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

A Thesis for the Degree of Doctor of Philosophy

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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.

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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.

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