



Copolymerization of polyethylene terephthalate and polycaprolactone using catalytic transesterification

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ARTICLE INFO

Keywords:

PET recycling
Catalytic transesterification
Melt blending
Copolymer characterisations
¹H NMR

ABSTRACT

A random copolymer between polyethylene terephthalate (PET) and polycaprolactone (PCL) is formed using catalytic transesterification in the melt. The copolymer, poly[(ET)₂-co-(CL)₂], has a backbone structure similar to that of polybutylene adipate terephthalate (PBAT) and could replace it at a lower cost, while simultaneously managing waste PET. Theoretically, a biodegradable copolymer is achieved when only two consecutive ET blocks remain. This degree of transesterification requires an active catalyst, capable of selective transesterification while limiting undesired chain scission. ¹H NMR spectroscopy revealed that titanium alkoxide catalysts were the most effective for rapid transesterification, leading to di-blocks of both ET and CL units. It was found that the random copolymer could only be produced by catalysts containing both highly acidic metal ions and highly basic, small linear ligands. These observations led to the proposal that catalytic transesterification is likely to occur via an insertion-coordination mechanism. Increasing catalyst loading from 0.35 to 1.1 parts per hundred when using Ti(OBu)₄ significantly accelerates transesterification, but a plateau is reached at about 0.85. Pleasingly, a reaction time of 2 min was sufficient for the reaction to be complete, suggesting reactive extrusion could be feasible. DSC thermograms of Ti(OEt)₄ and Ti(OBu)₄ catalysed blends have no observable recrystallization and melting peaks along with a sharp glass transition temperature suggesting the copolymer was highly amorphous with no unreacted homopolymers. Gel permeation chromatography of THF soluble blends revealed that a high extent of transesterification led to a decrease in chain length such that the Mn was reduced from about 68000 (PCL) to 13000–20000 (copolymer), suggesting that there is a need to use a minimum amount of catalyst to avoid excessive chain scission. The results demonstrate a proof-of-concept that transesterification of PET with PCL is possible to a high extent and that the reaction proceeds via an insertion-coordination mechanism. The results will inspire future research towards repurposing waste PET on extrusion scales and the creation of other biodegradable polyester materials using waste polymers.

1. Introduction

Polyethylene terephthalate (PET) is extensively used in packaging and textiles and accounts for a significant amount of plastic waste landfilled yearly [1]. Traditional recycling routes, like mechanical recycling, are limited by the different process requirements and contamination levels associated with municipal PET waste [2]. In addition, repeated heating cycles during the recycling process also cause hydrolytic degradation of PET and result in undesirable product properties [3,4].

Alternative options should be considered for polymers that cannot be

mechanically recycled, for example conversion to biodegradable polymers. Considering the repeat unit of polybutylene adipate terephthalate (PBAT) and the knowledge that it is biodegradable [5–8], it is unsurprising that many studies have attempted to create biodegradable blends of PET with biodegradable aliphatic polyesters [9–21]. The conversion of PET waste into a biodegradable polymer could provide an alternative recycling strategy for PET that cannot be recycled conventionally.

Polymer blending is an effective and inexpensive way to create new polymers with improved properties [22]. Yet, most polymer blends are immiscible, resulting in undesirable mechanical properties [23–26]. Blends of polymers with complementary properties, such as PET and

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<https://doi.org/10.1016/j.polymer.2023.126297>

Received 28 June 2023; Received in revised form 15 August 2023; Accepted 22 August 2023

Available online 23 August 2023

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polycarbonate (PC) [27–31] or polycaprolactone (PCL) [14–21], have been studied extensively to improve their compatibility by creating copolymers in the interfacial regions through transesterification (Scheme 1). Transesterification is the process of exchanging one ester's organic group with the organic group of another ester in the presence of a catalyst, resulting in block copolymers ranging in composition [32].

Synthesizing a biodegradable copolymer from polyester blends is challenging, and only limited success has been achieved [9–13,16,20,21]. In one of the few successful studies investigating the blending of PET with polybutylene succinate has found that degradation was primarily due to the aliphatic ester units, and the degradability depended on the length of the aliphatic units and hence the overall randomness of the copolymer [34]. Zhang et al. [18] have investigated synthesizing the copolymer by blending 50 wt% PET and PCL under a nitrogen atmosphere at 270 °C for 4–8 h without a catalyst. They concluded that while the size of the dispersed phase decreased over time, large amounts of unreacted homopolymers remained. Copolymerization using transesterification has been demonstrated using zinc (II) acetate and antimony (III) trioxide as the catalysts under a nitrogen atmosphere at 270 °C for 150 min. An average length of 2.9 PET and 1.8 PCL monomer units in the copolymer structure was estimated by ¹³C NMR spectroscopy; however, it had limited biodegradability [20]. The lack of biodegradability led to the conclusion that at a PET to PCL weight ratio higher than one, the resultant copolymer cannot be biodegradable, probably due to the length of PET units being more than two [35].

All of the catalysts reported for transesterification between polyesters are in the form of cation and anion pairs. As a result, the transesterification mechanism is believed to be either based on the Lewis acid, Lewis base, or the insertion-coordination mechanism (Scheme 1) [33]. The cations are crucial for activating the polyester's carbonyl carbon promoting the ester exchange and stabilising the coordinated complex for the Lewis acid (metal-based) mechanism. Increasing the metal ion's acidity should increase the carbonyl carbon's electrophilicity and thus promote the exchange reaction. However, the cation also promotes side reactions such as hydrolysis in the presence of moisture and end groups (alcoholysis and acidolysis). Considering ester groups are exchanged instead of cleaved, the Lewis acid mechanism should

retain the highest molecular weight and the narrowest molecular weight distribution.

For the Lewis base (ligand-based) mechanism, transesterification only depends on the anion acting as an initiator and generating an active polymeric alkoxide by attacking the ester groups. The active alkoxide (M-OR) can subsequently act as a nucleophile and attack other polyester chains, and thus, copolymers are created by cycles of addition-elimination reactions [19]. As a result, the nucleophilicity of anion is crucial for this pathway, and a strong nucleophile would enhance transesterification. However, chain cleavage involved in this mechanism will always result in reduced molecular weight and an increase in polydispersity.

The insertion-coordination mechanism is a combination of the two previous mechanisms in which the cation and anion are both required for the reaction. The cation is believed to enhance the reaction by coordinating the carbonyl group and the alkoxide species nearby. Since the cation and the anion are crucial for the reaction, transesterification by this pathway will be enhanced using a highly positively charged cation and a nucleophilic anion. As in the case of Lewis base mechanism, chain cleavage is inevitable.

Other mechanisms may also be effective for transesterification. Dibutyl tin (IV)oxide ((Bu)₂SnO) is postulated to catalyse the reaction by forming dimeric alkoxy and acyloxy distannoxane structures with the ester groups in situ. Transesterification is suggested to be propagated by the inter- and intramolecular exchange of these alkoxy and acyloxy distannoxane structures [36].

To synthesize a copolymer from melt blending of polyesters through transesterification, finding an effective catalyst is crucial. However, the absence of a unified view of transesterification mechanisms in literature makes it difficult to compare and quantify their effectiveness. A study by Pereira et al. using Brønsted acidic ionic liquids to investigate the compatibility of polylactide with ethylene-co-vinyl acetate suggested that solely changing the cations could promote transesterification even with a weakly nucleophilic chloride anion [37]. Meanwhile, another report has suggested that transesterification between PLA and PBAT is influenced by changing anions in phosphonium-based ionic liquids [38]. Additionally, metal ion-based catalysts have traditionally been selected based on their acidity and complex stability [39–41]. On the other hand, a recent study on PC transesterification suggested that the ligand's basicity is the sole factor determining catalyst efficiency. The authors suggested that despite the absence of the metal ion's influence on the reaction, a high degree of transesterification is still possible with a highly basic ligand [33]; however, chain scission promoted by a highly basic ligand may be inevitable [42,43]. It is possible that these proposed transesterification mechanisms may differ for different polyester blends, hence the contradictory effects of changing the cation and anion constituents reported in the literature.

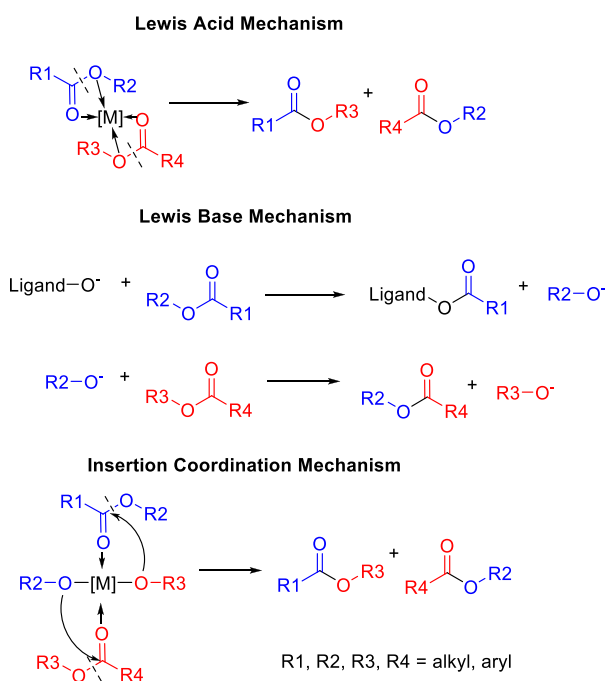
This paper investigates the catalytic transesterification of PET and PCL to create a random copolymer using melt blending. The work aims to understand the effect of varying the acidity and basicity of the metal ion and ligand, respectively, on the degree of transesterification and the reaction time required to produce a random copolymer with short blocks of ET units. The findings from this paper can be used to synthesize and characterize biodegradable copolymers from polyesters, which can provide valuable information as a first step to developing an alternative chemical recycling strategy.

2. Experimental

2.1. Materials

2.1.1. Polymers

Bottle grade polyethylene terephthalate (Papet Cool, IV 0.8 (dL/g)) and commercial grade polycaprolactone (CAPA™ 6500, Mw = 50000 g/mol) were both purchased from Avient New Zealand Limited and dried at 166 °C and at 50 °C for 24 h prior to the blending experiments.



Scheme 1. Proposed transesterification mechanisms involving either the cation (top) or anion (middle) or both (bottom) of the catalyst [33].

2.1.2. Catalysts

Several metal complexes (Table 1) with various metal ion acidities and ligand nucleophilicity strengths were selected to investigate their influence on transesterification.

Using a branched low basicity acetylacetonate bidentate ligand, the effect on transesterification as the metal ion acidity increases can be evaluated with the first four catalysts (Table 1). Furthermore, titanium complexes are ideal for investigating the effect of different ligands due to their high acidity and non-hazardous residue after blending. Ti(acac)₃, Ti(OiPr)₄, Ti(OBu)₄, and Ti(OEt)₄ are four titanium complexes that are used to study the influence of changes in ligand size, linearity, and basicity on transesterification. Combining a weakly acidic sodium ion and a highly basic small linear ligand such as NaOMe and NaOEt will allow for reliable comparisons of possible metal complex combinations. As the literature suggests, dibutyl tin(IV)oxide promotes transesterification in a different mechanistic route and is only included for comparison purposes [45].

2.2. Blend preparation

2.2.1. PET-PCL blends

An equimolar mixture of PET and PCL was chosen for all the experimented blends in this study to simplify the molar ratio adjustment when analysing ¹H NMR spectra.

The reactive blending between PET and PCL were performed in a discontinuous Brabender mixer with a 50 mL mixing chamber. A total of 40 g of polymeric materials (PET/PCL, 62.5%/37.5% w/w) were melt blended at 280 °C with a rotor speed of 50 rpm under a continuous nitrogen flow to minimize thermal oxidation and hydrolysis of the

Table 1

Summary of the metal complexes and their respective acidities and nucleophilicities used for the blending experiments. Catalysts are used without further purifications.

Catalysts and Purity	Supplier	Metal ion acidity (Z/R) ^a	Ligand nucleophilicity (pKa, dimension) ^b
Lanthanum (III) Acetylacetonate hydrate (La(acac) ₃ ·xH ₂ O), (100%, powder)	Sigma-Aldrich	2.91	8.93, branched
Iron (III) Acetylacetonate (Fe(acac) ₃), (Purum, 97%, powder)	Sigma-Aldrich	4.65	8.93, branched
Aluminium (III) Acetylacetonate (Al(acac) ₃), (ReagentPlus®, 99%, powder)	Sigma-Aldrich	5.61	8.93, branched
Titanium (IV) Acetylacetonate (Ti(acac) ₄), (63% in Isopropyl Alcohol)	AK-scientific	6.15	8.93, branched
Titanium (IV) Isopropoxide (Ti(OiPr) ₄), (≥97%)	Sigma-Aldrich	6.15	17.1, branched
Titanium (IV) Butoxide (Ti(OBu) ₄), (reagent grade, 97%)	Sigma-Aldrich	6.15	16.1, linear
Titanium (IV) Ethoxide (Ti(OEt) ₄), (Technical grade, 100%)	Sigma-Aldrich	6.15	15.9, linear
Sodium Ethoxide (NaOEt), (95%, powder)	Sigma-Aldrich	0.98	15.9, linear
Sodium Methoxide (NaOMe), (reagent grade, 95%, powder)	Sigma-Aldrich	0.98	15.3, linear
Dibutyl Tin (IV) Oxide ((Bu) ₂ SnO), (98%, powder)	Sigma-Aldrich	–	–

^a The acidity of the metal ion is estimated by their charge over ionic radius ratio. The ionic radius is approximated by assuming the metal ion is six-coordinate [44].

^b The ligand's nucleophilicity is estimated by their pKa and steric factor. The steric factor is classified by the linearity of the ligand.

polyesters. Blends with various catalysts, reaction time and the catalyst loadings (parts per hundred relative to polymer) were prepared (Table 2). To ensure all polymeric materials were properly melted and homogenized before the reaction, PET pellets were added to the mixer and completely melted over 3 min. PCL pellets were added to the melted PET after 3 min, and the blend was allowed to homogenize for another 2 min. After the 5 min of homogenization under a flow of nitrogen, the catalyst was added, and the reaction time was started. Upon reaching the desired reaction times, the blends were removed from the mixer and allowed to cool in air before the samples were taken for analysis. Solid catalysts were weighed and directly introduced to the melt blend, while liquid catalysts were added through a syringe, and respective density values determined the volumes at 25 °C.

2.2.2. Control samples

Various control samples were melt processed in a similar manner for comparison to the blends. These were pristine PET and PCL (from the supplier) as well as melt processed PET and PCL with and without a catalyst. Catalysed PCL control samples were prepared and analyzed using three metal complexes, Al(acac)₃, NaOMe, and Ti(OBu)₄, to investigate their effect on the PCL homopolymer due to different combinations of metal ion acidity and ligand nucleophilicity. The expected PCL alkoxide species (M-OR) created from the chain cleavage by the metal complexes would acidify and become a hydroxyl end group (-OH) upon contact with moisture in the air over time. From ¹H NMR spectroscopy, the change in methylene proton signals adjacent to the OH end group is used to estimate the number average molecular weight (Mn). For PET, only Ti(OBu)₄ was considered as part of the controls, after initial screening.

Uncatalyzed PET and PCL control samples were prepared by melting 30 g of respective polymers in the Brabender mixer at 280 °C with a rotor speed of 50 rpm under a continuous nitrogen flow for 20 min. 1.1 part per hundred (pph) (0.33 g) of specified catalysts was added to catalysed control samples, and the process conditions were identical to the uncatalyzed control samples.

2.3. Characterization

2.3.1. Nuclear Magnetic Resonance (NMR) spectroscopy

Solution phase NMR samples were prepared by dissolving samples in

Table 2

Summary of formulations and reaction times for all blends tested.

Sample	Catalyst	Catalyst loading (pph)	Blending time (minutes)
Blend 1	Al(acac) ₃	1.1	20
Blend 2	NaOMe	1.1	20
Blend 3	NaOEt	1.1	20
Blend 4	Fe(acac) ₃	1.1	20
Blend 5	La(acac) ₃	1.1	20
Blend 6	Ti(OBu) ₄	1.1	20
Blend 7	(Bu) ₂ SnO	1.1	20
Blend 8	Ti(OEt) ₄	1.1	20
Blend 9	Ti(OiPr) ₄	1.1	20
Blend 10	Ti(acac) ₄	1.1	20
Blend 11	Uncatalyzed	–	20
Blend 12	Ti(OBu) ₄	1.1	10
Blend 13	Ti(OBu) ₄	1.1	5
Blend 14	Ti(OBu) ₄	1.1	2
Blend 15	Ti(OBu) ₄	0.85	2
Blend 16	Ti(OBu) ₄	0.6	2
Blend 17	Ti(OBu) ₄	0.35	2
PCL control 0	–	–	–
PCL control 1	–	–	20
PCL control 2	Al(acac) ₃	1.1	20
PCL control 3	NaOMe	1.1	20
PCL control 4	Ti(OBu) ₄	1.1	20
PET control 0	–	–	–
PET control 1	–	–	20
PET control 2	Ti(OBu) ₄	1.1	20

0.5 mL CDCl₃. NMR samples for blends that were found to be partially soluble or insoluble in chloroform were prepared by dissolving in a 0.5 mL mixture of CDCl₃ and D-trifluoroacetic acid (70/30 v/v%). The NMR solutions were passed through a 22 μm PTFE filter to remove solid impurities. ¹H, COSY, HMQC, and HMBC NMR spectra were recorded by a Bruker AVIII - 400 MHz Spectrometer. All spectra were obtained at room temperature using trimethylsilane (TMS) as the internal standard.

2.3.2. Differential Scanning Calorimeter (DSC)

Differential scanning calorimetry (DSC) measurements were obtained using a TA instruments Q1000 with calorimetric precision ± 1% and sensitivity of 0.2 μW. DSC samples varied between 6 and 10 mg and were first heated to 260 °C at a rate of 10 °C/min with a continuous nitrogen purge (50 mL/min) to remove thermal history. Analytical measurements were taken by cooling the samples from 260 °C to −80 °C and subsequently heating them to 280 °C at a rate of 10 °C/min.

2.3.3. Gel permeation chromatography (GPC)

Molecular weight distributions of tetrahydrofuran (THF) soluble blends and PCL controls were determined using a GPC instrument equipped with three PS-DVB columns with particle sizes of 6 μm and pore sizes of 50 nm (Shimadzu, Shim-pack GPC-803) using a refractive index detector at 40 °C. Samples were dissolved in THF and filtered with a 22 μm PTFE filter, and the eluting THF flow rate was set at 0.5 mL/min. The exclusion limit of the columns is 7 × 10⁴ Mw of polystyrene (PS), and the calibrations were performed using PS standards with narrow polydispersity.

2.3.4. Solubility tests

Solubility tests were performed using five different organic solvents reported in the literature with high solubility for PBAT [46]. Solutions were prepared by adding 20 mg of polymer to 1 mL of solvent, and the solutions were sonicated at 40 °C for 10 min before visual inspection. Solubility was graded as high, partial, and insoluble according to their appearance. Samples resulting in a clear solution were graded high; solutions with an obvious weight loss and gel-like appearance were categorized as partial, and solutions with completely undissolved solid were deemed insoluble.

2.3.5. Tensile testing and sample preparations

Mechanical properties (Young's modulus, maximum tensile strength, and elongation at break) were recorded according to the testing standard ASTM-D882 using an Instron 5943 universal test machine with a maximum load limit of 1000 N. 30 g of DCM soluble copolymer was dissolved in 200 mL DCM and was stirred at ambient temperature (~25 °C) for 3 h until complete dissolution. Polymer solutions were then cast into a 26 mm diameter circular Teflon-coated casting pan, and the solvent evaporation rate was controlled to form a "bubble-free" uniform polymer film with a thickness of ~0.7 ± 0.05 mm. Dimensions of testing specimens were cut according to the specified testing standard with a gauge length of 50 mm. Testing specimens were dried for a minimum of 48 h before the tensile testing to prevent the influence of residue solvent. Test machine cross-head separation was set at a constant rate of 500 mm/min, and the reported mechanical properties were an average of five testing specimens for each sample.

3. Results and discussion

3.1. Copolymer structure

Transesterification between PET and PCL is a random process described as the repeating units of ET and CL are disconnected and reconnected randomly, resulting in a copolymer. As will be discussed in Section 3.1.2, a triad analysis is used to analyze the change in proton signals adjacent to the ester group with a typical shift of 4–5 ppm in ¹H NMR spectra from homopolymer to copolymer, as indicated by the star

sign in Fig. 1. These methylene proton signals in a PET homopolymer are symmetrically positioned between two electron-withdrawing aromatic groups, resulting in a higher chemical shift than the methylene proton signal in PCL positioned between two aliphatic groups. As a result of transesterification, the corresponding methylene protons on the copolymer are observed between the PET and PCL signals which are now inequivalent due to the adjacent aromatic and aliphatic groups, resulting in a discrete signal for each. This allows us to use the respective integral values to estimate the mole fraction of the homopolymer triads and copolymer triads present in the blend. As illustrated in Fig. 1, PET mole fractions (position (1), copolymer A (positions (2) and (3)) and double substituted copolymer, position (5)) are determined by dividing their integrals over the sum of methylene proton signals (1), (2), (3), and (5). PCL (position (6)) and copolymer B (position (4)) mole fractions are calculated by dividing the integrals of triads over the sum of the integrals of methylene proton signals (4) and (6). With the help of a statistical model [47], the mole fraction of triads can be used to quantify the degree of transesterification and the average PET and PCL block lengths present in the copolymer.

3.1.1. PCL and PET controls

The ¹H NMR spectra of the pristine unreacted PCL (Table 2, PCL control 0) and uncatalyzed PCL (Table 2, PCL control 1) were almost identical (Figs. S12 and S13). The absence of common PCL degradation products [48] found in the uncatalyzed PCL sample suggests that PCL is stable under the processing conditions. The spectra of catalyzed PCL control samples (Table 2, PCL controls 2–4) have a noticeable increase in the methylene proton signal at 3.62 ppm (Figs. S14–S16), suggesting an increase in OH end-groups which result from the ligand-facilitated cleavage of the PCL chains into smaller fragments. Therefore, the integrals of methylene proton signals adjacent to the hydroxyl end groups can be used to estimate the M_n in PCL control samples according to Equation (1), using 114.14 g/mol as the molecular weight of a CL repeat unit. In Equation (1), f_{4.04} is the mole fraction of the methylene protons adjacent to the oxygen of the ester group (δ_H = 4.04 ppm) and f_{3.62} is the mole fraction methylene protons adjacent to a hydroxyl active end (δ_H = 3.62 ppm). As shown in Table 3, the M_n of pristine PCL decreased the most, from 56365 g/mol to 9673 g/mol, when catalyzed by NaOMe (Table 2, PCL control 3). Use of 1.1 pph Ti(OBu)₄ similarly resulted in a decrease in M_n to 12373 g/mol (Table 2, PCL control 4). Therefore, methoxide and butoxide anions are highly nucleophilic ligands able to cleave PCL chains to produce shorter PCL fragments. Al(acac)₃ containing a weak nucleophilic ligand resulted in only marginal decrease in M_n relative to pristine PCL (Table 2, PCL control 2). Further discussion of the relationship between the molecular weight and corresponding transesterification mechanism(s) will be continued in Section 3.3.

Under the same processing conditions, the Ti(OBu)₄ catalyzed PET control sample exhibited negligible differences in the observed ¹H NMR spectra compared to pristine and uncatalyzed PET (Figs. S17–S19). This suggests that PET is not reactive with either highly acidic metal ions or nucleophilic ligands. Therefore, the catalyst likely reacts with PCL chains to initiate the transesterification reaction, generating reactive PCL alkoxide species, which can subsequently react with PET chains to propagate the reaction.

$$M_nPCL = \frac{f_{4.04}}{f_{3.62}} \times 2 \times 114.14 \quad (1)$$

3.1.2. Quantitative analysis and copolymer sequencing by ¹H NMR spectroscopy

The structures of the PET and PCL homopolymers can be represented by the various chemical moieties defined in Fig. 2. Assuming a Bernoulli distribution of repeating moieties along a copolymer backbone, past studies have established a protocol to estimate the structure and sequence of a copolymer through the triad analysis of ¹H and ¹³C NMR spectroscopy [47,49]. The triad analysis treats the backbone structure of

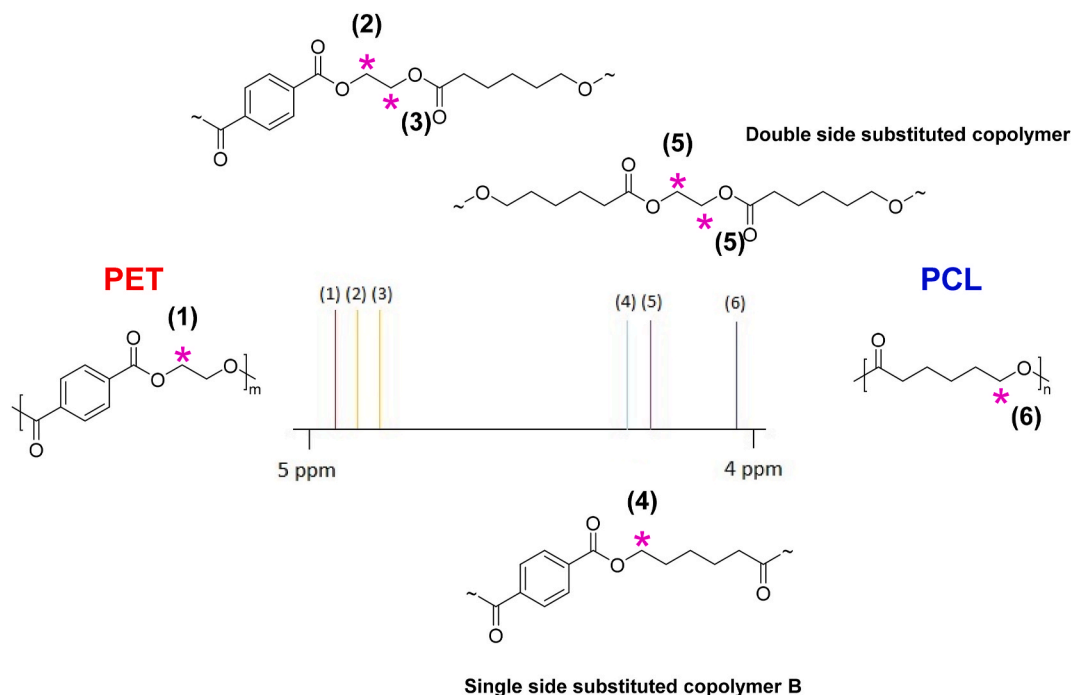


Fig. 1. The expected positions of the methylene proton signals and the structures of respective homopolymers and copolymers created through transesterification in a simulated ^1H NMR spectrum.

Table 3

Estimated number average molecular weight by ^1H NMR spectroscopy (Rounded to the nearest 100 units).

Sample	M_n (g/mol)
PCL control 0 (unreacted)	51900
PCL control 1 (uncatalyzed)	44300
PCL control 2 (1.1 pph $\text{Al}(\text{acac})_3$)	34900
PCL control 3 (1.1 pph NaOMe)	9700
PCL control 4 (1.1 pph $\text{Ti}(\text{OBu})_4$)	12400

a polymer as a summation of repeating moieties denoted as A1, B1, A2, and B2, as shown in Fig. 2. When copolymer A (Fig. 1) is created, triads around the ethylene unit (B1) will change from symmetrical (PET, A1B1A1) to asymmetrical (A1B1A2). Similarly, when copolymer B (Fig. 1) is created, triads centred around the B2 unit will change from symmetrical homopolymer (PCL, A2B2A2) to asymmetrical (A2B2A1).

As outlined in the opening paragraph, the degree of transesterification can be quantified and converted into a comprehensible description of the copolymer structure in terms of average block lengths of ET and CL units. This is done by measuring the change in integral ratios between symmetrical and asymmetrical triads based on the methylene proton signals in ^1H NMR spectra and convert this

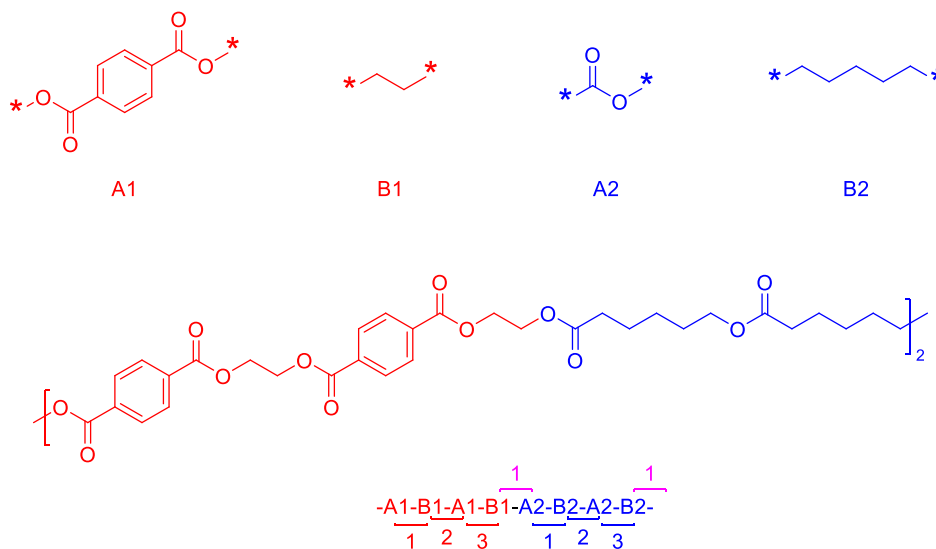


Fig. 2. Assigned notations for the different chemical moieties of the polymers. A1: terephthalate, B1: ethylene, A2: ester and B2: pentylene; and an example of an alternating di-block copolymer structure expressed in terms of the notations with the number of A1B1 (red), A2B2 (blue), B1A2 (purple) and B2A1 (purple) dyads. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

information into the mole fraction of triads e.g. f_{A1B1A1} which are summarised in Table S1. The mole fractions are subsequently converted into the number of polymeric sequences (number of dyads) present in bulk by applying Equations (2) and (3). Consequently, the average block length of ET and CL units in the copolymer structure can be determined by the ratio between homopolymer dyads (A1B1 for PET, A2B2 for PCL) and copolymer dyads (A1B2, A2B1).

$$N_{A1B1} = \frac{f_{A1B1A2}/2 + f_{A1B1A1}}{f_{A1B1A2}/2} \quad (2)$$

$$N_{A2B2} = \frac{f_{A2B2A1}/2 + f_{A2B2A2}}{f_{A2B2A1}/2} \quad (3)$$

The number of dyads, i.e., A1B1, A1B2, A2B1, and A2B2 in alternating di-blocks of copolymer (poly[(ET)₂-co-(CL)₂]), is shown in Fig. 2. In the alternating di-block structure, the dyad ratio between A1B1 and A2B1 is 3:1, as well as between A2B2 and A1B2. The dyad ratios for ET and CL blocks will vary depending on their length, such as a tri-block (poly[(ET)₃-co-(CL)₃]) with a dyad ratio of 5:1, a tetra-block with a dyad ratio of 7:1, etc. Based on the number of dyads, it is possible to estimate and describe the copolymer as poly[(ET)_x-co-(CL)_y], in which a and b are the varying number of repeating units/block lengths of ET and CL units present in the copolymer structure based on the degree of transesterification.

It is worthwhile to mention that double substitution is possible with both the copolymer A (A1B1A2), and copolymer B (A2B2A1)). However, only double substitution in copolymer A will result in a distinct signal as shown in Fig. 1. This is due to the asymmetrical nature of PCL ester structure, making double substitution in copolymer B indistinguishable in the ¹H NMR spectrum since the product will appear equivalent to single substituted copolymers A and B adjacent to each other as illustrated in Scheme S1.

As a result of a double substitution, the double-substituted triad A2B1A2 can be described as a B1 unit squeezed between two PCL units. The extra B1 units result in an increased number of A2B1 dyads estimated by ¹H NMR spectroscopy, which deviates the number of A2B1 dyads from 1, and the newly inflated number of A2B1 can be estimated by applying Equation (4). In relation to the overall composition of poly[(ET)_x-co-(CL)_y], the number of double-substituted triads should be trivial because the A1B1A2 triads require further transesterification, thus making poly[(ET)_x-co-(CL)_y] sequence descriptions based on the average length of ET and CL repeating units estimated by the amount of single substituted triads plausible.

$$N_{A2B1} = \frac{f_{A1B1A2}/2 + f_{A2B1A2}}{f_{A1B1A2}/2} \quad (4)$$

Another, simpler, way of quantifying the degree of transesterification is by calculating the ratio of the methylene proton signals between the mole fractions of copolymers and the homopolymers triads. The PET transesterification ratio ($T_{PET}\%$) can be therefore defined as the mole fraction of the homopolymer triads A1B1A1 converted into A1B1A2 and A2B1A2 using Equation (5). Similarly, Equation (6) can be used for the transesterification ratio of PCL ($T_{PCL}\%$).

$$T_{PET}\% = \frac{f_{A1B1A2} + f_{A2B1A2}}{f_{A1B1A1} + f_{A1B1A2} + f_{A1B1A2}} \quad (5)$$

$$T_{PCL}\% = \frac{f_{A1B2A2}}{f_{A1B2A2} + f_{A2B2A2}} \quad (6)$$

3.1.3. Catalytic activities of different catalysts

Blends 1–10 in Table 1 were prepared by mixing equimolar PET and PCL with ten different catalysts for 20 min to compare the transesterification effectiveness when combining metal ions and ligands with different acidities and nucleophilicity. From the ¹H NMR spectrum of the uncatalyzed blend (Table 4, Blend 11), two methylene proton signals

Table 4

Distributions of poly[(ET)_x-co-(CL)_y] estimated by ¹H NMR spectroscopy.

Samples ^a	Transesterification % ^b		Average lengths of repeating units ^c	
	PET	PCL	ET (x)	CL (y)
Blend 1	6.6	7.4	15	14
Blend 2	4.8	6.6	21	15
Blend 3	2.8	2.2	36	40
Blend 4	22.7	19.7	4–5	5
Blend 5	2.7	1.9	37	53
Blend 6	45.3	47.4	2	2
Blend 7	13.4	16.2	8	6
Blend 8	55.9	60.9	2	2
Blend 9	18.7	19.4	6	5
Blend 10	27.2	25.2	4	4
Blend 12	52.9	56.1	2	2
Blend 13	49.2	49.8	2	2
Blend 14	48.6	47	2	2
Blend 15	43.3	48.3	3	2
Blend 16	34.1	34.2	3	3
Blend 17	15	22.1	7	5

^a Sample entries refer to Table 1.

^b Fractions determined from ¹H NMR integrals of respective structure according to Table 2.

^c Estimated by the dyads ratio between homopolymers and copolymers as described in section 3.1.2.

were observed, as expected, at 4.80 ppm (PET) and 4.16 ppm (PCL) representing the methylene group adjacent to an ester group in the respective homopolymers (Fig. S1). As anticipated in Fig. 1, the emerging chemical shifts observed in ¹H NMR spectra when a catalyst was added (Blends 1–9, Figs. S2–S11) are evidence of the formation of copolymer links by transesterification.

Table 4 summarizes the transesterification ratios and block lengths of ET and CL units calculated using the previously described methods by ¹H NMR spectroscopy for blends catalysed by various catalysts (Table 4, blends 1 to 10), detailed information on mole fraction of triads and lengths of dyads are available in Table S2. The charge over ionic radius ratio (Z/R) is used to estimate the influence of metal ions' acidity on transesterification, with the order of acidity descending from Ti⁴⁺ > Al³⁺ > Fe³⁺ > La³⁺. Increasing the metal ions' acidity with a sterically hindered anionic ligand such as acetylacetonate (acac) resulted in shortening of ET repeating units as illustrated in Fig. 3 Although Fe³⁺ is less acidic than Al³⁺, it has a better catalytic activity towards transesterification. As a previous study investigating PET transesterification suggested, this observation may be due to a "dome-shaped" correlation between catalytic activity and complex stability [39]. Both PET and PCL transesterification ratios obtained from Equations (5) and (6) varies substantially among catalysts with acac ligands, with the highest transesterification ratio slightly above 27%. Nevertheless, it is evident that manipulating metal ions' acidity alone is insufficient to create a randomized copolymer.

The next step was to evaluate the effect of varying the nucleophilicity of the anionic ligands while keeping a highly acidic Ti⁴⁺ metal ion in the metal complex catalyst, as shown by the green bars in Fig. 3. Blends with catalysts consisting of linear ligands such as Ti(OBu)₄ (Table 4, Blend 6) resulted in a significant increase of copolymer signals in the ¹H NMR spectra (Fig. 4). In particular, and Ti(OEt)₄ (Table 4, Blend 8) were highly active, yielding a randomized copolymer with an estimated sequence of poly[(ET)₂-co-(CL)₂]. However, changing the ligand to branched anionic isopropoxide (iPrO⁻) (Table 4, Blend 9) resulted in a similar degree of transesterification as found with the Ti(acac)₄ (Table 4, Blend 10) with average block lengths of ca. 4–5, substantially less reactivity than with the linear alkoxy ligands. The inductive effect gives the iPrO⁻ ligand slightly higher basicity (pKa 16.5) than the EtO⁻ and BuO⁻ anions (pKa 16 for both). Therefore, in contrast to the previous study on transesterification between isosorbide polycarbonate [40], this observation suggests that basicity is not the dominant factor in deciding

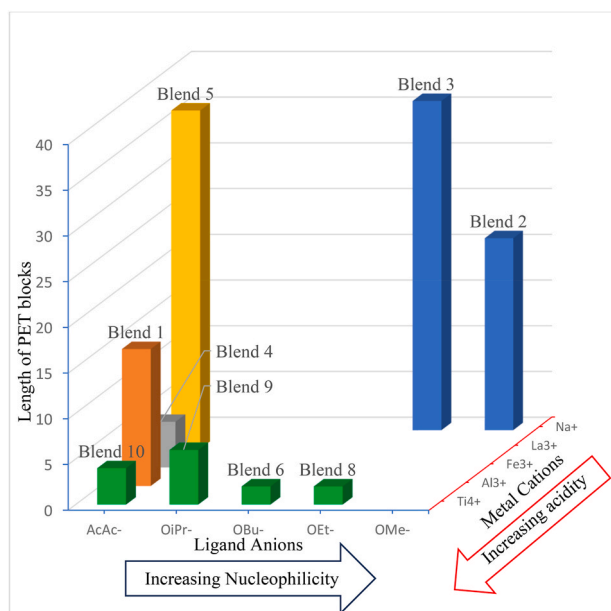


Fig. 3. Visualisation of the effect of changing the acidity and nucleophilicity of metal complexes on the length ET repeating units in the copolymer. Metal cations used in the experiments, Ti⁴⁺ (green), Al³⁺ (orange), Fe³⁺ (gray), La³⁺ (yellow) and Na⁺ (blue) are grouped along the z-axis with different color codes. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

insertion-coordination model in which metal ions and ligands work together to actively promote transesterification between PET and PCL.

Moreover, pairing a small and linear ligand with a weakly acidic metal ion did not result in a high extent of transesterification. The transesterification ratios for both sodium methoxide (Table 4, Blend 2) and sodium ethoxide (Table 4, Blend 3) were remarkably low. From Table 4, the estimated block lengths of ET and CL repeating units are exceptionally high for these two catalysts (Blends 2 and 3), and their spectra resemble an uncatalyzed blend. Therefore, the limited amount of transesterification products suggests that only copolymers with extremely long blocks of ET and CL repeating units were synthesized, and most likely a lot of unreacted homopolymers were also present in the blend.

In a study investigating the biodegradability of aromatic ester oligomers, Witt U et al. have suggested that based on a 40–50 mol% terephthalic acid to an aliphatic acid ratio (the standard formulation in commercial PBAT), 6–12% of the backbone of PBAT would contain consecutive aromatic ester units with average repeating units of two or higher [34]. The results suggest that PBAT's biodegradability could be due to its natural randomness from polycondensation and therefore having the majority of its aromatic ester units at a length of two or less. Therefore, to mimic the randomness of PBAT, poly[(ET)_x-co-(CL)_y] should target an average length of ET repeating units of two or less to be considered “randomized” enough to be theoretically biodegradable. From the ¹H NMR analysis, only Ti(OEt)₄ and Ti(OBU)₄ could achieve the desired poly[(ET)₂-co-(CL)₂] structure. While Ti(OEt)₄ has a higher activity than Ti(OBU)₄, it was determined that Ti(OBU)₄ is more practical for further investigation due to storage, lower rate of hydrolysis, price, and commercial availability.

3.1.4. Effect of blending time and catalyst loading

Finding the optimal blending time and catalyst loading is essential to evaluate the viability of upscaling the reaction to a continuous process and to avoid unwarranted chain cleavage from the presence of excess catalyst. From Fig. 5(B) and S23, the degree of transesterification was found to be relatively consistent from two to 20 min (Table 4, Blends 6, 12–14) in the presence of 1.1 pph of Ti(OBU)₄. This result implies that transesterification between PET and PCL reaches equilibrium within 2 min after adding the catalyst. In contrast, catalyst loadings significantly affect the degree of transesterification as supported by the change in intensities of copolymer signals in Fig. S24. From Table 4, reducing the loading from 1.1 to 0.6 pph of Ti(OBU)₄ (Table 4, Blends 6 and 16) resulted in the copolymer sequences changing from a poly[(ET)₂-co-(CL)₂] to a poly[(ET)₃-co-(CL)₃]. At 0.85 pph loading, the copolymer sequences can be described as a distribution of di-blocks and tri-blocks poly[(ET)₂₋₃-co-(CL)₂₋₃], as expected.

Further reducing the loading to 0.35 pph (Table 4, Blend 17) yielded a block copolymer with an estimated sequence of poly[(ET)₇-co-(CL)₅]. From the results, a tri-block structure with 0.6 pph of Ti(OBU)₄ is not ideal since biodegradability for an aromatic-aliphatic polyester is optimal with two or fewer consecutive aromatic units. Overall, the number of homopolymer dyads decreases as catalyst loading increased and plateaued at about 0.85 pph catalyst loading, as shown in Fig. 5(A). From the result, a blend of PET and PCL at equimolar ratios using a catalyst loading above 0.85 pph Ti(OBU)₄ is sufficient to synthesize a copolymer with lengths of ET repeating units amenable to biodegradation.

3.2. Thermal analysis of poly[(ET)_x-co-(CL)_y]

3.2.1. DSC characterisations

The DSC thermogram of an uncatalyzed blend of PET and PCL will show melting and recrystallization peaks corresponding to their respective homopolymers due to the absence of transesterification. With transesterification progressing and copolymers forming, the poly[(ET)_x-co-(CL)_y] structure will transition from longer to shorter blocks of

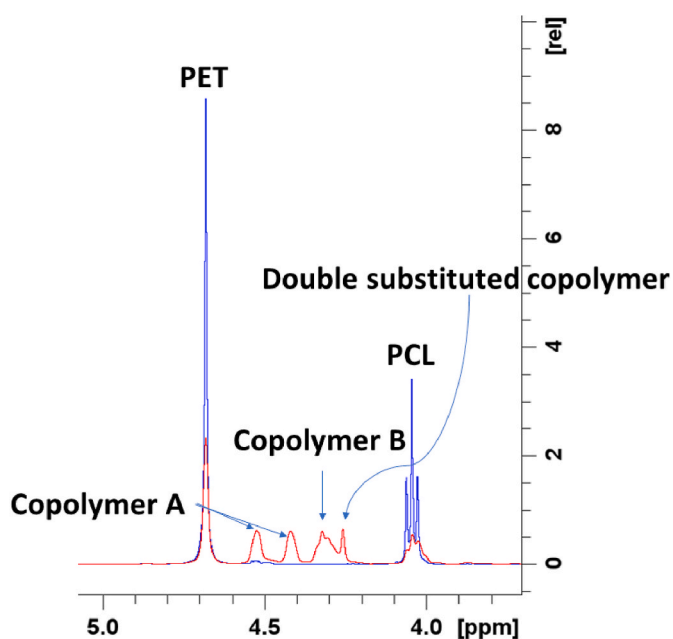


Fig. 4. A comparison between the ¹H NMR spectra of the methylene proton signals (Fig. 1) uncatalyzed (blue) and Ti(OBU)₄ catalyzed (red) blends. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

the ligand's potency. The decreased copolymer formation when comparing the *i*PrO⁻ ligands to EtO⁻ and BuO⁻, is likely due to steric factors, where catalysts with ligands of greater steric bulk (e.g. Ti(O*i*Pr)₄) are significantly less active. Among the various titanium complexes, Ti(OEt)₄ has the smallest ligand and exhibits the highest activity, further confirming the relationship between steric hindrance at the metal centre and catalytic activity. These observations coincide with the

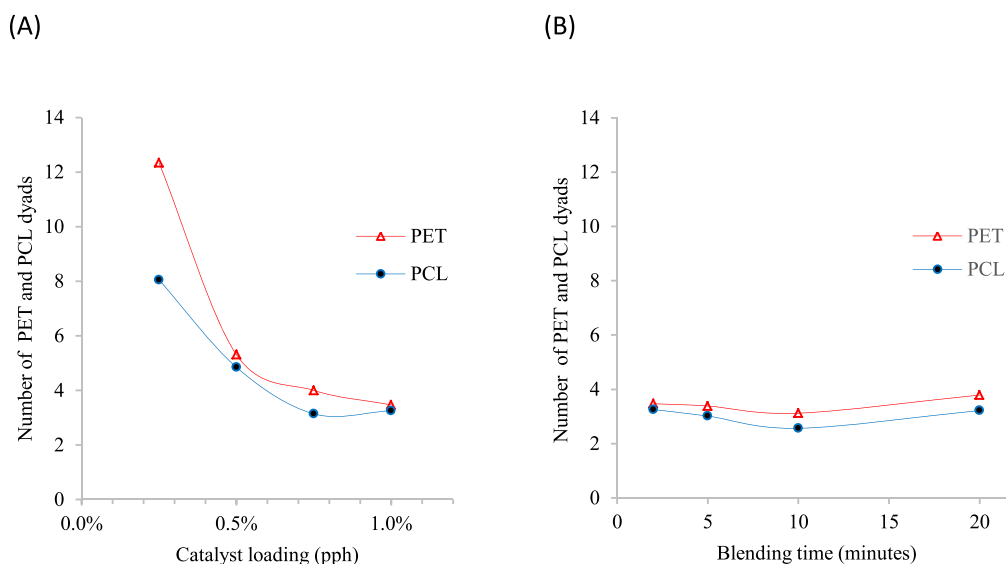


Fig. 5. The change in the number of homopolymer dyads in the equimolar blend of PET and PCL with an increase in $\text{Ti}(\text{O}i\text{Pr})_4$ catalyst loading (A) and increasing blending time with 1.1 pph $\text{Ti}(\text{O}i\text{Pr})_4$ (B).

repeating ET and repeating CL units. As a result, the crystallinity of ET and CL chains will gradually decrease until a point at which the length of ET and CL blocks is too short to recrystallize in the copolymer backbone. The visual loss in crystallinity and a singular glass transition temperature value close to the theoretical value calculated from Flory-Fox's equation observed in the DSC thermogram will prove that the blend has transformed into a bulk of monophasic poly[(ET)_x-co-(CL)_y] without any homopolymer left.

Fig. 6 (A, B) show the catalysed blends' cooling and second heating curves (Table 4, Blends 1–10) obtained with DSC. In Fig. 6 (A), cooling thermograms arranged by the catalysts' transesterification effectiveness determined by ^1H NMR spectroscopy indicated that with increased catalytic activity, PCL and PET homopolymer recrystallization peaks

gradually broaden, shift to a lower temperature, and eventually disappear. K.Y. Lim et al. has estimated that the minimum block lengths of ET and CL repeating units to recrystallize are three and six repeating units, respectively. Therefore, according to this result, as transesterification progresses, the length of ET and CL repeating units in the copolymer decreases until they are too short for recrystallization, as expected [25]. Notably, the recrystallization peaks of PCL disappear sooner than PET, possibly due to the combination of the higher reactivity of PCL with the catalyst and the shorter length of consecutive PET units required to recrystallize compared to PCL.

The recrystallization peak of PCL first disappears in the $(\text{Bu})_2\text{SnO}$ -catalysed blend (Table 4, Blend 7), while PET recrystallization peaks were visible in DSC thermograms of all catalysed blends except for Ti

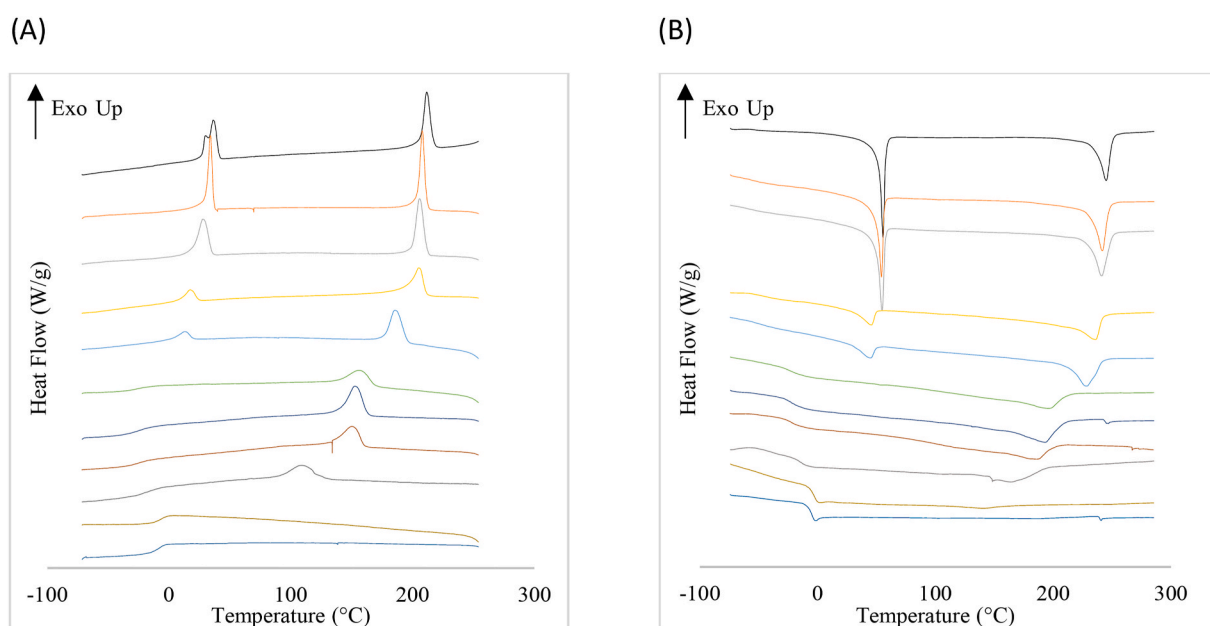


Fig. 6. Cooling curves at a rate of 10 °C per min of all the catalysed blends investigated in this study (A) and second heating curves of all the catalysed blends investigated in this study at a rate of 10 °C per min (B). Curves are arranged in the following order according to the catalysts' effectiveness determined by ^1H NMR spectroscopy: Uncatalysed (black), NaOEt (orange), La(acac)₃ (silver), NaOMe (yellow), Al(acac)₃ (light blue), SnO(Bu)₂ (green), Ti(OiPr)₄ (deep blue), Fe(acac)₃ (brown), Ti(acac)₄ (gray), Ti(OBu)₄ (golden) and Ti(OEt)₄ (light teal). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

(OEt)₄ and Ti(OBu)₄, as indicated by the gold and light teal curves (Fig. 6, A). Based on the block length estimated in Table 4, the DSC thermolysis indicates that ET and CL repeating units cannot recrystallize when their lengths are reduced to less than three and seven in the copolymer structure, respectively. Therefore, the recrystallization behavior observed in the DSC thermogram was consistent with the block lengths required for PET and PCL to recrystallize, as suggested by the literature [25], which validates the accuracy of block length of ET and CL repeating units estimates derived from ¹H NMR data.

Table S3 summarizes all the thermal properties obtained with DSC thermograms. Among the catalysed blends, the copolymer's new transition temperature (*T_g*) becomes more apparent as the catalytic activity increases, signalling the transition to an amorphous material. The observed *T_g* progressively merged from binary values of −56.6 °C and 78 °C, an uncatalyzed blend, to a singular value at −2.76 °C in the Ti(OBu)₄ catalysed blend. This gradual convergence in *T_g* can be explained by the reduction in flexibility of CL blocks when connected to the more rigid ET blocks in the copolymer and vice versa for the ET blocks. Therefore, the respective *T_g* of PCL and PET will shift closer as transesterification advances and become a singular *T_g* when a statistical copolymer is formed, as predicted by the Flory-Fox equation. Ti(OEt)₄ and Ti(OBu)₄ catalysed blends exhibit comparable *T_g* to the empirical *T_g* 7.55 °C calculated for an equimolar PET-PCL blend using Flory-Fox's equation, indicating that poly[(ET)₂-co-(CL)₂] synthesized using these catalysts is homogeneous.

The second heating curves show the gradual decline of the PET and PCL crystallinities in a similar trend as the recrystallization peaks. The crystallinities of PCL and PET were calculated using Equation (7), where *W_g* is the weight fractions of PET and PCL, Δ*H_m* is the melting enthalpy of individual polymers from the DSC curve, and Δ*H_m*^o is the melting enthalpy of their perfect crystals (PET = 140 J/g [50] and PCL = 136 J/g [51], respectively).

$$X_c \% = \frac{\Delta H_m}{\Delta H_m^o \times W_g} \times 100 \quad (7)$$

The immiscibility constraining the polymer chains can explain the slight drop in crystallinity in the uncatalyzed blend compared to the measurements of respective pure homopolymers. In addition to displaying a sharp singular *T_g*, the absence of crystallinity was observed in Ti(OEt)₄ and Ti(OBu)₄ catalysed blends, further corroborating that the poly[(ET)₂-co-(CL)₂] synthesized are highly amorphous, and no unreacted homopolymers were present. Similar to semicrystalline PBAT, some Ti(OBu)₄ catalysed blends show subtle melting peaks, which are possibly due to some regularities arising from a trivial amount of ET repeating units longer than 3 present in the copolymer backbone. It is worthy to note that the thermal properties suggest that copolymers, where the length of ET have been significantly reduced, may have limited application based on their low *T_g* and amorphous nature. It would therefore require a balance between desired mechanical properties and biodegradability, achieved based on the length of ET segments.

As the degree of transesterification significantly changes the thermal properties observed in the DSC thermogram, it is unsurprising to observe no disparity between various blending times from the DSC thermal analysis (Fig. S25). Accordingly, a blend catalysed by Ti(OBu)₄ 0.6 pph produces a broad PET melting and recrystallization peak, while an even less transesterified 0.35 pph Ti(OBu)₄ catalysed blend results in visible PET and PCL melting and recrystallization peaks (Fig. S26). These observations reaffirm that Ti(OBu)₄ loading at 0.6 pph or below is insufficient to yield a poly[(ET)_x-co-(CL)_y] with an average of ET repeat units lower than three from an equimolar blend.

3.3. Molecular mass and reaction mechanisms

The molecular weight distributions (Đ) obtained from GPC for THF soluble blends and PCL control samples are shown in Table 5. The *M_n* of PCL control samples obtained from GPC are in good agreement with

Table 5
Molecular weight distribution determined by GPC.

Samples ^a	<i>M_w</i> ^b	<i>M_n</i> ^b	Đ ^b
Pristine PCL	85500 ± 500	67800 ± 400	1.26 ± 0.01
PCL control 1	75300 ± 200	52500 ± 100	1.43 ± 0.01
PCL control 2	51600 ± 700	30700 ± 600	1.61 ± 0.11
PCL control 3	18700 ± 300	11000 ± 200	1.70 ± 0.00
PCL control 4	27000 ± 100	15500 ± 100	1.74 ± 0.01
Blend 6	31100 ± 470	16200 ± 280	1.92 ± 0.01
Blend 8	24100 ± 100	13700 ± 0	1.76 ± 0.00
Blend 12	30900 ± 300	17200 ± 200	1.79 ± 0.01
Blend 13	32700 ± 100	18300 ± 100	1.78 ± 0.00
Blend 14	29700 ± 200	18300 ± 500	1.63 ± 0.03
Blend 15	37600 ± 100	20700 ± 100	1.82 ± 0.01
Blend 16	36400 ± 300	20500 ± 200	1.77 ± 0.08
Blend 17 ^c	58700	47800	1.22
Commercial PBAT	67800 ± 900	43800 ± 4000	1.57 ± 0.14

^a Samples entry and the reaction conditions can be found in Table 1. Only blends that were soluble in THF were studied with GPC. *M_w* and *M_n* are rounded to the nearest 100 units and Đ to the nearest two decimal places.

^b Đ represents the average of three runs except for 0.35 pph Ti(OBu)₄ sample (blend 17). Experimental errors are calculated by the standard deviations of the triplicates GPC experiments on each sample.

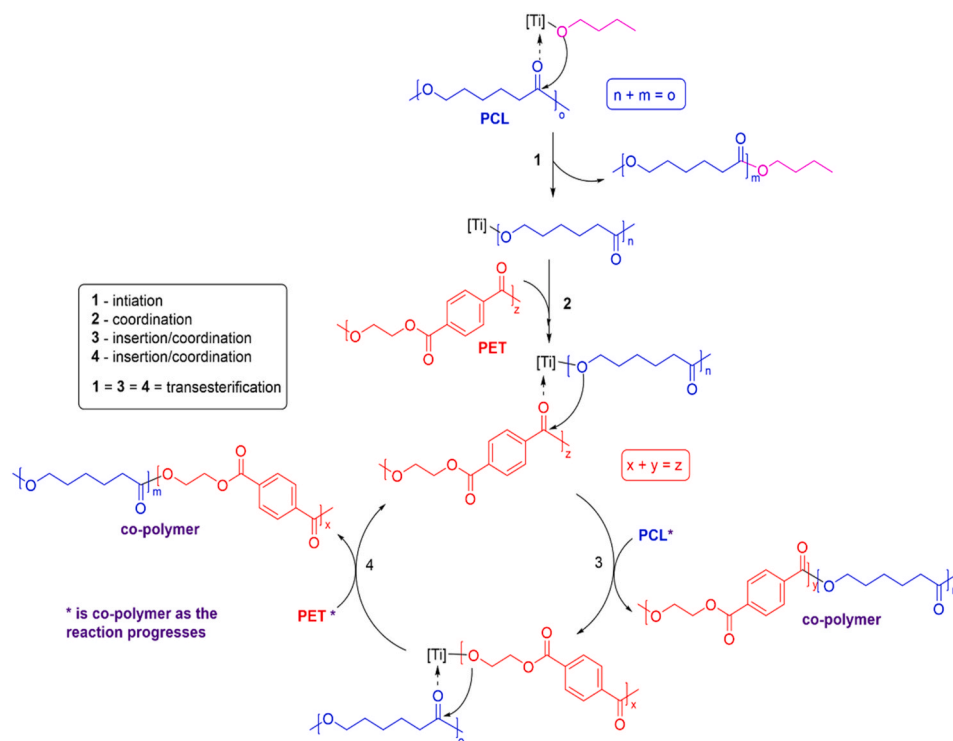
^c The samples were partial soluble in THF and the Đ data only reflect the soluble fraction and only single GPC measurement were obtained.

those of PCL control samples estimated from the ¹H NMR end group analysis (Table 3). Comparing the Đ of PCL control samples (Fig. S27), PCL catalysed by Al(acac)₃ (Table 5, PCL control 2) suffers the slightest reduction in the overall molecular weights (*M_n* and *M_w*) while PCL catalysed by NaOMe (Table 5, PCL control 3) had the most severe reduction. The lack of a potent nucleophilic ligand (acac[−]) in PCL control sample 2 likely minimizes chain cleavage and reduces the overall molecular weights; hence the Đ is similar to uncatalyzed PCL (Table 5, PCL control 1). The slight reduction in the overall molecular weights for the Al(acac)₃ sample compared to the uncatalyzed PCL sample is most likely due to unavoidable hydrolysis caused by the acidic Al³⁺ ion.

Ti(OBu)₄ and NaOMe catalysed PCL (Table 5, PCL control 3 and 4) resulted in significantly lower molecular weights than the other PCL controls. Although NaOMe is a poor transesterification catalyst, as indicated by NMR analysis, the ligand reduces the molecular weight of PCL most effectively (Table 5, PCL control 3). This result shows that the size of the ligand is the only factor that determines the amount of active PCL alkoxide generated via chain cleavage during the initial step of transesterification independent of the metal ion employed.

Since PET does not react with the catalyst as supported by the ¹H NMR spectra (Figs. S18–20), and uncatalysed PET and PCL did not result in observable evidence of transesterification, it is therefore reasonable to postulate that transesterification occurs as a two-step reaction, in which the ligand initiates the reaction with PCL to generate PCL alkoxide fragments (step 1, Scheme 2). With an acidic metal ion, PCL alkoxide fragments react with the PET carbonyl group, forming the first copolymer link that releases a PET alkoxide fragment (steps 2–3, Scheme 2). The PET alkoxide fragment, in turn, reacts with the PCL carbonyl group, forming the second copolymer link that recreates the PCL alkoxide fragment (step 4, Scheme 2), propagating transesterification through these cyclic exchanges of alkoxide species (steps 3 and 4).

The Đ graphs of catalysed blends share the same characteristic: a slight “shoulder” peak emerges from the central peak (Figs. S28 and S29). Since transesterification is postulated to occur through two steps of insertion-coordination which involves a random process of chain cleavages and reconnections during the formation of the copolymer structure, some lower molecular weight fragments are inevitable by-products. These fragments give rise to the visible “shoulder” peak on the Đ graphs. As a result, the polydispersity index (PDI) of poly[(ET)₂-co-(CL)₂] synthesized by Ti(OBu)₄ ranges from 1.6 to 1.9 (Table 5, Blends 6, 12–17). Furthermore, the average molecular weight of Ti(OEt)₄ catalysed blend (Table 5, Blend 8) is lower than Ti(OBu)₄



Scheme 2. The proposed transesterification pathways between PET and PCL through insertion-coordination mechanism.

catalysed blend (Table 5, Blend 6). The results show that a more active ligand will lead to a lower overall molecular weight as an inevitable side effect of forming a poly[(ET)_x-co-(CL)_y] with a short block of ET repeating units. Fig. 7 shows a steady decrease in number average molecular weight (M_n) as transesterification ratios rise to about 40% and then plateaus at about 50%.

The molecular mass measured by GPC does not change significantly with blending time (Fig. S29); however, PDI increases readily with longer blending time, suggesting that prolonged blending may induce

unwanted chain cleavage (Fig. S30). In Fig. S29, a comparison between poly[(ET)₂-co-(CL)₂] synthesized by 0.85 pph Ti(OBu)₄ (Table 5, blend 15) with a commercial PBAT sample indicates that poly[(ET)₂-co-(CL)₂] has a suboptimal molecular mass and could be improved by adding chain extenders.

3.4. Solubility and preliminary mechanical properties

Solubility in the same solvents is an excellent indicator of the miscibility and structural similarity between two polymers. poly[(ET)_x-co-(CL)_y] and PBAT are expected to have similar solubility parameters if their structures are similar. Therefore, poly[(ET)_x-co-(CL)_y] with randomized and short blocks of ET and CL repeating units should dissolve in common organic solvents that are highly soluble for PBAT, but poly[(ET)_x-co-(CL)_y] consists of long blocks or unreacted binary blend will remain insoluble; instead, these are more likely to dissolve in PET soluble solvents such as trifluoroacetic acid (TFA), and therefore, solubility test can also indicate the presence of unreacted PET homopolymers. Transesterification should progress the catalysed blends from insoluble to partially soluble before dissolving entirely in the solvents that are soluble for PBAT when length of ET blocks reduction reaches a critical length in the copolymer.

As discussed in the GPC section, the M_n of Ti(OBu)₄ catalysed blends (Table 5, Blends 6, 11–16) is substantially lower than commercial PBAT. For this reason, it is essential to find relevant solubility tests conducted on PBAT samples with comparable M_n (24400 g/mol) in the literature so that the solubility observed for poly[(ET)_x-co-(CL)_y] in the tested solvents is primarily due to the structural similarity and not influenced by the molecular weight [43].

Table 6 shows the different solubility of the blends catalysed by various catalysts in five organic solvents. Since PCL is highly soluble in all the tested solvents, the insolubility is postulated to be due to either unreacted PET or long ET blocks in poly[(ET)_x-co-(CL)_y]. Therefore, the solubility can be related to the maximum consecutive ET units in a poly[(ET)_x-co-(CL)_y] structure soluble in each solvent. For instance, chloroform and dichloromethane (DCM) display the highest tolerance for

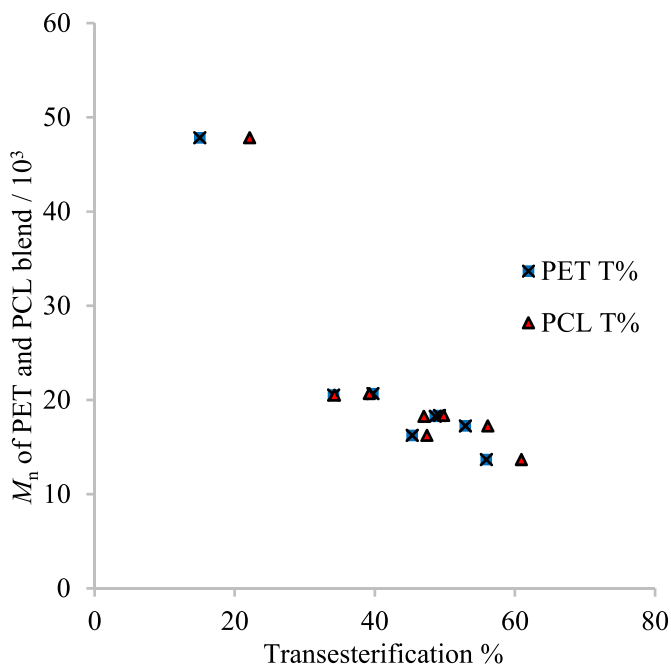


Fig. 7. The relationship between M_n of poly[(ET)_x-co-(CL)_y], determined by GPC, and transesterification ratios in THF soluble blends.

Table 6

Solubility of PET-PCL blends with different catalysts in solvents that are reported to be highly soluble for PBAT in literature [43].

Samples ^a	THF	Aniline	Chloroform	Chloroethylene	DCM
Blend 1	I ^b	I	I	I	I
Blend 2	I	I	I	I	I
Blend 3	I	I	I	I	I
Blend 4	I	I	S	I	S
Blend 5	I	I	I	I	I
Blend 6	S	P	S	S	S
Blend 7	P	P	P	P	P
Blend 8	S	S	S	S	S
Blend 9	I	P	P	P	P
Pristine PCL	S	S	S	S	S
Pristine PET	I	I	I	I	I

^a Sample entry refer to Table 1.

^b Solubility is based on visual inspection and examples are as shown in Fig. S31. I = Insoluble, P = Partial and S = Highly soluble.

repeating ET units and can completely dissolve poly[(ET)_x-co-(CL)_y] from the blend catalysed by Fe(acac)₃ (Table 6, Blend 4) with an estimated average block length of 4–5 ET repeating units. At the same time, tetrahydrofuran (THF) can only dissolve poly[(ET)_x-co-(CL)_y] when most of the backbone consists of two or fewer repeating ET units.

Samples that appear to be solid and insoluble must contain a lot of unreacted PET homopolymers. Meanwhile, partially soluble samples with gel-like appearances could be homogenized copolymers with long blocks of ET repeating units incorporated into the backbone without remaining unreacted PET homopolymer. Accordingly, blends catalysed by Ti(OBu)₄ and Ti(OEt)₄ (Table 6, Blends 6 and 8) were completely soluble in all tested solvents, demonstrating that poly[(ET)₂-co-(CL)₂] has both structural and intermolecular interactions similar to PBAT.

As mentioned in Section 3.2, the mechanical properties of poly[(ET)_x-co-(CL)_y] will vary significantly depending on the crystallinity due to the different degrees of transesterification. Since the most interesting copolymer synthesized with 0.85 pph of Ti(OBu)₄ (Blend 15, Table 2) is a translucent, flexible solid, and soluble in DCM at ambient conditions (25 °C, 1 bar), it is possible to prepare samples for mechanical testing by solution casting and compare them to commercial PBAT samples using the same method. Preliminary results indicated that this copolymer had a Young's Modulus of 64.0 ± 2.6 MPa and ultimate tensile strength of 6.7 ± 0.1 MPa, which are slightly lower than a commercial PBAT sample (Young's Modulus of 72.9 ± 0.9 MPa and ultimate tensile strength of 9.6 ± 0.6 MPa). The elongation at break of the copolymer sample is 125.6 ± 12.9%, substantially lower than 489.6 ± 78.4% for commercial PBAT. From Table 5, the difference in mechanical properties is likely attributed to the lower molecular mass of the copolymer compared to PBAT. Methods for mitigating this is the focus future work.

4. Conclusions

The activities of catalysts used in this study descend in the following order: Ti(OEt)₄ > Ti(OBu)₄ ≫ Ti(acac)₄ > Fe(acac)₃ ≥ Ti(OiPr)₄ > (Bu)₂SnO ≫ Al(acac)₃ > NaOMe ≫ NaOEt ≥ La(acac)₃.

Out of all the catalysts screened, only Ti(OEt)₄ and Ti(OBu)₄ successfully created a copolymer structure that resembles the randomness of PBAT. Blends catalysed by metal complexes cannot produce fully randomized copolymers without a highly acidic metal ion ligand or a basic and linear ligand. Furthermore, the steric bulk of the ligand significantly hinders the reaction, resulting in four to five average consecutive ET units in Ti(OiPr)₄ and Ti(acac)₄ catalysed blends, compared to two in Ti(OBu)₄ and Ti(OEt)₄ catalysed blends. Thus, a sterically unhindered nucleophilic ligand is preferred to maximize transesterification. As a result, metal ions and ligands both play essential roles in promoting transesterification between polyesters, which is consistent with the description of insertion-coordination mechanism. Nevertheless, it has been found that metal complexes composed of acidic

metal ions and bulky ligands, such as Ti(acac)₄, exhibit better catalytic activity than those composed of weakly acidic ions and nucleophilic ligands, such as NaOMe. Therefore, customizing the catalyst based on changing the metal ion could be helpful in polyester or polycarbonate blend compatibilization using catalytic transesterification.

Given that PET is not reactive with either catalyst and PCL alone, the molecular mass of PCL is significantly reduced with strong nucleophilic ligand and this help generating PCL alkoxide species is most likely to initiate transesterification. The result leads to the hypothesis that transesterification propagates through the exchange of cyclic PET and PCL alkoxide species.

With vanished recrystallization peaks in DSC and a singular T_g, it is evident that the binary blend of PET and PCL catalysed by Ti(OEt)₄ and Ti(OBu)₄ has become a monophasic poly[(ET)_x-co-(CL)_y] bulk with no remaining homopolymers present.

Solubility tests revealed that poly[(ET)₂-co-(CL)₂] is fully soluble in the same solvents that are common for PBAT, which also provides evidence of the absence of unreacted PET homopolymer. Different solvents have varied tolerance to the length of ET repeating units in the polymer's backbone. Chloroform and DCM, for instance, can dissolve poly[(ET)_x-co-(CL)_y] with an average number of ET repeat units of four, while THF can only dissolve poly[(ET)_x-co-(CL)_y] with an average of two. This difference in solubility could be useful in separating poly[(ET)_x-co-(CL)_y] with different lengths of ET repeating units through precipitation.

Overall, the randomness of poly[(ET)_x-co-(CL)_y] largely depends on the composition of the catalyst and their loadings. Contrary to this, blending time does not affect the extent of the reaction, and 2 min of blending time are sufficient to achieve reaction equilibrium. Therefore, synthesizing the copolymer can be upscaled to a more robust and continuous process, such as reactive extrusion without high operational costs.

A high extent of transesterification is likely accompanied by a significant reduction in molecular weight, based on the GPC analysis. For this reason, further research is underway focusing on the mechanical properties and changes in microstructure by altering blend formulations. This will provide the foundation for determining the optimal formulations to create the copolymer with biodegradability and mechanical properties comparable to PBAT.

CRedit authorship contribution statement

W.H. Leung: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft. **E.M. Leitao:** Methodology, Writing – review & editing, Supervision. **C.J.R. Verbeek:** Conceptualization, Funding acquisition, Methodology, Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymer.2023.126297>.

References

- [1] US EPA, O., Plastics: material-specific data, Retrieved Jun 23, 2023, from, <https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/plastics-material-specific-data>, 2017.
- [2] V. Jankauskaite, G. Macijauskas, R. Lygaitis, Polyethylene terephthalate waste recycling and application possibilities: a review, *Medziagotyra* 14 (2008) 119–127.
- [3] F. Welle, Twenty years of PET bottle to bottle recycling—an overview, *Resour. Conserv. Recycl.* 55 (11) (2011) 865–875, <https://doi.org/10.1016/j.resconrec.2011.04.009>.
- [4] A.M. Al-Sabagh, F.Z. Yehia, G. Eshaq, A.M. Rabie, A.E. ElMetwally, Greener routes for recycling of polyethylene terephthalate, *Egyptian Journal of Petroleum* 25 (1) (2016) 53–64, <https://doi.org/10.1016/j.ejpe.2015.03.001>.
- [5] U. Witt, R. Müller, W. Deckwer, New biodegradable polyester-copolymers from commodity chemicals with favorable use properties, *J. Environ. Polym. Degrad.* 4 (4) (1995) 215–223, <https://doi.org/10.1007/BF02068676>.
- [6] I. Kleiber, C. Hetz, R.M. Kroppenstedt, R.-. Müller, W.-. Deckwer, Biodegradation of aliphatic-aromatic copolyesters by thermomonospora fusca and other thermophilic compost isolates, *Appl. Environ. Microbiol.* 64 (5) (1998) 1731–1735, <https://doi.org/10.1128/AEM.64.5.1731-1735.1998>.
- [7] S.J. Kim, H.W. Kwak, S. Kwon, H. Jang, S. Park, Synthesis, characterization and properties of biodegradable poly(butylene sebacate-Co-terephthalate), *Polymers* 12 (10) (2020) 2389, <https://doi.org/10.3390/polym12102389>.
- [8] J. Jian, Z. Xiangbin, H. Xianbo, An overview on synthesis, properties and applications of poly(butylene-adipate-co-terephthalate)–PBAT, *Advanced Industrial and Engineering Polymer Research* 3 (1) (2020) 19–26, <https://doi.org/10.1016/j.aiepr.2020.01.001>.
- [9] I. Acar, A. Kaşgöz, S. Özgümüş, M. Orbay, Modification of waste poly(ethylene terephthalate) (PET) by using poly(L-lactic acid) (PLA) and hydrolytic stability, *Polym.-Plast. Technol. Eng.* 45 (3) (2006) 351–359, <https://doi.org/10.1080/03602550600553267>.
- [10] D.P.R. Kint, A. Alla, E. Deloret, J.L. Campos, S. Muñoz-Guerra, *Synthesis, Characterization, and Properties of Poly(ethylene Terephthalate)/poly(1,4-Butylene Succinate) Block Copolymers* Elsevier BV, 2003, [https://doi.org/10.1016/s0032-3861\(02\)00938-2](https://doi.org/10.1016/s0032-3861(02)00938-2).
- [11] Y. Maeda, T. Maeda, K. Yamaguchi, S. Kubota, A. Nakayama, N. Kawasaki, S. Aiba, Synthesis and Characterization of Novel Biodegradable Copolyesters by Transesterification of Poly(ethylene Terephthalate) with Copoly(succinic Anhydride/ethylene Oxide), Wiley, 2000, [https://doi.org/10.1002/1099-0518\(20001215\)38:24<4478::aid-pola170>3.0.co;2-a](https://doi.org/10.1002/1099-0518(20001215)38:24<4478::aid-pola170>3.0.co;2-a).
- [12] L. Tan, Y. Chen, W. Zhou, F. Li, L. Chen, X. He, Preparation and biodegradation of copolyesters based on poly(ethylene terephthalate) and poly(ethylene glycol)/oligo(lactic acid) by transesterification, *Polym. Eng. Sci.* 50 (1) (2010) 76–83, <https://doi.org/10.1002/pen.21513>.
- [13] S. Heidary, B. Gordon, Hydrolyzable poly(ethylene terephthalate), *J. Environ. Polym. Degrad.* 2 (1) (1994) 19–26, <https://doi.org/10.1007/BF02073483>.
- [14] F. Yang, Y. Chen, S. Rwei, Synthesis and characterization of the temperature controllable shape memory of polycaprolactone/poly(ethylene terephthalate) copolyester, *Fibers Polym.* 23 (9) (2022) 2526–2538, <https://doi.org/10.1007/s12221-022-0005-x>.
- [15] K.Y. Lim, B.C. Kim, K.J. Yoon, Structural and physical properties of biodegradable copolyesters from poly(ethylene terephthalate) and polycaprolactone blends, *J. Appl. Polym. Sci.* 88 (1) (2003) 131–138, <https://doi.org/10.1002/app.11597>.
- [16] E. Chiellini, A. Corti, A. Giovannini, P. Narducci, A.M. Paparella, R. Solaro, Evaluation of biodegradability of poly(ϵ -caprolactone)/poly(ethylene terephthalate) blends, *J. Environ. Polym. Degrad.* 4 (1) (1996) 37–50, <https://doi.org/10.1007/BF02083881>.
- [17] K.Y. Lim, B.C. Kim, K.J. Yoon, The effect of molecular weight of polycaprolactone on the ester interchange reactions during melt blending with poly(ethylene terephthalate), *Polym. J.* 34 (5) (2002) 313–319, <https://doi.org/10.1295/polymj.34.313>.
- [18] Z.-P. Zhang, X.-L. Luo, Yuchen Lu, D.-Z. Ma, Transesterification of poly(ethylene terephthalate) with poly(ϵ -caprolactone), *Chin. J. Polym. Sci.* 18 (5) (2000) 405–412.
- [19] J. Hsu, J. Wong, Kinetic Modeling of Melt Transesterification of Diphenyl Carbonate and Bisphenol, A Elsevier BV, 2003, [https://doi.org/10.1016/s0032-3861\(03\)00605-0](https://doi.org/10.1016/s0032-3861(03)00605-0).
- [20] Jun, H. S., Kim, B. O., Kim, Y. C., Ho, N., Chang, S. I., & Woo, Biodegradable Plastics and Polymers 498.
- [21] Y. Tokiwa, T. Suzuki, Hydrolysis of copolyesters containing aromatic and aliphatic ester blocks by lipase, *J. Appl. Polym. Sci.* 26 (2) (1981) 441–448, <https://doi.org/10.1002/app.1981.070260206>.
- [22] R.S. Porter, L. Wang, *Compatibility And Transesterification in Binary Polymer Blends* Elsevier BV, 1992, [https://doi.org/10.1016/0032-3861\(92\)90866-u](https://doi.org/10.1016/0032-3861(92)90866-u).
- [23] M. Coltell, C. Toncelli, F. Ciardelli, S. Bronco, Compatible blends of biorelated polyesters through catalytic transesterification in the melt, *Polym. Degrad. Stabil.* 96 (5) (2011) 982–990, <https://doi.org/10.1016/j.polydegradstab.2011.01.028>.
- [24] S.S. Park, S.H. Chae, S.S. Im, Transesterification and crystallization behavior of poly(butylene succinate)/poly(butylene terephthalate) block copolymers, *J. Polym. Sci., Part A: Polym. Chem.* 36 (1) (1998) 147–156, [https://doi.org/10.1002/\(SICI\)1099-0518\(19980115\)36:1<147::AID-POLA19>3.0.CO;2-J](https://doi.org/10.1002/(SICI)1099-0518(19980115)36:1<147::AID-POLA19>3.0.CO;2-J).
- [25] M.L. Di Lorenzo, P.L. Pietra, M.E. Errico, M.C. Righetti, M. Angiuli, Poly(butylene terephthalate)/poly(ϵ -caprolactone) blends: miscibility and thermal and mechanical properties, *Polym. Eng. Sci.* 47 (3) (2007) 323–329, <https://doi.org/10.1002/pen.20711>.
- [26] T. Bubmann, A. Seidel, V. Altstädt, *Transparent PC/PMMA Blends via Reactive Compatibilization In a Twin-Screw Extruder* MDPI AG, 2019, <https://doi.org/10.3390/polym11122070>.
- [27] M. Fiorini, F. Pilati, C. Berti, M. Toselli, V. Ignatov, *Reactive Blending of Poly(ethylene Terephthalate) and Bisphenol-A Polycarbonate: Effect of Various Catalysts and Mixing Time on the Extent of Exchange Reactions* Elsevier BV, 1997, [https://doi.org/10.1016/s0032-3861\(96\)00520-4](https://doi.org/10.1016/s0032-3861(96)00520-4).
- [28] F. Pilati, E. Marianucci, C. Berti, Study of the reactions occurring during melt mixing of poly(ethylene terephthalate) and polycarbonate, *J. Appl. Polym. Sci.* 30 (3) (1985) 1267–1275, <https://doi.org/10.1002/app.1985.070300330>.
- [29] L.C. Mendes, P.S.C. Pereira, V.D. Ramos, Effectiveness of the transesterification catalyst on the thermal, dynamic-mechanical and rheological properties of PET/PC reactive melting blends, *Macromol. Symp.* 299–300 (1) (2011) 183–189, <https://doi.org/10.1002/masy.200900112>.
- [30] O. Meziane, M. Guessoum, A. Bensedira, N. Haddaoui, Thermal characterization of reactive blending of 70PC/30PET mixtures prepared in the presence/absence of samarium acetylacetonate as a transesterification catalyst, *J. Polym. Eng.* 37 (6) (2017) 577–586, <https://doi.org/10.1515/polyeng-2016-0190>.
- [31] A.N. Wilkinson, E.M.I. Nita, M.L. Clemens, E. Jöbstl, J.P.A. Fairclough, Structure development in reactive polycarbonate-poly(ethylene terephthalate) melt blends, *J. Macromol. Sci. Phys.* 44 (6) (2005) 1087–1102, <https://doi.org/10.1080/00223405000364585>.
- [32] A.N. Wilkinson, D. Cole, S.B. Tattum, The effects of transesterification on structure development in PC-PBT blends, *Polym. Bull. (Berlin)* 35 (6) (1995) 751–757, <https://doi.org/10.1007/BF00294959v>.
- [33] S. Yan, W. Lai, M. Zhang, G. Wu, Reactive blending of isosorbide-based polycarbonates: catalytic selectivity and transesterification mechanism, *Polymer (Guilford)* 210 (2020), 122999, <https://doi.org/10.1016/j.polymer.2020.122999>.
- [34] D.P.R. Kint, A. Alla, E. Deloret, J.L. Campos, S. Muñoz-Guerra, *Synthesis, Characterization, and Properties of Poly(ethylene Terephthalate)/poly(1,4-Butylene Succinate) Block Copolymers* Elsevier BV, 2003, [https://doi.org/10.1016/s0032-3861\(02\)00938-2](https://doi.org/10.1016/s0032-3861(02)00938-2).
- [35] U. Witt, R.-. Müller, W.-. Deckwer, Evaluation of the biodegradability of copolyesters containing aromatic compounds by investigations of model oligomers, *J. Environ. Polym. Degrad.* 4 (1) (1996) 9–20, <https://doi.org/10.1007/BF02083878>.
- [36] I. Espinasse, R. Pétiaud, M. Llauro, A. Michel, Multinuclear NMR characterization of Co-cross-linking of ethylene-co-vinylacetate and ethylene-co-methylacrylate polymer blends in the presence of dibutyltin oxide, *Int. J. Polym. Anal. Char.* 1 (2) (1995) 137–157, <https://doi.org/10.1080/10236669508233869>.
- [37] E.C. Lopes Pereira, J.M. Farias Da Silva, R.B. Jesus, B.G. Soares, S. Livi, *Bronsted Acidic Ionic Liquids: New Transesterification Agents for the Compatibilization of Polylactide/ethylene-Co-Vinyl Acetate Blends* Elsevier BV, 2017, <https://doi.org/10.1016/j.eurpolymj.2017.10.003>.
- [38] L.C. Lins, S. Livi, J. Duchet-Rumeau, J. Gérard, Phosphonium ionic liquids as new compatibilizing agents of biopolymer blends composed of poly(butylene-adipate-co-terephthalate)/poly(lactic acid) (PBAT/PLA), *RSC Adv.* 5 (73) (2015) 59082–59092, <https://doi.org/10.1039/C5RA10241C>.
- [39] G.M. Gruter, L. Sipos, M. Adrianus Dam, Accelerating research into bio-based FDCA-polyesters by using small scale parallel film reactors, *Comb. Chem. High Throughput Screen.* 15 (2) (2012) 180–188, <https://doi.org/10.2174/138620712798868374>.
- [40] M.R. Meneghetti, S.M.P. Meneghetti, Sn(IV)-based organometallics as catalysts for the production of fatty acid alkyl esters, *Catal. Sci. Technol.* 5 (2) (2015) 765–771, <https://doi.org/10.1039/C4CY01535E>.
- [41] K. Tomita, H. Ida, Studies on the Formation of Poly(ethylene Terephthalate): 3. Catalytic Activity of Metal Compounds in Transesterification of Dimethyl Terephthalate with Ethylene Glycol Elsevier BV, 1975, [https://doi.org/10.1016/0032-3861\(75\)90051-8](https://doi.org/10.1016/0032-3861(75)90051-8).
- [42] L. Zhou, G. Zhao, W. Jiang, Effects of catalytic transesterification and composition on the toughness of poly(lactic acid)/Poly(propylene carbonate) blends, *Ind. Eng. Chem. Res.* 55 (19) (2016) 5565–5573, <https://doi.org/10.1021/acs.iecr.6b00315>.
- [43] Z. Wang, M. Zhang, Z. Liu, S. Zhang, Z. Cao, W. Yang, M. Yang, Compatibilization of the Poly(lactic Acid)/poly(propylene Carbonate) Blends through in Situ Formation of Poly(lactic Acid)-B -poly(propylene Carbonate) Copolymer Wiley, 2017, <https://doi.org/10.1002/app.46009>.
- [44] Atomistic simulation group in the materials department of imperial College. Database of ionic radii, Retrieved Jan 16, 2023, from, <http://abulafia.mt.ic.ac.uk/shannon/ptable.php>.
- [45] I. Espinasse, R. Pétiaud, M. Llauro, A. Michel, Multinuclear NMR characterization of Co-cross-linking of ethylene-co-vinylacetate and ethylene-co-methylacrylate polymer blends in the presence of dibutyltin oxide, *Int. J. Polym. Anal. Char.* 1 (2) (1995) 137–157, <https://doi.org/10.1080/10236669508233869>.
- [46] S. Khatsee, D. Daranarong, W. Punyodom, P. Worajittiphon, Electrospinning Polymer Blend of PLA and PBAT: Electrosustainability-Solubility Map and Effect of Polymer Solution Parameters toward Application as Antibiotic-Carrier Mats, Wiley, 2018, <https://doi.org/10.1002/app.46486>.
- [47] I.R. Herbert, *NMR Spectroscopy Of Polymers* (Softcover Reprint of the Original, first ed. 1993, Springer, 2012).
- [48] O. Persenaire, M. Alexandre, P. Degée, P. Dubois, Mechanisms and kinetics of thermal degradation of poly(ϵ -caprolactone), *Biomacromolecules* 2 (1) (2001) 288–294, <https://doi.org/10.1021/bm0056310>.
- [49] J. Devaux, P. Godard, J.P. Mercier, Bisphenol-A polycarbonate-poly(butylene terephthalate) transesterification. I. Theoretical study of the structure and of the degree of randomness in four-component copolycondensates, *J. Polym. Sci. Polym.*

- Phys. Ed 20 (10) (1982) 1875–1880, <https://doi.org/10.1002/pol.1982.180201010>.
- [50] M. Guessoum, N. Haddaoui, F. Fenouillot-Rimlinger, Effects of reactive extrusion and interchange catalyst on the thermal properties of polycarbonate/poly (ethylene terephthalate) system, *Int. J. Polym. Mater.* 57 (7) (2008) 657–674, <https://doi.org/10.1080/00914030801891195>.
- [51] M.V.B. Nicolino, A.d.A. Lucas, M.C. Branciforti, Reactive extrusion of poly (butylene succinate-co-adipate) and poly (ϵ -caprolactone) biodegradable blends through titanium-based transesterification catalyst, *Polym. Degrad. Stabil.* 181 (2020), 109320, <https://doi.org/10.1016/j.polymdegradstab.2020.109320>.