

A novel flame-retardant-free copolyester: cross-linking towards self extinguishing and non-dripping

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In this manuscript, contradiction between the non-flammability and non-dripping of polyesters could be solved by copolymerizing terephthalic acid and ethylene glycol together with a pendent phenylethynyl-based monomer named 4-(phenylethynyl) di(ethylene glycol) phthalate (PEPE), which exhibited a cross-linkable nature at a proper temperature. TG-DSC simultaneous thermal analysis, FTIR, dissolution tests and rheological investigations proved the thermal cross-linking behavior of the copolyester, which was not active at the temperature of polymerization and processing but could cross-link rapidly at higher temperature before burning. LOI tests, cone calorimetry and small-scale flame tests further confirmed the self-extinguishment and inhibition for melt-dripping could be achieved through the cross-linking during burning, despite the absence of any flame-retardant element (say, bromine, chlorine, phosphorus, or nitrogen, *etc.*). Rheological analyses and the SEM microphotographs of the char showed P(ET-co-P)s exhibited a greater complex viscosity through the cross-linking at high temperature, leading to compact char residue, flame-retardant and anti-dripping effects.

Introduction

Semi-aromatic polyesters, mostly polycondensated from diol and aromatic diacid, have found wide applications, such as beverage bottles, fibers and packaging materials to meet multifarious requirements in daily life.^{1,2} Despite the presence of benzene groups in the main chain, polyesters exhibit a flammable nature and a very limited tendency to charring; contrarily, aromatic-containing fragments of the polyester volatilize and feed the flame after ignition.³ To flame-retard these polyesters, conventional methods are to chemically incorporate flame-retardant elements into their molecular chains, or to physically add flame-retardants into the resin,³ otherwise to layover a functional coating through fabric/textile finishing.⁴⁻⁶ However, the environmental contamination and bioaccumulation of some halogenated flame-retardants therein, which harm the environment and human health, are particularly problematic.⁷⁻¹⁰ Phosphorus-containing flame-retardants are considered to have relatively low toxicity,¹¹⁻¹⁴ and copolymerizing phosphorus-containing monomers into polymer chains is considered to be one of the most efficient methods, while physical blending would compromise the spinning and durability of polyesters.¹⁵⁻¹⁸ Unfortunately, most phosphorus-containing

copolyesters can cause the polymers to seriously melt-drip during the fire, thus leading to secondary damage and immediate empyrosis during the fire.^{19,20} Therefore, how to address the contradiction between the flammability and dripping behavior for polyester through intrinsic flame-retardancy becomes a real challenge for both scientific and industrial fields.

A new idea is to design a novel polyester that can exhibit non-flammable properties with no dripping in the absence of flame-retardants. The key to discover inherently non-flammable and non-dripping polyesters is to understand the mechanism of polymer combustion, though the burning process of polyesters is extremely complex.²¹ Neat polyesters, such as poly(ethylene terephthalate) (PET) and poly(trimethylene terephthalate) (PTT) with simple linear structures, readily and completely burn with serious dripping behavior caused by very low melt viscosity and strength at high temperatures.²²⁻²⁴ Other polymers with stable cross-linked network structures, like some polyimides (PMR-15 for instance), are difficult to ignite and, even when ignited, are easy to self-extinguish.²⁵⁻²⁹ Also, these kinds of materials exhibit no melt-dripping during combustion. These phenomena should be attributed to the great thermal stability, high melt viscosity and high char-formation tendency during heating brought by the stable cross-linked networks.^{30,31} Thus, we can imagine that, if this stable cross-linked network or cross-linkable precursor can be incorporated into the molecular structure of a polyester just like the reported PMR-15, it should be anti-dripping and flame-retarded.

Ethynyl or phenylethynyl structures located either in the end or pendent groups of the polymer can be cured upon heating to

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afford highly cross-linked networks (Scheme 1), which is solvent resistant, thermally and thermo-oxidatively stable.^{32–34} Moreover, phenylethynyl groups can offer a combination of properties that are not available in other cross-linkable groups, such as long shelf life at room temperature, a wide processing window for the original material, and excellent mechanical properties for the cross-linked products.³⁵ Seemingly this alkynyl-based cross-linking structure was perfectly suitable for polyester and provided a new line of thought in polyester synthesis and application; however, to the best of our knowledge, there has been no further report on the flame-retardant performance of phenylethynyl-containing polymers, nor the synthesis and properties of polyesters containing ethynyl or phenylethynyl moieties.

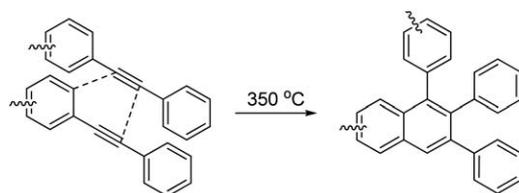
Phenylethynyl-containing compounds can also be utilized as additive-type flame-retardants to reduce the flammability and melt-dripping of polycarbonate. Morgan and Tour have synthesized a series of phenylethynyl-containing polymers and blended the polymers into polycarbonate.^{36,37} Multiple *o*-diaalkyne substitutions on the aromatic ring of the resulting polymers can be cross-linked at lower temperatures, which endows the blends with higher char yields, which correspondingly increases the flame-retardance and suppresses the melt-dripping. Unfortunately, flame-retardant elements, either bromine or phosphorus is still needed.

Adapting this concept, in this manuscript, PET has been chosen as the model polyester, and the phenylethynyl group has been selected as the cross-linkable precursor. The smart cross-linkable copolyester (entitled as poly(ethylene terephthalate-*co*-4-phenylethynylphthalate), P(ET-*co*-P)_{*n*}, where *n* denotes the molar parts of 4-phenyl acetylene glycol ester phthalate (PEPE) per hundred mole of TPA), which exhibits inactivity during synthesis and processing but can cross-link rapidly at higher temperatures before burning, was prepared *via* one-pot melt polycondensation. Thermal properties, cross-linking behavior, flame-retardant and anti-dripping performances of the resulting copolyesters were investigated.

Experimental

Chemicals and substrates

Terephthalic acid (TPA) was supplied by Jinan Chemical Fiber Co Ltd. (Jinan, China). 4-Phenylethynylphthalic anhydride (PEPA) was purchased from Changzhou Sunlight Pharmaceutical Co., Ltd. (Changzhou, China). Antimony trioxide (Sb₂O₃, AR), ethylene glycol (EG), methanol, phenol, tetrachloroethane, hexafluoro isopropanol, zinc acetate, sulfuric acid (CP) were all



Scheme 1 Cross-linking reaction of the phenylethynyl structure at high temperature.

manufactured by Chengdu Chemical Industries Co. (Chengdu, China) and used as received.

Synthesis of the cross-linkable monomer

PEPA was firstly methylated, and transesterificated in the presence of ethylene glycol to obtain the target cross-linkable monomer named 4-(phenylethynyl) di(ethylene glycol) phthalate (PEPE, dark-green viscous liquid, yield 89%) (Scheme 2). IR (KBr): $\nu = 3329$ (w), 2882–2997 (w), 1722 (s), 2210 cm⁻¹ (m); ¹H NMR (400 MHz, DMSO-*d*₆, δ): 6.9–7.6 (8H, Ar-*H*), 5.0 (2H, -OH), 4.4 (4H, -CH₂-OH), 3.7 (4H, -C(O)O-CH₂-).

Polymerization

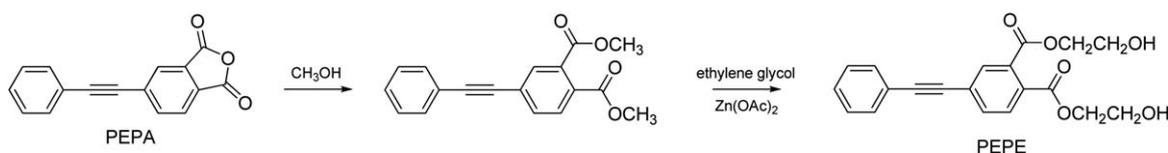
The synthetic routes for poly(ethylene terephthalate-*co*-4-phenylethynylphthalate abbreviated as P(ET-*co*-P) are shown as follows (Scheme 3). P(ET-*co*-P) was synthesized by melt polycondensation in a 2.5 L autoclave equipped with a nitrogen inlet, a condensation, and a mechanical stirrer. The route for preparation of P(ET-*co*-P)₁₀ was presented here as a representative example, where the number 10 denotes the molar parts of PEPE per hundred of TPA (say, PEPE : TPA = 10 : 100). 650 g (3.90 mol) TPA, 330 mL (5.80 mol) EG and 0.34 g (0.0012 mol) Sb₂O₃ were added to a 2.5 L autoclave. Prior to polymerization, nitrogen was purged into the autoclave to avoid any subsidiary reactions. A multistep temperature procedure was used for esterification. The reactor was firstly heated to 240 °C for 2 h and 260 °C for 1.5 h under high pressure (0.3–0.4 MPa), and water yielded was removed by fractionation. Then a vacuum was applied and reaction mixture was cooled to 240 °C slowly. Thereafter, 150 mL of an ethylene glycol solution of PEPE (2.6 mol L⁻¹) was added dropwise into the autoclave while keeping the temperature above 220 °C under a steady stream of nitrogen. Afterward, the mixture was heated to 260 °C, and during this period, the excess EG was continued to be distilled. Finally, the pressure of the mixture was reduced to lower than 60 Pa and the temperature was raised to 280 °C in 0.5 h and maintained for 2 h. The resulting polymer was extruded at the N₂ pressure through an orifice and cooled in water bath. Other examples were obtained according to a similar process. IR (KBr): 2882–2997 (w), 1722 (s), 2210 (m). ¹H NMR (CF₃COOD, δ , Fig. 1): 7.9 (Ar-*H* in terephthalic structure units), 7.3–7.6 (Ar-*H* in isophthalic structure units) 6.9–7.1 (Ar-*H* in 4-phenylethynyl structure unit) and 4.3–4.6 (-CH₂O-).

Thermal cross-linking of P(ET-*co*-P)

P(ET-*co*-P)s were firstly dissolved in hexafluoro isopropanol at a concentration of 5 mg mL⁻¹. The solution was cast on a glass plate, and dried at ambient temperature. The polymer films obtained were cross-linked at 340 °C for 30 min in nitrogen. PET was also thermal treated for better comparison.

Characterization

NMR spectrum (¹H, 400 MHz) were obtained at room temperature by a Bruker AVANCE AVII-400 NMR instrument, with CF₃COOD as the solvent, and tetramethylsilane as the internal standard. Fourier transform infrared spectroscopy (FTIR) was



Scheme 2 Synthesis process of 4-phenyl acetylene glycol ester phthalate (PEPE).

performed on a Nicolet 6700 spectrometer. GPC measurement was carried out on a Water 515 apparatus using polystyrene as a standard and CHCl_3 as an eluent. The intrinsic viscosities of the polyester were determined with an Ubbelohde viscometer with a concentration of 0.5 g dL^{-1} at 25°C in 1 : 1 (v/v) phenol-1,1,2,2-tetrachloroethane solution.

The solubility of the copolyesters was examined in phenol/tetrachloroethane and hexafluoro isopropanol at room temperature with a concentration of $0.1\text{--}1 \text{ g dL}^{-1}$. The gel content was determined by Soxhlet extraction with hexafluoro isopropanol (reflux 48 h). The ratio of the mass of insoluble materials remaining (dried to constant weight in vacuum) to the original mass was defined as the gel content for the sample. The gel content = mass of residue (g)/original mass (g) $\times 100\%$.

Cross-linking behavior was performed on a NETZSCH simultaneous TGA-DSC (449C) at a heating rate of $10^\circ\text{C min}^{-1}$ in N_2 .

The melting behaviors of neat PET and P(ET-co-P) copolyesters were measured with TA Q200 DSC apparatus, calibrated with pure indium and zinc standards. Samples ($5 \pm 0.5 \text{ mg}$) were melted and quenched in liquid nitrogen before testing. When tested, the samples were first equilibrated at 0°C in a nitrogen atmosphere with a purge flow of 50 mL min^{-1} , and was then heated to 250°C at a heating rate of $10^\circ\text{C min}^{-1}$. In this manuscript, heating curves and corresponding data of all testing samples were recorded.

Analysis of the thermal decomposition behavior of the polyesters was conducted on a NETZSCH TGA (209 F1) at a heating rate of $10^\circ\text{C min}^{-1}$. Char yields of the cross-linked copolyesters were determined from the mass of the residue remaining at 700°C in a nitrogen atmosphere.

The heat release rate (HRR), total heat release (THR), and the burning residues were measured by using an FTT cone calorimeter according to ISO 5660-1. The samples were molded to a size of $100 \times 100 \times 3 \text{ mm}^3$ at a heat flux of 50 kW m^{-2} using FERROMATIK MILACRON K-TEC 40 injection molding. The molding temperatures were 260°C , 240°C , 230°C , 210°C for PET, P(ET-co-P)₅, P(ET-co-P)₁₀ and P(ET-co-P)₂₀ respectively.

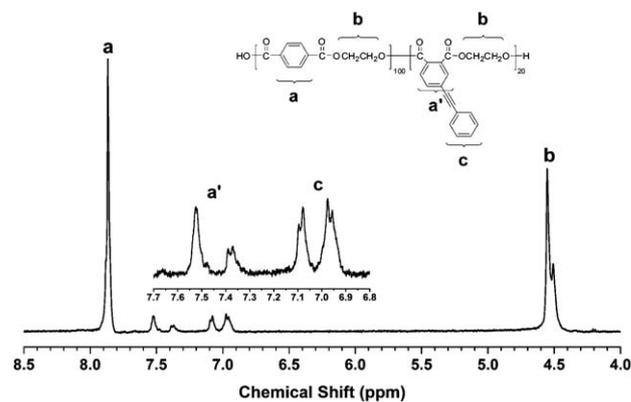


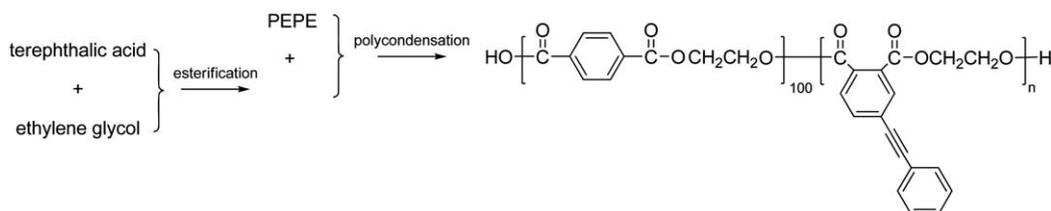
Fig. 1 ^1H NMR spectrum of P(ET-co-P)₂₀.

To observe the anti-dripping behaviors of the copolyesters, a small fire test was carried with a propane torch flame at different directions: on the one hand the samples were placed vertically and ignited in a propane torch flame at a 45° angle for 5–10 s with a 75% oxygen concentration; while on the other hand the propane flame was placed vertically, and the samples were kept at 45° angle and ignited for 5 s in air. Samples were molded to a size of $130 \times 6.5 \times 3.2 \text{ mm}^3$ through the aforementioned injection molding.

The LOI measurements were performed on the Oxygen Index Flammability Gauge (HC-2C) according to ASTM D 2863-97. The samples had a size of $120 \times 6.5 \times 3.2 \text{ mm}^3$.

The microstructures of the residual chars collected after the cone calorimeter tests were observed using scanning electron microscopy (JEOL JSM 5900LV) with an acceleration voltage of 10 kV. A thin layer of gold was sprayed on the surface prior to SEM observation.

Dynamic oscillatory rheological measurements of neat PET and copolyesters were performed with a parallel-plate fixture (25 mm diameter and 1 mm thickness) using an Advanced Dynamic Rheometric Expansion System (ARES, Bohlin Gemini 200) in an oscillatory shear mode. Temperature scanning tests at a fixed frequency of 0.1 Hz were in the range from 230, 230, 240

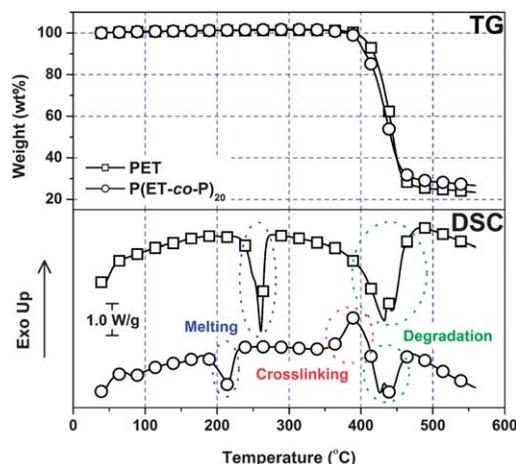
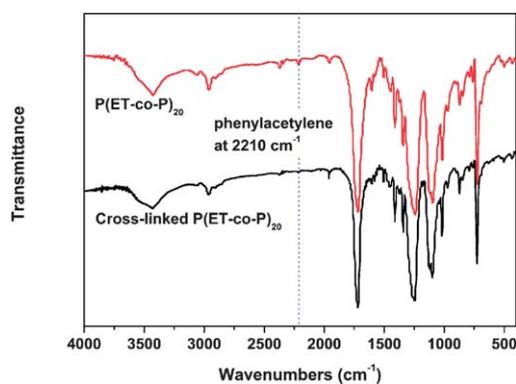


Scheme 3 Synthesis process of poly(ethylene terephthalate-co-4-phenylethynylphthalate), P(ET-co-P)_n, where *n* denotes the molar parts of 4-phenyl acetylene glycol ester phthalate (PEPE) per hundred mole of TPA, not the block length or repeating units.

Table 1 Basic characteristics of neat PET and P(ET-co-P) copolyesters

Samples	PEPE content (mol%)		$[\eta]$ (dL g ⁻¹)	Solubility ^b			
	Theo.	Test ^a		Original	Cross-linked ^c	Cross-linked gel (%) ^d	Cross-linked char (wt%) ^e
PET	—	—	0.68	+	+	—	10.9
P(ET-co-P) ₅	4.8	4.9	0.74	+	—	28.4	14.3
P(ET-co-P) ₁₀	9.1	8.9	0.85	+	—	42.6	18.0
P(ET-co-P) ₂₀	16.7	16.3	1.17	+	—	78.3	25.3
P(ET-co-P) ₄₀	28.6	28.0	1.24	+	—	—	30.6

^a Testing results were calculated from NMR. ^b Solubility of all samples were tested in both phenol-tetrachloroethane mixed solvent (60 : 40 w/w) and hexafluoro isopropanol (where “+” stands for soluble and “-” denotes insoluble). ^c Cross-linked at 340 °C for 60 min in N₂ for P(ET-co-P)_n (PET was also thermal treated). ^d Soxhlet extraction for 48 h with hexafluoro isopropanol. ^e Data of thermal treated PET and cross-linked copolyester obtained from TGA at 700 °C in nitrogen (heating rate at 10 °C min⁻¹).

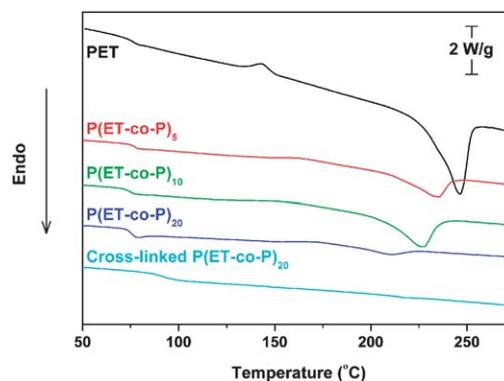
**Fig. 2** TG-DSC thermograms of PET and P(ET-co-P)₂₀ at a heating rate of 10 °C min⁻¹ in N₂.**Fig. 3** FTIR spectra of P(ET-co-P)₂₀ before and after heat-treatment at 340 °C for 30 min in N₂.

and 260 °C to 350 °C for P(ET-co-P)₂₀, P(ET-co-P)₁₀, P(ET-co-P)₅, and neat PET, respectively.

Results and discussion

Characterization of P(ET-co-P)s

P(ET-co-P) displayed yellow coloring from the conjugated acetylenic effects; and further turned to brown with increasing of

**Fig. 4** DSC thermograms for PET and P(ET-co-P) copolyesters in a nitrogen atmosphere at a heating rate of 10 °C min⁻¹.**Table 2** Thermal behaviors of PET and P(ET-co-P) copolyesters obtained from DSC

Sample	T_g (°C)	T_m (°C)	ΔH_m (J g ⁻¹)
PET	76.5	245.7	43.1
P(ET-co-P) ₅	77.5	232.9	31.3
P(ET-co-P) ₁₀	74.6	225.7	29.2
P(ET-co-P) ₂₀	76.1	207.8	6.1
Cross-linked P(ET-co-P) ₂₀	92.1	—	—

the content of PEPE. Molecular weight and polydispersity index (PDI) of P(ET-co-P)₂₀ were estimated by gel permeation chromatography (GPC); however, P(ET-co-P)₅ and P(ET-co-P)₁₀ were not dissolved in CHCl₃ for the GPC measurement. The GPC result showed a number-average molecular weight (M_n) and weight-average molecular weight (M_w) of P(ET-co-P)₂₀ which were 1.14×10^4 g mol⁻¹ and 4.12×10^4 g mol⁻¹, respectively (PDI = 3.6). Detailed parameters for the P(ET-co-P) copolyesters are listed in Table 1.

Thermal cross-linking analysis

In order to verify the hypothesis, that P(ET-co-P) copolyesters would conduct cross-linking reactions in the proper temperature range, which is lower than the decomposition temperature but

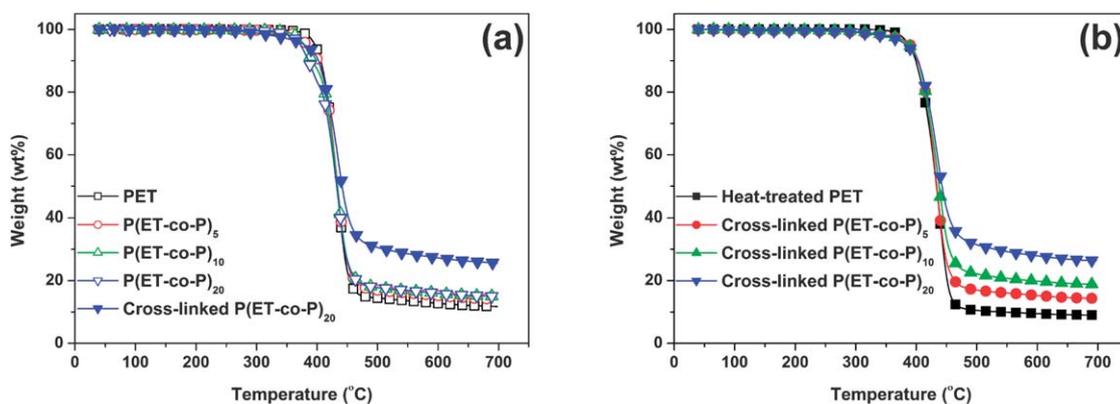


Fig. 5 TGA thermograms for PET and P(ET-co-P) copolyesters before (a) and after cross-linking (b) (cross-linked at 340 °C for 60 min in N₂ for P(ET-co-P)s, for comparison, PET was also thermally treated) in a nitrogen atmosphere at heating rate of 10 °C min⁻¹.

much above its processing temperature. The thermal behaviors of neat PET and P(ET-co-P)₂₀ were characterized by simultaneous thermogravimetry-differential scanning calorimetry (TG-DSC) in N₂ (Fig. 2). For the DSC thermogram of P(ET-co-P)₂₀, a notable exothermic process could be observed starting at 340 °C, just between the melting (*ca.* 220 °C) and the decomposition peak (*ca.* 440 °C), which should be attributed to the cross-linking reaction;^{32–39} while contrarily, neat PET directly decomposed after melting. It should be noted that the cross-linking peak was far away from the melting one, providing a wide processing window greater than 100 °C. From TGA curves, P(ET-co-P)₂₀ showed an initial decomposition temperature ($T_{5\%}$, defined as the temperature of 5 wt% weight loss) occurring at 392 °C, which is higher than the cross-linking temperature, indicating that the cross-linking reaction occurred prior to decomposition. Taken together, this unique thermal property confirmed the existence of cross-linking before decomposition without interfering in the processability of the copolyester.

Cross-linking of the P(ET-co-P)₂₀ copolyester was carried out at 340 °C for 30 min in nitrogen. Fig. 3 shows the FTIR spectra of P(ET-co-P)₂₀ before and after cross-linking. Noteworthy, is that a change in the FTIR spectrum could be observed after heating at 2210 cm⁻¹, suggesting that the alkynyl gradually disappeared during heating, which further indicated that the thermal cross-linking reaction had taken place (Scheme 1). In addition, no other significant changes could be found in the spectrum, indicating that the cross-linking was the major reaction at this temperature range, rather than thermal degradation.

Dissolution tests showed that the cross-linked P(ET-co-P) copolyesters were no longer soluble in the phenol-tetrachloroethane mixed solvent or hexafluoro isopropanol, even when the feed content of the third monomer was low; while all P(ET-co-P) copolyesters before heat treatment and PET were soluble in the above-mentioned solvent (Table 1). The degree of cross-linking was estimated by the gel content test for cross-linked P(ET-co-P) copolyesters *via* Soxhlet extraction for 48 h with reflux of hexafluoro isopropanol. With the introduction of PEPE, the gel contents of the cross-linked P(ET-co-P)s increased, which would provide more thermostable cross-linking networks during burning, and hence play a positive influence on flame-retardance and melt-dripping suppression.

DSC analysis

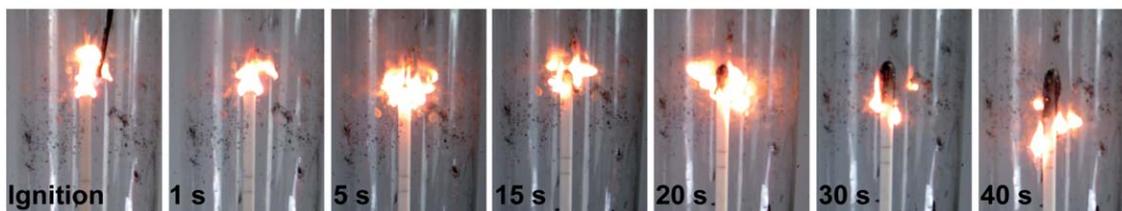
Fig. 4 shows the DSC thermograms of the P(ET-co-P) copolyesters and P(ET-co-P)₂₀ after cross-linking, in which the corresponding curve of neat PET was also included for comparison. Results indicated that PET and all P(ET-co-P) copolyesters before cross-linking were semicrystalline; however, both the melting temperature (T_m) and the corresponding enthalpy (ΔH_m) decreased with the increase of PEPE content incorporated (Table 2). On the one hand, the presence of bulky pendent phenylethynyl-containing side groups of PEPE disrupted the chain regularity and introduced irregular positions along the molecular chain axis due to the asymmetric hydroxyl groups of PEPE; thus, the resulting copolyesters exhibited lower crystallinity and melting temperatures. On the other hand, the presence

Table 3 TGA data of PET and P(ET-co-P) copolyesters before and after cross-linking

Sample	Before cross-linking				After cross-linking			
	$T_{5\%}$ (°C) ^a	T_{max} (°C) ^b	The rate of T_{max} (wt% min ⁻¹)	Residue at 700 °C (wt%)	$T_{5\%}$ (°C)	T_{max} (°C)	The rate of T_{max} (wt% min ⁻¹)	Residue at 700 °C (wt%)
PET	396.7	432.5	20.4	11.5	378.9	435.7	18.4	10.9
P(ET-co-P) ₅	383.2	433.6	19.0	14.2	390.2	434.0	18.3	14.3
P(ET-co-P) ₁₀	378.8	433.8	18.1	15.0	388.0	437.2	15.3	18.0
P(ET-co-P) ₂₀	372.5	435.2	16.6	15.2	384.1	432.8	13.1	25.3

^a $T_{5\%}$ defined as the temperature at which 5 wt% weight loss occurred. ^b T_{max} defined as the temperature at maximum weight loss rate.

PET (Oxygen Concentration: 23 vol%)



P(ET-co-P)₄₀ (Oxygen Concentration: 28 vol%)

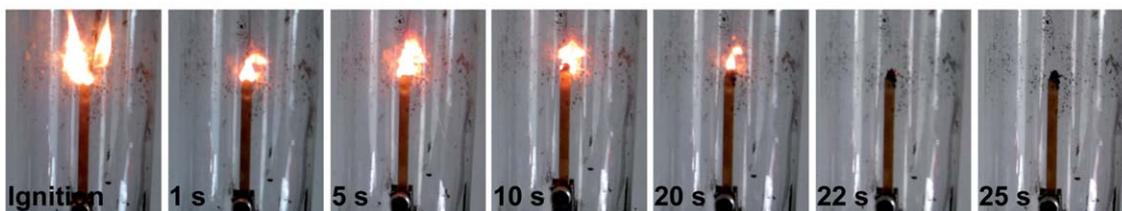


Fig. 6 Combustion processes of PET and P(ET-co-P)₄₀ at oxygen concentrations of 23 and 28 vol%, respectively.

of bulky pendent groups in P(ET-co-P) copolyesters hindered the molecular mobility, giving rise to the increase of glass transition temperatures (T_g). Apparently, the thermal behaviors of P(ET-co-P) could also be changed by cross-linking. The melting peak of P(ET-co-P)₂₀ disappeared after cross-linking, meaning that the crystalline form of the copolyester was completely destroyed. Furthermore, the T_g value of the cross-linked P(ET-co-P)₂₀ greatly increased compared with the value of the original one, suggesting a greater hindrance for chain mobility *via* the formation of the cross-linked networks.

Thermal stability

TGA results of the PET and P(ET-co-P) copolyesters before and after cross-linking under a nitrogen atmosphere were obtained and plotted in Fig. 5. $T_{5\%}$, T_{\max} , and the residue of all samples after the test are summarized in Table 3. For PET and P(ET-co-P) copolyesters before cross-linking (Fig. 5(a)), all samples exhibited

a single decomposition process, but the incorporation of the cross-linkable monomer slightly decreased the initial decomposition temperature and increased residual chars a little. However, compared with the original copolyesters, the $T_{5\%}$ of the cross-linked P(ET-co-P)s increased, suggesting the formation of the cross-linking structure. Furthermore, unlike the original copolyesters, residual chars of the cross-linked P(ET-co-P)s were much higher than that of PET (Fig. 5(b)). Higher residual chars at relatively high temperatures might be ascribed to the high char concentration of the phenylethynyl groups, suggesting that the pre-formed cross-linking networks were thermally stable as the literature reported,^{28,29} which might have a positive effect on flame-retardance and anti-dripping of the copolyester.

Burning behavior and anti-dripping analysis

The limit oxygen index (LOI) indicates the minimum oxygen concentration (vol%) which would support the combustion of a

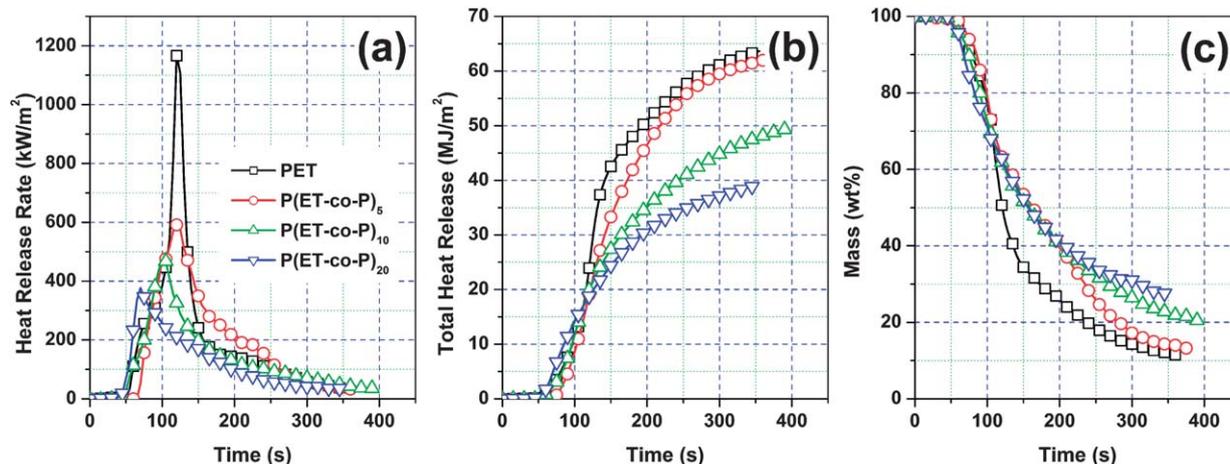


Fig. 7 Cone calorimetric results of PET and P(ET-co-P) copolyesters at an external heat flux of 50 kW m⁻² as a function of burning duration: (a) heat release rate, (b) total heat release and (c) residue mass.

Table 4 Detailed combustion results of neat PET and P(ET-co-P) copolyesters obtained from cone calorimetry

Samples	PET	P(ET-co-P) ₅	P(ET-co-P) ₁₀	P(ET-co-P) ₂₀
TTI (s) ^a	48	47	43	38
PHRR (kW m ⁻²)	1167	591	472	376
Time to PHRR (s)	120	120	100	70
FIGRA (kW m ⁻² s ⁻¹) ^b	9.7	4.9	4.7	5.4
Averaged HRR (kW m ⁻²)	205	203	139	126
THR (MJ m ⁻²)	63.5	62.1	49.5	39.0
Residue (wt%)	11	12	20	27

^a TTI stands for the time to ignition. ^b FIGRA is calculated by dividing the value of PHRR by the time to PHRR.

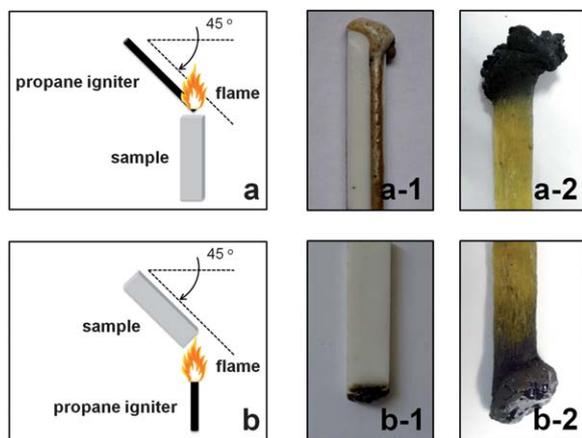


Fig. 8 Flammability in different small-scale flame test configuration: (a) vertically upward samples ignited at the top; (b) downward samples ignited at the bottom (1: neat PET; 2: P(ET-co-P)₂₀).

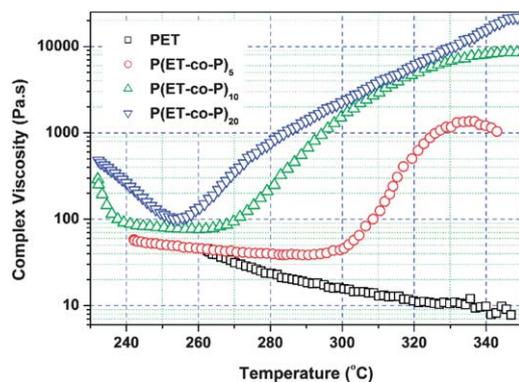


Fig. 9 Complex melt viscosity plotted against temperature at a heating rate of 10 °C min⁻¹ in an air atmosphere.

certain material. In this case, the LOI of PET, P(ET-co-P)₂₀ and P(ET-co-P)₄₀ was tested for estimating their flame-retardancy: LOI values increased from 22 to 25 and 28, respectively. In detail, the combustion processes of PET and P(ET-co-P)₄₀ were illustrated in Fig. 6. For PET, when the testing oxygen concentration was 23, the sample was ignited quickly with rapid flame propagation; while melt-dripping with fire could be observed after the burning duration reached 40 s. However, for the P(ET-co-P)₄₀ tested at an oxygen concentration of 28, when sample was

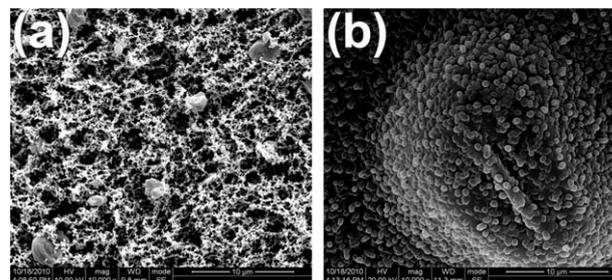


Fig. 10 SEM images of the char residue of P(ET-co-P)₂₀ after cone calorimetric analyses: (a) outer surface, (b) inner surface.

ignited, flame propagation was apparently slow; then the flame gradually became small, and finally extinguished within 25 s.

For the cone calorimeter test, an oxygen consumption technique similar to the real scale fire,^{40,41} was used to evaluate the combustion performance of the PET and P(ET-co-P) copolyesters (Fig. 7), and the detailed data is collected in Table 4. The heat release rate (HRR), in particular the peak value of HRR (PHRR), was considered as the most important parameter to evaluate fire safety of the flame-retardant materials, which determined the rate of fuel-feeding in the combustion and further rate of flame spread.^{42,43} Lower PHRR values denoted slower flame spread and minor fire hazard. In this work, with the introduction of PEPE, both the peak and average values of HRR of the copolyesters decreased significantly: PHRR of P(ET-co-P)₅ was about 591 kW m⁻², nearly half of that of PET; while for P(ET-co-P)₂₀, PHRR was only 376 kW m⁻² and decreased to 32% of that of PET. For flame-retardant polyesters, such low HRRs was much closer to the testing values of most phosphorus-containing polyesters.^{3,21-24} Thus, it was clear that PEPE could effectively reduce the HRR of copolyesters and slow down flame propagation. Also, with the incorporation of the functional monomer, the total heat release (THR) of the copolyester decreased with the increase of PEPE content: the value for neat PET was 63.5 MJ m⁻²; while the values for P(ET-co-P)₅, P(ET-co-P)₁₀ and P(ET-co-P)₂₀ were 62.1, 49.5 and 39.0 MJ m⁻², respectively. The mass curves for the four samples were very similar to the THR ones: P(ET-co-P)₂₀ exhibited the highest burning residues (27 wt%), meaning least fuel generation and feeding-back during combustion, which was in accordance with the TGA results of the cross-linked copolyesters rather than the results of un-treated samples. This phenomenon might be explained as follows: for cone calorimetry, the cross-linking

reaction of the copolyesters after ignition was much faster than that of the samples during TGA at a programmed heating rate to form a efficacious cross-linking structure; in other words, cross-linking reactions of the samples during TGA would compete with the rest of the side reactions, including chain scission and decomposition.

Consequently, the cone calorimeter tests strongly showed that these copolyesters had low flammability, despite the absence of traditional flame-retardants.

In a small-scale flammability test, the samples were firstly burned, as shown in Fig. 8(a). P(ET-co-P)₂₀ was seen to extinguish quickly following the removal of the igniter, leaving lots of intumescent char on the top of the sample, which played a positive role on anti-dripping; by contrast neat PET left a very clear trace of the flow after burning. When changing the direction of ignition (Fig. 8(b)), only little dripping was found for P(ET-co-P)₂₀ during the course of the test, and the char similarly maintained its shape. The non-flammability and non-dripping was achieved at the same time. It was a pity that P(ET-co-P)₂₀ still failed to pass vertical burning tests (UL-94), and a higher content of PEPE was needed. In our later work, P(ET-co-P)₈₀ (content of PEPE was about 44.4%) could reach V-0, and no any dripping appeared throughout the testing process.

Potential mechanism investigation

For better understanding of this flame-retardant and anti-dripping mechanism, dynamic oscillatory rheological measurements were introduced to investigate the viscoelastic behaviors of the testing samples during the heating process. Fig. 9 shows the temperature dependence of complex viscosity ($|\eta^*|$) of the P(ET-co-P) copolyesters and neat PET. Compared with neat PET, whose $|\eta^*|$ singly showed a linear decrease during the heating process, the $|\eta^*|$ of P(ET-co-P) copolyesters firstly experienced a decrease, and subsequently increased sharply from T_c (where $|\eta^*|$ starts to increase or cross-linking reaction occurs in other word^{44,45}), and the 'U-shape' change could be clearly observed in the whole temperature range. Furthermore, T_c values of all copolyesters were also between the melting temperature (T_m) and $T_{5\%}$, in accordance with the cross-linking behavior in N₂ from TG-DSC. This behavior could be explained as follows: upon heating, the easier movement of polymer chains resulted in a decrease in $|\eta^*|$ of the sample or the occurrence of the degradation of the polymer somewhat; however, for P(ET-co-P)s, the increase of $|\eta^*|$ (21 600 Pa s for P(ET-co-P)₂₀ at 350 °C) was due to the occurrence of a cross-linking reaction or the reaction overwhelming the decomposition of the copolyester. More importantly, it was reported that the high $|\eta^*|$ caused by cross-linking networks could effectively reduce the flammability of the polymer materials by suppressing the vigorous bubbling process in the course of degradation during combustion, and simultaneously inhibit the dripping effectively.^{20,44-47} As the degree of cross-linking further increased, a solid and char-like heat transfer barrier could be formed, which could play a positive role in maintaining the shape of the polymers and in extinguishing the materials. Moreover, P(ET-co-P) copolyesters with higher contents of PEPE exhibited a greater $|\eta^*|$, leading to higher char residues, better flame-retardant and anti-dripping effects, which was in agreement with the result of the cone calorimeter tests.

The surface morphology of the char could be very important for the solid-phase flame retardant. Fig. 10 presents the SEM microphotographs of the residue of P(ET-co-P)₂₀ after cone calorimeter measurements. Dramatically, a honeycomb-like char formation with a porous outer surface and compact inner surface was observed, and the particles of the inner surface were spherical in structure with an average diameter of about 500 nm. This interesting honeycomb-like char with compact particles probably exhibited excellent heat insulation and mechanical properties, providing outstanding flame-retardant and anti-dripping effects.

Conclusions

In summary, a novel high-temperature cross-linkable PET-based copolyester with phenylethynyl as a pendent group was successfully synthesized, and their flammability and anti-dripping performances suggested that the contradiction between the non-flammability and non-dripping for polyesters could be solved by copolymerizing the smart self cross-linking monomer. TG-DSC, FTIR, dissolution tests and rheological analyses proved the thermal cross-linking behavior of the copolyester. The cone calorimetric analyses and flammability tests further confirmed the self-extinguishment and inhibition for melt-dripping. Therefore, flame-retardation of the copolyester could be achieved only by cross-linking during burning, despite the absence of any flame-retardant element (say, bromine, chlorine, phosphorus, or nitrogen, *etc.*). This thermal cross-linkable copolyester had only carbon, hydrogen, and oxygen, which may be truly green and environment-friendly. In addition, this copolyester also provided a new strategy for preparing other polymers requiring low flammability and anti-dripping properties.

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