

Melt reaction and structural analysis based on poly(butylene terephthalate) and oligo(lactic acid) with addition of butanediol

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Abstract The poly(1,4-butylene terephthalate-co-DL-lactide) (BLA) copolymers were successfully prepared by the melt reaction between poly(1,4-butylene terephthalate) (PBT) and DL-oligo(lactic acid) (OLA) in the presence of 1,4-butanediol (BDO) without any catalysts. The transesterification between butylenes terephthalate (BT), 1,4-butanediol and lactide (LA) segments during the reaction was confirmed by the ^1H NMR analysis. The chemical structure of the copolymers was further investigated by the ^{13}C NMR and two-dimensional ^1H - ^{13}C HMQC (heteronuclear multiple quantum correlation) technique. The effect of reaction temperatures and the starting feed ratios on the molecular microstructures, molecular weights, solubility and thermal stability of the copolyesters was extensively studied. The sequence length of BT (N_{BT}) was found to play a vital role on the solubility and thermal behaviors of the resulting copolyesters. The copolyesters with N_{BT} in the range of 2.8 and 7.3 were soluble in chloroform. The $\text{B}_{10}\text{LA}_{40}$ copolyester with the shortest N_{BT} of 2.8 exhibited almost the lowest glass-transition temperature (T_g),

crystallization temperature (T_c), melting temperature (T_m), crystallization enthalpy (ΔH_c) and melting enthalpy (ΔH_m) as compared with the other copolyesters. The copolyester of $\text{B}_{10}\text{LA}_{40}$ was able to hydrolytically degrade and the fabricated scaffold that showed good biocompatibility towards the human bone marrow stromal cells.

Keywords Copolyesters · Poly(butylene terephthalate) · DL-oligo(lactic acid) · Biocompatibility

Introduction

In recent years, the amount of industrial and municipal waste has increased all over the world. For the non-degradable and petroleum-based commodity plastics, the typical method for disposing of these plastic wastes was landfills. Therefore, the design and development of materials capable of being degraded into safe components under specific environmental conditions have become increasingly important [1]. Up to now, many kinds of biodegradable polymers have been synthesized, including polylactide, polyglycolide, polycaprolactone, poly(α -amino acid)s, poly(orthoesters)s, polyanhydrides, etc. [2–5]. In order to obtain lower cost biodegradable polymers with both satisfactory physical properties and biodegradability, the method of incorporation of aromatic units into the main chain of degradable aliphatic polymers is involved. Blending and copolymerization techniques have been tried to obtain biodegradable polymers with improved properties [6–13].

A variety of random copolymers made by mixing of terephthalic acid/terephthalate and several aliphatic diacids with different diols have been prepared by melt polycondensation and characterized [14–16]. Furthermore, reactive

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blending of already existing homopolymers has proven to be a successful and inexpensive tool to produce new aliphatic/aromatic copolyesters with intermediate properties [17–23]. This technique has been recently used for the preparation of poly(1,4-butylene succinate)/poly(1,4-butylene terephthalate), poly(1,4-butylene adipate-co-succinate)/poly(1,4-butylene terephthalate), poly(1,4-butylene succinate)/poly(ethylene terephthalate) and poly(butylenes terephthalate/succinate/adipate) copolyesters [24–28].

In our previous work, the preparation and properties of the aliphatic/aromatic copolyesters by a melt bulk reaction between poly(butylenes terephthalate) (PBT) and DL-oligo(lactic acid) (OLA) has been reported [29, 30]. The copolyesters produced showed enhanced mechanical performance and sufficient biodegradability and could find use in the biomedical applications. In this study, in order to obtain poly(1,4-butylene terephthalate-co-DL-lactide) (BLA) with shorter averaged sequence length of butylene terephthalate (BT) segment and enough molecular weight, transesterification reactions of poly(butylenes terephthalate) (PBT) and DL-oligo(lactic acid) (OLA) were carried out with involving of 1,4-butanediol (BDO) in the absence of any additional catalyst.

Experimental

Materials and synthesis

Poly(butylene terephthalate) (PBT) (Aldrich) was powdered by cryogenic crushing and dried under vacuum overnight at 80 °C before use ($T_m = 227$ °C, $T_g = 66$ °C, $\overline{M}_\eta = 38,000$ g/mol from inherent viscosity measurements in 40/60 tetrachloroethane/phenol at 30 °C, using the molar mass-viscosity relationship $[\eta] = 1.166 \times 10^{-4} M^{0.871}$) [31]. The 1,4-butanediol (BDO) (CP grade) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). A 90% aqueous solution of racemic DL-lactic acid (Fluka) was heated stepwise to 200 °C and kept at this temperature in a vacuum for 4 h [32]. This procedure yielded α -hydroxy- ω -carboxyoligo(lactic acid) (OLA, $\overline{M}_w = 4500$ g/mol, $\overline{M}_n = 1700$ g/mol, $\overline{M}_w/\overline{M}_n = 2.60$).

Synthesis of copolyesters

The poly(1,4-butylene terephthalate-co-DL-lactide) (BLA) copolyesters were synthesized by reacting PBT, BDO and DL-oligo(lactic acid) (OLA) in the bulk and at high temperatures. PBT (8.8 g, 40 mmol), BDO (0.58 g, 8 mmol) and OLA (2.30 g, 32 mmol) were placed in a 50 mL glass reactor equipped with nitrogen inlet and outlet, and a central mechanical stirrer. A slow nitrogen stream was passed through the system. The reactor was placed in a salt

bath at 260 °C for 3 h under nitrogen, and then the reaction mixture was carried out at 260 °C for 1 h in a vacuum of 50 Pa. The polymer was allowed to cool to room temperature, dissolved in 50 mL of chloroform, isolated by precipitation in 800 mL of methanol, and collected on a filter. The white polymer was then dried at 40 °C for 24 h under vacuum.

Measurements

The ^1H - ^{13}C HMQC (heteronuclear multiple quantum correlation) experiments were performed on a Bruker ARX 400 MHz NMR spectrometer. The Gel permeation chromatography (GPC) was carried out on a Breeze Waters system consisting of a Rheodyne injector, a 1515 Isocratic pump and a Waters 2414 differential refractometer. The instrument was calibrated with monodisperse polystyrene standards. Thermogravimetric analysis (TGA) was performed under nitrogen with a Perkin-Elmer TGA 7 (heating rate 20 °C/min, sample size 8–10 mg). Differential scanning calorimetry (DSC) measurements of copolyesters were carried out on a Perkin-Elmer DSC 7 equipped with a liquid nitrogen cooling system under a nitrogen flow at a rate 40 mL/min. The surfaces of degraded samples after the hydrolytic degradation and growth of cells on the polyester scaffolds were observed with Philips 535 scanning electron microscopy (SEM) after gold vapor deposition onto the samples in an Edwards Auto 306.

Results and discussion

Synthesis of copolyesters

The aim of this work is the development of catalyst-free synthesis of high molecular weight copolyesters with biodegradable and aromatic moieties based on existing polymers. The poly(1,4-butylene terephthalate-co-DL-lactide) (BLA) copolyesters were synthesized by transesterification between PBT, BDO and OLA at 260 °C for 4 h in the bulk. During the synthesis of copolyesters, the transesterification between the reactants was almost unavoidable. Lactide and butanediol were built into the polymer chain during the reaction by transesterification, having the appropriate reactivity for incorporation and yielding a statistical product, poly(1,4-butylene terephthalate-co-DL-lactide) (BLA). Lactide units have two different functional groups and butanediol have two hydroxyl groups, so the polycondensation and the transesterification resulted in formation of butylene terephthalate (BT), and lactide (LA) units (or segments) in the copolyesters due to participation of butanediol producing same structure as butyleneoxy in PBT. The reaction took place without any additional

catalyst. Due to good solubility of oligo(lactic acid) in methanol, the copolyesters were re-precipitated from methanol. Any unreacted oligo(lactic acid) and butanediol contained in copolyesters could be extracted completely. The reaction took place without any catalyst.

“B” in the sample code is used for butanediol and “LA” is for OLA. The subscript numbers at the end of each initial denote their initial feed mole fractions (%) of either total diol or total OLA. For examples, B₁₀LA₄₀ represents a random copolyester synthesized with 10% butanediol, 40% OLA, and 50% PBT. The subscript number after a bracket in the sample code represents reaction temperature or reaction time. If no especial designation, the samples were synthesized at 260 °C for 4 h.

Structure characterization of copolyesters

In order to further confirm the correctness of the peak assignments, the two-dimensional ¹H–¹³C HMQC (heteronuclear multiple quantum correlation) technique was performed. From the ¹H–¹³C HMQC spectrum shown in Fig. 1, two cross-peaks of A and B can be discerned by the correlation of protons g at 4.270 ppm with carbon signal at 64.720 ppm and that of protons f at 1.851 ppm with a carbon signal at 25.120 ppm. On the basis of this, the signals at 64.720 and 25.120 ppm could be assigned to the carbon atoms attached to the protons g and f of the repeat units, respectively. The other cross-peaks produced by protons such as a, b, c, d and e and their corresponding attached carbons are easier to identify based on the analysis in Fig. 1. Therefore, the assignment of peaks at 4.270 (g) and 1.851 ppm (f) with their corresponding carbons at 64.720 and 25.120 ppm is correct based on the two-dimensional ¹H–¹³C HMQC technique analysis. It is concluded from the above results that the transesterification occurred between PBT and OLA in the presence of BDO.

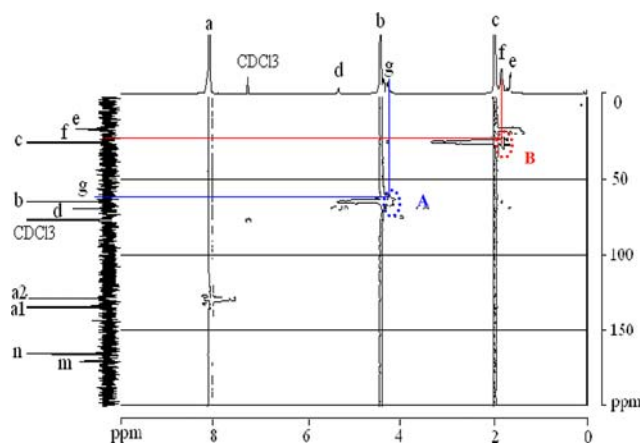


Fig. 1 ¹H–¹³C HMQC NMR spectrum of the copolyester B₂₀LA₃₀

As shown in Fig. 1, the integrals of the peaks at 5.362 (CH of LA units) and 4.436 ppm (OCH₂ of BT segments) provided the actual content of lactide (LA) and butylene terephthalate (BT) units (or segments) in the BLA copolyesters. The calculated molar ratios of BT/LA are shown in Table 1. The relative intensities of the dyad peaks for copolyesters BLA were used to calculate the number-average sequence lengths of the resulting copolyesters according to the following equation:

$$N_{BT} = (N_b/4)/(N_g/2) \quad (1)$$

where N_b and N_g represent the corresponding integral areas in ¹H NMR spectrum, respectively. The sequence lengths of the butylene terephthalate (BT) of the BLA copolyesters are listed in Table 1.

For the B₁₀LA₄₀ copolyester with PBT/BDO/OLA starting molar ratio of 50/10/40, the lowest sequence length of the BT (N_{BT}) and higher production yield were obtained when reaction temperature at 260 °C facilitated sufficient transesterification, with comparison to bulk reactions performing at 240 °C and 280 °C. The averaged sequence length of butylenes terephthalate (BT) of B₀LA₅₀ was 10.2 without involving of BDO. However, the N_{BT} 's of B₅LA₄₅ and B₁₀LA₄₀ were sharply reduced to 2.9 and 2.8 after the incorporation of 5% and 10% of BDO with maintaining 50% PBT addition, respectively. Either further increasing BDO addition while maintaining 50% PBT addition or decreasing BDO/OLA addition while maintaining molar ratio of BDO/OLA as 1/4 were against favorable to lower sequence length of the aromatic BT. The appropriate reaction times also played a vital role on lowering the sequence length of the BT in the copolyesters. The copolyester B₁₀LA₄₀ showed the shortest N_{BT} of 2.8 when reaction time of 4 h was applied. The shortening and prolonging reaction time resulted in longer sequence length of BT and lower product yield.

The copolyesters with lower sequence length of BT than three have excellent solubility in chloroform while the pristine PBT is only soluble in chloroform/phenol (4/6 v/v). Nevertheless, the copolyesters with sequence length of BT between three and eight are able to swelling in chloroform. Longer averaged sequence length of BT than 10 resulted in the copolyester insoluble in chloroform. It is believed that the solubility of the polymers was correlated with the sequence length of BT.

Due to the solubility of copolymers with short N_{BT} in chloroform, a conventional GPC with chloroform as eluent was used to measure the molecular weight of the copolyesters. The copolyester B₁₀LA₄₀ obtained at 260 °C for 4 h showed the number-average and weight-average molecular weight of 4.46×10^4 and 8.78×10^4 g/mol, respectively. The copolyesters obtained at 240 and 280 °C exhibited lower molecular weights due to the incomplete ester

Table 1 Composition and yields of the resulting copolyesters

Sample	Temp (°C)	Reaction time (h)	Feed molar ratio PBT/BDO/OLA	Composition ^a BT/LA	Yield (%)	N _{BT} ^b
(B ₁₀ LA ₄₀) ₂₄₀	240	4	50/10/40	74.1/25.9	78.4	3.0
B ₁₀ LA ₄₀	260	4	50/10/40	76.0/24.0	85.7	2.8
(B ₁₀ LA ₄₀) ₂₈₀	280	4	50/10/40	79.9/20.1	74.2	3.1
B ₀ LA ₅₀	260	4	50/0/50	90.4/9.6	72.9	10.2
B ₅ LA ₄₅	260	4	50/5/45	78.3/21.7	75.6	2.9
B ₁₀ LA ₄₀	260	4	50/10/40	76.0/24.0	85.7	2.8
B ₂₀ LA ₃₀	260	4	50/20/30	78.6/21.4	84.5	2.9
B ₃₀ LA ₂₀	260	4	50/30/20	83.7/16.3	83.2	5.8
B ₄₀ LA ₁₀	260	4	50/40/10	93.9/6.1	69.0	11.8
B ₁₀ LA ₄₀	260	4	50/10/40	76.0/24.0	85.7	2.8
B ₈ LA ₃₂	260	4	60/8/32	88.6/11.5	94.4	7.2
B ₆ LA ₂₄	260	4	70/6/24	88.8/11.2	89.6	7.3
(B ₁₀ LA ₄₀) _{2 h}	260	2	50/10/40	81.1/18.9	78.9	3.0
B ₁₀ LA ₄₀	260	4	50/10/40	76.0/24.0	85.7	2.8
(B ₁₀ LA ₄₀) _{6 h}	260	6	50/10/40	83.8/16.2	75.5	4.1

^a The molar ratio of butylene terephthalate (BT) and lactide (LA) segments (or units) in resulting copolyesters

^b The average sequence length of butylene terephthalate (BT) calculated from dyad peaks in NMR spectra

exchange reaction at relatively lower temperature of 240 °C and the decomposition at higher temperature of 280 °C. Both further increasing the reaction time to 6 h and decreasing the reaction time to 2 h showed disadvantageous influences on the molecular weights of the copolyesters.

Thermal behavior of copolyesters

The thermal properties were characterized by means of DSC and TG for the BLA copolyesters obtained from different PBT/BDO/OLA starting ratio and from different reaction temperatures. The copolyester prepared at reaction temperature of 260 °C showed higher decomposition temperature as 377.2 °C due to sufficient transesterification occurred. In the DSC cooling and heating curves of the copolyesters, the corresponding transition temperature values are listed in Table 2. Only one crystallization and melting peak were observed for the copolyesters. With comparison to those of the copolyesters obtained at 240 and 280 °C, the crystallization and melting peaks of the copolyester B₁₀LA₄₀ prepared at 260 °C were less sharp and smaller due to sufficient transesterification resulting in changes of crystallization and melting behaviors. Furthermore, the copolyester obtained at 260 °C showed the lowest melting temperature (T_m), crystallization temperature (T_c), melting enthalpy (ΔH_m) and crystallization enthalpy (ΔH_c) due to lower sequence length of segment from the substantial transesterification between PBT and OLA in the presence of BDO. It is believed that the transesterification between PBT and OLA in the presence

of BDO makes the BLA copolyester more random, thus restricting the crystallization of the copolyesters. The results suggested that the transesterification occurring at 260 °C could lower the sequence length of BT, as in accordance with the results of calculated sequence lengths of copolyesters. For the copolyester with the shorter sequence length of BT, the molecular chains are more difficult to crystallize during the cooling process, thus leading to the formation of less perfect crystals which melt at relatively lower temperatures.

All the copolyesters were less thermally stable but stable at around 360 °C as compared with the pristine PBT due to the incorporation of LA units. For the DSC cooling and heating curves for BLA copolyesters with different starting molar ratios and a constant 50% of PBT addition at 260 °C for 4 h, it is observed that all the copolymers exhibited one glass transition temperature. The B₁₀LA₄₀ copolyester showed the lowest glass transition temperature (T_g) as compared with the copolyesters with other initial mole ratio while maintaining a constant 50% PBT addition. The change of the T_m , T_c , ΔH_m and ΔH_c of the copolyesters with different BDO/OLA feed ratio were similar to that of T_g , and the B₁₀LA₄₀ copolyester exhibited the lowest values. The results are in accordance with the sequence lengths of BT as calculated from the NMR analysis. The shorter the sequence length of BT, the lower value of the T_g , T_m , T_c , ΔH_m and ΔH_c due to the transesterification between PBT and OLA in the presence of BDO forming more random molecular microstructures of the copolyesters. During the cooling process, the crystallization of the copolyesters was greatly restricted due to random copolymerization, leading

Table 2 Thermal properties of the resulting copolyesters

Sample	N _{BT}	T _g (°C)	T _{m1} (°C)	T _{m2} (°C)	ΔH _m (J/g)	T _c (°C)	ΔH _c (J/g)	T _d (°C)
(B ₁₀ LA ₄₀) ₂₄₀	3.0	31.8	–	175.3	35.6	145.2	33.2	363.8
B ₁₀ LA ₄₀	2.8	33.7	–	167.9	35.0	118.7	30.4	377.2
(B ₁₀ LA ₄₀) ₂₈₀	3.1	30.9	–	175.3	37.3	153.0	37.8	374.4
B ₀ LA ₅₀	10.2	42.9	205.1	216.1	46.2	188.2	47.7	364.3
B ₅ LA ₄₅	2.9	36.4	–	202.8	43.2	175.0	44.8	374.4
B ₁₀ LA ₄₀	2.8	33.7	–	167.9	35.0	118.7	30.4	377.2
B ₂₀ LA ₃₀	2.9	34.2	–	182.8	38.2	147.3	38.1	379.3
B ₃₀ LA ₂₀	5.8	35.0	–	197.7	43.0	162.4	46.6	379.4
B ₄₀ LA ₁₀	11.8	38.4	202.6	213.2	45.8	182.1	54.9	371.7

Note: Glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), crystallization enthalpy (ΔH_c) and melting enthalpy (ΔH_m) were registered by DSC at a cooling rate of 20 °C/min or at a second heating rate of 10 °C/min. T_d (–1.5 wt%) was measured by TG at a heating rate of 20 °C/min

to the crystallization at much lower temperatures. In the subsequent melting process, the copolyesters with shorter N_{BT} exhibited lower and broader melting peaks due to the formation of less perfect crystals during the crystallization. Longer sequence length of BT and LA resulted in double melting peaks during heating run. Therefore, the sequence length of BT (N_{BT}) is believed to play a vital role on the crystallization and melting behaviors of the copolyesters.

Hydrolytic biodegradability of copolyesters

For preliminary test of hydrolytic degradability, films of the copolyesters with thickness of 300 μm and weight of about 1.5 g were placed in 20 mL of a phosphate buffer solution at 37 °C. The samples were removed at predetermined time, rinsed with distilled water, dried, and weighed. Before continuing the experiment, the buffer solution was renewed. Surface morphology changes were investigated by scanning electron microscopy (SEM). Figure 2 shows the SEM images of the B₁₀LA₄₀ copolyester before and after hydrolytic degradation for 30 days. It is observed that the surface of the films was smooth without holes before the degradation. After degradation for 30 days, the dark areas and holes on the surfaces of the samples representing

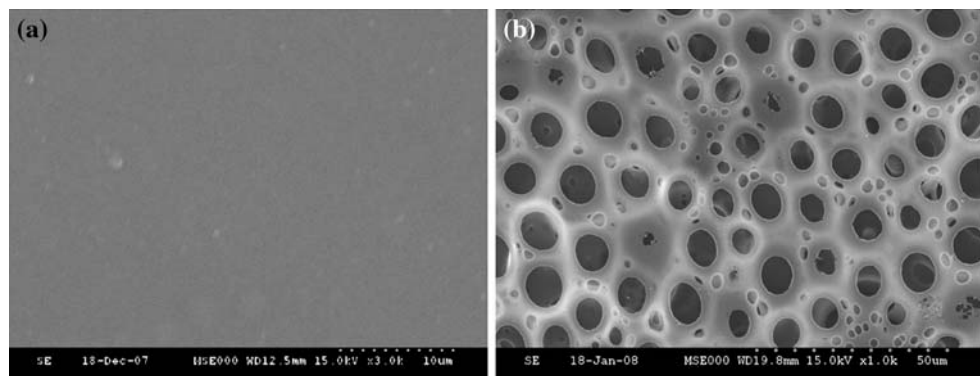
biodegraded parts were observed. The film became cracked or porous after 30 days due to the degradation of the lactide segments in random copolyesters.

Cytotoxicity and cell growth

The scaffolds of B₁₀LA₄₀ copolyester were fabricated using an established solvent-casting, particulate-leaching technique with NaCl as the porogen. The SEM images of the morphology of scaffolds show the interconnected pore structure (Fig. 3). The scaffolds resembled the macroscopic contours of the porogen assembly and had a pore size of 200–400 μm with good interconnectivity between pores. A large number of smaller pores of size 10–30 μm were also found in the skeletons, which might be produced by the bubbles formed during the evaporation of the solvent.

Bone marrow mesenchymal stem cells (MSCs) representing an ideal stem cell source and candidates for use in tissue repair and clinical applications were used in the study. Bone marrow mesenchymal stem cells (MSCs) were seeded on B₁₀LA₄₀ scaffolds. Both scanning electron microscope and immunofluorescence microscopy showed that cells grew well on scaffolds, and the number of cells increased gradually. The MSCs distributions within the pores of the

Fig. 2 SEM images of the surface of the B₁₀LA₄₀ copolyester film before and after hydrolytic degradation for 30 days



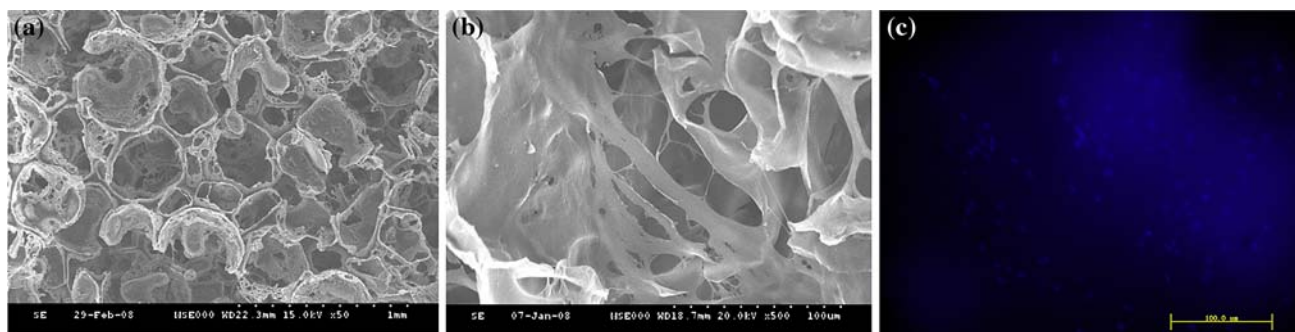


Fig. 3 SEM images of (a) the surface of B₁₀LA₄₀ copolyester scaffolds and (b) the MSCs seeded on the B₁₀LA₄₀ copolyester scaffold and cultured for 5 days, and (c) its immunofluorescence microscope image

scaffolds were shown in Fig. 3. It is observed that the bright dots distributed regularly on the background, indicating that the cells attached and grew well within the scaffolds. The porous structure of the scaffold provides more space for cell adsorption and makes the penetrating of the cells into the inside of the scaffold easier. In addition, high porosity is supposed to benefit the nutrient transformation and proliferation of the cells. Although mild acidic hydroxyl acids or oligomers were produced accompanying polymer degradation *in vitro* by analysis of degradation products, these influences might not be serious as they can diffuse from the inner of the scaffold to the outside through the pores. The result suggests that the porous scaffolds possessing a good biocompatibility are feasible for cell transportation. Cell morphology and cell-ECM interaction play a vital role in the strategy of tissue engineering. The attachment behavior of MSCs cultured on the scaffold was evaluated by SEM. Cells of polygonal, ellipsoidal and other shapes with several short pseudopods were observed on the surface of lumen within the scaffolds, suggesting that the cells are able to survive within the scaffolds. No evidence of toxicity or cell reactions to the scaffold was observed as there were no rounded cells, no inclusions or vacuoles in the cytoplasm and the nuclei contained many well formed and defined nucleoli by preliminary investigation. The cytoplasm also showed evidence of high synthetic activity showing rough endoplasmic reticulum. The preliminary investigation shows a strong cell attachment to the copolyester scaffold. It is believed that the copolymers are biocompatible with the cells and show no serious toxicity to the cells.

Conclusions

In this work, the biodegradable aliphatic/aromatic poly(1,4-butylene terephthalate-co-DL-lactide) (BLA) copolyesters were successfully synthesized by transesterification reactions of poly(butylenes terephthalate) (PBT) and DL-oligo(lactic acid) (OLA) were carried out with involving of

1,4-butanediol (BDO) in the absence of any additional catalyst in order to have shorter averaged sequence length of butylene terephthalate (BT) segment and enough molecular weight. The new peaks appeared in the ¹H NMR spectrum were assigned to the OCH₂ and CH₂ protons of the butylenedioxy group linking to a lactide by the further analysis of the two-dimensional ¹H–¹³C HMQC technique. The incorporation of the BDO facilitated the transesterification between PBT and OLA, thus leading to the formation of shorter sequence length of BT. The solubility and thermal behaviors of the copolyesters were determined by the sequence length of BT. The copolyesters with a relatively short N_{BT} ranging from 2.8 to 7.3 exhibit good solubility in chloroform. The number-average molecular weights of the BLA copolyesters are determined to be in range of 4.46×10^4 and 9.49×10^4 g/mol. The copolyester with a PBT/BDO/OLA starting molar ratio of 50/10/40 and reacted at 260 °C for 4 h exhibited the lowest values of T_c, T_m, ΔH_c, ΔH_m as compared with the copolyesters obtained at different reaction temperatures or with different starting molar ratios of BDO/OLA and a constant 50% of PBT addition, due to sufficient transesterification resulting in lowering sequence length of BT consequently changes of crystallization and melting behaviors. The B₁₀LA₄₀ copolyester showed good hydrolytic degradation behavior and the scaffold made from B₁₀LA₄₀ exhibited good biocompatibility.

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References

1. Nair LS, Laurencin CT. Biodegradable polymers as biomaterials. *Prog Polym Sci.* 2007;32:762–98.
2. Middleton JC, Tipton AJ. Synthetic biodegradable polymers as orthopedic devices. *Biomaterials* 2000;21(23):2335–46.

3. Gunatillake P, Mayadunne R, Adhikari R. Recent developments in biodegradable synthetic polymers. *Biotechnol Annu Rev*. 2006;12:301–47.
4. Heller J, Barr J, Ng SY, Abdelauoi KS, Gurny R. Poly(ortho esters): synthesis, characterization, properties and uses. *Adv Drug Deliv Rev*. 2002;54:1015–39.
5. Anastasiou TJ, Uhrich KE. Novel polyanhydrides with enhanced thermal and solubility properties. *Macromolecules* 2000;33:6217–21.
6. Fukuzaki H, Yoshida M, Asano M, Kumakura M, Imasaka K, Nagai T, et al. Synthesis of biodegradable copoly(L-lactic acid/aromatic hydroxy acids) with relatively low molecular weight. *Eur Polym J*. 1990;26:1273–77.
7. Pannu RK, Tanodekaew S, Li W, Collett JH, Attwood D, Booth C. A DSC study of the miscibility of poly(ethylene oxide)-block-poly(DL-lactide) copolymers with poly(DL-lactide). *Biomaterials* 1999;20:1381–7.
8. Bechtold K, Hillmyer MA, Tolman WB. Perfectly alternating copolymer of lactic acid and ethylene oxide as a plasticizing agent for polylactide. *Macromolecules* 2001;34:8641–8.
9. Ki HC, Park OO. Synthesis, characterization and biodegradability of the biodegradable aliphatic–aromatic random copolyesters. *Polymer* 2001;42:1849–61.
10. Nagata M, Goto H, Sakai W, Tsutsumi N. Synthesis and enzymatic degradation of poly(tetramethylene succinate) copolymers with terephthalic acid. *Polymer* 2000;41:4373–6.
11. Kim WS, Lim JC, Kim DJ, Soo KH. Synthesis and characteristics of biodegradable copolyesters from the transesterification of poly(butylene adipate-co-succinate) and poly(ethylene terephthalate). *J Appl Polym Sci*. 2004;92:3266–74.
12. Jin HJ, Lee BY, Kim MN, Yoon JS. Properties and biodegradation of poly(ethylene adipate) and poly(butylene succinate) containing styrene glycol units. *Eur Polym J*. 2000;36:2693–8.
13. Maeda Y, Maeda T, Yamaguchi K, Kubota S, Nakayama A, Kawasaki N, et al. Synthesis and characterization of novel biodegradable copolyesters by transreaction of poly(ethylene terephthalate) with copoly(succinic anhydride/ethylene oxide). *J Polym Sci A Polym Chem*. 2000;38:4478–89.
14. Chun BC, Cha SH, Chung YC, Cho JW. Enhanced dynamic mechanical and shape-memory properties of a poly(ethylene terephthalate)-poly(ethylene glycol) copolymer crosslinked by maleic anhydride. *J Appl Polym Sci*. 2001;83:27–37.
15. Pisula W, Pigłowski J, Kummerlöwe C. Preparation and characterization of copolyesters of poly(tetramethylene succinate) and poly(butylene terephthalate). *Polimery* 2006;51:341–50.
16. Li F, Xu X, Hao Q, Li Q, Yu J, Cao A. Effects of comonomer sequential structure on thermal and crystallization behaviors of biodegradable poly(butylene succinate-co-butylene terephthalate)s. *J Polym Sci B Polym Phys*. 2006;44:1635–44.
17. Deng LM, Wang YZ, Yang KK, Wang XL, Zhou Q, Ding SD. A new biodegradable copolyester poly(butylenes succinate-co-ethylene terephthalate). *Acta Mater*. 2004;52:5871–8.
18. Salhi S, Tessier M, Blais JC, Gharbi RE, Fradet A. Synthesis of aliphatic–aromatic copolyesters by a high temperature bulk reaction between poly(ethylene terephthalate) and cyclodi(ethylene succinate). *Macromol Chem Phys*. 2004;205:2391–7.
19. Wang L, Xie Z, Bi X, Wang X, Zhang A, Chen Z, et al. Preparation and characterization of aliphatic/aromatic copolyesters based on 1,4-cyclohexanedicarboxylic acid. *Polym Degrad Stab*. 2006;91:2220–8.
20. Kim YJ, Park OO. Miscibilities and rheological properties of poly(butylene succinate)-poly(butylene terephthalate) blends. *J Appl Polym Sci*. 1999;72:945–51.
21. Kang HJ, Park SS. Characterization and biodegradability of poly(butylene adipate-co-succinate)/poly(butylene terephthalate) copolyester. *J Appl Polym Sci*. 1999;72:593–608.
22. Park SS, Kang HJ. Sequence distribution and crystallization block copolyesters of poly(butylene glutarate-co-adipate-succinate) ternary random copolyester and poly(butylene terephthalate). *Polym J*. 1999;31:238–45.
23. Witt U, Einig T, Yamamoto M, Kleeberg I, Deckwer WD, Müller RJ. Biodegradation of aliphatic–aromatic copolyesters: evaluation of the final biodegradability and ecotoxicological impact of degradation intermediates. *Chemosphere* 2001;44:289–99.
24. Kint DPR, Alla A, Deloret E, Campos JL, Muñoz-Guerra S. Synthesis, characterization and properties of poly(ethylene terephthalate) /poly(1,4-butylene succinate) block copolymer. *Polymer*. 2003;44:1321–1330.
25. Shi XQ, Aimi K, Ito H, Ando S, Kikutani T. Characterization on mixed-crystal structure of poly(butylene terephthalate/succinate/adipate) biodegradable copolymer fibers. *Polymer* 2005;46:751–60.
26. Shi XQ, Ito H, Kikutani T. Characterization on mixed-crystal structure and properties of poly(butylene adipate-co-terephthalate) biodegradable fibers. *Polymer* 2005;46:11442–50.
27. Acar I, Kaşgöz A, Özgümüş S, Orbay M. Modification of waste poly(ethylene terephthalate)(PET) by using poly(L-lactic acid) (PLA) and hydrolytic stability. *Polym Plast Technol Eng*. 2006; 45:351–9.
28. Acar I, Pozan GS, Özgümüş S. Thermal oxidative degradation kinetics and thermal properties of poly(ethylene terephthalate) modified with poly(lactic acid). *J Appl Polym Sci*. 2008;109: 2747–55.
29. Zhu XJ, Chen YW, Su JY, He XH, Tan LC, Wang Y. Synthesis of aliphatic-aromatic copolyesters by a melting bulk reaction between poly(butylene terephthalate) and DL-Oligo(lactic acid). *High Perform Polym*. 2008;20:166–84.
30. Chen YW, Zhu XJ, Tan LC, Su JY. Melting bulk reaction between poly(butylene terephthalate) and poly(ethylene glycol)/DL-oligo(lactic acid). *J Appl Polym Sci*. 2008;108:2171–9.
31. Bormann WFH. Molecular weight-viscosity relationships for poly(1,4-butylene terephthalate). *J Appl Polym Sci*. 1978;22: 2119–26.
32. Asano M, Yoshida M, Kaetsu I. Biodegradability of a hot-pressed poly(lactic acid) formulation with controlled release of LH-RH agonist and its pharmacological influence on rat prostate. *Macromol Chem Rapid Commun*. 1985;6:509–13.