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Preparation of titania nanoparticles with tunable anisotropy and branched structures from core–shell molecular bottlebrushes

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ABSTRACT

Core–shell molecular bottlebrushes with various topologies and with poly (*tert*-butyl acrylate)-*b*-polystyrene (PtBA-*b*-PS) block copolymer side chains were synthesized via atom transfer radical polymerization (ATRP). After hydrolysis of the PtBA segments and their conversion to poly (acrylic acid) (PAA), the materials were used as templates to prepare titania nanoparticles. Transmission electron microscopy (TEM) images showed that the particles retained the characteristic shape of the templates, including cylindrical and cylindrical geometry. The cylindrical dimensions, i.e. diameter and length, were controlled by the number average degrees of polymerization of the PAA side-chain block and the polymethacrylate backbone, respectively. Thermogravimetric analysis (TGA) showed the weight fraction of inorganic content ranged from 17% to 35%, depending on the ratio of the length of PAA and PS blocks.

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1. Introduction

Molecular bottlebrushes are macromolecules containing long polymeric backbones with densely grafted polymeric side chains [1–3]. Owing to their unique architecture, molecular bottlebrushes exhibit distinct properties suggesting many potential applications including photonics [4–7], lubricants [8], stimuli-responsive materials [9–13], supersoft elastomers [14–17], porous materials [18,19], and drug delivery systems [20]. Molecular bottlebrushes can be synthesized via three strategies: “grafting through” [4,21], “grafting to” [22–24], and “grafting from” [25–27]. Development of reversible deactivation radical polymerization (RDRP) or controlled radical polymerization (CRP) procedures, including atom transfer radical (ATRP) [28,29], reversible addition–fragmentation chain transfer (RAFT) [30–33], and nitroxide-mediated polymerizations (NMP) [34] provided versatile routes for preparation of polymer brushes with controlled composition, molecular weight and dispersity of either or both backbones and side chains [35–46].

Although formally single molecules, molecular bottlebrushes have dimensions similar to some self-assembled nano-objects such

as polymer micelles. Due to strong steric repulsion between the densely grafted side chains, the bottlebrushes adopt extended, cylindrical conformations if the length of the backbone is significantly longer than that of the side chains. This allows molecular bottlebrushes with block copolymer side chains to be used as single-molecule templates for fabricating one-dimensional (1D) nanostructures such as nanowires and nanotubes [47–60]. Although sharing similar structures with micelles afforded by reversible self-assembly, molecular bottlebrushes do not undergo disassociation when the external environment is changed [61], offering unique opportunities for complexation and templating. Specific side chains can be incorporated to provide preferential affinities towards inorganic precursors. Therefore, composite materials with anisotropically arranged inorganic content could be selectively formed within these blocks, affording layered structures in the radial orientation. In this way, nanowires and nanotubes could be prepared using core–shell brush templates with the boundary of a nano-reactor defined by the core and the shell, respectively.

Due to their unique geometry and size-dependent optical, electronic, magnetic properties, 1D nanostructures are candidates for potential applications in the field of nanoelectronics, sensors, catalysis, energy harvesting, storage, and conversion [62–64]. Synthesis of branched inorganic nanostructures is an important research direction, which can generate hierarchical nanostructured networks with enhanced interconnectivity and percolation of

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nanoparticles [65,66]. For example, branched nanosized tetrapods offer the potential for charge transport in all spatial directions independent of their orientations [67,68].

This paper presents procedures for the synthesis of anisotropic titania hybrid nanocomposites. Molecular bottlebrushes with poly(acrylic acid)-*block*-polystyrene (PAA-*b*-PS) side chains were synthesized via “grafting-from” methods and used as templates to prepare hybrid nanocomposites. The PS segments not only define the boundaries of PAA (then titania) cores but also serve as shells outside titania nano-objects preventing crosslinking, aggregation and enhancing processability [69]. The synthetic strategy of “grafting-from” allows systematic tuning of the lengths and topologies of brushes during the preparation of backbones via ATRP [42,70,71]. Structural features of templates such as anisotropy and morphology of the branches were effectively transferred into hybrid nanocomposites. Isotropic nanoparticles were also prepared from star-like templates [72–78].

2. Experimental

2.1. Materials

(2-Trimethylsilyloxy)ethyl methacrylate (HEMA-TMS, Scientific Polymer Products), *tert*-butyl acrylate (*t*BA, 99%, Acros) and styrene (S, 99%, Aldrich) were purified by passing the monomer through a column filled with basic alumina to remove the inhibitor. Pentaerythritol tetrakis(2-bromoisobutyrate) (4f-BiB) was synthesized according to procedures reported in the literature [79]. Ethyl 2-bromoisobutyrate (EBiB, 98%, Acros), copper(I) bromide ($\text{Cu}^{\text{I}}\text{Br}$, 99.999%, Aldrich), copper(I) chloride ($\text{Cu}^{\text{I}}\text{Cl}$, $\geq 99.995\%$, Aldrich), copper(II) bromide ($\text{Cu}^{\text{II}}\text{Br}_2$, 98%, Acros), copper(II) chloride ($\text{Cu}^{\text{II}}\text{Cl}_2$, $\geq 99.995\%$, Aldrich), 4,4'-dinonyl-2,2'-bipyridine (dNbpy, 97%, Aldrich), N,N,N',N''-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), potassium fluoride (KF, 99%, Aldrich), tetrabutylammonium fluoride (TBAF, 1.0 M in THF, Aldrich), α -bromoisobutyryl bromide (98%, Aldrich), 2,5-di-*tert*-butylphenol (DTBP, 99%), triethylamine (TEA, $\geq 99\%$, Aldrich), trifluoroacetic acid (TFA, $\geq 98\%$, Aldrich), titanium(IV) 2-ethylhexanoate ($\text{Ti}(\text{EH})_4$, 97%, Alfa Aesar) and solvents were used as received without further purification.

2.2. Synthesis

2.2.1. Synthesis of PBiBEM (backbone macroinitiator)

The general procedure is described below for the synthesis of PBiBEM₅₆. A 25 mL Schlenk flask was charged with EBiB (67.2 mg, 0.345 mmol), HEMA-TMS (15.0 mL, 68.9 mmol), dNbpy (0.169 g, 0.414 mmol), $\text{Cu}^{\text{II}}\text{Cl}_2$ (12.9 mg, 0.0965 mmol), and anisole (1.7 mL). The solution was degassed by three freeze–pump–thaw cycles. During the final cycle, the flask was filled with nitrogen, and $\text{Cu}^{\text{I}}\text{Cl}$ (10.9 mg, 0.110 mmol) was quickly added to the frozen reaction mixture. The flask was sealed, evacuated, and backfilled with

nitrogen five times and then immersed in an oil bath at 60 °C. Polymerization was stopped when conversion reached 28.1% as determined by ^1H NMR spectroscopy. From the molar ratio of the reacted monomer to initiator, the degree of polymerization (DP) was calculated to be 56. The reaction mixture was diluted with methylene chloride, passed through neutral alumina column to remove the catalyst, then concentrated, and used in the next step without further purification.

A 50 mL round-bottom flask was charged with the product of last step (3.10 g, 15.4 mmol HEMA-TMS), KF (1.09 g, 26.1 mmol), DTBP (0.316 g, 1.53 mmol), and then dry THF (30 mL) was added under nitrogen. The reaction mixture was cooled down in an ice bath, followed by the injection of tetrabutylammonium fluoride (0.15 mL, 1.0 M in THF, 0.15 mmol) and subsequent dropwise addition of α -bromoisobutyryl bromide (4.2 g, 2.3 mL 18.4 mmol) over the course of 20 min. The reaction mixture was then allowed to reach room temperature and was stirred for another 24 h. Afterward the solids were filtered off and the mixture was precipitated by addition of the filtered solution to methanol/water (70/30), the solids were re-dissolved in methylene chloride (20 mL) and passed through the column filled with basic alumina. The product was re-precipitated three times in hexanes and dried overnight under vacuum. Apparent molecular weight determined by THF SEC: $M_{n,\text{SEC}} = 15,600$, and $M_w/M_n = 1.19$.

Three additional PBiBEM macroinitiators were prepared according to the above procedure using the stoichiometric ratios shown in Table 1.

2.2.2. Synthesis of PBiBEM-g-(PtBA-b-PS)

The general procedure for the synthesis of the bottlebrush macromolecules is described below for the synthesis of L₅₆ A₅₁ S₇₃ (Table 2). A 100 mL Schlenk flask was charged with PBiBEM₅₆ (0.191 g, 0.684 mmol initiator centers), *t*BA (50.0 mL, 342 mmol), dNbpy (0.349 g, 0.855 mmol), $\text{Cu}^{\text{II}}\text{Br}_2$ (2.4 mg, 0.85 mmol), and anisole (5.6 mL). The solution was degassed by three freeze–pump–thaw cycles. During the final cycle, the flask was filled with nitrogen, and $\text{Cu}^{\text{I}}\text{Br}$ (59.6 mg, 0.417 mmol) was quickly added to the frozen reaction mixture. The flask was sealed, evacuated, and backfilled with nitrogen five times and then immersed in an oil bath at 70 °C. Polymerization was stopped when conversion reached 10.8% as determined by ^1H NMR spectroscopy. From the monomer conversion and the initial ratio of initiator to monomer the DP of *t*BA side chains was calculated to be 51 (assuming 100% initiation efficiency from the multifunctional macroinitiator). Unreacted monomer was removed by ultrafiltration in MeOH/THF (50/50, vol%) solution using an ultrafiltration membrane (Biotech, Regenerated Cellulose, MWCO: 3500). The PtBA brush was dried under vacuum to a constant mass.

The PtBA brush (0.37 g, 0.0544 mmol chain end, assuming 100% initiation efficiency in last step), styrene (5.0 mL, 44 mmol), PMDETA (10.4 mg, 0.0599 mmol), $\text{Cu}^{\text{II}}\text{Br}_2$ (0.61 mg, 0.0027 mmol), and anisole (0.56 mL) were added to a 10 mL Schlenk flask. The solution was

Table 1
Experimental condition for the synthesis of PBiBEM.^a

Entry	M	dNbpy	CuX^b	CuX_2^b	Solvent	Conv. ^c	DP ^c	M_n^d	M_w/M_n^d
L ₅₆	200	1.2	0.32	0.28	10%	28.2%	56	15,600	1.19
L ₂₀₂	800	2.4	0.84	0.36	10%	25.3%	202	36,000	1.12
L ₃₇₂	1000	4.0	1.78	0.22	20%	37.2%	372	47,300	1.16
B ₂₀₅ ^b	4000	12	4.5	1.5	10%	20.5%	205 ^e	102,000	1.13

^a Numbers in the column of M, dNbpy, CuX and CuX₂ stand for relative ratios of initial monomer, ligand, CuX and CuX₂ to initiator (initiator = EBiB for L₅₆, L₂₀₂ and L₃₇₂; initiator = 4f-BiB for B₂₀₅) concentrations, respectively.

^b X = Cl for L₅₆, L₂₀₂ and L₃₇₂; X = Br for B₂₀₅.

^c Conversion based on the monomer to initiator ratio and the conversion of HEMA-TMS measured by ^1H NMR.

^d Determined by SEC using linear PMMA standards.

^e Averaged DP of repeat unit at each arm.

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