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A new approach to improving flame retardancy, smoke suppression and anti-dripping of PET: Via arylene-ether units rearrangement reactions at high temperature



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ABSTRACT

In order to avoid the serious melt-dripping problems caused by conventional phosphorus flame retardants, a new arylene-ether containing monomer named 2,2'-(4,4'-(1,4-phenylenebis(oxy))bis(4,1phenylene))bis(oxy) diethanol (PBPBD) was synthesized and introduced into the PET main-chain via condensation polymerization. With the incorporation of arylene-ether units, the thermal stability and the char residue from combustion of flame-retardant-element-free copolyesters containing PBPBD (BD_xPETs) increased dramatically. However, the crystallinity and melting temperature of these copolymers were lower than the same quantities for PET. Thermal degradation kinetic was investigated using the Ozawa-Flynn-Wall method, which illustrated that the apparent activation energy for decomposition of the copolyesters was enhanced with increasing the conversion and the content of PBPBD. Py-GC/MS results showed that the PBBPD structural units undergo rearrangement reactions at high temperature, and ultimately form conjugated heteroaromatic structures, which lead to the formation of stable char residues with unique "stick-shaped" micro-morphology. Due to these rearrangement reactions, BD_xPETs showed an expected flame retardant performance and a reduction in smoke generation during combustion. For example, the LOI value for BD₁₀PET was 28.4, and the total smoke production (TSP) was 10.4 m², much smaller than that for PET, 18.8 m². Moreover, melt-dripping was restricted. © 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Many different methods have been utilized to endow poly(ethylene terephthalate) (PET) with flame retardancy. Incorporating phosphorus entities into the main-chain of PET is considered to be one of the most efficient methods [1–4]. However, flame retardation of most phosphorus-containing copolyesters is achieved through melt dripping, specifically by removing heat from the

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Besides the functional groups above-mentioned, some wholly aromatic liquid-crystalline polyesters [10], all-aromatic poly(ether imide)s (PEIs) [11] and poly(ether ether ketone) (PEEK) [12,13], present excellent thermal properties and undergo thermal degradation with formation of char as a consequence of the presence of aromatic entities in the main-chain. Good thermal stability and char forming capability are beneficial for providing outstanding flame retardance and anti-melt-dripping property during a fire. Other similar polymers, such as those containing arylene-ether



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units, i.e., "Ar–O–Ar" structural units or "Ar–O–Ar-O–Ar" structural units may also display good flame retardance. These structural units may play a critical and positive role in enhancing char formation during thermal degradation thus improving the flame retardant performance of these materials.

In this work, 2,2'-(4,4'-(1,4-Phenylenebis(oxy))bis(4,1phenylene))bis(oxy) diethanol (PBPBD) containing arylene-ether units has been synthesized and then introduced into the mainchain of PET via melt polycondensation. The chemical structures of these novel flame-retardant-element-free copolyesters (BD_xPETs) were characterized using ¹H-NMR, ¹³C-NMR. Meltcrystallization behavior, thermal stability, thermal degradation kinetic, pyrolysis behavior, flame retardant performance, and char residue morphology were well investigated using DSC, TGA, Py-GC/ MS, LOI, cone calorimeter, and SEM.

2. Experimental section

2.1. Materials

Hydroquinone (AR grade), dimethylacetamide (DMAc, AR grade), chloroform (AR grade), methanol (AR grade), potassium carbonate (AR grade), potassium hydroxide (AR grade) and potassium iodide were received from Kelong Chemical Reagent Factory (Chengdu, China). Ethylene carbonate (AR grade) and 4'-fluo-roacetophenone (AR grade) were purchased from Aladdin-Reagent. *meta*-Chloroperoxybenzoic acid (m-CPBA, AR grade) was received from Hainachuan Technology Development Co., Ltd (Tianjin, China). Dimethyl terephthalate (DMT, AR grade), ethylene glycol (EG, AR grade), phenol, tetrachloroethane, and zinc acetate were all supplied by Chengdu Chemical Industries Co. (Chengdu, China). Tetrabutyl titanate was purchased from Kelong Chemical Reagent Factory, and dissolved in anhydrous toluene to prepare a 0.2 g/mL solution before use. Other materials were commercially available and used as received.

2.1.1. Synthesis of 1,1'-(4,4'-(1,4-phenylenebis(oxy))bis(4,1-phenylene))diethanone (PBBPD) [11,14]

The chemical structure of PBBPD is shown in Scheme 1, and its detailed synthesis process is: A 500 mL three-necked round bottom flask equipped with a magnetic stirrer, reflux condenser and nitrogen inlet was charged with hydroquinone (11.0 g, 0.1 mol), 4'-fluoroacetophenone (27.6 g, 0.2 mol), K₂CO₃ (27.6 g, 0.2 mol), and 250 mL DMAc. The mixture was stirred and refluxed for 12 h. The dark reaction product was cooled to room temperature and diluted

with water. After that, the brown product was collected, washed with water, and dried at reduced pressure. The PBBPD was obtained as brown powders. Yields: 85.3%; ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 2.60 (s, 6H), 6.98–7.09 (m, 4H), 7.12 (s, 4H), 7.86–8.10 (m, 4H).

2.1.2. Synthesis of 4,4'-(1,4-phenylenebis(oxy))bis(4,1-phenylene) diacetate (PBPD) [11,14]

PBBPD (34.6 g, 0.1 mol), 300 mL CHCl₃ and m-CPBA (27.6 g, 0.2 mol) were added into a 500 mL round bottom flask. The mixture was heated to reflux with stirring for 5 h, and then washed with saturated NaHSO₃ solution (250 mL), saturated NaHCO₃ solution (2 × 250 mL), and water (250 mL). The solvent was removed by distillation, and the crude product was recrystallized from methanol. The PBPD was acquired as golden crystals. The synthesis process is shown in **Scheme 1**. Yields: 80.2%; ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 2.32 (s, 6H), 6.84–7.19 (m, 12H).

2.1.3. Synthesis of 4,4'-(1,4-phenylenebis(oxy)) diphenol (PD) [11,14]

The PBPD (37.8 g, 0.1 mol) was dissolved in 50 mL methanol and treated with a 0.5 M KOH/methanol solution (30 mL). The reaction mixture was heated to reflux for 3 h. The solvent was removed by distillation, and the crude product was treated with a 1 M HCl solution. The product was collected by filtration, washed with water, and dried. The PD was gained as dark brown powders. The synthesis process is also presented in Scheme 1. Yields: 90.2%; ¹H-NMR (400 MHz, DMSO, δ , ppm): 6.73–6.78 (m, 4H), 6.82–6.87 (m, 4H), 6.88 (d, 4H), 9.30 (s, 2H).

2.1.4. Synthesis of 2,2'-(4,4'-(1,4-phenylenebis(oxy))bis(4,1-phenylene))bis(oxy) diethanol (PBPBD)

2,2'-(4,4'-(1,4-phenylenebis(oxy))bis(4,1-phenylene))bis(oxy) diethanol (PBPBD) was prepared as previously described [11,14–16], and its synthesis process is also given in Scheme 1. The detailed synthesis procedure is: PD (29.4 g, 0.1 mol), ethylene carbonate (17.6 g, 0.2 mol) and KI (0.2 g) were added into a 100 mL two-necked round bottom flask. With the protection of N₂ and a magnetic stirrer, the mixture was heated to 175 °C for 8 h, and then washed with a 2 M NaOH solution and water. After filtration and drying, the final product PBPBD was obtained as grey powders. Yields: 92.0%; ¹H NMR (400 MHz, DMSO, δ , ppm): 6.84–7.12 (m, 12H), 3.68–3.73 (t, 4H), 3.92–3.98 (t, 4H), 4.76 (s, 2H); ¹³C NMR (400 MHz, DMSO, δ , ppm): 155, 153, 150, 120, 119, 116, 70, and 60.



Scheme 1. Synthesis processes for PBBPD, PBPD, PD, and PBPBD.

2.2. Preparation of BD_xPETs

 BD_xPETs copolyesters were synthesized using DMT, EG, PBPBD as raw materials via transesterification and polycondensation. Zinc acetate and tetrabutyl titanate were used as the catalysts for the transesterification and polymerization, respectively. The preparation procedure is shown in Scheme 2.

The route for preparation of BD_xPETs containing 5 mol% PBPBD is presented here as a representative procedure: DMT (30.6 g, 0.1576 mol), EG (14.6 g, 0.2364 mol), PBPBD (2.95 g, 0.0078 mol), zinc acetate (0.08 g, 4.35×10^{-4} mol), and tetrabutyl titanate solution (0.05 mL, 4.35×10^{-4} mol) were added into a 100 mL polymerization bottle equipped with mechanic stirring and nitrogen inlet. Then the system was heated to 210–220 °C for 2 h under the protection of N₂, and the transesterification was carried out. After that, the mixture was heated to 270 °C, and the pressure of the system was reduced to lower than 50 Pa. The polycondensation was maintained for 3 h. Finally, the reactor was cooled to room temperature at reduced pressure. Other BD_xPET copolyesters were prepared by similar process.

2.3. Characterization

Intrinsic viscosities [η] of PET and BD_xPETs were determined with an Ubbelohde Viscometer at 25 °C in phenol/1,1,2,2-tetrachloroethane solution (v/v, 1/1).

The NMR spectra (¹H, 400 MHz; ¹³C, 400 MHz) for BD_xPETs were obtained with Bruker AVANCE AV II-400 NMR instrument, in which CF₃COOD was used as the solvent, and tetramethylsilane was the reference.

Differential scanning calorimetry (DSC) curves were recorded with a TA Q200 DSC apparatus, and calibrated with pure indium standards. The measurements were performed in aluminum pans with weighted samples of 5.0 ± 0.5 mg under nitrogen with a purge flow of 50 mL/min. The test procedure is given as follows: in order to eliminate the influence of thermal history and the effect of heat treatment on the crystalline structure of materials, the specimens were firstly heated at 280 °C and maintained for 5 min. Subsequently they were cooled down to 0 °C (i.e. 1st cooling), and then reheated to 280 °C (i.e. 2nd heating). All the scanning rates for this measurement were 10 °C/min.

The thermal stability and thermal degradation kinetic of the specimens in nitrogen atmosphere were performed using a NETZSCH TG 209 F1 apparatus. The samples (5.0 ± 0.5 mg) were heated from 40 to 700 °C at 10 °C/min. The Ozawa-Flynn-Wall method was used to analyze the thermal degradation kinetic parameters, and the samples (5.0 ± 0.5 mg) were heated from 40 to 700 °C at various rates: 5, 10, 20 and 40 °C/min.

Py-GC/MS tests were performed in a CDS5200 pyrolyzer. The pyrolysis chamber was under helium atmosphere, and the samples (300 μ g) were heated from ambient temperature to 500 °C at a rate of 1000 °C/min and kept for 20 s. The pyrolyzer was coupled with DANI MASTER GC-TOF-MS System, and helium was used as the carrier gas. For the operation, the temperature program of the

capillary column (DN-1701 FAST 10 m 0.10 mm 0.10 mm) of GC is as following: 2 min at 45 °C, after that the temperature was increased to 280 °C at a rate of 15 °C/min then kept at 280 °C for 5 min. The injector temperature was 280 °C. The MS indicator was operated in the electron impact mode at electron energy of 70 eV, and the ion source temperature was kept at 180 °C. The detection of mass spectra was carried out using a NIST library.

Cone calorimeter tests were carried out using a FTT cone calorimeter according to ISO 5660-1 standard. The specimens were prepared with a size of $100 \times 100 \times 3 \text{ mm}^3$ and a weight of 35 g, tested under a heat flux of 50 kW/m².

The LOI measurements were performed on the Oxygen Index Flammability Gauge (HC-2C) according to ASTM D2863-97 standard. The samples were compression molded, and cut into a standard size of $120 \times 6.5 \times 3.2 \text{ mm}^3$.

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

3. Results and disscussion

3.1. Structure characterization of BD_xPETs

The chemical structures of the resulting copolymers were characterized using ¹H-NMR and ¹³C NMR spectroscopy, which are shown in Fig. 1 and Fig. 2, respectively. The chemical shifts of 4.86 and 8.17 ppm in the ¹H-NMR spectrum are assigned to the ethylene glycol and terephthalic acid units, respectively. And their corresponding carbon chemical shifts are found at 57 (-CH₂-CH₂- in ethylene glycol units), 128, 130 (Ar-*C* in terephthalic acid units), and 169 ppm (*C*=O in terephthalic acid units). Besides, the resonance signals occurring at 4.50, 4.80 and 6.93–7.07 ppm in the ¹H-NMR spectrum are ascribed to PBPBD units, and associated with the peaks at 61, 58 ppm (-CH₂-CH₂- in PBPBD units), 147, 146, 145, 113 and 113 ppm (Ar-*C* in PBPBD units) in the ¹³C-NMR spectrum. The above results demonstrated that BD_xPETs were successfully obtained through the melt polycondensation.

The experimental content of PBPBD was calculated by the integral area ratio of I_{f+g+h} and I_a , and the detailed results are listed in Table 1. It is clear that over 80% PBPBD monomer is incorporated into the backbone of BD_xPET. The loss of PBPBD may be ascribed to its volatility during the polycondensation process at reduced pressure. And the intrinsic viscosities [η] of BD_xPETs are all more than 0.70 dL/g (PET), which illustrates that comparatively high molecular weight copolyesters are positively prepared.

3.2. Melting and crystallization behavior of BD_xPETs

The thermal transition behavior of BD_xPETs and PET were investigated using DSC. The glass transition temperature (T_g), the melting temperature (T_m), the crystallization temperature (T_c), and the corresponding enthalpies (ΔH_m and ΔH_c) are listed in Table 2 and Fig. 3 shows the second heating (a) and the first cooling



Scheme 2. Preparation process for BD_xPET, x denotes the molar content of PBPBD in the copolyester.



Fig. 2. ¹³C-NMR spectra of BD₂₀PET.

curves (b) of the samples. Considering the same thermal history of the prepared samples, the results of the second heating and the first cooling scans are discussed. It can be seen that, with increasing the content of PBPBD, the crystallization peak of BD_xPETs becomes duller and broader, while the T_c and ΔH_c decreases, indicating the

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Basic characteristics of samples.						
Samples	PBPBD (mol%)	[η] (dL/g)				
	Theoretical	Experimental ^a				
PET	_	-	0.70			
BD ₅ PET	5	4.3	0.84			
BD ₁₀ PET	10	8.3	0.74			
BD ₂₀ PET	20	18.2	0.82			

^a Calculated from ¹H-NMR.

Table 2 Thermal behavior of PET and BD_xPETs obtained from DSC.

Samples	Second heating scans			First cooling scans		
	<i>T</i> _g (°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	$\Delta H_c (J/g)$	
PET BD ₅ PET BD ₁₀ PET BD ₂₀ PET	78 83 81 81	243 238 220 210 ^a	31.7 32.1 15.2 -	172 155 145 –	40.0 27.0 4.7	

^a Measured using the Melting Point Apparatus.



Fig. 3. DSC thermograms of PET and BDxPETs for second heating scans (a) and first cooling scans (b) at 10 °C/min in N2.

the crystalline property decrease [17–19]. Therefore, the T_m of BD₁₀PET decreases from 238 °C (BD₅PET) to 220 °C. The T_m and T_c of BD₂₀PET have not been detected from DSC, which indicates that BD₂₀PET cannot crystallize during DSC testing.

3.3. Thermal stability of BD_xPETs

The thermal stability of the samples was evaluated by thermogravimetric analysis (TGA), and their TG as well as DTG curves under nitrogen atmosphere are shown in Fig. 4. The detailed data such as the initial decomposition temperature ($T_{5\%}$), the maximum rate decomposition temperature (T_{max}), and the residue at 700 °C of all samples are collected in Table 3. From Fig. 4, it is clear that all samples exhibit a single decomposition process. As seen in Table 3, $T_{5\%}$, T_{max} and the residue at 700 °C of copolyesters increase with increasing PBPBD content. Introducing only 5 mol% PBPBD into PET, the char residue increases sharply from 9.9% (PET) to 17.2% (BD₅PET). With further increasing the content of PBPBD, the char residue of BD₂₀PET reaches 22.5%, which achieves more than twice as that of PET. These results demonstrate that introducing PBPBD into the main-chain of PET can improve the thermal stability and the char forming capability of PET-based copolyesters significantly.

3.4. Thermal degradation kinetic

In order to illustrate the thermal degradation behavior of PET and BD_xPETs , Ozawa-Flynn-Wall method (Eq. (1)) is used [20–22].

$$log_{10}\beta = log_{10}\frac{AE}{R} - log_{10}F(\alpha) - 2.315 - 0.4567\frac{E}{RT} \tag{1}$$

Where A is the pre-exponential factor, E is the activation energy,

Table 3
TGA data of samples in N_2 atmosphere.

Samples	T _{5%} (°C) ^a	T_{\max} (°C) ^b	Residues at 700 °C (wt%)
PET	389.9	428.7	9.9
BD ₅ PET	394.0	430.8	17.2
BD ₁₀ PET	396.6	434.4	18.2
BD ₂₀ PET	402.0	438.3	22.5

^a Temperature of 5 wt% weight loss.

^b Temperature at the max rate weight loss.



Fig. 4. (a) TG and (b) DTG curves of samples in N₂ atmosphere.

β is the heating rate, T is the temperature, and F (α) is the integral function of the conversion. Via this method the apparent activation energy for decomposition of a reaction can be determined without specifically knowing its reaction mechanism. From Eq. (1), E can be calculated from the slope of a plot of logβ *versus* 1/T at a fixed weight loss. Fig. S1 shows the thermal degradation curves of PET and BD_xPETs at different heating rates. The thermal stability of the samples increases with increasing heating rates, as expected, given the time lag for thermal conduction and volatilization of the decomposition compounds [23]. Fig. S2 shows the plots of logβ *versus* 1/T at 5, 10, 20, 30, 40, 50, and 60% conversion (α%), and the fitted lines are nearly parallel as well as the correlation coefficients are almost above 0.99 (Table 4), which indicates that this method is valid. The calculated activation energy for decomposition of the samples with different conversion is also listed in Table 4.

It could be found that, as the conversion and the content of PBPBD monomer increasing, the activation energy for decomposition of the samples increases obviously. Higher activation energy means more energy is needed to break down the chemical bonds of the samples and their char formations become more and more stable. The above results indicate that the incorporation of PBPBD significantly improves the thermal stability of PET-based copolyesters, which is consistent with the TGA results.

3.5. Pyrolysis behavior

In order to further investigate the thermal degradation process of BD_xPET copolyesters, the pyrolysis GC/MS study was performed. The pyrograms of $BD_{20}PET$ and PET are presented in Fig. 5. Major corresponding peaks in Fig. 5 are numbered and their assignments are listed in Table 5.

As shown in Fig. 5 and Table 5, pyrolysis products of PET and

BD₂₀PET are very similar, which suggests that their degradation processes partly overlapped. The assigned structures of pyrolysis products of PET listed in Table 5 are: vinyl benzoate (peak 1), benzoic acid (peak 2), divinyl terephthalate (peak 3), dimethyl terephthalate (peak 4), methyl vinyl terephthalate (peak 3), dimethyl terephthalate (peak 4), methyl vinyl terephthalate (peak 5), [1,1'biphenyl]-4-carbaldehyde (peak 6), [1,1'-biphenyl]-4-carboxylic acid (peak 7), ethane-1,2-diyl dibenzoate (peak 8), and butane-1,4-diyl dibenzoate (peak 9). Based on our results and those previously reported [24–27], the proposed pyrolysis process of PET is given in Fig. 6. It can be sure that PET breaks down at the ester links according to the random chain scission mechanism, and the principal point of weakness in PET is the β -methylene group.

For pyrolysis products of BD₂₀PET, it is clear that one major difference from those of PET is the absence of methyl vinyl terephthalate (peak 5), [1,1'-biphenyl]-4-carbaldehyde (peak 6), and [1,1'-biphenyl]-4-carboxylic acid (peak 7), which come from the degradation of benzoic acid (peak 2; 2') or divinyl terephthalate (peak 3; 3') (Fig. 6). This phenomenon illustrates that, compared to neat PET, BD₂₀PET will release less volatile products at high temperature. The other major difference is the typical product of BD₂₀PET (peak 7'). From its assigned structure in Table 5, it can be deduced that this product may come from the rearrangement reactions of PBPBD structural units. During the decomposition process, some PBPBD units are separated from the main-chain of the copolyester, and then chain scissions occur at the "Ar-OCH₂CH₂O" links. With the electrical effects of the oxygen atoms linking the benzene rings, the adjacent carbon atoms become more active, and then link with the free radicals of ethy and ethoxyl [13.28]. After that, they undergo the dehydrogenation, ultimately forming the (E)-(14-methylchromeno[2,3-b]xanthen-7(14H)-ylidene) methanol (peak 7', assigned mass spectrum is shown in Fig. S3). Noteworthily, product of peak 7' is a stable and conjugated structure

 Table 4

 Decomposition Activation energy for samples determined by Ozawa-Flynn-Wall method.

α (%)) Activation energy (kJ/mol)		Correlation coefficient R ²					
	PET	BD ₅ PET	BD ₁₀ PET	BD ₂₀ PET	PET	BD ₅ PET	BD ₁₀ PET	BD ₂₀ PET
5	179	187	189	199	0.9999	0.9895	0.9920	0.9973
10	186	194	200	209	0.9998	0.9982	0.9994	0.9992
20	189	200	206	211	0.9992	0.9985	0.9985	0.9994
30	194	203	208	213	0.9995	0.9990	0.9987	0.9998
40	197	205	211	222	0.9998	0.9989	0.9971	0.9999
50	200	211	214	224	0.9998	0.9989	0.9954	0.9998
60	202	212	218	228	0.9996	0.9985	0.9884	0.9998



Fig. 5. The pyrograms of PET and BD₂₀PET.

with heteroaromatic rings, and this specific proposed pyrolysis process is given in Fig. 7. Combining the results of TGA and thermal degradation kinetic, i. e. considering the high thermal stability (5 wt% mass loss observed at 394–402 °C), the high char residue yield (17.2–22.5 wt%) and the comparatively high apparent decomposition activation energy for BD_xPETs, the formation of these conjugated heteroaromatic structures (peak 7') will play a flame-retardant role in condensed phase [1], which will be illustrated in the following parts.

3.6. Burning behavior of BD_xPETs

The combustion performance of BD_xPET copolyesters and neat PET, including heat release rate (HRR), total heat release (THR), smoke production rate (SPR) and total smoke production (TSP), are plotted in Fig. 8. And the detailed data are summarized in Table 6. The HRR, especially the peak value for HRR (PHRR), is considered as the most important parameter in evaluating the fire safety of materials, which determines the rate of fuel-feeding and flame spread in the combustion. A lower PHRR value denotes slower flame

Table 5 Compounds identified in the pyrograms of PET and BD₂₀PET.

Peak NO.	Retention time (min)	М	Assigned structure
1; 1′	6.02	148	0
			0
			vinyl benzoate
2; 2′	6.98	122	
			ОН
3; 3′	9.89	218	benzoic acid O
			o
			divinyl terephthalate
4; 4′	10.62	194	н ₃ соос———соосн ₃
			dimethyl terephthalate
5	11.18	206	o L
			° , o
			o
c.	12.24	102	methyl vinyl terephthalate
6	12.24	182	ОН
			[1,1'-biphenyl]-4- carbaldebyde
7	12.36	199	
			<hr/>
			[1,1'-biphenyl]-4- carboxylic acid
8; 5′	14.00	270	О С-О-СH ₂ -СH ₂ -О-СС-С-С-С-С-С-С-С-С-С-С-С-С-С-С-С-С-С
			ethane-1,2-diyl dibenzoate
9; 6′	16.41	298	0 — – – – – – – – – – – – – – – – – – – –
			butane-1,4-diyl dibenzoate
7′	17.13	328	ОН

(E)-(14-methylchromeno[2,3-b]xanthen-7(14H)ylidene)methanol



Fig. 6. Proposed pyrolysis process for PET.

spread and minor fire hazard, suggesting better flame retardance [7,29]. In this study, the introduction of PBPBD decreases the heat release of the copolyesters. The PHRR value for $BD_{10}PET$ is 734.2 kW/m², which is 73% of the value for neat PET; the PHRR value for $BD_{20}PET$ further decreases to 541.9 kW/m², which is nearly half of that for neat PET. Based on the HRR curves in Fig. 8 (a), fire growth rate (FIGRA) has been calculated through PHRR/t_{PHRR} to assess flame spread in developing fire, the scale of a fire, and the fire hazards of samples [30]. As well as the PHRR, the FIGRA of

copolyester is also decreased with the increase of the mole percent PBPBD. The FIGRA value for neat PET is 9.6, and the FIGRA values for BD_5PET , $BD_{10}PET$ and $BD_{20}PET$ decrease to 9.5, 7.7 and 6.4, respectively. Low FIGRA values indicate delayed times to flashover, which allows enough time to evacuate and/or for fire extinguishers to arrive [31]. And the THR values for BD_xPET copolyesters range from 53.4 to 57.3 MJ/m², which are close to the THR value for neat PET (55.5 MJ/m²), retaining an acceptable level.

Smoke produced in the fire is even the most important factor



Fig. 7. Proposed pyrolysis process for PBPBD structural units in BD₂₀PET.



Fig. 8. Cone calorimetric results of PET and BD_xPETs: (a) HRR; (b)THR; (c)SPR; (d)TSP.

which directly puts people to death by suffocation and/or inhalation of the toxic gases [32]. Thus, smoke suppression is really important for the flame-retardant polymers. As shown in Fig. 8 (d) and Table 6, the TSP values for BD₅PET, BD₁₀PET and BD₂₀PET are 10.2 m², 10.4 m², and 13.0 m², respectively. These values are much lower than the TSP value for neat PET (18.8 m²), which illustrates that the incorporation of PBPBD endows BD_xPETs with good smoke inhibition property. One reasonable interpretation should be that PBPBD structural units can ultimately form conjugated heteroaromatic structures, and release less volatile products compared to PET at high temperature, which suppresses the smoke generation effectively.

The limiting oxygen index (LOI) of the specimens was measured to estimate their flame retardance. The detailed LOI values are listed in Table 6. It can be seen that neat PET is a flammable material with a low LOI value of 22.0, and with the incorporation of PBPBD, the LOI value for BD₅PET increases to 26.1. Further increasing the content of PBPBD, the LOI value for BD₂₀PET reaches 32.0, meaning the copolyester obtains expected flame retardance. Fig. 9 shows the digital images of specimens after LOI test, serious melt-dripping and few char residue from combustion can be observed for neat PET. In contrast, apparently intumescent char formation and no melt-dripping phenomenon are observed for all the three samples of BD_xPETs.

All the results above-mentioned demonstrate that the incorporation of PBPBD can lower the HRR, FIGRA and TSP values while raise the LOI values for the copolyesters, providing outstanding flame retardant performance. Combining the pyrolysis GC/MS results, we can deduce that it is the formation of conjugated heteroaromatic structures through the rearrangement reactions of PBPBD structural units that promoted plenty of char formation during combustion, which can isolate the oxygen and the heat, suppress the smoke production simultaneously, as well as inhibit the dripping effectively.

3.7. Char residue morphology

To investigate the morphology of the char residues of BD_xPETs , SEM analysis was carried out. Inner surface images of char residues of PET and $BD_{20}PET$ after cone calorimeter measurements are given in Fig. 10. We can observe clearly that the char residue morphology of neat PET is smooth and with scattered ashes (Fig. 10 (a)). Compared with neat PET, in Fig. 10 (b), $BD_{20}PET$ presents rougher surface, and many grass-shape objects can be observed. After

Table 6	
Cone calorimetry and LOI results for PET and BD _x PETs.	

Samples	PET	BD ₅ PET	BD ₁₀ PET	BD ₂₀ PET
PHRR (kW/m ²)	1004.5	950.1	734.2	541.9
Av-HRR ^a (kW/m ²)	104.7	105.0	93.7	89.5
THR (MJ/m ²)	55.5	56.1	53.4	57.3
TSP (m ²)	18.8	10.2	10.4	13.0
t _{PHRR} ^b (s)	105	100	95	85
FIGRA ^c	9.6	9.5	7.7	6.4
LOI (vol%)	22.0	26.1	28.4	32.0

^a Av-HRR, the average value of HRR.

^b t_{PHRR} means Time to PHRR.

^c Fire Growth Rate, calculated by dividing the PHRR by the t_{PHRR}.



Fig. 9. Digital images of BD_xPETs and PET after LOI test.



Fig. 10. SEM images (500 \times ; zoom in part, 10000 \times) of the inner surfaces of residues: (a) PET; (b) BD₂₀PET.

magnification, it is clear that these grass-shape objects are actually "stick-shaped" char formations with a size of nearly 5 μ m long. These unique "stick-shaped" char residues should be ascribed to the formation of conjugated heteroaromatic structures via the rearrangement reactions of PBPBD structural units during combustion. And these "stick-shaped" char formations exhibit good heat insulation and smoke inhibition, providing outstanding flameretardant effects in a fire. Regrettably, like neat PET, BD₂₀PET contains only carbon, hydrogen and oxygen, thus it is difficult to further investigate the composition of its char residue from combustion.

4. Conclusion

In this study, a monomer containing arylene-ether units (PBPBD) and a series of novel flame-retardant-element-free PET based copolyesters using PBPBD as a comonomer (BD_xPETs) were synthesized successfully. Their chemical structures were confirmed using ¹H-NMR, ¹³C-NMR spectroscopy. With increasing the content of PBPBD, the thermal stability and the char residue from combustion of BD_xPETs increased dramatically, whereas the crystallinity and melting temperature of these copolymers decreased. The results of thermal degradation kinetic illustrated that the apparent decomposition activation energy for the copolyesters was enhanced with increasing the conversion and the content of PBPBD. The pyrolysis investigation showed that PBBPD structural units undergo rearrangement reactions at high temperature, ultimately forming conjugated heteroaromatic structures. And this formation made BD_xPETs have plenty of residues with special "stick-shaped" char morphology. Thanks to these efficient rearrangement and carbonization reactions promoted by PBPBD units, the flame retardance and smoke suppression of BD_xPETs were simultaneously enhanced significantly. Meanwhile, for BD_xPETs, no meltdripping but obvious intumescent char formation was observed after LOI test. Despite the absence of any flame retardant element, BD_xPETs copolyesters exhibited outstanding flame retardant performance and char forming capability. This modification might provide a new solution to flame retarded polymers, which is more friendly to environment and human body than traditional methods.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at 10. 1016/j.polymer.2015.09.016.

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