

Synthesis and self-assembly of carbazole-based amphiphilic triblock copolymers with aggregation-induced emission enhancement



Guang Li^{a,*}, Fanfan Du^b, Hu Wang^b, Ruke Bai^{b,*}

^a School of Materials Science and Engineering, Liaocheng University, Liaocheng 252059, China

^b CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, China

ARTICLE INFO

Article history:

Received 30 September 2013

Received in revised form 12 December 2013

Accepted 15 December 2013

Available online 22 December 2013

Keywords:

Aggregation-induced emission enhancement (AIEE)

Azide polymer

“Click” chemistry

Self-assembly

Vesicles

ABSTRACT

Well-defined amphiphilic triblock copolymers with carbazole pendants (PVACB-PEG2000-PVACB) were synthesized via the combination of reversible addition–fragmentation chain transfer (RAFT) polymerization and “click” chemistry. All of the intermediate and final products were characterized using ¹H NMR, FT-IR and GPC. Cup-shaped vesicles were then fabricated via self-assembly of the carbazole-containing amphiphilic triblock copolymers in aqueous solution, which were characterized by TEM and SEM. These novel carbazole-based polymeric vesicles were found to exhibit interesting aggregation-induced emission enhancement (AIEE) characteristics compared with the fluorescence intensity of the polymers in organic solution.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Over the past decades, considerable attention has been given to the synthesis of functional polymers with well-defined architectures due to their various functions stemming from their unique structures, such as block, graft and star copolymers [1,2]. Recent progress in controlled/living radical polymerization has facilitated the precise synthesis of novel and complex polymers with predetermined molecular weights and low molecular weight polydispersities, especially block copolymers [3,4]. Due to its applicability to a wide variety of monomers and the ease of processing under various conditions, reversible addition–fragmentation chain transfer (RAFT) polymerization has been considered as one of the most versatile controlled/living radical polymerization technologies for the preparation of well-defined polymers [5–8]. Since the term “click” chemistry was coined by Sharpless and co-workers in 2001 [9], it has been extensively studied as a powerful tool for the preparation of functional polymers [10–13]. The combination of RAFT polymerization and “click” chemistry has become a facile strategy for the synthesis of polymers with novel well-defined structures [14–17].

In solution, amphiphilic block copolymers can self-assemble into micelles or vesicles [18,19], which have potential biomedical appli-

cations [20–23]. Therefore, the self-assembly of amphiphilic copolymers has attracted considerable attention in the past decades. Although research on the self-assembly of π -conjugated fluorescent polymers into spheres [24–26] has attracted much interest, their poor water solubility restricts biological applications. Fluorescent vesicles may find significant applications in cellular tracking and drug delivery due to the better water solubility and easy identification. Generally, fluorescent vesicles are prepared by encapsulation of a fluorescent dye during vesicle formation [27,28], functionalization of the vesicles with luminophores [29–31], or self-assembly of fluorescent amphiphilic copolymers [32,33]. To the best of our knowledge, there have only been a few reports [32,33] on the preparation of aqueous dispersed fluorescent vesicles via the self-assembly of fluorescent amphiphilic copolymers because organic luminophores tend to aggregate when they are dispersed in water, which often leads to self-quenching of the luminescence [34]. Recently, an aggregation-induced emission enhancement (AIEE) phenomenon [35–39], in contrast to aggregation-induced quenching, has been observed, which provides a new approach for the design and synthesis of luminophore materials. Furthermore, it is more likely that fluorescent vesicles can be prepared from amphiphilic polymers exhibiting AIEE.

Herein, we present an effective approach for the synthesis of amphiphilic triblock copolymers containing luminophores through the combination of RAFT polymerization and “click” chemistry. The block copolymers consist of a hydrophilic block of polyethylene glycol (PEG) and two hydrophobic blocks with carbazole pendants.

* Corresponding authors. Tel.: +86 635 8230919; fax: +86 635 8230831 (G. Li). Tel.: +86 551 63600722; fax: +86 551 63631760 (R. Bai).

E-mail addresses: liguang@lcu.edu.cn (G. Li), bairk@ustc.edu.cn (R. Bai).

We found that the copolymers can self-assemble to form novel cup-shaped vesicles in aqueous solution. Most importantly, aggregation of the block copolymers in water leads to the AIEE phenomenon. To the best of our knowledge, this is the first report on the preparation of AIEE fluorescent vesicles *via* the self-assembly of fluorescent amphiphilic copolymers.

2. Experimental

2.1. Materials

Polyethylene glycol ($M_n = 2000$, Fluka, Switzerland) was dried by azeotropic distillation of a solution in toluene. Styrene (Shanghai Chemical Co., China) was purified by passing through a neutral alumina column before use. Azobisisobutyronitrile (AIBN, Shanghai Chemical Co., China) was recrystallized from ethanol. N-propargyl-carbazole [40], 4-vinylbenzyl azide [41] and S-1-Dodecyl-S'-(α, α' -dimethyl- α'' -acetic acid) trithiocarbonate [42] were synthesized using previously reported methods. All other chemicals were analytical-grade reagents and were used as received.

2.2. Synthesis of a macromolecular chain transfer agent (CTA-PEG2000-CTA)

PEG2000 (2.5 g, 1.25 mmol) was dissolved in 75 mL of dichloromethane with S-1-Dodecyl-S'-(α, α' -dimethyl- α'' -acetic acid) trithiocarbonate (1.82 g, 5 mmol) and a catalytic amount of DMAP (50 mg). When the solution was homogenized by stirring, DCC (1.01 g, 5 mmol) was added in one step to the solution. After stirring at room temperature for 48 h, the dicyclohexylurea precipitate was removed by filtration. The filtrate was concentrated and precipitated with an excess of diethyl ether. The crude product was dissolved in 100 mL of dichloromethane and was successively washed with water (100 mL \times 3) at pH 9–10. After drying over anhydrous sodium sulfate for 24 h, the organic solution was concentrated and precipitated with an excess of diethyl ether. CTA-PEG2000-CTA, which is yellow in color, was obtained by filtering and drying under vacuum at room temperature for 48 h (yield = 83.5%).

2.3. Synthesis of P(4-vinylbenzyl azide)-b-PEG2000-b-P(4-vinylbenzyl azide) (PVA-PEG2000-PVA)

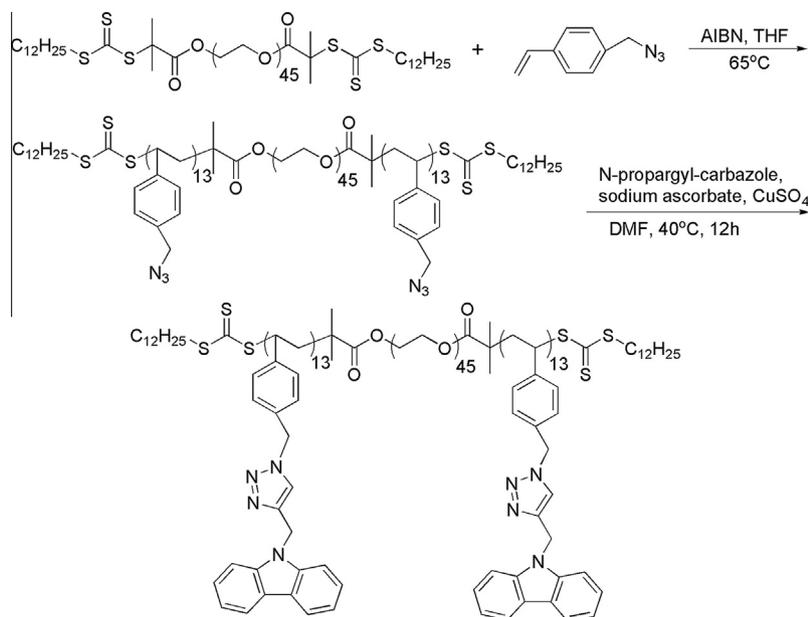
CTA-PEG2000-CTA (0.30 g, 0.11 mmol), AIBN (9.0 mg, 54.8 μ mol), 4-vinylbenzyl azide (0.66 g, 4.15 mmol) and tetrahydrofuran (1.0 mL) were placed in a glass tube. The glass tube was sealed under vacuum after degassing with three freeze–vacuate–thaw cycles and was then placed in an oil bath at 65 °C. After polymerization, the reaction mixture was precipitated in hexane. The polymer was collected by filtration and dried under vacuum at room temperature for 24 h.

2.4. “Click” reaction of PVA-PEG2000-PVA with N-propargyl-carbazole

In a typical synthetic procedure, PVA₁₃-PEG2000-PVA₁₃ (0.10 g, 0.4 mmol of azide groups) and N-propargyl-carbazole (0.15 g, 0.73 mmol) were dissolved in 3 mL of DMF. A solution of CuSO₄·5H₂O (5.7 mg, 22.8 μ mol) in 0.2 mL of water was added to the mixture, followed by the addition of a freshly prepared solution of sodium ascorbate (9.0 mg, 45.5 μ mol) in 0.2 mL of water. The mixture was heated at 40 °C overnight under an argon atmosphere. After the reaction, the solution was passed through a neutral Al₂O₃ column to remove the catalyst, using CH₂Cl₂ as the eluent. The obtained solution was then washed with an aqueous ammonia solution to remove all of the Cu^{II} trapped inside the polymer chains. After drying with anhydrous sodium sulfate for 24 h, the organic solution was concentrated and precipitated with an excess of hexane to remove the unreacted N-propargyl-carbazole. PVACB₁₃-PEG2000-PVACB₁₃, which has a light brown color, was obtained by filtering and drying under vacuum at room temperature for 24 h.

2.5. Self-assembly of PVACB-PEG2000-PVACB

In a typical preparation procedure, a round-bottom flask equipped with a stir bar was charged with 4.0 mg of PVACB₁₃-PEG2000-PVACB₁₃ and 4 mL of tetrahydrofuran (THF). The solution was stirred at room temperature for 1 h to ensure that the polymers were completely dissolved. Deionized water was added dropwise, with one drop added every 10–15 s. After 2.15 mL of water was added, aggregates



Scheme 1. Synthesis of PVACB-b-PEG2000-b-PVACB *via* RAFT polymerization and the “click” reaction.

Download English Version:

<https://daneshyari.com/en/article/5210007>

Download Persian Version:

<https://daneshyari.com/article/5210007>

[Daneshyari.com](https://daneshyari.com)