#### Polymer 70 (2015) 68-76

Contents lists available at ScienceDirect

# Polymer

journal homepage: www.elsevier.com/locate/polymer

# Block self-cross-linkable poly(ethylene terephthalate) copolyester via solid-state polymerization: Crystallization, cross-linking, and flame retardance

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#### ARTICLE INFO

Article history: Received 17 December 2014 Received in revised form 21 May 2015 Accepted 10 June 2015 Available online 12 June 2015

Keywords: Block copolyester Solid-state polymerization Crystallization Cross-linking Flame retardance

# ABSTRACT

A self-cross-linkable poly(ethylene terephthalate) block copolyester (SSP-PETPx) has been synthesized via solid-state polymerization (SSP). In the SSP process, a cross-linkable monomer named 4-(phenylethynyl) di(ethylene glycol) phthalate (PEPE) is incorporated into the amorphous phase of PET. The sequence distribution of the resulted copolyester SSP-PETPx is analyzed with <sup>1</sup>H NMR, showing that the SSP sample possesses block structure. Wide-Angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) show that SSP-PETPx is crystallizable benefitting from its block structure, while the corresponding random copolyester (RD-PETP) is totally amorphous. The segments containing PEPE determine the extent of crystallization. Simultaneous thermogravimetric-differential scanning calorimetry (TG-DSC) and rheological analysis prove the cross-linking behaviour of SSP-PETP although the block constitution slightly postpones cross-linking occurrence. The high complex viscosity of the SSP-PETP at 340 °C suggests good flame retardancy and anti-dripping properties. Micro combustion calorimeter (MCC) results prove both SSP-PETP and RD-PETP copolyesters have low flammability, which demonstrates that block structure of SSP-PETP doesn't have a negative impact on the flammability of copolyesters.

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# 1. Introduction

Poly(ethylene terephthalate) (PET), a partly aromatic semicrystalline polyester, has wide applications in our daily life such as beverage bottle, fiber and packing materials [1-3]. However, its fire risk seriously threatens human lives and property due to its flammable nature [4-6]. To obtain flame-retardant polyester material, conventional methods are incorporating flame-retardant elements into their main chains or side chains by polymerization, or adding flame retardants to their matrices [7-9]. Among them, copolymerizing phosphorus-containing monomers into polyester chains is considered to be one of the most efficient methods for preparation of flame-retardant fiber [10-12]. However, most phosphoruscontaining copolyesters cause serious melt-dripping during fire,

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leading to secondary damage and immediate empyrosis [13–17]. It is difficult to solve the contradiction between the flammability and dripping behaviour for polyester via copolymerization.

To overcome this problem, in our recent work, a kind of crosslinkable PET-based copolyester was designed and synthesized [18]. This copolyester is inactive at the temperature of synthesis and processing. But it can cross-link rapidly at higher temperature before burning, which endows copolyester with selfextinguishment and non-dripping behaviour. Besides, this thermal cross-linkable copolyester possesses only carbon, hydrogen, and oxygen elements, which is a truly green and environmentfriendly material. However, in order to obtain high flameretardancy and pass the UL-94 or LOI tests, high content of functional monomer is needed for this copolyester [19]. Without a doubt, the regularity and symmetry of polymer chain sharply decreases especially for the copolyesters with high content of functional monomer, and this will low their crystalline ability. For example, when the content of functional monomer is 16.3%, its





polyme



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melting enthalpy is decreased from 43.1 (for pure PET) to 6.1 J  $g^{-1}$  [18]. And it is well known that the crystalline ability of polymer has great relationship with its mechanical properties. Therefore, it is a key issue for this copolyester keeping good crystallinity and self cross-linking properties simultaneously.

Solid-state polymerization (SSP) is an effective method to synthesize copolyester with block constitution [20–22]. For polyester, SSP, is performed at the temperature below its melting temperature and higher than its glass transition temperature, which is usually used to increase the molecular weight. SSP occurs in the amorphous region of polyester while the chain motion in crystalline regions is restricted [23–27]. Based on this feature, the functional monomer can be incorporated into the amorphous regions of polyester via SSP, and the resulted copolyester possesses block constitution. Via SSP, Chen et al. [20,28] prepared a block phosphorus-containing poly(trimethylene terephalate) copolyester using the blends of 9,10-dihydro-10-[2,3-di(hydroxycarbonyl)propyl]-10-phospha-phenanthrene-10-oxide (DDP) ester and poly(trimethylene terephalate) (PTT) oligomer as raw materials. The crystallization behaviours of copolyesters were improved.

In this paper, self-cross-linkable block copolyesters were also synthesized via SSP. In SSP process, a cross-linkable monomer named 4-(phenylethynyl) di(ethylene glycol) phthalate (PEPE) was incorporated into the amorphous phase of PET. The sequence distribution and the randomness of the obtained copolyesters were analyzed by NMR. The detailed crystallization properties of copolyesters were investigated using DSC and WAXD. The cross-linking behaviours of the resulting copolyesters were discussed by TG-DSC and dynamic rheology. The relationship between the thermal behaviours and block constitution was investigated in detail. The flammability of the obtained copolyesters was examined by MCC.

# 2. Experimental

#### 2.1. Chemicals and substrates

Dimethyl terephthalate (DMT, CP grade) was provided by Sinopharm Chemical Reagent Co. Ltd (Shanghai China). Ethylene glycol (EG), antimony trioxide (Sb<sub>2</sub>O<sub>3</sub>, AR), methanol, phenol, tetrachloroethane, hexafluoro-isopropanol (HFIP), zinc acetate (CP) were obtained from Chengdu Chemical Industries Co. (Chengdu, China) and used as received. 4-phenylethynylphathalic anhydride (PEPA) was purchased from Changzhou Sunlight Pharmaceutical Co., Ltd. (Changzhou, China).

# 2.2. Pre-polymerization

PET prepolymer (p-PET) was prepared by transesterification method (Scheme 1). DMT and EG with molar ratio of 1:4 were added into a reaction apparatus with a nitrogen inlet, a condensation, and a mechanical stirrer. Transesterification catalyst zinc acetate and polycondensation catalyst Sb<sub>2</sub>O<sub>3</sub> were also added before reaction. The mixtures were kept at 180 °C with nitrogen protection and mechanical stir. After about 2 h, methanol was distilled out completely. Then, the reaction was further carried out under reduced pressure (40 Pa) for half an hour at 270 °C. <sup>1</sup>H NMR (CF<sub>3</sub>COOD,  $\delta$ ): 8.4 (Ar–*H*), 5.0 (–C(O)O–CH<sub>2</sub>CH<sub>2</sub>–O–(O)C–), 4.2 (-CH<sub>2</sub>–OH). The intrinsic viscosity of resulting p-PET was 0.19 dL/g.

Cross-linkable monomer PEPE was synthesized as our previous work [18]. PEPA was firstly ethoxylated in the presence of ethylene glycol (Scheme 1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>,  $\delta$ ): 7.6–8.5 (Ar–*H*), 5.0–5.4 (–C(O)O–*CH*<sub>2</sub>-), 4.3–4.6 (–*C*H<sub>2</sub>-OH).

p-PET and PEPE were dissolved into HFIP at 45 °C. After complete dissolution, the temperature was raised to 90 °C to remove the HFIP. Then, the obtained p-PET/PEPE mixture was ground into powder (particle size: 1.0–1.8  $\mu m,$  Fig. S1). Finally, the powdered p-PET/PEPE mixture was dried in oven at 80 °C for 24 h prior to further use.

#### 2.3. Solid-state polymerization (SSP)

SSP was carried out in a reaction tube under reduced pressure. The temperature was kept at 190 °C for 2 h, and then was raised to 205 °C. The tube was about 120 mm long, with the diameter of 15 mm. Reaction pressure was maintained at about 20–25 Pa, and reaction time were 0-8 h. The resulting SSP copolyesters are abbreviated as SSP-PETPx (Scheme 1), where the number x denotes the molar parts of PEPE per hundred of DMT. In this work, x is 30, 40, 60 or 80.

# 2.4. Melt polycondensation

For comparison, the random self-cross-linkable copolyester (RD-PETP<sub>40</sub>) and neat PET were prepared via one-pot melt polycondensation according to our previous work [18].

# 2.5. Characterization

NMR spectra of copolyesters (1H, 600 MHz; 13C, 400 MHz) with CF<sub>3</sub>COOD as the solvent, and tetramethylsilane as the internal stand, were obtained at room temperature by Bruker AVANCE AVII600 NMR and Bruker AVANCE AVII400 instrument, respectively. The intrinsic viscosities of p-PET were measured with an Ubbelohde viscometer with a concentration of 0.5 g/dL at 25 °C in 1:1 (v/ v) phenol-1,1,2,2-tetrachloroethane solution. The content of PEPE incorporated in PET chain was determined by <sup>1</sup>HNMR. Before NMR tests, all samples dissolved in CF<sub>3</sub>COOH with stirring for 30 min to make a solution, and then were precipitated by methanol. Via this treatment the unreacted PEPE was removed. The obtained products were dried in oven until constant weight.

#### 2.6. Crystallization characterization

The thermal transition behaviours of RD-PETPx and SSP-PETPx were measured with TA Q200 DSC apparatus, calibrated with pure indium and zinc standards. Samples (5  $\pm$  0.5 mg) were first heated to 270 °C for 3 min, to eliminate the influence of thermal history and the effect of heat treatment on the crystalline structure of materials. Then, the sample was cooled down to 40 °C to record the crystallization process, and reheated to 270 °C at a heating rate of 10 °C/min. WAXD measurements of RD-PETP<sub>40</sub> and SSP-PETP<sub>40</sub> were performed using an X-ray diffractometer (Philips X Pert X-ray diffractometer), with Cu K $\alpha$  radiation in a 2 $\theta$  ranges from 2 to 50°. All samples were annealed at 160 °C for 2 h before testing.

#### 2.7. Cross-linking behaviour

Cross-linking behaviours of copolyesters were investigated by a NETZSCH simultaneous TGA-DSC (449C) at a heating rate of 10 °C min<sup>-1</sup> in N<sub>2</sub>. Dynamic oscillatory rheological measurements of RD and SSP 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 1 rad/s in air were in the range of 200 or 240 °C–340 °C for RD and SSP samples at a heating rate of 10 °C min<sup>-1</sup>, respectively.



Scheme 1. Solid-state polycondensation route of SSP-PETPx.

#### 2.8. Flammability

Small scale flammability tests were performed on the FTT 0001 MCC Microscale Combustion Calorimeter (MCC). 5–10 mg samples were heated to 750 °C from 90 °C at a ramp rate of 1 °C/s in a stream of nitrogen flowing at 80 mL/min. The combustor temperature was set at 900 °C and oxygen/nitrogen flow rate was 20/80 mL mL<sup>-1</sup>.

#### 3. Results and discussion

# 3.1. Solid-state polymerization

To study the solid-state polymerization process, SSP-PETP<sub>40</sub> with solid polymerization time ( $t_{SSP}$ ) from 0 to 8 h was carried out. As shown in Scheme 1, transesterification reaction between PEPE and p-PET was main chemical reaction during SSP, and the chemical structure of the obtained copolyesters consisted of E-T and E-P unit, in which E stood for EG unit, T stood for DMT unit, and P stood for PEPE unit. The content of PEPE incorporated in PET chain was determined by <sup>1</sup>HNMR. Table 1 presents the change of reaction extent with  $t_{SSP}$  during SSP. The cross-linkable monomer PEPE showed a quick reaction with p-PET during the first 2 h reflected by the rapid increase of PEPE actual content. When  $t_{SSP}$  reached 8 h, almost all free PEPE monomer had been incorporated in the copolyester via transesterification reaction. At this time the actual PEPE content is 27.0%, which is almost as same as that of RD-PETP<sub>40</sub>.

# 3.2. Structure and sequential distribution analysis

As our design, the block constitution of SSP-PETPx is formed during SSP, because SSP only occurs in the amorphous area of polymer where the chains are mobile, as shown in Scheme 2. This block SSP-PETPx consisted of pure homopolymer polyester block (only TET repeat units) mainly in the crystalline domains and copolyester (both TEP and PEP units) in the amorphous parts. The chemical structure of SSP-PETP<sub>40</sub> was determined by <sup>13</sup>CNMR and <sup>1</sup>HNMR. Fig. 1 showed the <sup>13</sup>CNMR spectrum of SSP-PETP<sub>40</sub>  $(t_{SSP} = 8 h)$ , where the resonance signals occur at 87, 94, and 122–132 ppm were ascribed to the phenylethynyl groups. Fig. 2 showed the <sup>1</sup>HNMR spectra of SSP-PETP<sub>40</sub> ( $t_{SSP} = 8$  h) and RD-PETP<sub>40</sub>. Each spectrum was subjected to peak fitting using the curve fitting software MestReNova 6.1.0-6224. The resonance signal occurred at 8.25 ppm (a) was ascribed to the aryl of DMT (T), and the signals at 7.25–7.90 (b) ppm were assigned to the aryl of PEPE (P). During SSP, an ester bond will form when PEPE is incorporated into polymer chains. But PEPE has the same ester bond itself, that is to say, PEPE and SSP-PETP40 have very similar phenylethynyl group signals in NMR spectra, so, we cannot get the direct information about covalent links from their NMR spectra. Because the unreacted PEPE had been removed before NMR test, the signals of phenylethynyl groups in NMR spectrum of SSP-PETP<sub>40</sub> were ascribed to the PEPE segment in the copolyesters. And this illustrated that PEPE had been successfully incorporated into the copolyester chain via covalent bond. Especially, the signals at 4.65–5.05 in the Fig. 2 were caused by the methylene of EG with different combinations with DMT or PEPE. The possible combinations of TET, TEP (PET), and PEP were shown in Scheme 3. And the peaks at 4.92-5.05, 4.82-4.92, and 4.65–4.82 ppm were assigned to the methylene of TET (c), TEP (d), and PEP (e), respectively. In particular, the signals of PEP units only existed in SSP-PETP<sub>40</sub>, indicated that PEPE accumulated into homogeneous sequences in SSP. However, PEP signals cannot be observed in RD-PETP<sub>40</sub>. Actually, the concentration of PEPE units in

#### Table 1

	Basic	characteristic	of SSP	-PETP <sub>40</sub>	and I	RD-PETP40	copoly	esters.
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Samples	t <sub>SSP</sub> (h)	PEPE content (mol %)		Intensity of chemical shifts (%)			P <sub>TP</sub>	P <sub>PT</sub>	L <sub>nT</sub>	L <sub>nP</sub>	R
		Theo.	Actual <sup>a</sup>	с	d	e					
SSP-PETP40	1	28.6	17.3	77.7	10.0	12.3	0.06	0.28	16.7	3.6	0.34
	2		23.1	68.5	17.0	14.6	0.11	0.37	9.1	2.7	0.48
	4		27.0	62.0	21.8	16.2	0.15	0.41	6.7	2.4	0.56
	8		27.0	60.6	24.8	14.6	0.17	0.46	5.9	2.2	0.63
RD-PETP <sub>40</sub>	_	28.6	28.0	43.9	56.1	0	0.39	1	2.6	1	1.39

<sup>a</sup> Actual PETP contents were calculated from H NMR.



Scheme 2. Schematic representation of solid-state polymerization process of SSP-PETPx: (a) before SSP, (b) after SSP, (c) the formed SSP-PETPx block copolyester.

the amorphous phase during SSP is higher than its concentration in the melt during melt copolymerization, thereby enhancing the chance of PEP sequence formation. And this further demonstrates that our design is successful and block constitution of SSP-PETP<sub>40</sub> is obtained.

Furthermore, the degree of randomness of  $PEPT_x$  named R was calculated by <sup>1</sup>HNMR, and the compositions of each sequence were determined by Equations (1)–(3) [29–31].

$$P_{TP} = \frac{\frac{I_{TEP}}{2}}{\frac{I_{TEP}}{2} + I_{TET}} = \frac{\frac{I_d}{2}}{\frac{I_d}{2} + I_c} = \frac{1}{L_{nT}}$$
(1)



Fig. 1.  ${}^{13}$ C NMR spectrum of SSP-PETP<sub>40</sub> (t<sub>SSP</sub> = 8 h).

$$P_{PT} = \frac{\frac{I_{TEP}}{2}}{\frac{I_{TEP}}{2} + I_{PEP}} = \frac{\frac{I_d}{2}}{\frac{I_d}{2} + I_e} = \frac{1}{L_{nP}}$$
(2)

$$R = P_{TP} + P_{PT} \tag{3}$$

$$I_T = I_{TET} + \frac{I_{TEP}}{2} = I_c + \frac{I_d}{2}$$
(4)

$$I_P = I_{PEP} + \frac{I_{TEP}}{2} = I_e + \frac{I_d}{2}$$
(5)

Where  $I_T(I_a)$ ,  $I_P(I_b)$ ,  $I_{TET}(I_c)$ ,  $I_{TEP}(I_d)$ , and  $I_{PEP}(I_e)$  corresponded to the integrated intensities of a, b, c, d, and e, respectively. The  $P_{TP}$ stood for the probability of finding a P unit next to a T unit, and the  $P_{PT}$  stood for the probability of finding a T unit next to a P unit.  $L_{nT}$ meant the number-average sequential length of TET unit, and  $L_{nP}$ meant the number-average sequential length of PEP unit. In order to reduce the error,  $I_{TET}$ ,  $I_T$ , and  $I_P$  were directly obtained from <sup>1</sup>HNMR peak integration, while  $I_{TEP}$  and  $I_{PEP}$  were calculated by Equations (4) and (5).

As we know, the lower degree of randomness (R) denoted the units of copolymer tend to cluster together into blocks. In our investigation, the R value of SSP-PETP<sub>40</sub> ( $t_{SSP} = 8$  h) was 0.63, while the value for RD-PETP<sub>40</sub> with random structure was 1.39. It was clear that the repeating units of SSP-PETP<sub>40</sub> tend to accumulate into homogeneous sequences such as T-E-T-E-T or P-E-P-E-P, or block constitution, in another word [32,33].

The degree of randomness as a function of reaction time was also calculated and listed in Table 1. From Table 1, it was found that  $P_{TP}$  and  $P_{PT}$  of SSP-PETP<sub>40</sub> increased with the increase of t<sub>SSP</sub>, resulted in an increase of the degree of randomness. During SSP, the amount of PEPE incorporated in the polymer chains increased, and at the same time TET combination decreased. And TEP combination greatly increased, however, PEP combination increased a little. Thus, the degree of randomness increased. That is to say, the transesterification reaction between PEPE and p-PET in the



Fig. 2. <sup>1</sup>H NMR spectra of SSP-PETP<sub>40</sub> ( $t_{SSP} = 8$  h) (A), and RD-PETP<sub>40</sub> (B).



Scheme 3. Sequence distribution of T and P unit.

amorphous region plays an important role in increasing the R value [20,34]. The obtained copolyester kept the original crystalline region of PET, however, the new amorphous area actually became copolyester. With the increase of  $t_{SSP}$ , the copolyesters possessed more enough time for transesterification, resulting in more random copolyeser formation.

# 3.3. Crystallization behaviour

In order to investigate the crystallization behaviour of SSP-PETPx, WAXD measurement was used for SSP-PETP<sub>40</sub> ( $t_{SSP} = 8$  h) and RD-PETP<sub>40</sub> (Fig. 3). Before testing, all samples were treated

with same thermal conditions to maintain the same crystallization environment. SSP-PETP<sub>40</sub> showed a typical diffraction pattern as same as that of PET (Fig. 3) [5,35–38], indicating the introduction of PEPE segment didn't change the crystal structure of PET. For RD-PETP<sub>40</sub> obtained from melt polycondensation, a broad peak was observed indicated it lost crystalline ability and became amorphous. This illustrates, as we expected, SSP-PETP copolyester with the block constitution is crystallizable, which is beneficial to the application in the future [39,40].

The thermal transition behaviors of SSP-PETP<sub>40</sub> with different  $t_{SSP}$  are shown in Fig. 4. The detailed data are listed in Table 2. According with XRD results, SSP-PETP<sub>40</sub> showed obvious



**Fig. 3.** WAXD patterns of SSP-PETP<sub>40</sub> ( $t_{SSP} = 8$  h) and RD-PETP<sub>40</sub>.

crystallization and melting peaks, while RD-PETP<sub>40</sub> was completely amorphous and only glass transition temperature was found. The thermal transition behaviors of the blends of p-PET and PEPE were also investigated for comparison. Only a weak melting and crystallization peak ascribed to p-PET was found in DSC heating and cooling scan of the blends. This phenomenon illustrated there are no reaction occurrence when PEPE with p-PET was only simply blended. When the SSP was in progress, the reaction only occurred in the amorphous area of p-PET, which resulted in the constituents of crystallizable chain (part of TET) unchanged (Scheme 2). Besides this, more TEP combination formation due to the transesterification, and made the steric hindrance on crystallization caused by PEPE monomers alleviated. As a result, the obtained copolyester exhibited a good crystalline property, which was reflected by the increase of their melting point  $(T_m)$ , crystallization temperature  $(T_c)$ , and melting enthalpies with the increase of  $t_{SSP}$ .

Moreover, the PEPE content also affect the crystallization properties of SSP-PETPx. The thermal transition behaviors of SSP-PETPx ( $t_{SSP} = 8$  h) with different PEPE content were investigated by DSC (Fig. 5 and Table 3). It was found that the crystallization ability was decreased with the increase of PEPE content, embodied by the lower  $T_m$ ,  $T_c$  and  $\Delta H_m$ . Especially for SSP-PETP<sub>80</sub>, it did not show any crystallization peak in its cooling scan, and only very faint melting peak presented in its heating curve. It is well known that the relative crystallinity of polymer can be determined by the ratio of melting enthalpy  $(\Delta H_m)$  of samples to that of 100% crystalline polymer. At present, we cannot obtain the  $\Delta H_m$  value of 100% crystalline SSP-PETP<sub>x</sub>, and the detailed crystallinity of the obtained products did not be determined. But from the lower value of  $\Delta H_{\rm m}$ we can sure that the crystallinity was also decreased with the increase of PEPE content. The poor crystallization ability was due to the big steric hindrance of PEPE monomers, which retarded the chain motion of copolyester even it only appeared in the amorphous region of the obtained products. Fortunately, the obtained copolyester (such as SSP-PETP<sub>60</sub>) with relative high PEPE contents still showed an obvious crystallization and melting peak.

#### 3.4. Cross-linking behaviour

The cross-linking behaviours of SSP-PETPx were studied by TG-DSC simultaneous thermal analysis and dynamic rheometer, in which SSP-PETP<sub>40</sub> ( $t_{SSP} = 8$  h) and RD-PETP<sub>40</sub> were chosen as a representative and a control, respectively. From the DSC



**Fig. 4.** DSC thermograms of RD-PETP<sub>40</sub> and SSP-PETP<sub>40</sub> with different  $t_{SSP}$  and RD-PETP<sub>40</sub>: (a) the second heating scan, (b) the cooling scans at rate of 10 °C min<sup>-1</sup>.

thermogram of SSP-PETP<sub>40</sub> (Fig. 6), a notable exothermal process started at 336 °C was found, which is just between the melting and the decomposition peak [41–45]. This means at this temperature the cross-linking reaction occurred. The cross-linking reaction of copolyesters is caused by the cross-linking reaction of phenyl-ethynyl groups, in which two phenylethynyl groups reacted together and formed one triphenylnaphthalene cross-links [19]. Besides, a melting peak also can be obviously seen in its DSC curves. On the contrary, only cross-linking and decompositon peak were found for RD-PETP<sub>40</sub>. It was clear that after SSP, the copolyester kept crystallization and cross-linking property simultaneously, just as shown in Scheme 4.

Table 2 Thermal transition data of RD-PETP\_{40} and SSP-PETP\_{40} with different  $t_{SSP}$ 

Sample	$T_g$ (°C)	$T_c (^{\circ}C)$	$\Delta H_c (J g^{-1})$	$T_m(^\circ C)$	$\Delta H_m  (J \; g^{-1})$
RD-PETP <sub>40</sub>	81.7	_	_	_	_
Blends (0h)	58.1	127.7	2.1	195.2	6.5
SSP-PETP <sub>40</sub> -2h	75.0	149.7	9.2	207.8	13.0
SSP-PETP <sub>40</sub> -4h	79.3	159.8	12.3	229.0	16.2
SSP-PETP <sub>40</sub> -8h	80.1	170.4	22.0	233.5	20.9



Fig. 5. DSC thermograms of SSP-PETPx ( $t_{SSP} = 8 \text{ h}$ ): (a) the second heating scan, (b) the cooling scans at rate of 10 °C min<sup>-1</sup>.

If we observed carefully, some differences can be found in Fig. 6. The cross-linking peak of RD-PETP<sub>40</sub> started at 314 °C, however, the cross-linking peak of SSP-PETP<sub>40</sub> occurred later at about 336 °C. This means the block constitution of copolyester after SSP inhibited the cross-linking occurrence slightly. As we know, for SSP-PETPx, the cross-linkable chains concentrated at amorphous region, which made copolyester having big steric hindrance than that of RD-PETP. The bigger steric hindrance meant that the cross-linking groups were more difficult to contact, that is, cross-linking reaction is hard to happen.

Furthermore, as the most significant effect caused by selfthermal cross-linking, the complex viscosity ( $\eta^*$ ) of the testing samples during the heating process, which play a crucial role in flame retardancy and anti-dripping [46–50], was investigated by dynamic oscillatory rheological measurements in air (Fig. 7).

Table 3	
Thermal transition data of SSP-PETPx ( $t_{SSP} = 8$ h	ı).

Sample	Tg (°C)	T <sub>c</sub> (°C)	$\Delta H_c (J g^{-1})$	$T_m$ (°C)	$\Delta H_m \left(J \; g^{-1}\right)$
SSP-PETP <sub>30</sub> SSP-PETP <sub>40</sub> SSP-PETP <sub>60</sub> SSP-PETP <sub>80</sub>	79.0 80.1 81.6 80.9	190.4 170.4 156.0	26.3 22.0 5.4	234.7 233.5 225.8 221.7	21.0 20.9 9.5 1.4



Fig. 6. TG-DSC thermograms of SSP-PETP\_{40} ( $t_{SSP}=8~h)$  and RD-PETP\_{40} at rate of 10  $^\circ C~min^{-1}$  in  $N_2.$ 

Similar with random self-cross-linking copolyester, the  $\eta^*$  of SSP-PETP<sub>40</sub> experienced a decrease firstly and subsequently increased sharply at the cross-linking temperature, at which  $\eta^*$  starts to increase or cross-linking reaction occurs in other words [46,47]. And a 'U-shape' change was clearly observed in the whole temperature range. Besides this, SSP-PETP<sub>40</sub> with block constitution had higher cross-linking temperature than that of RD-PETP<sub>40</sub>, which was accord with the results of TG-DSC. From Fig. 7, it can also be seen that compared with RD-PETP<sub>40</sub>, SSP-PETP<sub>40</sub> showed a relatively low melt viscosity at the whole investigated temperature. This meant that the increase of  $\eta^*$  of SSP-PETP<sub>40</sub> became difficult due to its block constitution. But the complex viscosity of SSP-PETP<sub>40</sub> at the temperature of 340 °C was still very high (more than 10000 Pa s), illuminated it will endow the copolyester with good flame retardancy and anti-dripping. And this will be investigated later.

# 3.5. Flammability

The flammability characteristics of RD-PETP<sub>40</sub> and SSP-PETP<sub>40</sub> were examined by MCC, which is a new and useful method developed in recent years for investigating the combustion properties of polymer materials [51,52]. And neat PET was also investigated for comparison. Several parameters, such as heat release rate capacity (HRC), total heat release (THR) and temperature at the maximum heat release rate ( $T_{max}$ ), were obtained and presented in Table 4. HRC is the peak heat release rate (HRR) normalized to the heating rate, and low values of HRC indicate low flammability and low full-scale fire hazard. As shown in the HRR curves (Fig. 8), neat PET underwent heat release with a sharp peak, and exhibited a high HRC value of 472 J g<sup>-1</sup> K. In the case of RD-PETP<sub>40</sub> and SSP-PETP<sub>40</sub>,



Scheme 4. Schematic representation of cross-linking and crystallization process of SSP-PETPx.



**Fig. 7.** Complex melt viscosity of SSP-PETP<sub>40</sub> ( $t_{SSP} = 8 h$ ) and RD-PETP<sub>40</sub> plotted against temperature at rate of 10 °C min<sup>-1</sup> in an air atmosphere.

two heat release peaks with a broad region were observed. Meanwhile, compared with neat PET, they showed much lower HRC values of 303 J g<sup>-1</sup> K and 311 J g<sup>-1</sup> K, respectively, indicating they have lower flammability. Also, RD-PETP<sub>40</sub> and SSP-PETP<sub>40</sub> had lower THR values of 15.8 kJ g<sup>-1</sup> and 16.0 kJ g<sup>-1</sup>, while neat PET give a value of 17.2 kJ g<sup>-1</sup>. It meant that more volatile products were carbonized to participate in the charring process, rather than transferred into the MCC combustor [53].

In addition, it is noteworthy that the HRR curve of SSP-PETP<sub>40</sub> almost coincides with that of RD-PETP<sub>40</sub>, and they have similar HRC and THR values. This illustrates that no matter what structure of PETP<sub>40</sub> has, it almost exhibit same flame retardance. That is to say, the block structure of SSP-PETP<sub>40</sub> doesn't have a negative impact on the flammability of copolyesters. Actually, the action of cross-linking monomer in reducing the flammability of polymers is attributed to the improving the melt viscosity and compact char

Table 4	
MCC data of neat PET, RD-PETP <sub>40</sub> , and SSP-PETP <sub>40</sub> ( $t_{SSP} = 8$ h).	

Sample	HRC (J $g^{-1}$ K)	THR (J $g^{-1}$ K)	T <sub>max</sub> (°C)
PET RD-PETP <sub>40</sub> SSP-PETP <sub>40</sub>	472 303 311	17.2 15.8 16.0	442.8 437.1 439.6
SSP-PETP <sub>40</sub>	311	16.0	439.6



Fig. 8. Heat release rate curves of neat PET, RD-PETP<sub>40</sub>, and SSP-PETP<sub>40</sub> ( $t_{SSP} = 8 \text{ h}$ ).

[18]. As mentioned earlier, the cross-linking reaction of SSP-PETPx is just slightly postponed, and SSP-PETP<sub>40</sub> and RD-PETP<sub>40</sub> show very similar cross-linking behaviours. Consequently, SSP-PETP<sub>40</sub> has low flammability just as RD-PETP<sub>40</sub>.

# 4. Conclusion

In summary, self-cross-linkable block copolyesters have been successfully synthesized using PET prepolymer and PEPE as raw materials via SSP. <sup>1</sup>H NMR analysis shows the SSP-PETPx copolyester has a block chemical structure, i.e. one block is "PET crystalline region", and another one is "P(ET-co-P) random copolyester region". Transesterification reaction only occurs in the amorphous phase of p-PET. With the decrease of t<sub>SSP</sub>, the degree of randomness of copolyesters decreases. WAXD and DSC results demonstrate that after SSP the copolyesters are crystallizable, even for the samples with high PEPE content. This can be ascribed to their block structure, while the corresponding random copolyester is totally amorphous. The segments containing PEPE in amorphous area of SSP-PETPx determines its crystallization ability. The higher PEPE content introduced into PETPx copolyester lowers its crystallization ability. The SSP-PETPx keep the cross-linking properties although the cross-linking reaction has been slightly postponed compared with random copolyester. The complex viscosity of SSP-PETPx at high temperature is as high as 10000 Pa s, which will contribute to the flame retardancy and anti-dripping properties. MCC results suggest both SSP-PETPx and RD-PETP copolyesters have similar and small HRC and THR values, indicated they have low flammability. Via SSP, the crystallization ability of the obtained copolyesters was improved, and at the same time they still possess good flame retardance.

# Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (50933005, 51421061), and the Excellent Youth Foundation of Sichuan (2011]Q0007).

#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2015.06.012.

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