

## Preparation and thermal properties of a novel flame retardant copolymer

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### ABSTRACT

A monomer, acryloxyethyl phenoxy phosphorodiethyl amidate (AEPPA), was synthesized and characterized using Fourier transform infrared (FTIR), <sup>1</sup>H nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR) and <sup>31</sup>P NMR. The copolymer with various amounts of styrene (St) was obtained by the free radical bulk polymerization between AEPPA and St, and characterized using <sup>1</sup>H NMR. The thermal properties of the copolymers were investigated with thermogravimetric analysis (TGA) in air and nitrogen atmosphere, and differential scanning calorimetry (DSC). The TGA results in air indicated the copolymers with AEPPA show higher thermal stability than those without AEPPA. However, the TGA results in nitrogen showed that the decomposition temperature decreased and the char residue increased with the increase of AEPPA. The glass transition temperature (*T<sub>g</sub>*) of the copolymers from DSC indicated that an inverse proportion was observed between *T<sub>g</sub>* and the amount of AEPPA incorporated. The flammability of the copolymers was evaluated by microscale combustion calorimeter (MCC). The MCC results showed that AEPPA can decrease the peak heat release rate (PHRR) and the heat release capacity (HRC), and the sample CP10 shows the lowest PHRR and HRC.

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### 1. Introduction

Polystyrene (PS) is widely used in many fields because of its outstanding properties, such as low density, excellent mechanical durability and chemical resistance, and convenience of processing and moulding. However, the high flammability of PS limits its further application in some areas. In order to improve its flame retardancy, various flame retardant additives have been employed [1]. It has been reported halogen-containing compounds are flame retardant additives, which have very good flame retardant effect for PS resin [2,3]. But, halogen compounds can lead to environmental problems. Therefore, more and more researchers have been devoting themselves to exploring effective halogen-free flame retardants.

Recently, phosphorus-containing compounds, as halogen-free flame retardants, have received considerable attention [4]. These compounds with good efficiency are environmental friendly, and

they mainly act on condensed phase flame retardant mechanism. There are two methods used to prepare flame retardant PS composites. One method is to add phosphorus-containing flame retardant additives into PS during processing [5]. In order to get high flame retardancy, it needs high loading of these flame retardants, which will deteriorate the physical and mechanical properties of the PS composites. Furthermore, some additives may be leached from the composites. The alternative strategy is to use some reactive flame retardants in terms of chemical modification of the preformed homopolymers or simple copolymerization of monomers [1,6]. It is believed that this method just needs lower loading than the 'additive' approach. Therefore, an effective monomer is very important for the copolymerization. It has been reported that various phosphorus-containing compounds were used to copolymerize with styrene (St), and limiting oxygen index (LOI) and char yields increase with the content of phosphorus [7–10].

In this article, a novel monomer containing phosphorus and nitrogen was synthesized and copolymerized with St to prepare flame retardant PS. The structure of the monomer and copolymers were characterized by <sup>1</sup>H NMR, <sup>31</sup>P NMR and FTIR. The thermal properties of the copolymers were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). And, the flame retardant properties of these copolymers were also studied with microscale combustion calorimeter (MCC).

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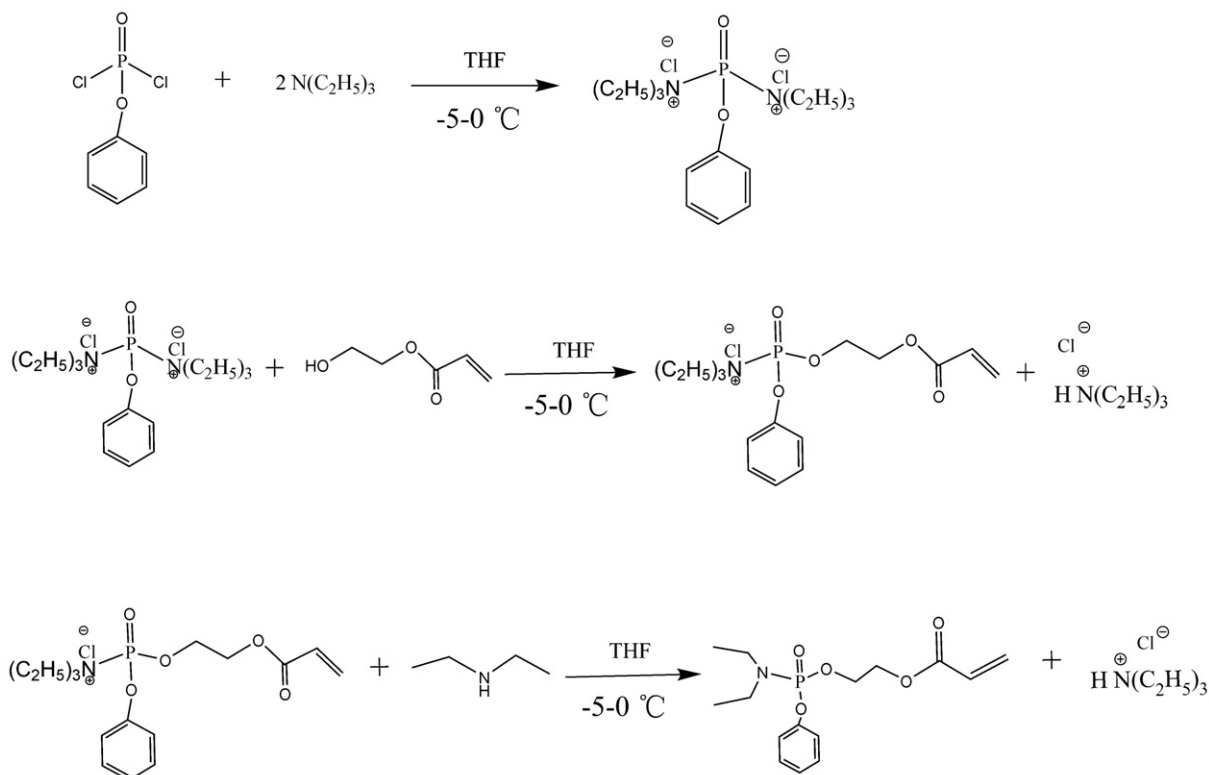
## 2. Experimental

### 2.1. Materials

Phenyl dichlorophosphate (PDCP) was offered by Deheng Chemical Corp (Shijiazhuang, China), and was freshly distilled before use. Triethylamine (TEA), diethylamine and hydroxyethyl acrylate (HEA) were obtained from the China Medicine (Group) Shanghai Chemical Reagent Corp (Shanghai, China), and they were purified by distillation. Tetrahydrofuran (THF) was refluxed with the sodium, and then was distilled. Styrene was first washed with NaOH solution to remove the inhibitor and followed with water and then distilled under reduced pressure. 2,2-Azobisisobutyronitrile (AIBN) was purified by recrystallizing from methanol. All of the other chemicals were used as received.

### 2.2. Synthesis of acryloxyethyl phenoxy phosphorodiethyl amidate (AEPPA)

PDCP (42.2 g, 0.2 mol), was dissolved in 160 ml dry THF in a 500 ml three-neck flask fitted with a mechanical stirring. Then, triethylamine (42.4 g, 0.42 mol) was added into the above blends and the system was cooled to  $-5^{\circ}\text{C}$ . After 20 min, HEA (23.2 g, 0.2 mol) in 40 ml of THF was added dropwise over a period of 2 h and then kept isothermal for 4 h. Subsequently, the diethylamine (15.33 g, 0.21 mol) in 40 ml THF was added dropwise over a period of 1.5 h and kept isothermal for 4 h. Finally, the mixture was warmed to room temperature, stirred for a further 10 h. After the precipitated triethylamine hydrochloride had been filtered, the solution was then rotary evaporated to remove the solvent and the unreacted reactants under reduced pressure. A brown viscous liquid was obtained. The synthesis route was illustrated in Scheme 1.



Scheme 1. Synthesis of AEPPA.

Yield 52.2 g (76.5%);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm)  $\delta$  7.1–7.3 (5H, aromatic proton), 6.4 and 5.8 (2H, vinyl), 6.1 (1H,  $\text{CH}=\text{CH}_2$ ), 4.4 (2H,  $=\text{CO}-\text{CH}_2-$ ), 4.2 (2H,  $\text{P}=\text{O}-\text{CH}_2-$ ), 3.1 (4H,  $=\text{CH}_2\text{CH}_3$ ), 1.06 (6H,  $=\text{CH}_3$ );  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , ppm),  $\delta$  7.4 (singlet peak); IR (neat liquid,  $\text{cm}^{-1}$ ), 3068 (w, aromatic  $\text{C}=\text{H}$ ), 2974 and 2880 (s,  $\text{CH}_3$  and  $\text{CH}_2$ ), 1730 (s,  $\text{Cz.dbnd;O}$ ), 1637 (w, vinyl), 1264 (s,  $\text{P}=\text{O}$ ).

### 2.3. Preparation of poly(St-co-AEPPA) copolymers

Copolymer of St with various amounts of AEPPA was prepared by free radical bulk polymerization in a two-step process. In the first stage, in a 150 ml three-neck flask with a magnetic agitator,  $\text{N}_2$  gas was placed St (45 g) and AEPPA (5 g). Then the mixture was heated to  $90^{\circ}\text{C}$  and AIBN (147 mg, 0.2 mol% relative to monomers) was added to pre-polymerize it. The mixture was cooled until a critical viscosity was reached. In the second stage, AIBN (73 mg, 0.1 mol%) was added again to the viscous mixture, and then the mixture was poured into a glass mould at  $60^{\circ}\text{C}$  in an oven for 22 h. Afterwards, the glass mould was kept at  $80^{\circ}\text{C}$  for 16 h. Finally, the glass mould was removed to yield a copolymer sheet with 10 wt% AEPPA. Other copolymers with various amounts of AEPPA were obtained by the same procedure. The AEPPA/St copolymer with 0 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt% AEPPA are labeled PS, CP5, CP10, CP15, CP20, respectively. In the experiment, the initiator used was 0.3 mol% of monomers. The schematic process of the reaction is presented in Scheme 2.

PS:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 7.2–6.2 (Ar-H), 2.4–1.6 (C=H), 1.6–1.2 ( $\text{CH}_2$ ). IR ( $\text{cm}^{-1}$ ): 3063–3020 (w, aromatic  $\text{C}=\text{H}$ ), 2923 (w, aliphatic  $\text{C}=\text{H}$ ), 1600 (w, aromatic  $\text{C}=\text{C}$ ). Copolymer:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 7.2–6.2 (Ar-H), 2.4–1.6 (C=H), 1.6–1.2 ( $=\text{CH}_2-$ ), 4.1–3.6 ( $=\text{O}-\text{CH}_2-\text{CH}_2-$ ), 3.1–2.9 ( $=\text{N}-\text{CH}_2-$ ), 1.1–0.9 ( $=\text{CH}_3$ ). IR ( $\text{cm}^{-1}$ ): 3060–3020 (w, aromatic  $\text{C}=\text{H}$ ), 2924 and 2851 (s,  $\text{CH}_3$  and  $\text{CH}_2$ ), 1734 (s,  $\text{C}=\text{O}$ ), 1599 (w, aromatic  $\text{C}=\text{C}$ ), 1267 (s,  $\text{P}=\text{O}$ ).

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