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# New application for aromatic Schiff base: high efficient flame-retardant and anti-dripping action for polyesters

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#### ABSTRACT

Bonding aryl groups with carbon-nitrogen double bond is a critical structural factor for the self-crosslinking of Schiff bases at high temperature. In this study, a novel aromatic Schiff base "5-(benzylidene-amino)-isophthalic acid dimethyl ester (BA)" has been designed as a self-crosslinking monomer for poly(ethylene terephthalate) (PET) based copolyesters (BA<sub>n</sub>PETs). The cross-linking behaviors, flame retardancy and non-dripping performance of BA<sub>n</sub>PETs have been investigated by simultaneous thermal analysis (TG-DSC), dynamic rheology, limiting oxygen index (LOI), UL-94 vertical burning and cone calorimetry tests. It is found that BA units can cross-link during combustion resulting in high melting viscosity and enhance char forming for BA<sub>n</sub>PETs, which endows the copolyesters with excellent flame retardancy and non-dripping behavior. Incorporating of BA with a low content (only 7.7 mol%), the

LOI value of copolyester increases from 22.0% to 31.0%, and at the same time it achieves V-0 rating in the UL-94 vertical burning test. The mode action of Schiff bases on flame retardation and anti-dripping of copolyesters also has been investigated, and the results show that the aromatic Schiff base groups can lead copolyesters to form nitrogen-containing cross-linkable networks and further transform into compact char layer during combustion. The char layer which acts as an effective barrier, cuts off oxygen, hinders the volatilization of combustible gas and isolates unburned polymer from fire resource. This work suggests that using Schiff base as a self-crosslinkable monomer is a new and effective way for fire-safe polymeric materials.

Key words: Schiff Base; PET; Cross-linking; Flame Retardance; Anti-dripping

#### 1. Introduction

Schiff bases, known as azomethines, exhibit interesting properties due to the presence of C=N imine groups. Structural diversified Schiff bases and their metal complexes have been extensively applied in diverse areas, such as biomedicine, [1, 2] self-healing materials, [3-5] fluorescent sensors, [6-8] corrosion inhibitors, [9, 10] catalysts, [11, 12] electrode materials [13, 14] and photochromic materials [15, 16]. Recently, Prof. Bourbigot's group have synthesized Salen-based Schiff bases and find they have an intriguingly combative response to an elevated temperature/fire scenario, which can be used as additive flame retardant for polyamide-6 by forming an ablative surface.[17] Analogously, highly  $\pi$ -conjugated Schiff base can significantly improve

the thermal stability of liquid crystal diepoxide polymer, probably ascribable its effective charring ability retarding a further degradation of polymer. [18] These results illustrate that Schiff bases can change their "soft" molecular structure to achieve thermal protection via precise selecting their substituents. [17]

Poly(ethylene terephthalate) (PET), has been widely used as textiles and engineering plastics because of its excellent comprehensive properties and low cost. [19-22] However, the fire risk and serious melt-dripping during burning limit its application in many fields. To improve both fire resistance and anti-dripping behaviors of PET, our laboratory has put forward a new solution i. e. designing some intelligent cross-linkable precursors and introducing them into the chemical structure of PET via copolymerization. [23-32] These chemical or physical cross-linkable units can form stable cross-linked networks in a certain temperature range which is higher than the processing temperature but lower than the decomposition temperature. Therefore, the obtained PET-based copolyesters show enhanced thermal stability, higher melt viscosity and stronger char-formation ability during combustion, and simultaneously display good self-extinguishing and anti-dripping performances. Deficiently, some of these cross-linkable precursors are expensive, and some of them need complicated synthesis procedures. [25, 26, 29] To promote the industrial application of these self-extinguishing and anti-dripping PET-based copolyesters, it is urgent to find out some new intelligent cross-linkable precursors with low cost and convenient synthesis process.

Recently, Zhang's work reveals that aromatic Schiff base exists dynamic

exchange among C=N double bonds at room temperature, when both nitrogen and carbon atoms in Schiff base are connected to aryl group. [3] Based on this dynamic equilibrium, the cross-linked polyacrylate possesses self-healing ability and reprocessability. The cross-linked networks are dynamic at room temperature, thus they may be stable at higher temperatures such as during combustion. That is to say, an aromatic Schiff base perhaps is a potential self-crosslinking unit for achieving PET flame retardant and anti-dripping performances.

To verify this idea, in this manuscript, a kind of aromatic Schiff base, 5-(benzylidene-amino)-isophthalic acid dimethyl ester (BA), has been synthesized and used as a cross-linkable flame retardant monomer for PET, because of its potential self-crosslinking property, containing ignition-proof element "nitrogen" and low cost. As we expect, this new aromatic Schiff base can cross-link at high temperature and results in the formation of stable networks during combustion, further to endow PET-based copolyesters with excellent self-extinguishing and anti-dripping properties. The thermal properties, cross-linking behaviors, flame-retardance, anti-dripping performances and residue chars of the copolyesters have been elaborately investigated.

#### 2. Experimental

#### 2.1 Materials

Dimethyl terephthalate (DMT, CP), zinc acetate (99.5%) and antimony trioxide (Sb<sub>2</sub>O<sub>3</sub>, AR) were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai,

China). 5-amino-isophthalic acid dimethyl ester was purchased from Lideshi Chemical Technology Co., Ltd. (Beijing, China). Benzaldehyde (AR), ethylene glycol (EG, AR), phenol, 1,1,2,2-tetrachloroethane, methanol, hexafluoro isopropanol and anhydrous ethanol were all provided by Chengdu Chemical Industries Co., Ltd. (Chengdu, China).

#### 2.2 Synthesis of 5-(benzylidene-amino)-isophthalic acid dimethyl ester (BA)

The Schiff base precursor BA was prepared by aldimine condensation according to the literature [33] and the synthetic route is shown in Scheme 1. The detailed synthesis processes are shown as follow: 31.8 g (0.3 mol) benzaldehyde and 150 mL anhydrous ethanol were mixed together and heated to reflux (85 °C) in a 500 mL three-necked round bottom flask equipped with a nitrogen inlet, reflux condenser and magnetic stirrer. Then 62.7 g (0.3 mol) 5-amino-isophthalic acid dimethyl ester was added into the flask in batches and the reaction mixture was stirred and refluxed for 6 h. After that, the mixture was cooled down to room temperature and the white powder was collected by filtration. Finally, the obtained product was recrystallized with anhydrous ethanol and dried under vacuum.



Scheme 1 Synthesis route of 5-(benzylidene-amino)-isophthalic acid dimethyl ester (BA).

BA: white crystals, yield: 87 %, m.p: 115 °C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm, shown in Fig. S1): 8.78 (1H, -N=CH-), 8.35-8.37 (1H, Ar-H), 8.03-8.05 (2H,

Ar-H), 7.98-8.03 (2 H, Ar-H), 7.52-7.63 (3H, Ar-H), 3.92 (6H, -OCH<sub>3</sub>).

#### **2.3 Polymerization**

The PET copolyesters (BA<sub>n</sub>PETs, the number n denotes the molar content of BA per hundred mole of DMT) containing Schiff base BA were fabricated by esterification and melt polycondensation (shown in Scheme 2). The synthesis procedures of BA<sub>10</sub>PET, serves as an example, are shown as follows: Under a nitrogen atmosphere, 25.4 g (0.1 mol) bis-hydroxyethyl terephthalate (BHET, transesterified by 0.1 mol DMT and 0.22 mol ethylene glycol), 3.0 g (0.01 mol) BA, 0.16 g ( $8.7 \times 10^{-4}$  mol) zinc acetate and 0.012 g ( $4.1 \times 10^{-5}$  mol) antimony trioxide were melted and transesterified at 200 °C for 3 h in a 100 mL three-necked polymerization bottle equipped with a mechanical stirrer. Then, the reactor was heated to 240 °C and the mixture was stirred for 2 h with the pressure of system reduced to lower than 70 Pa for polycondensation to obtain BA<sub>10</sub>PET copolyester. Other copolyesters were obtained by similar procedures.

<sup>1</sup>H NMR (400 MHz, CF<sub>3</sub>COOD-d<sub>6</sub>, δ, ppm, shown in Fig. S2): 8.53 (-N=CH-), 8.24 (Ar-H), 8.10 (Ar-H), 7.87-7.94 (Ar-H), 7.72 (Ar-H), 7.50-7.67 (Ar-H), 4.42 (-CH<sub>2</sub>-O-), 4.20 (-CH<sub>2</sub>-O-). <sup>13</sup>C MAS NMR (500 MHz, δ, ppm, shown in Fig. S3): 194 (-CH=N-), 165 (O-C=O), 131 (Ar), 61 (-CH<sub>2</sub>-).



Scheme 2 Synthesis processes of  $BA_nPET$ , where n denotes the molar content of BA per hundred mole of DMT (BA : DMT = n : 100 in mol), not the block length or repeating units0.

Based on the integral area of C=N and benzene ring of BHET obtained from their <sup>1</sup>H NMR spectra, for all copolyesters, it is found that more than 80% monomers are successfully introduced in the molecular chain of PET. In addition, the intrinsic viscosities [ $\eta$ ] of pure PET and copolyesters are similar and all over 0.7 dL g<sup>-1</sup>.

#### 2.4 Characterization

The intrinsic viscosities [ $\eta$ ] of PET and BA<sub>n</sub>PETs were measured by an Ubbelohde viscometer at 25 °C with a concentration of 0.5 g dL<sup>-1</sup> in 50/50 (v/v) of phenol/1,1,2,2-tetrachloroethane solution.

The <sup>1</sup>H NMR spectra (400 MHz) for BA and BA<sub>n</sub>PETs were obtained with Bruker AV II 400 MHz NMR instrument, in which DMSO- $d_6$  and CF<sub>3</sub>COOD were used as the solvent, respectively, and tetramethylsilane (TMS) was the reference. Before testing, the copolyesters were treated as follows: copolyesters were firstly dissolved into 50/50 (v/v) of phenol/1,1,2,2-tetrachloroethane solution, then precipitated with methanol, and finally dried in vacuum oven at 100 °C for 24 h. The <sup>13</sup>C MAS NMR spectra (500 MHz) for BA<sub>10</sub>PET was performed on Bruker AVANCE III 500 MHz solid NMR spectrometer.

The differential scanning calorimetry (DSC) tests were performed on a TA Q200 DSC apparatus with pure indium as standards. With a nitrogen flow of 50 mL min<sup>-1</sup>, aluminum pans contained  $5.0 \pm 0.5$  mg samples. Neat PET, BA<sub>5</sub>PET, BA<sub>10</sub>PET and BA<sub>15</sub>PET were firstly heated at 280 °C, 260 °C, 250 °C and 230 °C, respectively, and maintained for 3 min. Then all samples were cooled down to 40 °C and subsequently

reheated to 280 °C (marked as 2nd heating scans). The scanning rates for tests were 10 °C min<sup>-1</sup>.

Thermogravimetric analysis (TGA) were recorded using a NETZSCH TGA (209 F1) thermal analyzer under nitrogen and air atmosphere respectively. The tests were performed in Al<sub>2</sub>O<sub>3</sub> pans with 5.0  $\pm$  0.5 mg samples and heated from 40 °C up to 700 °C at a heating rate of 10 °C min<sup>-1</sup>.

Cross-linking behaviors of copolyesters were measured with NETZSCH simultaneous TG-DSC (449 C) with a nitrogen flow of 50 mL min<sup>-1</sup>. In aluminum pans, samples were heated from 40 °C to 550 °C at a 10 °C min<sup>-1</sup> heating rate.

Dynamic oscillatory rheological tests of neat PET and BA<sub>n</sub>PETs were performed with an Advanced Dynamic Rheometric Expansion System (TA, Discovery HR-2). The size of samples were 25 mm in diameter and 1 mm in thickness. Temperature scanning tests were in the range from 270 °C, 250 °C, 240 °C, 230 °C to 310 °C for PET, BA<sub>5</sub>PET, BA<sub>10</sub>PET, BA<sub>15</sub>PET, respectively. And time scanning tests were performed at a fixed 280 °C for 600 s. All tests were at a fixed frequency of 1 Hz.

Capillary rheological behaviors of neat BA<sub>n</sub>PETs were measured by a Rosand RH7D capillary rheometer. The tests were performed at 250 °C, 230 °C and 225 °C, respectively, with the shear rate ranged from 50 s<sup>-1</sup> to 2000 s<sup>-1</sup>.

Flame retardancy and non-dripping behaviors of neat PET and  $BA_nPETs$  were appraised by Limiting oxygen index (LOI) and Underwriter Laboratory 94 vertical burning (UL-94) tests. LOI tests were performed on a HC-2C oxygen index flammability gauge according to the ASTM D 2863-97 with a dimensional size of 130

 $\times$  6.5  $\times$  3.2 mm<sup>3</sup>. UL-94 tests were conducted with a CZF-2 apparatus according to the ASTM D 2863-97 with a dimensional size of 130  $\times$  13  $\times$  3.2 mm<sup>3</sup>. The results of each sample were obtained from at least five measurements.

Cone calorimetric tests were carried out with a FTT (UK) calorimeter according to the ISO 5660-1 at a 50 kW m<sup>-2</sup> heat flux and the testing samples were molded to a size of  $100 \times 100 \times 3.2 \text{ mm}^3$ . The average values of each sample were obtained from at least four measurements, and the experiment error was about  $\pm 10\%$ .

The gaseous products of neat PET and  $BA_{15}PET$  were investigated by thermogravimetry-infrared spectrometer (TG-IR) using the NETZSCH TGA (209 F1) thermogravimetric analyzer that was linked to the Nicolet 6700 FT-IR spectrophotometer at a 10 °C min<sup>-1</sup> heating rate from 40 °C to 700 °C in nitrogen atmosphere (flow rate: 50 mL min<sup>-1</sup>).

X-ray photoelectron spectroscopies (XPS) were performed on XSAM 800 spectrometer (Kratos Co., UK), with Al K $\alpha$  excitation radiation (1486.6 eV), operated at 12 kV and 15 mA. Bing energies were referenced to the carbonaceous carbon at 285.0 eV.

Fourier transform infrared (FTIR) spectra of the char residues of  $BA_{10}PET$  and PET were obtained by a Nicolet FTIR 170SX spectrometer. The wavenumber range from 500 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> using KBr disk method.

The microstructures of residual chars of cone tests were observed by scanning electron microscopy (SEM, JEOL JSM-5900LV) at a 10 kV acceleration voltage. Samples were over gilded using an Eiko IB-3 ion coater instrument before test.

Raman spectroscopies of residual chars of cone tests were performed on a LabRAM HR800 Raman spectrometer (SPEX Co., USA) with a 532 nm laser line.

The mechanical properties of PET and  $BA_nPETs$  were determined using INSTRON F563-44 according to ASTM D-638 at 1 mm/min cross-head speed. The specimen has a width of 4.0 ± 0.1 mm and thickness of 2.0 ± 0.1 mm. The results of each sample were obtained from at least five measurements.

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#### **3. Results and discussion**

#### 3.1 Cross-linking behavior

To investigate the cross-linking ability of BA unit,  $BA_{10}PET$  as an example is tested by TG-DSC at a heating rate of 10 °C min<sup>-1</sup> in nitrogen while pure PET is also measured for comparison. The TG-DSC curves of neat PET and  $BA_{10}PET$  are shown in Fig. 1. From the DSC curve of  $BA_{10}PET$ , it is noted that an obvious exothermic peak appears between the melting and decomposition peaks, and reaches at a maximum at 348 °C, while neat PET has no exothermic process and directly decomposes after melting. This special exothermic peak for  $BA_{10}PET$  proves that the cross-linking action caused by BA structure occurs at this temperature range in nitrogen. [23, 25, 26, 29]

Dynamic oscillatory rheological measurements are used to further validate the cross-linking behavior of copolyesters during the heating processes, and the corresponding results are shown in Fig. 2 (a). For pure PET, its complex viscosity decreases evidently with the increasing temperature, behaving as a typical

pseudoplastic fluid. [34-36] On the contrary, the complex viscosity of  $BA_nPETs$ increases sharply during heating. The complex viscosity of  $BA_{10}PET$  and  $BA_{15}PET$ nearly reach to 10000 Pa·s when the temperature is about 310 °C. This behavior illustrates that some stable cross-linking networks formed at high temperature restricting the mobility of the chains of  $BA_nPETs$ , thus leading to the increase of the complex viscosity. As we know, low melting viscosity at high temperature directly causes serious dripping behavior for pure PET, so the high complex viscosity of copolyesters will play a positive role for improving their anti-dripping.



Fig. 1 TG-DSC thermograms of neat PET and BA10PET in nitrogen at a heating rate of 10 °C

min<sup>-</sup>

The variation trends of complex viscosity of  $BA_nPETs$  display dissimilar to our previous reported self-crosslinking polymers: their complex viscosity firstly present a decrease with increasing temperature, and subsequently increase sharply when cross-linking reaction occur, showing "U-shape" curves. [25, 26, 29] This

phenomenon means that a few of BA<sub>n</sub>PETs copolyesters have formed cross-linking structures during preparation, but the cross-linking networks are too slight to influence their solubility or processing. The obtained BA<sub>n</sub>PETs can dissolve in phenol-tetrachloroethane mixed solvent or hexafluoro isopropanol, so their intrinsic viscosities can be got. In addition, BA<sub>n</sub>PETs copolyesters still maintain their processibility which have been tested by high pressure capillary rheometer. As shown in Fig. S4, we can see that the shear viscosity of BA<sub>n</sub>PETs declines sharply with increasing shear rate, as same as pure PET. But when BA<sub>n</sub>PETs copolyesters are treated at 300 °C for 10 min, they are insoluble in the above-mentioned solvent, illustrating a large quantity of stable cross-linking networks formed at high temperature.



Fig. 2 Dynamic oscillatory rheological results of neat PET and  $BA_nPETs$  in air atmosphere: (a) Complex melt viscosity plotted against temperature; (b) Complex melt viscosity plotted against time at a fixed temperature of 280 °C.

The relationship between the content of monomer BA and the cross-linking rate

is also investigated by dynamic oscillatory rheology at a fixed temperature. The increased rates of the complex viscosity at a constant temperature (280 °C) as reflected their cross-linking rates are shown in Fig. 2 (b). PET shows no increase in complex viscosity, while  $BA_nPETs$  copolyesters present linearly increased against time. The slopes of the lines become bigger with the increase of BA content, which means the more the incorporated BA units, the faster cross-linking rate at high temperature. And the formed cross-liking structure will be deduced in the following part based on the XPS spectra of  $BA_{10}PET$  char residue and TG-IR spectra of  $BA_{10}PET$  pyrolysis products.

#### 3.2 Melting behavior, mechanical properties and thermal stability

DSC is used to investigate the melting behaviors of BA<sub>n</sub>PETs copolyesters. Fig. 3 displays the second heating scans of neat PET and BA<sub>n</sub>PETs, and the detailed thermal transition data are listed in Table 1. From Fig. 3 we can see that all BA<sub>n</sub>PETs copolyesters are semicrystalline like pure PET. Compared to PET, the glass transition temperature ( $T_g$ ) of BA<sub>n</sub>PETs copolyesters are higher due to the large bulky pendent aromatic Schiff base groups. Meanwhile, both the melt temperature ( $T_m$ ) and the correlative enthalpy ( $\Delta H_m$ ) of copolyesters decrease with increasing content of BA. This phenomenon reveals that the incorporation of BA breaks the symmetry and regularity of the chain segments, and limits the movement of chains, resulting in the decline of the copolyesters' crystallization ability. [37-39] Nevertheless, in comparison to PET-based copolyesters containing phenylmaleimide/phenylacetylene, [25, 29] BA<sub>n</sub>PETs show better crystallization ability.



Fig. 3 DSC thermograms of neat PET and  $BA_nPETs$  for second heating scans in nitrogen at a

heating rate of 10 °C min<sup>-1</sup>.

		· <b>j</b>		п		
Sample –	BA content	t (mol%)	[η]	$T_{ m g}$	$T_{\rm m}$	$\Delta H_{ m m}$
	Theoretical	Actual <sup>a</sup>	$(dL g^{-1})$	(°C)	(°C)	$(J g^{-1})$
PET	0	0	0.79	79	247	35.6
BA <sub>5</sub> PET	4.8	3.9	0.76	84	232	33.0
BA <sub>10</sub> PET	9.1	7.7	0.78	86	224	24.7
BA <sub>15</sub> PET	13.0	11.1	0.74	86	206	18.8

Table 1 Intrinsic viscosity and DSC data of neat PET and BA<sub>n</sub>PETs.

<sup>a</sup>: Actual BA contents were calculated from <sup>1</sup>H NMR.

The mechanical properties of  $BA_nPETs$  and the control sample (neat PET) have been investigated, and the detailed data are collected in Table S1. Compared with neat PET, the elongation at break of  $BA_5PET$  and  $BA_{10}PET$  are almost as same as that of PET, however, their tensile strength are lower. It is well known that the mechanical properties of polymer materials are affected by many factors, such as chain structure, crystallinity, phase morphology, compatibility, etc. Because of the strong rigidity of

aromatic Schiff base units and low crystallization, the tensile strength and elongation at the breaks of  $BA_{15}PET$  decline dramatically compared to PET.

The thermal stability of BA<sub>n</sub>PETs is evaluated by TGA both in nitrogen and air atmosphere, and their TGA and DTG curves are shown in Fig. 4. The detailed decomposition temperatures obtained from Fig. 4 are listed in Table 2. Under nitrogen atmosphere, all samples show one decomposition process. Compared to pure PET, the initial decomposition temperatures ( $T_{5\%}$ ) of BA<sub>n</sub>PETs have tiny decrease (from 390 °C to 388 °C), while the temperatures at maximum weight loss rate ( $T_{max}$ ) exhibit an evident increase (from 429 °C to 435 °C). It is noteworthy that the residue at 700 °C increases sharply with the increase of BA content. For BA<sub>15</sub>PET containing 11.1 mol% BA, its residue char reaches to 22.0 wt% which is more than twice of PET (9.8 wt%). The improvement of residue char is attributed to the cross-linking reaction of BAnPETs, which can form stable networks and make copolyesters degrade difficultly at high temperature. As we know, the flame retardance of polymers are directly related to their char-forming abilities. The high char residue can prevent the materials from heat and oxygen by acting as physical barriers, so, it will endow materials with good flame retardancy.

In air atmosphere, pure PET and BA<sub>n</sub>PETs show two main decomposition steps in the degradation process.  $T_{5\%}$  of copolyesters decrease slightly with increasing BA content. The first maximum degradation temperature ( $T_{max1}$ ) of the copolyesters are similar to the value of pure PET, however, their second maximum degradation temperatures ( $T_{max2}$ ) have a drastically rise. This suggests that the cross-linkable



structures of BA in the copolyesters lead to the formation of stable cross-linking networks in the first step, which will retard the second decomposition.

Fig. 4 TGA and DTG thermograms of neat PET and BA<sub>n</sub>PETs in nitrogen (a, b) and air (c, d)

atmosphere at a heating rate of 10 °C min<sup>-1</sup>.

Table - Forreau of neur EFF and Bright EF6 in mit ogen and an atmosphere.							
	Nitrogen			Air			
Sample	<i>T</i> <sub>5%</sub> (°C)	T <sub>max</sub> (°C)	CR (wt%)	<i>T</i> <sub>5%</sub> (°C)	$T_{\text{max1}}$ (°C)	T <sub>max2</sub> (°C)	CR (wt%)
PET	390	429	9.8	385	434	535	0.2
BA <sub>5</sub> PET	389	435	14.3	386	435	575	0.1
BA <sub>10</sub> PET	388	432	17.0	379	433	595	0.1
BA <sub>15</sub> PET	388	434	22.0	377	432	610	0.1

Table 2 TGA data of neat PET and BA<sub>n</sub>PETs in nitrogen and air atmosphere.

 $T_{5\%}$ : defined as the temperature where 5% of the sample weight lost.

 $T_{\text{max}}$ : defined as the temperature at maximum weight loss rate.

CR: defined as the char residue at 700 °C.

#### **3.3 Flame retardancy**

The flame retardance of BA<sub>n</sub>PETs are firstly assessed by LOI and UL-94 tests. The corresponding results are summarized in Table 3. The LOI value increases from 22.0% of PET to 31.0% of BA<sub>10</sub>PET and BA<sub>15</sub>PET. From the digital images of the residue of pure PET and BA<sub>10</sub>PET after LOI tests (Fig. 5a), significant difference can be observed. For PET, severe melt-dripping occurs and bare char residue remains; for BA<sub>10</sub>PET, distinct intumescent char forms and no melt-dripping happens. This bulky intumescent char as protective layer of unburned material isolates combustible gas and heat during combustion, which make the sample quick self-extinguish in LOI test (Fig. 5b).



Fig. 5 Digital pictures: (a) PET and  $BA_{10}PET$  after LOI test with 22% and 31% oxygen concentration, respectively, (b)  $BA_{10}PET$  during combustion process in LOI test with 31% oxygen

C	Table 3 Detailed combustion results of neat PET and BA <sub>n</sub> PETs.							
S	ample	TTI (s)	PHRR (kW m <sup>-2</sup> )	THR (MJ m <sup>-2</sup> )	$\frac{\text{TSR}}{(\text{m}^{-2} \text{ m}^{-2})}$	LOI (%)	UL-94 Rating	
P	ΈT	47	761	75	1736	22.0	N.R.	
В	A <sub>5</sub> PET	41	586	63	1122	29.0	V-2	
В	A <sub>10</sub> PET	43	514	67	1113	31.0	V-0	
В	A <sub>15</sub> PET	36	502	64	1064	31.0	V-0	

TTI: defined as the time to ignition.

concentration.

Because of the low melt viscosity at high temperature, pure PET exhibits serious dripping behavior and ignites absorbent cotton during the UL-94 test. For BA<sub>5</sub>PET with low content of cross-linkable units, the melt-dripping behavior still can be seen during the test, and the cotton is ignited by dripping. That indicates the quantity of cross-linkable monomer isn't enough to inhibit melt-dripping. With the increase of BA content, the melt-dripping is totally suppressed. Both BA<sub>10</sub>PET and BA<sub>15</sub>PET copolyesters have no dripping in the UL-94 tests and achieved V-0 rating. After removing the igniter, a lot of intumescent char are left on their surface. This means the cross-linking actions of BA improve the melting viscosity and the carbonization of copolyesters at high temperature. The high melting viscosity and a great deal of intumescent char formed in fire effectively suppress the dripping behavior and retard the burning of copolyesters.

Cone calorimeter testing has been widely used to evaluate the flammability of materials. [40, 41] Fig. 6 shows heat release rate (HRR), total heat release (THR) and total smoke release (TSR) curves of neat PET and BA<sub>n</sub>PETs, and the detailed data are presented in Table 3. It has been well known that HRR, especially the peak heat release rate (PHRR) is a significant parameter to estimate the safety of materials in fire. The lower PHRR value suggests the better fire safety. For BA<sub>n</sub>PETs, their peak heat release rates are obviously decreased. For example, the PHRR of BA<sub>5</sub>PET is 586 kW m<sup>-2</sup>, decreases to 77% of that of neat PET; the PHRR of BA<sub>15</sub>PET dwindles to

502 kW  $m^{-2}$  which is only two-thirds of that of neat PET. These results demonstrate that the introduction of BA can effectively retard flame propagation.



Fig. 6 Cone calorimetric results of neat PET and BA<sub>n</sub>PETs: (a) HRR, (b) THR and (c) TSR.

In addition, the copolyesters containing Schiff-based functional groups reveal a distinct reduction in THR and TSR, as shown in Figure 6 and Table 3, which also owe to the formation of thermal insulation char from cross-linking. However, the THR of copolyesters do not decrease with the increasing content of BA. All copolyesters exhibit low and similar TSR values, and their THR values slightly increase with the increasing of BA content. These phenomenon can be explained as follow: the cross-linking reaction caused by BA is sufficient in cone test because of long heating time and higher temperature, and an effective flame retardant efficiency can be achieved at low BA content. For LOI and UL-94 tests, the cross-linking action is not adequate due to short heating time and low temperature, so, better flame retardancy of copolyesters can only be achieved for that containing more BA (BA<sub>10</sub>PET and BA<sub>15</sub>PET). The results of LOI, UL-94 and Cone tests clearly demonstrate that BA

monomer with Schiff base groups can effectively suppress the melt dripping and reduce the flammability of copolyesters with a low loadings.

#### 3.4 Effect of cross-linking on Flame-retardant mechanism

As talked above, the large melt viscosity and the intumescent char derived from cross-linking reaction are considered as the key to achieve anti-dripping and flame retardancy of the copolyesters. To get a better understanding of the relationship between the cross-linking reaction and flame retardant mechanism as well as non-dripping action of the copolyesters, TG-IR tests have been used to investigate the gaseous products during the heating processes, which can reveal the thermal degradation products. Fig. 7 displays three-dimensional TG-IR spectra and FTIR spectra of the gaseous products from the decomposition of neat PET and BA<sub>10</sub>PET at different temperatures in nitrogen atmosphere. There is almost no absorption peaks other than CO<sub>2</sub> in the spectra of BA<sub>10</sub>PET below 380 °C, indicating that no special gas produced in the cross-linking progress. With the temperature increasing to  $T_{\rm max}$ (430 °C), both PET and BA<sub>10</sub>PET decompose and produce lots of gases. These products have no difference and exhibit characteristic bands for aliphatic ether (1050-1175 cm<sup>-1</sup>), hydrocarbon (1300-1450 cm<sup>-1</sup>), RCHO (1761 cm<sup>-1</sup> and 2733 cm<sup>-1</sup>), RCOOH (1761 cm<sup>-1</sup> and 3550 cm<sup>-1</sup>), carbon monoxide (2137 cm<sup>-1</sup>) and carbon dioxide (2334 cm<sup>-1</sup> and 671 cm<sup>-1</sup>). These gaseous products are as same as those reported for PET, [42, 43] illustrating the cross-linkable monomer BA does not change the constitution of PET pyrolysis products in the gaseous phase. This means



that the function of BA for flame retardancy of polyesters should be played in the condensed phase.

**Fig. 7** Three-dimensional TG-IR spectra and FTIR spectra of gasified pyrolysis products for neat PET and BA<sub>10</sub>PET.

Thus, the char residues of PET and BA<sub>10</sub>PET are characterized by FT-IR to find out what chemical structure has been formed in the solid phase (Fig. S5). From the spectrum of PET, two characteristic absorption peaks of the skeleton vibration of aromatic ring and the stretching vibration of C-O-C group can be found at 1638 cm<sup>-1</sup> and 1125 cm<sup>-1</sup>, respectively. [44] For BA<sub>10</sub>PET, a new absorption peak at 1400 cm<sup>-1</sup> can be found besides these absorption peaks, which is ascribed to N-containing six-membered ring heterocyclic compounds. [44]

Table 4 Elements content and C/O fatto of original and heat treated D/10 E1.						
Sample	C (%)	O (%)	N (%)	C/O		
BA <sub>10</sub> PET	74.1	25.0	0.9	3.0		
BA10PET-330	77.1	21.6	1.3	3.6		
BA10PET-380	89.2	9.0	1.8	9.9		
BA10PET-430	92.3	5.8	1.9	15.9		
BA10PET-550	93.6	4.7	1.7	19.9		

**Table 4** Elements content and C/O ratio of original and heat-treated BA<sub>10</sub>PET.

To further determine the chemical structure of these N-containing heterocyclic compounds and the chemical bond changes in condensed phase during the thermal degradation process, XPS spectra have been collected. The elements content of original and heat-treated BA10PET (heated at 330 °C, 380 °C, 430 °C and 550 °C in  $N_2$  for 10 min, respectively) obtained from XPS are summarized in Table 4. The  $C_{1s}$ and  $N_{1s}$  XPS spectra of  $BA_{10}PET$  are shown in Fig. 8 and Fig. 9. The  $C_{1s}$  XPS result of BA10PET is distinguished as five peaks: C(O)O (288.7 eV), C-O (286.5 eV), C=N (286.0 eV), C=C (284.9 eV) and C-C (284.4 eV). [29, 45, 46] Because the decarboxylation process of the copolyester happens at high temperature, the peak of C(O)O decreases with the increase of treating temperature and disappears at 430 °C. There is an amplifying enhancement for the peak area of C=C and C-C, indicating some conjugated structures formed during heating treatment via cross-linking reaction. The C/O ratio of samples also gradually increases with the rise of treating temperature, suggesting that the carbonization process is combined by a decarboxylation and an aromatization process.



Fig. 8 C<sub>1s</sub> XPS spectra of original and heat-treated BA<sub>10</sub>PET.



Fig. 9 N<sub>1s</sub> XPS spectra of original and heat-treated BA<sub>10</sub>PET.

From Table 4, we can see the content of nitrogen does not decline during the decomposition of copolyester, in contrast, after heat treatment the nitrogen content is enhanced. It is testified that the nitrogen atoms retain in the condensed phase after cross-linking reaction. In the  $N_{1s}$  XPS spectrum of original BA<sub>10</sub>PET, there is only one peak at 399.2 eV, attributed to C=N of aromatic Schiff base group. [47] After heating at 330 °C for 10 min, a new binding energy is found at 399.9 eV (Fig. 9),

which can be assigned to amine nitrogen (-C-N-) according to the literature. [48] Further enhancing the temperature, the amine nitrogen slowly converts to pyridine-like nitrogen which is more thermal stable. This conversion process often happens during the pyrolysis of nitrogen-containing carbonaceous materials. [49, 50] According to the changes of chemical bonds based on XPS spectra, the cross-linking mechanism for  $BA_nPETs$  is proposed in Scheme 3. Between the melting and decomposition temperature, three -C=N- groups undergo a chemical reaction to form a hexatomic ring structure. These hexatomic ring structures make copolyesters form cross-linked networks and endow them with high melt viscosity during combustion.



Scheme 3 Conjectural cross-linking structure of Schiff base groups in BA<sub>n</sub>PETs.

The inner surface morphology of the char residues is important for the solid phase flame retardance, which is investigated by SEM. Fig. 10 presents the inner surface images of char residues of pure PET and BA<sub>n</sub>PETs after cone tests. From their amplified images, we can see clearly that the char residue morphology of PET is smooth and lots of bubbles spread all over the surface, while for BA<sub>n</sub>PETs, their char residues are all rougher and many worm-like objects bestrew on their char surfaces. These specific compact worm-shaped particles exhibit good heat insulation and

smoke inhibition, providing outstanding flame-retardant and non-dripping effects in combustion.



**Fig. 10** Low (500×) and high resolution (20000×) **SEM** images of the inner surfaces of char residues after cone calorimetric test: (a<sub>1</sub>, a<sub>2</sub>) neat PET; (b<sub>1</sub>, b<sub>2</sub>) BA<sub>5</sub>PET; (c<sub>1</sub>, c<sub>2</sub>) BA<sub>10</sub>PET; (d<sub>1</sub>, d<sub>2</sub>) BA<sub>15</sub>PET.

Raman spectroscopy is a suitable method to investigate the structure of carbonaceous materials formed during burning. The residue chars of PET and BA<sub>n</sub>PETs copolyesters after cone test also have been studied by Raman spectroscopy (shown in Figure 11). And the peak fitting mode is based on the Gaussian model. All samples display overlapped peaks with intensity maxima at 1350 cm<sup>-1</sup> (called D band) and 1585 cm<sup>-1</sup> (called G band), which stand for the typical polyaromatic species or graphitic structures. The D band corresponds to disordered graphite or glassy carbons and the G band represents the organized graphitic structures of the char layer. More importantly, the peak area ratio of D and G bands ( $A_D/A_G$ ) is related to the

microcrystal size of the char layer. Larger  $A_D/A_G$  value indicates a smaller size of carbonaceous microstructures, which means better flame retardance. As shown in Figure 11, it is found that the  $A_D/A_G$  ratio follows the sequence of PET (2.29) <  $BA_5PET$  (2.43) <  $BA_{10}PET$  (2.58) <  $BA_{15}PET$  (2.72). The char layer becomes more compact with the increase of BA content according to the results of  $A_D/A_G$  ratio. Therefore, the copolyester with the more cross-linkable group shows the better flame-retardant and anti-dripping performance, which is agree with the results of fire tests.



Fig. 11 Raman spectra of the residue char of neat PET and BA<sub>n</sub>PETs after cone calorimetric tests.

#### 4. Conclusion

Breaking the traditional application, aromatic Schiff bases show a new function in flame-retardant and non-dripping materials due to their self-crosslinked ability at high temperature. Connected to aryl group, Schiff based structure unit in PET copolyester can form nitrogen-containing hexatomic ring during combustion. This formed stable cross-linking network is the critical factor for the formation of a thermal-protective coating on the surface and increasing the melting viscosity for copolyesters at high temperature. Benefitting from this action, the obtained PET copolyesters show excellent flame-retardant and anti-dripping behaviors. Besides, due to its high efficiency, only 7.7 mol% of self-crosslinkable monomer is needed for the copolyester to achieve a UL-94 V-0 rating and an LOI value of 31.0%. Meanwhile, this self-crosslinking mainly occurs between the melting and decomposition temperature, which does not affect the processability of the copolyester. Because of its low cost and facile synthesis process, this self-crosslinkable monomer shows great potential applications.

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#### **Supporting Information**

<sup>1</sup>H- and <sup>13</sup>C-NMR spectra of BA and  $BA_nPETs$ ; Shear viscosities of  $BA_nPETs$  as a function of shear rate at different temperature; Mechanical properties of PET and  $BA_nPETs$ ; FTIR spectra of the char residues of PET and  $BA_{10}PET$ 

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#### **Figure and Table Captions**

Figure 1 TG-DSC thermograms of neat PET and  $BA_{10}PET$  in nitrogen at a heating rate of 10 °C min<sup>-1</sup>.

Figure 2 Dynamic oscillatory rheological results of neat PET and  $BA_nPETs$  in air atmosphere: (a) Complex melt viscosity plotted against temperature; (b) Complex melt viscosity plotted against time at a fixed temperature of 280 °C.

Figure 3 DSC thermograms of neat PET and  $BA_nPETs$  for second heating scans in nitrogen at a heating rate of 10 °C min<sup>-1</sup>.

**Figure 4** TGA and DTG thermograms of neat PET and BA<sub>n</sub>PETs in nitrogen (a, b) and air (c, d) atmosphere at a heating rate of 10 °C min<sup>-1</sup>.

**Figure 5** Digital pictures: (a) PET and  $BA_{10}PET$  after LOI test with 22% and 31% oxygen concentration respectively, (b)  $BA_{10}PET$  during combustion process in LOI test with 31% oxygen concentration.

**Figure 6** Cone calorimetric results of neat PET and BA<sub>n</sub>PETs: (a) HRR, (b) THR and (c) TSR.

Figure 7 Three-dimensional TG-IR spectra and FTIR spectra of gasified pyrolysis

products for neat PET and BA<sub>10</sub>PET.

Figure 8 C<sub>1s</sub> XPS spectra of original and heat-treated BA<sub>10</sub>PET.

Figure 9  $N_{1s}$  XPS spectra of original and heat-treated BA<sub>10</sub>PET.

**Figure 10** Low (500×) and high resolution (20000×) SEM images of the inner surfaces of char residues after cone calorimetric test:  $(a_1, a_2)$  neat PET;  $(b_1, b_2)$  BA<sub>5</sub>PET;  $(c_1, c_2)$  BA<sub>10</sub>PET;  $(d_1, d_2)$  BA<sub>15</sub>PET.

Figure 11 Raman spectra of the residue char of neat PET and BA<sub>n</sub>PETs after cone calorimetric tests.

Scheme 1 Synthesis route of 5-(benzylidene-amino)-isophthalic acid dimethyl ester (BA).

Scheme 2 Synthesis processes of  $BA_nPETs$ , where n denotes the molar content of BA per hundred mole of DMT (BA: DMT = n: 100 in mol), not the block length or repeating units.

Scheme 3 Conjectural cross-linking structure of Schiff base groups in BA<sub>n</sub>PETs.

 Table 1 Intrinsic viscosity and DSC data of neat PET and BAnPETs.

Table 2 TGA data of neat PET and BA<sub>n</sub>PETs in nitrogen and air atmosphere.

Table 3 Detailed combustion results of neat PET and BA<sub>n</sub>PETs.

Table 4 Elements content and C/O ratio of original and heat-treated BA<sub>10</sub>PET.

#### Highlights

1. A novel monomer containing aromatic Schiff base was incorporated into PET.

2. Cross-linking reaction occurs among the -CH=N- structure units at high temperature.

3. Cross-linking promotes char formation and melting viscosity increasing.

4. PET copolyesters with no-dripping and low smoke release show improved fire

#### **Graphical Abstract**

# New application for aromatic Schiff base: high efficient flame-retardant and anti-dripping action for polyesters

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