



Synthesis and application of polyethylene-based functionalized hyperbranched polymers



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ARTICLE INFO

Article history:

Available online 28 January 2015

Keywords:

Functionalized polyethylene
Chain walking polymerization
Hyperbranched polymers
Microstructure

ABSTRACT

Polyethylene is one of the largest volume commodity polymers, with excellent physical and chemical properties. Polyethylene-based functionalized hyperbranched polymers are newly developed materials with unique structures and properties. Their architecturally complex structure – topology, composition and functionality – may be designed for different applications, with reduction of complexity and cost in preparation. This review focuses on the synthesis strategies and applications of polyethylene-based functionalized hyperbranched polymers.

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1. Introduction

Highly branched polymers have been studied extensively in recent years. Compared to the corresponding linear polymer, highly branched polymers, such as dendrimer and hyperbranched polymers, possess unique physical properties stemming from their different architectures. Dendrimers are well-defined, highly ordered molecules with three-dimensional structures. By employing suitable synthetic strategies, functional groups in dendrimers are located at pre-designed sites, resulting in adjustable properties. The unique structure of dendrimers leads to some exceptional properties promising for particular applications, such as drug delivery [1], gene carriers [2], templates for mesoporous materials [3], molecular recognition [4,5], signal amplification [6,7], catalysis [8–10] and pollution removal [11]. However, preparation of dendrimers, which usually contains multistep synthesis and purification, is tedious and costly. It is desired to develop new efficient methodologies to produce dendrimers or replacements.

Conventional synthesis of dendrimers is inconvenient and time-consuming using a chain of iterative growth and activation steps. Although some revised strategies have been developed to simplify the synthesis, the design and preparation of monomers are still challenging for commercial production. Despite their imperfection in symmetric topology, hyperbranched polymers, featuring a multitude of branches and three-dimensional fractal structure with cores, branches and peripheries, still retain exceptional chemical and physical properties similar to dendrimers. The preparation of hyperbranched polymers greatly reduces synthetic cost and time compared with dendrimers. They are often easily produced in one-pot and one-step, suitable for industrial application in a large scale without stepwise sophisticated reactions and costly purifications. Consequently, less costly and easily obtained hyperbranched macromolecules are desired to replace dendrimers in some particular applications.

Large scale polyethylene production is often performed in the present of early transition metal catalysts. Because of their high oxophilicity, early transition metal catalysts tend to be poisoned by polar comonomers. Therefore, it is difficult to functionalize polyethylene through direct copolymerization, desirable for industrial production. Conversely, late transition metal catalysts have lower oxophilicity tolerant toward polar comonomers. However, before 1995, due to β -hydride elimination, only dimers or oligomers could be produced with late transition metal catalysts under mild conditions [12–15]. Introducing bulky, aryl substituents in α -diimine Ni or Pd, enable the synthesis of high molecular weight polyethylene with such catalysts [16]. In addition, Pd α -diimine catalysts enable copolymerization of ethylene with polar monomers [17]. The functionalized polyethylenes possess a high branching degree, with the incorporated polar groups dominantly located at the end of the branches. Based on the discovery of these new catalysts, Guan showed that the topology of polyethylenes produced by using Pd α -diimine catalysts may be controlled by adjusting the polymerization conditions [18] characterizing the control mechanism as

a “chain-walking polymerization” (CWP). At a relatively low pressure of feeding ethylene, chain walking leads to the formation of branch-on-branch structures, namely, a hyperbranched topology. As revealed by light scattering and ^{13}C NMR, the topology of polyethylenes changes with polymerization pressure from linear to hyperbranched to dendritic [19]. Chen et al. reported that polar ethylene copolymers initiated by Pd α -diimine catalysts can also be topologically controlled by changing the ethylene pressure [20].

Polyethylene-based functionalized hyperbranched polymers are promising materials for replacing dendrimers in certain suitable areas, offering significant reduction in production time and cost. Tunable topology and functionality of this new class of polyethylenes has attracted attentions from industry and academia. However, limited work has focused on the application of this class of polymer. Although hyperbranched polyethylene (HBPE) has been reviewed, the functionalization and applications of this new polymer has not been introduced fully and completely [21,22]. The aim of this article is to shed light on different strategies and applications of polyethylene-based functionalized hyperbranched polymers.

2. Incorporation of functionality into polyethylene-based functionalized hyperbranched polymers

Owing to competing β -hydride elimination, late transition metal catalysts are more prone to oligomerize or dimerize ethylene compared to early transition metal catalysts. In 1995, Brookhart M. et al. reported a new class of Ni- and Pd-based catalysts **1–5** (Fig. 1) for polymerization of ethylene or α -olefin [16].

The incorporation of bulky α -diimine ligand onto the metal center can weaken β -hydride elimination, so that polyethylenes with average molecular weight ranging from 1.8×10^3 to 1.6×10^6 g/mol can be successfully prepared. The branching degree may be calculated from ^1H NMR integration of the methyl, methylene and methine groups. For example, polyethylene produced by complex **1a** has 106 branches per 1000 carbon atoms. These α -diimine catalysts develop a new class of polyethylenes that possesses a high branching degree.

The formation of branches is derived from combined processes of β -hydride elimination, bond rotation and reinsertion. The polymerization mechanism of branched polyethylene initiated by Ni and Pd α -diimine is shown in Scheme 1. The polyethylene propagation contains two processes: ethylene coordination and following insertion. After β -hydride elimination, the alkyl species **C2** is converted to rest state **C3**. The generation of methyl branches is caused by basic step in CWP: rotation of end olefin group around coordination bond and following reinsertion [18,23]. Further repetition of chain walking produces a longer branch. Complex **C3** can be trapped by ethylene to give both complex **C6** and olefin end-capped polymer chain. However, the bulky α -diimine ligand retards the association displacement and chain transfer that results in production of high molecular weight polyethylene. Alkyl

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