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Synthesis, crystallization and hydrolysis of aromatic–aliphatic copolyester: Poly(trimethylene terephthalate)-*co*-poly(L-lactic acid)

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ABSTRACT

In this study, poly(trimethylene terephthalate)-*co*-poly(L-lactic acid) (PTT-*co*-PLLA) copolyesters with different compositions were synthesized by melt polycondensation. The crystal morphologies of PTT-*co*-PLLA copolyesters were investigated with polarized light microscope (PLM). It was found that PTT-*co*-PLLA copolyesters exhibited banded spherulites with smaller band spacing at the same degree of super-cooling compared with PTT homopolymer. The PLLA segments in those copolyesters ranged from 0 to 28.4 mol% and did not form crystals during crystallization. Hydrolysis study on PTT homopolymer and PTT-*co*-PLLA copolyesters was carried out in buffer solutions. PTT-*co*-PLLA copolyesters represented pronounced hydrolytic degradation, which increased with the content of lactyl units. And it was concluded that degradation of PTT-co-PLLA was mainly attributed to the scission of PLLA segments.

1. Introduction

Prompted by environmental concern, socio-economical reasons and oil crisis, interest toward the exploitation of biodegradable polymers as a primary substitute for chemical products and biomaterials have been witnessed increasing in last decades [1]. It is known that most of the chemosynthesized biodegradable polymers are aliphatic polyesters, such as poly(lactic acid) (PLA), poly (butylene succinate) (PBS), poly(ε-caprolactone) (PCL), and poly (glycolic acid) (PGA) etc. However, the applications of these aliphatic polyesters are greatly limited because of the low thermal properties [2–4].

In order to obtain biodegradable polymer with both excellent physical and thermal properties, serials copolyesters composed of aromatic and aliphatic units. Such as poly(ethylene adipate-*co*-terephthalate) copolyesters [5,6], poly(ethylene terephthalate)-*co*-poly(ε-caprolactone) [7,8], poly(ethylene terephthalate)-*co*-poly (butylene adipate-*co*-succinate) [9], Poly(ethylene-co-diethylene terephthalate)-co- poly(L-lactic acid) [10] and poly(ethylene terephthalate)-*co*-poly(1,4-butylene succinate) copolyesters [11] were prepared. Generally, aromatic–aliphatic copolyesters with up to 40 mol% degradable aliphatic units are biodegradable [12–14].

Up to now, several commercial biodegradable aromatic–aliphatic copolyesters, such as BASF Ecoflex®, the copolyester of poly(butylene terephthalate) and poly(butylene adipate), are available. Ecoflex® is a completely biodegradable and compostable plastics [15]. It can be processed like low density polyethylene into films, bags or coatings. However, the melting point of Ecoflex® is 110–120 °C, which greatly limit its application.

To prepare a bio-based and degradable polymer with higher thermal resistance than Ecoflex®, PTT-*co*-PLLA copolyesters were synthesized in this study. It is well-known that PLLA is an excellent biodegradable polymer due to the two-fold environmental advantage of being prepared from renewable resources and being biodegradable. On the other hand, PTT, similar to PET and PBT, is a semicrystalline thermoplastic. PTT has several excellent properties, such as high crystallization rate and excellent elastic recovery [16]. Moreover, the monomer 1,3-propanediol can be obtained commercially through bio approaches. All these advantages of PLLA and PTT make it interesting to synthesize a copolyester of PTT and PLLA. It is designed to be sensitive to hydrolysis and biodegradability due to the ester bonds of PLLA segments in the PTT-*co*-PLLA chain. However, there are many difficulties in the synthesis of PTT-*co*-PLLA copolyester. For example, it is difficult to limit the thermal degradation of PLLA at the high reaction temperature.

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The aim of this study was to synthesize a high-molecular-weight poly(trimethylene terephthalate)-*co*-poly(L-lactic acid) (PTT-*co*-PLLA) copolyester and to investigate the influence of PLLA segments on the crystallization and hydrolysis behaviors. PTT-*co*-PLLA copolyesters were prepared via esterification and polycondensation from prepolymers of PTT and PLLA with particular molecular weight. In this paper, chemical structures, crystallization and hydrolysis behaviors of the resulting copolyesters were shown.

2. Experimental

2.1. Materials and methods

2.1.1. Materials

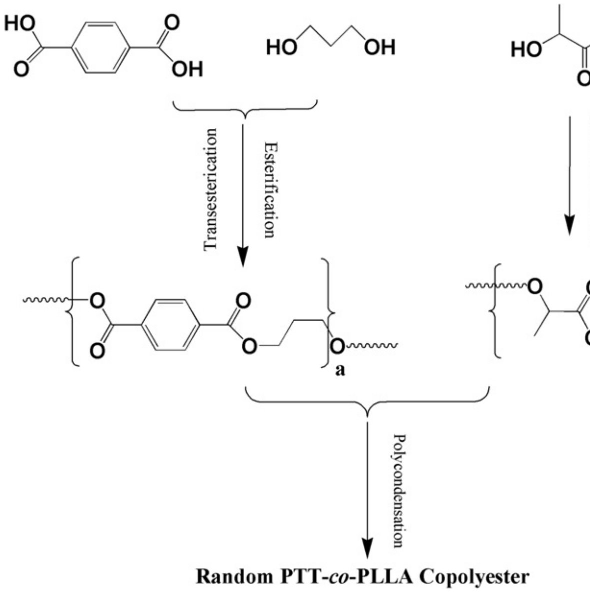
Purified terephthalatic acid (PTA) was obtained from *Yangzi Petrochemical Company Ltd*. 1,3-propanediol (PDO) was purchased from *Cell Ltd*. L-lactic acid aqueous solution was obtained from *PURAC Ltd*. All the other reagents were purchased from *Sinopharm Chemical Reagent Co*., *Ltd*.

2.1.2. Synthesis of PTT-co-PLLA copolyesters

PLLA with M_w of 5.6 kg/mol was prepared by melt polycondensation of dehydrated L-lactic acid. The reaction mixture was kept at 160–165 °C under a vacuum of 0.03 kPa in a round-bottom flask. PTT was synthesized through the two-step process: direct ester interchange of PTA and PDO monomers at 250 °C under 0.3–0.4 MPa with zinc acetate as the catalyst and melt polycondensation at 260 °C under 15 Pa with titanium butoxide as the catalyst. And then, blends of PTT oligomer with [η] of 0.15 dL/g, PLLA and composite catalysts composed of titanium dioxide, antimonic oxide, polyphospholic acid and tetrabutyl titanate, were placed in a 1 L rotating steel reactor. The reaction blends were kept at 225–230 °C and under a vacuum of 10 Pa for 3–5 h. High-molecular-weight PTT-*co*-PLLA copolyesters were obtained. The reaction route for the synthesis of the PTT-*co*-PLLA copolyester was shown as Scheme 1.

2.1.3. Purifying of obtained copolyesters

Firstly, PTT-*co*-PLLA copolyester were dissolved in the mixture of chloroform/trifluoroacetic acid (1/3 v/v) and then filtered to eliminate impurity. Secondly, the obtained filtered liquor was precipitated by petroleum ether and filtered in order to remove OLLA and PLLA. This process was repeated for three times and then the last filtered cake was collected and dried at 60 °C under vacuum for 48 h.



Scheme 1. Reaction route of PTT-*co*-PLLA copolyester.

2.2. Characterizations

2.2.1. Molecular parameters

Intrinsic viscosities of PTT-*co*-PLLA copolyesters in mixture solvents ($c = 5$ g/dL) of phenol and 1,1,2,2-tetrachloroethane (3/2 w/w) were examined using a *AV370 Ubbelohde* viscometer at 25 °C.

The chemical structures of PTT-*co*-PLLA copolyesters were characterized using a *Bruker AVIII 400* MHz nuclear magnetic resonance (NMR) spectrometer. Trifluoroacetic acid-*d* was used as the solvent and all experiments were carried out at 25 °C.

The optical rotations of PTT-*co*-PLLA copolyesters were characterized with a *SGW-1* Automatic Polarimeter. It was found that all the PTT-*co*-PLLA copolyesters have lost optical rotation.

2.2.2. Crystal structures and thermal properties

Wide angle X-ray diffractograms (WAXD) at room temperature were acquired by using a *Bruker D8* diffractometer, using Ni-filtered Cu Ka radiation at 40 kV and 30 mA. Each specimen for WAXD was made through three steps. Firstly, the sample was made into a film

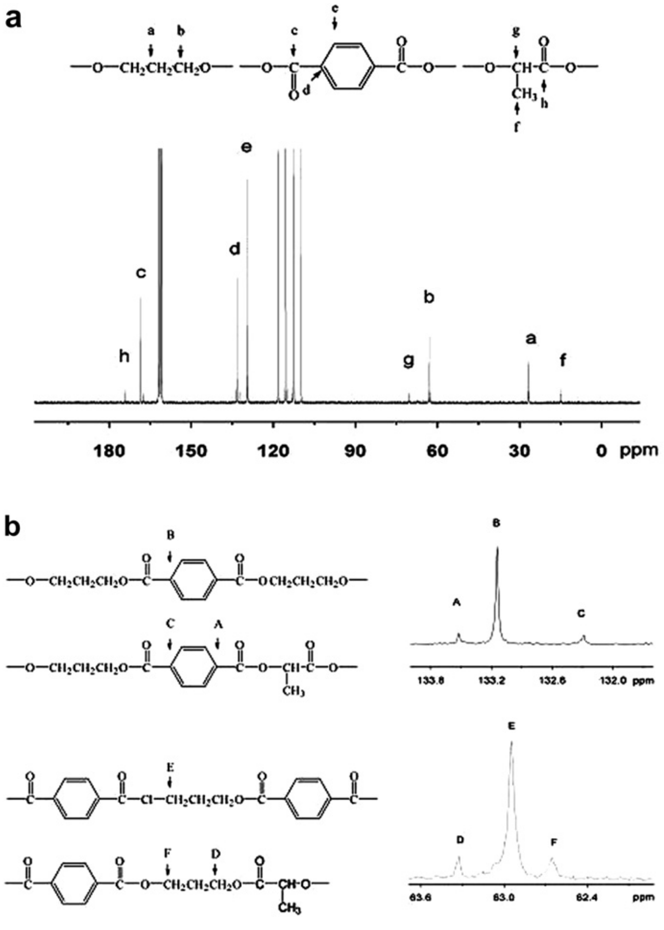


Fig. 1. a) ^{13}C NMR spectrum of PTT-*co*-PLLA2 copolyester and the peak assignments. b) enlarged spectrum in the range of quaternary aromatic carbons d and the methylene carbons b in the $-OCH_2CH_2CH_2O-$ units.