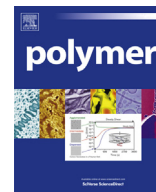




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Synthesis of star-brush polymer architectures from end-reactive molecular bottlebrushes

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ABSTRACT

Reactive bottlebrush-linear block copolymers with poly(methyl methacrylate) side chains and linear poly(glycidyl methacrylate) (PGMA) end blocks were utilized for the fabrication of brush-star architectures. Well-defined bottlebrush copolymers with reactive end blocks were prepared by a grafting-from method, where a block copolymer backbone was synthesized by sequential reversible addition–fragmentation chain transfer (RAFT) polymerization of functionalized monomers, while side chains were installed by atom transfer radical polymerization (ATRP) of methyl methacrylate initiated from the bromide groups of the backbone. LiBr-catalyzed ring-opening of epoxides in the presence of ethylenediamine at room temperature was utilized for efficient cross-linking of PGMA blocks leading to star-brush architectures. Various structural parameters, such as side chain length and reactive end block length, were found to impact the efficacy of the cross-linking step. The developed method provided means to connect giant bottlebrush copolymer arms ($M_n > 300$ kg/mol) into a star architecture in an effective and tunable manner.

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1. Introduction

The synthesis of polymers with well-defined architectures and various topological structures are of considerable interest due to their featured applications. Recent advances in polymer synthetic methods have allowed for the preparation of a variety of branched polymer architectures, such as star, comb, brush, hyperbranched, and dendritic. Among these, star polymers are characterized by having multiple polymer segments emanating from a single junction point or a densely cross-linked core [1,2] and exhibit distinct physical and mechanical properties compared to their linear analogs of the same molecular weight [3–6]. In particular, the unique branched architecture of star polymers manifests itself in a compact globular shape and low solution viscosity, which creates an attractive platform for a variety of applications, such as drug delivery vehicles, nanoparticle templates, tougheners, and rheological modifiers [6–10]. Star polymers are typically synthesized by either arm-first [11–16] or core-first [17–20] methods, which are classified depending on the order of construction of arm and core units. Such macromolecules can be tailored for specific applications

by introducing desired functionalities in the central core and arm segments using available synthetic methods [21–25].

Bottlebrush copolymers, as a specific class of grafted polymers, have been widely investigated over the past decade due to a set of unique properties and synthetic challenges [26–29]. These comb-like copolymers consist of shorter side chains that are densely grafted along a longer polymeric backbone. Steric repulsions between densely grafted side chains force the backbone to stretch out resulting in stiff macromolecules characterized by a persistent cylindrical shape in solution and low density of entanglements in melt [30–34]. Different synthetic methods, such as grafting-from [35], grafting-through [36] and grafting-onto [37,38], have been utilized for the preparation of bottlebrush copolymers. Synthetic control over the macromolecular dimensions, composition and topology allows for the preparation of uniquely shaped and structured bottlebrush copolymers for a variety of applications, such as photonic crystals [39–41], supersoft elastomers [42], molecular sensors [43], nanotubes [44–46], nanoporous materials [47,48], shape-persistent surfactants [49], nanoparticle templates [50,51], and drug delivery vehicles [52–54].

Star-brush copolymers, which combine the properties of both star and bottlebrush polymers, contain densely grafted brush-like arms radiating from a central core [55]. The development of fundamental understanding of structure–property relationships in

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these newly emerged macromolecular architectures requires robust synthetic methods that allow one to access complex architectures in a modular fashion. Compared to typical star polymers, the synthesis of star-brush copolymers presents additional challenges due to the complexity of the targeted architecture and steric hindrance provided by the densely grafted arms. Reported methods for the preparation of star-brush copolymers mostly rely on the synthesis of a star-shaped backbone first, followed by grafting of polymer side chains by either polymer–polymer coupling reactions (grafting-onto) or polymerization initiated from the star backbone (grafting-from) [56–59]. In this report, we describe a new method for the preparation of star-brush copolymers by an arm-first approach, based on the controlled cross-linking of giant bottlebrush copolymer arms containing reactive linear end blocks (Fig. 1). We show that relative lengths of the bottlebrush side chains and the reactive linear end block play a critical role in controlling the successful outcome of the star formation.

2. Experimental section

2.1. Materials

Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol and dried under vacuum before use, CH_2Cl_2 was dried using a commercial solvent purification system (Innovative Inc.). Glycidyl methacrylate (GMA), and methyl methacrylate (MMA) were passed through a basic alumina column before polymerization to eliminate the radical inhibitor. All other chemicals were used as received unless stated otherwise.

2.2. Measurements

^1H NMR spectra were recorded on a Varian Inova-500 spectrometer (500 MHz) by using CDCl_3 or CD_3CN as a solvent. Size exclusion chromatography (SEC) data was obtained using Viscotek's GPCmax and TDA302 Tetrade detector Array system equipped with two PolyPore columns (Polymer Labs, Agilent). The detector unit contained a refractive index, UV, viscosity, low angle (7°) and right angle (90°) light scattering modules. Tetrahydrofuran (30°C , 1 mL/min) was used as the mobile phase. The system was calibrated with 10 linear polystyrene standards from 1.2×10^6 –500 g/mol. The refractive index increment (dn/dc) for poly(GMA) was measured to be 0.087 mL/g in THF ($T = 30^\circ\text{C}$, $\lambda = 630\text{ nm}$), which was used to determine absolute molecular weights of the poly(GMA) homopolymer. SEC analysis in DMF (0.01 M LiBr) was carried out at 55°C on a Viscotek GPC system equipped with a VE-3580 refractive index (RI) detector, two mixed bed (PolyAnalytik) organic columns (PAS-103M and PAS-105M). The system was calibrated with 10 polystyrene standards from 1.2×10^6 –500 g/mol. TEM images were obtained using a JEOL 2010 TEM instrument. Samples were prepared by dip-coating a 400 mesh carbon coated

copper grid from a dilute (1 mg/mL) sample solution.

2.3. Synthesis of BIEM

The synthesis of 2-(2-bromoisobutyryloxy) ethyl methacrylate (BIEM) was carried out according to the procedures described previously [60,61]. A solution of 2-hydroxyethyl methacrylate (7.00 mL, 58 mmol) and pyridine (5.36 mL, 66 mmol) in CH_2Cl_2 (75 mL) was stirred at 0°C for 45 min under nitrogen, and 2-bromoisobutyryl bromide (7.72 mL, 64 mmol) was added dropwise over 30 min. The mixture was stirred at 0°C for 6 h, during which time the formation of a white precipitate was observed. The mixture was filtered to remove the white precipitate and the solids were washed with CH_2Cl_2 . The filtrate was washed with deionized water ($2 \times 100\text{ mL}$), 10% NaHCO_3 solution ($2 \times 100\text{ mL}$), and a saturated NaCl solution ($2 \times 100\text{ mL}$) and then dried over MgSO_4 . The MgSO_4 was filtered off and the CH_2Cl_2 was evaporated. The product was purified by vacuum distillation (84°C , 0.02 mmHg) to provide the desired compound in 75% yield. ^1H NMR (500 MHz, CDCl_3 , δ): 6.16 (s, 1H, $\text{CH}=\text{C}$ trans), 5.62 (s, 1H, $\text{CH}=\text{C}$ cis), 4.45 (s, 4H, $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$), 1.97 (3H, α - CH_3), 1.95 (s, 6H, $-\text{C}(\text{Br})(\text{CH}_3)_2$).

2.4. Synthesis of poly(GMA)

GMA (1 mL, 7.4 mmol), 2-cyano-2-propyl 4-cyanodithiobenzoate (CPCDB, 36.2 mg, 147.0 μmol), and AIBN (2.4 mg, 14.7 μmol) were dissolved in benzene (2 mL) in a Schlenk flask, and the mixture was degassed by three freeze–pump–thaw cycles. The polymerization was performed at 60°C under stirring. After 16 h, the reaction was quenched by cooling to room temperature. The mixture was then diluted with CH_2Cl_2 , the polymer was precipitated from 20-fold excess of methanol three times and dried in a vacuum oven overnight to produce 0.932 g polymer as a pink powder. SEC (light scattering detector): $M_n = 10.5\text{ kg/mol}$, $D = 1.13$.

2.5. Synthesis of poly(GMA-*b*-BIEM) diblock copolymer

Poly(GMA) ($M_n = 10.5\text{ kg/mol}$, 75 mg) was dissolved in a mixture of BIEM (0.38 mL, 1.71 mmol) and toluene (0.4 mL) in a Schlenk flask. AIBN (0.115 mg, 0.7 μmol) was then added to the mixture in the reaction flask, and the mixture was degassed by three freeze–pump–thaw cycles. The reaction was performed at 65°C for 18 h and then quenched by cooling down to room temperature under running water. The final product was diluted with CH_2Cl_2 , precipitated from 20-fold excess of methanol three times, and dried in a vacuum oven overnight to produce 0.413 g polymer as a pink powder. SEC (polystyrene standards): $M_n = 72.2\text{ kg/mol}$, $D = 1.16$.

2.6. End group modification of poly(GMA-*b*-BIEM)

The characteristic pink color of polymers synthesized by reversible addition–fragmentation chain transfer polymerization is due to the thiocarbonylthio moiety present at the end of the polymeric chain. To remove the dithiobenzoate end group of the polymeric chain and to produce poly(GMA-*b*-BIEM) diblock copolymer with a cyanoisopropyl end group, the polymer was treated with excess amount of AIBN initiator according to the literature procedure [62]. Poly(GMA-*b*-BIEM) (0.2 g, 2.8 μmol) was dissolved in tetrahydrofuran (1.5 mL) in a 10-mL round-bottom flask and 20-fold excess of AIBN (11.4 mg, 69.3 μmol) was then added to the flask. The solution was purged with N_2 gas, sealed, and placed in an oil bath at 80°C for 2.5 h. After the reaction, the polymer was precipitated in 20-fold excess of cold hexanes, and

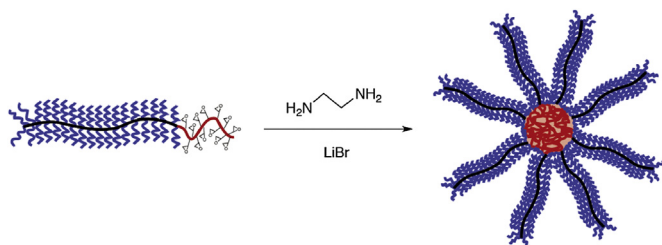


Fig. 1. Synthesis of core-cross-linked star-brush copolymers from end-reactive bottlebrush copolymers.

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