

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

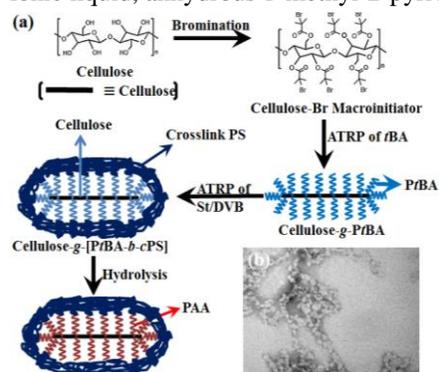
Zhiqun Lin, Georgia Institute of Technology, Atlanta, GA 30332

### Research Progress Report (09/01/2017-08/31/2018)

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

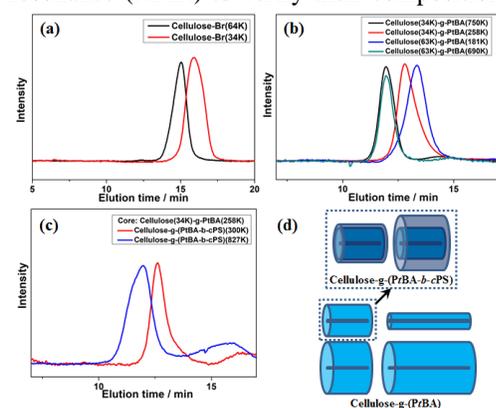
#### 1. Linear Bottlebrush Cocoons

For bottlebrush cocoons, we started from cellulose as the rigid backbone to craft rod-like cocoons (**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-pyrrolidone (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 (*t*BA) and styrene and divinyl benzene were performed to yield cellulose-grafted poly(*t*BA)-*block*-poly (styrene and divinyl benzene) (denoted cellulose-g-(*Pt*BA-*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 (*c*PS) cocoon. The DVB/St comonomer ratio was set to be 5% to provide moderate crosslink density while maintaining the solubility of molecular cocoons in organic solvent. The inner *Pt*BA block was then hydrolyzed into PAA block by trifluoroacetic acid (TFA), converting the resulting bottlebrush copolymer into amphiphilic macromolecule. In both *Pt*BA and PS/DVB polymerization, CuBr and PMDETA were used as the catalyst and ligand. All cellulose initiators and bottlebrush copolymers were characterized by gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) to verify their compositions and MWs. The bromination efficiency of cellulose was determined



**Figure 1.** (a) Synthetic route to rod-like bottlebrush cocoons. (b) TEM image of stained bottlebrush cellulose-g-(PAA-*b*-*c*PS) cocoons.

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 *Pt*BA were grown, yielding bottlebrush polymer with MW of 258K and 750K, respectively (**Figure 2b**). For 64K cellulose-Br, two different MWs of *Pt*BA were synthesized, yielding bottlebrush polymer with MWs of 181K and 690K, respectively (**Figure 2c**). All polymers had PDI below 1.2. Cellulose-g-*Pt*BA with a MW of 258K was further used as the macroinitiator to grow the second block (i.e., crosslinked PS; *c*PS). Two *c*PS with different MWs were grown, yielding cellulose-g-(*Pt*BA-*b*-*c*PS) with a total molecular weight of 300K and 827K respectively.



**Figure 2.** GPC curves of (a) cellulose-Br, (b) cellulose-g-*Pt*BA, and (c) cellulose-g-(PAA-*b*-*c*PS). Architecture of synthesized bottlebrush cocoons, where *c*PS (upper two panels) grows from cellulose-g-*Pt*BA (lower and central four panels).

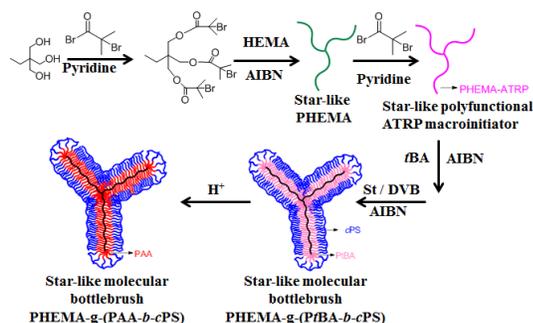
**Figure 1b** shows TEM image of stained cellulose-g-(PAA-*b*-*c*PS) after hydrolysis of *Pt*BA into PAA blocks with a total MW of 300K. The staining agent selectively dyed the *c*PS shell, revealing the cocoon structure of the bottlebrush copolymer with low aspect ratio.

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

For the future work next year, all other cellulose-g-*PtBA* 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 Fe<sub>3</sub>O<sub>4</sub> 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 *PtBA* 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



**Figure 3.** Synthesis of star-like PHEMA-g-(PAA-*b*-cPS) bottlebrush by ATRP.

(*PtBA-b-cPS*). After hydrolyzing *PtBA* into PAA, star-like bottlebrush trilobes were obtained. The structure of PHEMA-g-(PAA-*b*-cPS) was characterized by <sup>1</sup>H NMR, FT-IR and GPC. The typical proton peaks located at 7.3-7.5 ppm can be assigned to benzene groups in PS. The total disappearance of tertbutyl group at 1375 cm<sup>-1</sup> in the FT-IR further verified the successful hydrolysis of *PtBA* block. The MW of star-like PHEMA-g-(*PtBA-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.