Synthesis and applications of compartmentalised molecular polymer brushes

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Abstract: Polymer science is rapidly advancing towards the precision-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, offering immense potential for the production of tailor-made nanomaterials. Here, 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 amongst 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, equipping 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 the access to complex – but uniform – building blocks improved and their supramolecular behaviour became better understood. Advanced polymer self-assembly 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 review, 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 via block copolymer assembly 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 articles.[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 via orthogonal synthetic protocols which in turn yield covalently bound and uniform building blocks for supramolecular self-assembly applications. In this review, 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 as the z-direction here), with pendant secondary chains protruding in the xy directions (Fig. 1A). Steric repulsion between adjacent pendant chains imparts rigidity to the assembly, 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 they are capable of liquid crystalline behaviour[10] in bulk. This absence of entanglement significantly reduces the energetic barriers to reorganisation, 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 (Fig. 1B), yielding a block copolymer (block-type) brush,[11] or in the xy directions to produce a core-shell brush (Fig. 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, using grafting-through, grafting-onto, or grafting-from approaches (Fig. 2).

The grafting-through approach involves the homo- or co-polymerrisation of macromonomers, generating structures of high grafting density and allowing for complete characterisation of the side-chains prior to their incorporation into the primary backbone of the polymer (Fig. 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[13] triblock brushes with impressively low dispersities. The orthogonality of ROMP and radical-based polymerisation methods allow 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, affording access to architectures with compartmentalisation in both the xy and z directions.

Wooley has demonstrated the versatility of norbornyl-bearing trithiocarbonate chain transfer agents to synthesise polystyrene (PS),[16] poly(tert-butyl acrylate) (P(tBA)),[16] poly(hydroxyxystyrene),[17] poly(lactic acid) (PLA)[18] and fluorinated polymers[19,19] with excellent control over dispersity. Sequential ROMP of these macromonomers using a modified second generation Grubbs’ catalyst then yielded compartmentalised molecular brushes of various morphologies, notably a ‘dumbbell’-like architecture.[19]

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 hydroxyl functionality onto the norbornyl unit allows for ROP of cyclic monomers including L-lactide,[20] whilst addition of a bromide functionality permits the ATRP of various monomers including styrene[20] and poly(ethylene glycol) methacrylate.[21] Norbornyl or other polymerisable units may be installed to 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-azole cycloaddition (CuAAC)[22] with alkynyl-functionalised norbornenes, to yield macromonomers of PS,[23] P(tBA)[23,24] and poly(tert-butyl acrylate).[25] Esterification has also been used extensively to install norbornyl units onto pre-formed polymer chains, notably by Matsen, Hillmyer, Bates and coworkers,[26] who used this approach to generate diblock molecular brushes consisting of atactic polypropylene and PS. The grafting-through approach allowed a straightforward synthesis of a molecular brush library with alterations in block sizes, which in turn, aided the validation of a quantitative self-consistent field theory for the melt state of diblock brushes.

Key
- grafting-from initiator site
- cyclic olefin
- coupling site

Fig. 1. The construction of molecular brushes via various approaches. The ‘grafting-through’ method relies on the polymerisation of (meth)acrylates or cyclic olefin-based monomers using a controlled polymerisation technique e.g. 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 via a ‘click’-type coupling ends the construction process. The ‘grafting-from’ approach uses a polymer chain (backbone) with multiple functionalities to enable controlled polymerisation of pendant polymer chains, e.g. 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.
The grafting-onto approach involves the attachment of polymeric side-chains to a pre-formed polymer backbone, with components bearing complementary functional groups (Fig. 2B). This strategy allows for the separate preparation and characterisation of both backbone and graft components, which can lead to well-defined architectures, but its success may be limited by both kinetic and thermodynamic factors. With increasing grafting density, 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 to the generation of molecular brushes. Poly(chloroethyl vinyl ether) backbones can undergo highly efficient two-step coupling with anionically polymerised (‘living’) polyisoprene and PS chains via nucleophilic substitution, yielding random copolymer brushes with dispersities below 1.10. Studies by the same group have demonstrated the usefulness of grafting-onto and grafting-from onto strategies for the formation of z-compartmentalised brushes, using analogous coupling methodologies. 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 Fig. 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 (Fig. 2C). This method allows for the production of brushes of relatively high grafting densities 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).

Grafting-from methodologies have also been used extensively to produce compartmentalised nano-architectures, offering ample flexibility in choice of synthetic routes. ROMP has been used to enable the production of very high molecular weight diblock polymers with one block displaying pendant ATRP-initiating groups, 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. Secondary RAFT functionalities may also be installed as post-polymerisation modifications, enabling the construction of ABC triblock molecular brushes with an impressive dispersity of 1.3.

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

3. Applications of compartmentalised molecular polymer brushes

The advances in synthetic methodology discussed above, enabled primarily by the revolution of controlled polymerisation techniques, has propelled the study of molecular brushes from their first emergence in the 1980s to sophisticated highly functional architectures. Molecular copolymer brushes have been employed for applications as diverse as nanofabrication, cellular imaging and even to mimic complex biological functions such as size/charge selective molecular transport. The following section highlights key roles of compartmentalised molecular brushes in various applications in solution, thin and bulk films and at the interface (Fig. 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 have used sequential RAFT polymerisations to produce α-norbornyl ABC block copolymers (macromonomers) which, once grafted through using ROMP, yielded xy-compartmentalised molecular brushes (core-shell-corona) which self-assembled in aqueous solution to produce...
cylindrical nanostructures (Fig. 4A). Rzayev and Huang have used compartmentalisation to obtain soft brush templates for producing various hollow and open-end polymer nanotubes.\[35-37\] For example, the core of a core-shell-corona brush template was degraded to form a hollow nanotube, of which the interior wall was formed by a negatively charged polyelectrolyte shell, while a crosslinked corona stabilised the construct.\[35\] 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 differing in hydrodynamic diameter by only 2 nm (Fig. 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, 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 work of Defieux and co-workers, who have produced z-compartmentalised diblock molecular brushes\[28\] by the sequential grafting of living polystyryl and polyisopropyl chains onto a poly(2-chloroethylvinylether)-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 non-compartmentalised 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 assemblies in the solid state, demonstrating the utility of molecular compartmentalisation as a tool to direct macroscopic properties. When a similarly random distribution of
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 (Fig. 4B), or in the xy directions to yield core-shell amphiphilic architectures (Fig. 4C).

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 in the solid state, but these self-assembly processes can be frustrated by the introduction of asymmetry to 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. In solution, however, engineering the symmetry of the grafted architecture can be used to control interfacial curvature of assemblies, allowing precision control over the resultant supramolecular architecture. Rzayev and co-workers have generated a series of amphiphilic molecular brushes and explored the shape-morphology relationships that determine the resulting architectures. Using z-compartmentalised brushes featuring PLA and poly(ethylene glycol) methyl ether methacrylate grafts which vary in length, they have produced a selection of supramolecular assemblies, 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 assemblies of low CMC can be useful in drug delivery applications. Z-compartmentalised amphiphilic molecular brushes incorporating a cholesterol-functionalised hydrophobic block, along with a hydrophilic polyelectrolyte 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 for in vitro circulation time (Fig. 4E).

Molecular brushes, with their large molecular weights, also display promise for the delivery of larger 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, which can lead to cytotoxicity. Schmidt and co-workers have constructed xy-compartmentalised polymer brushes with a poly(Lysine) core capable of binding siRNA, and a neutral poly(Sarcosine) shell to mask positive charges. 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, in which the morphology may be adjusted via control of the composition and architecture of the molecular brush. Block copolymers with incompatible blocks may phase separate, yielding domains with dimensions typically defined by block lengths. For structures with domain sizes > 100 nm, this approach becomes frustrated by chain entanglement, as beyond its critical entanglement molecular weight the viscosity of the material increases significantly, necessitating annealing temperatures 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.

One such area of application is in the fabrication of photonic crystals, e.g. ordered composite structures of high- and low-refractive index materials with periodicity comparable to the wavelength of light. 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. Longer wavelengths may be achieved by induced domain swelling via addition of other components to the mixture (like solvent, nanoparticles or homopolymers) 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. Brushes of similar composition and dimensions but different arrangements of the side-chains were observed to phase separate differently, demonstrating the influence of the individual compartments in terms of achievable domain spacings. 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, SANS) and determined by the overall side chain length. Interestingly, the domain spacing was noted to be insensitive to the backbone length, suggesting 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 spacing over 100 nm were observed by SANS (Fig. 5C). These lamellar domains had dimensions which depended on the backbone length, and were large enough to reflect visible light.

Molecular brushes may offer easier tunability when selecting building blocks for self-assembly than their linear analogues, as the lamellar spacing can be simply adjusted by a change in 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 (Fig. 5D).\[52\] Increases in the degree of polymerisation of the brush backbone led to increasing domain spacing in respective thin films, impressively following a near-linear relationship. This relationship between molecular weight and wavelength of maximal reflectance has been demonstrated to be sufficiently accurate to allow prediction of the optical properties of the resultant material (Fig. 5E).\[20a\] Domain spacing may also be adjusted by altering self-assembly conditions, such as changing annealing solvent and temperature\[20a\] as well as blending in additives (e.g. gold nanoparticles) (Fig. 5G/H).\[53\] This highly combinatorial approach of 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 confinement (e.g. emulsion droplets) to yield (nano)particles with internal structure,\[54\] which may results in unique optical properties.

The introduction of a third block in z-compartmentalised molecular brushes may lead the formation of diffuse or mixed interfaces. ABC triblock brushes composed of PLA, poly(methyl

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Fig. 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 with permission from Xia, et al.\[25\] Copyright 2009 American Chemical Society. (D) The lamellar period measured in bulk self-assembled block brushes increases with the length of the backbone but also with the grafting density of the architectures. Reproduced with permission from Lin, et al.\[52\] 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 and the wavelength of maximal reflectance vs. molecular weight plot follows a near-perfect power law. (F) Besides molecular weight and side-chain grafting, the experimental setup used to produce thin film also determined the periodicity of the lamellar structure and therefore the colour reflected by the material. E/F reproduced with permission from Sveinbjörnsson, et al.\[20a\] 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) that gives the thin film optical properties. G/H reproduced with permission from Song, et al.\[53\] 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). Adapted with permission from Bolton, et al.\[32c\] Copyright 2011 American Chemical Society.
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. Similarly Grubbs and co-workers studied ABC triblock brushes composed from polymers with low interaction (χ) parameters. In contrast to linear analogues that typically form two- or three-domain lamellar morphologies, their study revealed brush self-assembly 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, accessing not only lamellar but even cylindrical morphologies. 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. The achievable pore size was dependent on the architecture of the diblock copolymer used. Films obtained via the self-assembly of diblock brushes exhibited larger pore sizes compared to pores obtained when using 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 above, diblock brushes may display similar behaviour to linear block copolymers in solution, thin films and bulk. However, due to 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 but interestingly, these brushes also allow for swelling the lamellar domains using homopolymers in order to increase the spacing between the lamellae and consequently tune the optical properties of the polymer films. 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. [PS]-b-[PLA] brushes were also used by Lin and co-workers to study their behaviour at the air/water interface using a Langmuir-Blodgett approach. Compared to linear PS-b-PLA block copolymer analogues, the diblock brushes required more space per molecule due to their bigger molecular weight. Already at low pressures, architecture-dependent differences were observed within Langmuir monolayers using AFM. Furthermore, the pressure-area isotherms revealed unique interfacial self-assembly as a function of surface pressure which differed much
from the assembly behaviour known for amphiphilic block copolymers (Fig. 6E/F). Surprisingly, limited work has been done to date studying 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 to date. As a surface coating, diblock brushes have been spin-coated onto silicon wafers to form a monolayer of upright molecular brushes that 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 predicts an exciting future for molecular brushes. The preparation of compartmentalised molecular brushes, whilst still synthetically demanding, is no longer a stumbling block to the realisation of nano-sized building blocks for self-assembly. While this compartmentalisation has already proved valuable in bulk and thin films, enabling fast phase separation and tuneable optical and surface properties, the behaviour in solution is currently less well understood, presenting interesting opportunities for further study. Such endeavours will undoubtedly be inspired by the fascinating hierarchical structures achieved via the self-assembly of compartmentalised molecular brushes.

Fig. 7. Prospective applications of covalently-fixed, stable and shape-anisotropic molecular brush building blocks in the fabrication of solution self-assembled structured materials. 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.

First examples of the use of molecular brushes in particle-particle assembly have been recently demonstrated by controlling their end-to-end connection via DNA hybridisation\[^{57}\] or hydrophobic interactions.\[^{58}\] Unlike the use of diblock brushes as surfactants (i.e. high molecular weight amphiphiles),\[^{21, 59}\] this brush-brush interaction may be directional into one, two or three dimensions – depending on the brush architecture (Fig. 7) – largely attributed to the covalently-fixed nature of molecular brushes. Their stable architecture may be a notable advantage over self-assembled components (such as multicompartment micelles or crystallisation-derived micelles), endowing 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 (Fig. 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 (Fig. 8B/D).\[^{63}\] Moreover, they have been used to aid the dispersion of carbon nanotubes (Fig. 8C)\[^{64}\] and the processing of otherwise immiscible polymer blends (Fig. 8E).\[^{65}\] 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 (Fig. 8F). Yang and co-workers have recently reported the synthesis of asymmetric Janus molecular brush nanorods that adopt a vertical orientation at the emulsion interface. These stimulating applications of Janus particles in combination with the delicate control over molecular architecture and composition further motivate the use of molecular brushes at interfaces. Pickering emulsions, polymer processing and surface coatings may benefit from such tuneable synthetic additives.

Compartmentalisation in the xy direction has been shown in the form of core-shell and core-shell-corona molecular brushes and used to produce templated organic and inorganic nanomaterials, demonstrating applications beyond soft matter. The exploitation of the z-direction is at 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 to produce molecular brushes with multiple compartments which themselves are built from multiblock polymer grafts. Matson synthesised tapered brushes (‘cone-shaped’ along the z-direction) via sequential addition of macromonomers of decreasing molecular weight.

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 the 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 has already provided impressive control over their grafting density, providing another emerging strategy to the realisation of truly tailor-made nanoscale architectures.
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Hairy compartments. The methodical compartmentalisation of molecular polymer brushes offers immense opportunity to develop tailor-made advanced nanomaterials with applications in nanofabrication, optics and functional materials.