Spherical polymer micelles: nanosized reaction vessels?

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Supramolecular self-assembly techniques have provided a versatile means by which to selectively assemble polymeric molecules into well-defined three-dimensional nanostructures. The stabilization and tailoring of these dynamic nanostructures can be achieved using a range of chemistries to afford functional robust nanoparticles. Many examples of the stabilization, functionalization and application of these nanoparticles have been reported in the literature, and this paper will focus on these areas in the context of their potential application as nanometre-sized reaction vessels.

Keywords: polymer; micelles; nanoreactors; nanoparticles

1. Introduction

The control of the size, shape and function of molecular constructs on the nanoscale, using both covalent and non-covalent interactions, has received increasing interest due to their wide-ranging applications from medicine to materials science (Hawker & Wooley 2005). The facile synthesis of these polymeric nanostructures is achieved using a hierarchical assembly approach in which covalent interactions are first used to form a large robust building block such as a block copolymer, which can then undergo assembly via non-covalent interactions, with a relatively small number of other chains, to form nanometre-sized polymer nanostructures such as micelles and vesicles (Klok & Lecommandoux 2001). Thus, ‘weak’ non-covalent interactions can be used in concert with ‘strong’ covalent interactions to form structures with large nanoscale dimensions (of approx. tens to hundreds of nanometres) with tunable properties and function. This hierarchical assembly approach has been inspired by the self-assembly processes which are evident in nature and been used in many aspects of synthetic materials science, biology and chemistry (Whitesides 2002).

A key aspect of this self-assembly approach is in the synthesis of suitable building blocks which can be readily and specifically assembled into three-dimensional nanostructures. A number of different building blocks can be used, but our interest is primarily in the application of well-defined polymers as building blocks. To enable the synthesis of well-defined and functional nanostructures, it must be possible to synthesize well-defined and functional polymeric building blocks. This has been
achieved in recent years using a number of novel polymerization strategies, and our main interest is in the application of controlled radical polymerization strategies. Controlled radical polymerization techniques allow for precision polymer synthesis and have provided great opportunity in terms of flexibility, diversity and functionality in the synthesis of the polymeric building blocks (Kamigaito et al. 2001; Matyjaszewski & Xia 2001; Perrier & Takolpuckdee 2005).

This synthetic versatility allows for control over the building block composition, size and shape which, in turn, provides a handle for varying the afforded nanoscale objects’ morphology and dimensions upon self-assembly. This represents an important aspect of polymer self-assembly as it enables the construction of polymers with a high degree of control over molecular weight, sequence and end functionalization, and this has facilitated their application in many areas of science such as in synthesis and fabrication. In particular, this review will focus on the application of these synthetic techniques towards the facile synthesis of well-defined functionalized hydrophobic (water-repelling) and hydrophilic (water-loving) or ‘amphiphilic’ block copolymers. The area of solution amphiphilic block copolymer self-assembly has represented an important advance in the field of polymer and materials science, by allowing the self-assembly of blocks into well-defined specific nanostructures with a range of morphologies. The desire to develop such precise synthetic building blocks is driven by the target of achieving a high level of structural control which would enable the polymers to self-assemble with complexity and precision which is evident in natural systems such as enzymes and viruses.

Many nanostructure architectures, such as spheres, toroids, helices, rods, discs, vesicles and tubes, can be accessed by controlling both the conditions under which polymer solution self-assembly is conducted and by altering the block copolymer composition. For example, altering the relative block compositions changes the subsequent packing parameter, $p$ (where $p = v/la$, in which $a$ is the surface area of the hydrophilic or head group and $v$ and $l$ are the volume and length of the hydrophobic segment) and allows access to a range of morphologies (figure 1), such as hollow cage-like or vesicle-type structures and worm-like cylinder micelles (Isrealachvili et al. 1976). This area of solution self-assembly and the generation of a wide range of morphologies is beyond the scope of this review, but the reader is directed to a recent paper in the area (Lowik & van Hest 2004). Overall, the ability to control the assembly product provides an exciting opportunity in the manufacture of unique materials that demonstrate properties that are not otherwise accessible by conventional techniques.

Spherical polymeric micelles and nanoparticles are perhaps the most exciting functional assemblies, due to their well-defined phase-separated core–shell morphology and confined hydrophobic core domain (Webber 1998). Spherical polymer micelles have recently found numerous diverse applications such as delivery vehicles for therapeutics, as smart materials and nanosized devices (Wooley 2000; Rosler et al. 2001; Torchilin 2004; Vriezema et al. 2005). It has been recognized that the ability to further tailor the physical, chemical and biological properties of these nanostructures is central in the development of their future applications. Thus, there has been great recent interest in the development of methodologies for the synthesis, cross linking and functionalization of polymeric micelles (O’Reilly et al. 2006a). For example, these synthetic spherical polymeric nanostructures can be compared with natural architectures.

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such as viruses, given their self-assembled shells and nanometre length-scales (Wooley 2000). Given this analogy, it is unsurprising that the design of complex synthetic nanoparticles primarily uses techniques that are based on the basic construction tools found in nature, such as the combination and balance of weak and strong interactions, such as the hydrophobic effect and covalent bonds.

In this review we concentrate on the assembly, stabilization and functionalization of amphiphilic block copolymers into spherical nanostructures. We will highlight the selective functionalization of their core domain to enable their application as functional self-assembled nanoreactors. This is an exciting area of research due to the potential application of the resulting materials as novel supported catalyst systems. The covalent attachment of specific catalytic or functional groups within the hydrophobic core, which are protected from hydrolysis or degradation by the surrounding hydrophilic corona, allows for the selective reaction of hydrophobic reagents within a hydrophilic or aqueous environment. However, the functionalization of the core domain within polymeric micelles has received relatively limited attention, due to the difficulty in incorporating functionality within the hydrophobic block.

There are numerous other classes of self-assembled polymeric nanostructures and hybrid structures that have been used as nanoreactors. In addition, extensive and pioneering work has been performed in the development of biomacromolecular nanoreactors; however, as these structures constitute a whole other category in themselves, they will not be included in this review and instead readers are directed towards an excellent recent review which covers this work (Vriezema et al. 2005).

Figure 1. Schematic of the different aggregate morphologies predicted by the packing parameter \( p \). (Reprinted with permission from Vriezema et al. (2005).)
2. Solution self-assembly of amphiphilic block copolymers into spherical micelles

The simplest and most common method for the assembly of synthetic polymer chains into well-defined structures of nanoscale dimensions involves the solution formation of polymer micelles (Reiss 2003). Polymer micelles are formed spontaneously using the solution self-assembly (figure 2) of amphiphilic multi-block copolymers, which consist of a hydrophobic and hydrophilic chain segments. This process involves using the differing solubility and solution interaction of the segments of amphiphilic block copolymers to enable association of segment(s) into a particular solvent system. The association of a segment or segments of the copolymer chains, when placed in a solvent system that solvates only a portion of the overall chain, at concentrations at or above the critical micelle concentration (cmc) affords nanosized particles. That is to say at concentrations below the cmc, only unimer–polymer chains exist but as the polymer chain concentration increases beyond the cmc the polymer chains associate to form aggregates such as micelles. Experimentally, this is achieved by dissolving the amphiphilic copolymer in a good solvent for both the blocks and then gradually adding a non-solvent for the hydrophobic block; the micelles can then be kinetically trapped by complete replacement of the good solvent by the non-solvent via dialysis. This produces well-defined spherical aggregates, known as polymer micelles which in aqueous solution consist of a central hydrophobic core domain surrounded by a hydrophilic corona or shell.

The major driving force behind the self-assembly of amphiphilic copolymers is the decrease in free energy of the system due to the removal of the hydrophobic fragments from the incompatible aqueous environment by the formation of a micelle core which is stabilized and ‘protected’ from the surrounding aqueous media by the hydrophilic blocks via the hydrophobic effect (Tanford 1973). It is this protected hydrophobic core environment which is of interest as a confined environment in which to perform chemistry. It should be noted that conversely, reverse micelles can be formed by adding a non-solvent for the hydrophilic block to afford phase separation in which the hydrophilic core is surrounded by a hydrophobic shell in a hydrophobic surrounding media (Jung et al. 2003).

The properties of polymeric micelles are very tunable allowing for the tailoring of material and mechanical properties as well as their shapes and sizes. For example, the properties of a polymer micelle can be readily altered by choice of polymer comprising the core domain and can be varied to include glassy, crystalline or fluid-like materials. The core can also be removed to afford a solvent-filled nanocage or even hydrolysed to produce an entirely hydrophilic structure (Huang et al. 1999; Zhang et al. 2000; Turner & Wooley 2004). The ability to readily control the particle diameters in the range of 10–100 nm by controlling the block copolymer chain lengths and the ability to establish a hollow polymeric nanocage by removal of the core domain represent a significant advantage over other macromolecular constructs, such as linear polymers, surfactants or dendrimers. In addition, polymer micelles have been demonstrated to be more stable and also have a significantly lower cmc than surfactant micelles. Further discussion of surfactant micelles is beyond the scope of this paper and instead the reader is directed to a recent review article (Liu & Armes 2001b).
The characterization of the size, shape and distribution of these spherical polymeric micelles can be achieved using a plethora of techniques such as dynamic light scattering, static light scattering, transmission electron microscopy, atomic force microscopy, analytical ultracentrifugation (AU), viscometry, size exclusion chromatography and small-angle neutron scattering.

3. Stabilization of polymer micelles by cross-linking

Polymeric micelles are unstable at elevated temperature, at concentrations below their cmc and to changes in solvent composition. Given the need for well-defined robust nanostructures for applications as vessels for supported catalysis and delivery vehicles, there has been significant interest in the stabilization of these micelles. In nature, stabilization of self-assembled structures is often achieved by covalent cross links, and by analogy it has been demonstrated that the selective formation of such cross links between the polymer chains that compose a specific segment of a block copolymer micelle affords a single, nanostructured macromolecule or nanoparticle (Thurmond et al. 1996). The overall effect is that the formation of covalent cross links throughout a specific domain offers stability to the nanostructured assemblies by providing reinforcement to the weak hydrophobic interactions that enable polymer micelle assembly and existence. There are several potential locations for cross-linking within the polymeric micelles, including at the core chain end, within the core domain, at the core–shell interface and throughout the shell layer (figure 2). The location of the cross-linked domain can dramatically affect the chemical and physical properties of the resulting materials, and the extent of the cross-linking can also impact the stability, structure and thus applications of the resultant materials.

There are a number of primary chemistries which have been employed for the cross-linking and stabilization of the core domain of micellar particles, and they include the incorporation of polymerizable or photo/UV cross-linkable groups (Prochaska & Baloch 1979; Guo et al. 1996; Henselwood & Liu 1997), the introduction of cross-linking reagents (Iijima et al. 1999) and the application of external stimuli (Sumerlin et al. 2004; Bronich et al. 2005; Li et al. 2006). Recent work by the author has reported the application of mild and efficient...
copper-catalysed 1,3-dipolar cycloaddition or ‘Click’ \cite{Rostovtsev2002} chemistry for the core cross-linking of polymer micelles using tunable dendritic cross-linkers \cite{OReilly2007}.

Chemical fixation of either the core or shell domain is of interest due to the increased stability and robustness of the nanoparticles relative to their precursor micelles. It has also been proposed that cross-linking the core or shell domain alters the permeability of the respective domain, and thus significantly affects their potential as delivery vehicles or nanosized reaction vessels \cite{Kataoka2001; Rosler2001}. The majority of work in this area has focused on the cross-linking of the shell domain through functionalities located on the backbone of corona polymer chains, to afford a central core domain which comprises linear chains that are covalently linked to the inner surface of a permeable cross-linked shell layer. These shell cross-linked nanostructures have been demonstrated to have great potential as encapsulation and delivery agents due to their higher core mobility and more rigid form compared with core cross-linked particles. The cross-linking of the shell was first reported using radical polymerization techniques \cite{Thurmond1996}, then by condensation reactions \cite{Huang1997} and more recently by copper-catalysed 1,3-dipolar cycloaddition chemistry \cite{Joralemon2005a}, all of which are very efficient and generate robust phase-separated nanostructures which contain a permeable corona layer.

The permeability of the shell layer is the key when considering the desired applications of these polymer micelles as the ingress and release of small molecules is of paramount importance to their application as reaction vessels and delivery agents \cite{Murthy2001}. The methodologies outlined above all allow for the complete ‘protection’ of the core domain by the uniformly stabilized shell layer, while maintaining the desired nanoscale particle diameters with narrow size distributions (with distributions of approx. 1–5 nm)—thus providing a confined hydrophobic environment within the core domain in which chemistry can be performed.

This chemistry is only limited by the preparation of an appropriate amphiphilic diblock copolymer and the structure and chemical composition of the resultant nanoparticles can be readily tuned using the wide range of block copolymers which are synthetically available. A broad range of polymers have been used as the core hydrophobic domain of shell cross-linked nanoparticles and include styrene, isoprene, butadiene, caprolactone, poly(ethylene oxide) and methyl methacrylate. Monomers which have been used to prepare the hydrophilic water-soluble domain include, among others, acrylic acid, 4-vinylpyridine, (meth)acrylic acid, 2-dimethylaminoethyl methacrylate and N-isopropylacrylamide.

It is important that the cross links are limited to intramicellar rather than intermicellar reactions, and this is conventionally achieved by performing the cross-linking at high diblock copolymer dilution, to avoid the formation of large (micrometre-sized) covalently bound aggregates. However, recent work by Armes has elegantly used novel cross-linking concepts to create three-layer onion cross-linked micelles in which the central layer of a triblock copolymer is cross-linked \cite{Butun2000; LiuArmes2001a}. These triblock copolymers offer the advantage over conventional diblock copolymers that they allow inner-shell cross-linking to be carried out at high polymer concentrations without intermicellar cross-linking and aggregation due to the confined nature of the

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cross-linking reactions. This, in addition to the tunable nature of the micelle structures, has been proposed to facilitate laboratory scale-up and also improve their commercial viability.

An important development in the field of polymeric micelle stabilization, but which is beyond the scope of this review, is the recent report of reversible and tunable cross-linking chemistries. This has been very elegantly demonstrated by the groups of Kataoka and McCormick, and the resultant materials have been demonstrated to have great potential in the field of drug delivery due to the selective cleavage of the cross links to enable a controlled release and targeted delivery approach (Kakizawa et al. 1999; Li et al. 2006).

Overall, the potential uses of these cross-linked materials are improved by their increased stability towards environmental changes such as concentration and temperature, compared with their non-cross-linked micellar precursors. The subsequent covalent attachment of moieties to the cross-linked self-assembled architectures further extends the potential application of these materials towards their development as well-defined confined nanoreactors.

4. Subsequent chemical modification of cross-linked micelles

The functionalization of polymeric nanoparticles can be achieved at various locations, thereby allowing for the tailoring of these materials towards specific applications such as nanoreactors. There are three major classes of functional polymeric nanoparticles (figure 3). The first two classes of nanoparticles contain functional groups at the surface or within the shell domain of the particle and are envisaged to allow for the targeted and directed delivery of the vehicle to a particular site and are available as reactive handles for cross-linking of the corona or can present functionality on the nanoparticle surface. The third class of functional nanoparticles which is of greatest interest in this review contain reactive groups located in the hydrophobic core domain and may be used to cross-link the core or introduce further functionality into the nanoparticle core domain.

The selective functionalization of the core domains of polymeric micelles is an exciting area of research due to the potential application of the resulting materials as novel carrier or reaction vessels. The covalent attachment of specific groups within the hydrophobic core, which can be protected from hydrolysis or degradation by the surrounding hydrophilic corona, allows for the delivery or confinement of hydrophobic moieties in a hydrophilic or physiological environment. However, the functionalization of the core domain within polymeric micelles and nanoparticles has received relatively limited attention, due to the difficulty in incorporating functionality within the hydrophobic block.

5. Core functionalization and reactivity

The area of bioconjugation or attachment of biological molecules to the polymeric assemblies has been the primary functionalization strategy of nanoparticles to allow for the production of diagnostic and therapeutic products. Polymeric materials functionalized with sugars, peptides, targeting ligands, antibodies and other moieties have received considerable interest as a means to generate structures capable of polyvalent specific binding interactions (Liu et al. 2001; Bae et al. 2003;
Bes et al. 2003; Pan et al. 2003, 2004; Becker et al. 2004; Joralemon et al. 2005b). However, a drawback of the methodologies often employed is that often the reactive functionality is not compatible with the required polymerization conditions, for example often relatively complicated synthetic procedures were required for the functional diblock copolymer synthesis.

Another strategy that is perhaps more synthetically versatile and straightforward is the synthesis of latent functionalized monomers, which can be incorporated selectively into the hydrophobic domain to allow for the selective and versatile functionalization of the core region post-assembly and stabilization. Using Click reactive groups as the latent functionality, within a polystyrene core domain, Click-functionalized micelles were isolated which could be cross-linked in an intramicellar fashion via amidation reactions within an acrylic acid shell layer to afford nanoparticles bearing alkynyl or azido groups within the core domains (O’Reilly et al. 2005). The azido or alkynyl functionality that was embedded and dispersed throughout the hydrophobic styrenic core of the polymeric micelles was demonstrated to be available for further chemical modification using copper-catalysed 1,3-dipolar cycloaddition chemistry with complementary Click-functionalized fluorescent dyes to allow for the versatile chemical modification of the core domain (figure 4).

Functionalization and subsequent use of the functional handles embedded within the nanoparticle core require a number of issues to be considered. For example, for reactions to occur within this domain, reagents and substrates must transverse the shell layer and core–shell interface while still being soluble in the hydrophobic environment of the core. These issues were recently addressed, and it was reported that by tailoring the reaction conditions a fluorophore could be covalently attached to the core of a polystyrene–polyacrylic acid polymer micelle with a hydrodynamic diameter of approximately 20 nm (O’Reilly et al. 2006b). The covalent attachment versus sequestration was confirmed using AU analysis.
and also a pro-fluorophore coumarin dye (Yee et al. 2004). Thus, it was demonstrated that the fluorogenic reaction between a 3-azidocoumarin and alkynyl functionality located within the hydrophobic core domain of a shell cross-linked nanoparticle was successful based on the generation of fluorescence upon alteration of the coumarin electronic structure. This allowed for the confirmation of the covalent copper-catalysed 1,3-dipolar cycloaddition attachment of the coumarin within the nanoparticle rather than sequestration. This represented an important breakthrough in the application of polymer micelles as nanoreactors, as it provided evidence that the shell layer is permeable to small molecules and also that reactive functionality embedded within the core domain is available for further chemistry.

6. Polymer nanoreactors

Today’s environmental consciousness favours aqueous medium as a reaction solvent, as does its low cost; despite this, organic solvents are still the primary media used in organic synthesis. Unfortunately, the applicability of water as a reaction medium is limited due to the insolubility of many commonly used substrates and also the decomposition or deactivation of reactants/products under aqueous conditions. To overcome these challenges, surfactants, watersoluble dendrimers and organic hosts have been used to conduct such reactions in
aqueous media (Menger et al. 1975; Twyman et al. 2002). The development of novel catalytic functional polymeric nanostructures is of great interest and application to many different aspects of chemistry. The advantages of such nanostructures over traditional supports are numerous and include their ease of synthesis, versatility in size and functionalization as well as the potential application of these systems for selective catalysis in primarily aqueous media. This may be achieved by the inclusion of a reactive/catalytic group within the polymer nanoparticle core domain.

Micellar catalysis is a well-explored field with many examples of both reaction rate enhancement and retardation (Fendler & Fendler 1975; Bunton et al. 1991). These micellar effects are important; however, unlike the well-defined diblock copolymer systems we are interested in, they often use unstabilized and often commercially available surfactant-based micelles. These functionalized micelles can be described and used as nanoreactors, but the relatively undefined and dynamic nature of these micelles has somewhat limited their application. These unstabilized structures are not considered further in this paper and, instead, the reader is directed to a recent review of this area (Lindström 2002).

There have been a small number of recent reports on the applications of amphiphilic block copolymer micelles as nanoreactors (Vriezema et al. 2005). One recent example has reported that the assembly of a grafted amphiphile into a polymer micelle in aqueous media affords a conformation which consists of the hydrophobic units tucked inside to form a unique hydrophobic pocket that is capable of sequestering hydrophobic guest molecules (Arumugam et al. 2005). These hydrophobic pockets with dimensions of approximately 50 nm have been demonstrated to provide a unique reaction environment, which provides better selectivity to the reaction products than conventional surfactant micelles. This is achieved due to the confined encapsulation of the substrate, intermediate and products on the time scale of the reaction within the hydrophobic core, which leads to a cage effect and thus reaction selectivity.

An alternative strategy, which uses micelle-forming amphiphilic block copolymers in the stabilization of metal nanoparticles, has been extensively studied and can be described as nanoreactors, as the metal colloids are synthesized within their interior (Forster & Antonietti 1998). This has enabled the formation of nanosized (1–2 nm) metal colloids or clusters within PS-b-PVP micellar assemblies, with diameters of approximately 30 nm, and these metal colloid-functionalized polymer micelles can also be used as nanoreactors, owing to the presence of the catalytically active colloid within the micelle core domain. These assemblies have been suggested to combine the advantages of heterogeneous and homogeneous catalysis, given their solubility in organic solvents yet facile catalyst recovery using ultrafiltration or precipitation. These metal-functionalized micelles have been used in a range of catalysis reactions such as hydrogenations, oxidations and reductions (Roucoux et al. 2002).

Polymer–metal nanoparticles have been explored as nanoreactors for C–C coupling reactions such as in the Pd-catalysed Heck reaction (Klingelhofer et al. 1997; Le Bars et al. 1999). The authors suggest that the unique structure of these nanoreactors affords increased metal colloid lifetimes and comparable catalytic activity compared with low-molecular-weight Pd complexes. In addition, the colloidal catalysts showed no change in particle size or distribution after catalysis and demonstrated good catalytic reproducibility. However, these block
copolymer-supported catalysts demonstrated limited reactivity towards non-activated arenes and further work is required to tailor the complexing ligand on the metal to allow for higher reactivity. Recently, the formation of smaller clusters (ca 0.7 nm) has been reported using block copolymer cross-linked micelles of various architectures as templates and they have demonstrated activity in hydrogenation and Heck reactions (Okamoto et al. 2005).

Although these metal-functionalized nanoparticles can behave as nanoreactors, the ill-defined size and colloidal nature of the catalyst sites have thus far limited their further development and scope. Of significant interest would be the synthesis of well-defined single-site catalytic nanoparticles which should display comparable catalytic activities to their unsupported analogues yet offer the advantage of improved recyclability and recovery. The development of synthetic strategies for the selective incorporation of catalytic groups at specific locations within a three-dimensional polymeric array thus remains an important target. Moreover, the ease of tailoring of the nanoparticle facilitates extensive investigation and development of these catalytic systems to include stimuli-responsive nanostructures. This objective has not yet been fully realized and represents a whole new field of supported catalysis that may offer significant advances over existing polymeric systems.

7. Future outlook

Although the self-assembly of amphiphilic block copolymers has been an area of great interest for chemists for some time, quite recently the activities in the areas of functional/catalytic-stabilized polymer micelles have begun to intensify. The availability and realization of new synthetic controlled radical polymerization methods offer the opportunity to synthesize tailor-made, well-defined and specifically functionalized di- and triblock copolymers, thus providing an increase in synthetic versatility and may explain this increase in interest. The current research has begun to realize the full potential of these polymer micelles as delivery agents and the next stage in their development is in their application as supports for catalysis and investigation of them as nanoreactors. There has been little previous work on the introduction of single-site catalysts within polymeric micelles, and this may be due to the perceived lack of rigidity of micelles in solution which can lead to a lack of structural stability and conformation fixation of substrates compared with dendrimers. However, unlike dendrimers, which require elaborate and sometimes challenging synthesis, the preparation of polymer micelles is relatively straightforward and also extremely versatile, especially given the recent advances in stabilization chemistries. A significant advantage of using these polymeric scaffolds as catalyst supports is the ability to modify and thus tune the properties of the scaffolds by altering the surrounding solution conditions, and to develop responsive or ‘smart’ catalytic nanoreactors for improved separation and recovery.

Overall, block copolymer micelles and nanoparticles hold great promise as nanometre-sized reaction vessels, primarily due to their distinct and confined core environment. This phase-separated core–shell morphology and the potential for catalyst tethering within the hydrophobic core domain enable the possibility of selectively introducing reactive or catalytic handles into the core domain.

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As a consequence of the unique morphology of these nanostructures, it can be envisaged that the hydrophilic corona acts as a stabilizing shell and ‘protects’ the contents of the hydrophobic core domain in aqueous media. Thus, it should be possible to perform catalysis which is incompatible or currently unachievable in water within the hydrophobic core of the nanoparticle in a primarily aqueous solution. It is also proposed that there will be an environmental concentration effect within the core of the nanostructure, which will allow for an accumulation of hydrophobic substrates within this domain and enable closer proximity to the catalytic moieties than would be possible in a conventionally supported polymer catalyst or free catalyst system. Interest is now growing in the application of new cross-linking and functionalization strategies for these polymer assemblies to further enable their potential in advanced applications.

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