



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



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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 ¹H 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 semi-crystalline 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 phosphorus-containing copolyesters cause serious melt-dripping during fire,

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 cross-linkable 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 self-extinguishment and non-dripping behaviour. Besides, this thermal cross-linkable copolyester possesses only carbon, hydrogen, and oxygen elements, which is a truly green and environment-friendly material. However, in order to obtain high flame-retardancy 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

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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 terephthalate) copolyester using the blends of 9,10-dihydro-10-[2,3-di(hydroxycarbonyl)propyl]-10-phospha-phenanthrene-10-oxide (DDP) ester and poly(trimethylene terephthalate) (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 (Sb₂O₃, AR), methanol, phenol, tetrachloroethane, hexafluoro-isopropanol (HFIP), zinc acetate (CP) were obtained from Chengdu Chemical Industries Co. (Chengdu, China) and used as received. 4-phenylethynylphthalic 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 Sb₂O₃ 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. ¹H NMR (CF₃COOD, δ): 8.4 (Ar-H), 5.0 (-(C(O)O-CH₂CH₂-O-(O)C-), 4.2 (-CH₂-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). ¹H NMR (400 MHz, DMSO-d₆, δ): 7.6–8.5 (Ar-H), 5.0–5.4 (-(C(O)O-CH₂-), 4.3–4.6 (-CH₂-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 μm, 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-PETP_x (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-PETP₄₀) 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 CF₃COOD 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 ¹H NMR. Before NMR tests, all samples dissolved in CF₃COOH 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-PETP_x and SSP-PETP_x were measured with TA Q200 DSC apparatus, calibrated with pure indium and zinc standards. Samples (5 ± 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-PETP₄₀ and SSP-PETP₄₀ were performed using an X-ray diffractometer (Philips X Pert X-ray diffractometer), with Cu Kα radiation in a 2θ 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⁻¹ in N₂. 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⁻¹, respectively.

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