



# A novel phosphazene cyclomatrix network polymer: Design, synthesis and application in flame retardant polylactide

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## ABSTRACT

A novel phosphazene cyclomatrix network polymer poly(cyclotriphosphazene-co-pentaerythritol) (PCPP) was synthesized and characterized based on an attempt to look for a high efficient and green intumescent flame retardant. A series of flame retardant polylactide (FR-PLA) composites containing PCPP were prepared by melt blending method. Thermal degradation behavior and combustion properties of FR-PLA composites were evaluated through thermogravimetric analysis, UL-94 experiments, limiting oxygen index and cone calorimeter tests. It is found that the weight of residues for FR-PLA composites improved greatly with the addition of PCPP. Additionally, PCPP show a high flame retardant efficiency for PLA, UL-94 V-0 could be passed only containing 5 wt% PCPP. Fourier transform infrared spectra and scanning electronic microscopy investigations reveal that the residual chars are compact and foaming containing P–O–C structure, which restrains the development of fire and increases the flame retardant properties.

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## 1. Introduction

Overuse of traditional resins caused the extensive problems including deterioration of environmental pollution and the quick decrease of the petroleum energy sources, which has raised the demand for biodegradable polymers derived from renewable resources [1–3]. Among commercially available biodegradable plastics, polylactide (PLA) can be most reasonably used as promising alternative to the petroleum-based plastics, because of its high biocompatibility, good biodegradability and mechanical properties [4,5]. PLA and its copolymers have been used successfully in packaging, agricultural films, coatings, textiles, medical and pharmaceutical applications [6–8]. Unfortunately, inherent flammability and melt dripping restricted its further applications in many important fields such as housing and electronic devices etc [9].

It is a common method to protect PLA against attack by fire through addition of flame retardants [10], especially halogen containing additives for their good ratio of property to price. However there has been a considerable trend towards increasing application of green flame-retardant strategy because of environmental and safety concerns [11–14]. Recently, intumescent flame retardant (IFR) technology has been used as one of the green methods for

polymeric materials due to its advantages of little smoke and low toxicity etc [15–17]. An IFR system is usually composed of three components: an acid source, a char forming agent and a blowing agent. Réti et al. [18] evaluated the efficiency of different IFR systems combined ammonium polyphosphate (APP) with pentaerythritol (PER), lignin (LIG) or starch (ST). The results indicated at 40 wt% loading of additives, the feature of the systems containing APP/LIG or APP/ST are V-0 classification while PLA-APP/PER is only V-2 rating. Hu's group [19] synthesized a monomeric IFR triazine phosphamide which exhibited high efficiency in PLA, the limiting oxygen index (LOI) value could reach 38 with 25 wt% additive and V-0 rating was obtained. However, when the content decreased to 15 wt%, only V-2 rating was obtained with slightly dripping, although the LOI value was still as high as 33.5. There are some other researches that have been devoted to promote the flame retardant properties of PLA [20–23]. But the results implied it was still hard to obtain a high flame retardant PLA without dripping at low content of additives. Thus, it is highly desired to seek a high efficient IFR for the further development of PLA materials.

Polyphosphazenes are a unique class of inorganic-organic materials with high thermal and chemical stabilities. They can improve thermal and flame-retardant properties of reinforced polymers and composites. The most widely studied polyphosphazenes have a linear backbone of alternating phosphorus and nitrogen atoms with two organic groups linked to each phosphorus atom. Despite the many attributes and potential uses of them, their relatively low yield and high cost has slowed their

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commercialization. One attractive alternative is a class of readily modified macromolecules known as cyclomatrix-type polyphosphazenes, which includes network and cycloliner polymers. More research has been focused on the generation of the former because the complexities involved with the synthesis of the latter severely limit their desirability. A series of cyclomatrix network polyphosphazenes have been prepared and their thermally decomposed properties have been discussed [24–27]. The studies demonstrated that the polyphosphazene structure and high crosslink density were very conducive for their high char-yield and excellent self-extinguishability. To our surprise, little research is concerned with their further application in flame retardant polymer materials, let alone PLA.

In this article, we report our efforts on preparation of a phosphazene cyclomatrix network polymer poly(cyclotriphosphazene-co-pentaerythritol) (PCPP) and its application in PLA. Its structure is well confirmed by nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectra. The flame retardant PLA composites with and without PCPP were prepared. Their thermal degradation behavior and flammability properties were investigated by thermogravimetric analysis (TGA), limiting oxygen index (LOI), UL-94 vertical and cone calorimeter (CC) experiments. The residues after combustion were investigated by scanning electronic microscopy (SEM) and FTIR.

## 2. Experimental

### 2.1. Materials

PLA (2002D) were supplied by Nature Works. Hexachlorocyclotriphosphazene (HCCP; Changzhou New Area Jili chemical Co. LTD) was recrystallized from dry hexane followed by sublimation twice. All other reagents were purchased from Shanghai Chemical Reagent Co. LTD and used as received unless otherwise stated.

### 2.2. Synthesis of PCPP

The synthesis route of PCPP is depicted in Scheme 1. HCCP (139.06 g, 0.40 mol), PER (122.54 g, 0.60 mol), sodium hydroxide

(96 g, 2.4 mol), and 300 mL of tetrahydrofuran were placed in 1000 mL flask connected with a drying tube. The mixture was refluxed for 6 h under N<sub>2</sub>, and then cooled to room temperature and precipitated in 10-fold excess water. The solid was filtered and washed with water and acetone. The white product PCPP was dried at 80 °C under vacuum to a constant weight (92.7% yields).

### 2.3. Preparation of composites

The formulations of PLA samples are presented in Table 1. All composites were prepared on a Brabender mixer at the temperature 180 °C with the roller speed 50 rpm for 8 min. The mixed samples were transferred to a mold and preheated at 185 °C for 5 min, then pressed at 10 MPa, and successively cooled to room temperature while maintaining the pressure to obtain the composite sheets for further measurements. Before mixing, all materials were dried in vacuum oven at 80 °C for at least 12 h.

### 2.4. Instrumentation

The <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded with an AVANCE 400 Bruker spectrometer using DMSO-*d*<sub>6</sub> as a solvent. FTIR spectra were obtained using a Nicolet 510P FTIR spectrometer using KBr pellets.

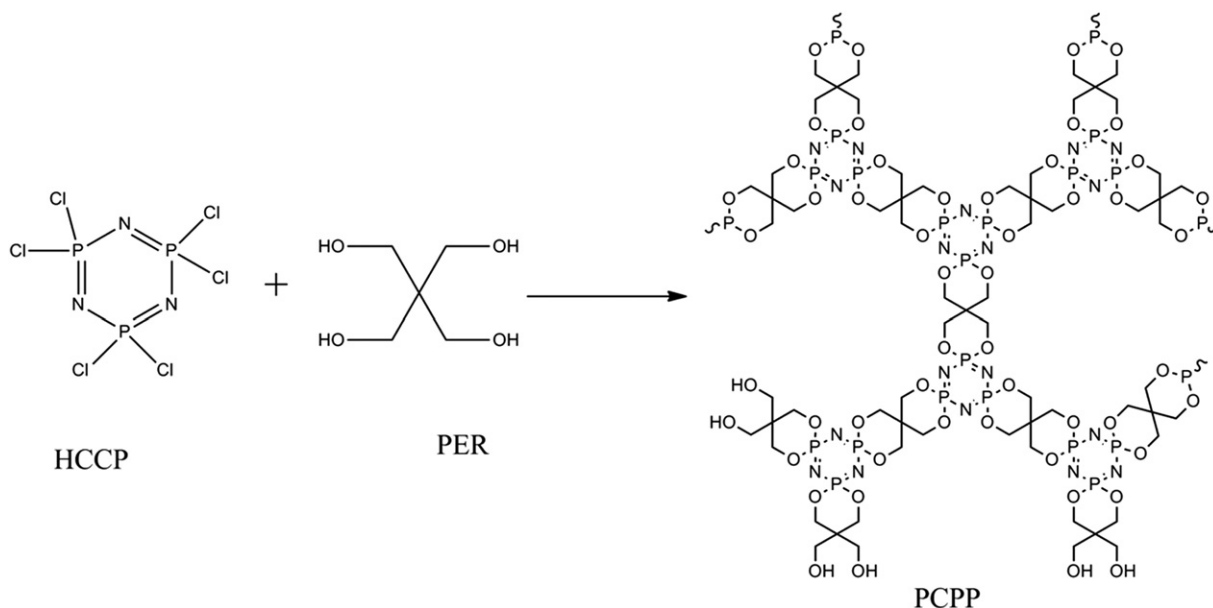
TGA of samples were examined on a METTLER TOLEDO TGA/DSC1 Analyzer, in a range from 30 °C to 800 °C at a heating rate of 10 °C/min.

LOI was measured according to ASTM D2863. The apparatus used was an HC-2 oxygen index meter (Jiangning Analysis Instrument Co., China). The specimens used for the test were of dimensions 100.0 × 6.5 × 3.0 mm and prepared by moulding.

The UL-94 vertical test was carried out on an AG5100B vertical burning instrument (Jiangning Analysis Instrument Co., China) according to the UL 94 test standard. The specimens used were 100.0 × 13.0 × 3.0 mm in dimension.

The CC tests were carried out in an FTT cone meter according to ISO5660 under a heat flux of 35 kW/m<sup>2</sup>. The sheets for the test are 100.0 × 100.0 × 3.0 mm in dimension.

The char formed after CC testing was first sputter-coated with a conductive layer, and then its surface morphology was observed



Scheme 1. The synthesis road of cyclomatrix network polyphosphazene PCPP.

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