

6. Conclusions

In this thesis, work has been presented concerning an investigation into the use of microphase separated block copolymers as templates in the cross-phase assembly of segmented nanorods, which involved an initial proof of principle experiment to determine if cross-phase alignment of selectively functionalized, bisegmented nanorods can be made to occur under optimized experimental conditions, followed by further experiments to investigate the influence of different experimental parameters upon this process.

Critical to this work, as outlined in chapter 1, is the implementation of experimental conditions that are optimised for this cross-phase alignment; conditions that maximize the enthalpic drive towards cross-phase alignment while minimizing the entropic penalty associated with doing so. The principal challenge in achieving such conditions is the formation of segmented nanorods with dimensions smaller than the microphases of the block copolymer template, as virtually no literature deals with such materials. Thus, much of the work described in this thesis concerns the preparation of these materials, with the further aim of preparing a range of different materials to facilitate experiments on the effect of changes in the experimental conditions.

In chapter 2, the preparation of the microphase separated block copolymers is described, with lamellar and spherical microphase morphologies of the weakly segregating PMMA-*b*-PBMA and strongly segregating PS-*b*-P2VP polymers being targeted. It was found that while PS-*b*-P2VP could be prepared with microphases sufficiently large for use in this work, PMMA-*b*-PBMA could not be synthesized with the required properties. In chapter 3, a methodology for the preparation of single segment nanorods with pure composition and good control over the segment length at the required dimensions was developed. This method was extended to multi-segment nanorods in chapter 4, where it was found that

nanorods with the required properties could be formed, but that the conditions required for the collection of the nanorods in the absence of polymer residues lead to mechanical deformation. In the case of freshly prepared nanorods, brittle fracture of the gold segments occurred whereas older nanorod samples underwent a combination of either breakage at the inter-segment interfaces or plastic deformation of the gold segments accompanied by brittle fracture of the nickel segment surface layers.

Despite these deformations, some of the nanorods in aged samples retained the required dimensions for use in the proof of principle experiments (chapter 5), in which it was found (in all observed instances) that cross-phase alignment of small, intact segmented nanorods occurs without any noticeable disruption of the microphase separation of the surrounding block polymer, and only a small degree of local change in microphase order (although it was also noted that difficulties in observing statistically significant numbers of such nanorods prevented a more quantitative analysis being performed in this work). Further experiments investigating the influence of changes in the experimental conditions on this process were also carried out, although the reliance on a limited supply of aged nanorods restricted the number of experiments that were performed. In one experiment, it was found that (in all observed instances) selective functionalisation is not necessarily required for cross-phase alignment to occur; weaker enthalpic driving forces are sufficient as cross-phase orientation appears to result in a smaller decrease in entropy for such large nanoparticles. In another experiment, it was found that when the length of the nanorod segments exceeded the dimensions of the sequestering microphases, the microphase structure in the surrounding polymer is severely disrupted, meaning that nanorods must have segment dimensions smaller than those of the microphases if cross-phase alignment is to occur. This result was also observed in the case of block copolymers with spherical microphase morphology, although the disruption to the surrounding microphase structure occurred to a lesser degree.

The results of this work have a number of implications. First and foremost is the fact that this method of controlled nanoparticle alignment can be made to work under these optimized conditions, which means that this method can potentially be used to extend the range of nanoparticle assembly structures that may be formed with this form of template. However, it was also shown that this process is strongly affected by a number of factors, which may limit the usefulness of this method. One such limit is the nanorod concentration, as nanorods of these dimensions in close proximity appear to disrupt the microphase separation of the block copolymer (ascribed to the excessive polymer chain stretching required to accommodate the nanorods overcoming the copolymer block repulsion). Another limiting factor is the dimensions of the nanorods relative to the microphases; longer nanorods appear to disrupt the microphase structure of the polymer, whereas relatively large diameters appear to help drive the cross-phase alignment through entropic considerations in the absence of a strong enthalpic driving force (at least in the case of a lamellar block copolymer).

Thus, future work on this method should be targeted to address these limitations, particularly through the development of methods for the formation of segmented nanorods with smaller dimensions, which are anticipated to yield a reduced degree of polymer chain stretching upon their inclusion into the polymer microphases. Future work should also address the mechanical deformation of these nanorods upon their collection by centrifugation, necessitating a study into this phenomenon to better understand its origins. Finally, other studies should also be performed to investigate the influence of a wider range of experimental parameters upon this templating process, such as the use of weakly segregated block copolymers (using a different synthesis technique for the production of PMMA-*b*-PBMA or even a different block copolymer).

A further implication of this work involves the observation that the block copolymer morphology alters to accommodate large nanorods. Such alterations in local microphase morphology may be useful in a range of applications that require localized control over the block copolymer microphase structure (such as

the newly emerging field of block copolymer photolithography), which may be implemented in a controlled fashion through patterning of a surface with large features through lithography.