Journal of Organometallic Chemistry xxx (2016) 1–6

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Construction of ferrocene-containing nanomaterials via self-assembly of ferrocenyl hyperbranched polyethylene

Zheng Deng [a], Haojie Yu [a, *], Li Wang [a, **], Xiaoting Zhai [a], Yongsheng Chen [a], Sergey Z. Vatsadze [b]

[a] State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China
[b] Chemistry Department, Lomonosov Moscow State University, Leninskie Gory 1/3, 119991 Moscow, Russia

ARTICLE INFO

Article history:
Received 30 December 2015
Received in revised form
14 March 2016
Accepted 15 March 2016
Available online xxx

Keywords:
Multimetallic compounds
Ferrocene
Hyperbranched polyethylene
Self-assembly

ABSTRACT

Self-assembly of ferrocene-containing copolymers has been proved to be a convenient way to construct various functional nanomaterials. Thus, (hyperbranched polyethylene)-*grafted*-(poly(2-(methacryloyloxy)-ethyl ferrocenecarboxylate)) (HBPE-*g*-PFcEMA) was synthesized. It's self-assembly properties in the THF/*n*-hexane solvent mixture and *n*-hexane were explored. In the THF/*n*-hexane solvent mixture, spherical micelles were obtained at low concentration of HBPE-*g*-PFcEMA. However, at higher concentration, only irregular nanoparticles were observed. In contrast, the HBPE-*g*-PFcEMA micelles prepared in *n*-hexane by solvent diffusion method were with well-defined structures whether at low or high concentration of HBPE-*g*-PFcEMA. Furthermore, the nanostructures of these assemblies in *n*-hexane could be controlled to be sheet, hollow or patchy sphere simply by adjusting the concentration of HBPE-*g*-PFcEMA. Therefore, a novel and convenient way was provided to construct ferrocene-containing nanomaterials with various nanostructures from the same ferrocenyl hyperbranched copolymer by controlling its concentration. These ferrocene-containing nanomaterials might find their application as precursor in preparing functional iron oxide nanomaterials.

1. Introduction

Well-defined functional nanomaterials have attracted significant interest in the past decades, due to their potential applications in biomedicine [1,2], optoelectronic [3] and energy devices [4] etc. The self-assembly of block copolymers has been proved to be an efficient way to construct various complex nanomaterials including spherical, cylindrical or wormlike micelles, and vesicles etc. [5–7] by changing their molecular weight and composition. In particular, the ferrocene-containing block copolymers (FcBCP) have been widely adopted to prepare functional nanomaterials because of their redox and electro-chemical properties [8,9].

FcBCP can be briefly classified into main-chain and side-chain FcBCP according to the position of ferrocene in the polymer chain [10]. The self-assembly properties of main-chain FcBCP, mainly polyferrocenylsilane (PFS)-based block copolymers, have been extensively studied by Manners and Winnik et al. [11]. They found that PFS formed cylindrical micelles in the selective solvent by a crystallization-driven living self-assembly method. Epitaxial growth from the crystalline micelles ends on further addition of unimers was revealed. By this method, various well-defined micelles/co-micelles with different structures were prepared [12–15]. However, the polyferrocenylsilane-based polymers were mainly synthesized by anionic, cationic, and photolytic anionic ring-open polymerization methodologies [16], which imposed obstacles in their applications because of the harsh preparation condition required.

In contrast, well-defined side-chain FcBCP can be synthesized in an easier way termed as controlled radical polymerization (e.g. atom transfer radical polymerization (ATRP) and reversible addition fragmentation chain transfer (RAFT) polymerization etc.) [10,17]. The self-assembly properties of side-chain FcBCP in selective solvents were also studied. Selection of solvents plays a crucial role in the self-assembly of side-chain FcBCP. In general, a good solvent for both blocks is required to dissolve the FcBCP totally. Then, the self-assembly is induced in the selective solvent, which is

---

* Corresponding author.
** Corresponding author.

E-mail addresses: dz0909@qq.com (Z. Deng), hjyu@zju.edu.cn (H. Yu), opl_wl@dial.zju.edu.cn (L. Wang), 1052204961@qq.com (X. Zhai), josephchan0314@gmail.com (Y. Chen), szv@org.chem.msu.ru (S.Z. Vatsadze).

http://dx.doi.org/10.1016/j.jorganchem.2016.03.016
0022-328X/© 2016 Elsevier B.V. All rights reserved.

Please cite this article in press as: Z. Deng, et al., Journal of Organometallic Chemistry (2016), http://dx.doi.org/10.1016/j.jorganchem.2016.03.016

a good solvent for only one of the blocks. In aqueous systems, the ferrocene-containing segment was usually utilized as a water-insoluble core while other common water-soluble polymers such as poly(ethylene oxide)/poly(ethylene glycol) [18–22], poly(*N*,*N*-diethylacrylamide) [23] and poly(2-vinylpyridine) [24] etc. were used as water-swollen shell. The redox properties of ferrocene moieties endowed the FcBCP self-assembled micelles with redox-responsive properties [18,25,26], which could be employed for selective release of the hydrophobic payloads [27,28].

In organic solvent systems, the ferrocene-containing segment can be utilized as either solvent-insoluble core or solvent-soluble shell depended on the solubility of the second block and the solvent selected. Tang et al. synthesized cobaltocenium and ferrocene heterobimetallic diblock copolymer poly(2-(methacrylolyoxy)ethyl cobaltoceniumcarboxylate hexafluorophosphate)-*b*-poly(2-(methacrylolyoxyl)ethyl ferrocenecarboxylate) (PMAECoPF$_6$-*b*-PMAEFc) via sequential RAFT polymerization. Dimethyl formamide (DMF) was found to be a good solvent for both PMAECoPF$_6$ and PMAEFc blocks. However, only PMAECoPF$_6$ was soluble in acetonitrile (MeCN) while only PMAEFc was soluble in tetrahydrofuran (THF). Hence, spherical micelles of PMAECoPF$_6$-*b*-PMAEFc were obtained in DMF/MeCN (ferrocene in the core) and DMF/THF (ferrocene in the shell), which were used as precursors to prepare nanostructured cobalt/iron hybrid materials [29,30]. Gallei and Frey et al. synthesized poly(vinylferrocene)-*b*-poly(lactide) (PVFc-*b*-PLA) diblock and miktoarm star polymers respectively. Compared with PLA, the PVFc block was poorly soluble in CH$_2$Cl$_2$. Thus, spherical micelles were obtained in CH$_2$Cl$_2$ successfully with a ferrocene-containing core for both of the linear block copolymers and star-shaped copolymers [31]. However, to the best of our knowledge, the self-assembly properties of ferrocene-containing hyperbranched copolymer, which have found their applications in anionic ion recognition [32], burning rate catalyst [33] and carbon nanomaterials synthesis [34], in selective organic solvent have not been explored.

Herein, the ferrocene-containing hyperbranched polyethylene (HBPE-*g*-PFcEMA) was synthesized by combining the chain walking copolymerization with ATRP. The self-assembly behavior of HBPE-*g*-PFcEMA was explored in both of the THF/*n*-hexane solvent mixture and *n*-hexane, in which PFcEMA was insoluble but HBPE was soluble. Several interesting nanostructures were obtained simply by controlling the concentration of HBPE-*g*-PFcEMA. These self-assembled nanostructures might be utilized as procures in preparing iron oxide nanomaterials.

2. Experimental details

2.1. Materials and methods

All manipulations that involving moisture- or air-sensitive chemicals were conducted using Schlenk techniques. Pd-diimine catalyst [35], 2-(2-bromoisobutyryloxy) ethyl acrylate (BIEA) [36] and 2-(methacryloyloxy)-ethyl ferrocenecarboxylate (FcEMA) [32,37] were synthesized according to the literature. 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, 98%) and Copper (I) bromide (CuBr, 98%) were purchased from J&K Scientific Ltd. Dichloromethane (CH$_2$Cl$_2$, AR), anisole (AR), tetrahydrofuran (THF, AR) and *n*-hexane (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. CuBr was purified according to the literature [38]. CH$_2$Cl$_2$ was dried with activated 4A- type molecular sieve followed by distillation over calcium hydride prior to use. Other chemicals were used without further purification.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker Avance III 400 NMR spectrometer using CDCl$_3$ as solvent. Fourier transform infrared (FT-IR) spectra were recorded on Nicolet 5700. Gel permeation chromatography (GPC) was performed on a Waters Wyatt GPC instrument with a light scattering (LS) detector. Differential scanning calorimetry (DSC) curves were obtained from TA-Q200 at a heating rate of 10 °C/min. Transmission electron microscopy (TEM) images were taken with Hitachi HT-7700 TEM. Scanning electron microscope (SEM) images were taken with Hitachi SU-8010 SEM.

2.2. Synthesis of HBPE-g-PFcEMA

HBPE-g-PFcEMA was synthesized according to our previous paper with minor modification [33]. Typically, the hyperbranched polyethylene macro-initiator (HBPE-Br) was firstly synthesized by chain walking copolymerization of ethylene with BIEA in CH$_2$Cl$_2$ with a Pd-diimine catalyst at 25 °C under ethylene pressure of 1 atm. Then, HBPE-Br was utilized as macro-initiator for the ATRP of FcEMA in anisole at 90 °C for 6 h. The mole ratio of [monomer]:[CuBr]:[PMDETA]:[Br] was 300:5:5:1. The ^{1}H NMR data of HBPE-g-PFcMEA were summarized as follow [33]: $\delta = 4.84$ ppm (*s*, 2H, Hd), 4.43 ppm (*s*, 4H, Hc), 4.36 ppm (*s*, 2H, He), 4.22 ppm (*s*, 5H, Hf), 1.97 ppm (*br. s*, 2H, Ha), 1.26 ppm (methylene), 1.22 ppm (methine) 1.12, 1.00 ppm (*s*, 3H, Hb) and 0.88, 0.83 ppm (methyl). The FT-IR data of HBPE-g-PFcEMA were ascribed as follow [33,39]: 3097 cm^{-1} ($\nu_{(C-H)}$, ferrocene), 2926, 2854 cm^{-1} ($\nu_{(C-H)}$, $-CH_3$, $-CH_2-$), 1716 cm^{-1} ($\nu_{(C=O)}$), 1461 cm^{-1} ($\delta_{(C-H)}$, $-CH_2-$, $-CH_3$), 1377 cm^{-1} ($\delta_{s\ (C-H)}$, $-CH_3$), 1277 cm^{-1} ($\nu_{(C-O)}$, $-(C=O)-O$) and 1135 cm^{-1} ($\nu_{(C-O)}$, $R-C-O-$). 1053, 1026, 822 cm^{-1} ($\tau_{(C-H)}$, ferrocene).

2.3. Self-assembly of HBPE-g-PFcEMA in the solvent mixture of THF/n-hexane

A series of HBPE-g-PFcEMA/THF solution with different concentration were prepared by dissolving a certain amount of HBPE-g-PFcEMA in THF at room temperature. In six 10 mL vials equipped with stir bars, 2.0 mL HBPE-g-PFcEMA/THF solution with certain concentration was added individually. Then, 2.0 mL *n*-hexane was added drop-wise into each vial. The resultant mixtures, in which the concentration of HBPE-g-PFcEMA was varied from 0.1 to 10.0 mg/mL, were stirred vigorously for 30 min and then left undisturbed for another 30 min. The obtained solution was used for further analysis.

2.4. Self-assembly of HBPE-g-PFcEMA in n-hexane

A series of HBPE-g-PFcEMA/THF solution with different concentration were prepared by dissolving a certain amount of HBPE-g-PFcEMA in THF at room temperature. In six 10 mL vials equipped with stir bars, 2.0 mL HBPE-g-PFcEMA/THF solution with certain concentration was added individually. Then, 2.0 mL *n*-hexane was added drop-wise into each vial. The resultant mixtures, in which the concentration of HBPE-g-PFcEMA was varied from 0.1 to 10.0 mg/mL, were stirred vigorously for 30 min. Then, the mixtures were transferred into a dialysis tube (MWCO = 8000–14,000 Da) and dialyzed against *n*-hexane respectively. During dialysis, fresh *n*-hexane was replaced about every 6 h. After 2 days, the HBPE-g-PFcEMA micelles were formed, and the micellar solution was collected for further analysis.

3. Results and discussion

3.1. Synthesis and characterization of HBPE-g-PFcEMA

As shown in Scheme 1, the HBPE-g-PFcEMA with a core-shell structure was synthesized in two steps according to our previous

Please cite this article in press as: Z. Deng, et al., Journal of Organometallic Chemistry (2016), http://dx.doi.org/10.1016/j.jorganchem.2016.03.016