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Rational Design and Synthesis of Well-defined Organic Linear and Janus-type Molecular Bottlebrush Cocoonas well as Star-like Molecular Bottlebrush Trilobes

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The PI proposes to synthesize well-defined organic linear and Janus-type molecular bottlebrush cocoonas as well as star-like molecular bottlebrush trilobes. To date, linear bottlebrush cocoonas and star-like bottlebrush trilobes have been synthesized.

1. Linear Bottlebrush Cocoonas

For bottlebrush cocoonas, we started from cellulose as the rigid backbone to craft rod-like cocoonas (Figure 1a). To obtain single cellulose chain with certain length, cellulose was first brominated in a mixed solvent containing ionic liquid, anhydrous 1-methyl-2-pyrrolidione (NMP), and DMF, followed by fractional precipitation to divide the cellulose into a series of size with each of low dispersity. Different fractions with different molecular weights (MWs) were used as the macroinitiator to synthesize core-shell bottlebrush cocoon with varied backbone length. Sequential atom transfer radical polymerization (ATRP) of tert-butyl acrylate (tBA) and styrene and divinyl benzene were performed to yield cellulose-grafted poly(tBA)-block-poly (styrene and divinyl benzene) (denoted cellulose-g-(PtBA-b-cPS). ATRP is a living free-radical polymerization technique, affording excellent molecular weight control and enabling the precise design of bottlebrush block copolymer with a tunable MW and narrow distribution for each constituent block. Divinyl benzene (DVB) is a bifunctional crosslinker which can copolymerize with styrene (St) to form a crosslinked PS (cPS) cocoon. The DVB/St comonomer ratio was set to be 5% to provide moderate crosslink density while maintaining the solubility of molecular cocoonas in organic solvent. The inner PtBA block was then hydrolyzed into PAA block by trifluoroacetic acid (TFA), converting the resulting bottlebrush copolymer into amphiphilic macromolecule. In both PtBA and PS/DVB polymerization, CuBr and PMDETA were used as the catalyst and ligand. All cellulose initiators and bottlebrush copolymeres were characterized by 1H gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) to verify their compositions and MWs. The bromination efficiency of cellulose was determined by NMR to be 100%, suggesting all -OH groups on cellulose were converted into ATRP initiator. Two different fractions of cellulose initiators were acquired by prep-GPC with MWs of 34K and 64K, respectively (Figure 2a). For 34K cellulose-Br which has a backbone length of around 30 nm, two different MWs of PtBA were grown, yielding bottlebrush polymer with MW of 258K and 750K, respectively (Figure 2b). For 64K cellulose-Br, two different MWs of PtBA were synthesized, yielding bottlebrush polymer with MWs of 181K and 690K, respectively (Figure 2c). All polymers had PDI below 1.2. Cellulose-g-PtBA with a MW of 258K was further used as the macroinitiator to grow the second block (i.e., crosslinked PS; cPS). Two cPS with different MWs were grown, yielding cellulose-g-(PtBA-b-cPS) with a total molecular weight of 300K and 827K respectively.

Figure 1b shows TEM image of stained cellulose-g-(PAA-b-cPS) after hydrolysis of PtBA into PAA blocks with a total MW of 300K. The staining agent selectively dyed the cPS shell, revealing the cocoon structure of the bottlebrush copolymer with low aspect ratio.

Figure 2. GPC curves of (a) cellulose-Br, (b) cellulose-g-PtBA, and (c) cellulose-g-(PAA-b-cPS). Architecture of synthesized bottlebrush cocoonas, where cPS (upper two panels) grows from cellulose-g-PtBA (lower and central four panels).
For the future work next year, all other cellulose-g-PrBA with different backbone length and aspect ratios will be further grafted with crosslinked PS to form cocoons. They will be characterized by NMR, GPC, DLS, AFM, TEM. The cocoons will then be loaded with small molecule dye or biomolecules to investigate their potential for controlled release. Additionally, they will be converted into a variety of inorganic nanorods such as Fe₃O₄ nanorod to further verify their rod-like structures and investigate the physical properties of nanorods.

2. Star-like Bottlebrush Trilobes

**Figure 3** shows synthesis of star-like bottlebrush trilobes. Star-like bottlebrush trilobes PHEMA-g-(PAA-b-cPS) was achieved by sequential ATRP of 2-hydroxyethylmethacrylate (HEMA), tert-butyl acrylate (tBA), styrene (St)/divinylbenzene (DVB, as cross-linker, 5%), followed by hydrolysis of the intermediate PrBA blocks into PAA. At first, PHEMA backbone was synthesized using a trifunctional ATRP agent (TMP-ATRP) prepared by reacting a trifunctional alcohol of 2-ethyl-2-(hydroxymethyl)propane-1,3-diol (TMP) with 2-bromoisobutyryl bromide (Bibb). The MW of PHEMA was tunable by varying the reaction time, that is, 62 K (PDI 1.16) and 79 K (PDI 1.25) when reacting for 0.5 h and 1.5 h, respectively. The resulting star-like PHEMA was then be transformed into a star-like polyfunctional macroinitiator (PHEMA-ATRP) by brominating the terminal hydroxyl groups on each TMP arm with Bibb. The esterification reaction between PHEMA and Bibb had nearly 100% conversion, as confirmed by ¹H NMR spectroscopy of PHEMA-ATRP, where the proton peak at 5 ppm assigned to the -OH group in PHEMA disappeared. Subsequently, the first side-chain PrBA was grafted from the PHEMA-ATRP backbone. The characteristic proton –CH of PrBA appeared at 2.25 ppm together with tertbutyl group at about 1375 cm⁻¹ in FT-IR substantiated the successful synthesis of PHEMA-g-PrBA. By adjusting the reaction and the feed ratio of PHEMA-ATRP and tBA, PrBA blocks with MWs of 20 K and 32 K were obtained. Furthermore, St was polymerized with a 5% mole ratio of crosslinker DVB, yielding the targeted PHEMA-g-(PrBA-b-cPS) bottlebrush trilobes was calculated to be 116 k with a PDI of 1.45.

For the future work next year, star-like bottlebrush trilobes PHEMA-g-(PAA-b-cPS) will be used as template to yield perovskite star-like trilobes using the supersaturated recrystallization method to further corroborate the .

3. Janus-type Bottlebrush Cocoons

Synthesis of Janus-type bottlebrush cocoons will be the focus of the project next year. The proposed strategy starts with sequential RAFT polymerization of HEMA as backbone. The resulting Janus bottlebrush cocoons will have a bifunctional core, one side of PAA and the other side of P4VP with a completely crosslinked PS shell. As PAA and P4VP carries opposite charges in the Janus cocoon, they can be loaded with positively charged and negatively charged compounds, respectively, to achieve bifunctional delivery. Moreover, the Janus cocoons are expected to be capitalized as nanoreactor to synthesize Janus nanorods which has unique physical properties and much advanced applications.

**Research Impact**

This project allows the PI to build a new research direction in constructing polymers and block copolymers with complex architectures that are amenable to well-established living or controlled living polymerization techniques. The research project involves a set of polymer synthesis and a variety of characterization techniques. Two graduate students have been working on this project. The students working on the project have gained extensive knowledge on polymer architecture design and been familiar with several controlled free radical polymerization techniques such as atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain-transfer polymerization (RAFT). This project also provided good opportunity for students to learn a suite of polymer characterization techniques, including GPC for measuring MW, NMR for evaluating chemical composition, AFM and TEM for examining morphology.