Article:

Pelras, Théophile, Mahon, Clare Sarah and Muellner, Markus (2018) Synthesis and Applications of Compartmentalised Molecular Polymer Brushes. Angewandte Chemie International Edition. pp. 6982-6994. ISSN 1433-7851

https://doi.org/10.1002/anie.201711878

Synthesis and Applications of Compartmentalised Molecular Polymer Brushes

Théophile Pelras,[+,a,b] *Dr. Clare S. Mahon,*[+,a,c] *Dr. Markus Müllner**[a,b]

[a] Key Centre for Polymers and Colloids, School of Chemistry, The University of Sydney, Sydney, NSW 2006 (Australia)
E-mail: markus.muellner@sydney.edu.au
[b] The University of Sydney Nano Institute (Sydney Nano), Sydney, (Australia)
[c] Department of Chemistry, University of York
Heslington, York, YO10 5DD (UK)
[+] These authors contributed equally to this work.

Abstract: *Polymer science is rapidly advancing towards the precise construction of synthetic macromolecules of formidable complexity. Beyond the impressive advances in control over polymer composition and uniformity enabled by the living polymerisation revolution, the introduction of compartmentalisation within polymer architectures can elevate their functionality beyond that of their constituent parts, thus offering immense potential for the production of tailor-made nanomaterials. In this Minireview, we discuss synthetic routes to complex molecular brushes with discrete chemical compartments and highlight their potential in the development of advanced materials with applications in nanofabrication, optics and functional materials.*

1. Introduction

Compartmentalisation, a feature which is ubiquitous in living systems, has captured the imagination of researchers striving to rival the complexity of the self-ordered systems found in nature. State-of-the-art polymers have moved far beyond the simplicity and functionality of commodity plastics to become tailor-made building blocks capable of self-organising to form complex and well-ordered soft matter.[1] Progress has been predominately enabled through breakthroughs in synthetic polymer chemistry, which has equipped researchers with powerful tools to steer polymer composition and architectures with unprecedented precision. These developments have created new opportunities to direct the self-assembly of soft matter as access to complex - but uniform - building blocks has improved and their supramolecular behaviour has become better understood. Advanced self-assembly of polymers is now at a stage where multiblock copolymers can be organised into patchy or compartmentalised nanoparticles, which themselves may continue to (co-)assemble into highly ordered matter.[2] In this Minireview, the term "compartmentalised particles" refers to nanoparticles containing at least two distinct, chemically different, compartments----with the simplest case being either a Janus or core--shell particle.

The production of compartmentalised nanoparticles by the assembly of block copolymers has already benefitted enormously from improvements in control over monomer sequence and polymer composition, as well as control of overall molecular weight and dispersity. The area of multicompartment polymer particles has been summarised in recent reviews.[3] Impressive progress in synthetic chemistry has provided new routes to compartmentalised soft nanoparticles and building blocks for self-assembly, by finely controlling the polymer architecture. Aside from the more established miktoarm star polymers,[4] a highly promising candidate comes in the form of a grafted architecture, namely molecular polymer brushes.[5] The synthetic construction of molecular brushes enables direct compartmentalisation by orthogonal synthetic procedures which in turn yield covalently fixed and uniform building blocks for supramolecular self-assembly applications. In this Minireview, we introduce block-type molecular polymer brushes, an emerging class of nanomaterials in the synthesis of nanostructured soft matter with distinct chemical compartments. We discuss promising strategies that allow convenient control over architecture and connect the unique properties of molecular brushes to current and prospective fields of application.

2. Molecular Polymer Brushes

A molecular brush - cylindrical polymer brush or bottlebrush polymer - consists of a primary polymer backbone (defined here as the z-direction) with pendant secondary chains protruding in the xy directions (Figure 1A). Steric repulsion between adjacent pendant chains imparts rigidity to the assembly, thereby resulting in a rod-like architecture which in turn endows molecular brushes with unusual material properties.[6] The unique brush architecture and associated properties have been comprehensively summarised in focussed reviews.[7] Molecular brushes in solution avoid the interchain entanglement observed in solutions of linear polymers,[8] with the macromolecules effectively behaving as discrete entities,[9] and are capable of liquid-crystalline behaviour[10] in the bulk. This absence of entanglement significantly reduces the energetic barriers to reorganisation, thereby enabling molecular brushes to act as "building blocks" for more complex molecular architectures. Molecular brushes, by their nature, are well-suited to the design of compartmentalised materials, where the compartmentalisation may be incorporated along the z-direction of the polymer (Figure 1B) to yield a block copolymer (block-type) brush,[11] or in the *xy* directions to produce a core--shell brush (Figure 1C).[12] Molecular brushes may also be used as supramolecular building blocks to construct compartmentalised nanostructures.[13]

2.1. Strategies for the Synthesis of Molecular Brushes

Several reviews have explored the unique properties of molecular brushes as well as basic strategies for generating brush architectures,[5, 6, 14] so only a brief overview will be provided here. These routes can be best categorised according to the strategy used to generate or attach side chains by using grafting-through, grafting-onto or grafting-from approaches (Figure 2).

The grafting-through approach involves the homo- or co-polymerisation of macromonomers, which leads to the generation of structures with a high grafting density and allows for complete characterisation of the side chains prior to their incorporation onto the primary backbone of the polymer (Figure 2A). The increasing steric constraints of the growing architecture may, however, limit the overall length of the macromolecule generated, with the purification of brushes prepared in this manner often frustrated by the presence of remaining high-molecular-weight side-chain components.

Ring-opening metathesis polymerisation (ROMP) allows for the convenient production of multiblock polymers of very well-defined chain lengths, which has enabled the production of ABA[13b] and ABC[15] triblock brushes with impressively low dispersities. The orthogonality of ROMP and radical-based polymerisation methods allows for the preparation of norbornyl macromonomers with a high degree of precision. Such macromonomers (i.e. polymers with a polymerisable end group) may comprise multiple blocks and may be sequentially polymerised to afford access to architectures with compartmentalisation in both the *xy* and *z* directions.

Wooley and co-workers have demonstrated the versatility of norbonyl-bearing trithiocarbonate chain-transfer agents by the synthesis of polystyrene (PS),[16] poly(*tert*-butyl acrylate) (P*t*BA),[16] poly(hydroxystyrene),[17] poly(lactic acid) (PLA)[18] and fluorinated polymers[17, 19] with excellent control over the dispersity. Sequential ROMP of these macromonomers using a modified second generation Grubbs catalyst then yielded compartmentalised molecular brushes of various morphologies, including a "dumbbell"-like architecture.[18]

Atom-transfer radical polymerisation (ATRP) and ring-opening polymerisation (ROP) may also be used for the construction of norbornyl macromonomers without initiating ROMP. Conjugation of a hydroxy functionality onto the norbornyl unit allows for ROP of cyclic monomers, including L-lactide,[18, 20a-d] whilst the addition of a bromide functionality permits the ATRP of various monomers including styrene,[20] poly(ethylene glycol) methacrylate (PEGMA) [13c] and fluorinated monomers.[21] Norbornyl or other polymerisable units may be installed into linear polymers as part of a post-polymerisation modification. This is often conveniently achieved by substituting ATRP-initiating halides with azides and subsequent copper-catalysed alkyne-azide cycloaddition (CuAAC)[22] with alkynyl-functionalised norbornenes to yield macromonomers of P*t*BA,[23] PS[24] and poly(*n*-butyl acrylate).[25] Esterification has also been used extensively to install norbornyl units onto preformed polymer chains, notably by Matsen, Hillmyer, Bates and co-workers,[26] who used this approach to generate diblock molecular brushes consisting of atactic polypropylene and PS. The grafting-through approach allowed the straightforward synthesis of a library of molecular brushes with variations in block sizes, which in turn aided the validation of a quantitative self-consistent field theory for the melt state of diblock brushes.

The grafting-onto approach involves the attachment of polymeric side chains to a preformed polymer backbone, with components bearing complementary functional groups (Figure 2B). This strategy allows for the separate preparation and characterisation of both the backbone and graft components, which can lead to well-defined architectures, but its success may be limited by both kinetic and thermodynamic factors. As the grafting density increases, steric hindrance along the backbone may impede the attachment of further grafts, with this process already bearing a high entropic cost as randomly coiled grafts are forced to adopt a more "stretched" conformation. Incomplete coupling of side chains may also lead to challenges in the purification of brushes prepared in this manner.

The grafting-onto approach has largely been avoided, but Deffieux and co-workers have elegantly demonstrated the utility of this approach for the generation of molecular brushes. Poly(chloroethyl vinyl ether) (PCEVE) backbones can undergo highly efficient two-step coupling with anionically polymerised "living" polyisoprene and PS chains by nucleophilic substitution to yield random copolymer brushes with dispersities below 1.10.[27] Studies by the same group have demonstrated the usefulness of grafting-onto[28] and grafting-from/onto[29] strategies for the formation of *z*-compartmentalised brushes by using analogous coupling methods. Possible alternative coupling reactions to install side chains are plentiful, and a general example of how grafting-onto may be exploited in future studies to produce *z*-compartmentalised polymer brush nanoparticles is shown in Figure 2B.

The grafting-from approach requires the formation of a backbone containing reactive sites which allow for the generation of side chains by another polymerisation technique (Figure 2C). This method allows the production of brushes of relatively high grafting densities by using straightforward purification techniques. Grafting-from routes may, however, require the use of multiple protection and deprotection steps and, therefore, still constitute complex multistep procedures. The grafting-from approach remains the most effective route to produce compartmentalised brushes along the *xy* direction (core-shell and core-shell-corona brushes).[30]

Grafting-from methods have also been used extensively to produce compartmentalised nanoarchitectures, since they offer ample flexibility in the choice of synthetic routes. ROMP has been used[31] to enable the production of very high molecular weight diblock polymers with one block displaying pendant ATRP-initiating groups, thus allowing for the growth of styrene grafts to produce *z*-compartmentalised structures of various molecular architectures. Rzayev and co-workers have used successive reversible addition-fragmentation chain-transfer (RAFT) polymerisations to construct polymer backbones containing functionalities to enable sequential ATRP and ROP.[32] Secondary RAFT functionalities may also be installed as post-polymerisation modifications,[33] thereby enabling the construction of ABC triblock molecular brushes with an impressive dispersity of 1.3.

A table showing the most recent *z*-compartmentalised block brushes, including their synthesis strategies and features, is available in the Supporting Information (Table S1).

3. Applications of Compartmentalised Molecular Polymer Brushes

The advances in synthetic methods discussed above, enabled primarily by the revolution of controlled polymerisation techniques, has propelled the study of molecular brushes from their first emergence[34] in the 1980s to sophisticated highly functional architectures. Molecular copolymer brushes have been employed for applications as diverse as nanofabrication,[17a, 19] cellular imaging[35] and even to mimic complex biological functions such as size- and charge-selective molecular transport.[36] The following section highlights key roles of compartmentalised molecular brushes in various applications in solution, thin and bulk films and at the interface (Figure 3).

3.1. In Solution

The discrete nature of molecular brushes, combined with the high level of control accessible over their synthesis and resulting molecular architectures, renders them highly attractive building blocks for the design and engineering of complex supramolecular assemblies in solution.

Wooley and co-workers[13a] used sequential RAFT polymerisations to produce α-norbornyl-ABC block copolymers (macromonomers) which, once grafted through ROMP, yielded *xy*-compartmentalised molecular brushes (core-shell-corona) that self-assembled in aqueous solution to produce cylindrical nanostructures (Figure 4A). Rzayev, Huang et al. have used compartmentalisation to obtain soft brush templates for the production of various hollow and open-end polymer nanotubes.[32a,36,37] For example, the core of a core--shell--corona brush template was degraded to form a hollow nanotube with an interior surface consisting of a negatively charged polyelectrolyte, while a cross-linked corona stabilised the construct.[36] The resultant amphiphilic nanotubes were found to be capable of selectively encapsulating guest molecules, discriminating on the basis of charge and, remarkably, the size-selective uptake of one of two polyamidoamine dendrimers with hydrodynamic diameters differing by less than 2 nm was observed (Figure 4B). In conceptually similar approaches, the same authors synthesised hollow nanocapsules with hydrophobic interiors using *xy*-compartmentalised molecular brushes.[38] The exterior surface was decorated after polymerisation with various oligo(ethylene glycol) substituents, thereby enabling the tuning of cellular uptake and demonstrating promise for future drug-delivery applications.

The influence of compartmentalisation in the formation of self-assembled architectures is demonstrated by the studies of Deffieux and co-workers, who have produced *z*-compartmentalised diblock molecular brushes[28] by the sequential grafting of "living" polystyryl and polyisopropyl (iPP) chains onto a PCEVE-derived backbone. These polymers were demonstrated by atomic force microscopy (AFM) and light-scattering techniques to self-assemble into hyperbranched micellar structures. In contrast, analogous noncompartmentalised brushes[27] produced by the random grafting of polystyryl and polyisopropyl chains onto the same backbone existed as isolated macromolecules in solution, but were capable of forming lamellar structures in the solid state, thus demonstrating the utility of molecular compartmentalisation as a tool to direct macroscopic properties. When a similarly random distribution of polystyryl and polyisopropyl chains were installed onto a macrocyclic polymer backbone,[39] the resultant cyclic polymer brushes were demonstrated to yield *xy*-compartmentalised cylindrical supramolecular structures in certainsolvents (Figure 4C).

Polymeric surfactants generally display lower critical micelle concentrations (CMCs) than analogous small-molecule amphiphiles, a feature which can be further extended in the case of molecular brushes. The use of side-chain-grafted architectures also allows access to enhanced levels of complexity in the design of surfactants. Amphiphilic compartmentalisation can readily be incorporated in the synthesis of molecular brushes either in the *z*-direction to yield block copolymer surfactants or in the *xy* directions to yield core--shell amphiphilic architectures.

Key to controlling the self-assembly of molecular brush surfactants is the symmetry of the brush architecture. Diblock molecular brushes with similar graft lengths have been demonstrated to assemble into lamellar phases[32c] in the solid state, but these self-assembly processes can be frustrated by the introduction of asymmetry into the architecture. Highly asymmetric diblock brushes are unable to maintain the constant cross-sectional area required for lamellar assembly, whilst the rigid nature of the backbone prevents the adoption of structures featuring curved interfaces.[32b] In solution, however, engineering of the symmetry of the grafted architecture can be used to control the interfacial curvature of assemblies, thus allowing precise control over the resultant supramolecular architecture. Rzayev and co-workers[32d] have generated a series of amphiphilic molecular brushes and explored the shape--morphology relationships that determine the resulting architectures. By using *z*-compartmentalised brushes featuring PLA and poly(ethylene glycol) methyl ether methacrylate grafts which vary in length (Figure 4D), they have produced a selection of supramolecular structures ranging from spherical and cylindrical micelles to bilayers. These micellar aggregates display improved thermodynamic stability relative to the corresponding assemblies of diblock copolymer surfactants, with CMCs as low as 1 nM reported.

The ability of molecular brushes to yield supramolecular structures of low CMC can be useful in drug-delivery applications.[40] *Z*-compartmentalised amphiphilic molecular brushes[41] incorporating a cholesterol-functionalised hydrophobic block along with a hydrophilic polyethylene oxide block were prepared by ROMP and shown to assemble into micellar structures. A cytotoxic drug was encapsulated in the core of the micelles, which enabled efficient cellular uptake and drastic enhancements in circulation times in vivo (Figure 4E).

Molecular brushes, with their high molecular weights, also display promise for the delivery of large therapeutic entities, such as nucleosides. The challenge of delivering RNA-based therapeutics to cells is often approached through their complexation with positively charged synthetic polymers or lipids,[42] which can lead to cytotoxicity. Schmidt and co-workers have constructed *xy*-compartmentalised polymer brushes with a polylysine core capable of binding siRNA, and a neutral poly(sarcosine) shell to mask positive charges.[43] Polymers were shown to deliver siRNA to cells and effectively silence a leukemia-associated gene during in vitro experiments, whilst displaying low cytotoxicity.

3.2. In Thin and Bulk Films

Block-type molecular brushes are highly applicable in the assembly of structured matter, since the morphologies may be adjusted by control of the composition and architecture of the molecular brush. Block copolymers with incompatible blocks may phase separate and yield domains with dimensions typically defined by the block lengths. For structures with domain sizes >100 nm, this approach becomes frustrated by chain entanglement, as the viscosity of the material increases significantly beyond its critical entanglement molecular weight,[44] thus necessitating annealing temperatures that are sufficiently high to damage the material or affect its properties. Molecular brushes avoid such entanglement issues as they exist as isolated polymer chains in solution, a feature which enables their use for the convenient preparation of nanostructures with large domain sizes.[20b,c,45]

One such area of application is in the fabrication of photonic crystals, for example, ordered composite structures of high- and low-refractive index materials with periodicity comparable to the wavelength of light.[46] Although photonic crystals can be formed using ultrahigh molecular weight linear block copolymers, chain entanglement limits the accessible domain sizes and, therefore, restricts achievable colours to wavelengths below the green region of the visible spectrum.[47] Longer wavelengths may be achieved by induced domain swelling by adding other components to the mixture (such as solvent,[48] nanoparticles[49] or homopolymers),[50] but these processes introduce further layers of complexity into the manufacturing process. Grubbs and co-workers have made significant advances in the fabrication of photonic materials using block copolymer brushes.[20a, 20d, 51] Brushes of similar composition and dimensions but different arrangements of the side chains were observed to phase-separate differently,[25] thus demonstrating how the arrangement of the individual compartments can influence the achievable domain spacings (Figure 5A). When the brushes had randomly localised side chains (i.e. no "fixed" compartments), the domain spacing of the resulting thin films was relatively small (14 nm by small-angle X-ray scattering, SAXS) and determined by the overall length of the side chain (Figure 5B). Interestingly, the domain spacing was noted to be insensitive to the backbone length, which suggested the brushes were undergoing phase separation of their side chains, with the backbone confined at the interface between the two polymers and the side chains segregated to opposite sides (i.e. along the *x*-axis). Conversely, when the brushes were compartmentalised along the *z*-axis, large and well-ordered lamellar domains with spacings over 100 nm were observed by SAXS (Figure 5C). These lamellar domains had dimensions which depended on the backbone length and were large enough to reflect visible light.

When selecting building blocks for self-assembly, molecular brushes may offer easier tunability than their linear analogues, as the lamellar spacing can be simply adjusted by a change in the brush grafting density (but retaining the same backbone dimensions). Molecular brushes with comparable backbone lengths but different grafting densities produced lamellar bulk morphologies where larger domains were accessible through brushes with higher grafting densities (Figure 5D).[52] Increases in the degree of polymerisation of the brush backbone led to increasing domain spacing in the respective thin films, with a remarkable near-linear relationship observed. This relationship between molecular weight and the wavelength of maximal reflectance has been demonstrated to be sufficiently accurate to allow prediction of the optical properties of the resultant material (Figure 5E).[20a] Domain spacing may also be adjusted by altering the self-assembly conditions, such as changing the annealing solvent and temperature,[20a] as well as by the blending in of additives (e.g. gold nanoparticles; Figure 5G,H).[53] This highly combinatorial approach to tuning the optical properties of polymer films demonstrates the versatility of molecular brushes in the fabrication of photonic coatings. Given their unique phase separation, block-type brushes may also be self-assembled in confined spaces (e.g. emulsion droplets)[54] to yield (nano)particles with internal structure, such as axially stacked lamellae.[55]

The introduction of a third block in *z*-compartmentalised molecular brushes may lead to the formation of diffuse or mixed interfaces. ABC triblock brushes composed of PLA, poly(methyl methacrylate) (PMMA) and PS - with similar block and side-chains lengths - revealed similar behaviour to a diblock copolymer with fully segregated PLA and mixed PS/PMMA phases, despite the general immiscibility of PS and PMMA and the miscibility of PLA and PMMA.[33] Similarly Grubbs and co-workers studied ABC triblock brushes composed of polymers with low interaction (χ) parameters.[15b] In contrast to linear analogues that typically form two- or three-domain lamellar morphologies, their study revealed the self-assembly of brushes into lamellar domains with a unique block domain connectivity.

Tuning the symmetry of diblock molecular brushes adds an additional means to direct their self-assembly in the bulk phase and allows access not only to lamellar but even cylindrical morphologies.[32c] The cylindrical domain may subsequently be etched to produce porous polymer films for prospective use in filtration or templating applications. In this context, Rzayev and co-workers have used cone-shaped [PLA]-*b*-[PS] diblock brushes and selectively hydrolysed self-assembled polymer films to produce well-defined nanoporous materials (Figure 5).[32c] The achievable pore size was dependent on the architecture of the diblock copolymer used. Films obtained by the self-assembly of diblock brushes exhibited larger pore sizes than those obtained from conventional linear diblock polymers.

3.3. At the Interface

The intramolecular segregation of chemical properties motivates the use of block-type brushes at interfaces. As shown in Section 3.1, diblock brushes may display similar behaviour as linear block copolymers in solution, thin films and bulk. However, as a consequence of their particulate character, they may further be employed as compatibilisers in polymer melts and mixtures. Grubbs and co-workers have shown that [PLA]-*b*-[PS] brushes can separate into lamellar structures,[20a] but interestingly, these brushes also allow the lamellar domains to be swelled by using homopolymers to increase the spacing between the lamellae and consequently tune the optical properties of the polymer films (Figure 6A-D).[20d] Here, the brushes prevent macroscopic demixing of homopolymers and sustain the order of the phase-separated film by stabilising the interface between the individual polymer domains. Lin and co-workers also used [PS]-*b*-[PLA] brushes and a Langmuir--Blodgett approach to study their behaviour at the air/water interface.[56] Compared to linear PS-*b*-PLA block copolymer analogues, the diblock brushes required more space per molecule because of their higher molecular weight. Architecture-dependent differences were already observed within Langmuir monolayers at low pressures by AFM. Furthermore, the pressure--area isotherms revealed unique interfacial self-assembly as a function of the surface pressure, which is highly different from the assembly behaviour known for amphiphilic block copolymers (Figure 6E,F). Surprisingly, limited work has been done to date on studying the surface-pressure-induced morphological changes of amphiphilic block-type brushes at interfaces. However, as shown in Section 3.1, amphiphilic diblock brushes have already been synthesised. Diblock brushes have been used as a surface coating by spin-coating them onto silicon wafers to form a monolayer of upright molecular brushes that could be rendered into a high-resolution negative-tone photoresist surface.[17a] Similar future applications may make use of the fast phase-separation of block-type brushes as well as their unique ability to form light-interactive surface coatings (as discussed in Section 3.2). This advance might enable roll-to-roll processing of photonic coatings in the future. The final section will elaborate on prospective applications of compartmentalised molecular brushes.

4. Perspective and Future Applications

The acceleration of progress in polymer and colloidal self-assembly enabled by advances in synthetic polymer chemistry suggests molecular brushes have an exciting future. The preparation of compartmentalised molecular brushes, whilst still synthetically demanding, is no longer a stumbling block to the realisation of nanosized building blocks for self-assembly. While this compartmentalisation has already proved valuable in bulk and thin films for fast phase separation and tuneable optical and surface properties, the behaviour in solution is currently less well understood and offers interesting opportunities for further study. Such endeavours will undoubtedly be inspired by the fascinating hierarchical structures achieved by the self-assembly of multicompartment micelles in the last decade.[3] The first examples of the use of molecular brushes in particle-particle assembly have been recently demonstrated by controlling their end-to-end connection through DNA hybridisation[57] or hydrophobic interactions.[58] Unlike the use of diblock brushes as surfactants (i.e. high molecular weight amphiphiles),[32d, 59] this brush--brush interaction may be directional in one, two or three dimensions - depending on the brush architecture (Figure 7) - largely because of the covalently fixed nature of molecular brushes. Their stable architectures may be a notable advantage over self-assembled components (such as multicompartment micelles or crystallisation-derived micelles) and endow these building blocks with substantial tolerance to environmental changes. Recently, molecular brush templated organic nanotubes have shown pH-dependent end-to-end association in water.[60] Freed from solvent limitations, we anticipate that many of the micelle-based superstructures observed in the past decade can be translated into aqueous environments to demonstrate their full potential.

Similar inspiration could be taken from Janus particles, especially polymer Janus nanoparticles,[61] as the straightforward compartmentalisation of molecular brushes may be used to tailor Janus-like polymer nanoparticles of various compositions (Figure 8A). In recent years, Janus particles have featured as key parts in several intriguing studies.[62] Janus spheres, cylinders and platelets with the same chemical make-up showed shape- and aspect-ratio-dependent interfacial behaviour at liquid--liquid interfaces (Figure 8B).[63] Moreover, they have been used to aid the dispersion of carbon nanotubes (Figure 8C)[64] and the processing of otherwise immiscible polymer blends (Figure 8D).[65] A recent example by Matyjaszewski and co-workers used the in-situ formation of Janus-type molecular copolymer brushes to stabilise water-in-oil emulsions (Figure 8E).[66] Yang and co-workers have recently reported the synthesis of asymmetric Janus molecular brush nanorods that adopt a vertical orientation at the emulsion interface.[67] These exciting applications of Janus particles in combination with the precise control over the molecular architecture and composition further motivate the use of molecular brushes at interfaces. Pickering emulsions,[68] polymer processing[65] and surface coatings[69] may benefit from such tuneable synthetic additives.

Compartmentalisation in the *xy* direction has been achieved in the form of core--shell and core--shell--corona molecular brushes and used to produce templated organic and inorganic nanomaterials,[30, 70] thus signifying applications beyond soft matter. The exploitation of the *z*-direction is still in the early stages, but may lead to multiple and sequential compartmentalisation, which may be useful in the design of cascade reactions. Perrier and co-workers have recently used the versatility of the RAFT shuttle approach[71] to produce molecular brushes with multiple compartments that are themselves built from multiblock polymer grafts.[72] Matson synthesised tapered brushes ("cone-shaped" along the *z*-direction) by sequential addition of macromonomers of decreasing molecular weight,[73] thereby highlighting the complexity of compartmentalised architures that may be obtained by incorporating an element of sequence control.

A central challenge in contemporary polymer science is the realisation of the ability of the chemist to precisely direct the construction of synthetic materials to rival the complexity and homogeneity observed in nature’s macromolecules, particularly proteins, which display multiple "layers" of self-organisation. Ultimately, the intricacies of protein architecture which enable their diverse functionalities in self-assembly, recognition and catalysis are conferred by precise control of their monomer sequence during polymerisation----a level of control that many polymer chemists are striving to emulate and will surely be realised. The addition of sequence control in the construction of molecular brushes[74] has already provided impressive control over their grafting density, thus illustrating another emerging strategy for the realisation of truly tailor-made nanoscale architectures.

Acknowledgements

T.P. thanks the University of Sydney Nano Institute (Sydney Nano) for a Postgraduate Top-Up Scholarship. C.S.M. is a grateful recipient of a Marie Skłodowska-Curie Global Fellowship; this project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 702927. M.M. acknowledges the Faculty of Science (University of Sydney) Seed funding scheme, the Selby Research Foundation and the Australian Research Council for a Discovery Early Career Researcher Award (DE180100007).

References

[1] J.-F. Lutz, J.-M. Lehn, E. W. Meijer, K. Matyjaszewski, *Nat. Rev. Mater.* **2016**, *1*, 16024.

[2] (a) H. Gröschel, F. H. Schacher, H. Schmalz, O. V. Borisov, E. B. Zhulina, A. Walther, A. H. E. Müller, *Nat. Commun.* **2012**, *3*, 710; (b) D. J. Lunn, J. R. Finnegan, I. Manners, *Chem. Sci.* **2015**, *6*, 3663—3673; (c) A. H. Gröschel, A. Walther, T. I. Löbling, F. H. Schacher, H. Schmalz, A. H. E. Müller, *Nature* **2013**, *503*, 247-251; (d) H. Qiu, Z. M. Hudson, M. A. Winnik, I. Manners, *Science* **2015**, *347*, 1329—1332.

[3] (a) A. H. Gröschel, A. H. E. Müller, *Nanoscale* **2015**, *7*, 11841—11876; (b) J. Du, R. K. O’Reilly, *Chem. Soc. Rev.* **2011**, *40*, 2402—2416.

[4] (a) A. Hanisch, A. H. Gröschel, M. Förtsch, M. Drechsler, H. Jinnai, T. M. Ruhland, F. H. Schacher, A. H. E. Müller, *ACS Nano* **2013**, *7*, 4030—4041; (b) Z. Li, E. Kesselman, Y. Talmon, M. A. Hillmyer, T.P. Lodge, *Science* **2004**, *306*, 98—101.

[5] M. Zhang, A. H. E. Müller, *J. Polym. Sci. Part A* **2005**, *43*, 3461—3481.

[6] S. S. Sheiko, B. S. Sumerlin, K. Matyjaszewski, *Prog. Polym. Sci.* **2008**, *33*, 759—785.

[7] (a) R. Verduzco, X. Li, S. L. Pesek, G. E. Stein, *Chem. Soc. Rev.* **2015**, *44*, 2405—2420; (b) J. Yuan, A. H. E. Müller, K. Matyjaszewski, S. S. Sheiko in *Polymer Science: A Comprehensive Reference*, Elsevier, Amsterdam, **2012**, pp. 199—264; (c) J. Rzayev, *ACS Macro Lett.* **2012**, *1*, 1146—1149.

[8] (a) Y. Tsukahara, J. Inoue, Y. Ohta, S. Kohjiya, *Polymer* **1994**, *35*, 5785—5789; (b) Y. Tsukahara, *Kobunshi* **1997**, *46*, 738—740.

[9] (a) Y. Tsukahara, K. Tsutsumi, Y. Okamoto, *Makromol. Chem. Rapid Commun.* **1992**, *13*, 409—413; (b) S. Namba, Y. Tsukahara, K. Kaeriyama, K. Okamoto, M. Takahashi, *Polymer* **2000**, *41*, 5165—5171.

[10] Y. Tsukahara, Y. Ohta, K. Senoo, *Polymer* **1995**, *36*, 3413—3416.

[11] K. Ishizu, J. Satoh, A. Sogabe, *J. Colloid Interface Sci.* **2004**, *274*, 472—479.

[12] H. G. Börner, K. Beers, K. Matyjaszewski, S. S. Sheiko, M. Möller, *Macromolecules* **2001**, *34*, 4375—4383.

[13] (a) Z. Li, J. Ma, N. S. Lee, K. L. Wooley, *J. Am. Chem. Soc.* **2011**, *133*, 1228—1231; (b) C. M. Bates, A. B. Chang, N. Momčilović, S. C. Jones, R. H. Grubbs, *Macromolecules* **2015**, *48*, 4967—4973; H. Unsal, S. Onbulak, F. Calik, M. Er-Rafik, M. Schmutz, A. Sanyal, J. Rzayev, *Macromolecules* **2017**, *50*, 1342—1352.

[14] (a) H.-i. Lee, J. Pietrasik, S. S. Sheiko, K. Matyjaszewski, *Prog. Polym. Sci.* **2010**, *35*, 24—44; (b) C. Feng, Y. Li, D. Yang, J. Hu, X. Zhang, X. Huang, *Chem. Soc. Rev.* **2011**, *40*, 1282—1295.

[15] (a) L. Su, G. S. Heo, Y.-N. Lin, M. Dong, S. Zhang, Y. Chen, G. Sun, K. L. Wooley, *J. Polym. Sci. Part A* **2017**, *55*, 2966—2970; (b) A. B. Chang, C. M. Bates, B. Lee, C. M. Garland, S. C. Jones, R. K. W. Spencer, M. W. Matsen, R. H. Grubbs, *Proc. Natl. Acad. Sci. USA* **2017**, *114*, 6462—6467.

[16] Z. Li, J. Ma, C. Cheng, K. Zhang, K.L. Wooley, *Macromolecules* **2010**, *43*, 1182—1184.

[17] (a) G. Sun, S. Cho, C. Clark, S.V. Verkhoturov, M. J. Eller, A. Li, A. Pavía-Jiménez, E. A. Schweikert, J. W. Thackeray, P. Trefonas, K. L. Wooley, *J. Am. Chem. Soc.* **2013**, *135*, 4203—4206; (b) S. Cho, F. Yang, G. Sun, M. J. Eller, C. Clark, E. A. Schweikert, J. W. Thackeray, P. Trefonas, K. L. Wooley, *Macromol. Rapid Commun.* **2014**, *35*, 437—441.

[18] A. Li, Z. Li, S. Zhang, G. Sun, D. M. Policarpio, K. L. Wooley, *ACS Macro Lett.* **2012**, *1*, 241—245.

[19] G. Sun, S. Cho, F. Yang, X. He, A. Pavía-Sanders, C. Clark, J. E. Raymond, S. V. Verkhoturov, E. A. Schweikert, J. W. Thackeray, P. Trefonas, K. L. Wooley, *J. Polym. Sci. Part A* **2015**, *53*, 193—199.

[20] (a) B. R. Sveinbjörnsson, R. A. Weitekamp, G. M. Miyake, Y. Xia, H. A. Atwater, R. H. Grubbs, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 14332—14336; (b) W. Gu, J. Huh, S.W. Hong, B. R. Sveinbjornsson, C. Park, R. H. Grubbs, T. P. Russell, *ACS Nano* **2013**, *7*, 2551—2558; (c) S. W. Hong, W. Gu, J. Huh, B. R. Sveinbjornsson, G. Jeong, R. H. Grubbs, T. P. Russell, *ACS Nano* **2013**, *7*, 9684—9692; (d) R. J. Macfarlane, B. Kim, B. Lee, R. A. Weitekamp, C. M. Bates, S. F. Lee, A. B. Chang, K. T. Delaney, G. H. Fredrickson, H. A. Atwater, R. H. Grubbs, *J. Am. Chem. Soc.* **2014**, *136*, 17374—17377; (e) M. B. Runge, S. Dutta, N. B. Bowden, *Macromolecules* **2006**, *39*, 498—508.

[21] Xu, W. Wang, Y. Wang, J. Zhu, D. Uhrig, X. Lu, J. K. Keum, J. W. Mays. K. Hong, *Polym. Chem.*, **2016**, *7*, 680-688.

[22] J. E. Hein, V. V. Fokin, *Chem. Soc. Rev.* **2010**, *39*, 1302—1315.

[23] D.-P. Song, C. Li, N. S. Colella, W. Xie, S. Li, X. Lu, S. Gido, J.-H. Lee, J. J. Watkins, *J. Am. Chem. Soc.* **2015**, *137*, 12510—12513.

[24] D.-P. Song, Y. Lin, Y. Gai, N. S. Colella, C. Li, X.-H. Liu, S. Gido, J. J. Watkins, *J. Am. Chem. Soc.* **2015**, *137*, 3771—3774.

[25] Y. Xia, B. D. Olsen, J. A. Kornfield, R. H. Grubbs, *J. Am. Chem. Soc.* **2009**, *131*, 18525—18532.

[26] S. J. Dalsin, T. G. Rions-Maehren, M. D. Beam, F. S. Bates, M. A. Hillmyer, M. W. Matsen, *ACS Nano* **2015**, *9*, 12233—12245.

[27] D. Lanson, F. Ariura, M. Schappacher, R. Borsali, A. Deffieux, *Macromolecules* **2009**, *42*, 3942—3950.

[28] D. Lanson, M. Schappacher, R. Borsali, A. Deffieux, *Macromolecules* **2007**, *40*, 5559—5565.

[29] F. Ariura, M. Schappacher, R. Borsali, A. Deffieux, *React. Funct. Polym.* **2009**, *69*, 402—408.

[30] M. Müllner, A. H. E. Müller, *Polymer* **2016**, *98*, 389—401.

[31] (a) M. B. Runge, N. B. Bowden, *J. Am. Chem. Soc.* **2007**, *129*, 10551—10560; (b) M. Byun, N. B. Bowden, Z. Lin, *Nano Lett.* **2010**, *10*, 3111—3117; (c) M. B. Runge, J. Yoo, N. B. Bowden, *Macromol. Rapid Commun.* **2009**, *30*, 1392—1398.

[32] (a) K. Huang, J. Rzayev, *J. Am. Chem. Soc.* **2009**, *131*, 6880—6885; (b) J. Bolton, T. S. Bailey, J. Rzayev, *Nano Lett.* **2011**, *11*, 998—1001; (c) J. Rzayev, *Macromolecules* **2009**, *42*, 2135—2141; (d) R. Fenyves, M. Schmutz, I. J. Horner, F. V. Bright, J. Rzayev, *J. Am. Chem. Soc.* **2014**, *136*, 7762—7770.

[33] J. Bolton, J. Rzayev, *Macromolecules* **2014**, *47*, 2864—2874.

[34] Y. Tsukahara, K. Mizuno, A. Segawa, Y. Yamashita, *Macromolecules* **1989**, *22*, 1546—1552.

[35] (a) Z. Zheng, A. Daniel, W. Yu, B. Weber, J. Ling, A. H. E. Müller, *Chem. Mater.* **2013**, *25*, 4585—4594; (b) M. A. Sowers, J. R. McCombs, Y. Wang, J. T. Paletta, S. W. Morton, E. C. Dreaden, M. D. Boska, M. F. Ottaviani, P. T. Hammond, A. Rajca, J. A. Johnson, *Nat. Commun.* **2014**, *5*, 5460; (c) M. F. Fouz, K. Mukumoto, S. Averick, O. Molinar, B. M. McCartney, K. Matyjaszewski, B. A. Armitage, S. R. Das, *ACS Cent. Sci.* **2015**, *1*, 431—438.

[36] K. Huang, J. Rzayev, *J. Am. Chem. Soc.* **2011**, *133*, 16726—16729.

[37] K. Huang, D. P. Canterbury, J. Rzayev, *Macromolecules* **2010**, *43*, 6632—6638.

[38] K. Huang, A. Jacobs, J. Rzayev, *Biomacromolecules* **2011**, *12*, 2327—2334.

[39] M. Schappacher, A. Deffieux, *Science* **2008**, *319*, 1512—1515.

[40] M. Müllner, *Macromol. Chem. Phys.* **2016**, *217*, 2209—2222.

[41] T.-H. Tran, C. T. Nguyen, L. Gonzalez-Fajardo, D. Hargrove, D. Song, P. Deshmukh, L. Mahajan, D. Ndaya, L. Lai, R. M. Kasi, X. Lu, *Biomacromolecules* **2014**, *15*, 4363—4375.

[42] F. Geinguenaud, E. Guenin, Y. Lalatonne, L. Motte, *ACS Chem. Biol.* **2016**, *11*, 1180—1191.

[43] C. Hörtz, A. Birke, L. Kaps, S. Decker, E. Wächtersbach, K. Fischer, D. Schuppan, M. Barz, M. Schmidt, *Macromolecules* **2015**, *48*, 2074—2086.

[44] M. Rubinstein, R. H. Colby, *Polym. Phys.*, Oxford University Press, Oxford, **2003**.

[45] A. Noro, Y. Tomita, Y. Matsushita, E. L. Thomas, *Macromolecules* **2016**, *49*, 8971—8979.

[46] J. D. Joannopoulos, S. G. Johnson, J. N. Winn, R. D. Meade, *Photonic Crystals*: *Molding the Flow of Light*, 2nd ed., Princeton University Press, Princeton, **2008**.

[47] (a) J. Yoon, R. T. Mathers, G. W. Coates, E. L. Thomas, *Macromolecules* **2006**, *39*, 1913—1919; (b) P. D. Hustad, G. R. Marchand, E. I. Garcia-Meitin, P. L. Roberts, J. D. Weinhold, *Macromolecules* **2009**, *42*, 3788—3794.

[48] Y. Kang, J. J. Walish, T. Gorishnyy, E. L. Thomas, *Nat. Mater.* **2007**, *6*, 957.

[49] C. Kang, E. Kim, H. Baek, K. Hwang, D. Kwak, Y. Kang, E. L. Thomas, *J. Am. Chem. Soc.* **2009**, *131*, 7538—7539.

[50] A. Urbas, Y. Fink, E. L. Thomas, *Macromolecules* **1999**, *32*, 4748—4750.

[51] (a) G. M. Miyake, V. A. Piunova, R. A. Weitekamp, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2012**, *51*, 11246--11248; *Angew. Chem.* **2012**, *124*, 11408—11410; (b) G. M. Miyake, R. A. Weitekamp, V. A. Piunova, R. H. Grubbs, *J. Am. Chem. Soc.* **2012**, *134*, 14249—14254.

[52] T.-P. Lin, A. B. Chang, S.-X. Luo, H.-Y. Chen, B. Lee, R. H. Grubbs, *ACS Nano* **2017**, *11*, 11632—11641.

[53] D.-P. Song, C. Li, N. S. Colella, X. Lu, J.-H. Lee, J. J. Watkins, *Adv. Opt. Mater.* **2015**, *3*, 1169—1175.

[54] M. P. Kim, G.-R. Yi, *Front. Mater.* **2015**, *2*, 45.

[55] A. Steinhaus, T. Pelras, R. Chakroun, A. H. Gröschel, M. Müllner, *Macromol. Rapid Commun.* **2018,** DOI 10.1002/marc.201800177

[56] L. Zhao, M. Byun, J. Rzayev, Z. Lin, *Macromolecules* **2009**, *42*, 9027—9033.

[57] X. Lu, E. Watts, F. Jia, X. Tan, K. Zhang, *J. Am. Chem. Soc.* **2014**, *136*, 10214—10217.

[58] Y. Yamauchi, K. Yamada, N. N. Horimoto, Y. Ishida, *Polymer* **2017**, *120*, 68—72.

[59] D. Zehm, A. Laschewsky, M. Gradzielski, S. Prévost, H. Liang, J. P. Rabe, R. Schweins, J. Gummel, *Langmuir* **2010**, *26*, 3145—3155.

[60] S. Onbulak, J. Rzayev, *J. Polym. Sci. Part A* **2017**, *55*, 3868—3874.

[61] A. Walther, A. H. E. Müller, *Soft Matter* **2008**, *4*, 663—668.

[62] A. Walther, A. H. E. Müller, *Chem. Rev.* **2013**, *113*, 5194—5261.

[63] (a) T. M. Ruhland, A. H. Gröschel, A. Walther, A. H. E. Müller, *Langmuir* **2011**, *27*, 9807—9814; (b) T. M. Ruhland, A. H. Gröschel, N. Ballard, T. S. Skelhon, A. Walther, A. H. E. Müller, S. A. F. Bon, *Langmuir* **2013**, *29*, 1388—1394.

[64] A. H. Gröschel, T. I. Löbling, P. D. Petrov, M. Müllner, C. Kuttner, F. Wieberger, A. H. E. Müller, *Angew. Chem. Int. Ed.* **2013**, *52*, 3602--3606; *Angew. Chem.* **2013**, *125*, 3688—3693.

[65] (a) A. Walther, K. Matussek, A. H. E. Müller, *ACS Nano* **2008**, *2*, 1167—1178; (b) R. Bahrami, T. I. Löbling, A. H. Gröschel, H. Schmalz, A. H. E. Müller, V. Altstädt, *ACS Nano* **2014**, *8*, 10048—10056.

[66] G. Xie, P. Krys, R. D. Tilton, K. Matyjaszewski, *Macromolecules* **2017**, *50*, 2942—2950.

[67] F. Jia, F. Liang, Z. Yang, *Langmuir* **2018**, *34*, 1718-1724.

[68] C. Kaewsaneha, P. Tangboriboonrat, D. Polpanich, M. Eissa, A. Elaissari, *Colloids Surf. A* **2013**, *439*, 35—42.

[69] S. L. Pesek, Y.-H. Lin, H. Z. Mah, W. Kasper, B. Chen, B. J. Rohde, M. L. Robertson, G. E. Stein, R. Verduzco, *Polymer* **2016**, *98*, 495—504.

[70] (a) J. Yuan, A. H. E. Müller, *Polymer* **2010**, *51*, 4015—4036; (b) M. Müllner, J. Yuan, S. Weiss, A. Walther, M. Förtsch, M. Drechsler, A. H. E. Müller, *J. Am. Chem. Soc.* **2010**, *132*, 16587—16592; (c) M. Morits, V. Hynninen, Nonappa, A. Niederberger, O. Ikkala, A. H. Gröschel, M. Müllner, *Polym. Chem.* **2018**, 9, 1650; (d) M. Müllner, T. Lunkenbein, J. Breu, F. Caruso, A. H. E. Müller, *Chem. Mater.* **2012**, *24*, 1802—1810; (e) M. Müllner, T. Lunkenbein, M. Schieder, A. H. Gröschel, N. Miyajima, M. Förtsch, J. Breu, F. Caruso, A. H. E. Müller, *Macromolecules* **2012**, *45*, 6981—6988.

[71] Z. Zheng, J. Ling, A. H. E. Müller, *Macromol. Rapid Commun.* **2014**, *35*, 234—241.

[72] A. Kerr, M. Hartlieb, J. Sanchis, T. Smith, S. Perrier, *Chem. Commun.* **2017**, *53*, 11901—11904.

[73] S. C. Radzinski, J. C. Foster, S. J. Scannelli, J. R. Weaver, K. J. Arrington, J. B. Matson, *ACS Macro Lett.* **2017**, *6*, 1175—1179.

[74] T.-P. Lin, A. B. Chang, H.-Y. Chen, A. L. Liberman-Martin, C. M. Bates, M. J. Voegtle, C. A. Bauer, R. H. Grubbs, *J. Am. Chem. Soc.* **2017**, *139*, 3896—3903.

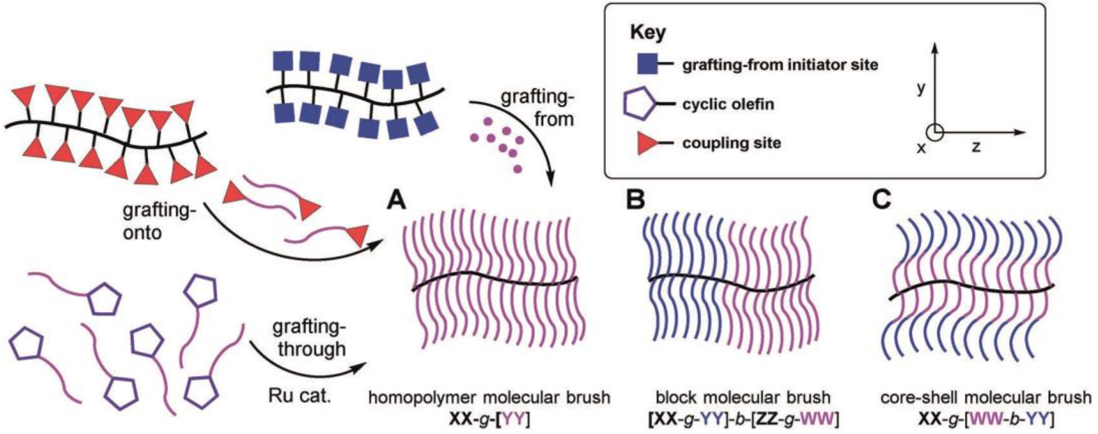

Figure 1 The construction of molecular brushes by various approaches. The "grafting-through" method relies on the polymerisation of (meth)acrylates or cyclic olefin-based monomers (by using a controlled polymerisation technique for example, RAFT, ATRP or ROMP). "Grafting-onto" requires the formation of a backbone featuring coupling sites and side chains that have complementary coupling functions; the assembly by a "click'-type coupling ends the construction process. The "grafting-from" approach uses a polymer backbone with multiple functionalities to enable controlled polymerisation of pendant polymer chains, for example, initiation sites for ATRP or ROP, or groups to mediate RAFT or nitroxide-mediated polymerisation. Examples of molecular brush architectures are shown: (A) homopolymer molecular brush, (B) block-type or Janus molecular brush and (C) core--shell molecular brush.

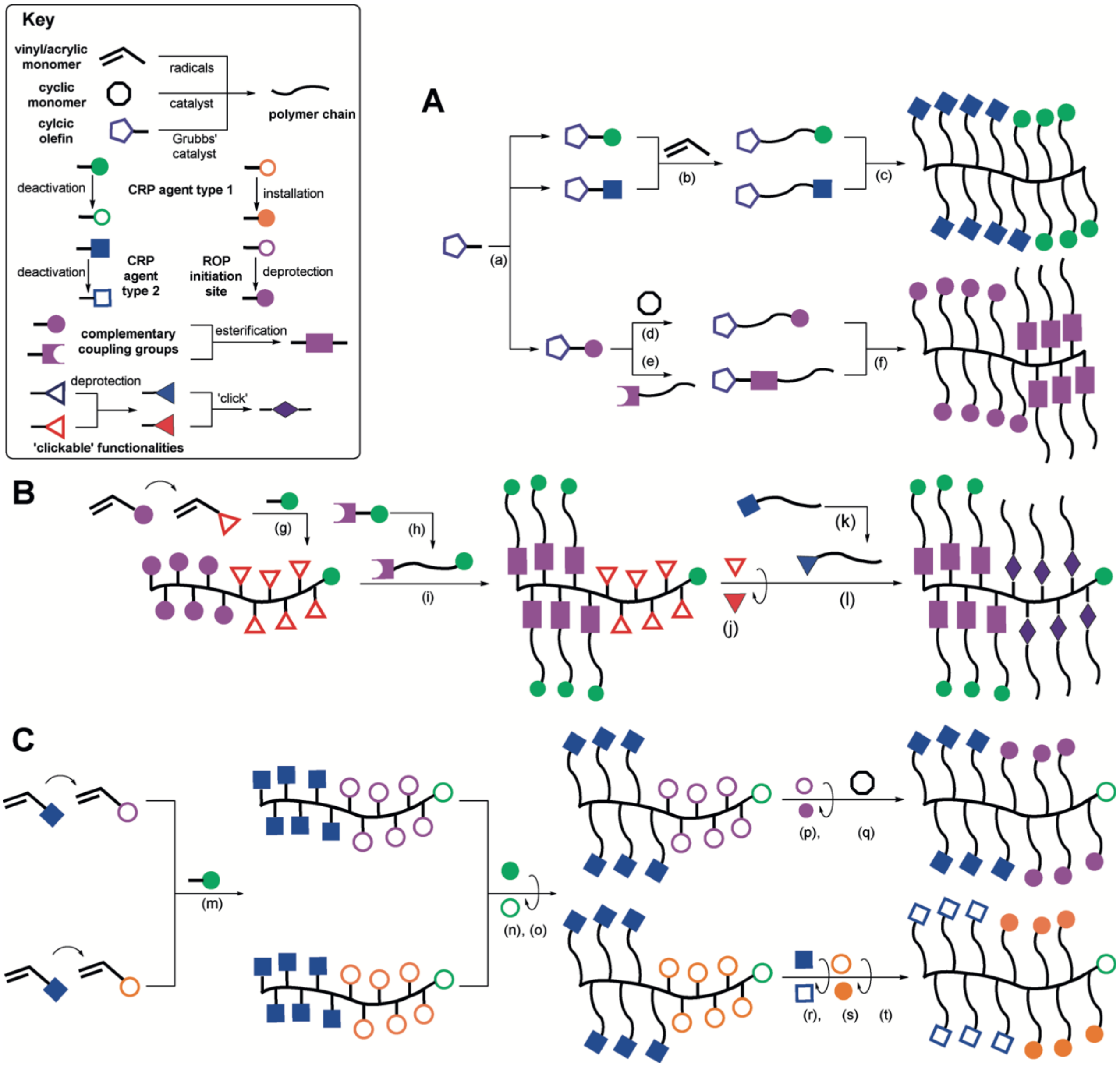

Figure 2 (A) The sequential construction of compartmentalised block-type brushes by a grafting-through method. (a) A cyclic olefin is modified to bear groups which can mediate controlled radical polymerisation (CRP) or hydroxy functions. (b) The CRP-olefins are used to form macromonomers that (c) can be sequentially reacted to form a block-type brush. Alternatively, the hydroxy functionalities are used as (d) ROP initiation sites or (e) for the coupling of polymer chains before (f) sequential polymerisation to form a block-type brush. (B) The sequential construction of a compartmentalised block-type brush using a grafting-onto method. (g) A diblock copolymer backbone is synthesised by sequential CRP. (h) CRP is also used to prepare side chains with reactive pendant groups that (i) enable the first coupling step. (j) Side-chain functionalities are deprotected, whilst (k) new side chains with a "clickable" functionality are synthesised and (l) subsequently attached on the brush backbone to yield a diblock molecular brush. (C) The sequential construction of compartmentalised block-type brushes by a grafting-from method. (m) A diblock copolymer backbone is synthesised by sequential CRP. (n) The CRP-mediating terminal groups of the backbone are removed, and (o) a further CRP is initiated to enable the first grafting-from step. (p) The protecting groups are removed from the ROP initiation site and (q) the last grafting step is performed. Alternatively, (r) the CRP-mediating groups at the end of the side chains are removed, (s) another CRP mediating group is installed and (t) the last grafting step is performed.

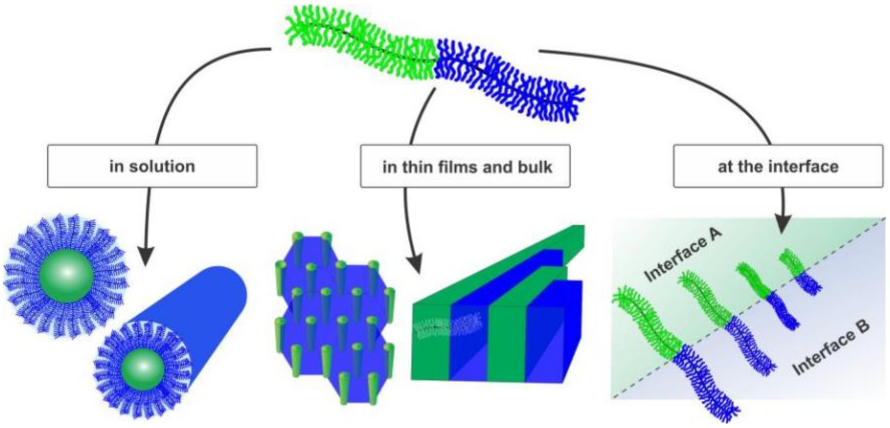

Figure 3 Molecular brushes can be compartmentalised to yield discrete domains with distinct chemical properties. Compartmentalised nanoparticles show promise for self-assembly applications in solution, in thin films and in the bulk phase, and have emerged as promising stabilisers at interfaces.

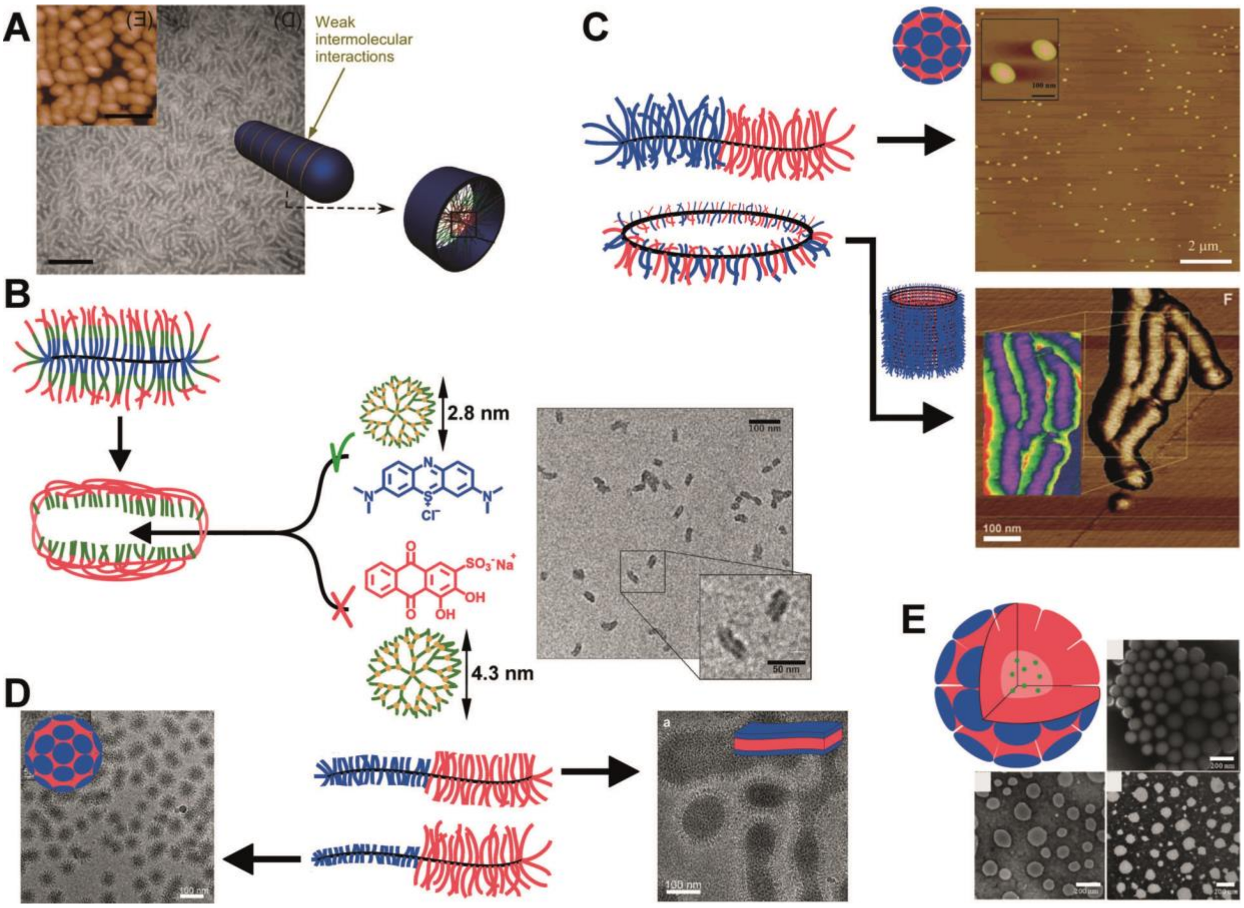

Figure 4 (A) *xy*-Compartmentalised molecular brushes were shown to self-assemble into cylindrical nanostructures (scale bar=200 nm). Adapted from Ref. [13a] with permission. Copyright 2011 American Chemical Society. (B) Compartmentalised molecular brushes were used to construct well-defined hollow nanotubes with negatively charged interiors that were capable of size- and charge-selective guest encapsulation (scale bars=100 nm in main Figure and 50 nm in inset). Adapted from Ref. [36] with permission. Copyright 2011 American Chemical Society. (C) *z*-Compartmentalised molecular brushes were shown to self-assemble in certain solvents to yield micellar structures, whilst cyclic molecular brushes with randomly grafted side chains were demonstrated to yield cylindrical supramolecular assemblies when exposed to a solvent selective for one of the grafted polymers (scale bars=2 µm for the top and 100 nm for the bottom pictures). Adapted from Ref. [28] with permission. Copyright 2007 American Chemical Society, and from Ref. [39] Copyright 2008 American Association for the Advancement of Science. (D) Tuning the symmetry of amphiphilic molecular brushes termed "bottlebrush surfactants" can allow the production of a range of supramolecular architectures (scale bars=100 nm). Adapted from Ref. [32] with permission. Copyright 2014 American Chemical Society. (EE) Giant micelles achieved from block brushes can be used in drug-delivery applications through the loading of therapeutics inside their core (scale bars=200 nm). Adapted from Ref. [41] with permission. Copyright 2014 American Chemical Society.

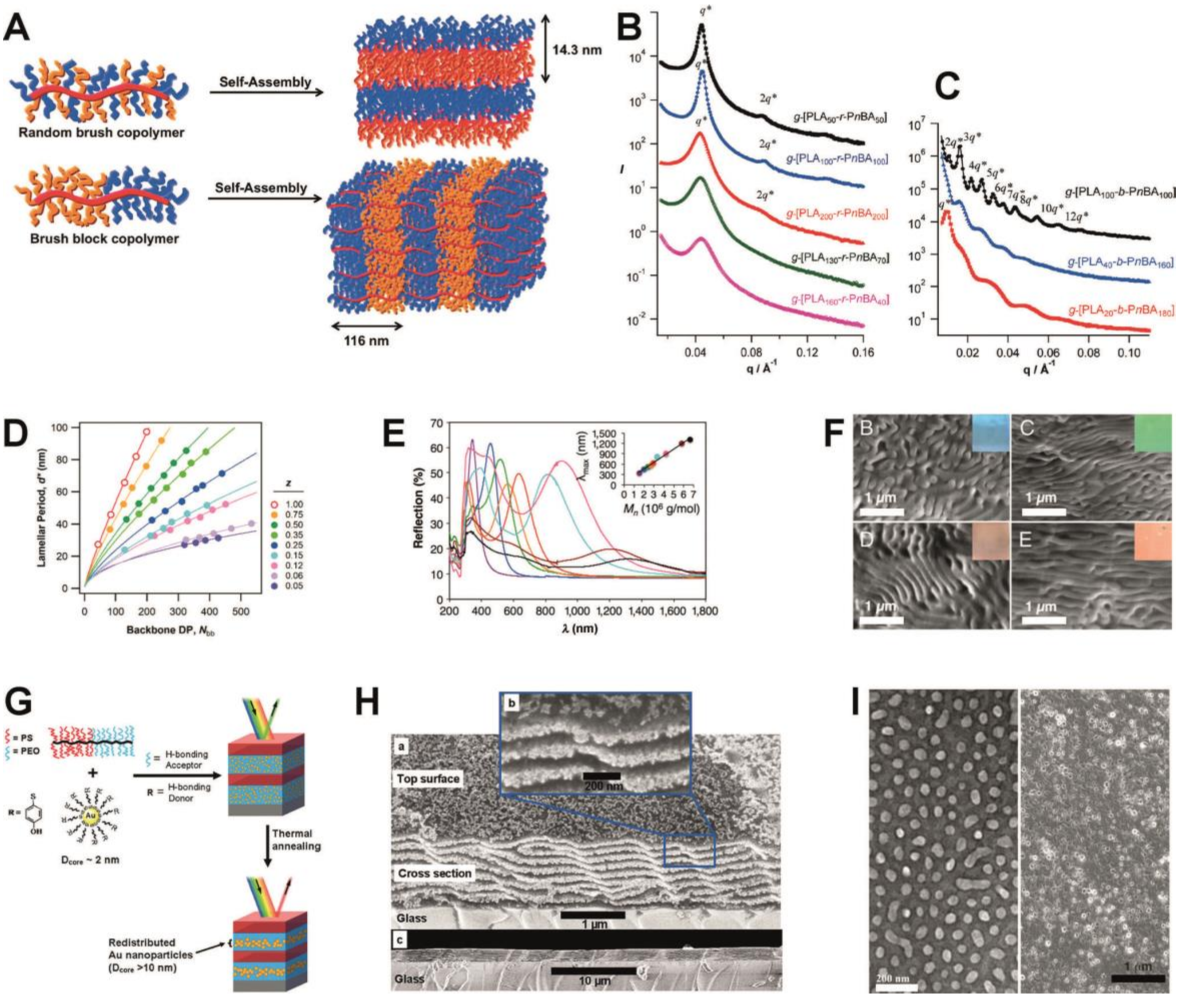

Figure 5 (A) The segregation of side chains along the *z*-axis yields much larger lamellar structures (and with a higher degree of organisation) than in a random configuration, as measured by SAXS on (B) random copolymer brushes and on their (C) block analogues. (A)—(C) Reproduced from Ref. [25] with permission. Copyright 2009 American Chemical Society. (D) The lamellar period measured in bulk self-assembled block brushes increases with the length of the backbone (DP=degree of polymerisationbut also with the grafting density of the architectures. Reproduced from Ref. [52] with permission. Copyright 2017 American Chemical Society. (E) The reflectance of the bulk self-assembled thin films is related to the molecular weight of the compartmentalised brushes. The plot of the wavelength of maximal reflectance versus molecular weight follows a near-perfect power law. (F) Besides controllingthe molecular weight and side-chain grafting, the experimental set-up used to produce thin films also determined the periodicity of the lamellar structure and therefore the colour reflected by the material (scale bars=1 µm). (E), (F) reproduced from Ref.[20a] with permission. Copyright 2012 National Academy of Sciences. The loading of gold nanoparticles into a block copolymer brush and the annealing of the material (G) redistributes the inorganic components into a thin layer, (H) which gives the thin film optical properties [scale bars=1 µm for top picture in (H) and 10 µm for bottom picture in (H)]. (G), (H) Reproduced from Ref. [53] with permission. Copyright 2015 John Wiley & Sons. (I) Cone-shaped block brushes self-assemble into nanocylinders (TEM, left), and a nanoporous material can be obtained after selective degradation of the cores of the cylinders (SEM, right; scale bars=200 nm for the left and 1 µm for the right picture). Adapted from Ref. [32c] with permission. Copyright 2011 American Chemical Society.

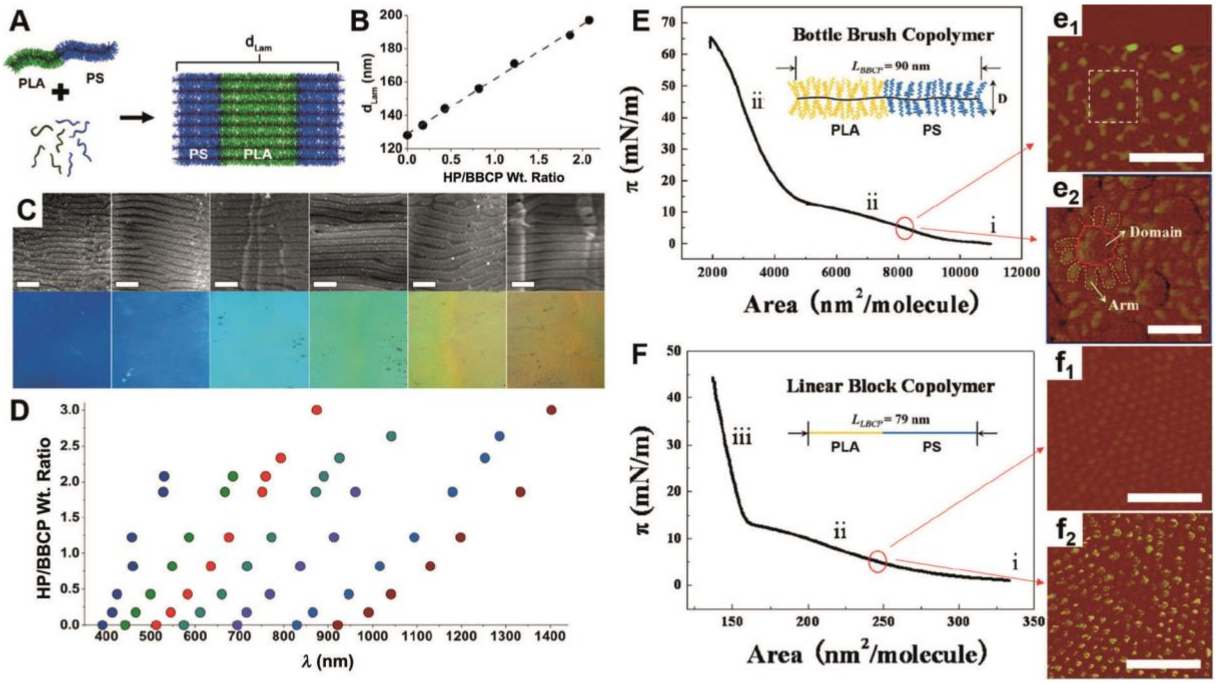

Figure 6 (A) Blending homopolymers (HPs) of PS and PLA with [PLA]-*b*-[PS] brush block copolymers (BBCPs) enabled control over the domain spacing of the resulting lamellar morphology. (B) Increasing the weight ratio of HP/BBCP allowed further increasing of the domain spacing, thereby resulting in various optically active polymer surfaces (C) with tuneable photonic band gaps; (D) each colour corresponds to a specific BBCP. (A)—(D) Reproduced from Ref. [20d] with permission. Copyright 2014 American Chemical Society. (E) [PS]-*b*-[PLA] diblock brushes and (F) PS-*b*-PLA linear diblock copolymers differ in their self-assembly at the air/water interface. At relative low pressures of 5 mN m^{-1}, Langmuir monolayers revealed the formation of distinct morphologies/domains [see AFM height (e_1) and phase (e_2) images], whereas the linear counterpart showed a well-ordered monolayer [see AFM height (f_1) and phase (f_2) images] (scale bars=500 nm for e_1, f_1 and f_2 and 100 nm for e_2). (E),(F) Adapted from Ref. [56] with permission. Copyright 2009 American Chemical Society.

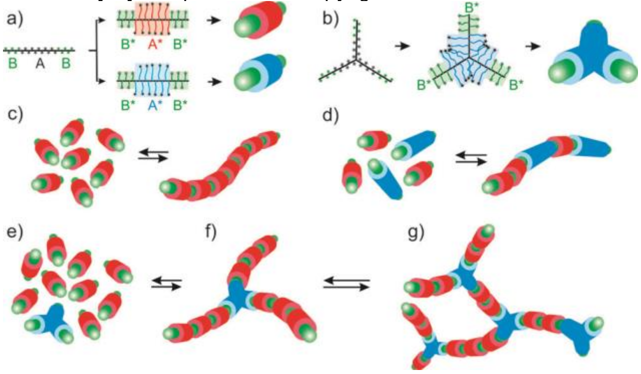

Figure 7 Prospective applications of covalently fixed, stable and shape-anisotropic molecular brush building blocks in the fabrication of self-assembled structured materials in solution. Compartmentalised (A) linear or (B) branched molecular brushes may enable the directional and reversible self-assembly of soft matter in multiple dimensions. Building blocks may be synthesised to be symmetrical and (C) identical in composition and aspect ratio or (D) different in aspect ratio and composition. Given the nature and stability of molecular brushes, the building blocks (E) may be designed to facilitate assembly in (F) two or (G) three dimensions.

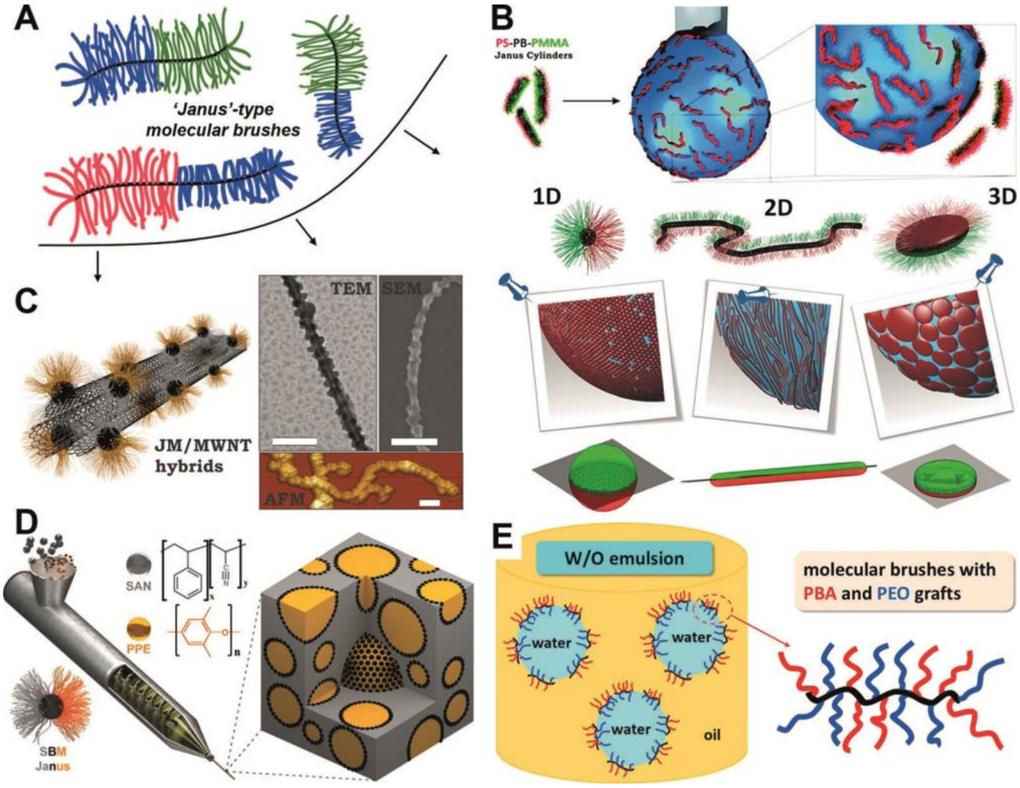

Figure 8 (A) Prospective applications of block-type molecular brushes. Depending on their composition and block ratio, Janus brush nanoparticles present analogues to block-copolymer-derived Janus particles. Such materials may find application as (B)—(D) surface or interface stabilisers in emulsions and dispersions. (B) Reproduced from Ref. [63] with permission. Copyright 2011/2013 American Chemical Society. (C) Reproduced from Ref. [64] with permission. Copyright 2013 John Wiley & Sons. (D) Similar Janus micelles have been used in polymer blend processing. Reproduced from Ref. [65b] with permission. Copyright 2014 American Chemical Society. (E) Random copolymer brushes may form Janus character in situ, which can then be utilised in the stabilisation of water/oil emulsions. Reproduced from Ref. [66] with permission. Copyright 2017 American Chemical Society.