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Cyclic polymers as a building block for cyclic brush polymers and gels

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ABSTRACT

Cyclic polymers, as one of the oldest topological polymers, are undergoing resurgence. This is largely ascribed to the significant achievements in modern polymer chemistry. The novel ring-expansion techniques have conveniently produced varied cyclic polymers with highly topological purity and on large scales, which should facilitate their use in the near future. Beyond the monocyclic molecular conformations, the combination of controlled polymerization techniques and click chemistry have established a robust strategy for preparing cyclic polymers with more complex architectures, such as theta, eight, and tadpole shapes. This diversification in cyclic polymer composition and conformation significantly broadens interest in the cyclic polymers. However, compared to the synthesis achievements, the exploration of cyclic polymer property and application are lagging behind. Recently, we explored the ring-expansion metathesis polymerization on various functional ring-strained olefin monomers to produce cyclic functional polymers, which were then used as the building blocks to fabricate cyclic brush polymers and cyclic gel materials and will be discussed here.

1. Introduction

Cyclic polymers have received significant attention recently with several important reviews [1–7] and a specific cyclic polymer symposium celebrated at the 245th ACS national meeting. Due to their unique endless molecular topology, cyclic polymers have markedly different characteristics from their linear counterparts, including a smaller hydrodynamic volume and radius of gyration, lower melt viscosity, higher thermostability, and increased rate of crystallization [1–7].

To date, known synthetic strategies for cyclic polymers can be generalized into two categories: ring-closure and ring-expansion methods both have advantages and disadvantages. In the ring-closure method, cyclic polymers are prepared by applying highly efficient coupling chemistry to end-functionalized linear telechelic polymers. Progress in combining click chemistry with controlled polymerization has increased the viability of this method for synthesizing cyclic polymers with controlled molecular weight and low polydispersity, but there are still limitations. To assure high topological purity, ring-closure reactions typically require dilute conditions leading to reduced yields. In addition, it is difficult to obtain cyclic polymers with high molecular weight by this method. Alternatively, ring-expansion is based on the insertion of monomer units into an activated cyclic chain. Because the cyclic polymers remain intact during the whole ring-expansion process, this method can produce high molecular weight cyclic polymers with high purity, even from concentrated solutions or the bulk. One disadvantage is that it can be difficult to control the molecular weight and polydispersity of the resultant cyclic polymers. The ring-closure and ring-expansion methods have enabled the preparation of many types of cyclic polymers, including cyclic polystyrene [8], polymethacrylate [9], polyacrylate [10] polyacrylamide [11] polyester [12] polycyclooctene [13] and polynorbornene [14]. In addition, cyclic polymers with complex architectures have been developed, including those with theta [15], eight [15], tadpole [16], block [17], and brush [18–20] shapes. The various synthetic methods, polymer types, and various cyclic architectures have been thoroughly described in recent reviews [1–7].

As a complement in this tutorial review, we mainly focus on the recent progress on cyclic polymers from our research group focused on ring-expansion metathesis polymerization (REMP) to produce the functional cyclic polyolefins, which were then used as the universal building blocks to prepare cyclic brush polymers and cyclic gels.

2. Ring-expansion metathesis polymerization

REMP was firstly reported by Grubbs and coworkers in 2002 [13]. Following significant contributions from Bielawski, Boydston,

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and Xia in the Grubbs's research group, REMP has become a powerful method for preparing cyclic polyolefins [13,14,19,21–23]. Fig. 1 shows the key mechanistic steps involved in REMP. Initiation occurs via the cyclic olefin monomer inserting into the Ru-alkylidene bond to expand the cyclic catalyst ring. Propagation then proceeds by a repeated insertion of monomer into the growing cyclic polymer. As monomer is consumed, a competing intramolecular chain transfer reaction decreases the molecular weight of the growing cyclic polymer, broadens its polydispersity, and generates cyclic polymers. An additional catalyst release process can produce the original catalyst and more catalyst-free cyclic polymer.

To date, two series of cyclic Ru-alkylidene catalysts (UC series and SC series) of five main types (UC-5, 6, 7 and SC-5, 6) (Fig. 2) have been developed. It was found that both the heterocycle size and the N-heterocyclic carbene (NHC) ligand electronics significantly impact the catalyst efficiency and the polymerization behavior as well. The catalyst with larger ring leads to faster polymerization rates and lower catalyst release from cyclic polymer. The saturated NHC ligand endows the catalyst with much faster polymerization rate than that of the unsaturated NHC ligand. Furthermore, various cyclic olefin monomers have been successfully polymerized by REMP. As shown in Fig. 2, they are composed of not only the commercial available cyclic olefins and their simple derivatives having a small functional group, but also those having bulky side groups such as dendrons and even polymers.

As is typical of ring-expansion approaches, REMP can produce large amounts of pure cyclic polymers at high polymerization concentrations. Furthermore, REMP is unique in that it can obtain cyclic polymers with the highest reported molecular weight. This makes it a good candidate to prepare cyclic polymer building blocks for the fabrication of cyclic materials, such as the nano-scale cyclic brush polymers and the macro-scale cyclic gels.

3. Cyclic brush polymers

Brush polymers are composed of a long polymer backbone with densely grafted polymer side chains. Due to the steric repulsion between densely grafted bulky side chains, these macromolecules have an extended, rigid worm-like conformation when the backbone is much longer than the side chains [24,25]. It is this unique molecular conformation that renders brush polymers as a unique building block for generating advanced nanomaterials, such as creating well-defined single-molecular hybrid nano-objects and for fabricating periodic nanomaterials with large domain spacings by self-assembly [26]. In addition to the linear morphology, the molecular shapes of brush polymers can be enriched by manipulating the backbone topology [27–30]. When cyclic polymers are chosen as backbones, the novel cyclic brush polymers are designed to bear a donut-like molecular topology.

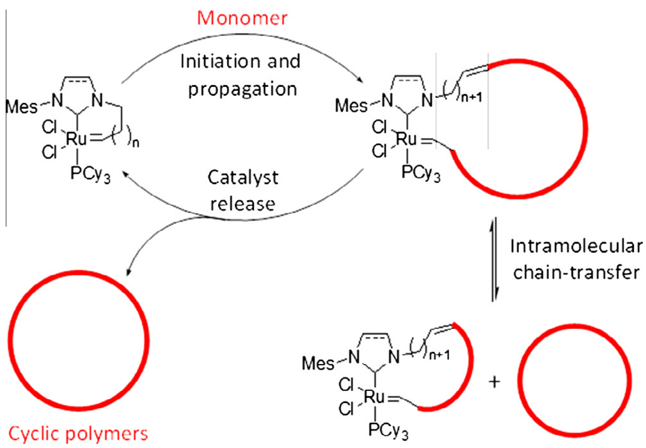

Fig. 1. Key mechanistic steps involved in REMP [22].

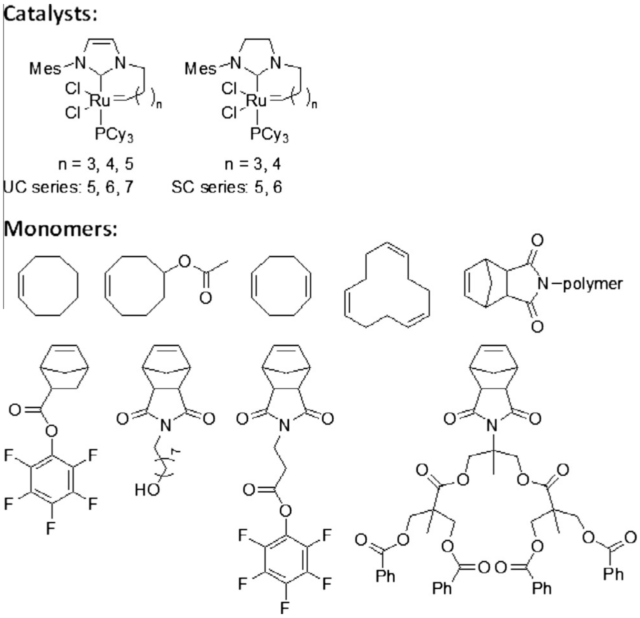

Fig. 2. Cyclic Ru-alkylidene catalysts and appropriate cyclic olefin monomers.

Although a few reports have been published on synthesizing cyclic brush polymers [18,31–33], the preparation of brush polymers demonstrating stiff toroidal macromolecular topologies has remained elusive [13,23,34,35]. REMP is unique here because it meets many of the necessary requirements for building the backbone of cyclic brush polymers. Inspired by this, REMP has been successfully utilized to prepare cyclic brush polymers by Grubbs' and Tew's research groups independently [14,19,20,36,37]. Applying the three traditional routes to linear brush polymers, [grafting through (polymerization of macromonomers), grafting onto (coupling of side chains to backbone), and grafting from (polymerization of side chains from a backbone macroinitiator)], cyclic brush polymers have been prepared by REMP.

4. Grafting through

The first report to synthesize and visualize cyclic dendronized polymers by the grafting through technique was published by the Fréchet and Grubbs' research groups in 2009 [14]. A norbornene-based macromonomer was designed with a second generation dendron side chain. When using the SC-5 or UC-6 as catalyst, the cyclic dendronized polymers were obtained by REMP (Fig. 3A). The donut-like molecular topology was visualized by AFM with a diameter of 30–40 nm (Fig. 3B). Following the same concept, they further investigated the direct REMP of norbornene-based macromonomers with a bulky polymer side chain (Fig. 3C) [19]. A series of cyclic brush polymers were then produced with ultra-high molecular weight and various polymer side chains, including polystyrene, polylactide, and poly(n-butyl acrylate). In this work, the macromonomers were efficiently prepared by controlled polymerization techniques and click chemistry. For a moderate to high polymerization conversion of these bulky macromonomers, the more active SC-series catalysts were required. The donut-like molecular topology was visualized by AFM and most cyclic brush polymers have diameters in the range of 100–180 nm (Fig. 3D), which is much larger than that from the cyclic dendronized polymers. The increased molecular size is presumably caused by the