

Synthesis and Characterization of Aliphatic-Aromatic Copolyesters PET-PLA From PET Waste and Lactide

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Abstract

Copolyesters containing aliphatic units in the main chain were obtained by reacting Bis(2-hydroxy ethyl terephthalate) (BHET) with Lactide at a high temperature in bulk in presence of tin (II)octoate as the catalyst. Various copolyesters were synthesized by using BHET/Lactide mass ratio ranging from 70/30 to 40/60. Thermal properties were studied by DSC and TGA, and structural characterization was carried out by ¹H NMR spectroscopy. These techniques confirm the insertion of lactide units in PET chains. All copolyesters exhibit some block copolymer character.

Keywords: Copolymerization, Melt polycondensation, Bis(2-hydroxy ethyl terephthalate), Lactide, Random microstructure.

1. Introduction

Poly(ethylene terephthalate) (PET) is a thermoplastic polymer, which is used as fibres, sheets and soft drink bottles. (1)

PET is strong and durable, chemically and thermally stable, has low gas permeability and is easily processed and handled. (2, 3) This combination of properties makes PET a desirable material for a wide range of applications and a significant component of worldwide plastic consumption.

As a result of the diversity of this applications in a high volume of consumer products, large amount of PET waste is also generated, which includes polymer manufacturing waste as well as the products after the end of their useful life. With the increasing pressure of keeping the environment clean, recycling the PET waste in an ecofriendly manner is the only solution.

Post-consumer PET can be recycled into new items or into monomers or oligomers which are generally hydroxy-terminated and can be used for the synthesis of derived polyesters of PET such as PET - poly(lactide), PET -poly(glycolide), or PET - poly(ϵ -caprolactone).(3)

Chemical recycling of PET by glycolysis has been the focus of many research studies.(4-7)

In the recent years, the synthesis of biodegradable copolyesters of PET has received a growing interest.

A number of aliphatic-aromatic copolyesters have thus been produced e.g. poly(butylene succinate)/poly(butylene terephthalate) (8-11), poly[(butylene adipate)-co-(butylene succinate)]/poly(butylene terephthalate) (12), poly(butylene succinate)/poly(ethylene terephthalate) (13), poly(ethylene terephthalate)/poly(ethylene succinate) (14), poly(ethylene adipate)/poly(ethylene terephthalate) (15), poly(ethylene terephthalate)/poly(ϵ -caprolactone)(4,16-18), poly(ethylene terephthalate)/polylactide (19-21) and poly(ethylene terephthalate)/Polyglycolide . (22)

Some methods have been reported for the synthesis of PET-PLA copolymers such as (i) the melt transesterification reaction between bis-hydroxyethyl terephthalate and PLA oligomers (19) and (ii) the reaction between DMT,EG and lactic acid (20) or bis-hydroxyethyl terephthalate with lactic acid. (21)

The reaction of commercial BHET with Lactide has been much less investigated. However, this reaction *presents two major advantages*: (i) no release of by-products, (ii) obtaining of copolyesters with high molecular weight.(23)

In this paper, we describe the synthesis of novel biodegradable copolyester PET- PLA prepared by melt polycondensation from bis-2-hydroxyethyl terephthalate (BHET) and Lactide. Their structure, microstructure and degradation were investigated.

2. Experimental Part

a. Materials

Lactide (99%) was obtained from Sigma Aldrich, Stannous Octoate((Oct)₂Sn), Ethane-1,2-diol (EG-99,8%) and cobalt(II) acetate tetrahydrate(+98%) were purchased from Sigma-Aldrich (Germany) and used without further purification.

b. Synthesis

Synthesis of bis(2-hydroxyethyl terephthalate) (BHET) by glycolysis of poly(ethylene terephthalate). (4)

Bottles of mineral water were washed, cut into slices and finely ground. In a reactor equipped with a magnetic stirring, 80 g of PET flakes (0.42 mol of ethylene terephthalate units), 160 g (2.57mol) of EG and 0.249 g (0.001 mol) of cobalt acetate tetrahydrate as catalyst were charged at T = 190 ° C. After 3 hours of reaction, 400 ml of boiling water was added to the reactor and the mixture was stirred vigorously.

The obtained product was filtered to separate the oligomers from PET of high mass. The filtrate was placed at 4°C for 48 h. The white crystalline flakes of BHET were filtered and dried. A yield of 90% BHET with high purity was attained.

Synthesis of BHET-Lactide copolyesters by ring-opening polymerization.

BHET (0.0118mol,3.00g), Lactide (0.0208 mol,3.00g) and 0,1 % (mass) Stannous Octoate((Oct)₂Sn) were placed in a 50-mL glass reactor equipped with a mechanical stirrer and a nitrogen inlet. The reactor was heated gradually from 160 to 180°C under nitrogen (3 h). After cooling to 160°C, vacuum (0.01mbar) was applied and temperature was raised again gradually to 180°C for 1 h. The reaction was continued for 4 h to carry out the reaction of polytransesterification. All copolymers were characterized without any purification.

c. Measurements

¹H NMR spectra were recorded on a Bruker DRX 400 spectrometer. BHET/Lactide copolyesters were dissolved in CDCl₃ solvent. Chemical shifts were referenced to residual CHCl₃ at 7.26 ppm. The infrared spectrum ...

Molecular weight (M_n) and molar mass dispersity (Đ_n) of all copolyesters were determined using size exclusion chromatography (SEC) analyses performed on a Shimadzu LC-20AD liquid chromatography equipped with two Varian PL gel 5 μm MIXED-C columns (column, injection and refractometer temperature: 30°C; injection volume: 100 μL) and a refractive index detector (Shimadzu RID-10A). THF was used as the eluent at a flow rate of 1.0 mL/min. The molecular characteristics were determined relative to linear polystyrene calibration standards. All polymers were dissolved in THF (10 mg mL⁻¹).

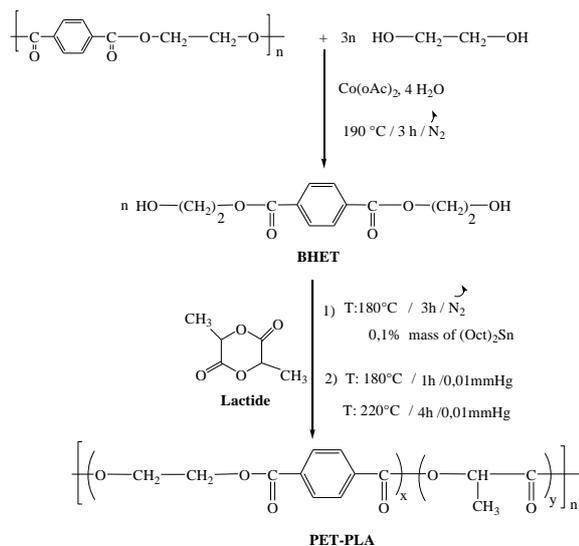
Differential Scanning Calorimetry (DSC) was carried out on a DSC Q2000-Modulated TA Instruments apparatus equipped with a liquid nitrogen cooling accessory, at cooling and heating rates of 20 °C. min⁻¹. Non hermetic aluminum capsules containing about 10 mg of polymer were subjected to two successive temperature ramps under nitrogen from -80°C to 360°C. Melting temperatures (T_m) were taken at the minima of the melting endotherms and glass transition temperatures (T_g) at the inflection point.

Thermogravimetric Analysis (TGA) was carried out on a TA Instruments Q500 thermogravimetric analyzer system at a heating rate of 10°C.min⁻¹ under a nitrogen atmosphere.

The inherent viscosity [η_{inh}] of the copolyesters samples in chloroform was measured at 25 °C in a constant-temperature bath using a UBBELOHDE viscometer. From the time flow of solvent and solution, the inherent viscosity [η_{inh}] was calculated.

3. Results and discussion

The reaction between BHET and Lactide was carried out at 160°C and 220°C for 8h in the bulk, in the presence of Stannous Octoate((Oct)₂Sn) as a catalyst (0,1% mass) (scheme1). A possible reaction mechanism could involve the homopolymerization of lactide and the formation of copolymer by PET-poly lactide ester interchange.



Scheme 1. synthesis of BHET-Lactide copolyesters.

The infrared spectrum of BHET/Lactide copolymer is shown in Fig. 1. It can be clearly seen that the spectrum contains aliphatic CH at 2961 cm^{-1} , aromatic CH at 1452 and 1409 cm^{-1} , C-O single bond and ester carbonyl at 1244 cm^{-1} and at 1714 cm^{-1} respectively.

Depending on composition and reaction time, these copolyesters may be random or may exhibit some block copolymer character. The structure and microstructure of these copolyesters were, therefore, investigated by ^1H NMR spectroscopy.

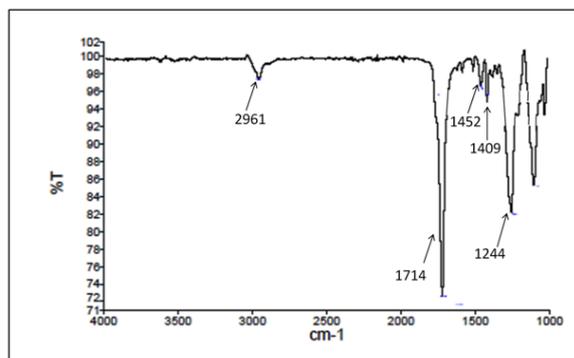
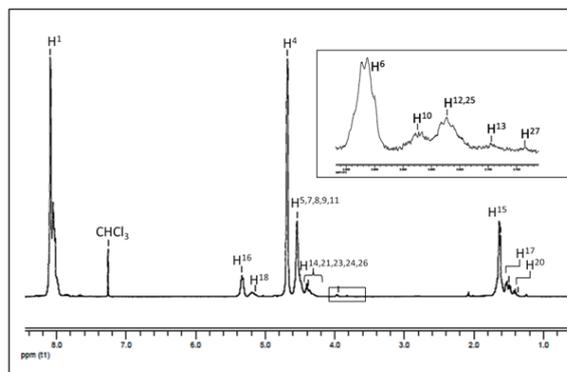


Figure 1. FTIR spectrum of BHET/lactide copolymer (50/50).

^1H NMR study of BHET-Lactide copolyesters

In addition to PET signals, the ^1H NMR spectra of copolyesters obtained using various initial (BHET/Lactide) ratios displayed a series of peaks in the 4.2–4.8 ppm region, which can be assigned to the

species depicted in table 1. As an example, the ^1H NMR spectrum of the 50/50 PET/PLA copolyester was given in Fig. 2.

Figure 2. ^1H NMR spectrum of copolyester BHET-Lactide (50/50) (in CDCl_3).

TET (H^1 , 4.67 ppm); TEL+LET ($\text{H}^{7,8}$, 4.54 ppm) and LEL (H^{23} , 4.38 ppm) triads are easily identified in the spectrum (T=Terephthalate, L=Lactide, E=1,2-ethylene). (Table 1)

The existence of TEL triads, is evidence of Lactide insertion in PET chains.

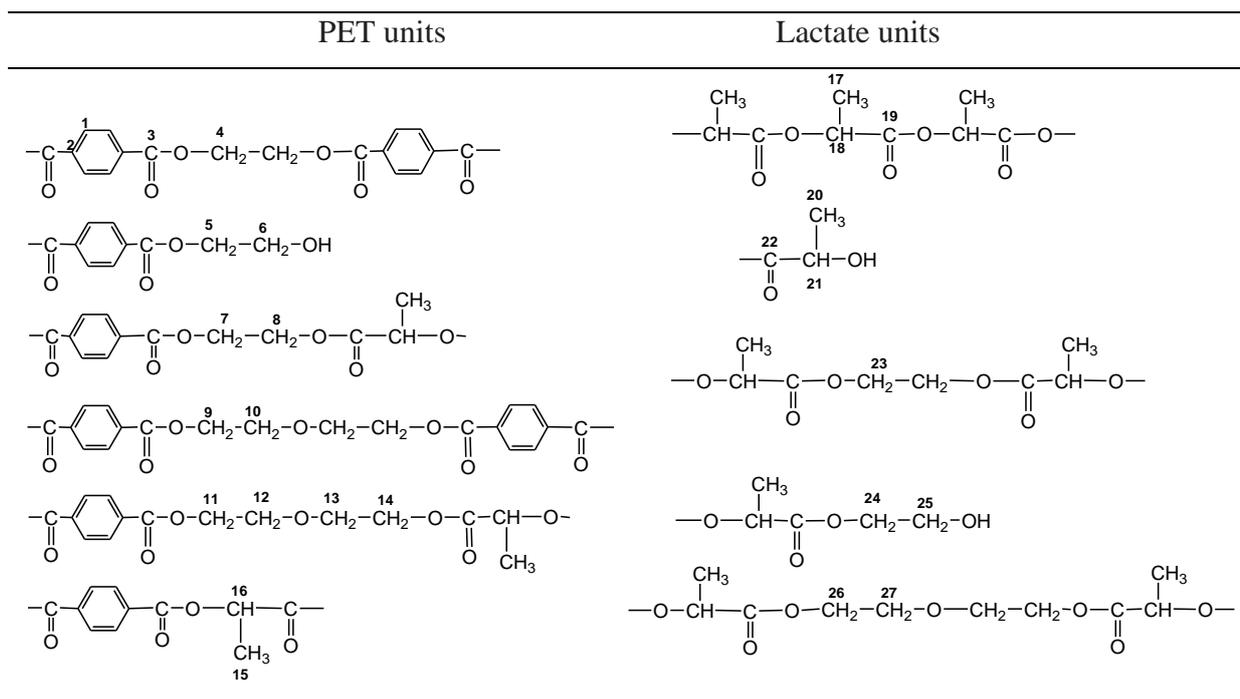
The number-fractions F_{E} (TET), F_{E} (TEL+LET) and F_{E} (LEL) of TET, TEL and LEL E-centered triads in PET-PEL copolyesters were determined by integrating the corresponding NMR peaks. F_{E} (TET), F_{E} (TEL+LET) are proportional to $I_{\text{T}}/4$ and $(I_{\text{T}}+I_{\text{L}})/4$ respectively, where I is the integration of the H_n resonance

The actual terephthalate (T)/lactate (L) mol ratio was easily determined from the total integrations of aromatic protons (H^1 at 8.1 ppm) and lactate methyl resonances ($\text{H}^{15,17,20}$ at 1.3–1.8 ppm). Due to sublimation of lactide, the T/L mol ratio final in copolyesters is significantly lower than the starting one, $(\text{T/L})_0$ (Table 2).

The new signal at 1.63 ppm (H^{15}) corresponds to T-L diads. The signal at 5.32 (H^{16}) and 5.19 ppm (H^{18}) correspond to L-T and L-L diads, respectively.

The peak at 4.67 ppm is assigned to T-E-T triads (H^5). A number of signals are superimposed at ca. 4.54 ppm: $\text{H}^{7,8}$ of T-E-L triads and methylenes in β -position to OH endgroups (H^9) and to ether oxygens (H^{11}). In the same way, the signal of L-E-L triads at 4.38 ppm (H^{23}) overlaps with a series of peaks corresponding to groups linked to lactate units ($\text{H}^{12,25}$) and to $-\text{CH}(\text{CH}_3)-\text{OH}$ end-groups (H^{27}). (T=terephthalate, L=Lactide, E=1,2 ethylene).

Table 1. Atom numbering in BHET -Lactide copolyesters.

Table 2. Chain microstructure in BHET/Lactide copolymers: Number-fractions of TET, TEL, LEL triads, F_E (TET), F_E (TEL+LET) and F_E (LEL),

Samples	F_E (TET) ^{b)}	F_E (TEL) ^{b)}	F_E (LEL) ^{b)}	F_{T0}/F_{L0} ^{c)}	F_T/F_L ^{d)}
BHET/Lactide(70/30) ^{a)}	0.571	0.369	0.058	56.89/43.10	62.5/37.5
BHET/Lactide(60/40) ^{a)}	0.577	0.378	0.043	45.92/54.07	55.5/44.4
BHET/Lactide(50/50) ^{a)}	0.591	0.343	0.066	36.19/63.80	62.0/37.9
BHET/Lactide(40/60) ^{a)}	0.539	0.380	0.079	26.47/73.52	56.4/43.5

a) (m_1/m_2) represents the initial BHET/Lactide mass ratio.

b) fraction of TET, TEL and LEL in final copolymers

c) Initial mole fraction of T and Lactide units in initial reaction mixture.

d) Mole fraction of T and Lactide units in final copolymer.

Moreover, hydroxy end group and oxydiethylenemoieties linked to different neighboring entities can also be identified.

The "degree of randomness", R , introduced by Yamadera (24) as a parameter for characterizing the extent of randomization in condensation copolymers, was used to characterize the extent of randomization in these copolymers.

$$R = \frac{F(TEL)}{2F_L} + \frac{F(TET)}{2F_T} = P_{LT} + P_{TL}$$

F_T and F_L represent the molar fraction of terephthalate and lactide units in copolymer and are determined from NMR spectra.

P_{TL} and P_{LT} are the probability of finding an ET repeating unit next to a Lactide repeating unit, and a Lactide repeating unit next to an ET repeating unit when going from one chain end to the other, respectively.

Table 3. Chain microstructure of BHET-Lactide copolyesters: number-average block length of T and L units in ethylene terephthalate and Lactide blocks, $\overline{L_{n,T}}$ and $\overline{L_{n,L}}$, degree of randomness, R.

Sample	$\overline{L_{n,T}}$	$\overline{L_{n,L}}$	R
BHET/Lactide(70/30) ^{a)}	3.38	2.03	0.787
BHET/Lactide(60/40) ^{a)}	2.94	2.35	0.765
BHET/Lactide(50/50) ^{a)}	3.62	2.21	0.728
BHET/Lactide(40/60) ^{a)}	2.97	2.29	0.772

a) (m₁/m₂) represents the initial BHET/lactide mass ratio.

The degree of randomness R is equal to 0 for blends, to 1 for random copolymers and varies between 0 and 1 for block copolymers. $1 < R < 2$ for copolymers having a tendency to form alternating structure.

The R values and the number-average block lengths calculated from NMR spectra are reported in Table 3. All copolyesters exhibit some block copolymer character ($R < 1$) due to the sublimation of the lactide. Therefore final Lactide fraction in the copolymer is lower than of terephthalate fraction.

Table 4. Inherent viscosity and molecular weight data of BHET/Lactide copolyesters.

Samples	$[\eta]_{inh}$ (dl/g) ^{b)}	M_n (g/mol) ^{c)}	M_w (g/mol) ^{c)}	\overline{D}_M ^{c)}
BHET/Lactide (40-60) ^{a)}	0.227	13.900	39.100	2.8
BHET/Lactide (50-50) ^{a)}	0.262	17.000	54.200	3.1
BHET/Lactide (60-40) ^{a)}	0.210	14.500	38.500	2.6
BHET/Lactide (70-30) ^{a)}	0.187	* d)	* d)	* d)

a) (m₁/m₂) represents the initial BHET/Lactide mass ratio.

b) 1.5g/l of polymer in CHCl₃ at 25°C.

c) Determined by SEC using polystyrene calibration standards.

d) Insoluble in THF.

Thermal properties

BHET/Lactide(70/30) semi-crystalline copolyester is and exhibit one glass transition temperature (T_g) and one melting temperature (T_m) which are lower than those of PET ($T_g = 83^\circ\text{C}$, $T_m = 255^\circ\text{C}$) (4) but higher

SEC study of BHET-Lactide copolyesters

The SEC analysis was therefore carried out on BHET-lactide 60/40 to 40/60, which exhibits good solubility in THF. The values of the average molar masses determined by SEC and by using polystyrene calibration are reported in Table 4.

The number-average molar masses of this copolyesters were $M_n = 13.900$ to 17.000 g/mol

M_n values are more interesting than these obtained by E. Olewnik ($M_n = 6100$ for 50/50 copolyester), (19) the synthesis of aliphatic-aromatic copolyesters from a cyclic ester allows the obtaining of high molar mass copolyesters.

\overline{D}_M is significantly higher to 2 because of the presence of side reaction such as etherification and formation of cyclic species which are inevitable in polycondensation reactions.

The M_w of these copolyesters could not be determined from NMR spectra due to (i) the very low amount of end groups and (ii) the partial overlapping of the resonances of end groups ($H^{6,20}$) and ether groups (H^{12}) arising from etherification side reactions during the second reaction step.

than those of PLA homopolymers ($T_g = 52^\circ\text{C}$, $T_m = 156^\circ\text{C}$) (19), which reflects the insertion of lactate units in the copolyesters chains. (Figure 3).

BHET/Lactide 60/40 to 40/60 copolyesters are amorphous, which can easily be understood in view of their very short sequence length (Table 5).

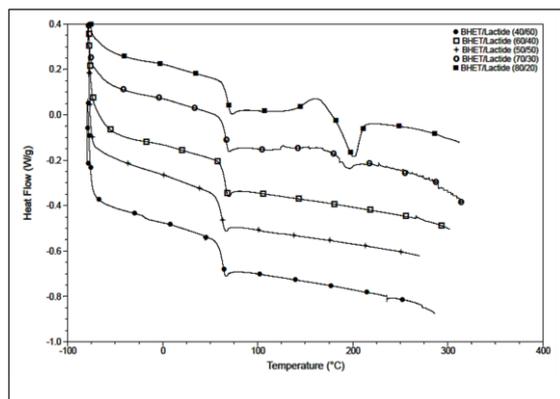


Figure 3. DSC curves of PET-PLA copolymers

Table 5. Thermal analysis data of copolyesters.

Samples	T _g ^{°C} ^(a)	T _m ^{°C} ^(a)	T _{d,5%} ^{°C} ^(b)
PET ⁽¹⁹⁾	83.0	255.0	360
BHET/Lactide (70/30)	66.78	194.43	341
BHET/Lactide (60/40)	66.29	*	325
BHET/Lactide (50/50)	62.52	*	293
BHET/Lactide (40/60)	58.73	*	310
PLA ⁽¹⁹⁾	52	156	221

The TGA analysis showed a good thermal stability for all copolyesters. (Fig.4).

The temperature of degradation of copolyesters is slightly above that of PLA, but much lower than that of PET homopolymer.

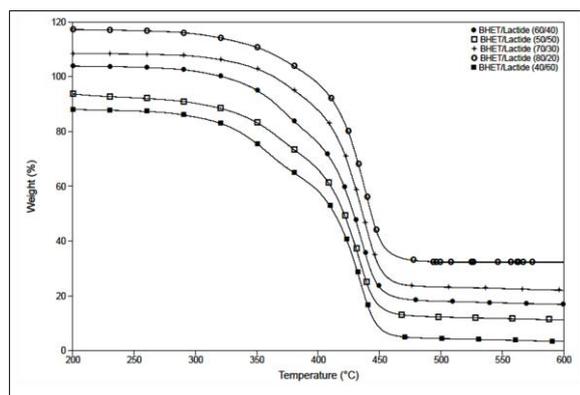


Figure 4. TGA curves of PET-PLA copolymers

Conclusion

This work showed that the insertion of lactate units into PET chains by a reaction between bis (2-hydroxy ethyl terephthalate) and Lactide in both easy and efficient, leading to high molar mass copolyesters.

As expected, ¹H NMR spectra also reflect the insertion of lactate units in PET polymer chains and allows the study of chain microstructure.

The degree of randomness of copolyesters is significantly lower than unity, indicating that they present some block copolymer character. This appears rather surprising in view of the high reaction temperature.

Copolyesters thermal properties were studied by DSC and TGA. The thermogravimetric analysis reveals fairly good thermal stabilities for all PET/PLA copolyesters.

The glass transition and melting temperatures of all copolyesters are lower than those of PET but higher than those of high molar mass PLA and are relatively higher than those of PET/PLA copolyesters synthesized from a mixture of homopolymer (19).

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