

Phosphorus-containing copolyesters: The effect of ionic group and its analogous phosphorus heterocycles on their flame-retardant and anti-dripping performances



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ABSTRACT

A series of copolyesters containing ionic groups (PETIs-K) were synthesized by melt co-polycondensation using terephthalic acid, ethylene glycol, and potassium salt of bishydroxyethyl ester of 10-hydroxy-10-oxo-10H-phenoxaphosphine-2,8-dicarboxylic acid (DHPP0-K) as monomers. The copolyesters only with analogous phosphorus-containing heterocycles (PETPs) were also synthesized and used as a control. The dynamic rheological behaviors confirmed that the complex viscosity of PETIs-K increased with increasing temperature due to the existence of ionic aggregates, which restricted melt dripping, while PETPs had flow behaviors similar to PET: the complex viscosity decreased with increasing temperature. The ionic groups induced the decomposition of the polymer backbone to form a more stable residue at high temperatures, which made PETIs-K exhibit good flame retardancy even with low phosphorus contents. Cone test showed the peak heat release rate and total smoke production of PETP5 decreased to 34% and 58% of pure PET. Compared with PETP5, these values for PETI5-K were reduced by 31% and 50%, respectively. EDX and ICP-AES results demonstrated that 92% of phosphorus for PETI10-K remained in char residues; however, this value for PETP10 was only 45%. Combined with results of XPS, Raman spectroscopy and Py-GC/MS, it can be proved that the ionization of phosphorus took main effects in condensed phase via promoting carbonization to form stable graphitic char, which avoided the decrease of carbonization due to the competitive effects of phosphorus in gas phase.

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1. Introduction

Poly(ethylene terephthalate) (PET), one of the most important commercial polymers, possesses excellent chemical resistance, thermal stability, spinnability, and good mechanical properties [1–4]; it has been widely used as films, synthetic fibers, bottles, and engineering plastics. Unfortunately, PET is flammable and exhibits serious melt-dripping during combustion, which limits its application in some fields. At present, methods for endowing PET with flame retardancy are common, and some have been incorporated into industrialize processes. Some of these methods are, for example: adding flame retardants into PET by blending, incorporating flame-retardant monomers into PET chains via

polymerization, or finishing the fabrics/textile in a solution containing flame retardants [5–8]. Among these methods, introducing phosphorus-containing monomers into the PET backbone is an efficient way for improving PET flame retardancy, as it avoids poor durability and compatibility problems caused by the other methods [9–12]. These phosphorus-containing PET copolyesters usually achieve flame retardancy through removing heat from the burning surface, which enhances the melt-dripping of PET [13]. Therefore, how to resolve the conflict between the flammability and melt-dripping behavior has become a challenge for the development of flame-retardant PET in real applications.

In our previous work, we found if some unsaturated conjugated groups (such as azobenzene groups and phenylethynyl groups, etc.) were introduced into the PET backbone, these copolyesters could self-crosslink during combustion via chemical cross-linking [4,14,15]. This self-crosslinking reaction created copolyesters with high melting viscosity, giving both flame retardancy and anti-dripping simultaneously. Unfortunately, high cross-linkable-

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monomer dosage was needed in order to achieve good flame retardancy, and this destroyed the crystalline properties of PET seriously.

Recently, our research group introduced the ionomer concept to the field of phosphorus-containing copolyesters, and found the conflict between the flame retardance and melt-dripping of PET could be resolved in this manner [16–18]. In our previous work, it was found that when DHPPO-Na (the sodium salt of 10*H*-phenoxaphosphine-2,8-dicarboxylic acid 10-hydroxy-,2,8-dihydroxyethyl ester 10-oxide) was introduced into PET backbone, the melt viscosity of PET was increased greatly via ionic aggregation. Also, the char of this PET ionomer formed rapidly during decomposition, which restricted melt-dripping [19]. The thermal behavior, especially the crystallization ability, of this ionomer was similar with pure PET, indicating this ionomer with thermo-reversible physical crosslinking (ionic aggregation) had better processability and spinnability than the aforementioned chemical cross-linking copolyesters.

Some literatures reported that different alkaline metal ions had different flame-retardant effects on the bio-materials (jute, wood based material etc.) [20–22]. The greater the ionic radius, the lower the thermal stability for alkali group [23]. And potassium-catalyzed cellulose pyrolysis considerably increased the char yields and promoted the generation of phenol and phenol derivatives, which would form polycyclic aromatic hydrocarbons at high temperature [24,25].

Therefore, in this work, we changed our previous ionic monomer DHPPO-Na to DHPPO-K (the potassium salt of 10*H*-phenoxaphosphine-2,8-dicarboxylic acid,10-hydroxy-,2,8-dihydroxyethyl ester, 10-oxide), and introduced it into the PET backbone via melt polymerization. For better understanding the influence of ionic groups on flame retardancy, thermal stability, anti-dripping behavior, and pyrolysis behavior, an analogous, comparative, phosphorus heterocycles monomer without an ionic group was prepared and copolymerized with terephthalic acid and ethylene glycol to prepare another PET copolyesters (PETPs).

2. Experimental

2.1. Materials

Terephthalic acid (TPA, fiber grade) was purchased from Jinan Chemical Fiber Co. Ltd. (Jinan, China). Ethylene glycol (EG, industrial grade) was provided by Xilong Chemical Industries Co. Ltd. (Chengdu, China). 4,4'-dimethyldiphenylether (AR grade) was provided by Jiaying Sicheng Chemicals Co. Ltd. (Jiaying, China). Phenylphosphonous dichloride (AR grade), phosphorus trichloride (AR grade), aluminum trichloride (AR grade), potassium permanganate (KMnO₄, AR grade), and tetrabutyl titanate (AR grade) were

all obtained from Kelong Chemical Industrial Reagent Co. (Chengdu, China). Tetrabutyl titanate was dissolved into anhydrous toluene to prepare a 0.2 g/ml solution before use. Other materials were used as received.

2.2. Preparation of PET copolyesters containing phosphorus heterocycles (PETPs)

The exact synthesis procedure for PETPs was described as follows (Scheme 1): PET prepolymer was prepared via esterification and polycondensation reaction of TPA and EG in a 1-L autoclave. The mixture of PET prepolymer and DCPPO-Ph (its preparation procedure and structure characterization are shown in supporting information, Scheme S1 and Fig. S1(b)), was melted under N₂, and then a quantity of tetrabutyl titanate was added as a catalyst. The copolyesters were obtained after polycondensation at 240–280 °C under vacuum. ¹H NMR (Fig. S2(a), CF₃COOD, δ, ppm): 4.76 (s, 4H); 8.08 (s, 4H); 8.31–8.50, 7.36–7.60 (m, 11H). ³¹P NMR (CF₃COOD, δ, ppm): 2.68 (s).

2.3. Preparation of PET copolyester ionomers (PETIs-K)

Ionic monomer, DHPPO-K was prepared according to our previous work (structure characterization shown in Fig. S3) [19]. Poly(ethylene terephthalate)s-based ionomers (PETIs-K) were prepared in a same way (Scheme 2). ¹H NMR (Fig. S2(b), CF₃COOD, δ, ppm): 4.49 (s, 4H); 7.18 (m, 2H); 7.80 (s, 4H); 8.07 (m, 2H); 8.48 (m, 2H). ³¹P NMR (CF₃COOD, δ, ppm): 8.36 (s).

The basic parameters of PETPs and PETIs-K are shown in Table 1.

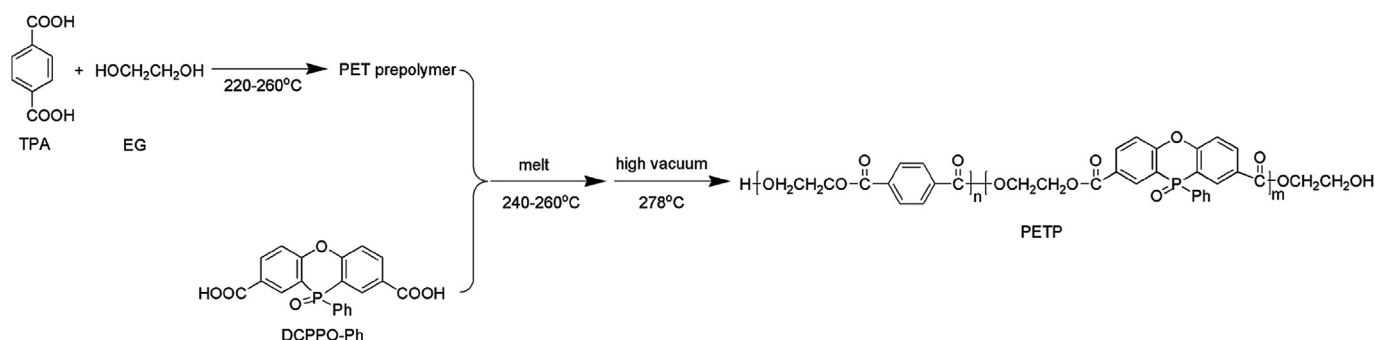
2.4. Characterization

Intrinsic viscosities [η] of samples were measured in an Ubbelohde viscometer at 25 °C in phenol/1,1,2,2-tetrachloroethane solution (v/v, 50/50) at a concentration of 5 g polymer/L solvent.

NMR spectroscopy was carried out on a Bruker AVANCE operating at 400 MHz for ¹H and at 161.9 MHz for ³¹P (DMSO-d₆ or CF₃COOD was used as solvent and tetramethylsilane was used as reference).

The actual phosphorus contents of the purified samples were determined by oxygen flask combustion-inductively coupled plasma atomic emission spectroscopy (ICP-AES) method.

The rheological properties were determined with a TA DHR-2 rheometer in air atmosphere. Disk-like samples with a size of 2.5 mm diameter and 1 mm thickness were dried under vacuum at 120 °C for 12 h. The complex viscosity (η) was measured as function of temperature ranging from 250 to 330 °C for PETP3 and PETI3-K, from 230 to 330 °C for PETP10 and PETI10-K, and from 260 to 330 °C for neat PET, each at a fixed frequency of 1 Hz.



Scheme 1. Synthesis process of PETP, where *m* and *n* denote the mole of DCPPO-Ph and TPA, respectively, not the block length or repeating units.

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