Huge Polymer Circles

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Synthesis and Direct Imaging of Ultrahigh Molecular Weight Cyclic Brush Polymers**

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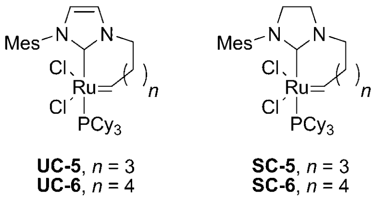
Polymer architectures and nanostructures have profound effects on the materials properties, and significant progress has been made in controlling polymer architectures with the development of new polymerization techniques.[1] Brush polymers or densely grafted polymers represent an important class of nanoscale macromolecular architectures.[2] The extremely high congestion arising from the high density of side chains forces the macromolecular backbone to adopt an extended conformation that forces brush polymers into worm-like nanoscale structures and bestows unique properties in comparison with conventional coiled polymers.[3]

Over the past decade, linear and star-shaped brush polymers have been synthesized and molecular imaging has shown their distinct worm-like and star-like nanostructures.[4] However, cyclic graft polymers that exhibit toroidal nanostructures remain very rare, partly due to the challenging synthesis of high MW cyclic polymers with high grafting density required to achieve nanoscale features. An inspiring example of high MW cyclic brush polymers was recently reported by Deffieux and co-workers.[5] In their synthesis, an ABC triblock linear copolymer was used in order to prepare high MW cyclic polymer by ring-closing under high dilution conditions, and subsequent grafting of living anionic polystyrene chains to the backbone afforded cyclic brush polymer. Atomic force microscopy (AFM) clearly revealed the toroidal nanostructures of cyclic brush polymers on the surface, but linear, figure-eight, tadpole, and catenane shapes were also observed as a result of side reactions during the ring-closing reaction.[6] Since the synthesis involved multiple steps and required high dilution and stringent conditions, we sought an alternative route to synthesize high MW brush polymers and achieve cyclic nanostructures. Our group has developed a series of Ru-based catalysts (Scheme 1) that mediate ring-expansion metathesis polymerization (REMP) to produce high MW cyclic polymers under simple experimental conditions without necessitating high dilution conditions by an end-linking approach.[7] With the Frechét group, we recently showed that cyclic dendronized polymers synthesized using these catalysts indeed adopted toroidal shapes with internal diameters of 5–7 nm.[8] During publication of this manuscript, the Tew group also reported the use of REMP for the synthesis of cyclic polymer templates that were converted to cyclic brush polymers via a “graft-to” approach.[9] Herein, we report the synthesis of ultrahigh MW cyclic brush polymers by a one-pot “graft through” approach, and direct imaging of their large toroidal nanostructures by AFM.



Scheme 1. Cyclic olefin metathesis catalysts.

We investigated direct REMP of macromonomers (MMs) that we have used previously for the synthesis of linear brush polymers.[10] Initial attempts using less active cyclic catalysts **UC-5** and **UC-6** were unsuccessful, with only minimal conversion of MMs. In contrast, when more active catalysts (**SC-5** and **SC-6**) were used, moderate to high conversions were obtained within a few hours for each of the MMs attempted, giving highly viscous or solidified reaction media. Notably, each of the obtained brush polymers was readily redissolved in good solvents (e.g., CH_2Cl_2, THF, toluene, etc). Their MWs were all extremely high in the range of 1.9 to 26×10^6 Da and exceeded our GPC separation limit. Thus, absolute MWs were determined by static light scattering and used to calculate the degree of polymerization (DP) of the brush polymer backbones. To our knowledge, the MWs of these cyclic brush polymers are among the highest for any structure of graft/brush polymers reported to date. The MW distribution was broad as a result of slow initiation of REMP catalysts. The MM conversion was dependent on a combination of catalyst activity as well as MM structure and MW. In general, the MM conversion and DP of cyclic brush polymer decreased with increasing MW of the MM. For example, when the MW of ω-norbornenyl polystyrene MM (Scheme 2) increased from 2200 to 6600 Da, the conversion decreased from 93% to 65%, with concomitant decrease in DP from 4100 to 880 (Table 1). Notably, the MWs of these cyclic brush polymers significantly exceeded those of the linear brush polymers we previously synthesized using ring-opening metathesis polymerization (ROMP).[10]

We have previously used AFM to directly image individual linear brush polymers prepared from these MMs, and observed linear, extended worm-like nanostructures.[10a]

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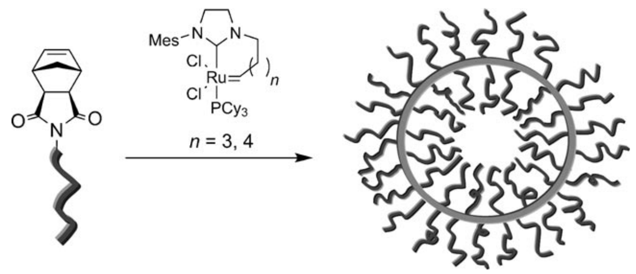

Scheme 2. Synthesis of cyclic brush polymer from REMP of ω-norbornenyl MM.

Table 1: REMP of Macromonomers.[a]

No.	Macromonomer[b]	Cat.	M_w ($\times10^6$ Da)[c]	PDI[d]	$DP_{back.}$[e]	Conv.[f]
1	**NB(PS)2200**	**SC-5**	9.1	1.2	4100	93%
2	**NB(PS)3200**	**SC-5**	6.2	1.1	1900	74%
3	**NB(PS)6600**	**SC-5**	5.8	1.1	880	67%
4[g]	**NB(PS)6600**	**SC-5**	5.7	1.2	860	55%
5	**NB(PLA)4400**	**SC-5**	13	1.4	3000	92%
6	**NB(PLA)8700**	**SC-5**	26	1.1	3000	79%
7	**NB(PS)2200**	**SC-6**	2.4	1.2	1100	89%
8	**NB(PS)6600**	**SC-6**	6.5	1.1	1000	78%
9	**NB(P*n*BA)4000**	**SC-6**	4.0	1.3	1000	>99%
10	**NB(PLA)4400**	**SC-6**	1.9	1.5	430	>99%
11	**NB(PLA)8700**	**SC-6**	6.0	1.4	690	98%

[a] Conditions: [MM]/[catalyst] = 50, 55 °C, in benzene unless otherwise noted. [b] MMs were named in a format of NB(X)Y, with X the type of polymer and Y the M_n of MM. [c] Determined by multi-angle laser light scattering, using $dn/dc = 0.180\ \mathrm{mL\,g^{-1}}$ for PS, $0.049\ \mathrm{mL\,g^{-1}}$ for PLA, and $0.055\ \mathrm{mL\,g^{-1}}$ for P*n*BA. [d] Determined by GPC in THF. PDI is likely underestimated due to the ultrahigh MWs that exceed the GPC column size exclusion limit. [e] DP of the brush polymer backbones. [f] Conversion of MM is determined by comparing the peak areas of brush polymer and residual MM from GPC measurement of the crude product. [g] THF was used as solvent.

Herein, we used identical sample preparation and imaging conditions to image the cyclic brush polymers. Brush polymers with large PS side chains (**NB(PS)6600**) on graphite surface gave the clearest AFM images of individual molecules. As shown in Figure 1, various large ring-shaped nanostructures were clearly observed, either as small aggregates or as individual rings, together with some linear chains. All the observed nanostructures, both cyclic and linear, had uniform width of 30–40 nm and height of 1–2 nm, which are consistent with the linear brush polymer we previously prepared by ROMP of the same MMs. Most cyclic structures have diameters in the range of 100–180 nm, corresponding to contour lengths of 310–560 nm. We have previously measured the average length per monomeric unit to be 0.6 nm,[10a] using uniform, narrowly dispersed linear brush polymers with the same side chain. Therefore, a contour length of 310–560 nm corresponds to a backbone DP of ca. 500–900, which is close to the calculated backbone DP (880) based on the absolute MW measured by light scattering. Additionally, all the cyclic structures exhibited loop-like shapes with large open pores, different from our previously reported cyclic dendronized polymers, which presented as donut-like shapes with small pores of only 5–7 nm.[8] This is presumably due to the high MWs of both side chain and backbone and the significantly extended backbone conformation. Interestingly, we also observed structures where cyclic loops either partially stacked or crossed (Figure 1 e), and the cross-sectional analysis

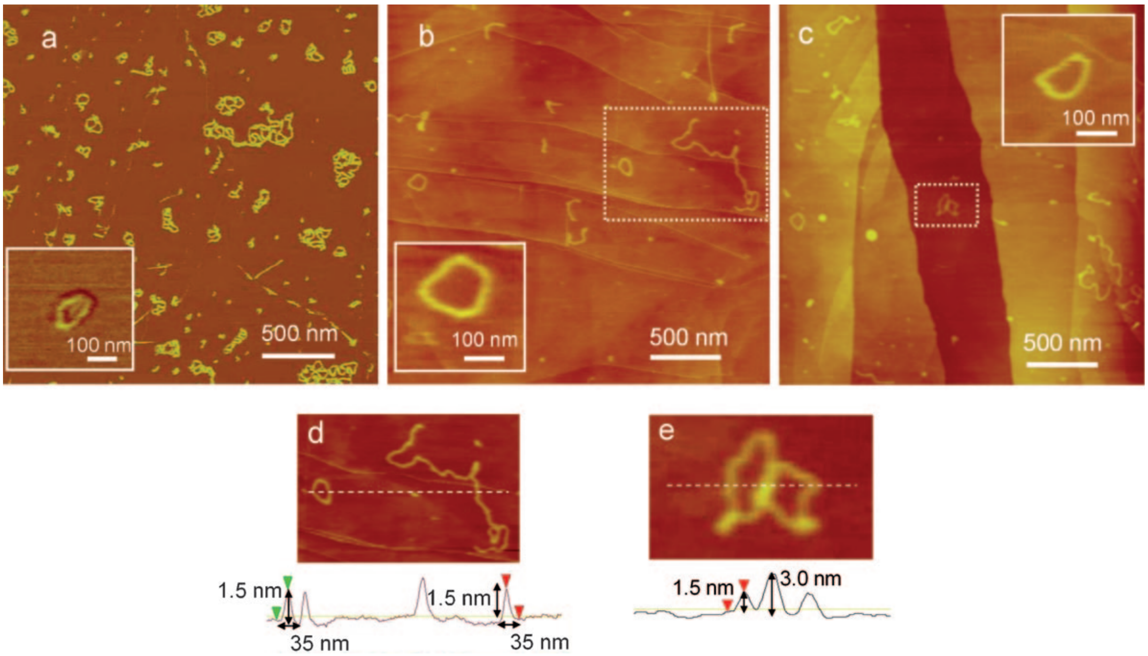

Figure 1. Topographic AFM images of REMP brush polymer **PNB(PS)6600** (Table 1, entry 3) on graphite: a) spin-coated from $0.01\ \mathrm{mg\,mL^{-1}}$ solution; b,c) spin-coated from $0.001\ \mathrm{mg\,mL^{-1}}$ solution. Inserts are magnified images of individual cyclic brush polymers; d) cross-sectional analysis of a cyclic and a linear brush polymer in the highlighted area in (b); e) cross-sectional analysis of either stacked or crossed rings in the highlighted area in (c).

showed that the stacked portion had a height twice that of the non-overlapping portion. We believe this structure is more likely to be from physically, partially overlapped rings during spin-coating and drying process, as opposed to catenated rings. Formation of catenanes during metathesis polymerization of norbornenyl MMs is very unlikely because chain transfer between greatly hindered polynorbornene backbones should not be possible.

Although of lower imaging quality, we also observed cyclic structures for brush polymers made with other MMs, such as **NB(PLA)8700**, and the largest observed loop contour length was nearly 2.5 μm. The extremely large loop was highly elongated in order to minimize side chain congestion (Figure 2).

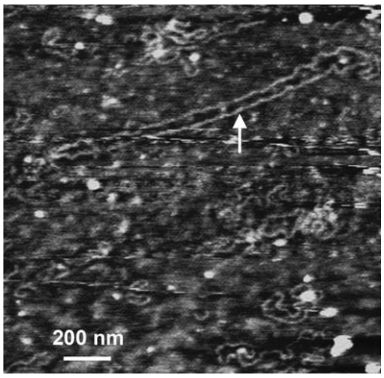

Figure 2. Topographic AFM image of REMP brush polymer **NB-(PLA)8700** (Table 1, entry 5) on mica. Arrow points to a cyclic polymer with contour length of nearly 2.5 μm.

In addition to cyclic structures, linear contaminants were observed at variable lengths, some even exceeding 1 μm. Individual brush polymers with lengths more than 1 μm have been rare in the literature, and this length was even unattainable with our previous synthesis of linear brush (co)polymers using living ROMP (Supporting Information, Figure 2S).

Matyjaszewski, Sheiko, and co-workers have recently found that high MW, densely grafted polymers are prone to rapid mechanical degradation through backbone scission.[11] This spontaneous phenomenon was attributed to the concentrated tension at the backbone due to adsorption of high density, long side chains at surfaces. They observed very rapid degradation of brush polymers that were 500 nm in length within the first hour of adsorption, and degradation rates slowed exponentially as the length reached 100–200 nm. In light of their findings, ultrahigh MW cyclic brush polymers may be even more susceptible to cleavage considering the additional stress in the backbone from the forced curving. In fact, we observed ring scission of individual cyclic brush polymer after leaving on graphite surface for 2 h (Figure 3). This ring scission closely resembles the previously reported cleavage of cyclic DNA plasmid on mica surface.[12] Additionally, we have also reported rapid mechanical degradation of cyclic dendronized polymers upon sonication.[8] Collectively, these observations may suggest the vulnerable nature of ultrahigh MW cyclic brush polymers toward mechanical ring-cleavage events.

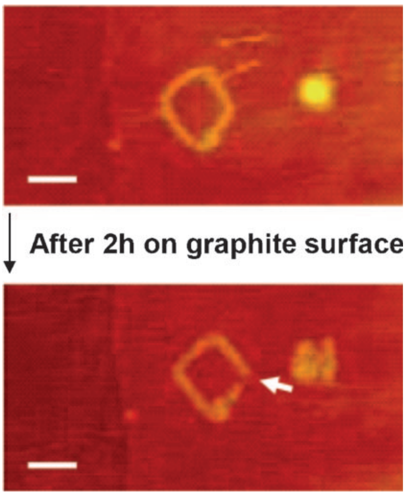

Figure 3. Topographic AFM images of a cyclic brush polymer **PNB(PS)6600** undergoing ring cleavage on graphite surface after 2 h at room temperature. The arrow points to the cleavage site. The scale bar is 100 nm.

In conclusion, we have demonstrated the direct synthesis of various ultrahigh molecular weight cyclic brush polymers by using ring-expansion metathesis polymerization of macromonomers, and toroidal shapes with large opening pores were visualized by AFM. Although we have observed linear contamination (manifesting in linear nanostructures) in our preliminary results, REMP of MMs affords facile access to large cyclic organic nanostructures with different functionalities that would be otherwise challenging to achieve.

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