



Synthesis and self-assembly in aqueous solution of amphiphilic diblock copolymers containing hyperbranched polyethylene



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ABSTRACT

In this paper, the well-defined amphiphilic diblock copolymers, hyperbranched polyethylene-*b*-poly(ethylene oxide) (HBPE-*b*-PEO) and hyperbranched polyethylene-*b*-poly(acrylic acid) (HBPE-*b*-PAA), were synthesized by combing chain walking ethylene polymerization in the presence of 4-vinylbenzyl chloride catalyzed with Pd- α -diimine and click chemistry or atom transfer radical polymerization (ATRP). The self-assembly behavior in water, a selective solvent for PEO and PAA, and the micelle morphology of HBPE-*b*-PEO and HBPE-*b*-PAA were investigated by laser light scattering (LLS), transmission electron microscopy (TEM) and atomic force microscopy (AFM). The resultant diblock copolymers can self-assemble into spherical vesicles as demonstrated by LLS and TEM, which become collapsed on mica surface during drying as showed by AFM.

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1. Introduction

Since the explorations made by Brookhart et al. and Guan et al. over a dozen years ago [1,2], hyperbranched polyethylene (HBPE) obtained at low pressure based on “chain walking” polymerization (CWP) using Pd- α -diimine catalyst has attracted considerable attention due to its unique chain structure. Distinct from linear polyethylene (PE), HBPE has structure and topology similar to that of dendrimer, and possesses some strikingly superior material properties, such as improved processability [3,4], enhanced solubility [5–7] and low melt viscosity [8–10]. For low- and medium-molecular-weight HBPE, it is even an oily liquid at room temperature [10]. To date, HBPE has been found its application for lubricant formulation [8–10], polymer extrusion processing [3,4] and solubilization of carbon nanotubes in organic solvents [5–7].

Another potential application for HBPE is as a building block for constructing polymers of various well-defined chain architectures [11–14], for instance, the hyperbranched-linear block copolymers [11,12]. It has been demonstrated that dendritic-linear block

copolymers have interesting self-assembling feature, novel interfacial properties, and special phase separation behavior, promising applications in thin film, drug delivery, biomaterials and coatings [15–17]. Unfortunately, dendritic structure often requires tedious synthetic procedures. Hyperbranched structure, as an alternative, is much easier to synthesize and incurs lower cost [18,19]. HBPE is such an option, which can easily obtain at low pressure catalyzed by Pd- α -diimine catalyst. There have been a few studies on hyperbranched-linear diblock copolymers containing an HBPE block reported in the literature [11,12]. Utilizing the unique reaction of styrene derivatives with cationic Pd species, Ye et al. demonstrated a quantitative end-capping chemistry for efficient synthesis of narrowly distributed telechelic hyperbranched polyethylenes (HBPEs) containing a functional ω -terminal group (*i.e.*, mono end-capped HBPEs with only one functional group at the ω chain end) [11]. Later, these mono end-capped HBPEs were successfully used as precursors for further synthesis of diblock copolymers of HBPE and polystyrene (HBPE-*b*-PS) or poly(methyl methacrylate) (HBPE-*b*-PMMA) *via* atom transfer radical polymerization (ATRP) [12]. Note that, all the blocks of these reported hyperbranched-linear diblock copolymers containing an HBPE block are hydrophobic. In order to exploit their application in biomaterials or drug delivery, it is necessary to synthesize several HBPE diblock copolymers with a hydrophilic block.

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On the other hand, a number of dendritic/hyperbranched polyethylene graft copolymers have been synthesized by combining CWP with ATRP, reversible addition fragmentation transfer (RAFT) polymerization or click chemistry. Chen et al. first developed a tandem CWP-ATRP approach for constructing dendritic polyethylene with reactive surface functionalities [20]. Later, Zhang et al. showed the synthesis of HBPE tethered with PMMA side chains (HBPE-*g*-PMMA) via a similar procedure [13]. Our group also developed a tandem CWP-RAFT approach for the synthesis of HBPE grafted with poly(*N,N*-dimethylaminoethyl methacrylate) chains (HBPE-*g*-PDMAEMA) [14]. More recently, we further grafted poly(ethylene oxide) (PEO) chains onto a dendritic polyethylene core (DPE-*g*-PEO) through CWP combining azide-alkyne click chemistry [21].

The self-assembly of various hyperbranched polymers and linear-hyperbranched polymers have been widely investigated in the literature [22–27]. However, only one study has been concerned about amphiphilic polymers containing HBPE segments [14]. The self-assembly of amphiphilic HBPE graft copolymers tethered with water-soluble chains in water was first investigated by our group recently [14]. These HBPE graft copolymers have been found to self-assemble into vesicles in aqueous solution. To date, there is still a lack of studies on the self-assembly of amphiphilic HBPE diblock copolymers (i.e., hyperbranched-linear diblock copolymers consisting of an HBPE block and a water-soluble linear block). Furthermore, it is essential to measure the exact nanostructures of the hydrated state aggregates when concerning their specific applications. So far, the nanostructures of the HBPE-based aggregates are investigated on the basis of transmission electron microscopy (TEM) and atomic force microscopy (AFM) observations [14]. Note that both measurements are performed after the aggregates become dry. Considering the HBPE block as an oily liquid at room temperature, the morphologies of the aggregates might change during the sample preparation. Thus, it is necessary to measure the nanostructures in aqueous solution for the HBPE-based aggregates.

In this study, we employed the general technique of end-capping chemistry to synthesize two HBPE precursors. Then click chemistry and ATRP were respectively carried out to obtain two amphiphilic hyperbranched-linear diblock copolymers, hyperbranched polyethylene-*b*-poly(ethylene oxide) (HBPE-*b*-PEO) and hyperbranched polyethylene-*b*-poly(acrylic acid) (HBPE-*b*-PAA). Both diblock copolymers consisting of a long HBPE block and a short water-soluble block were used to study their self-assembly in aqueous solution. A detailed laser light scattering (LLS) study on the HBPE-based aggregates was reported, providing the clear nanostructures for the hydrated state aggregates in aqueous solution. TEM and AFM observations were also used to give an image for the aggregates in their dried state.

2. Experimental section

2.1. General procedure and materials

All manipulations of air- and/or moisture-sensitive compounds were carried out under a dry argon atmosphere by using standard Schlenk techniques or under a dry argon atmosphere in glovebox unless otherwise noted. The Pd- α -diimine catalyst [(Ar-N=C(Me)-C(Me)=N-Ar)-Pd(II)(Me) (N \equiv CMe)]⁺ BAF⁻ [Ar = 2,6-(iPr)₂C₆H₃] (**1**) was prepared according to the literature [1,28,29]. Dichloromethane was refluxed over CaH₂ and distilled before use. Toluene was refluxed over potassium with benzophenone as indicator and distilled under argon atmosphere prior to use. *N,N*-dimethylformamide (DMF) and *tert*-butyl acrylate (*t*BuA) were obtained from Aladdin and distilled under vacuum before use. CuCl

(97%, Aladdin) and CuBr (99%, Aldrich) were purified by washing with acetic acid, ethanol, and diethyl ether in order. 4-vinylbenzyl chloride (VBC, 90%), *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA, 99%), NaN₃ (99%) and CF₃COOH (99%) were obtained from Aldrich and used without further purification. Mono-alkynyl-terminated PEO (PEO_{2k}≡, *M*_n = 2.0 × 10³ g mol⁻¹) was synthesized according to the literature [30]. Other reagents if not specified were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received.

2.2. Synthesis of mono VBC end-capped hyperbranched polyethylene (HBPE-VBC)

Two mono VBC end-capped hyperbranched polyethylenes (HBPE-VBC-1 and HBPE-VBC-2) were synthesized according to the method reported by Li and Ye [11]. Typically, ethylene “living” polymerizations were carried out with 0.1 mmol Pd- α -diimine catalyst (**1**) at 15 °C under ethylene pressure of 1 atm. in 50 mL dichloromethane. After a prescribed period of polymerization time, VBC of 300 equiv to the catalyst was injected to allow end-capping of PE chains for 1 h. Volatile components were removed by a rotary evaporator to yield a yellow product. The product was redissolved in petroleum ether, filtered through a short plug containing neutral alumina and silica gel to remove catalyst residues, and precipitated by a large amount of methanol for three times. The final colorless oily product was dried overnight under vacuum at 50 °C.

2.3. Synthesis of azido-terminated HBPE (HBPE-N₃)

To a Schlenk flask equipped with a magnetic stirring bar, HBPE-VBC-1 (1.044 g, 5.60 × 10⁻⁵ mol), NaN₃ (0.036 g, 5.60 × 10⁻⁴ mol) and 30 mL DMF/toluene (2:3 v/v) solution were introduced under N₂. The reaction mixture was placed in an oil bath held at 80 °C. After stirring for 18 h, the polymer solution was diluted with 20 mL toluene, and washed with large amount of water. The organic layer was collected and dried over anhydrous MgSO₄. The solvent was removed under vacuum, yielding a colorless oily product.

2.4. Synthesis of HBPE-*b*-PEO

HBPE-N₃ (0.988 g, 5.30 × 10⁻⁵ mol), PEO_{2k}≡ (0.128 g, 6.40 × 10⁻⁵ mol, 1.2 equiv to azido group), CuBr (1.5 equiv to azido group) and 20 mL anhydrous toluene were added to a 50-mL Schlenk flask under N₂. The mixture was degassed through three freeze-pump-thaw cycles and then left under N₂. Degassed PMDETA (1.5 equiv to azido group) was then injected via gastight syringe. The mixture was stirred at 100 °C for 18 h in an oil bath. After reaction, the solvent was removed under vacuum. The resultant solid was dissolved in THF and precipitated into an excess of water/methanol (1:1 v/v) mixture to remove the copper catalyst and excess PEO. This dissolution/precipitation procedure was repeated until the polymer became colorless. The final product was dried overnight under vacuum at 50 °C, yielding a semitransparent viscous solid.

2.5. Synthesis of HBPE-*b*-PtBuA

The synthesis of HBPE-*b*-PtBuA was accomplished by the ATRP of *t*BuA with HBPE-VBC-2 as macroinitiator. A typical procedure [12] was started with the ratio of reagents [*t*BuA]₀/[HBPE-VBC-2]₀/[CuCl]₀/[PMDETA]₀ = 1700/1/8/8.8. HBPE-VBC-2 (5.78 × 10⁻⁵ mol), PMDETA (5.09 × 10⁻⁴ mol), *t*BuA (9.83 × 10⁻² mol), and toluene (15 mL) were placed in a 50-mL Schlenk flask under N₂ and degassed through bubbling with dry N₂ for 15 min. CuCl (4.63 × 10⁻⁴ mol) was then added to the mixture under N₂. The

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