Pyridine dicarboxylic acid derived polyesters: Prospects for developing safe, circular and sustainable materials

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The use of aromatic chemicals as key ingredients in (bulk) applications such as coatings, paints, and packaging materials is inevitable. The high dependency on the aromatics is due to their rigid characteristics that offer enhanced properties resulting in superior application performance. The development of biobased aromatic chemicals (drop-in's) or renewable rigid alternatives is necessary for the transition towards sustainable products and to alleviate society's reliance on fossil feedstock primarily being used to produce such aromatic chemicals. This mini-review highlights the potential of renewable rigid pyridine dicarboxylic acid building blocks in producing polyesters with intriguing properties for various applications.

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Introduction

Aromatics such as benzene, toluene, and xylene (BTX), and similar structurally related chemicals are primarily used in bulk application areas including coatings and paint, engineering plastics, polymers and rubber, and packaging. These base chemicals alone account for over 40 % of the total volume that is industrially produced from fossil feedstocks with the consequences of negative environmental impacts, including (toxic) waste production, pollution, high energy consumption, and CO_2 emissions. The transition towards sustainable chemical production for a safer and circular economy can significantly mitigate these problems. This transition can be achieved by either developing cost-effective strategies to produce the base chemicals from feedstocks such as biomass, algae, and agricultural waste, or by developing renewable alternatives that outperform or perform similarly to base chemicals in the targeted applications.

Over the last decade, academic and industrial researchers have made several efforts to investigate the efficient synthesis of aromatic base chemicals using lignocellulosic and other biomass as feedstocks [1]. Despite significant progress, none of the strategies explored have reached commercial-scale production for various reasons. The key issues include a lack of technological developments in obtaining target chemicals with a high yield and selectivity and higher associated production costs compared to benchmarked standards due to complex and multistep downstream processing. Nevertheless, many biobased drop-in chemicals and renewable alternatives have been explored for various applications ranging from home and personal care products to automotive and aerospace industries [2−4].

2,5-Furandicarboxylic acid (2,5-FDCA) is an excellent example of a renewable alternative to terephthalic acid (PTA) in polyester synthesis with superior gas barrier properties and mechanical performance [5]. These characteristics enhance the potential of poly(ethylene furanoate) (PEF) polymers for everyday applications such as bottles, packaging materials, textiles, and coatings [6].

Pyridine dicarboxylic acid (PDC) is a renewable building block currently under investigation, especially in producing polyester polymers and associated applications. Six isomers are known to exist in the PDC family. Among them, quinolinic acid (2,3-PDC), cinchomeronic acid (3,4-PDC), and dinicotinic acid (3,5-PDC) are rarely investigated as no (recent) literature was found describing their polymer properties. Quinolinic acid is known to be highly toxic (an excitotoxin in the central nervous system), explaining its negligence in any applications [7]. However, no clear arguments were found for the other two isomers (3,4 and 3,5-PDC). The remaining three isomers in the PDC family, namely, lutidinic acid (2,4-PDC), isocinchomeronic acid (2,5-PDC), and dipicolinic acid (2,6-PDC) have gradually been receiving attention lately in polyester synthesis for their potential applications in packaging and other areas.

Given its versatility, polyethylene terephthalate (PET) is widely used in various applications, such as

textile fibres, packaging (beverage and food industries), household products, and electrical appliances. The global demand is anticipated to rise to 35.7 million metric tonnes by 2030, up from the volume of 25.5 million metric tonnes in 2022. The quest for a transition towards biobased chemicals and materials for a sustainable, safe, and circular economy led to the identification of PEF as a renewable alternative to PET. The furanic structure of PEF not only brings in the renewable counterpart, but it also provides the superior properties (gas barrier performance, mechanical strength, and heat resistance) of polyester, which expands PEF's potential in several other applications beyond the products where PET is primarily used.

While the potential of PDC-derived polymers is being progressively explored in various application areas, the key properties such as glass transition (T_g) and melting transition (T_m) of polyesters synthesised from EG using the isomers of aromatics (p-terephthalic acid-PTA, isophthalic acid-IPA, and phthalic acid-PA), furanics (2,5-furandicarboxylic acid-2,5-FDCA, 2,4-furandicarboxylic acid-2,4-FDCA, and 3,4-furandicarboxylic acid-3,4-FDCA), and pyridinics (2,6-PDC, 2,5-PDC, and 2,4-PDC) have been compared and are presented in Table 1. Given the commercial relevance of EG-derived polymeric materials in various applications, it is intriguing to compare the available properties data of PDC-derived polymers with the other two analogues.

Among the three isomers, only 2,6-PDC has been investigated thus far for synthesising polyester using EG. The preliminary data reveals that the polyester has a T_g of 75 °C which is 2 °C higher than PET and 4 °C lower than PEF. The authors did not observe the

melting transition in differential scanning calorimetry (DSC) when measured up to 300 °C [8]. Unfortunately, no information was available on whether the crystallinity can be induced by an annealing procedure to determine the T_m. Though the polymer properties of the other two isomers (2,5- and 2,4-PDC) have not yet been investigated, it is too early to establish the structure and property correlations between the isomers.
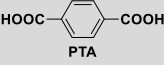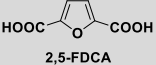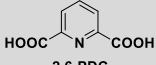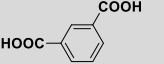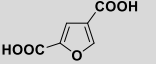
This perspective will mainly emphasise the three isomers of PDC that have been studied as monomers in synthesising various polyesters via different techniques. The orientation of the carboxylic acid groups at different positions in the isomers results in polymers with distinct properties that enhance their prospective contributions in developing green and sustainable materials for a range of applications.

Synthesis of pyridine dicarboxylic acids (PDCs)

Very few reports describe sustainable routes to synthesise pyridine dicarboxylic acids. For instance, lignin was used as a feedstock to produce the two isome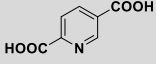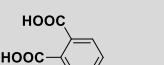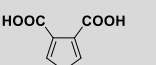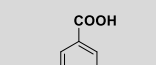rs of PDC, i.e., 2,4-PDC and 2,5-PDC via enzyme-mediated pathways [10,11]. The key intermediate, protocatechuic acid, is synthesised from vanillin which in turn is obtained via the oxidation of lignin using a bacterium *Rhodococcus jostii* RHA1 (*R.jostii*). The enzymes protocatechuate 4,5-dioxygenase and protocatechuate 2,3-dioxygenase catalyse the conversion of protocatechuic acid into 2,4-PDC and 2,5-PDC respectively. The protocatechuate dioxygenases favor the metacleavage followed by cyclisation using a nitrogen source (NH_4Cl) to give PDC (Scheme 1) [10,11]. McClintock and co-workers used glucose as a feedstock to demonstrate the gram scale production of the third isomer 2,6-pyridine

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Table 1

Thermal properties of EG-derived polyesters with aromatics, furanics [9], and pyridinic dicarboxylic acid isomers.

Aromatics	EG polyester		Furanics	EG polyester		Pyridinics	EG polyester	
	T_g (°C)	T_m (°C)		T_g (°C)	T_m (°C)		T_g (°C)	T_m (°C)
PTA	73	243	2,5-FDCA	79	209	2,6-PDC	75	–
IPA	55	235	2,4-FDCA	73	–	2,5-PDC	N.A.*	N.A.
PA	38	–	3,4-FDCA	35	155	2,4-PDC	N.A.	N.A.

*Data not available.

Scheme 1
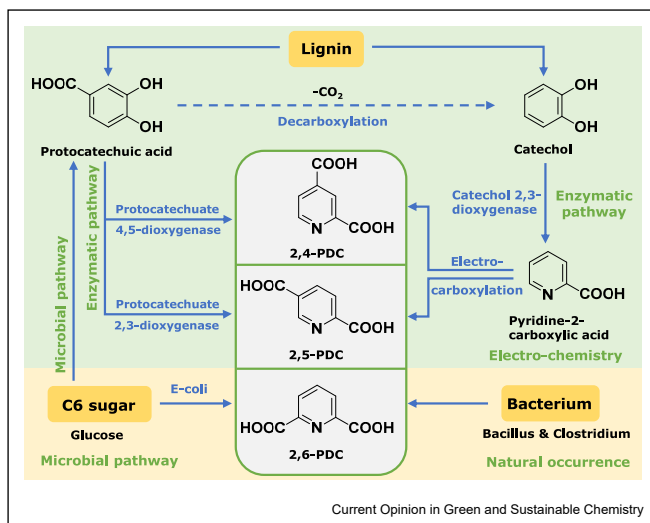
An overview of synthetic routes to produce 2,4-PDC and 2,5-PDC from lignin and glucose via protocatechuic acid or catechol using enzymes and electrochemistry (top section). The microbial pathway to produce 2,6-PDC from glucose and its natural occurrence in the bacterium is depicted at the bottom section of the scheme.

dicarboxylic acid (2,6-PDC) also known as dipicolonic acid, by using an industrial workhorse organism, *E. coli* [12]. Besides *E-coli*, the *Bacillus* and *Clostridium* species produce 2,6-PDC naturally up to 15 % of the dry weight of bacterial spores [13].

Next to the biotechnological strategies, an electrochemical process to produce 2,4-PDC and 2,5-PDC via the direct carboxylation of methyl pyridine-2-carboxylate in the presence of CO_2 has been described recently [14]. The selectivity of the carboxylation reaction was tuned by an undivided electrochemical cell, favoring the formation of 2,4-PDC and 2,5-PDC in a 6:1 ratio [14]. The catechol is a key intermediate in this strategy, which can be directly derived from lignin or obtained via the decarboxylation reaction of protocatechuic acid [15,16]. It was shown that the enzyme pseudomonas catechol 2,3-dioxygenase produces an unstable intermediate, 2-hydroxymuconic semialdehyde, from catechol, which is then cyclized in the presence of ammonia, yielding pyridine 2-carboxylic acid [17]. Besides lignin as a feedstock, an improved method to produce both protocatechuic acid and catechol from glucose via microbial synthesis was also reported by Wensheng et al. [15].

Polyesters derived from pyridine dicarboxylic acid

Polycondensation reactions are typically performed at higher temperatures in the presence of a catalyst to achieve high molecular weights and the required properties suitable for application demands. PET is one such polyester that is industrially produced via a melt condensation procedure in the presence of an antimony or titanium catalyst at temperatures between 275 and 285 °C under vacuum conditions. The high molecular weight PET (bottle-grade) is achieved further via a solid-state post condensation (SSPC) process. The new, renewable PEF is also synthesised under similar conditions, however, at a slightly lower temperature due to the thermal stability limitations of the furan moiety, resulting nonetheless in a polyester with a superior gas barrier and mechanical performance compared to PET [5].

It is known that introducing a bridging group between the benzene ring reduces the aromaticity of the cyclic system and decreases its thermal stability. Pyridine dicarboxylic acid is such a molecule and to be utilized as an effective monomer in polyester synthesis, its thermal stability must meet the conditions required for the polycondensation reaction.

In 1992, Briehl and Butenuth used thermogravimetric analysis (TGA) and DSC to examine the thermoanalytical behaviour of all six isomeric PDC thoroughly. The authors found that the isomers 2,4-PDC, 2,5-PDC, and 2,6-PDC with the carboxylic substituent in the 2 position, are thermally unstable at high temperatures (235−255 °C) and show low enthalpies of decomposition (melting followed by decomposition [29]. The nitrogen atom in the heterocyclic ring is hypothesized to be involved in the cleavage of CO_2 under elevated temperatures. Among the six isomers, it is found that the least stable isomer is 2,3-PDC (165 °C)

and the most stable are 3,4-PDC and 3,5-PDC, which have a decomposition temperature above 311 °C. The higher thermal stability of the latter isomers are due to the unlikely intermolecular hydrogen bond formation between the nitrogen atom and the carboxylic groups in the meta and para positions [29].

Enzymatic polymerisation

Given the poor thermal stability and the possible complexation (chelation) of the pyridine moiety with metals like Ti(IV), which is commonly used as a trans-esterification catalyst in the polycondensation reaction, Pellis et al. examined the use of enzymes as biocatalysts to synthesize polyesters from all three PDC isomers at moderately low temperatures (85 °C) [24]. The lipase B from Candida antarctica (CaLB) was employed as a catalyst for bulk (neat) and solution polymerization carried out in diphenyl ether as a solvent at 85 °C. The bulk approach was ineffective and resulted in oligoesters with molecular weights below M_n 1800 g mol^{-1} for all three diols, 1,4-butane diol (1,4-BDO), 1,6-hexane diol (1,6-HDO), and 1,8-octane diol (1,8-ODO) that were studied in combination with diethyl esters of 2,4-, 2,5-, and 2,6-PDC, respectively (Table 2). The solution method gave reasonably higher molecular weight polyesters especially when 1,8-ODO was used. For example, a polyester with M_n 14,300 g mol^{-1} was obtained by reacting 2,4-diethyl pyridine dicarboxylate with 1,8-ODO. The other two isomers, 2,5- and 2,6-PDC produced polyesters with molecular weights M_n of 8100 g mol^{-1} and M_n 3200 g mol^{-1} respectively [24]. Later, the authors attempted to increase the low molecular weight oligomers produced via the bulk technique. A two-step strategy was proposed in which the first step is bulk polymerisation, and followed by a thermal treatment of the obtained oligoesters in the second step. Several polyesters were investigated by subjecting the polymer to a thermal treatment of up to 180 °C for 24 h under air, nitrogen, and vacuum conditions. Even though not significant, a 2.7-fold increase in the molecular weight, i.e., from M_w 1000 to 2700 g mol^{-1} was observed for poly(1,4-butylene 2,4-pyridinedicarboxylate) [25].

Solution polymerisation

For decades, there has been an interest in investigating the polycondensation reaction under various conditions, such as low-to-high reaction temperatures, different feed ratios of the monomers employed, types of catalysts and their loading, and use of coupling reagents and solvents. In 1982, Tanaka et al., investigated the use of picryl chloride as a condensation agent for the reaction of 2,5-PDC with different aliphatic diols at room temperature in the presence of pyridine as a solvent (Table 2). A polyester yield of up to 89 % and a solution viscosity ca.1.0 was achieved within a reaction time of 5.0 h performed at 30 °C [19]. It is believed that the trinitrophenyl ester is an active intermediate that is formed when a carboxylic acid reacts with the salt that is produced by the reaction of pyridine and picryl chloride. The ester intermediate then rapidly reacts with an alcohol to form the new ester linkages building in the polyester chains [19]. Two decades later, Doan et al., followed the same procedure to produce polyesters using 2,6-PDC and various poly(ethylene glycol)s. The authors found that yields were satisfactory when 1.5 equivalents of picryl chloride-to-carboxylic acid groups were used [21]. Isfahani and Faghihi used a different approach to perform the polycondensation reaction. Starting from diacid chlorides of 2,5-PDC, various aromatic diols were reacted in the presence of pyridine as base and N,N′-dimethyl acetamide (DMAc) as solvent. The polyesters had yields above 80 % and molecular weights ranged from M_n 14,000 and 22,000 g mol^{-1} [22].

Melt polycondensation

The first known melt polycondensation reaction of pyridine dicarboxylic acid was reported 62 years ago. In 1962, Broadhead and coworkers of the Standard Oil company (currently known as ExxonMobil), developed water-soluble resins for the coating industry using 2,5-PDC and diethylene glycol. Without using a catalyst, the two monomers were mixed at a 1:1 ratio and heated to 200 °C for 30 min and at 175 °C for 8 h resulting in a resin that was used as a protective coating material and eventually dissolved in an aqueous solution at temperatures ranging between 15 °C and 80 °C [18]. Using a Titanium(IV) isobutoxide (Ti(O-Bu)$_4$) or Titanium(IV) isopropoxide (Ti(O-iPr)$_4$) catalyst in the melt polycondensation reaction between 2,6-PDC and with various aliphatic diols resulted in the formation of the oligomers. The polymerisation reaction performed at 260 °C using 1,3-propane diol (1,3-PDO) resulted in a material with a glass transition (T_g) 30 °C and a melting transition (T_m) of 162 °C [20]. In another study, the polycondensation reaction was performed at a slightly lower temperature (180 °C). Inherent viscosities in the range 0.29–0.30 g dL^{-1} were reported when using diols such as EG, 1,4-BDO, and 1,6-HDO [8].

A patent application from Biome Bioplastics, describes the synthesis of a copolyester polybutyrate adipate pyridine dicarboxylate (PBAP) that was prepared using the diethyl ester of 2,4-PDC and 2,5-PDC in combination with diethyl adipate, respectively and with 1,4-BDO [30]. In line with previous reports, Ti(O-Bu)$_4$ was used as a catalyst and the polymerization reaction was performed at 180 °C for 17 h. The molecular weights of the resulting polymers were determined by ^{1}H NMR (using repeating units) and estimated to be 4000 g mol^{-1} for 2,4-PBAP and 4200 g mol^{-1} for 2,5-PBAP. Thermal analyses of 2,5-PBAP showed two distinct T_gs (−35.3 °C and 41.9 °C) and one T_m at 105.9 °C. In the case of 2,4-PBAP, only one T_g

Table 2

Summary of PDC-derived polyesters and their properties.

Entry	PDC	Diol(s)	Type	Polymerization conditions				M_n (10^4) (g mol^{-1})	T_g (°C)	T_m (°C)	Year
				Solvent	Catalyst	Temp. (°C)	Time (h)				
1	2,5-PDC	DEG[a]	Melt	–	–	175/200	8	N.A.*	N.A.	40−50	1962 [18]
2	2,5-PDC	C2−C12[b]	Solution	Pyridine	Picryl-Cl	RT[c]	5−18	N.A.	N.A.	N.A.	1982 [19]
3	2,6-PDC	1,3-PDO	Melt	–	Ti(O-Bu)$_4$	260	1.5−2	N.A.	30	162	2003 [20]
4	2,6-PDC	PEG 400−1000[d]	Solution	Pyridine	Picryl-Cl	RT[c]	2−50	2.1−3.31	–30	–	2006 [21]
5	2,5-PDC-Cl[e]	HO-Ar-OH[f]	Solution	Pyridine	DMAc[g]	0−80	12	1.4−2.2	N.A.	N.A.	2009 [22]
6	2,6-PDC-Et[h]	C2−C6[i]	Melt	–	Ti(O-iPr)$_4$	90−180	1	N.A.	8−161	N.A.	2011 [8]
7	2,4-& 2,5-PDC-Et + DEA[j]	1,4-BDO	Melt	–	Ti(O-Bu)$_4$	110−180	20	0.4−0.42	−31 to −35	106	2016 [11]
8	2,6-PDC-Me + DEBF[k]	EG	Melt	–	Zn(OAc)$_2$ + Ti(O-Bu)$_4$	180−240	3−6	1.3−2.6	62−66	–	2016 [23]
9	2,4-,2,5-& 2,6-PDC-Et[l]	C4,C6,C8	Neat & Solution	Diphenyl ether	iCaLB	85	90	0.18−1.43	−10 to −29	88−133	2019 [24]
10	2,4-PDC-Et[m]	1,4-BDO	Melt	–	–	140−180	24	0.16	N.A.	N.A.	2020 [25]
11	2,5-& 2,6-PDC-Cl[n]	1,10-DD[o]	Melt	–	–	80−140	5	2.4−2.5	0 to −6	110−124	2022 [26]
12	2,6-PDC-Cl + C$_{10}$-Cl[p]	Is or Im[q]	Solution	Pyridine + Toluene	–	80−115	12−24	1.0−1.1	40−64	–	2022 [27]
13	2,6-PDC-Cl[r]	Is+1,10-DD[o]	Melt	–	–	80−140	3−5	0.4−1.7	6−12	97−110	2024 [28]
14	2,6-PDC-Cl[r]	Ii or CBDO[s]	Melt	–	–	175−190	2−3	0.5	112−124	–	2024

[a] Diethylene glycol.

[b] Except for C$_7$, C$_8$, and C$_{11}$ all other diols were investigated.

[c] Room temperature.

[d] Polyethylene glycol 400 and 1000.

[e] 2,5-pyridinedicarboxylic acid dichloride.

[f] Range of aromatic diols were used.

[g] Dimethyl acetamide.

[h] 2,6-pyridine dicarboxylic acid diethyl ester.

[i] EG, 2,2-dimethyl-1,3-propanediol, 1,4-BDO, 1,6-HDO and DEG.

[j] 2,4-and 2,5-pyridine dicarboxylic acid diethyl esters in combination with diethyl adipate.

[k] 2,6-pyridine dicarboxylic acid dimethyl ester in combination with diethyl bisfuran.

[l] 2,4−2,5- and 2,6-pyridinedicarboxylic acid diethyl esters.

[m] 2,4-pyridinedicarboxylic acid diethyl ester.

[n] 2,5- and 2,6-pyridinedicarboxylic acid dichlorides respectively.

[o] 1,10-decane diol.

[p] 2,6-pyridinedicarboxylic acid dichloride in combination with sebacoyl chloride.

[q] Isosorbide or Isomannide.

[r] 2,6-pyridinedicarboxylic acid dichloride.

[s] Isoidide or 2,2,4,4-tetramethyl-1,3-cyclobutanediol.

* Not available.

at −31.7 °C was recorded. The mechanical properties of 2,5-PBAP exhibit a similar Young's Modulus (90.6 vs. 100.8 MPa) when the polyesters were compared to commercial polybutylene adipate terephthalate (PBAT). However, the tensile strength (expressed in MPa) and elongation at break (%) values of 2,5-PBAP are both far below the benchmark values [30]. Another study describing the use of 2,6-PDC dimethyl ester as a comonomer with feed ratios varying from 20 to 60 mol%

to the bis-furoate (main monomer) was reported in 2016 by Bougarech and co-workers [23]. The authors used a second catalyst (Ti(O-Bu)$_4$) during the poly-condensation reaction to address the likelihood of the pyridine moiety deactivating the first catalyst (Zn(OAc)$_2$) by chelation. As evidenced by previous reports, increasing pyridinic moieties leads to a decrease in the molecular weight of the resulting copolyesters (Table 2). On the other hand, the amorphous

characteristics and high T_g values were attributed to the rigid backbone from the pyridine structure that hampers the crystallisation phenomenon [23].

Recently, Liu and coworkers examined a different strategy to address the challenges associated with using a metal catalyst and the poor thermal stability of pyridine carboxylic acids, i.e., melting followed by decomposition at temperatures typically used in the polycondensation reactions. Instead of starting from the diacid or diester of PDCs ($T_{m\ diacid}$ 235–250 °C, $T_{m\ diester}$ 130–170 °C), the authors used dichlorides of PDCs as the monomers that have lower melting points ($T_{m\ dichloride}$ 55–65 °C). The dichloride derivatives are reactive substrates that can be used without a catalyst in polycondensation reactions at temperatures between 115 and 140 °C to produce reasonably higher molecular weight polyesters (M_n 24,500 g mol^{-1}). Using 2,6-PDC dichloride as a comonomer in the copolyester synthesis reduces the molar weight but positively affects the T_g, consistent with previous reports. The liquid water and dynamic vapor sorption exhibited higher values for the copolyesters prepared using pyridine monomers. This could be due to the hydrophilic nature of the pyridine structure in the polymer backbone. Next to this, the presence of a pyridine moiety showed a positive influence in enhancing the water and gas barrier properties of the copolyester [27]. These values were comparable to PET (semicrystalline) but lower than that of PEF. The homo polyester poly(decylene 2,6-pyridinedicarboxylate) – PDe26PD prepared from 2,6-PDC dichloride with 1,10-decane diol (1,10-DDO) is semicrystalline (T_m 110 °C) and displayed a molecular weight M_n 24,500 g mol^{-1}. These values are slightly higher for the 2,5-isomer. (M_n 25,700 g mol^{-1} and T_m 124 °C). Despite lower thermal stabilities compared to the aromatic analogues (e.g. polydecylene isophthalate - PDeIP), the mechanical properties of PDe26PD such as Young's modulus (E) were over five times, and the strength (σ_b) 2–4 folds higher compared to PDeIP [26]. The gas barrier properties for the polyester prepared using 2,6-PDC dichloride are found to be superior compared to the one obtained from the 2,5-isomer. The ring-flipping in the nonsymmetrical 2,6-isomer is hindered similar to 2,5-FDCA (PEF). Thus the molecular motions are restricted causing lower diffusion coefficients of gases like O_2 and CO_2 [26]. The effect of the incorporation of the rigid diol (isosorbide-Is) was found to positively influence the thermal and mechanical properties of the resulting copolyester poly(decylene 2,6-pyridinedicarboxylate isosorbide) – PDe26PDIs [28]. For example, as low as 8 mol% incorporation of Is could increase the thermal stability by 8 °C and T_g by 6 °C. The mechanical properties were significantly improved in the copolyester compared to the homopolyester (PDe26PDIs $vs.$ PDe26PD), Young's modulus (E) 1390 ± 170 $vs.$ 770 ± 25 MPa, and

mechanical strength (σ_b) 31.6 ± 2.7 $vs.$ 12.5 ± 4.8 MPa. The increase in these values was attributed to the intrinsic rigidity of the isosorbide structure in the polymer backbone and its stronger intramolecular interactions [28]. These results indicate that the physical and chemical properties of pyridinic polyesters can be tuned, expanding the scope of these materials in a wide range of applications.

The thermal properties of the polyesters obtained from 2,6-PDC dichloride in combination with the rigid diols such as isoidide (Ii) (one of the reactive isomers in the isohexide family) and 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO) were investigated for its suitability in durable applications (e.g. industry packaging, automotive, and building and construction materials). Despite low molecular weights, the polyester's thermal stabilities and T_g were significantly improved. Both the diols (Ii and CBDO) in combination with 2,6-PDC dichloride respectively were rapidly crystallised during the polymerisation, hence the temperature was raised until the melt was obtained and the polycondensation reactions proceeded. Thus, poly(isoidide-2,6-pyridinedicarboxylate) – PIi26P was synthesised at 165–175 °C resulting in polyester with T_g 112 °C, whereas poly(cyclobutane-2,6-pyridinedicarboxylate) – PC26P at 180–190 °C to give a polyester with T_g 124 °C (see structures in Figure 1). No T_m was observed for both polyesters. Although mechanical performance tests were not investigated, preliminary thermal properties highlight similarities to polystyrene polymer, which is widely used in applications such as foams (insulation material) and packaging materials.

Though not a polyester, Lubrizol Corporation patented a trimer comprised of 2,5-PDC and 2,6-PDC with 2-ethylhexanol respectively, as suitable additives in formulating lubrication oils for internal combustion engines. The antiwear and/or extreme pressure performance of PDC-derived trimers was found to be superior to the conventional zinc dialkyldithiophosphate (ZDDP) additive which has a detrimental effect on the fuel economy and efficiency [31].

Conclusions and outlook

The potential of PDC to be used as an effective monomer is hindered by the chelation of metal catalysts typically used in polymer synthesis and the poor thermal stability of carboxylic acid groups, especially adjacent to the nitrogen atom. Researchers have developed various polymerisation strategies to overcome these challenges and improve their effectiveness as monomers in producing polyesters with interesting properties:

- The enzyme CaLB-mediated polymerisation, a promising method that uses lower temperatures and solvents, produces pyridinic polyesters with molecular

Figure 1
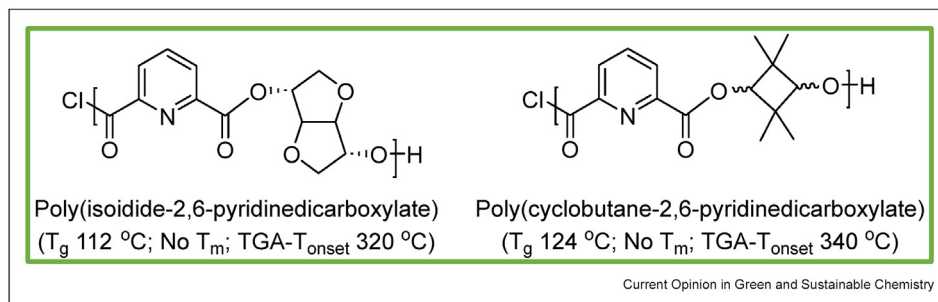
Structures of PIi26P (left) and PC26P (right) derived from 2,6-PDC dichloride with Ii and CBDO respectively.

Figure 2

Overview of PDC and derivatives that were used in combination with diols for producing polyesters. The summary of the significance of polyester properties and its potential applications is given at the bottom of the figure.

weights up to M_n 14,300 g mol^{-1} without metal catalysts.

• The polycondensation reaction, which can be performed at room temperature using reactive picryl chloride as a condensation reagent, is not attractive due to the challenges of handling the highly explosive nature of picryl chloride in large quantities.

• The diacid or diester of PDCs typically requires an esterification or transesterification catalyst and higher temperatures for oligomerisation and subsequent polymerisation reactions. However, the innovative strategy of employing dichloride derivatives, which are reactive monomers, is an interesting approach as they do not require a catalyst and can be performed at moderate temperatures.

Standard Oil Company demonstrated the use of water-soluble pyridinic polyester resins for coatings several decades ago. However, this is the only available report

and no further efforts have been made to develop the potential of PDC-derived polyesters in the coating and paint applications.

Lubrizol Corporation demonstrated that PDC can be beneficial in the automotive sector, as its oligomers are suitable additives for formulating lubrication oils for internal combustion engines, enhancing fuel economy.

PBAT, a biodegradable polymer, is ideal for blending with rigid polymers like plastic bottles due to its high flexibility and toughness properties. Biome Bioplastics developed a pyridinic version of PBAT, which shares mechanical properties (e.g. Young's Modulus) with the benchmark PBAT. This suggests that the pyridine moiety has the potential to replace the terephthalate unit in PBAT production, retaining its original properties.

An overview of PDC and its derivatives when used in combination with different diols to produce polyesters with superior properties, and the potential applications of these materials, is shown in Figure 2.

The rigid structure of PDC provides several advantages when incorporated into a polymer backbone. These advantages are:

1. Enhanced biodegradability
2. Chelating agent for extraction of metal ions from the compatible medium
3. Enhancement in water and gas barrier properties
4. Higher T_g values
5. Influence on the stacking/crystallisation behaviour
6. Positive effect on liquid water and dynamic vapor sorption due to hydrophilic nature
7. Tuneable morphology of the polymer

These characteristics are significantly interesting in developing sustainable, safe, and circular materials for various applications.

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 article.

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Data availability

No data was used for the research described in the article.

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