



Synthesis, thermal properties, and crystallization kinetics of novel biodegradable poly(ethylene succinate-co-diethylene glycol succinate) copolyesters



Peng Xue, Zhaobin Qiu *

State Key Laboratory of Chemical Resource Engineering, MOE Key Laboratory of Carbon Fiber and Functional Polymers, Beijing University of Chemical Technology, Beijing 100029, China

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ABSTRACT

Biodegradable poly(ethylene succinate-co-diethylene succinate) (P(ES-co-DEGS)) copolyesters with different diethylene glycol succinate (DEGS) compositions and the homopolymer poly(ethylene succinate) (PES) were successfully synthesized by a two-stage melt polycondensation method. The crystal structures, basic thermal properties, crystallization kinetics, and spherulitic morphologies of P(ES-co-DEGS) and PES were extensively investigated. Relative to PES, the glass transition temperature values of the copolyesters are slightly reduced, while their melting temperature and equilibrium melting temperature values obviously become smaller. The crystal structures of the copolyesters are the same as PES, while their degree of crystallinity values are slightly reduced. Relative to PES, the crystallization rates of the copolyesters become smaller, while the crystallization mechanisms remain almost unchanged. The morphology study revealed that the enhanced spherulite size and lowered nucleation density were observed with increasing crystallization temperature for all of the samples.

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1. Introduction

The development and practical application of the aliphatic polyesters from the renewable resources are important and attractive issues in research and industrial fields during the past several decades [1–4]. Poly(L-lactide) (PLLA) is a typical member of the biodegradable aliphatic polyesters, which has been widely used in biomedical and packaging applications [5–7]. Similar to PLLA, poly(ethylene succinate) (PES) and poly(butylene succinate) (PBS) are also two important members of biodegradable aliphatic polyesters, which can be prepared from the condensation of succinic acid (SA) and diol. It is well worth noting that SA is a new type of platform chemical derived from renewable resources [8]. Therefore, similar to PLLA, PES and PBS may also be regarded as biodegradable polyesters, which can be prepared from renewable resources from this viewpoint.

PES may be recognized as one of the most potential substitutes for the traditional plastics, such as polypropylene (PP) and polyethylene (PE), for its biodegradability and excellent mechanical property [9–11]. It has a chemical structure of

$-(\text{OCH}_2\text{CH}_2\text{OOCCH}_2\text{CH}_2\text{CO})_n-$ and can be prepared by the melt polycondensation of SA and ethylene glycol (EG). The chemical structure, basic thermal properties, nonisothermal and isothermal melt crystallization kinetics, crystalline morphology, crystal structure, crystal transition mechanism, thermal stability, and other properties of PES homopolymer have been extensively reported [12–17]. To develop the PES based multicomponent materials with the desired properties, some polymers were utilized to blend with PES, such as poly(vinyl phenol) (PVPh), poly(ethylene oxide) (PEO), and PLLA [18–21]. PES was found to be miscible with PVPh and PEO [19,20], while the immiscibility and phase separation were found in the PLLA/PES blends [21]. In addition to polymer blending, some PES based copolyesters containing ethylene succinate (ES) unit have also recently been synthesized and studied through a copolymerization method, such as poly(butylene succinate-co-ethylene succinate) (P(BS-co-ES)), poly(ethylene succinate-co-ethylene adipate) (P(ES-co-EA)), poly(hexamethylene succinate-co-ethylene succinate) (P(HS-co-ES)), poly(ethylene succinate-co-trimethylene succinate) (P(ES-co-TS)), etc. [22–26].

In literature, the introduction of the ether linkage into the backbone chain of some aliphatic polymers has already been extensively investigated, which may influence the flexibility, crystallinity and other properties of the synthesized aliphatic

* Corresponding author. Fax: +86 10 64413161.

E-mail address: qiuzb@mail.buct.edu.cn (Z. Qiu).

copolyesters with respect to their parent homopolyesters [26–30]. In this work, several poly(ethylene succinate-co-diethylene glycol succinate) (P(ES-co-DEGS)) copolyesters with different diethylene glycol succinate (DEGS) compositions were prepared through a two-step melt polycondensation for the first time. Moreover, the crystal structure, basic thermal properties, isothermal crystallization behavior, and spherulitic morphology and growth kinetics of P(ES-co-DEGS) with different DEGS contents and the homopolymer PES were systematically investigated and discussed. The aims of this research are not only to develop a new family of the PES based copolyesters but also to investigate the effect of the DEGS unit with the ether linkage on the thermal properties and crystallization kinetics of P(ES-co-DEGS), relative to PES. Such research results may be of interest and importance from both academic and practical viewpoints for the development and investigation of novel biodegradable polymers.

2. Experimental

2.1. Materials

The monomers SA, EG, and diethylene glycol (DEG) were purchased from Tianjin Fuchen Chemical Reagents Factory, Beijing Chemical Works, and Xilong Chemical Co., Ltd., respectively. The catalyst titanium tetrabutoxide ($\text{Ti}(\text{OBu})_4$) and the stabilizer polyphosphoric acid (PPA) were bought from Beijing Jingxiang Chemical Factory and Sinopharm Chemical Reagent Co., Ltd., respectively. All of the reagents were directly used without any purification.

2.2. Synthesis of PES and P(ES-co-DEGS)

The synthesis of the copolymers and PES was performed through a typical two-step melt polycondensation (esterification and polycondensation) [23]. The detailed synthesis process was similar to that of our previous work [23], which was not shown here in detail for brevity. The obtained copolyesters in this study were labeled as PEDEGSX, where X was the molar ratio of DEGS unit of P(ES-co-DEGS).

2.3. Characterization

Proton Nuclear Magnetic Resonance (^1H NMR). The compositions and chemical structures of the prepared samples were ensured by a Bruker AV 600 MHz instrument in deuterated chloroform.

Gel Permeation Chromatography (GPC). The molecular weights were analyzed with a Waters 515HPLC GPC (Waters Company, USA), using chloroform as the solvent.

Wide-Angle X-ray Diffraction (WAXD). The WAXD profiles were recorded on a Rigaku d/Max2500 VB2+/PC X-ray Diffractometer at 40 kV and 200 mA.

Differential Scanning Calorimetry (DSC). A TA Instrument DSC Q100 was used to investigate the thermal properties and crystallization behaviors. The samples were annealed at 130 °C for 3 min to eliminate the previous thermal history before any thermal analysis.

Polarized Optical Microscope (POM). The POM measurements were performed on an Olympus BX51 POM with a Linkam THMS600 temperature controller.

3. Results and discussion

3.1. Synthesis, characterization, and crystal structures of PES and P(ES-co-DEGS)

^1H NMR is a powerful method that may calculate the exact composition of the copolymers rapidly and precisely. The chemical structure of P(ES-co-DEGS) is shown in Fig. 1a, labeling the different protons of ES and DEGS units specifically. To better understand the chemical structure, the different resonance peaks corresponding to the different protons of ES and DEGS units from the ^1H NMR spectrum of PEDEGS11 are collected in Fig. 1b. The peak at 4.30 ppm is assigned to the resonance of H1 protons, while the resonance peaks at 4.25 ppm and 3.69 ppm are caused by the H3 and H4 protons, respectively; moreover, the peak at 2.67 ppm is arisen from H2 and H2' protons. The exact molar compositions of the copolymers may be calculated through the following equation:

$$\frac{\text{ES}}{\text{DEGS}} = \frac{I_{\text{H1}}}{I_{\text{H3}}} = \frac{I_{\text{H1}}}{I_{\text{H4}}} \quad (1)$$

where I is the intensity of the resonance peak corresponding to the different protons of the ES and DEGS units. From Fig. 1, the composition results are listed in Table 1, showing that the molar ratio is almost identical with the molar ratio in feed. Table 1 also provides the molecular weights of all of the samples.

Cao et al. once synthesized a series of P(BS-co-ES) copolymers through a typical two-step melt polycondensation, calculated the degree of randomness of the copolymers with ^{13}C NMR, and found that the obtained copolymers were random copolymers [26]. Gigli et al. also synthesized a series of novel eco-friendly copolyesters of PBS containing ether-linkages using the similar method, evaluated the distribution of the comonomeric sequences along the polymer chain by means of ^{13}C NMR, and concluded that the degree of randomness was close to 1, indicative of the random nature of the obtained copolymers [28]. In this work, we synthesized the PEDEGS copolymers via a similar synthesis process; therefore, it is expected that the obtained copolymers may be random copolymers. The degree of randomness of PEDEGS should also be evaluated with ^{13}C NMR, which will be reported in the forthcoming work.

To extensively investigate the crystal structures of PES and its copolymers, the WAXD patterns of these samples are collected in Fig. 2 after crystallizing at 56 °C from the crystal-free melt for 2 days. PES has two different crystal forms, i.e., α form and β form; however, the β form appears only under the strain condition [12]. In Fig. 2, three intense diffraction peaks ((0 2 1), (1 2 1), and (2 0 0) planes), corresponding to the α form of PES, are present [13]; furthermore, the increment of the DEGS unit does not obviously influence the peak positions of the WAXD profiles. Consequently, the similar diffraction peaks are present for P(ES-co-DEGS), despite the DEGS contents, except some slight changes in the intensity.

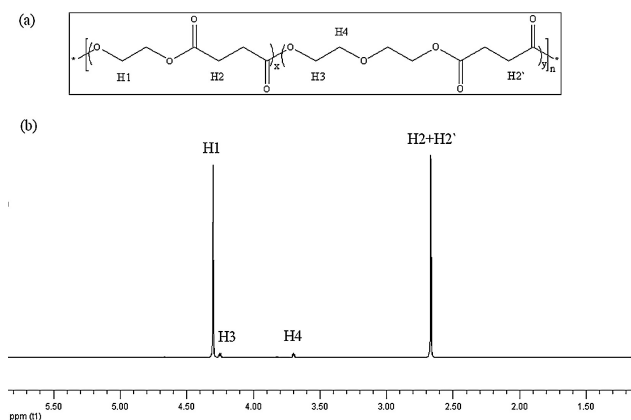


Fig. 1. (a) Chemical structure of P(ES-co-DEGS) and (b) ^1H NMR spectrum of PEDEGS11.

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