



## Regular Article

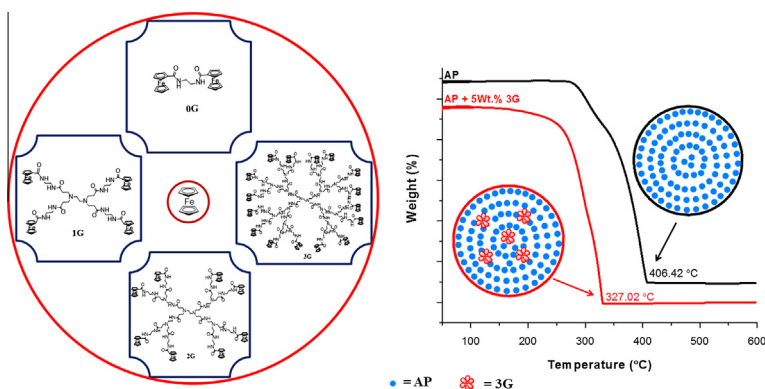
## Synthesis of ethylene diamine-based ferrocene terminated dendrimers and their application as burning rate catalysts



Zain-ul-Abdin, Li Wang\*, Haojie Yu\*, Muhammad Saleem, Muhammad Akram, Hamad Khalid, Nasir M. Abbasi, Xianpeng Yang

State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 16 July 2016

Revised 26 September 2016

Accepted 2 October 2016

Available online 4 October 2016

## Keywords:

Ferrocene terminated dendrimers

Electrochemical properties

Ammonium perchlorate

Anti-migration behavior

Burning rate catalysts

## ABSTRACT

Ferrocene-based derivatives are widely used as ferrocene-based burning rate catalysts (BRCs) for ammonium perchlorate (AP)-based propellant. However, in long storage, small ferrocene-based derivatives migrate to the surface of the propellant, which results in changes in the designed burning parameters and finally causes unstable combustion. To retard the migration of ferrocene-based BRCs in the propellant and to increase the combustion of the solid propellant, zero to third generation ethylene diamine-based ferrocene terminated dendrimers (**0G**, **1G**, **2G** and **3G**) were synthesized. The synthesis of these dendrimers was confirmed by  $^1\text{H}$  NMR and FT-IR spectroscopy. The electrochemical behavior of **0G**, **1G**, **2G** and **3G** was investigated by cyclic voltammetry (CV) and the burning rate catalytic activity of **0G**, **1G**, **2G** and **3G** on thermal disintegration of AP was examined by thermogravimetry (TG) and differential thermogravimetry (DTG) techniques. Anti-migration studies show that **1G**, **2G** and **3G** exhibit improved anti-migration behavior in the AP-based propellant.

© 2016 Elsevier Inc. All rights reserved.

## 1. Introduction

Composite solid propellants are the energy sources, which are used in rocket motors for the propulsion of launch vehicles [1,2].

Usually, propellants consist of an inorganic oxidizer, ammonium perchlorate (AP), metallic fuel (aluminum), binder (hydroxyl terminated polybutadiene (HTPB)) and a small amount of other constituents such as plasticizer, curing agent, stabilizers and burning rate catalysts (BRCs) [3]. Various kinds of BRCs like nano-metal particles, transition metal oxides, metal chelates and ferrocene-based derivatives have been used for AP-based propellants [4–6].

\* Corresponding authors.

E-mail addresses: [opl\\_wl@dia.zju.edu.cn](mailto:opl_wl@dia.zju.edu.cn) (L. Wang), [hjyu@zju.edu.cn](mailto:hjyu@zju.edu.cn) (H. Yu).

Among these BRCs, ferrocene-based derivatives received much attention due to their good ignitability in the propellant, microscopic homogeneities in distribution [7,8] and good compatibility with organic binder [9–11].

Small ferrocene-based derivatives exhibit intrinsic disadvantages as BRCs, such as their migration to the surface of the solid propellant in long-time storage and sublimation or evaporation loss during processing [12]. These disadvantages result in irreproducible properties, such as poor aging of the propellant [13,14], which alter the designed burning parameters, reduces service life and may cause surprise ignition [15]. The burning rate properties of ferrocene-based polymers and derivatives depend on their chemical structures, miscibility, mobility and effective Fe contents [16]. The best known ferrocene-based BRCs are *n*-butyl ferrocene (NBF), *tert*-butyl ferrocene (TBF) and 2,2-bis[(ethylferrocenyl)propane] (catocene). [17,18] However, NBT and TBF exhibit migration problems due to the short carbon chain on ferrocene and their low molecular weight. Catocene was then prepared to overcome migration problems [19–21]. Though, these drawbacks have not been overcome obviously and after long-time storage, catocene still showed obvious migration to surface of the propellant [18]. Therefore, the study on migration is still continued to find cheap and effective way to overcome these problems.

Ferrocene terminated dendrimers are a class of functionalized-materials, which have received much attention of the scientists due to their special topology, low viscosity, high molecular weight good catalytic behavior and redox properties [22–24]. However, the incorporation of ferrocene into the dendrimers is a challenge, as ferrocene terminated dendrimers show distinctive redox behavior of ferrocene and high thermal stability. It has been found that grafting of ferrocene onto the dendrimers [25] is the one of the effective ways to retard the migration of the BRCs in the solid propellant and to increase its burning rate. Xiao and co-workers synthesized ferrocene functionalized polyester and amine ester dendrimers as ferrocene-based BRCs [3,14,26], showing good burning rate catalytic properties on thermal decomposition of AP-based propellant but on prolonged storage, they showed obvious signs of migration to the interface of the propellant. We have designed ferrocene terminated dendrimers containing large number of oxygen and nitrogen especially N–H groups. Perhaps, the existence of large number of oxygen atoms attached with carbonyl groups and (N–H) groups results in improved anti-migration properties of the ferrocene terminated dendrimers.

Here, we synthesized zero to third generation ethylene diamine-based ferrocene terminated dendrimers (**0G**, **1G**, **2G** and **3G**) by Michael addition reaction [27,28] followed by the reaction with ethylene diamine and then by the condensation reaction with ferrocene monocarbonyl chloride. An understanding of the electrochemical properties of ferrocene terminated dendrimers is very important, when identifying their potential applications. Generally, redox processes involve the gain and loss of electrons, while combustion of the propellant also involves transfer of electrons. Therefore, the electrochemical properties of **0G**, **1G**, **2G** and **3G** were investigated by cyclic voltammetry (CV). The catalytic behavior of **0G**, **1G**, **2G** and **3G** on thermal decomposition of AP was studied by thermogravimetry (TG) and differential thermogravimetry (DTG). Anti-migration properties of **1G**, **2G** and **3G** in comparison to ferrocene and catocene were also investigated.

## 2. Experimental

### 2.1. Materials

Ethylene diamine, methyl acrylate, methanol, petroleum ether and pyridine were obtained from Sinopharm-Chemical Reagent

Co., Ltd. and used after drying with molecular sieves (4 Å-type). Dichloromethane (DCM), tetrahydrofuran (THF) and triethyl amine (TEA) were also obtained from Sinopharm-Chemical Reagent Co., Ltd. and used after drying with molecular sieves (4 Å-type) followed by reflux. Ferrocenemonocarboxylic acid, oxalyl chloride and NaHCO<sub>3</sub> were obtained from Sinopharm-Chemical Reagent Co., Ltd. and used as received. Tetrabutylammonium tetrafluoroborate (Bu<sub>4</sub>NBF<sub>4</sub>) was obtained from J & K Co., Ltd. and ammonium perchlorate (AP), hydroxyterminated polybutadiene and isophorone diisocyanate were obtained from Aladdin Co., Ltd. and used as received.

### 2.2. Synthesis

#### 2.2.1. Ferrocenemonocarbonyl chloride

Ferrocenemonocarbonyl chloride was prepared by the substitution reaction of ferrocene-monocarboxylic acid with oxalyl chloride in freshly distilled dichloromethane (DCM) using pyridine as a catalyst. Typically, ferrocenemonocarboxylic acid (20.7140 g, 83.92 mmol) was dried at 40 °C under reduced pressure for about 4 h. The freshly dried ferrocenemonocarboxylic acid was dissolved in 150 mL DCM. Pyridine (14.5 mL) was added to ferrocenemonocarboxylic acid solution and the resulting solution stirred at room temperature (25 °C) for about 15 min. Oxalyl chloride (15.5 mL, 180.72 mmol) was dropwise added to ferrocenemonocarboxylic chloride solution prepared in DCM at room temperature. The resulting mixture was again stirred for 30 min at 25 °C and then it was refluxed for 6 h. Solvent (DCM), extra amount of pyridine and oxalyl chloride were evaporated under reduced pressure and then the obtained residue was extracted with 200 mL of petroleum ether at 90 °C to get ferrocenemonocarbonyl chloride. The obtained product was stored under Ar atmosphere.

#### 2.2.2. Ethylene diamine-based amine terminated dendrimers

Ethylene diamine-based amine terminated dendrimers (**0.75G**, **1.75G** and **2.75G**) were synthesized by the Michael addition reaction followed by the reaction with ethylene diamine [28]. The synthesis of **0.5G**, **1.5G** and **2.5G** was the same. So, synthesis of **0.5G** is taken as an example. Typically, ethylene diamine (4.00 mL, 59.90 mmol) was dissolved in 40 mL methanol in an ice bath under Ar gas. Methyl acrylate (108.56 mL, 1198.00 mmol) was dropwise added in the ethylene diamine solution. The resulting solution was stirred at 0 °C for 1 h. Afterward, the resulting solution was stirred at 25 °C for 2 days. The solvent and excess amount of methyl acrylate was evaporated on a rotary evaporator at 50 °C yielding the final product.

The synthesis of amine-terminated dendrimers (**0.75G**, **1.75G** and **2.75G**) was the same. So, synthesis of **0.75G** is taken as an example. Typically, **0.5G** (29.0560 g, 71.88 mmol) was dissolved in 40 mL methanol in an ice bath under Ar atmosphere. Ethylene diamine (28.80 mL, 431.28 mmol) was dropwise added in **0.5G** solution prepared in methanol. The resulting solution was stirred at 0 °C for 1 h. Afterward, the resulting solution was stirred at 25 °C for 2 days. The solvent with any excess ethylene diamine was evaporated on a rotary evaporator at 70 °C yielding the final product.

#### 2.2.3. Ethylene diamine-based ferrocene terminated dendrimers

Ethylene diamine-based ferrocene terminated dendrimers (**0G**, **1G**, **2G** and **3G**) were synthesized by the condensation reaction of ethylene diamine, **0.75G**, **1.75G** and **2.75G** with ferrocenemonocarbonyl chloride in freshly distilled DCM. The synthesis of **0G**, **1G**, **2G** and **3G** was the same. So, synthesis of **0G** is taken as an example. Typically, ethylene diamine (0.800 mL, 11.98 mmol) was dried under vacuum. The dried ethylene diamine was dissolved in 60 mL DCM. A solution of ferrocenemonocarbonyl chloride

Download English Version:

<https://daneshyari.com/en/article/4985417>

Download Persian Version:

<https://daneshyari.com/article/4985417>

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