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Novel phosphorus-containing hyperbranched polysiloxane and its high performance flame retardant cyanate ester resins

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ABSTRACT

A novel phosphorus-containing hyperbranched polysiloxane (P–HSi) with a great amount of phosphaphenanthrene and silanol groups was synthesized by a hydrolysis of self-made phosphorus-containing triethoxysilane. Based on this, P–HSi was used to develop a new high performance flame retardant cyanate ester (CE) resin with simultaneously improved integrated properties. A small addition of P–HSi (5 wt%) to CE can remarkably increases the flame retardancy of CE resin, where the content of P element is only as low as about 1.8 wt%. More attractively, the incorporation of P–HSi to CE resin significantly improves the thermal stability and mechanical properties, completely overcoming the disadvantages of phosphorus flame retardants. Specifically, for the modified CE resin with 15 wt% P–HSi, its initial degradation temperature is about 58 °C higher than the corresponding value of original CE resin; moreover, its impact and flexural strengths are about 2.7 and 1.5 times of the corresponding values of CE resin, respectively. In addition, the P–HSi/CE resins have obviously decreased curing temperature and improved dielectric properties. These outstanding integrated properties of P–HSi/CE resins show that P–HSi is an effective and multi-functional flame retardant for developing high performance resins.

1. Introduction

High performance thermosetting resins with good flame retardancy are increasingly required by many cutting-edge industries including aerospace, microelectronic, and transportation, etc. [1–3]. However almost all resins do not have suitable flame retardancy.

To-date, adding flame retardant to a resin has been proved to be a common and effective method to endow the resin with good flame retardancy [4–6]. Phosphorus compounds become the main kind of flame retardants owing to their environment-friendly and high efficiency [7–9]. Among them, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) has received notable attention of scientists and engineers worldwide because of its additional merits such as good thermal stability, less toxicity, outstanding oxidation and water resistance [10–12]. Qian's group synthesized a new DOPO-containing flame retardant (HAP–DOPO) which was then used to modify epoxy resin, and found that the modified epoxy resin has higher char yield and lower heat release rate [13]. Our group prepared a novel modified bismaleimide (BMI) resin system by copolymerizing BMI with DOPO, and found that the modified BMI resin with a very low content of phosphorus element (1.25 wt%) has significantly improved flame retardancy [14]. Recently, Schartel's group published a series of papers on the flame redardancy and fire behavior of modified resins and carbon fiber-reinforced composites based on DOPO-containing flame retardants. They found that the flame retardancy of a resin is almost independent on the size of the flame retardants, but is closely related to the interaction between the DOPO-containing flame retardant and the resin, while the release of phosphorous compounds results in significant flame inhibition [15–18].

These researches prove that DOPO has a unique effect of improving the flame retardancy of resins. However, it is worthy to note that, compared with the original resin, the introduction of DOPO into the resin not only decreases the initial degradation temperature (T_{di}), leading to poor thermal stability, but also declines the mechanical properties (e.g. flexural strength) [19,20]. In fact, similar problems also exist in other phosphorus flame retardants [21–23]. Therefore, how to overcome these bottlenecks without worsening the advantages of DOPO is a very interesting issue.

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Recently, our group synthesized a series of hyperbranched polysiloxanes, which were then used to prepared high performance thermosetting resins. Results show that the hyperbranched polysiloxane with a suitable structure will improve the integrated performance of the resin. A typical example is the fully end-capped hyperbranched polysiloxane with large branching degree and amine-groups (Am—HBPSi), its modified BMI resin simultaneously has improved flame retardancy, toughness, strength and thermal stability [24]. However, Am—HBPSi does not have a long-term storage stability owing to its high activity.

The paper reports the synthesis of a new phosphorus flame retardant, which is a phosphorus-containing hyperbranched polysiloxane with a great amount of DOPO and silanol groups (P—HSi); based on this, P—HSi was used to develop high performance flame retarding cyanate ester (CE) resin. CE resin was chosen as the base resin owing to its great potential in many cutting edges including electric and electronic industries, aerospace and aviation, etc. [25–27]. The effect of P—HSi on the structure and integrated performances (including curing behavior and mechanism, mechanical and dielectric properties, flame retardancy and the mechanism) were intensively investigated.

2. Experimental

2.1. Materials

CE used in this research was 2,2′-bis(4-cyanatophenyl)isopropylidene, which was bought from Jiangdu Resin Plant in China. Azobisisobutyronitrile (AIBN, 99.5%), ethanol, and concentrated hydrochloric acid (HCl, 36.5%) were purchased from Beijing Chemical Works, China. DOPO was obtained from Eutec Trading (Shanghai) Co. Vinyltriethoxy silane (VTES) was bought from Zhejiang Chem-tech Group Co., Ltd. Distilled water was produced in our lab.

2.2. Synthesis of P—HSi

The synthesis mechanism of phosphorus-containing hyperbranched polysiloxane with a great amount of DOPO and silanol groups (P—HSi) was shown in Fig. 1.

10 g VTES, 0.164 g AIBN and 10.8 g DOPO were added to a 500 mL reactor with a magnetic stirrer and a reflux condenser under a nitrogen atmosphere. The temperature was kept at 80 °C for 8 h to obtain a light yellow liquid, coded as DTES.

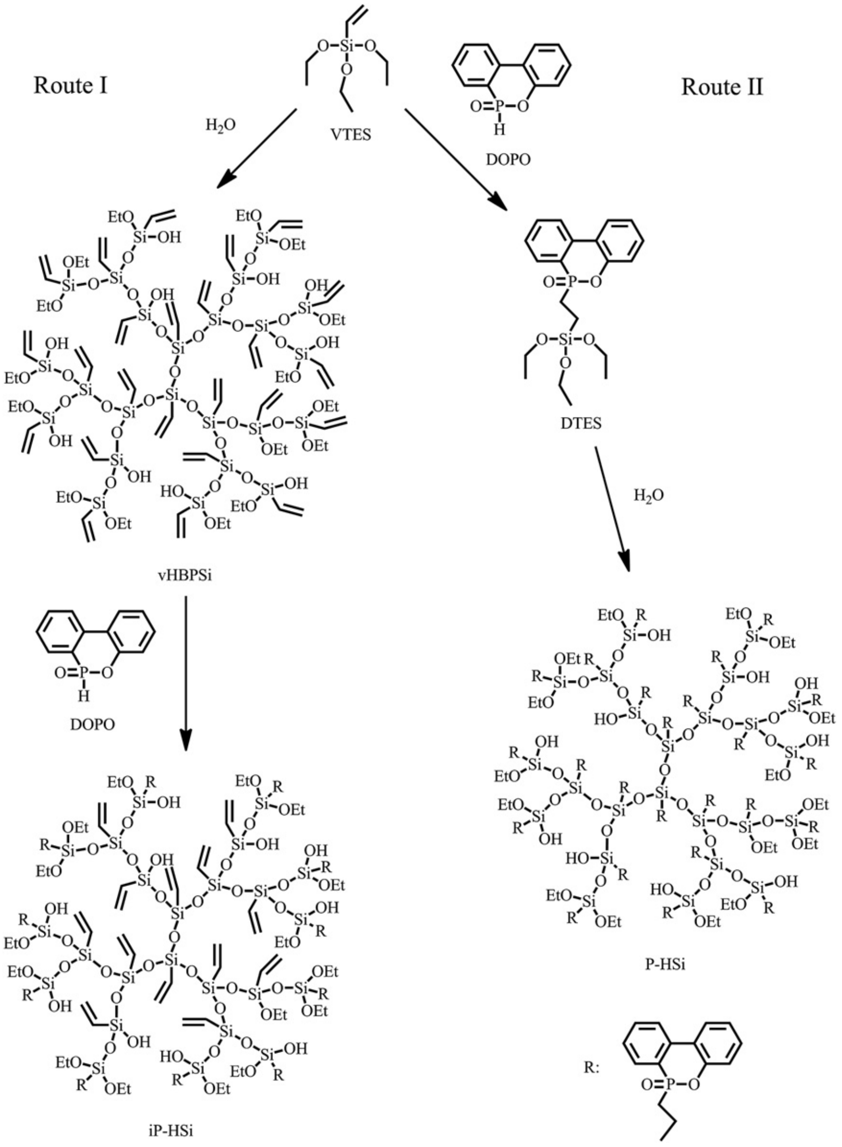

Fig. 1. Synthesis of iP—HSi and P—HSi.