



Synthesis of ferrocenyl functionalized hyperbranched polyethylene and its application as low migration burning rate catalyst



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ABSTRACT

Ferrocene based burning rate catalysts (BRCs) play an important role in the solid rocket propellants. However, the migration problem during curing and storage limits their application in the solid rocket propellants. To tackle this problem, the ferrocenyl functionalized hyperbranched polyethylene (HBPE-g-PFcEMA) with high molecular weight was synthesized as low migration BRCs. HBPE-g-PFcEMA was characterized by ¹H NMR, FT-IR, GPC and XPS. The electrochemical properties of HBPE-g-PFcEMA were evaluated by cyclic voltammetry. TGA results revealed that the HBPE-g-PFcEMA was quite stable under 210 °C. The catalytic efficiency of HBPE-g-PFcEMA for thermal decomposition of ammonium perchlorate (AP) was evaluated by TGA method. When 17 wt% of HBPE-g-PFcEMA was added, the final decomposition temperature of AP was decreased dramatically from 417 °C to 339 °C and the maximum weight loss temperature of AP was decreased from 408 °C to 328 °C. The migration property of HBPE-g-PFcEMA was studied and compared with ferrocene. Ferrocene migrated out of the migration tube after 6 days storage while the HBPE-g-PFcEMA only showed little migration even after 31 days storage at 50 °C. Therefore, the HBPE-g-PFcEMA was a low migration BRC with high catalytic efficiency for thermal decomposition of AP, which might find its application in aerospace.

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1. Introduction

Burning rate catalysts (BRCs) are one of the significant ingredients in the solid rocket propellants, which play an important role in enhancing the burning rate of the propellants to provide enough driving force for the rocket [1]. In order to achieve a stable burning rate and provide a low pressure exponent to the propellants, various BRCs have been developed including nano-metal particles [2–4], metal chelates [5], transition metal oxides [6,7] and ferrocene derivatives [8–10]. Among these, ferrocene derivatives such as tert-butylferrocene, 2,2-bis(ethylferrocenyl)propane and n-butylferrocene etc. [11] have been commonly used due to their good catalytic performance, facile preparation, and good compatibility with organic binders [12]. However, these ferrocene derivatives are small molecule and volatile. Thus, they tend to migrate to the surface of the propellants during curing and storage, which may damage the propellants [13,14].

To solve this migration problem, specially designed ferrocene based BRCs, such as ferrocene-containing polymers [15], polar groups functionalized ferrocene compounds [10] and ionic ferrocene compounds [11] were developed. Among these, ferrocene-containing polymers attracted significant interest, due to their excellent thermal stability, catalytic properties, and anti-migration properties [16,17]. Gao et al. synthesized both the main- and side-chain ferrocene-containing linear polymers as BRCs [15], and they found that these ferrocene-containing linear polymers were low migration BRCs with excellent catalytic efficiency for thermal decomposition of ammonium perchlorate (AP). Compared with ferrocene-containing linear polymers, the ferrocene-containing dendrimer and hyperbranched polymers were considered as better low migration BRCs attributed to their special architecture, such as with plenty of terminal groups and inner cavities. Xiao et al. synthesized a series of ferrocenyl functionalized polyester dendrimers, and they found that the functionalized dendrimers showed excellent catalytic performance for thermal decomposition of AP [18]. Hyperbranched polymer is the mimics of dendrimer which can be synthesized in an easier way while possess the good properties of dendrimer. Thus, Xiao et al. synthesized a series of ferrocenyl terminated hyperbranched polyether and poly(amine)

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ester [19–21]. Later, Sun et al. synthesized a novel ferrocenyl functionalized hyperbranched polyether by self-condensing ring opening polymerization [22]. Those ferrocenyl functionalized hyperbranched polymers were all found to be efficient BRCs.

However, in these cases, although these ferrocenyl functionalized hyperbranched polymers exhibited good catalytic efficiency, their molecular weights were low (less than 8000 g/mol) and their migration properties were not elaborate clearly. Considering that the ferrocenyl functionalized polymers with higher molecular weight may have greater resistance to migrate in the solid propellant [13], therefore, synthesis of ferrocenyl functionalized hyperbranched polymer with high molecular weight may provide a new direction to prepare better low migration BRCs.

Hyperbranched polyethylene (HBPE), which is synthesized via Pd-diimine catalyzed chain walking polymerization (CWP), is well-known for its highly branched even branches on branches structure [23]. The combination of CWP and atom transfer radical polymerization (ATRP) provide a convenient way to synthesize various functionalized HBPE [24,25]. Among these, the ferrocenyl functionalized HBPE attracted significant attentions due to their unique electrochemical and catalytic properties [26,27]. Xiao et al. synthesized the ferrocenyl functionalized HBPE via sequential Pd-diimine catalyzed CWP and ATRP process, and they found that the ferrocenyl functionalized HBPE exhibited good recognition ability of H_2PO_4^- [28]. Furthermore, the ferrocenyl functionalized HBPE was found to be an efficient catalyst for the synthesis of carbon nanomaterials [29].

Herein, ferrocenyl functionalized hyperbranched polyethylene (HBPE-g-PFcEMA) with high molecular weight was synthesized as low migration BRCs via Pd-diimine catalyzed CWP followed by ATRP. The HBPE-g-PFcEMA was characterized by ^1H NMR, GPC, FT-IR and XPS. Its electrochemical property and thermal stability were studied. Furthermore, the catalytic efficiency and migration property of HBPE-g-PFcEMA were evaluated.

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 [30], 2-(2-bromoisobutyryloxy) ethyl acrylate (BIEA) [31] and 2-(methacryloyloxy)-ethyl ferrocenecarboxylate (FcEMA) [28] were synthesized according to the literature. Copper (I) bromide (CuBr, 98%) was obtained from J&K Scientific Ltd and was purified according to the literature [32]. 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, 98%) was obtained from J&K Scientific Ltd. Anisole (AR), tetrahydrofuran (THF, AR) and anhydrous methanol (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Hydroxyl-terminated polybutadiene (HTPB, technical grade) was purchased from China Haohua Chemical Group Co., Ltd. Isophorone diisocyanate (IPDIC, AR) and ammonium perchlorate (AP, AR) were purchased from Aladdin. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker Avance-400 DMX NMR spectrometer using CDCl_3 as solvent. Gel permeation chromatography (GPC) was performed on a Waters Wyatt GPC instrument with a differential refractive index (DRI) detector using polystyrene as standard. Fourier transform infrared (FT-IR) spectra were recorded on Nicolet 5700. X-ray photoelectron spectroscopy (XPS) spectra were acquired with a VG ESCALAB MARK II XPS system. Cyclic voltammograms were recorded with a CHI660A analyzer. A platinum working electrode and an Ag/Ag^+ reference electrode were used. The concentration of HBPE-g-PFcEMA and $n\text{-Bu}_4\text{PF}_6$ in CH_2Cl_2 were 0.5 mg/mL and 0.1 mol/L respectively. Thermogravimetric analysis (TGA) was

performed on TA-Q500 at a heating rate of 10 °C/min in nitrogen atmosphere.

2.2. Synthesis of HBPE-g-PFcEMA

HBPE-g-PFcEMA was synthesized by combining the Pd-diimine catalyzed CWP with ATRP. The hyperbranched polyethylene macro-initiator (HBPE-Br, $M_n = 17.9$ kg/mol, branching density = 104 branches/1000C and initiating site = 13.6 sites/mol) was synthesized by chain walking copolymerization of ethylene with BIEA according to the previously reported literature [24]. Then, HBPE-Br was utilized as macro-initiator for the ATRP of FcEMA. The typical ATRP procedure was described as follow [28]. FcEMA (0.95 g, 2.78 mmol, 300 equiv.) was dissolved in 4.0 mL anisole in a 10.0 ml Schlenk flask equipped with a stirring bar. The FcEMA/anisole solution was degassed by three freeze–pump–thaw cycles and finally filled with argon gas. A deoxygenated solution of $[\text{Cu}^{\text{I}}(\text{PMDETA})\text{Br}]$ (0.2 M, 0.046 mmol, 5 equiv.) in anisole was added into the Schlenk flask via syringe. The resulting mixture was heated to 90 °C and the polymerization was initiated by addition of deoxygenated HBPE-Br/anisole solution (0.013 M, 0.0092 mmol (mole of initiating site), 1 equiv.). The polymerization was quenched using liquid nitrogen after 8 h. The copper complex was removed by passing through a short neutral alumina column. The resultant solution was then concentrated and precipitated in methanol. The crude product was further purified by three precipitation (in methanol) and dissolution (in THF) cycles. The final orange powder was dried under vacuum at 35 °C for 48 h. The ^1H NMR data of HBPE-g-PFcEMA were summarized as follow: $\delta = 4.83$ ppm (s, 2H, Hd), 4.42 ppm (s, 4H, Hc), 4.36 ppm (s, 2H, He), 4.20 ppm (s, 5H, Hf), 1.87, 1.57 ppm (br. s, 2H, Ha), 1.26 ppm (methylene), 1.23 ppm (methine) 1.13, 1.01 ppm (s, 3H, Hb) and 0.88, 0.85 ppm (methyl).

2.3. Preparation of the samples for thermogravimetric analysis measurement

The samples of AP/HBPE-g-PFcEMA mixture with HBPE-g-PFcEMA content varied from 0 to 17 wt% for TGA measurement were prepared by grinding the mixture carefully in an agate mortar. Then, the mixture was dried under vacuum at 35 °C for 24 h before being sent for TGA measurement.

2.4. Migration studies

In order to study the migration behavior of the HBPE-g-PFcEMA, the HBPE-g-PFcEMA migration tube was prepared according to the previously reported process with a few modification [13,15]. The typical procedure was described as follow: HBPE-g-PFcEMA (57.0 mg) and AP (2.8220 g) were mixed together in a 25 mL beaker. Then, the binder (HTPB, 0.45 mL) and crosslinker (IPDIC, 0.3 mL) were added. The resulting mixture was stirred vigorously, and the yellow sludge-like mixture was finally obtained. The obtained mixture (AP/HTPB/IPDIC/HBPE-g-PFcEMA) was all packed into a glass tube (length: 65 mm, outer diameter: 10 mm, thickness: 0.5 mm), and the end of the tube was then filled with AP/HTPB/IPDIC mixture. As a contrast, the ferrocene migration tube was prepared in a similar way. The two migration tubes were then placed in the oven at 50 °C for further migration study.

3. Results and discussion

3.1. Synthesis and characterization of HBPE-g-PFcEMA

HBPE-g-PFcEMA was synthesized by CWP of ethylene with BIEA followed by ATRP of FcEMA (Scheme 1). The chemical structure of

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