/PMDETA catalyst system and EBrIB as the initiator in 50 vol% methoxybenzene. Each data point is the average of 3 separate polymerisations161

Fig 2.6: Molecular weight as a function of monomer conversion for the ATRP of PMMA macroinitiator using the CuBr/PMDETA catalyst system and EBrIB as the initiator in 50 vol% methoxybenzene. Each data point is the average of 3 separate polymerisations	163
Fig 2.7: Molecular weight distribution as determined by GPC for PMMA macroinitiator samples prepared by ATRP using the CuBr/PMDETA catalyst system and EBrIB as the initiator in 50 vol% methoxybenzene	165
Fig 2.8: H ¹ -NMR spectrum of PMMA-Br macroinitiator	167
Fig 2.9: Molecular weight distribution as determined by GPC of (□) PMMA macroinitiator and (◇) PMMA-b-PBMA block copolymer prepared using this macroinitiator	170
Fig 2.10: H ¹ -NMR of PMMA-b-PBMA block copolymer	171
Fig 2.11: Image of an iodine stained, microphase separated PS-b-P2VP film (lamellar morphology) on an epoxy substrate	174
Fig 2.12: TEM image of the cross-section of an iodine stained, microphase separated PS-b-P2VP film showing a well ordered lamellar morphology	175
Fig 2.13: TEM image of the cross-section of the PS-b-P2VP film's epoxy substrate	176
Fig 2.14: Close up TEM images of the cross-section of an iodine stained, microphase separated PS-b-P2VP film showing the dimensions of the microphase lamellae	177
Fig 2.15: Image of an iodine stained, microphase separated PS-b-P2VP film (spherical morphology) on an epoxy substrate	178
Fig 2.16: TEM image of the cross-section of an iodine stained, microphase separated PS-b-P2VP film showing a well ordered spherical morphology	180
Fig 2.17: TEM image of the cross-section of an iodine stained, microphase separated PS-b-P2VP film showing a well ordered spherical morphology	181
Fig 3.1: SEM images of the filtration surface of a commercially available porous anodic alumina filtration membrane (nominal 10nm pore diameter)	191
Fig 3.2: SEM images of the cross-section of a commercially available porous anodic alumina membrane (nominal 10nm pore diameter) showing the (top) pore structure in the bulk of the membrane and (bottom) the asymmetric pore structure at the branched (filtration) surface.	192
Fig 3.3: SEM images of the surface of a commercially available track etched polycarbonate membrane	194
Fig 3.4: Porous membrane with a damaged/delaminated conductive backing exhibiting (a) a reduction in nanorod yields and (b) increased variation in nanorod length	195
Fig 3.5: SEM of a 200nm thick Ag layer sputter coated onto a track etched polycarbonate membrane, which exhibits a largely pin-hole free surface	197
Fig 3.6: Porous membrane with a conductive coating containing voids and pin-hole defects that are (a) filled by electrodeposition of a sacrificial layer of metal followed by (b) deposition of the metal comprising the nanorods	198
Fig 3.7: Setup of the electrodeposition apparatus	203

Fig 3.8: procedure for the unfurling of the Ag coated polycarbonate membrane onto (a) the metal contact plate which has (b) 1-2 drops of water deposited onto it near the edge. The curled up membrane is then placed onto these drops such that (d) the membrane may unfurl to cover the metal contact plate.....	204
Fig 3.9: SEM images of (a) Ag treated polycarbonate and (b) untreated polycarbonate membrane.....	210
Fig 3.10: SEM image of Ag treated polycarbonate at high magnification.....	211
Fig 3.11: TEM images of Ni nanorods synthesized under literature derived conditions.....	214
Fig 3.12: EDAX spectrum of Ni nanorods.....	215
Fig 3.13: High resolution TEM image of nickel nanorods synthesized under literature derived conditions.....	215
Fig 3.14: TEM image featuring the perforate, plate like fragments of material observed in the nickel nanorod samples.....	216
Fig 3.15: EDAX of the perforated, plate like fragments of material in TEM images of nickel nanorods.....	217
Fig 3.16: A typical current vs. time data for the electrodeposition of nickel from a nickel sulfamate plating solution into the pores of a polycarbonate filtration membrane.....	218
Fig 3.17: Current vs. time data for the deposition of gold.....	220
Fig 3.18: TEM image of Au nanorods synthesized under literature conditions.....	222
Fig 3.19: EDAX spectra of (A) the solid nanorod segments and (B) the porous “tails”.....	223
Fig 3.20: High resolution TEM images of (a) porous gold “tails” and (b) solid gold nanorod segments.....	224
Fig 3.21: TEM images of Au nanorods formed with a passed charge of (a) 0.025C and (b) 0.1C.....	226
Fig 3.22: TEM image of an Au nanorod without nitric acid treatment (bottom) EDAX spectra of (A) the left segment and (B) the right segment.....	228
Fig 3.23: TEM image of a Ni nanorod without nitric acid treatment (bottom) EDAX spectra of (A) the right segment and (B) the left segment.....	231
Fig 3.24: TEM image of gold nanorods resulting from metal deposition where rinsing of the membrane between depositions is accompanied by mild sonication.....	234
Fig 3.25: SEM image of the surface of a track etched polycarbonate membrane after exposure to pH 11 KOH solution for 1 hour.....	235
Fig 3.26: Current vs. time data for the electrodeposition of residual silver species in a KOH electrolyte.....	236
Fig 3.27: TEM image of gold nanorods formed following the electrodeposition of residual silver species.....	237
Fig 3.28: (a) TEM image of gold nanorods formed following deposition of a nickel barrier segment (b) EDAX analysis of the gold segments showing the gold Ma and La peaks and the Ka peaks due to copper.....	238

Fig 3.29: Photo of a polycarbonate membrane containing gold nanorods (after nitric acid treatment). Note the visibly preferential deposition at the edge of the deposition area	241
Fig 3.30: TEM image of nanorods including those resulting from metal deposition in the outermost segment of the synthesis template	244
Fig 3.31: TEM image of nanorods excluding those resulting from metal deposition in the outermost segment of the synthesis template	245
Fig 3.32: Length distributions of gold nanorods (a) including and (b) excluding those formed from metal deposition at the edge of the cathode	246
Fig 3.33: Length distribution of gold nanorods formed with (a) a 1mA current limit and (b) no current limit	249
Fig 3.34: current vs. time data for gold deposition at a current limit of 1mA	250
Fig 3.35: Length distribution of gold nanorods formed with a 0.1mA current limit	251
Fig 3.36: current vs. time data for gold deposition at a current limit of 0.1mA	252
Fig 3.37: length histogram for gold nanorods synthesized under a current limit of 1mA with sonication during the deposition	253
Fig 3.38: current vs. time data for gold deposition (a) under a current limit of 1mA and (b) under a current limit of 1mA with sonication	254
Fig 3.39: TEM image of nanorods collected using the standard literature method of multiple centrifugation and re-suspension steps	257
Fig 3.40: TEM image of a nanorod coated in a low electron density residue	258
Fig 3.41: TEM images of low electron density spheres present in nanorod samples treated using the standard literature method	259
Fig 3.42: TEM image showing the absence of residual polymer when the nanorods are treated with extensive sonication during the re-suspension stage of nanorod collection	261
Fig 3.43: TEM image showing the near complete absence of residual polymer adhering to nanorods that are treated with extensive sonication during the re-suspension stage of nanorod collection	262
Fig 3.44: diagram showing the chemical attack of polycarbonate by base hydrolysis of the carbonate group	263
Fig 3.45: TEM image of nanorods collected after treatment with 30% ammonia solution	264
Fig 3.46: TEM images of nanorods collected after treatment with 30% ammonia solution, exhibiting the presence of smears of residue material	265
Fig 3.47: diagram depicting the chemical attack of poly(vinyl pyrrolidone) by hydrogen peroxide	266
Fig 3.48: TEM images of nanorods treated with 30% ammonia solution followed by 30% hydrogen peroxide solution	267
Fig 3.49: diagram depicting the conversion of carboxylic acid by products of poly(vinyl pyrrolidone) into corresponding amides by ammonia	268
Fig 3.50: TEM images of nanorods treated with ammonia solution and hydrogen peroxide	270

Fig 4.1: TEM image of a Ni-Au-Ni-Au segmented nanorod.....	280
Fig 4.2: EDAX analysis of Ni-Au-Ni-Au segmented nanorods	281
Fig 4.3: TEM image of Ni-Au-Ni-Au segmented nanorods formed under optimized conditions	283
Fig 4.4: Depiction of attack of nickel nanorod segments within the synthesis template by nitric acid (top) before exposure to nitric acid (bottom) after exposure to nitric acid	284
Fig 4.5: TEM image of Ni-Au-Ni-Au segmented nanorods formed under optimized conditions, excluding the use of nitric acid or sonication	285
Fig 4.6: TEM image of Ni-Au-Ni-Au segmented nanorods formed under optimized conditions, excluding the use of sonication	286
Fig 4.7: TEM image of Ni-Au-Ni-Au segmented nanorods formed under optimized conditions, with no sonication and treatment with 4:1:1 methanol:30% NH ₃ :30% H ₂ O ₂ to remove deposited silver	288
Fig 4.8: TEM image of Ni-Au-Ni-Au segmented nanorods formed under optimized conditions, with sonication and treatment with 4:1:1 methanol:30% NH ₃ :30% H ₂ O ₂ to remove deposited silver	289
Fig 4.9: current vs. time data for the deposition of subsequent gold segments in a Ni-Au-Ni-Au sample (top) with sonication (bottom) without sonication	290
Fig 4.10: TEM image of (0.08C) Ni – (0.08C) Au nanorods	292
Fig 4.11: TEM image of (0.06C) Ni – (0.12C) Au nanorods	293
Fig 4.12: TEM image of (0.04C) Ni – (0.04C) Au nanorods	293
Fig 4.13: TEM image of (0.04C) Ni – (0.04C) Au nanorods	294
Fig 4.14: (top) TEM image of Au-Ni nanorods treated under conditions optimized for use with block copolymers (bottom) EDAX analysis of the observed nanoparticles	298
Fig 4.15: TEM images of small particles dispersed within traces of residual polymer	299
Fig 4.16: EDAX of residue polymer smears containing dispersed particulates as shown in fig 4.15	300
Fig 4.17: TEM of Au-Ni-Au nanorod at 200kV showing the polycrystalline nature of the deposited metal	304
Fig 4.18: TEM of Au-Ni nanorods (top) before polymer removal and centrifugation (bottom) after such treatment	307
Fig 4.19: TEM of 0.04C-0.04C Au-Ni nanorods after polymer removal and centrifugation	308
Fig 4.20: TEM of 100nm-100nm long Au-Ni nanorods showing shrinkage of the nickel segment	309
Fig 4.21: TEM of 100nm-100nm long Au-Ni nanorods showing the plastic deformation of the gold segments along with the presence of voids	310
Fig 4.22: TEM of 100nm-100nm long Au-Ni nanorods showing the breakage of some of the nanorods into individual segments	311

Fig 5.1: SEM image of the surface of a track etched polycarbonate membrane serving as a synthesis template for the segmented nanorods (pores are highlighted in yellow)	320
Fig 5.2: TEM image of a cross-section of the microphase separated block copolymer / nanorod films in regions absent of nanorods	326
Fig 5.3: TEM image depicting cross-phase templating of segmented nanorods	328
Fig 5.4: TEM image depicting cross-phase templating of segmented nanorods. Note that the apparent diameter of the nanorod in this image is larger than expected, and is most likely two nanorods at different depths within the cross-section	329
Fig 5.5: TEM image showing changes in microphase morphology to accommodate a single segment nanoparticle	330
Fig 5.6: TEM image depicting changes in microphase morphology around nanorods in close proximity	331
Fig 5.7: TEM image showing cross-phase templating of Au-Ni nanorods in PS-b-P2VP without surface functionalisation	334
Fig 5.8: TEM image showing disruption of the local microphase separation in the presence of non-functionalised nanorods	335
Fig 5.9: TEM image showing disruption of the local microphase ordering in the presence of long nanorods	336
Fig 5.10: TEM image showing disruption of the local microphase ordering in the presence of long nanorods	337
Fig 5.11: TEM image showing the BCC spherical morphology block copolymer in the absence of nanorods	339
Fig 5.12: TEM image showing the effect of both single and bi-segmented nanorods on the microphase structure of PS-b-P2VP with a BCC spherical morphology	340
Fig 5.13: TEM image showing the effect of both a cluster of nanorods on the microphase structure of PS-b-P2VP with a BCC spherical morphology	341

LIST OF TABLES

Table 2.1: Data related to the determination of equilibrium microphase periodicity relative to total degree of polymerisation for a diblock copolymer.....	142
Table 2.2: Mark-Houwink parameters for PMMA and PBMA in THF at 30°C.....	155
Table 3.1: Current limits for the deposition of metals (given as current per unit electrode area).....	206

ACKNOWLEDGEMENT

First, I would like to acknowledge Assoc. Prof. Janis Matisons for giving me the opportunity to engage in study at a post-graduate level, as well as for his advice and encouragement along the way. I would also like to acknowledge the assistance of a number of other people for their contributions to this work; David Uhrig for the synthesis of PS-b-P2VP block copolymer along with Kerry Gascoigne, Lyn Waterhouse and Peter Self for their advice and assistance with imaging of samples by electron microscopy. Finally, I would like to thank the members of the Flinders Nanomaterials group, both past and present, for the help and support they have offered over the course of my post-graduate studies.