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Characterization, crystallization kinetics and melting behavior of poly(ethylene succinate) copolyester containing 5 mol% trimethylene succinate

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Abstract

Copolyester was synthesized and characterized as having 94.4 mol% ethylene succinate units and 5.6 mol% trimethylene succinate units in a random sequence as revealed by NMR. Differential scanning calorimeter (DSC) was used to investigate the isothermal crystallization kinetics of this copolyester in the temperature range (T_c) from 30 to 80 °C. The melting behavior after isothermal crystallization was studied by using DSC and temperature modulated DSC (TMDSC) by varying the T_c, the heating rate and the crystallization time. DSC and TMDSC curves showed triple melting peaks. The melting behavior indicates that the upper melting peaks are primarily due to the melting of lamellar crystals with different stabilities. A small exothermic curve between the main melting peaks gives a direct evidence of recrystallization. As the T_c increases, the contribution of recrystallization gradually decreases and finally disappears. The Hoffman–Weeks linear plot gave an equilibrium melting temperature of 108.3 °C. The kinetic analysis of the spherulitic growth rates indicated that a regime II → III transition occurred at ∼65 °C.

Keywords: Copolyester; Poly(ethylene succinate); Crystallization

1. Introduction

Polymers universally used such as polyethylene (PE), polypropylene (PP) and polystyrene have caused considerable environmental pollution since they are not degradable but stable. With the rise of concern to global environment in recent years, much attention has been focused on biodegradable and biocompatible polymers. According to the difference in the preparation methods, biodegradable polymers can be classified into two types. One is the biosynthetic polymer, such as bacterial polyhydroxyalkanoates (PHAs). The other is the chemosynthetic polymer, such as aliphatic polyesters. Aliphatic polyesters are considered to be biodegradable plastics owing to their susceptibilities to enzymes and microorganisms. Poly(ethylene succinate) (PES) has a comparatively high melting point (103–106 °C) [1] and some good mechanical properties, which are comparable with some of the extensively used polymers like low density PE (LDPE), PP, etc.

Among the properties of biodegradable polymeric materials, biodegradation rate is the most important for practical application. Numerous factors affect the biodegradation rates of polymers, such as chemical composition, crystalline structure, and morphology [2]. Many researchers have found that the degree of crystallinity, spherulite size and lamellar structure of the aliphatic polyesters can influence the biodegradation rate, because biodegradation first takes place at the amorphous parts of polymers [3]. Accordingly, crystallization kinetics and melting behaviors should be carefully considered, since they affect not only the crystallinity of polymers but also the final physical properties and biodegradability.

Poly(trimethylene succinate) (PTS) is a new polyester with an odd number of methylene groups in its respective diol monomer. Poly(butylene succinate) (PBS), PTS and PES are only different in their numbers of methylene groups between

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the two ether groups, namely 4, 3 and 2, respectively. It was found that PTS which had the lowest crystallinity degraded faster than PBS and PES [4]. The crystal structure [5–8] and the crystal growth kinetics [2,9] of PES have been studied. The molecular weight dependence of the crystallization rate and the primary nucleation rate of PES have also been investigated [10,11]. Only a few studies on the multiple melting behavior of PES have been published [2,9,12–14].

Tsai et al. synthesized PES, PTS and a series of their copolymers [1]. They identified that the distribution of ethylene succinate (ES) and trimethylene succinate (TS) units in these copolyesters is random. Results of wide-angle X-ray diffraction (WAXD) and heating thermograms for the measurements of melting (T_m) and glass transition (T_g) temperatures indicate that the incorporation of TS units into PES significantly inhibits the crystallization behavior of PES. The crystallinity falls from 34 to 8% as the TS content increases from 0 to 50%. Additionally, the value of T_g decreases from −9.9 to −31.5 °C as TS increases from 0 to 100%. Therefore, in this study, PES copolymer with only 5 mol% TS was synthesized and characterized. To the best of our knowledge, poly[(ethylene succinate)-*co*-(5 mol% trimethylene succinate)] (PES-*co*-5%PTS) has not been reported so far in the literature. In this study, the differential scanning calorimetric (DSC) data were analyzed over a wide range of isothermal crystallization temperature (T_c) using the Avrami equation [15,16]. The origin of the multiple melting behavior of isothermal crystallized specimens was elucidated using WAXD, DSC and temperature modulated DSC (TMDSC) by varying the T_c, the crystallization time and the heating rate. The linear growth rates of spherulites were obtained using a polarized light microscope (PLM) and the regime transition temperature was determined from the Lauritzen–Hoffman (LH) equation [17].

2. Experimental

2.1. Synthesis and characterization

Ethylene glycol (EG) (Showa, 99.5%), 1,3-propanediol (PD) (Acros, 98%) and succinic acid (SA) (Acros, 99%) were used without purification. Titanium tetraisopropoxide (TTP) (Acros, 98+%) was used as received. Other solvents for analysis were also used without further purification. The reaction mixture was charged into a 1-L stainless reactor with the molar ratios of EG:PD:SA = 0.95:0.05:1. TTP was used as a catalyst with 0.1 mol% based on the amount of diacid used. PES-*co*-5%PTS copolyester was synthesized by a two-step esterification reaction in the melt. It was purified after dissolving in chloroform and precipitating into 10-fold amount of vigorously stirred ice-cooled methanol. The precipitate was filtered, washed with methanol, and dried under reduced pressure at room temperature.

This copolyester had an intrinsic viscosity [η] of 1.01 dL/g, measured in phenol/1,1,2,2-tetrachloroethane (3/2, w/w) at 30 °C. The number and weight average molecular weights, M_n and M_w, were 8.4×10^4 and 1.37×10^5 g/mol relative to poly(methyl methacrylate), respectively. A detailed report of characterization of a series of other PES/PTS random copolymers simply referred our most recent work [1]. The T_g of an amorphous specimen was obtained with a Perkin–Elmer Pyris 1 DSC at a heating rate of 10 °C/min. The corresponding T_g was −11.6 °C (261.5 K).

All the PES-*co*-5%PTS sheets were prepared in a hot press machine. The compressed sheet had a thickness of about 0.2 mm for DSC studies or about 0.5 mm for WAXD patterns. Both purified PES-*co*-5%PTS and sheets were dried at room temperature in a vacuum oven for 12 h to remove moisture before use.

2.2. ^{13}C NMR analysis

The NMR spectrum of $CDCl_3$ solution was recorded using a Varian UNITY INOVA-500 NMR spectrometer at 295.5 K. Fig. 1 presents the ^{13}C NMR spectrum of the copolymer and the peak assignments. The two chemical shifts at 61.19–62.34 and 28.73–28.90 ppm are associated with the methylene carbons α and β to the ester oxygen in the trimethylene group [1]. The diol carbon atoms of ethylene group are at 62.35 ppm (C_2). The chemical shifts of methylene group and the carbonyl group of succinic acid are at 27.80–27.84 (C_1) and 172.89–173.05 (C_5) ppm, respectively. In a closer view of the ^{13}C NMR spectrum, the carbonyl carbons (C_5) were split into three peaks, as shown in the inset of Fig. 1. The assigned b–d peaks represent the carbonyl carbons of EST-T side, EST-E side and ESE structures, respectively (where E represents EG unit, S represents SA unit, and T denotes PD unit).

A detailed determination of compositions and the ester sequence distribution of a series of other PES/PTS random copolymers were reported in our most recent work [1]. This copolyester is characterized as having 94.4% ES units and 5.6% TS units, based on the analysis of carbonyl carbons. ES and TS units had average-number sequence length of 16.8 and 1.0, respectively. The randomness, B, is 1.06, which is within experimental error, $B = 1.0$ for a random copolyester. Therefore, the distribution of ES and TS units in this

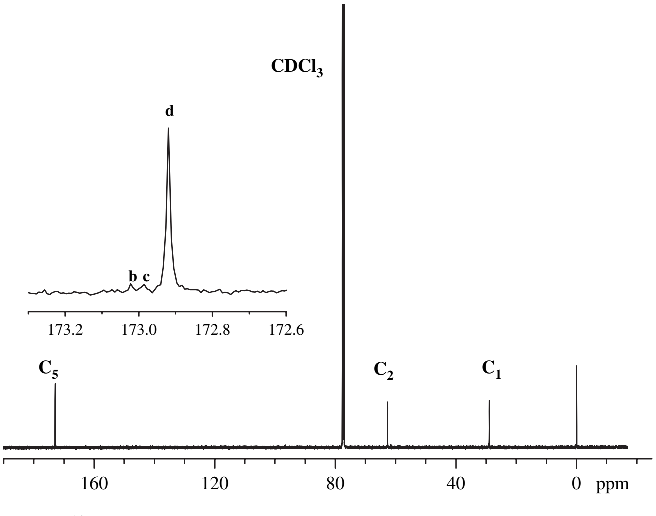

Fig. 1. ^{13}C NMR spectrum (solvent: $CDCl_3$ at 295.5 K) and its peak assignments.