



Synthesis of a novel macromolecular charring agent with free-radical quenching capability and its synergism in flame retardant polypropylene



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ABSTRACT

Fabricating an effective synergism between the condensed phase (char-forming) and the gas phase (free-radical quenching) is recently considered to be a very promising way to prepare high-efficient intumescent flame retardants. In this work, a novel hindered amine phosphorous-nitrogen macromolecular charring agent (HAPN) with free-radical quenching capability was synthesized and characterized. Then it was combined with ammonium polyphosphate (APP) to flame-retard polypropylene (PP). The flame retardancy and thermal stability of PP/HAPN/APP mixtures were investigated by limiting oxygen index (LOI), vertical burning test (UL-94), cone calorimetric test (CCT) and thermogravimetric analysis (TGA). When the content of HAPN/APP was 25 wt%, PP/HAPN/APP could self-extinguish at 36 s after igniting in the oxygen concentration of 29.5% and achieve a UL-94 V-0 rating. Meanwhile, the peak heat release rate (PHRR), total heat release rate (THR), average heat release rate (AV-HRR) and average mass loss rate (AV-MLR) were significantly decreased. The flame retardant mechanism of HAPN/APP was explored and the results revealed that there was an effective synergism between the condensed phase and the gas phase during the combustion. In the condensed phase, HAPN could make PP involve into the char-forming reaction to promote the formation of compact and firm intumescent char layer. Simultaneously, the nitroxyl radical generated by HAPN could effectively restrain and even extinguish the flame in the gas phase by quenching the active free-radicals.

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1. Introduction

In recent years, intumescent flame retardant (IFR) is regarded as one of the most promising halogen-free flame retardants because of its low smoke, non-toxicity, anti-dripping and being environmental-friendly [1–3]. Generally, IFR exhibits flame retardation by forming intumescent char layer on the surface of polymer [4]. Therefore, the flame retardant efficiency of IFR mainly depends on the physical barrier effect of the char layer [5]. However, the traditional IFR systems such as ammonium polyphosphate/pentaerythritol (APP/PER) system are consisted of small molecular compounds [6], by which the char layers formed are loose and fragile and thus their flame retardant efficiency is relatively poor

[7,8]. To overcome this disadvantage, many meaningful researches [9–11] have been done, and synthesizing macromolecular charring agents to displace small molecular ones was proved to be a feasible way because the macromolecular ones have better char-forming ability and thermostability [12–14].

Recently, it is reported that hindered amines have great synergistic effect with many kinds of flame retardants (such as IFR) because of their outstanding active free-radical quenching capability in the gas phase [15,16]. Cao and co-workers [17] synthesized a hindered amine containing silane (Si-NOR) by sol-gel reaction and used it as the flame retardant synergist of IFR. They found that Si-NOR could effectively improve the flame retardant efficiency of IFR. In our previous work [18], a hindered amine NOR116 was combined with APP/PER to flame-retard polypropylene (PP) and found that NOR116 showed a great synergistic effect with APP/PER because NOR116 could effectively weaken the heat flux, air flow and melting drip by quenching the active free-radicals in both the gas phase and the condensed phase during combustion. Accordingly, it appears that hindered amines have enormous potential in

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improving the flame retardancy of IFR. However, in the existing works, the hindered amine compounds were added directly with IFR into polymer by physical blend and acted as the synergists of the flame retardant. It was difficult for the mixtures to fully show their synergism because the addition amounts of the compounds were very small (<0.5 wt%) and the mixing evenness was a big challenge [19]. Besides, many hindered amine compounds are highly volatile and would lose at the processing temperature [20]. Therefore, introducing the hindered amine group into macromolecular charring agent by covalent bond is a promising way since it could not only resolve the problems mentioned above, but also make the interactions between the charring agent and the hindered amine group much more efficient within one molecule unit.

In this work, a novel macromolecular charring agent containing hindered amine group named HAPN was synthesized, and it was combined with APP to flame-retard PP. The structure of HAPN was characterized by Fourier transform infrared spectrometry (FTIR) and nuclear magnetic resonance spectroscopy (^1H NMR and ^{31}P NMR). The flame retardancy and thermal stability of PP/HAPN/APP system were investigated. The flame retardant mechanism of HAPN/APP was also explored and revealed by FTIR, thermogravimetry-Fourier transform infrared (TG-FTIR), pyrolysis gas chromatography mass spectroscopy (Py-GCMS) and scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX).

2. Experimental

2.1. Materials

Cyanuric chloride (CNC) was provided by Aladdin Industrial Co., Ltd., China. Triacetonediamine was purchased from Zhengzhou Alfa Chemical Co., Ltd., China. Ethanediamine was produced by China Sun Specialty Products Co., Ltd., China. Phenylphosphonic dichloride was provided by Zhengzhou Huiju Chemical Co., Ltd., China. Sodium hydroxide (NaOH) was purchased from Tianjin Qilun Chemical Technology Co., Ltd., China. Polypropylene (PP, T30S) was provided by Maoming Petrochemical Co., China. All the materials for synthesis were analytically pure and were used directly without further purification.

2.2. Synthesis of hindered amine phosphorous-nitrogen macromolecular charring agent (HAPN)

The synthesis route of HAPN is shown in Scheme 1.

The synthesis of N, N'-bis(2-aminoethyl)-phenyl phosphorodiamidate (BPPA): BPPA was synthesized according to the literature [21]. Ethylenediamine (31.25 g, 0.52 mol) and chloroform (100 mL) were added in a 250 mL four-neck flask equipped with a

thermometer, a stirrer and a constant pressure dropping funnel. Under vigorous mechanical stirring, a solution of phenylphosphonic dichloride (29.25 g, 0.15 mol) in chloroform (50 mL) was added dropwise within 3 h at 0–5 °C, and the reaction was lasted for another 6 h. Then the mixture was filtered and the filtrate was further distilled under reduced pressure to remove chloroform and the residual ethylenediamine. At last, light yellow transparent viscous liquid was obtained.

Afterwards, cyanuric chloride (27.66 g, 0.15 mol) and dioxane (200 mL) were added in a 500 mL four-neck flask equipped with a thermometer, a stirrer and two constant pressure dropping funnel. Under vigorous mechanical stirring, a solution of triacetonediamine (23.44 g, 0.15 mol) in dioxane (50 mL) and a solution of sodium hydroxide (6 g, 0.15 mol) in deionized water (24 mL) were added dropwise simultaneously within 3 h at 0–5 °C, and the reaction was lasted for another 5 h. Then the reaction temperature was increased to 55 °C. Simultaneously BPPA (36.34 g, 0.15 mol) and sodium hydroxide (12 g, 0.3 mol) were dissolved in deionized water (24 mL). Half of the mixed aqueous solution was added dropwise to the flask within 1.5 h and the reaction was further carried out for another 4 h. Then the reaction temperature was increased to 105 °C. The other half of the mixed aqueous solution was added dropwise to the flask within 1.5 h and the reaction was continued for another 5 h. Then the mixture was filtered and the residue was further washed with dioxane and ethanol for several times to remove the residual reactants. After dried at 100 °C under vacuum to a constant weight, the macromolecular charring agent containing hindered amine group (HAPN) was obtained (yield: 83.1%).

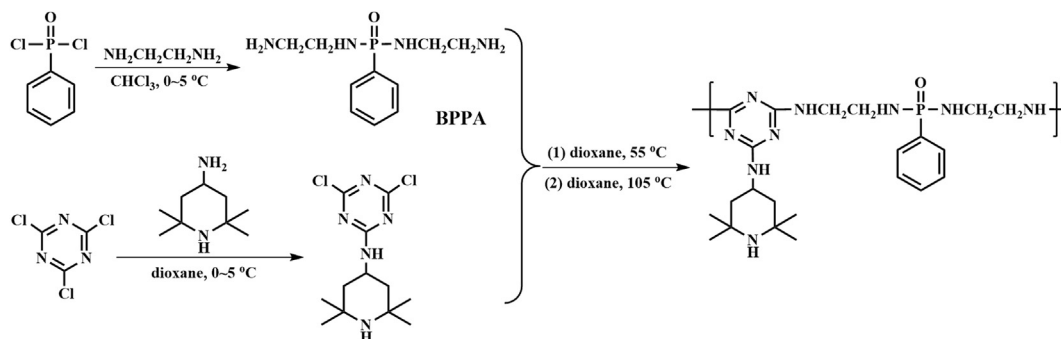
2.3. Preparation of flame retardant PP

PP, HAPN and APP were dried at 100 °C under vacuum for 6 h before use. Then PP, HAPN and APP were melt-mixed on a two-roll mill (XK-160, Changzhou Shuangfeng Machinery Factory, China) at 175 °C for 15 min. The prepared mixtures were molded under compression (15 MPa) at 180 °C for 6 min and cooled to room temperature naturally. The obtained flame retardant PP sheets with standard size would be used for further testing. The formulations of the flame retardant PP are listed in Table 1.

2.4. Characterization

2.4.1. Fourier transform infrared spectrometry (FTIR)

The samples were mixed with KBr powder and pressed into a tablet. The measurements were carried out by using a Tensor 27 spectrometer (Bruker Optics Inc., Germany). The FTIR spectra of the samples were collected in the optical range of 4000–400 cm^{-1} under a resolution of 4 cm^{-1} .



Scheme 1. Synthetic route of HAPN.

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