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# Multistep pyrolysis behavior of core-shell type hyperbranched azide copolymer: Kinetics and reaction mechanism *via* experiment and simulation

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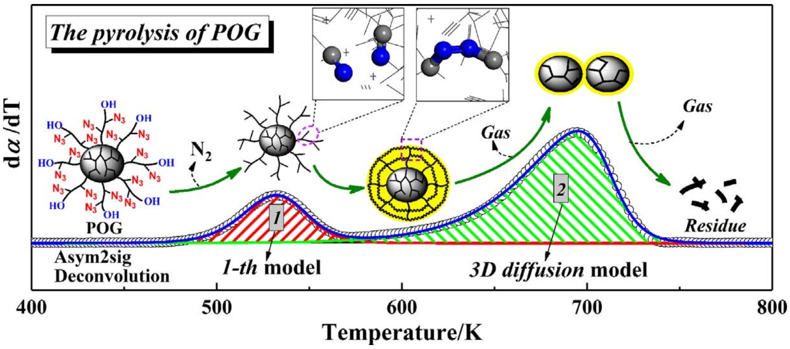
## GRAPHICAL ABSTRACT



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## ABSTRACT

As an attractive new energetic fuel, core–shell type hyperbranched azide copolymer (POG) have been investigated with regard to its pyrolysis kinetics and mechanism. Through Asymmetric Double Sigmoidal (Asym2sig) function deconvolution, POG pyrolysis profiles could be separated into two reactions well (the first and second step). Based on reasonable kinetics analysis methods, mechanism functions of the first and second step reactions were constructed to *n*-th order reaction model of $f_1(\alpha_1) = (1-\alpha_1)^{1.05}$ and 3D diffusion model of $f_2(\alpha_2) = 1.95(1-\alpha_2)^{2/3}[1-(1-\alpha_2)^{1/3}]^{-0.54}$. The gaseous products and residual morphology in different pyrolytic steps are identified by TG-FTIR-MS and SEM. Through molecular simulation, the intermediate reactions between the first and second step were successfully captured, and then the detailed pyrolysis mechanism of POG was established. In the initial stage of POG pyrolysis, thermal cracking of $-N_3$ generates nitrenes and releases $N_2$ (fitting *n*-th order model). Next, the intermolecular crosslinking and intramolecular cyclization reactions of nitrenes form a new cross-linked layer on the outside of hyperbranched polyether core of POG (PEHO-*c*), delaying the decomposition of inner PEHO-*c*. Furthermore, pyrolysis of cross-linked layer and PEHO-*c* is gradually performed by 3D diffusion model from outside to inside, which is very suitable for 3D core-shell structure of POG.

## 1. Introduction

Azide polymers have received extensive attention and been the subject of much research because of the azido groups which can release additional heat and provide a higher temperature and specific impulse on combustion as a component of high-energy fuel [1], such as glycidyl azide polymers (GAP) [2–4], poly(3-azidomethyl-3′-methyl oxetane) (PAMMO) [5,6], poly (3,3′-bis-azidomethyl oxetane) (PBAMO) [7,8], as

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well as corresponding copolymers [9–13]. GAP, as a typical representative, is considered as a kind of perfect materials to be used as the fuel binder of composite propellants and solid fuel of hybrid rocket and ducted rocket [14] due to its high density, low sensitivity, low characteristic signals, high energetic level, *etc*. [7,15,16]. Nevertheless, GAP exhibits poor low-temperature properties because of the bulky side group and low molecular weight, that reduce backbone flexibility [17], consequently, limiting its development and application to some extent. To improve these problems, we have successfully prepared core-shell type multi-arm azide copolymer (POG) based on typical three-dimensional (3D) hyperbranched polyether core and GAP shell, which possesses some noticeable properties (higher molecular weight, lower glass transition temperature and viscosity) in comparison with common linear GAP [18]. In the ongoing studies, we are initially finding that they can provide good practical performances in casting and extruding solid propellants as binder or additive. These characteristics mean that POG is promising compounds regarding potential application as novel energetic materials.

Pyrolysis behavior of thermal hazard substance plays a crucial role in burning rate, gas production performance, and safe characteristics for propellants [19], especially for new energetic material. At present, the thermal kinetics and pyrolysis mechanisms of linear GAP or its derivatives have been widely studied. It is generally accepted that their thermal decomposition could be mainly divided into two stages [20–22]: Firstly, the azido groups rupture and produce energy, and secondly, polyether backbone can be broken down at higher temperature. In Chen's literature, its thermal decomposition behaviors were investigated in nitrogen, which indicated the activation energy is *ca* 146 kJ/mol and the *n-th* kinetic model is suitable for the first step reaction [23]. Tang and co-workers submitted that the decomposition of GAP at atmospheric pressure in argon was dominated by the condensed phase chemistry and few reactions occurred in the gas phase [24]. Wang et al. [1] investigated the details of thermal decomposition reactions and products of GAP at low pressure. It is observed that the pyrolysis began at *ca* 70 °C and some free radicals, such as $C_2H_3O$, $C_3H_5O$, $C_6H_6O$, were detected. Furthermore, they discussed the formation mechanisms of some important radicals and proposed the most probable reaction routines. Recently, a few researchers have focused their attention on the decomposition behavior of GAP derivatives due to much better practical applications than that of GAP homopolymer. The pyrolysis behaviors of energetic thermoplastic elastomer based on GAP or PBAMO/GAP were examined, and relatively kinetics parameters and reaction mechanisms of azido-groups decomposition were confirmed [17,25]. Zhao et al. [13] studied the thermal decomposition behavior of BAMO-GAP and BAMO-GAP/nano-CuO using DSC-TG-FTIR-MS coupling technique and identified their major gaseous products. It was suggested that nano-CuO enhanced the N—N bond breaking in azido groups and more $N_2$ was released. Huang and co-workers synthesized a new fullerene-GAP (C60-GAP), and found that C60-GAP decomposition showed complex three-step thermal process [26]. From the above literatures, we can observe that the decomposition of GAP involves a complex process, especially, the copolymer of GAP and other compounds. Consequently, pyrolysis kinetics of GAP or its derivatives are generally investigated only in the stage of azido-group decomposition due to the complex multistep overlapping process [13,17,25,27,28]. Although the pyrolysis mechanisms of GAP have been preliminary confirmed by deducing based on the pyrolytic products detected using different methods and devices, there is no direct and valid evidence for the intermediate reaction process, especially, the decomposition process after azido group rupture. Hence, a more effective strategy is crucially needed to explore the multistep pyrolysis process of complex azide copolymers.

Nowadays, in order to simplify the multistep reaction, mathematical deconvolution method using a statistical function was used to separate the overlapping kinetic rate data. This approach assumed that the component reaction steps were not mutually dependent [29].Up to now, many particular peak functions have been used in the kinetic studies of multistep thermal decomposition reaction, such as Gaussian [30], Bi-Gaussian [31], Lorentz [30], Logistic [32], and so on. Thus, the selection of a proper peak function is very important for specific system [33]. Asymmetric Double Sigmoidal (Asym2sig) is a commonly used function for asymmetric signal deconvolution, for example, complex light or electrical signal [34–36]. There are relatively less studies about Asym2sig deconvolution for pyrolytic curves. Walters et al. [37] separated pyrolysis profiles of cyanate ester resin into two reaction steps by using Asym2sig function deconvolution, but not gave the detailed calculative process. Chen et al. applied Asym2sig function deconvolution to multiple pyrolysis kinetic study of bamboo waste, and obtained satisfying results, as well as analyzed the relationship between Asym2sig and pyrolysis parameters in detail [38]. Furthermore, combining with the characteristics of POG pyrolysis curves, we try to use a deconvolution procedure with Asym2sig function for POG pyrolytic kinetics in this article. In addition, the intermediate reactions are difficult to detect by experimental studies alone due to highly reactive in an extremely short period of time. Therefore, a computationally feasible method is needed to study the pyrolysis mechanisms of POG. Reactive Force Field Molecular Dynamics (ReaxFF-MD) simulation has been developed by Van Duin et al. [39] for exploring chemical reactions. Many papers use ReaxFF-MD for studying the pyrolysis characteristics and reaction mechanisms of organics [40–44], especially, energetic materials [45–47]. To the best of our knowledge, the two methods used to investigate the thermal kinetics and pyrolysis mechanism of azide polymers have been rarely reported. Inspired by the literatures, these strategies used to evaluate the pyrolysis behavior of POG are a desirable alternative.

The pyrolysis process of POG could be more complex than that of linear azide polymer due to its 3D spatial arrangement of molecular chains. In this article, a deconvolution procedure with Asym2sig function was used for POG pyrolytic kinetics. In addition, the common methods of model-free, kinetic compensation effects, integral master-plots, and kinetic mechanism function construction were also used to determine kinetic triplets of multistep pyrolysis of POG. Meanwhile, the pyrolysis mechanism of POG was deduced by ReaxFF-MD simulation and pyrolytic products analysis. Furthermore, the relationship of kinetic models and pyrolysis mechanisms of POG was discussed. The research not only presents the pyrolysis behavior of POG in detail, but also may provide some methods for studying the complex pyrolysis process of similar energetic polymers.

## 2. Experimental methodology

### 2.1. Materials

Core-shell type hyperbranched azide copolymer (POG, $\boldsymbol{M_n}$ = 5870 g/mol, the molar ratio of core to shell is around 1:2) was synthesized at the laboratory [18].The hyperbranched polyether (PEHO, $\boldsymbol{M_n}$ = 2120 g/mol, the degree of branching is 0.42) was synthesized according to the literature [18,48]. The chemical structures of PEHO and POG are shown in Fig. 1.

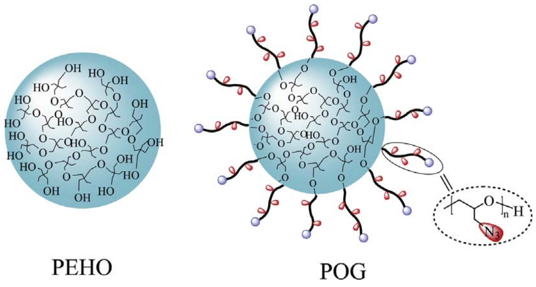

**Fig. 1.** The molecular structural formula of PEHO and POG.