



Synthesis and characterization of poly(ester ether urethane)s block copolymers based on biodegradable poly(butylene succinate) and Poly(ethylene glycol)



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ABSTRACT

A series of poly(ester ether urethane)s (PEEUs) block copolymers composed of dihydroxy-terminated poly(butylene succinate) (HO-PBS-OH) as the hydrophobic part and poly(ethylene glycol) (PEG) as the hydrophilic part were successfully synthesized and investigated with various PEG mass fraction using isophorone diisocyanate (IPDI) as a chain-extender. Nonisothermal melt-crystallization kinetics and subsequent melting behavior of PEEUs have been investigated by differential scanning calorimetry (DSC). The Avrami equation modified by Jeziorny and Mo's method were applied to describe the kinetics of the crystallization process. Meanwhile, the effects of PEG on the crystalline morphology and crystal structure of PEEUs were studied by wide-angle X-ray diffraction (WAXD), polarized optical microscope (POM). The analysis of nonisothermal crystallization kinetics showed that the crystallization rate of PBS segment within PEEUs was improved by the introduction of high PEG content. Additionally, banded spherulites were observed regardless of composition for all copolymers. Their biodegradability was investigated by the enzymatic degradation using *Pseudomonas cepacia* lipase. Experimental data showed that biodegradation rate increased with the increasing of PEG content, and a significant rate of degradation was occurred in the PEEU sample with 60 wt% PEG content.

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1. Introduction

In recent years, potential applications of biodegradable aliphatic polyesters, such as poly(butylene succinate) (PBS), polylactic acid (PLA), poly(ϵ -caprolactone) (PCL) and so forth, expand rapidly in various fields of medicine and industry [1,2]. Because of their favorable properties of biodegradability and biocompatibility, they are widely utilized in biomedical applications, such as scaffold for the tissue engineering of bone and matrix for drug controlled release system, as well as in packaging and mulching film [3–5]. Among these biodegradable polymers, PBS has attracted a great deal of interest due to its biodegradability, thermal properties, and acceptable mechanical properties [6].

However, PBS has some hurdles such as low biodegradation rate to overcome which restrict its further application in various field. Hence, the copolymerization of other component into PBS chains

would be expected to improve its biodegradability and mechanical properties. Amin Cao et al. [7] reported the syntheses of PBSC copolyesters via polycondensation of succinic acid, 1,4-butanediol and ϵ -caprolactone. They found that biodegradation rate of the PBSC copolyesters using soil composting test increased considerably compared to the pristine PBS and the more CL units incorporated, the higher the biodegradability of the copolyester was observed. Therefore, they concluded that the chain flexibility was another main factor affecting the biodegradability of the copolyester besides the specificity of the unit chemical structure and morphology. In this paper, PEG was introduced into PBS by chain extension reaction using IPDI as a chain-extender.

In the early study, diphenylmethane diisocyanate (MDI) was commonly used as a chain extender for PBS. The melt viscosity of the PBS material after the chain extension was improved, the thermal stability was enhanced, and the material had higher mechanical properties. However, the biodegradability of PBS after chain extension deteriorated compared with pure PBS material. The reason for the decrease of biodegradability was the increase of molecular weight and the introduction of benzene

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ring structure after chain extension. Compared with MDI, the aliphatic chain structure of IPDI is more suitable as a chain extender for PBS resin. IPDI was an alicyclic isocyanate containing two –NCO groups in the molecule. The two –NCO groups were attached to the aliphatic chain and the aliphatic ring respectively. The difference of activity was between 0.2/1–12/1 [8]. In the urethane reaction, the activity of the two groups usually depended on the reaction temperature, the type of catalyst and the type of hydroxyl groups of the reaction [9]. In the process of urethane reaction, the advantage of this difference in reactivity was the low viscosity of the product, the narrow molecular weight distribution, and the small amount of free IPDI monomer in the product. Industrial grade IPDI was a mixture of cis and trans isomers, and the two isomers had reaction selectivity. Generally, aliphatic diisocyanates such as IPDI had good flexibility and could impart good mechanical properties to the polyurethane material [10]. In addition, IPDI had good compatibility with co-reactants and solvents.

As a semicrystalline copolyester with non-toxic, non-antigenic and non-immunogenic, PEG exhibited excellent hydrophilicity and biocompatibility and incorporation of PEG into PBS had shown the increasing of the biodegradability. Zhou [11] reported the synthesis of PBSEG copolyesters through a two-step process of esterification and polycondensation from succinic acid, 1,4-butanediol and PEG, and the effect of content of PEG on physical properties and hydrolysis degradation behavior were thereby studied.

As a kind of biodegradable aliphatic polyester, the biodegradability property of PBS, as well as its copolyesters, has been widely studied. And a great deal of fundamental studies showed that the biodegradability of aliphatic polyesters turned out to depend on many factors such as the chain flexibility, degree of crystallinity, hydrophilic/hydrophobic balance within the main chain and so forth. V. Tserki et al. [12] prepared a series of aliphatic homopolyesters and copolyesters from 1,4 butanediol and dimethylesters of succinic and adipic acids by a two-step process of transesterification and polycondensation, the biodegradation of the polymers by soil compost and enzymatic hydrolysis have been studied, and they suggested that the key factor affecting material degradation was its crystallinity.

Polymers with elastomeric mechanical properties, adjustable biodegradability and cell compatibility are ideal for many biomedical applications [13]. In this study, we prepared a series of poly(ester ether urethane)s (PEEUs) copolymers composed of PBS and PEG by using IPDI as a chain-extender, and focused on the influence of PEG on crystal structure, mechanical and degradation properties of the copolyesters. Meanwhile, DSC was used to study the nonisothermal crystallization kinetics of the PEEUs, and the avrami equation modified by Jeziorny method were applied to describe the kinetics of the crystallization process. The degradation of the PEEUs under enzymatic hydrolysis condition was also studied.

2. Experimental

2.1. Materials

In this study, Succinic acid (SA) and 1,4-butanediol (1, 4-BD) were obtained from Sinopharm Chemical Reagent Co., Ltd (China). isophorone diisocyanate (IPDI) and PEG of Mn = 2000 g/mol were provided by Tianjin Chemical Reagent Co. Inc., China. Stannous chloride and 4-Methylbenzenesulfonic acid were purchased from North Tian-yi Chemical Reagent Factory (Tianjin, China) and Yingda Xi-gui Chemical Reagent Factory (Tianjin, China), respectively. Pseudomonas cepacia lipase was supplied by Novocata Co. Ltd, China with a specific activity of 40 U/mg.

2.2. Synthesis of dihydroxy-terminated poly(butylene succinate) (HO-PBS-OH)

HO-PBS-OH prepared in this work was synthesized by a two-step esterification and polycondensation reaction as previous reports [14]. First, SA and BD were added into a 250 ml four necked flask with the diacid and diol molar ratio of 1/1.2, and a suitable amount of stannous chloride and 4-methylbenzenesulfonic acid as co-catalysts was placed into the flask. Then the flask was equipped with a thermometer, water separator, mechanical stirrer, and nitrogen inlet pipe. The mixture was stirred and melted at 140 °C for 2 h in N₂ atmosphere to complete the esterification reaction. During the polycondensation process, a suitable amount of stannous chloride was added again into the esterification product and the temperature was gradually raised to 230 °C, and the pressure was reduced to 50 Pa for 2 h. The solid was dissolved in chloroform and then precipitated in excessive methanol. The white product was dried at 80 °C under vacuum to a constant weight (98.7% yields). The number average molecular weights of the HO-PBS-OH was 3820, polydispersity index was 2.3.

2.3. Synthesis of the PEEU copolymers

A set of PEEU copolymers was synthesized by chain extension reaction as following the calculated HO-PBS-OH and PEG weight ratio: 100/0, 80/20, 60/40 and 40/60 wt%, and they were defined as PEU, PEEU-1, PEEU-2, PEEU-3 respectively. The synthesis process was as follows: predetermined amounts of HO-PBS-OH and PEG were placed into the flask, and the mixture was melted and agitated at 160 °C under N₂ atmosphere. When the mixture was completely molten, a predetermined amount of IPDI was injected into the flask. Then the reaction mixture was stirred mechanically for 1 h. Subsequently, the resulting product was purified as described above. The reaction scheme for the synthesis of the PEEU copolymers is shown in Scheme 1.

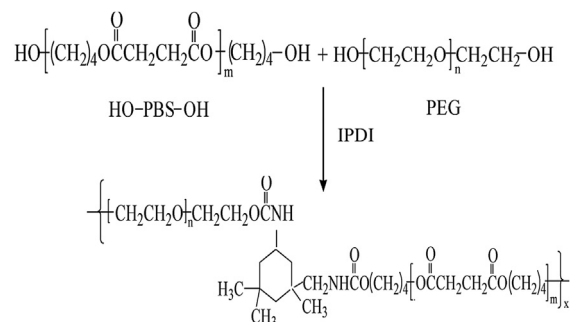
2.4. Characterizations

2.4.1. FTIR

The FTIR spectra was recorded between 400 cm⁻¹ and 4000 cm⁻¹ on a TENSOR 27 FT-IR spectrometer (Bruker spectrometer, Germany). The sample was coated on a KBr plate, and the adsorption bands of functional group were collected.

2.4.2. ¹H NMR

¹H NMR spectra of the copolymers were recorded on a Bruker 400 MHz spectrometer at room temperature. CDCl₃ was used as solvent and tetramethylsilane (TMS) as internal reference.



Scheme 1. Synthesis of PEEU copolymers from HO-PBS-OH, PEG and IPDI.

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