



Synthesis of a novel bridged-cyclotriphosphazene flame retardant and its application in epoxy resin



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ABSTRACT

A novel flame retardant, named bisphenol-A bridged penta(anilino)cyclotriphosphazene (BPA-BPP), was successfully synthesized. Its chemical structure was characterized by Fourier transform infrared (FTIR), ¹H NMR and ³¹P NMR. Then, different amounts of BPA-BPP were mixed with diglycidyl ether of bisphenol-A (DGEBA) to fabricate flame retardant epoxy resin (EP). Nonisothermal differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) tests were used to study the curing kinetics and thermal degradation behaviors of flame retardant EPs. The results of limiting oxygen index (LOI), vertical burning tests (UL-94) suggested that BPA-BPP exhibited good flame-retarded efficiency on the EP loaded with low phosphorus content. Compared with the neat EP, the LOI value of EP/9%BPA-BPP increased from 21.0 vol% to 28.7 vol%. Furthermore, the peak of heat release rate (PHRR), total heat release (THR), total smoke production (TSP) of the same sample, obtained from cone calorimetry, were declined obviously, suggesting excellent flame retardancy and smoke inhibition. The morphology and chemical structures of the char layers were analyzed by SEM, Raman and FTIR. The Py-GC/MS was used to investigate the pyrolysis behavior and flame-retardant mechanism of BPA-BPP. In the process of heating, aniline, diphenylamine and NH₃ were released from BPA-BPP in gaseous phase, and phosphorus-rich carbonaceous chars were left in condensed phase. BPA-BPP could promote EP to form intumescence protective char layers, enhancing flame retardancy of EP effectively.

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1. Introduction

Epoxy resins (EPs) have been widely applied as matrix resin in many fields due to their ease of curing and processing, good dimensional stability, superior electrical, chemical and mechanical properties [1–3]. However, inflammability of epoxy resin limits their wide-spread application in fields requiring high fire resistance. Although traditional halogen-containing EPs have been well developed to meet the considerable secure requirements in these fields, halogen additives will cause environmental toxicity as well as health hazards because of the generation of highly toxic and potentially carcinogenic substances during combustion [4,5]. Therefore, a growing interest has been focused on halogen-free solutions, which allows for green chemistry and sustainable development [6,7].

Over the past decade, many efforts have been made to achieve

high flame retardancy of EPs by using phosphorus- and nitrogen-containing additives [8–10], monomers [5,11] or hardeners [12,13]. Among them, phosphazene derivatives have aroused great attention due to they are good candidates as the flame retardants for EPs [10,11,14,15]. On one hand, cyclotriphosphazene as the matrix of phosphazene derivatives can provide the synergism of the phosphorus-nitrogen combination, which result in good fire resistance and auto-extinguish ability in polymers [16–19]. This advantage could be ascribed to its unique molecular framework of cyclotriphosphazene based on alternation of P and N atoms in a conjugative mode [20]. On the other hand, substitution chemistry at phosphorus atoms particularly provides a multiple synthetic methodology for creating cyclotriphosphazene-based derivatives with varied substituent groups, which allows us to obtain multifunctional reactive and additive types flame retardants with ease [21–23]. Researchers have paid much attention to obtain new derivatives of cyclotriphosphazene to prepare flame retardant EPs [11,14,15,24]. These studies display clearly that the cyclotriphosphazene structure contribute to high char-yield and excellent self-extinguish ability in EPs.

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In this work, a novel flame retardant bisphenol-A bridged penta (anilino) cyclotriphosphazene (BPA-BPP) was synthesized successfully through nucleophilic substitution reaction of hexachlorocyclotriphosphazene, bisphenol-A and aniline. The chemical structure of BPA-BPP was characterized via Fourier transform infrared spectroscopy (FT-IR), ^1H NMR, and ^{31}P NMR. Then flame-retardant EPs with 3 wt%, 6 wt% and 9 wt% BPA-BPP were prepared and studied. The results of the thermogravimetric analysis (TGA), LOI, UL-94, microscale combustion calorimeter (MCC) and cone calorimeter revealed that the incorporation of BPA-BPP changed the thermal degradation behavior and enhanced the flame retardancy of EP. Meanwhile, the graphitizing structure and morphology analysis of the residual chars as well as pyrolysis behavior of BPA-BPP have been investigated systematically.

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene (HCCP) was obtained from Zibo Lanyin Chemical Co., Ltd., (Zibo, China), purified by recrystallization from *n*-heptane prior to use. Bisphenol-A (BPA), aniline and 4,4'-Diamino-diphenylmethane (DDM) were purchased from Aladdin Industrial Corporation, (Shanghai, China). Potassium carbonate (K_2CO_3), Sodium hydride (NaH), sodium sulfate (Na_2SO_4), potassium hydroxide (KOH), tetrahydrofuran (THF), petroleum ether, dichloromethane (CH_2Cl_2), ethyl ether and *n*-heptane were purchased from Tianjin Guangfu Fine Chemical Research Institute, (Tianjin, China). THF was distilled from sodium benzophenone ketal before use, and the other chemicals and reagents were used without further purification. Diglycidyl ether of bisphenol-A (DGEBA) (NPEL128, epoxide equivalent weights = 185 g/eq) was commercially available.

2.2. Synthesis of bisphenol A bridged chlorocyclotriphosphazene (BPA-BCP)

NaH (60% in mineral oil, 4.0 g) was added to a solution of HCCP (34.8 g) in THF at $-20\text{ }^\circ\text{C}$ under nitrogen protection. A solution of BPA (11.4 g) in THF was added dropwise into the suspension over 2 h with agitation, followed by stirring for 12 h at $-20\text{ }^\circ\text{C}$. Then solution was stirred for 2 h at room temperature. After the reaction was completed, the reaction mixture was filtered and then washed repeatedly with deionized water. The organic layer was dried with anhydrous Na_2SO_4 and concentrated on a rotator evaporator under reduced pressure, leaving a white solid. The residue was purified by silica gel chromatography (silica gel, 40 vol% of CH_2Cl_2 /60 vol% of petroleum ether) to obtain white solid of BPA-BCP (31.9 g, yield 75.1%). M.p.: $114.0\text{--}114.9\text{ }^\circ\text{C}$; ^1H NMR (DMSO- d_6 , TMS): δ /ppm 7.19–7.17 (d, 4H), 7.09–7.07 (d, 4H), 1.62 (s, 6H); ^{31}P NMR (DMSO- d_6 , 85% H_3PO_4): δ /ppm 22.74–22.35 (d, 2P) and 12.12–11.35 (t, 1P); FTIR: ν/cm^{-1} = 1180 and 1150 (P=N), 1014 and 967 (P–O–C), 591 and 515 (P–Cl).

2.3. Synthesis of bisphenol A bridged penta(anilino) cyclotriphosphazene (BPA-BPP)

BPA-BCP (25.5 g) was added to a suspension of K_2CO_3 (41.5 g) in aniline (93.1 g) under nitrogen protection. This reaction mixture was stirred at room temperature for 2 h. Then it was heated to $150\text{ }^\circ\text{C}$ and maintained for 8 h. Subsequently, the mixture was cooled to room temperature prior to filtration. The excess aniline was removed under reduced pressure yielding brown solid. The solid was treated with aqueous KOH and extracted with diethyl ether. Finally, the diethyl ether solution was added into petroleum

ether (200 mL), then the white precipitate formed and the solvent was removed by filtration. The precipitate was washed with petroleum ether (100 mL) and dried under vacuum for 12 h. The white product BPA-BPP was obtained in 87.3% yield (37.1 g). M.p.: $109.0\text{--}110.4\text{ }^\circ\text{C}$; ^1H NMR (DMSO- d_6 , TMS): δ /ppm 7.41 (s, 4H), 7.29 (s, 4H), 7.24–7.11 (m, 20H), 7.06–6.99 (m, 30H), 6.73–6.66 (m, 10H), 1.37 (s, 6H); ^{31}P NMR (DMSO- d_6 , 85% H_3PO_4): δ /ppm 8.88–8.19 (t, 1P) and 2.85–2.51 (d, 2P); FTIR: ν/cm^{-1} = 3361 (–NH–), 1173 and 1150 (P=N), 1029 and 1000 (P–O–C).

2.4. Preparation of epoxy thermosets

EP/BPA-BPP samples were prepared via a thermal curing process. At first, BPA-BPP and DDM were mixed at $120\text{ }^\circ\text{C}$ for 20 min, giving a homogenous liquid. DGEBA was previously heated to $50\text{ }^\circ\text{C}$. The mixture of BPA-BPP and DDM was added into DGEBA under vigorous stirring. It was degassed under vacuum for 10 min to remove trapped air, then poured directly into a preheated teflon mould. A two-step curing procedure was carried out to obtain the thermosetting resins. The epoxy mixture was cured in air convection oven for 2 h at $90\text{ }^\circ\text{C}$ and then 2 h at $130\text{ }^\circ\text{C}$. All the details of formula are listed in Table 1.

2.5. Measurement and characterization

Fourier transform infrared (FTIR) spectra were directly recorded by attenuated total reflection (ATR) adjunct of Nicolet IS50 spectrometer over the frequency range from 500 to 4000 cm^{-1} , the resolution factor of FTIR spectrometer was 4 cm^{-1} and 16 scans.

^1H NMR and ^{31}P NMR spectra were conducted on a Bruker AV II-400 MHz at room temperature using DMSO- d_6 as the solvent.

The curing kinetics of EP/DDM and EP/DDM/BPA-BPP samples were studied by nonisothermal differential scanning calorimetry (DSC) testing (DSC-1, METTLER TOLEDO), operating at a heating rate of 5, 10, 15 and $20\text{ }^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

Thermogravimetric analysis (TGA) was performed on a TA Instruments Q50 thermal gravimetric analyzer in a temperature range of $40\text{--}700\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$, and sample weight was in the range of 6–8 mg. According to our TGA measurement, the residue mass reproduction of each sample was within $\pm 1\%$.

Limiting oxygen index (LOI) test was accorded to standard method ASTM D2863-00 performing with a Motis oxygen index test instrument (Suzhou, China). The dimensions of the specimen were $130\text{ mm} \times 6.5\text{ mm} \times 3.2\text{ mm}$. The Vertical burning tests (UL-94) were measured on CZF-5 instrument (Nanjing Jiangning Instrument Factory, China) based on ASTM D3801/UL-94V standard. The sample size was $125\text{ mm} \times 13\text{ mm} \times 3.2\text{ mm}$.

Pyrolysis combustion flow calorimeter (PCFC) tests were performed using a FAA Microscale combustion calorimeter (Fire Testing Technology, UK) according to ASTM D7390. 5 ± 0.5 samples were heated from $100\text{ to }700\text{ }^\circ\text{C}$ at a heating rate of $1\text{ }^\circ\text{C}/\text{s}$ at a nitrogen flowing rate of $80\text{ mL}/\text{min}$. The fire behavior of the EPs was evaluated via a cone calorimeter device (Fire Testing Technology,

Table 1
Formulas of the cured EP composites.

Sample	DGEBA (g)	DDM (g)	BPA-BPP	
			(g)	(wt%)
EP	80	21.5	–	–
EP/3%BPA-BPP	80	21.5	3.1	3.0
EP/6%BPA-BPP	80	21.5	6.5	6.0
EP/9%BPA-BPP	80	21.5	10.0	9.0

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