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Cylindrical polymer brushes – Anisotropic building blocks, unimolecular templates and particulate nanocarriers

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ABSTRACT

This article presents an overview of the latest key developments and research activities in the area of cylindrical polymer brushes (CPBs), also known as ‘molecular bottlebrushes’. CPBs consist of a polymer backbone containing polymer side chains that cause the backbone to extend and adopt a worm-like conformation. The extent of backbone stretching and the aspect ratio of CPBs is determined by the length and grafting density of the side chains. The latest developments in controlled/living polymerisation techniques led to novel and more efficient ways of producing delicate polymer architectures, such as block copolymer CPBs, and resulted in a considerable expansion of the field of application for these soft anisotropic materials. In this feature article, we focus on important recent findings and applications in the areas concerning solution and bulk self-assembly of block copolymer CPBs, unimolecular templating and brush-based drug delivery systems in nanomedicine.

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1. Introduction

Cylindrical polymer brushes (CPBs) are giant macromolecules with particle dimensions. Frequently, they are also referred to as ‘molecular brushes’ or ‘bottlebrushes’, highlighting their single molecule character and shape. CPBs have polymer side chains attached to a linear polymer backbone. The close proximity of the side chains, particularly at high grafting densities, drives them to avoid entanglement and stretches the backbone. This in turn gives access to unique polymer architectures comprising a characteristic cylindrical or worm-like conformation and remarkable spatial dimensions. Moreover, the properties and behaviour of CPBs are very different to those of linear polymers, which has prompted extensive research activities of both experimental and theoretical scientists.

CPBs were discovered in the late 1980s [1]. However, early synthesis efforts predominantly focused on merely realising these complex polymer architectures through new synthesis strategies [2–4]. Today, greatly owing to the contributions of controlled/living polymerisation techniques, in particular ring opening metathesis polymerisation (ROMP) and controlled radical polymerisation

(CRP), CPBs are no longer just an artistic polymeric construct, but rather a modular toolbox for the design of functional nanomaterials with tailor-made properties. The fact that the shape-persistent nature of CPBs is independent of the chemical composition but stems from its intrinsic architecture, enables a modular synthesis of distinct and complex macromolecules through various polymerisation strategies.

In this article, we take a look at some of the key areas where CPBs shape up to be next-generation nanomaterials, suitable for a range of applications in the fields of hybrid materials, energy, sensing, photonics and nanomedicine. Over the past decade, a number of excellent reviews have been dedicated to the ever-growing field of CPBs [5–11], and the field is continuously expanding due to the aforementioned achievements in synthetic polymer science. Several review articles have focussed in detail on the synthesis, characterisation and unique properties of CPBs. Accordingly, we will only briefly discuss the various syntheses of these elaborate polymer architectures. Rather the focus of this feature article is on the properties of CPBs, their behaviour in self-assembly and their application as template materials and drug delivery vehicles.

As nomenclature, we adopt square brackets to describe the composition of CPBs. Polymers in square brackets represent the composition of one grafted side chain. For example, [XX-*b*-YY] describes CPBs with diblock side chains, whereas [XX]-*b*-[YY]

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indicates a diblock copolymer CPB, where two brushes are connected to each other (Scheme 1).

2. Strategies toward cylindrical polymer brushes

The synthesis of CPBs is categorised according to the strategy by which the side chains are formed or attached. In general, there are three grafting strategies, namely *grafting-from*, *grafting-to* and *grafting-through* (Scheme 1). Each of the three grafting approaches has its inherent advantages and disadvantages; however, several studies have already demonstrated that it is possible to overcome strategy-specific difficulties. For example, the development of highly efficient coupling reactions and the steady advances in polymerisation techniques have helped to overcome some of the inherent hurdles of producing CPBs and have, more generally, eased their synthesis. Note that densely grafted CPBs can also be produced via self-assembly of block copolymers in bulk [12–15]. However, this article will solely focus on molecular CPBs.

The homopolymerisation of macromonomers (that is, the grafting-through approach) yields CPBs with maximum grafting density and allows the precise characterisation of the polymer side chains prior to brush formation. A limiting factor of this approach is the increasing steric constraints of bulky macromonomers, which limit the overall brush length. High viscosities at already low conversion may prevent the synthesis of long CPBs with side chains of high molecular weight and add additional steps to the purification of unreacted macromonomers. Highly active catalysts employed in ROMP emerged as particularly useful in the polymerisation of macromonomers and improved the poor length control of CPBs using conventional radical polymerisation [16,17]. Recently, atom transfer radical polymerisation (ATRP) at higher pressures enabled the synthesis of CPBs from macromonomers with high efficiencies [18].

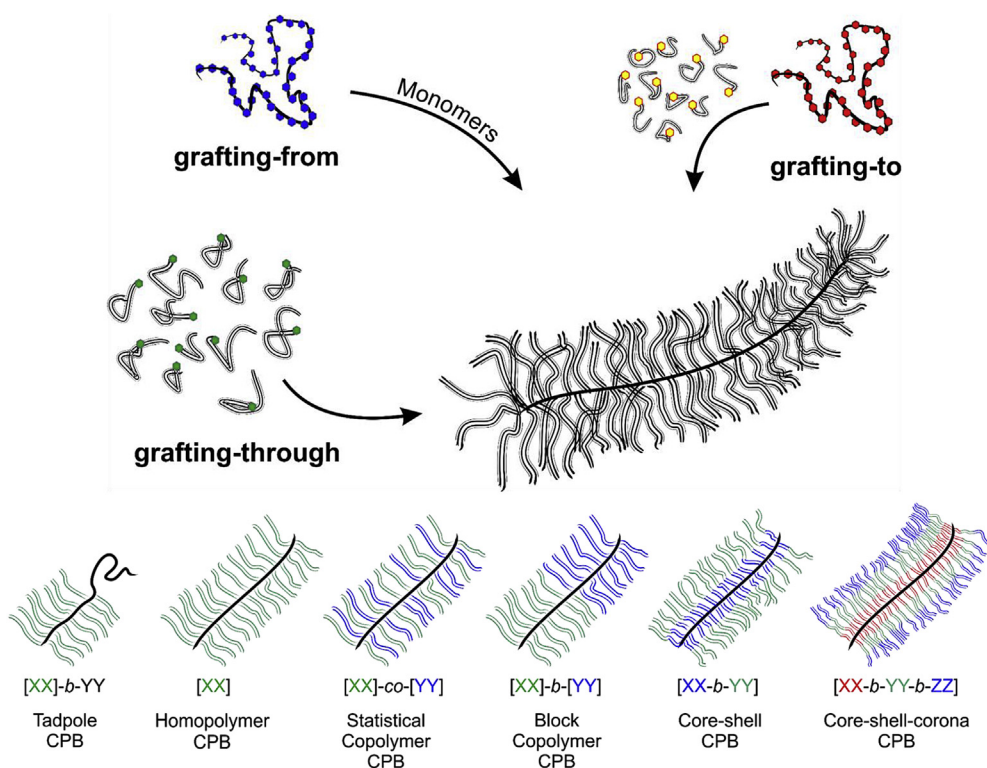
The attachment of separately prepared side chains to a polymer backbone (that is, the grafting-to approach) enables detailed

characterisation of the individual components before the brush formation. However, powerful coupling reactions are required to graft side chains onto a polymer backbone with sufficient density. The limiting factor is the steric demand of the side chains, often leading to low grafting densities and in turn to additional purification steps. Click chemistry, amongst other polymer-analogous reactions, provides increased control for the grafting of the side chains onto a functional backbone. However, the intrinsic limitation preventing high grafting efficiencies has only been overcome by a small selection of relatively short side chains [19,20].

The polymerisation of the individual side chains from a poly-initiator backbone (that is, the grafting-from approach) provides a compromise between the two other approaches in terms of grafting efficiency and allows a tailoring of the composition and the length of the side chains during polymerisation. The grafting-from method typically uses CRP and/or ring opening polymerisation (ROP) for side chain growth, in order to produce a diverse range of tailor-made CPBs with well-defined compositions. CPBs with very long backbones can be prepared. However, the initiator efficiency is compromised due to steric hindrance of the monomers, leading to typical grafting densities of 50–90% [21–25]. Precipitation or dialysis then allow for straightforward removal of unreacted monomers. Yet, precise characterisation of the side chains remains a multi-step procedure.

Using the individual grafting methods separately or in conjunction with each other has proved to be a powerful tool in realising complex and compartmentalised CPBs. In addition, sequential grafting and the combination of several polymerisation techniques enable the tailoring of the composition, size and functionality of these nanostructures. In particular, the grafting-from and the grafting-through approaches give access to various compartmentalised CPBs, which present a hot topic in current CPB research.

In this context, the grafting-from method is particularly powerful in producing concentric CPBs, such as core-shell-corona



Scheme 1. An illustration of the three grafting strategies to produce CPBs and some of their many compositions.

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