Poly(alkylene terephthalate)s: from current developments in synthetic strategies towards applications

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Abstract

Poly(ethylene terephthalate) (PET), poly(trimethylene terephthalate) (PTT) and poly(butylene terephthalate) (PBT) are widely known and the mostly studied polymers belonging to the poly(alkylene terephthalate) (PAT) family, but there are many other polymers in this family of which the full potential has not yet been disclosed. Herein, we provide an overview of the state-of-the-art of this specific polyester type. In a first part, the various synthesis methods including melt polycondensation, solution polycondensation and ring-opening polymerisation together with their advantages and disadvantages are discussed. Next, an overview of the polymer properties and a comparison of their thermal and mechanical behaviour are provided. Due to the increasing interest in sustainability (e.g. production of PATs from bio-based monomers) and recycling aspects (e.g. depolymerisation), recent progress on PATs in these particular fields is also highlighted. Currently, PET, PTT and PBT are exploited in many applications while research is striving to broaden their application field.

Keywords: poly(alkylene terephthalate), synthesis methods, polymer properties, recycling, applications

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1. Introduction

The main synthesis route for polyesters is through a polycondensation between a di- or polyfunctional carboxylic acid and a di- or polyfunctional alcohol.[1–6] Depending on the starting materials, a variety of polyesters with tuneable properties can be synthesised.[7,8] The first generation of polyesters exhibited issues upon applying processing techniques such as electrospinning. When polyesters based on terephthalic acid were synthesised, they exhibited a high melting point and enabled fibre formation which rendered them industrially relevant.[1] The overall name for polyesters constituting a rigid aromatic terephthalate group and a flexible alkyl moiety is poly(alkylene terephthalate)s (PATs).[6,9,10] The general structure of these polymers is depicted in **Figure 1**. Variation in the number of methylene groups constituting the alkyl chain leads to polymers with different properties.[11–13] Poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) were the first polymers from the PAT family being synthesised while shortly after, PET films and fibres were produced to serve a plethora of applications. Later on, PBT, which was more easily processable compared to PET, was applied as construction material. The name and abbreviation of various PATs are listed in **Table 1**. The abbreviations PET, poly(trimethylene terephthalate) (PTT) and PBT are generally known and accepted.[9,13–17] For the other PATs, the nomenclature has been inconsistent over the years and there are different abbreviations currently circulating (e.g. pGT with p representing the number of methylene groups and GT referring to glycol terephthalate).[18,19] Throughout the current review, the abbreviations listed in **Table 1** will be used.

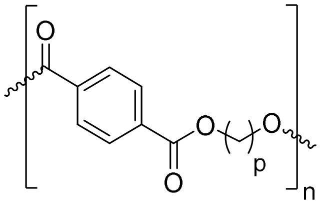

Figure 1. The general structure of PATs with p being the number of methylene groups constituting the alkyl chain.

Table 1. The denotation of various PATs referred to in this review with p being the number of methylene groups constituting the alkyl chain as indicated in Figure 1.

Name	p	Abbreviation
Poly(ethylene terephthalate)	2	PET
Poly(trimethylene terephthalate)	3	PTT
Poly(butylene terephthalate)	4	PBT
Poly(pentamethylene terephthalate)	5	$PAT_{(p=5)}$
Poly(hexamethylene terephthalate)	6	$PAT_{(p=6)}$
Poly(heptamethylene terephthalate)	7	$PAT_{(p=7)}$
Poly(octamethylene terephthalate)	8	$PAT_{(p=8)}$
Poly(nonamethylene terephthalate)	9	$PAT_{(p=9)}$
Poly(decamethylene terephthalate)	10	$PAT_{(p=10)}$

The most frequently reported PATs include the high-performance thermoplastic polyesters PET and PBT. Currently, PET is the most used polymer worldwide as it is applied as feedstock in numerous of products such as textile, beverage bottles, packaging material, etc.[2,6,20,21] In 2016, up to 30 % of the total amount of PET produced was used for bottle production.[20] PET bottles are desirable since the polymer is strong, lightweight, transparent, shatterproof and readily available.[20,21] This makes the bottles inexpensive and easy to transport. PET is also useful in aerospace applications, but since it needs to withstand extreme conditions, higher molar masses of 120 000 g/mol of polymer is required (see 2.2.1).[22]

PBT is structurally very similar to PET, but it has a longer alkyl chain in between two terephthalate moieties which makes the polymer more flexible.[14,23] This results in faster crystallisation which is desired for injection moulding. PBT has already been applied in a plethora of commercial applications like automotive parts, consumer goods which are exposed to high temperature or electrical stress (e.g. egg boilers, hairdryers and oven or iron handles, gear wheels, etc).[2,24]

More recently, investigation towards PTT has gained increasing attention for its potential use in commercial applications like carpets and other textiles, films and food packaging.[2,25–31] Investigations concerning PATs with $p > 4$ are limited and mainly cover alternative synthesis methods along with a study describing their crystallisation behaviour.[32–36] The industrialisation of these PATs is troublesome, mostly because of the limited availability of the raw materials, the high cost and the complexity of the processes.[37] Yet, due to technological advances, it is only a matter of time before these polyesters are also easily produced on a large scale and at a reasonable cost.

In 2003, an extensive review covering PET, PTT, PBT and copolyesters thereof, has already been published.[2] It addresses the history, the technology and chemistry concerning the polyesters up to then. Herein, more recent developments will be addressed and PATs with a larger number of methylene groups will be highlighted.

2. Synthesis methods

The first synthesis of an aliphatic-aromatic PAT was conducted around 1940 by Schlack, who produced PBT, as well as Whinfield and Dickson, who synthesised PET.[2,4,38–40] Both polymers were produced via a two-step melt polymerisation. Since then, also solution polymerisation strategies such as ring-opening polymerisation (ROP) and single-step solution polymerisation have been explored for the synthesis of PATs.[6,39] Also for the production of the required monomers, various possibilities have been explored, including the synthesis from fossil-based or biological resources.

2.1. Monomer synthesis

2.1.1. Monomer synthesis on industrial scale

PTT, PBT and PET are produced on industrial scale via the polycondensation between terephthalic acid (TPA) or dimethyl terephthalate (DMT) and a diol. Currently, these monomers for commercial PAT synthesis are mainly obtained from fossil-based resources. Both TPA and DMT are produced starting from para-xylene.[41–43] Xylenes are aromatic hydrocarbons and are mainly produced via catalytic reforming, which is a processing step in the oil refinery of crude oil. This chemical process converts naphtha into higher-octane products and aromatics. A mixture of multiple aromatic compounds is thereby obtained but para-xylene is easily isolated based on the difference in freezing point.[43] Para-xylene is almost exclusively used for the production of TPA and DMT. To obtain TPA and DMT, the methyl groups on the aromatic hydrocarbon need to be oxidised first in the presence of a catalyst. The currently most employed oxidation method of xylene was already commercialised in 1970 as the AMOCO process and involves acetic acid as solvent, oxygen as oxidant and a cobalt/manganese/bromine catalyst system (**Figure 2**).[42] For this reaction, the temperature is increased to 175-225 °C and oxygen is provided at a pressure of 1.5-3 MPa. Terephthalic acid is formed as a solid with a selective yield of 95 % which is subsequently subjected to a purification process. Despite the high yield of the reaction, it causes some environmental issues and safety concerns. The bromide ions that are used in the catalyst system can form methyl bromide, which is toxic. Therefore, milder oxidation reactions of xylenes have been investigated but a suitable alternative to produce TPA on industrial scale has not been identified yet. Esterification of the formed TPA with methanol, leads to the production of DMT. Another commonly applied method to produce DMT from *p*-xylene is via the multistep Witten process, which is represented in **Figure 3**.[41,44]

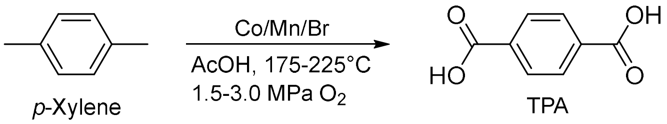

Figure 2. The AMOCO process to convert *p*-xylene into terephthalic acid (TPA) in 8-24 hours.[42]

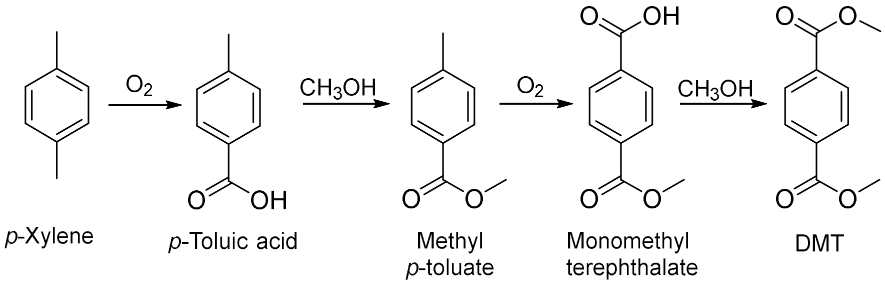

Figure 3. The Witten process to convert p-xylene in dimethyl terephthalate (DMT).[41]

Besides a difunctional terephthalate, also a diol is necessary for the production of PATs. In case of PET, ethylene glycol (EG) is required. The currently applied commercial production of EG starts with the oxidation of ethylene to form ethylene oxide, which is subsequently hydrolysed with water.[1,45] Ethylene is mainly obtained from steam cracking, which is also a process in oil refinery.[46] Since ethylene oxide reacts more easily with ethylene glycol than with water, also di-, tri-, tetra- and polyethylene glycols are formed. However, their production is minimised (< 10 %) by the addition of a large excess of water. Via vacuum distillation, by-products and water are removed to obtain EG with high purity, which is used as raw material for polyester synthesis or as anti-freeze.[47]

The monomer required for the synthesis of PBT is 1,4-butanediol (1,4-BDO). There are five chemical processes known for the commercial production of this diol, as represented in **Figure 4**.[48,49] The Reppe method, which is the most common, includes the reaction between acetylene and formaldehyde to form 2-butyne-1,4-diol. Catalytic hydrogenation of the latter results in 1,4-BDO (**Figure 4 A**).[50,51] Another multistep pathway to form 1,4-BDO, the Lyondell process, involves the isomerisation of propylene oxide into allyl alcohol which subsequently undergoes hydroformylation. The end product is obtained by the hydrogenation of 4-hydroxybutyraldehyde (**Figure 4 B**). The third process is the synthesis pathway patented by Mitsubishi-Kasei, which involves three steps. The catalytic reaction of butadiene, acetic acid and oxygen yields 1,4-diacetoxy-2-butene and subsequent hydrogenation results in another intermediate which is hydrolysed to 1,4-BDO (**Figure 4 C**).[50] In the fourth process, butane is oxidised into succinic anhydride which reacts with methanol to dimethyl succinate and further hydrogenation leads to the diol. This production pathway is known as the Huntsman process (**Figure 4 D**). The McKee process also starts from butane but this is first converted into maleic anhydride.[52] 1,4-BDO is formed by subsequent esterification and hydrogenation (**Figure 4 E**).

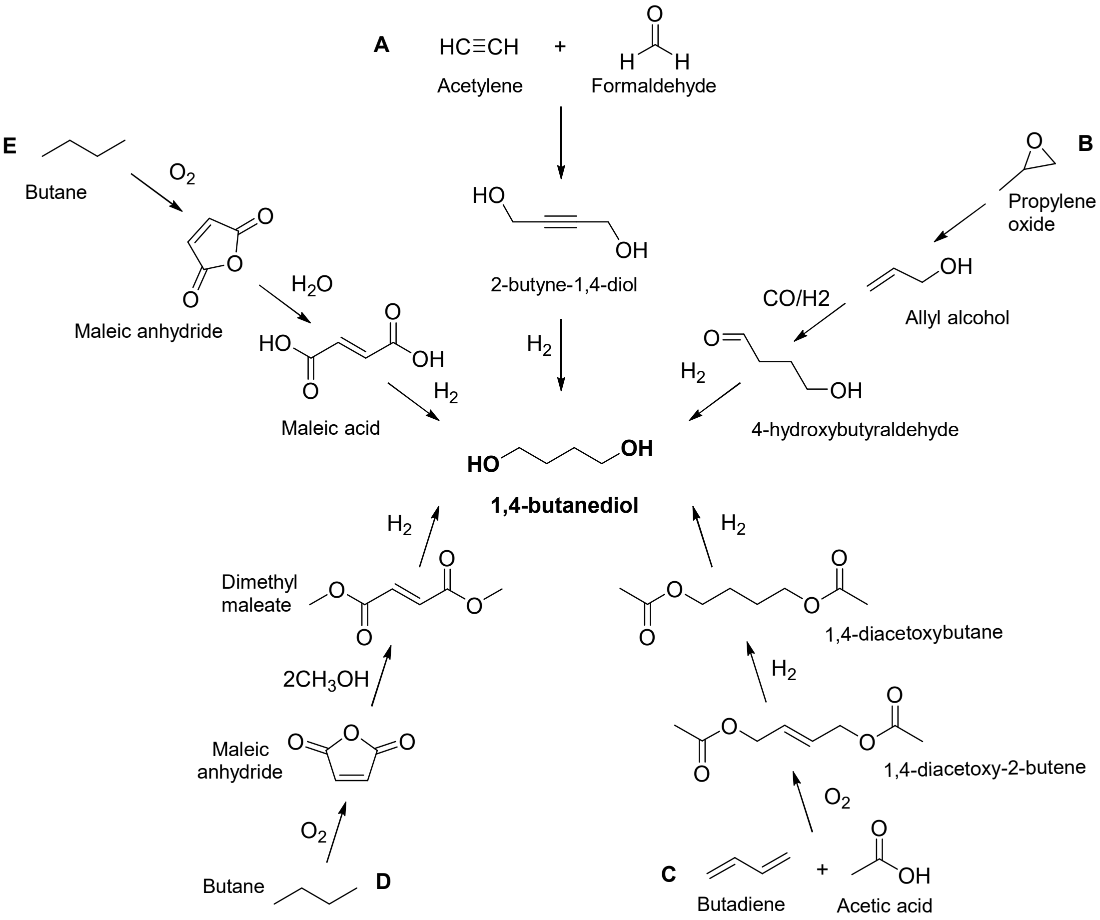

Figure 4. Different synthesis methods of 1,4-butanediol. (A) Reppe process, (B) Lyondell process, (C) Mitsubishi-Kasei process, (D) Huntsman process and (E) Davy McKee process.[49]

The low availability of 1,3-propanediol (1,3-PDO) has initially limited the production of its respective polymer PTT, even though the latter can be synthesised in the same way as PET and PBT.[53] In the 1990s, economically feasible production pathways for the monomer have been developed independently by Degussa, Shell and DuPont which led to the synthesis of PTT on industrial scale.[16,54,55] The starting materials in the processes of the former two companies are derived from petroleum and will therefore be discussed in this section. The production of 1,3-PDO starting from glucose, which is a renewable source, will be explained in the upcoming section (see 2.1.2).

The production method developed by Degussa starts from acrolein which is first converted into 3-hydroxypropionaldehyde by the addition of water and subsequently reduced to 1,3-PDO (**Figure 5**).[56,57] The first step in this method is catalysed by an acidic cation exchanger and for the second step, a hydrogenation catalyst is used, such as Raney nickel and platinum or ruthenium supported on metal oxides or activated carbon. After work-up, it was found that the product still contained a few thousands ppm of residual carbonyls. To reduce this, a second high temperature (110-150 °C) hydrogenation step was necessary.[58] Acrolein itself can be obtained via the oxidation of propylene or can be derived from glycerol.[57] In an alternative synthesis method, used by Shell Oil Company, ethylene oxide and syngas react to β-hydroxyaldehyde which is hydrogenated to 1,3-PDO.[56,57] This reaction can proceed in a single step if a homogeneous bimetallic cobalt-ruthenium catalyst is used in combination with bis(phospholano)alkane catalyst precursors (**Figure 5**).[59] The Shell trademark name for their PTT is Corterra.[60]

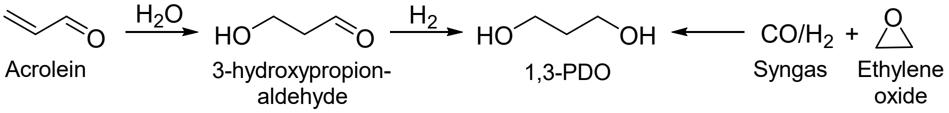

Figure 5. The synthesis pathways for the production of 1,3-propanediol (1,3-PDO) used by Degussa (left pathway) and Shell (right pathway).

2.1.2. Alternative monomer synthesis

The commercial bio-based PTT, produced by DuPont (Sorona) since 2000, is synthesised with 1,3-PDO originating from glucose. The latter is extracted from biological materials, which reduces the greenhouse gas emission and energy consumption accompanying PTT production (**Figure 6**).[61–63] The 1,3-PDO synthesis from glucose can proceed via two steps with natural organisms or via one step, if the organisms are genetically engineered for that purpose.[64,65] It has been shown that monomers synthesised via this method contain less impurities than the 1,3-PDO produced from petroleum-based reagents.[57]

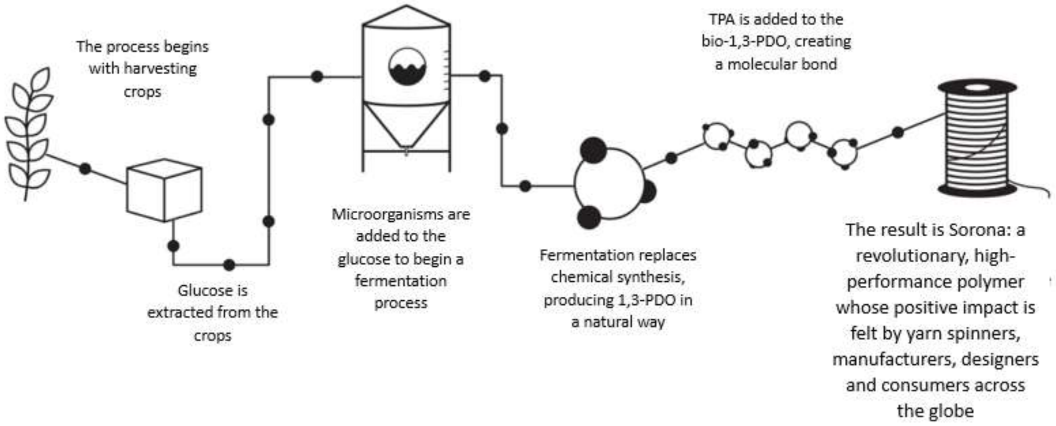

Figure 6. The production method of Sorona (PTT) from bio-based 1,3-propanediol (1,3-PDO) according to DuPont.[62]

In 2018, Lu *et al*. referred to the synthesis of 1,5-pentanediol from biomass, which could be scaled up to industrial level at low cost.[37] The production includes the conversion of furfural to the diol via multiple hydrogenation steps (**Figure 7**).[66–71] Furfural can be derived from biomass, such as sawdust and corncobs, by the hydrolysis of hemicellulose into xylose which is subsequently hydrogenated. Recent developments in the synthesis of bio-based 1,5-pentanediol lead to opportunities for the commercial production of one of the starting products of $PAT_{(p=5)}$ and will therefore initiate investigations towards a wider range of applications for this particular polymer.

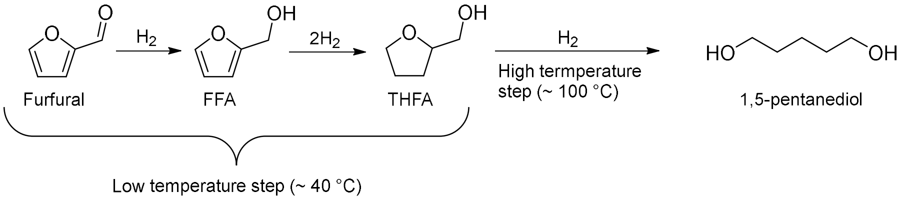

Figure 7. The reaction pathway to obtain 1,5-pentanediol via multiple hydrogenation processes of furfural with furfuryl alcohol (FFA) and tetrahydrofurfuryl alcohol (THFA) as intermediates.[72]

Also for PATs containing more methylene units, alternatives for the synthesis of the starting diols, preferably from renewable sources, are investigated. The production of $\text{PAT}_{(p=10)}$ requires 1,10-decanediol and to obtain this monomer, a bio-based synthesis route is available.[64,73] Castor oil is obtained from plants and can be converted into sebacic acid via treatment with a strong base at elevated temperature (250 °C). Hydrogenation of the acid results in 1,10-decanediol, as indicated in **Figure 8**.

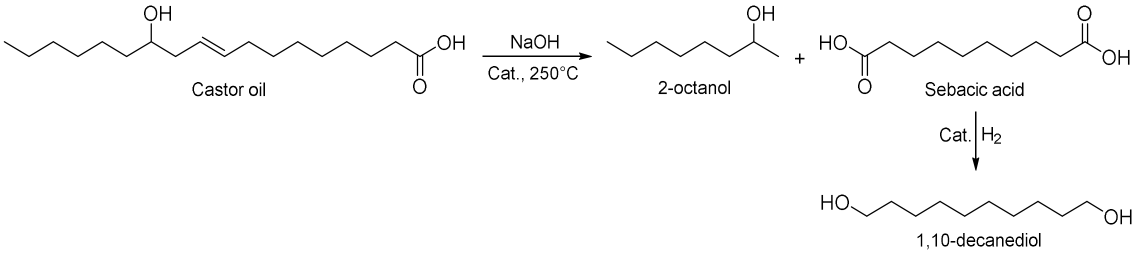

Figure 8. The production of 1,10-decanediol from castor oil with sebacic acid as intermediate.

2.2. Polymer synthesis

2.2.1. Melt polycondensation

Melt polycondensation is the first synthesis method that was developed to produce PATs and is still used on industrial scale and in a research context.[2,6] This step-growth polymerisation involves two metal-catalysed steps, as indicated in **Figure 9**.[7,74] First, an intermediate prepolymer is obtained by means of an esterification or a transesterification. The former comprises a reaction between the appropriate diol and TPA, while for the latter DMT is used. This step is generally performed at 190-230 °C under inert conditions, established via a nitrogen or argon flow.[3,4,75] The end of the (trans)esterification is indicated by the theoretical amount of alcohol or water that is distilled. Since this is an equilibrium reaction, the removal of the by-product is also necessary to shift the equilibrium towards the prepolymer site. The second step includes the polycondensation of the intermediates to form the end product. Therefore, the pressure is reduced and the temperature is increased to 250-275 °C. The polycondensation is terminated when a certain melt viscosity is reached.[1] Zinc- , titanium-, antimony- and tin-based catalysts are frequently applied to accelerate the processes at moderate temperature.[2,76,77] Melt polymerisation is used for the industrial production of PET since it offers several advantages including large scale production possibilities via a continuous polymerisation process without the need for purification.[78]

During the first years after the development of this synthesis method, DMT could be easily obtained in high purity which favoured the transesterification pathway.[2] Only in the 1960s, TPA could be produced in sufficiently high purity on industrial scale. The synthesis of PATs with p up to 20 was already realised with this method.[79–81] PET obtained via melt polycondensation, generally had a molar mass of about 25 000 g/mol which is suitable for film production but insufficient to enable compression moulding.[1,7,22] The production of higher molar mass polymers with melt polycondensation is difficult, because the high melt viscosity complicates the removal of the by-product and high temperatures are necessary to enhance the reaction rate. This leads to an increasing number of degradation reactions that can occur. To obtain PET with suitable characteristics for compression moulding, a solid-phase polycondensation can be performed following on the melt polycondensation. Herein, the reaction temperature is lowered to 200-240 °C, which is above the T_g but below the T_m of PET, causing the rate of the degradation reactions to reduce significantly while the polycondensation can still proceed. Moreover, remaining impurities like diols, acetaldehyde and water are efficiently removed. The additional solid state polymerisation provides PET with a suitable molar mass to be used for demanding applications (i.e. aerospace applications).[10,22,82]

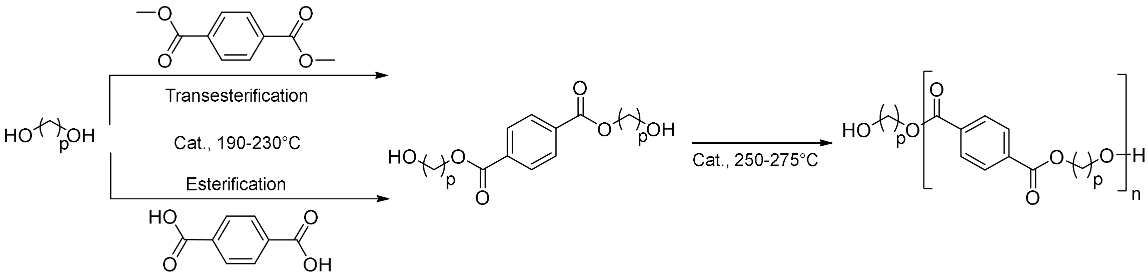

Figure 9. Reaction pathway of the step-growth polymerisation for the synthesis of PATs.

The described melt polycondensation is not ideal since high temperatures and vacuum are necessary to establish the molten state of the polymer together with by-product removal. These harsh conditions result in monomer sublimation and diffusion constraints, which in turn create stoichiometric imbalances and can lead to side reactions such as chain scission, chain defects, end group modification and cyclic oligomer formation.[83–85] With the aim of solving some of these issues, several catalysts have been investigated and it was shown that antimony-, tin- and titanium-based catalysts were the most suitable options for polycondensation.[2] However, as the titanium-based catalyst renders a yellow colour, the antimony-based catalyst is associated with possible toxicity issues and some catalysts accelerate side reactions, they introduced new problems to the synthesis.[2,6] In addition, removing the catalyst from the end product is both technically and economically difficult.[86] Although the antimony trioxide catalyst is widely used and excellent for the acceleration of the polymerisation of e.g. PET, several attempts have been carried out over the last decade to replace the current catalysts with a superior catalyst system, thereby addressing issues associated with the former.[10,86,87] It is desired to develop a catalyst with an activity comparable to the organometallic catalysts but which is more benign, operates at lower temperatures and which is easier to remove after synthesis.[88] Therefore, scientists are exploring the organocatalytic field to identify small organic molecules as potential catalysts.[89] Some examples that have shown to be successful for the polymerisation of PET include 1,5,7-triazabicyclo[4.4.0]dec-5-ene and a salt of 1,8-diazabicyclo[5.4.0]undec-7-ene and benzoic acid.[86,90] The main limitations of the organocatalysts include their often poor thermal stability which results in partial or complete degradation during synthesis. Hence, polymers with a lower molar mass are obtained compared to those polymerised through organometallic catalysis.

2.2.2. Solution polycondensation

Solution polymerisation was proposed as alternative for melt polymerisation in order to obtain polyesters.[91–93] During a solution polymerisation, all reactants are dissolved in a common inert solvent.[94] This provides a more homogeneous mixture and the reaction can proceed under milder conditions compared to melt polymerisation. Additionally, the viscosity of the reaction medium is sufficiently low to allow stirring, which is not always the case for melt polymerisation. The main disadvantages associated with solution polymerisation are the additional costs and scale-up issues related to the use of a solvent including the extra processing steps required for the separation of the solvent after reaction.[95] Furthermore, organic solvents exploited for this purpose often impose additional safety issues due to e.g. toxicity and flammability.[96]

A large number of solution polycondensation reactions between a glycol and a diacid chloride have already been reported.[97] For the synthesis of aromatic polyesters, (anhydrous) pyridine with chlorinated aliphatic hydrocarbons or picryl chloride were already used as reaction media.[91] In case of picryl chloride, PAT syntheses at room temperature were even feasible.[98] However, PET did not dissolve in pyridine which resulted in a heterogeneous mixture.

2.2.2.1. Single-step solution polycondensation

In 2018, Giol *et al.* reported a novel, catalyst-free synthesis method for PATs that proceeds via solution polycondensation.[6,99] This procedure includes a single-step reaction between terephthaloyl chloride (TCL) and the corresponding diol resulting in the desired polymer and hydrogen chloride (HCl), as shown in **Figure 10**. The single-step solution polycondensation was applied for PATS with an alkyl chain length varying from 5 to 10 methylene units (p=5-10). The temperature at which optimal synthesis was realised, was investigated by executing the reaction at both room and elevated temperature (160 °C). The latter resulted in higher molar masses (from 3 to 5 kg/mol respectively) and increased polymer yield (from 18 to 63 %). Although the selection of an appropriate solvent was a challenge for this synthesis approach, various suitable solvents have been reported including tetrahydrofuran, chloroform, 1,1,2,2–tetrachloroethane and 1,2-dichlorobenzene (DCB).[93] It has been shown that DCB results in the highest yield (> 70 %) and molar mass (> 10 kg/mol).

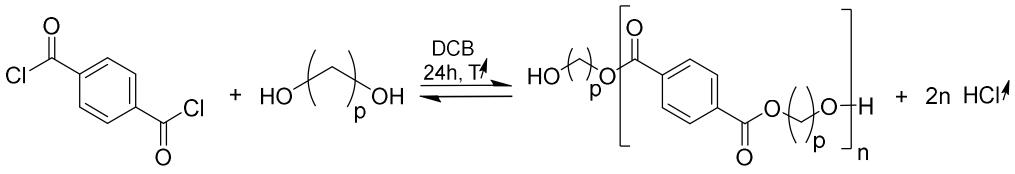

Figure 10. Single-step solution polymerisation for the synthesis of PATs starting from TCL and a diol with an alkyl chain length varying from 5 to 10 methylene groups (p=5-10).

Since polycondensations are equilibrium reactions, removal of the HCl by-product favours polymer formation. Therefore, an acid-capturing agent like triethyl amine or pyridine was added to the solution to form a salt with the released acid. However, this approach demands multiple time-consuming washing steps in order to separate the salt from the polymer. An alternative approach is through flushing of the solution with an inert gas like nitrogen or argon in order to remove the by-product. To avoid a corrosive and toxic environment, neutralisation of the gas flow in an alkaline solution follows. This procedure is more efficient as HCl-removing strategy. Giol *et al*. compared both options and observed a higher yield (72 %) and molar mass (> 10 kg/mol) with the flushing method which makes it even more beneficial. Solution polymerisation provides high purity and well-defined end products which can be used for high-end applications such as biomedical and automotive purposes. This synthesis method is more appealing than the melt polymerisation as it includes only one step, proceeds at lower temperatures and does not involve the use of any toxic catalyst.[6] The latter is expected to be beneficial when using these polymers for biomedical applications.

2.2.2.2. Ring-opening polymerisation

An alternative solution polymerisation method is ring-opening polymerisation (ROP).[100] ROP is a chain-growth polymerisation technique in which the polymer is formed starting from cyclic monomers.[101] Via ring-opening, the monomers are sequentially added to the active centre of the growing polymer chain. In this mechanism, the ring-opening of the monomers is the driving force for the synthesis of the polymer.[102] Diverse polymer architectures have already been synthesised via this way including block copolymers, star-shaped polymers and graft copolymers.[103] Also the PATs can be formed by ROP of a corresponding cyclic monomer (**Figure 11**).

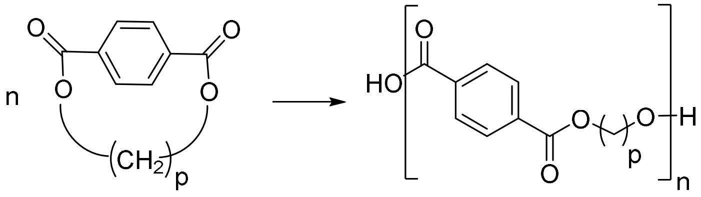

Figure 11. Ring-opening polymerisation of cyclic monomers into PAT.

The synthesis of PATs via ROP has already been investigated and it was demonstrated that the characteristics and properties of polymers produced via this method are the same as those of PATs obtained via polycondensation.[77] The main limitation of ROP appears to be the availability of cyclic polyesters as starting reagents. Initially, these macrocyclic alkylene terephthalates were frequently produced via multi-step high-dilution techniques, such as the reaction between an oligomeric diol and an oligomeric diacid chloride performed by Zahn *et al.* (**Figure 12**).[104,105] Since very low levels (< 3 %) of cyclic oligomers were also formed as by-product during the melt polymerisation of PBT and PET, extraction from the reaction mixture was another technique to obtain ROP reagents.[106–111]

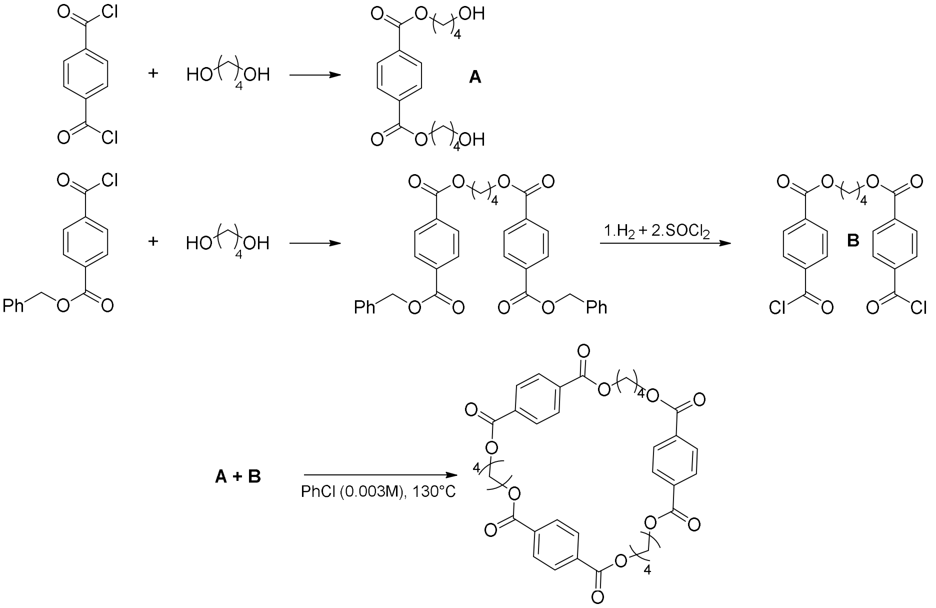

Figure 12. Preparation of cyclic PBT oligomers via multi-step high-dilution condensation of oligomers.[2,104,105,112]

These approaches only yielded a small amount of cyclic oligoesters (< 8 %) which rendered ROP unsuitable for large scale production. This remained an issue until Brunelle *et al.* reported a direct synthesis technique for cyclic oligoesters by combining a diol with a diacid chloride which resulted in the corresponding cycles and only a minor amount of linear derivatives (< 2 %) (**Figure 13**).[112] The latter needed to be removed prior to ROP to achieve high molar mass products (~50 kg/mol).[83] This pseudo-high dilution condensation is catalysed by unhindered amines such as 1,4-diazabicyclo[2.2.2]octane (DABCO), also known as triethylenediamine.

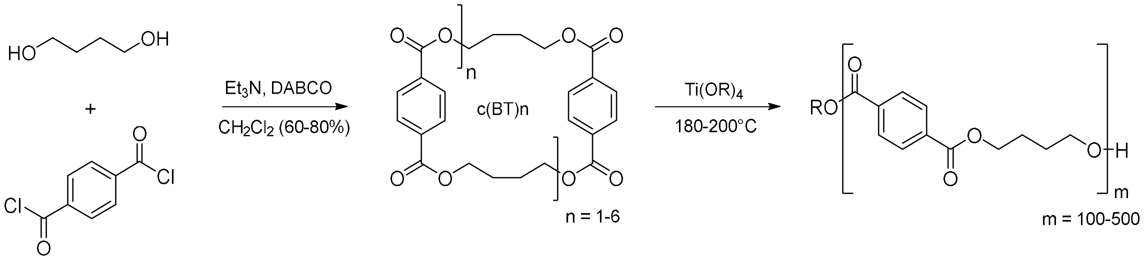

Figure 13. Direct synthesis method for cyclic butylene terephthalate and polymerisation to PBT.[112]

Another promising method for the production of cyclic alkylene terephthalates is via cyclo-depolymerisation. This is not only a suitable way to obtain cyclic monomers, but it can also be seen as a recycling method for PATs.[113] For these reasons, multiple depolymerisation methods have already been investigated for various polyesters.[108,114–120] For the production of PBT cyclic oligomers for example, a tubular reactor has been designed that depolymerises high molar mass PBT into o-xylene at 240 °C.[76,121] After 5-10 min, 70-80 % of the PBT is already converted into cyclic oligomers.

The cyclo-depolymerisation of $PAT_{(p=6)}$ in order to obtain hexamethylene terephthalate cyclic oligomers has also been reported.[77] These oligomers are abbreviated as $c(HT)_n$ with n being the number of hexamethylene terephthalate units in the cyclic molecule. They can be used as reagents to produce for example copolyesters. Since PAT$_{(p=6)}$ has excellent mechanical properties, chemical resistance and is not biodegradable, a copolyester with e.g. poly(ε-caprolactone), which is biodegradable but has rather unsatisfactory thermal and mechanical behaviour, can result in a copolymer with tuneable properties.[122–124] For the cyclo-depolymerisation, PAT$_{(p=6)}$ was dissolved in DCB and 3 mol% dibutyltin oxide was added. After 4 days reacting at 180 °C, a mixture of cyclic oligomers ranging from the dimer to the nonamer (c(HT)$_{2\text{-}9}$) was obtained, which could be used for ROP. Due to the broad cycle range, this mixture was suitable for the investigation of the influence of the ring size on the ROP.[113] González-Vidal *et al*. synthesised PAT$_{(p=6)}$ from a c(HT)$_{2\text{-}5}$ and a c(HT)$_{6\text{-}7}$ mixture to compare the reactivity. They found that the former had a lower ROP reactivity than the latter and that a higher molar mass polymer (from 39 to 50 kg/mol) could be obtained from the hexamer- and heptamer-enriched fraction.

Recently, Flores *et al*. reported alternative synthesis conditions for the production of PAT$_{(p=6)}$ which allowed cyclo-depolymerisation after the synthesis with the same catalyst exploiting other conditions.[83] The synthesis route is visualised in **Figure 14**. In a first step, 1,6-hexanediol and DMT reacted in a highly diluted toluene solution with *Candida Antarctica* lipase B (CAL B) as enzymatic catalyst to form cyclic oligomers.[83,125] After 24 hours, only cyclic species were present in the reaction mixture ranging from dimers to heptamers c(HT)$_{2\text{-}7}$ with decreasing abundance. Subsequently, ROP of the cyclic oligomers was executed in a concentrated (50 g/l) toluene solution in the presence of CAL B. PAT$_{(p=6)}$ with an average molar mass of 8.9 kg/mol was obtained after 24 hours. The subsequent cyclo-depolymerisation was performed in the same conditions as the first step and oligomeric cycles ranging from dimers to heptamers were obtained after 72 hours but with the trimer c(HT)$_3$ being the most abundant species. The depolymerisation did not proceed in the absence of CAL B. This method is promising since it avoids the use of acid chloride derived reagents, does not require an organometallic catalyst and has the ability to efficiently recycle PAT$_{(p=6)}$. The main drawback of the reaction is that longer reaction times are necessary than with ROP using (organo)metallic catalysts but, according to the authors, this issue can be tackled by finding a more efficient enzyme that functions at higher temperatures. The authors also believe that this method can be applied to PATs of greater industrial interest like PET and PBT.

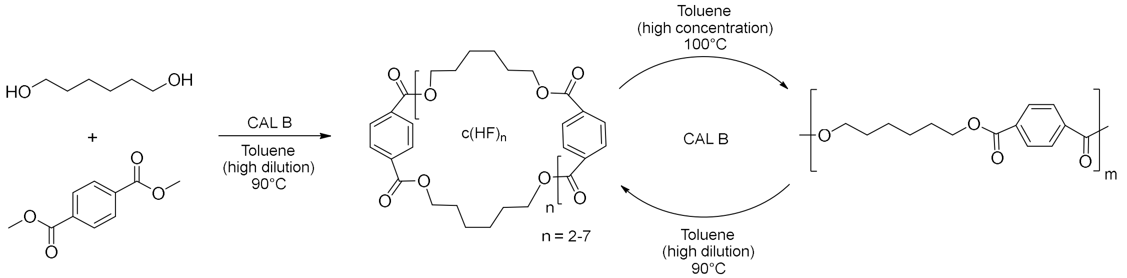

Figure 14. The enzymatic synthesis of c(HT)$_n$ cyclic oligomers, the ring-opening polymerisation and cyclo-depolymerisation.

Pseudo-high-dilution techniques and cyclo-depolymerisation are frequently applied methods for the production of cyclic esters and render the synthesis of high molar mass (> 100 kg/mol) polyesters via ROP possible.[2,39,83] Currently, they are still used although also other approaches like the polymer-supported cyclo-oligomerisation are available.[126–128] These techniques increase the potential of ROP as commercial synthesis method for PATs or copolymers thereof.

The ROP proceeds when an active chain end is created, which is realised via the addition of an initiator that opens one of the cyclic monomers (**Figure 15**).[129] For this purpose, tin- and titanium-based initiators were found to be the most effective. After creating the active chain end, the cyclic oligomers are propagating in order to increase the chain length until no cyclic oligomers are left and a polymer is obtained. Given the mechanism of the polymerisation, the initiator is incorporated within the polymer. The polymerisation was completed within minutes and a high molar mass (> 100 kg/mol) polyester could be obtained.[39,76] ROP offers multiple advantages including milder reaction conditions, shorter reaction times, no heat production and the absence of by-products which makes it an attractive alternative synthesis method.[2,129]

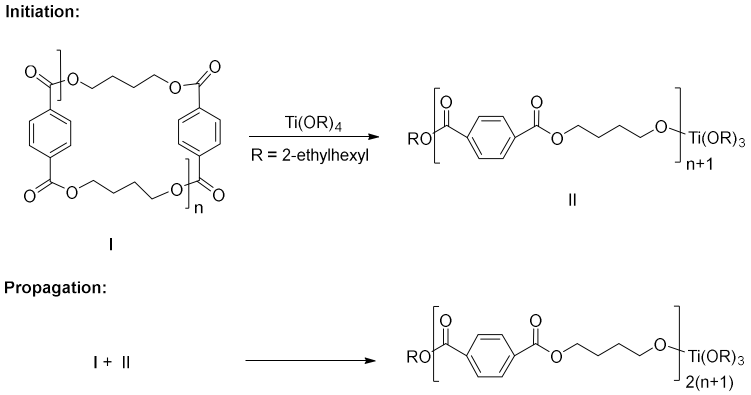

Figure 15. Ring-opening polymerisation of cyclic oligomeric PBT monomers.[129]

3. Polymer properties

The properties of the commercial polyesters PET, PTT and PBT are the best known since they have been already thoroughly investigated. All three are non-biodegradable and semi-crystalline thermoplastic polymers with good chemical resistance and limited water absorption.[2,115,130,131] In the following paragraph, the thermal and mechanical properties of commercial and non-commercial PATs will be discussed in greater detail.

3.1. Thermal properties

The thermal properties of polymers are mainly determined via thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in order to obtain characteristics like the degradation temperature (T_{deg}), the glass transition temperature (T_g), the melting temperature (T_m) and the (cold) crystallisation temperature ($T_{(c)c}$). A summary of these values for PET, PTT, PBT and $PATs_{(p=5-12)}$ can be found in **Table 2**.

Table 2. An overview of the thermal properties of various PATs obtained from DSC and TGA measurements.

PAT	T_g (°C)	T_{m1} (°C)	T_{m2} (°C)	T_c (°C)	T_{cc} (°C)	T_{deg} (°C)	Reference
PET	67^a-81^b	-	256-267	200	110-150	445	[11,13,64,132–134]
PTT	45-60^a	-	220-231	-	193	430	[18,26,131,135–138]
PBT	25^a-52^b	-	220-224	172	-	398-416	[6,13,18,64,139]
$PAT_{(p=5)}$	11-15^b	-	122-132	64	72	404	[6,37]
$PAT_{(p=6)}$	9-13^b	132-134	140-148	98-125	-	386	[77,113,140,141]
$PAT_{(p=7)}$	-2-3^b	-	90-96	-	-	403	[6,142]
$PAT_{(p=8)}$	8^{a*}	118	131	79	-	404	[6,75]
$PAT_{(p=9)}$	-3-0^b	-	90-92	-	-	388	[6,143]
$PAT_{(p=10)}$	5^{a*}	115	127	88	-	404	[6,13,19]
$PAT_{(p=12)}{}^{\circ}$	-1^b	-	121	-	-	415	[35,141]

**Determined via rapid heat-cool calorimetry.*
[a] Amorphous polymers
[b] Semi-crystalline polymers

The T_{deg} represented in **Table 2** corresponds to the maximum of the first order derivative of the TGA thermogram.[6] This is also known as the inflection point or first derivative peak temperature and corresponds to the maximum degradation rate of the sample.[144,145] The values ranges from 390 to 415 °C for every polymer except for PTT and PET, which are more resistant to thermal degradation. One report compared the thermal stability of $PAT_{(p=5)}$ with the commercial PATs and mentioned that its decomposition temperature is comparable to that of PBT. Generally, PATs are stable up to 300 °C and they degrade in a one-step decomposition process.[6,146] Although the decomposition of polyesters is complex, it is believed that a simultaneous cleavage of ester and aliphatic bonds occurs, which is often observed for polyesters containing aliphatic and aromatic moieties.[6,7,147,148] The degradation behaviour of PET at high temperatures has already been studied and indicates that, due to thermal and/or oxidative degradation reactions, by-products including formaldehyde (FA), acetaldehyde (AA) and other cyclic oligomers are formed. The formation of these by-products is important considering the fact that PET is abundantly applied as packaging material for food and beverages. Both FA and AA can leach out from PET and the latter gives rise to an undesirable taste or odour to the content of the package. [149,150] There are multiple ways in which FA and AA can be generated in PET including via thermal degradation during the solid state polymerisation or injection moulding and through by-product formation during melt polycondensation of PET.[151] Villain *et al.* reported on the degradation of PET and showed that a mass loss of 0.5 % was reached after exposing a sample to 300 °C for approximately 20 minutes in an inert atmosphere.[152] In air, a mass loss of more than 2 % was observed after 20 minutes at 270 °C. Liu *et al*. have proposed a thermal degradation mechanism for PTT as indicated in **Figure 16**.[16] First, a McLafferty rearrangement splits the polymer chain which results in a carboxylic acid and an allyl ester end-group product. Decarboxylation of the former results in carbon dioxide and de-esterification of the latter produces carbon monoxide and acrylaldehyde. Also some other fragments like phenyl-containing chains were identified.[38,136]

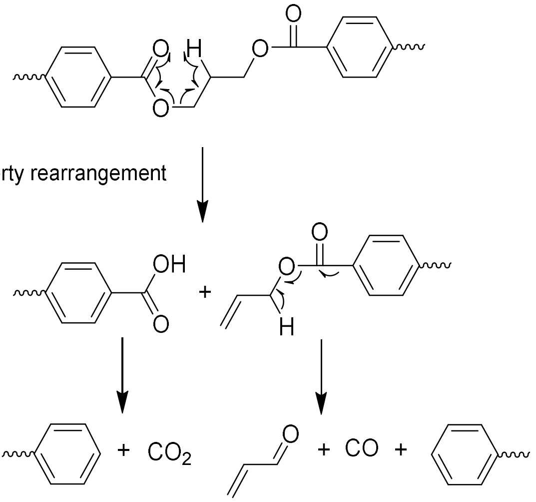

Figure 16. Thermal degradation mechanism of PTT according to Liu *et al.*[16]

The T_g of PET depends among others on the degree of crystallinity. For highly crystalline PET, a T_g of 81 °C was observed while this was 67 °C for its quasi-fully amorphous equivalent.[132] These values are higher compared to those for PBT, for which T_g's up to 52 °C have been reported for semi-crystalline samples.[153,154] This trend can be observed for the entire PAT series since the flexibility of the polymer chains increases with p, which will result in a decreasing T_g. Moreover, research has shown that the T_g of the polymers with an odd number of methylene groups, e.g. $PAT_{(p=5)}$, $PAT_{(p=7)}$ and $PAT_{(p=9)}$ is lower compared to the ones with an even number of methylene moieties, e.g. $PAT_{(p=4)}$, $PAT_{(p=6)}$, $PAT_{(p=8)}$, $PAT_{(p=10)}$ and $PAT_{(p=12)}$ when recorded via rapid heat-cool calorimetry. Knowing that a semi-crystalline polymer will possess a slightly higher T_g than its amorphous analogue, it is believed that this could be an explanation for the observed odd-even pattern.[6,155] Since the T_g depends on many different parameters including the synthesis pathway and the cooling and heating rate, the odd-even effect is only apparent for the PATs ranging from 4 to 10 methylene groups in Table 2. Of these PATs, T_g's originating from the same research are plotted as a function of the chain length in order to visualise the odd-even pattern (**Figure 17**).

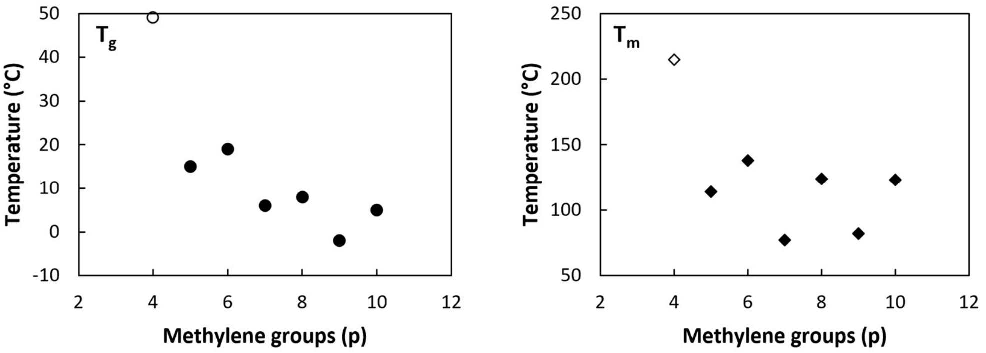

Figure 17. Visualisation of the odd-even trend in the T_g (left) and T_m (right) of $PATs_{(p=4-10)}$. The values were recorded with rapid heat-cool calorimetry.[6] PBT is indicated with an open symbol because the authors used this PAT as reference material but did not synthesise it themselves.

PET is characterised by a single melting temperature of approximately 265 °C.[156] In the DSC thermograms of $PAT_{(p=6)}$, $PAT_{(p=8)}$ and $PAT_{(p=10)}$ on the other hand, two partially overlapping melting endotherms can be distinguished. The melting temperatures corresponding to these endotherms are reported in **Table 2** as T_{m1} and T_{m2}. The multiple melting peaks have already been investigated and are hypothesised to originate from a melt-recrystallisation model.[23,157–160] During heating, the original and less stable polymer crystals melt, which results in the first melting peak. Simultaneously, recrystallisation occurs and upon further increase of the temperature, melting of the recrystallised crystals follows, which gives rise to the second melting peak. Just like with the T_g, the T_{m2} also shows an odd-even trend (**Figure 17**) and generally decreases with increasing p, which can be interesting in view of specific applications.[6,19,138] Dyeing of PTT for example requires less energy compared to PET because the melting temperature, and as a result also the dyeing temperature, of the former is lower.[131] Furthermore, various authors have already studied the odd-even effect of the T_m and attributed this to the crystallisation behaviour. Goodman *et al*. described the odd-even trend for PATs with p ranging from 2 to 10 and hypothesised that the higher melting temperature resulted from a more intimate crystal packing of the even series.[161] Tasaki *et al*. have determined the chain conformation of PATs with X-ray structure analysis.[81,162] They showed that the odd-numbered PATs form *gauche* bonds around the ester moiety and therefore adopt a kinked conformation (**Figure 18**). The even-numbered series on the other hand had a fully extended conformation because of the formation of all-*trans* bonds. This difference in chain conformation leads indeed to a difference in packing structure between the odd- and even-numbered PATs and causes an odd-even pattern in the T_m. However, the trend in chain conformation only accounts for p up to 14 because longer PATs were also expected to take the all-*trans* conformation, irrespective of the value of p.

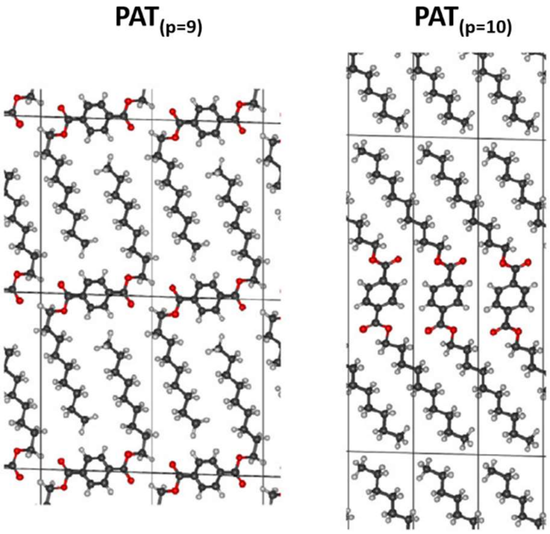

Figure 18. Chain conformation of PAT$_{(p=9)}$ and PAT$_{(p=10)}$, with respectively a kinked conformation because of the *gauche* bonds around the ester moiety and a fully extended conformation because of the all-*trans* bonds. Figure adapted from Tasaki *et al.*[81]

A study comparing the crystallisation rates of PET, PTT, PBT and PAT$_{(p=5)}$ revealed that it decreases in the following order: PBT > PTT > PET > PAT$_{(p=5)}$.[163] In case of the latter, it has been proven that the polymer crystallises slower from the melt than from the glassy state.[37] The rapid crystallisation rate of PBT compared to PET makes the former more suitable for injection moulding since shorter production cycles can be established.[1,2] Also for PAT$_{(p=7)}$, multiple authors mention the slow crystallisation of the polymer which made it difficult to determine the T_{cc} with DSC.[36,37]

3.2. Mechanical properties

In **Table 3**, some characteristics of PATs determined via tensile testing are overviewed. Tensile tests have only been performed on a restricted number of PATs which made the available literature in this regard rather limited. It should be noted that it is difficult to compare properties resulting from various studies because of the different conditions and experimental parameters applied.

Table 3. An overview of the mechanical properties of various PATs obtained from tensile testing.

PAT	Young's modulus (MPa)	Ultimate tensile strength (MPa)	Stress at break (MPa)	Elongation at break (%)	Reference
PET	2000-5300	62	-	4-600	[2,164,165]
PTT	1600-3000	62	32	5-300	[24,37]
PBT	2340-2800	57	-	250	[18,37]
PAT$_{(p=5)}$	650-1000	-	21	448	[37,166]
PAT$_{(p=6)}$	531-740	-	15-20	2-16	[113,140,146]
PAT$_{(p=8)}$	450	-	-	-	[166]
PAT$_{(p=10)}$	400	-	-	-	[166]

Ward *et al.* compared the mechanical properties of PET, PTT and PBT and found that PTT and PBT have a lower Young's modulus than PET and that PTT shows superior elastic recovery compared to the other two polymers.[167] Also in this case, the difference in chain conformation (*vide supra*) is believed to be the reason for this phenomenon. Since PTT contains only three methylene units, it will adopt a highly contracted zigzag conformation, while both PET and PBT will be fully extended because of their even number of methylene groups.[15] The difference in conformation can possibly explain the superior elastic recovery and resilience of PTT over PET and PBT.[2,26,118,137] However, several properties of PTT, like the crystallisation rate and the T_g, are in between those of PET and PBT.[5,25,56] As a result, PTT can be processed through a similar strategy as exploited for PBT, while maintaining mechanical characteristics comparable to those of PET (e.g. high young's modulus and tensile strength).[26] Other research compared the young's moduli up to $PAT_{(p=10)}$ and found that it decreased with increasing number of methylene moieties in the repeating unit.[166]

Stress-strain curves from samples prepared via injection moulding and exposed to compression indicated that the processing method highly influences the tensile properties of $PAT_{(p=5)}$.[37] This is also one of the reasons that the mechanical properties of the PATs indicated in **Table 3** entail broad ranges. Due to its lower glass transition temperature and melting temperature (*vide supra*), $PAT_{(p=5)}$ is less rigid compared to PET, PTT and PBT.[166] This manifests itself in a lower modulus and breaking strength. However, the lower T_g and the longer aliphatic moiety is expected to result in a superior impact strength above room temperature along with improved flexibility, elasticity and ductility compared to PTT.

From the above paragraphs, it can be understood that the properties of the PATs partially match, but that there are some variations due to the difference in chain length which make them suitable for diverse applications. PBT for example exhibits good electrical insulation and very fast crystallisation, while PTT has potential due to its high elasticity, outstanding elastic recovery, good dyeability and softness.[1,130,168] PET on the other hand is the toughest material, but reveals poor fatigue resistance and impaired recovery from strains exceeding 5 %.[2]

In addition, the properties of PATs can be easily altered in combination with an additive like a stabiliser, plasticiser or another polymer.[18] In the case of PET, a lot of research has already been done towards the addition of fillers for improved mechanical properties. The investigated fillers included carbon fibres, carbon nanotubes, glass fibres and flame retardants.[169–175] The use of fillers was also investigated for PATs with longer alkyl chain lengths.[140,176–180] The tensile modulus and strength of injection moulded PTT increased when 0.05-0.3 wt% carboxylated multi-walled carbon nanotubes (MWCNTs) were incorporated.[136] Moreover, the nanocomposites were less brittle and their conductivity increased with 60 %. Furthermore, also electrospun PBT fibres showed a three times higher modulus measured via atomic force microscopy (AFM) when 5 wt% MWCNTs were added.[139] Another option to differentiate the mechanical properties for various applications, is via the synthesis of copolymers. Varma *et al*. investigated copolymers of PET with $PAT_{(p=6)}$, $PAT_{(p=8)}$ and $PAT_{(p=10)}$, which resulted in a decreasing modulus when PATs with longer alkyl chain were combined with PET. The highest moisture regain and dye uptake was noticed when $PAT_{(p=10)}$ was included in the copolymer because of the lower T_g which increased the segmental mobility and free volume.[11,181] In 2019, Xu *et al*. proved an enhanced ductility when bio-based 1,10-decanediol was incorporated in PBT via a green polycondensation-coupling ring-opening polymerisation.[182] As eco-friendly and sustainable alternative for packaging, Chebbi *et al*. synthesised a series of biobased copolyesters starting from 1,10-decanediol, isosorbide and dimethylfuran-2,5-dicarboxylate monomers.[183] This $PAT_{(p=10)}$ copolymer showed improved mechanical properties (i.e. tensile modulus, ultimate strength and elongation at break) when isosorbide was included at lower concentrations (5-15 mol%) and it was sensitive to biodegradation assays in soil.

4. Polymer recycling

As PET and PBT are used in a plethora of commercial applications ranging from automotive to food packaging, they are produced in high quantities on industrial scale. Therefore, both are highly abundant in plastic waste and play a crucial role in pollution.[184–188] In order to avoid plastic waste and achieve a circular economy, recycling is gaining increasing attention.[189] In 2017, more than 70 % of the PET bottles in Europe were recycled. Plastic waste can be reused (e.g. PET bottles after thorough cleaning) or processed into lower grade products (e.g. fibre fillings for pillows or carpets from PET bottles).[190] In the past years, recycling of PATs, and more precisely PET, was already described in various extended reviews and therefore only covered briefly in this review.[191–200] In the context of recycling, two processes are applied, including chemical and mechanical recycling.

4.1. Chemical recycling

One of the recycling techniques that has already been investigated for commercial PATs is chemical recycling. This includes the total or partial depolymerisation of polymers towards their corresponding monomers or oligomers respectively. These could in turn be used as raw materials to synthesise new polymers.

Soon after the commercialisation of PET, a lot of chemical recycling techniques for this polymer have been reported including hydrolysis with hot compressed water [115,119,201,202], alcoholysis with methanol [120] and glycolysis with ethylene glycol.[2,203–206] Since water is a cheap, readily available and environmentally friendly solvent, it is more attractive than alcohols to use in a reaction. When water reaches temperatures of 240-320 °C, it diffuses in the polymer and hydrolyses the ester bonds which cleaves the polymer into smaller fragments. Via this way, it gradually dissolves PET and forms a homogeneous solution. As the hydrolysis continues, TPA, ethylene glycol and some by-products are formed. If the reaction proceeds at 300 °C for 10 minutes, 90 % TPA and 70 % ethylene glycol are formed, while longer residence times decrease the yield of the latter since it is prone to dehydroxylation in the presence of dicarboxylic acid.[201] In the case of methanolysis, DMTA and ethylene glycol are formed. It can be concluded that both processes result in the starting monomers required for the PET synthesis. A disadvantage of chemical recycling of PET is the high cost related to the high processing temperature and pressure which are required.

Also for PTT and PBT, successful depolymerisation methods, mainly based on methanolysis, have been published.[114,118,207,208] It was recently shown that the monomers of PTT and

PBT could be obtained in a high yield via hydrolysis (70 % 1,3-PDO, 95 % 1,4-BDO and 90% TPA).[115,119,201,202] For PTT, a reaction at 300 °C for 15 minutes seemed to be optimal, as the highest yields (90.5 % TPA and 69.03 % 1,3-PDO) were obtained and longer reaction times led to an increase in formed by-products (**Figure 19**).[115] 1,4-butanediol, produced by the depolymerisation of PBT, was converted into THF when reaction times exceeded 15 minutes.[119]

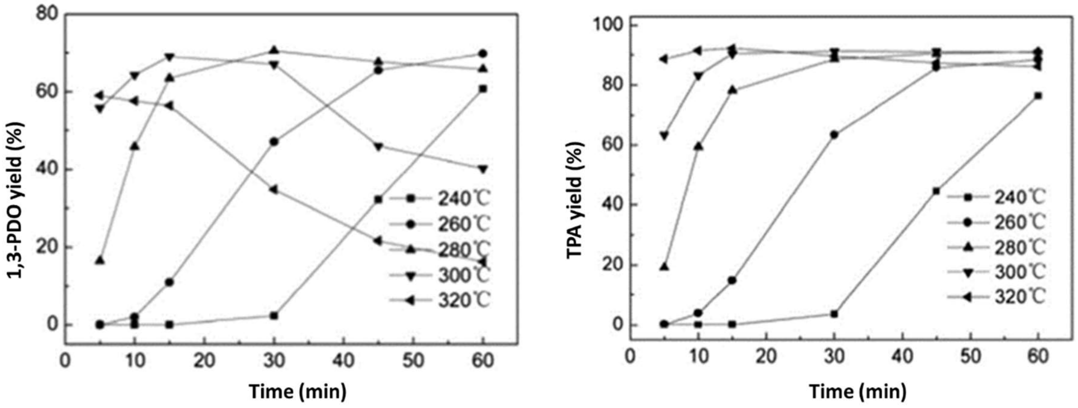

Figure 19. The yield of 1,3-propanediol (left) and TPA (right) as a function of time for the depolymerisation of PTT in hot compressed water at different temperatures.[115]

More recently, enzymes have been screened and investigated to be applied in the recycling process of aromatic polyesters.[209] Because of the industrial relevance of PET recycling, a substantial amount of research has been devoted to the biodegradation of this polymer. As a result, recent reviews covering this topic are abundant.[210–213] Several enzymes can hydrolyse the surface chains of PET but for recycling, the building blocks should be degraded. Müller *et al.* reported that an enzyme isolated from *Thermobifida fusca* (TfH) could hydrolyse aliphatic−aromatic copolyesters such as poly(butylene terephthalate-co-adipate).[214,215] Later, TfH was the first enzyme of which was demonstrated that it was capable of depolymerising PET.[216,217] The hydrolysis products included terephthalic acid, benzoic acid and bis(2-hydroxyethyl terephthalate).[218] To date, numerous PET hydrolases have already been identified. The majority of them belong to the cutinase group (i.e. hydrolases that can degrade cutin of the cuticular layer in leaves). When combined with fungal proteins, the cutinase activity can be stimulated and the rate of enzymatic PET degradation is increased.[219,220] However, there are several factors that affect the biodegradability of polymers including the crystallinity, surface topography and the temperature at which the degradation takes place. In highly crystalline materials, the mobility of the polymer chains is restricted, thereby reducing the probability for enzymatic degradation to occur. As a result, amorphous regions are more easily hydrolysed by polyesterases. Depending on the final application, the polymers exhibit a different degree of crystallisation. PET bottles and textiles for example have a crystallinity of 30-40 % while PET used for packaging is only corresponding with a crystallinity of 8 %. Additionally, when the degradation temperature is close to the T_g of the polymer, the chain mobility will be increased, thereby facilitating enzymatic degradation.[217] The difficult depolymerization of highly crystalline PET waste and the high temperatures at which the enzymes should remain active limit the biocatalytic depolymerization capabilities of PET on an industrial scale.[221] It might be interesting to investigate to what extend PET hydrolases are also capable of degrading other PATs, beyond PET.

4.2. Mechanical recycling

Mechanical recycling is another recycling process which is widely applied for various plastics including PET. Although, to the best of our knowledge, literature for other PATs is non-existing.[191,196,222,223] Mechanical recycling involves the remelting of the plastics, either alone or with raw material, to reprocess them into granulates by melt extrusion. Prior to the remelting, the PET waste is sorted and separated from other plastics in order to avoid contamination and deterioration of the PET. Thereafter, the PET materials are washed, either with water or with organic solvents (e.g. tetrachloroethylene). Subsequently, a drying step is applied to remove any water or solvents left from washing in order to minimise the moisture content. The latter would degrade the polymers because of hydrolytic chain scission during melting. For PET, maximum 50 ppm water is allowed and therefore, dryers at 170 °C for 6 hours are used.[223] In general, mechanical recycling is a more environmentally friendly process compared with chemical recycling. Furthermore, it is relatively simple and only low investment costs are required. Although mechanical recycling does not alter the basic material, as contaminants are removed, the material properties will vary. In each recycling cycle, the molar mass will decrease due to the hydrolytic chain scissions. Since the standards of recycled PET intended for food packaging are high, chemical recycling is favoured over mechanical recycling in that field.

5. Overview of application potential

As mentioned earlier *(vide supra)*, a plethora of applications exist for the PATs produced on industrial scale while for the other PATs, investigation towards their application potential is ongoing or should still be conducted. An overview of the current applications of PATs is given in **Figure 20**.

5.1. Non-biomedical applications

The first PET production plant was built in 1959 and allowed the synthesis of PET on industrial scale. This, together with the versatility of the polymer, resulted in commercial applications.[2] PET is often exploited in the packaging industry because of its low cost, transparency and limited permeability towards several gases including oxygen. To exemplify, the oxygen permeability of PET is 1.5 cm^3 mm/m^2 atm day while this corresponds with 60 cm^3 mm/m^2 atm day for high density polyethylene. These barrier properties render PET an excellent material for the preservation of food, beverages, pharmaceuticals, etc, which are prone to oxidation. A substantial amount of research concerning the barrier properties of PET can be consulted in literature.[224–228] Since the polymer shows low permeability against carbon dioxide and certain organic aroma compounds, it is also preferred for packaging of carbonated soft drinks.[39,227,228] Furthermore, PET can be drawn into long fibres that are durable and resistant to shrinkage and stretching, making them excellent to become processed into clothing. More than 60 % of all PET produced worldwide is consumed in the textile industry, often in blends with other materials such as cotton.[229,230] With a conductivity of $1*10^{-18}$ S/cm, PET is considered an insulating material which is applied as electrical insulator in e.g. cables and motors. A wide variety of PET-based copolymers and blends have already been examined to tune the properties towards different applications.[11,39,231–234] Recycled PET from PET bottles is also used in lower grade products, for example carpets and fibre filling for pillows.[190]

PTT has only been commercialised relatively recently and is currently sold under the trade mark Corterra by Shell and bio-based Sorona by Dupont.[53,235] Nylon 6,6 used to be the standard polymer to produce carpets and apparel.[236–238] However, as PTT can be dyed more easily, has a softer feel and superior stain resistance, stretch and recovery, this polymer has become increasingly appealing for these applications since its initial commercialisation. The PTT fibres, commercially known as Triexta, are also used in pillowcases and swimwear. The polymer is investigated as engineering thermoplastic and for films and food packaging.[53,57,131] Currently, PET and nylon layers are present in retort pouches. Since PTT exhibits the transparency and heat resistance of PET but a flexibility and elasticity comparable to that of nylon, the polymer has been investigated to replace both layers in retort pouches.[237,239] Recently, filaments for extrusion-based 3D printing were produced from PTT blended with biocarbon.[240]

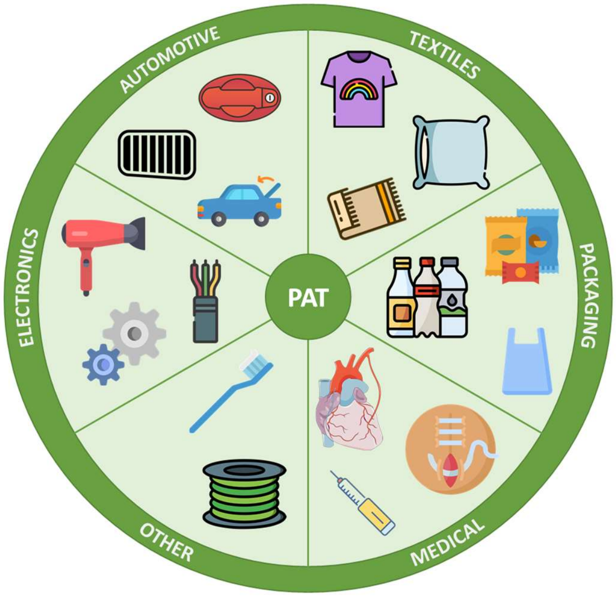

Figure 20. Overview of applications in which PATs are used. The included sectors are electronics (e.g. hairdryer, cable insulation, gear wheel), automotive (e.g. door handle, trunk lid, radiator grill), textiles (e.g. carpet, pillowcase, apparel), packaging (e.g. beverage bottles, grocery bag, food packaging), medical (e.g. insulin pen, sutures, bypass graft) and other (e.g. toothbrush bristles and 3D printing filament).

PBT is sold under a lot of tradenames including Crastin by Dupont and Pocan by Lanxess.[241,242] PBT is frequently applied for electronic components in the automotive industry (*vide supra*).[1,130] Dupont for example applies PBT in a vehicle lighting system because of its hydrolysis and high-temperature resistance in combination with the suitable strength, toughness and processibility of the material. Since PBT is FDA-approved for food contact purposes, exhibits a low moisture absorption, and a high resistance to staining, it is typically used in food processing machinery components. This polymer can also be found in some fibre applications, such as toothbrush bristles and is present in food contact materials and certain cosmetics.[2,243,244] PBT is readily processable by means of extrusion and injection moulding. Polymer blends of PBT with poly(ε-caprolactone) can be found in the exterior and interior of cars as bumpers, radiator grills, door handles, trunk lids, etc.[1,245] Recently, the polymer has been investigated to serve many other applications including, yet not limited to bead foam,[246] antimicrobial packaging[247] and flame retardant materials.[248]

Despite the low T_g and moderate T_m of $PAT_{(p=6)}$ (**Table 2**), the polymer is investigated for its use in laminating processes. To this end the thermal and mechanical behaviour should be improved and the melt viscosity increased. For this purpose, $PATs_{(p=6)}$ have been adapted by replacing an increasing amount (5 to 50 mol%) of terephthalates with 5-sulfoisophthalate sodium salt (SI) units.[146] The authors found that the thermal stability and T_m of the copolyester decreased while the T_g increased with the number of SI units. The Young's modulus and melt viscosity of the polymer increased gradually with the SI content and also the elongation at break increased drastically but only for a low amount of SI units. Since the SI moieties are more hydrophilic, the copolyesters experienced an enhanced hydrolytic degradability.

For the other PATs, research on possible commercial applications is ongoing or should still commence and is mainly limited by the low availability of the reagents which prevents the production on industrial scale.[37] However, once the commercialisation is realised, the future of this polymer class looks promising. $PAT_{(p=5)}$ for example could be excellent for melt processing due to its low T_m and high thermal stability.[2] All the properties of $PAT_{(p=5)}$ also indicate that the polymer could be used in elastic fibres, toughening additives for rigid polyesters and hot melt adhesives.[37] Moreover, copolymers with PATs also possess interesting features for various applications. If copolymers of $PAT_{(p=6)}$ and biodegradable poly(ε-caprolactone) are further investigated, they could be used as biodegradable alternatives for PET plastic packaging.[77,249]

5.2. Biomedical applications

The investigation of PBT and PET for biomedical applications already started around the 1990s. Both biocompatible polymers induce only a minor inflammatory response and can therefore be used as biomaterials.[250–253] Currently, PET is applied as synthetic bypass graft for the replacement of large diameter (> 6 mm) blood vessels.[254–257] However, using the polymer in small-diameter (< 6 mm) grafts, remains challenging because of thrombogenicity issues.[258] The latter is the formation of a blood clot inside blood vessels which obstructs the blood flow and results in failure of the graft. One of the causes for thrombosis to occur is the absence of a complete endothelium, i.e. a single layer of endothelial cells on the graft wall.[257,259] $PAT_{(p=5-10)}$ are currently investigated as alternatives for PET bypass grafts because preliminary assays showed promising results regarding their endothelial cell interactivity and indicated that the mechanical properties of PATs might more closely resemble the ones of native vessels.[99,260,261] PET is also exploited as surgical suture membrane,[234] angioplasty balloon,[262] support in breast implants,[263] scaffold for tissue engineering[264] and ligament prosthesis.[258] This enumeration indicates that PET is used for a lot of biomedical purposes but, due to the hydrophobic nature of the polymer, surface modifications are frequently required to realise a successful application in this field. Multiple approaches have already been described, including grafting of a more hydrophilic polymer, plasma treatment to create polar functional groups, the immobilisation of a coating, etc (**Figure 21**). For the latter, a wide variety of coatings like fluoropolymers,[265] collagen, heparin derivatives,[266] fibroblast growth factor [267] and gelatin [256,268] have already been applied. When a PET graft was used as ligament prosthesis, the hydrophobic polymer induced the formation of scar tissue around the graft which frequently resulted in graft rupture. Therefore, surface modifications on the PET graft, which could improve the cell compatibility of the prosthesis, were investigated.[269] Coatings containing hydroxyapatite, bioactive glass or hydroxypropyl cellulose have been applied onto the PET surface. Also, the immobilisation of polystyrene sodium sulfonate was realised with the "grafting from" technique. A review from 2014 by Smith *et al.* discusses a plethora of polymer coatings for biomedical applications.[270] For the PATs, reports regarding their surface modification strategies are limited and could be an interesting research topic.[271]

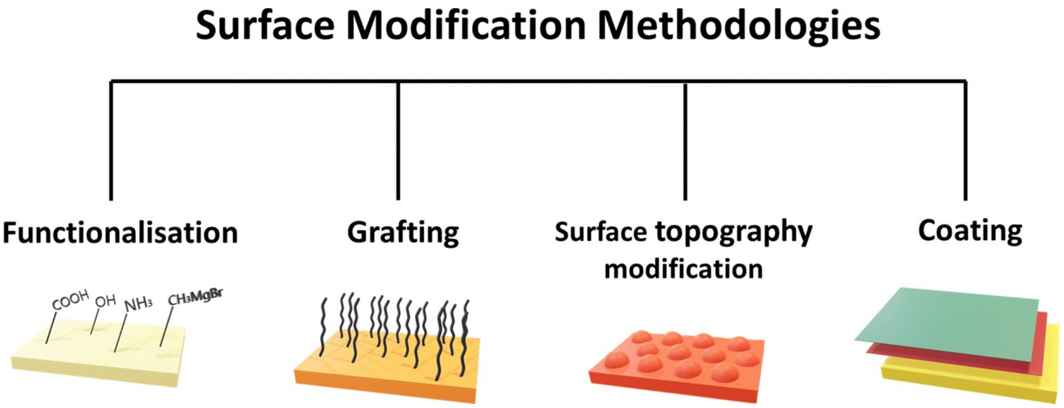

Figure 21. Some of the surface modification methodologies used for PET.[272]

Just like PET, PBT has shown its potential in the biomedical field but mainly in combination with other polymers. Copolymers composed of poly(ethylene oxide terephthalate) and PBT (PEOT/PBT) have induced *in vivo* calcification and bone bonding which led to the investigation of this block copolymer as possible scaffolding material for (bone) tissue engineering.[130] Furthermore, PEOT/PBT has also been studied as bone filler,[273] dental implant[274] and for the treatment of bone defects.[275] Surface modifications, like gas plasma treatment and the incorporation of hydroxyapatite have appeared to be necessary in some cases, including for the *in vitro* culture of bone marrow stromal cells.[276] Moreover, PEOT/PBT scaffolds were found to be successful to function as gradual drug release system.[277,278] In addition, other polymer combinations containing PBT have also been investigated for tissue engineering.[279] A copolymer of PBT with poly(ethylene oxide) (PEO) was examined for protein release by the combination of matrix degradation and diffusion. Bezemer *et al*. found that the release rates could be tuned depending on the content and molar mass of PEO.[280] This copolymer is also applied in other biomedical fields such as in bone replacement[281] and to create artificial skin.[282] Moreover, PBT is also used in filtration applications for biomedical purposes. One report indicated that PBT with a thin layer of hydroxyapatite can function as a blood filter for the selective removal of leukocytes (white blood cells).[283] Furthermore, PBT has shown to be biocompatible and haemocompatible in a composite with wollastonite, a component known to enhance the mechanical performance.[284,285] The polyester has also been incorporated in an insulin pen, rendering it light, strong and affordable to aid diabetes patients.[286]

6. Conclusions and future perspectives

Throughout the past decades, PET, PTT and PBT have been dominating the large-scale production for their use in many commercial applications. Industrially, melt polymerisation is still the method of choice, but new approaches have been investigated. Solution polymerisation has emerged as an alternative since it provides polymers via a single-step method without the need for a catalyst. However, solvent related issues such as toxicity and the necessity for additional purification steps must be taken into account. Despite the multiple advantages of ROP, the limited availability of cyclic reagents currently renders the technique unsuitable for large scale production. Recent discoveries related to synthesis methods of cyclic oligomers could provide a solution for this issue. Due to the global awareness that emerged recently, a more sustainable consumer flow is desired and research towards a circular economy became increasingly important. Recycling is desired, especially for PET, PTT and PBT, which are used for many single use plastic applications and therefore play a crucial role in pollution. To this end, alternative reaction conditions for PATs with the possibility for chemical recycling (e.g. via (cyclo-)depolymerisation) were investigated during the past few years. Methods for the extraction of monomers from naturally occurring raw materials to realise the production of PATs from renewable building blocks also received a lot of attention. The thermal properties of the PATs up to $p=12$ have already been examined but literature on the mechanical properties of PATs with $p > 4$ is scarce, indicating that these should be further explored. The different properties of the PATs make them suitable for various applications. PET, PTT and PBT are already applied in a lot of fields and recently, the potential applications of some of the PATs with more than 4 methylene moieties have been studied, although these investigations are still in an early stage.

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References

[1] E. Gubbels, T. Heitz, M. Yamamoto, V. Chilekar, S. Zarbakhsh, M. Gepraegs, H. Köpnick, M. Schmidt, W. Brügging, J. Rüter, W. Kaminsky, Polyesters, Ullmann's Encycl. Ind. Chem. (2018) 1–30. https://doi.org/https://doi.org/10.1002/14356007.a21_227.pub2.

[2] J. Scheirs, T.E. Long, Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters, John Wiley & Sons, 2003.

[3] X. Lefèbvre, M.H.J. Koch, H. Reynaers, C. David, Thermal behavior of poly(hexamethylene terephthalate) oligomers. I. Melting behavior and morphology of the crystalline phase, J. Polym. Sci. Part B Polym. Phys. 37 (1999) 1–18. https://doi.org/10.1002/(SICI)1099-0488(19990101)37:1<1::AID-POLB1>3.3.CO;2-2.

[4] J.R. Whinfield, J.T. Dickson, Polymeric linear terephtalic esters, US Patent 2465319A, 1949.

[5] W. Schmidt, U. Thiele, S. Schauhoff, D. Yu, Process for production of polypropylene terephthalate, 5798433, 1998.

[6] E.D. Giol, N. Van den Brande, B. Van Mele, S. Van Vlierberghe, P. Dubruel, Single-step solution polymerization of poly(alkylene terephthalate)s: synthesis parameters and polymer characterization, Polym. Int. 67 (2018) 292–300. https://doi.org/10.1002/pi.5508.

[7] K. Ravindranath, R.A. Mashelkar, Polyethylene terephthalate-I. Chemistry, thermodynamics and transport properties, Chem. Eng. Sci. 41 (1986) 2197–2214. https://doi.org/10.1016/0009-2509(86)85070-9.

[8] J.G. Smith, C.J. Kibler, B.J. Sublett, Preparation and Properties of Poly (methylene terephthalates), J. Polym. Sci. Part A-1. 4 (1966) 1851–1859. https://doi.org/https://doi.org/10.1002/pol.1966.150040719.

[9] A. Martínez De Ilarduya, S. Muñoz-Guerra, Chemical structure and microstructure of poly(alkylene terephthalate)s, their copolyesters, and their blends as studied by NMR, Macromol. Chem. Phys. 215 (2014) 2138–2160. https://doi.org/10.1002/macp.201400239.

[10] M.A. Villalobos, J. Debling, Bulk and Solution Processes, in: Handb. Polym. Synth. Charact. Process., 2013: pp. 273–294. https://doi.org/10.1002/9781118480793.ch13.

[11] D.S. Varma, R. Agarwal, V. I.K., Poly(ethylene Terephthalate)/ Poly(alkylene Terephthalate) Copolyester Fibers : Mechanical and Physical Properties, Text. Res. J. (1986) 364–369. https://doi.org/https://doi.org/10.1177/004051758605600604.

[12] G. Botelho, A. Queiro, S. Liberal, P. Gijsman, Studies on thermal and thermo-oxidative degradation of poly(ethylene terephthalate) and poly(butylene terephthalate), Polym. Degrad. Stab. 74 (2001) 39–48. https://doi.org/https://doi.org/10.1016/S0141-3910(01)00088-X.

[13] I.C. McNeill, M. Bounekhel, Thermal degradation studies of terephthalate polyesters: 1. Poly(alkylene terephthalates), Polym. Degrad. Stab. 34 (1991) 187–204. https://doi.org/10.1016/0141-3910(91)90119-C.

[14] J.H. Chang, Comparison of thermomechanical properties and morphologies of polyester nanocomposite fibers: PBT, PET, and PTT, Polym. - Plast. Technol. Eng. 47 (2008) 791–801. https://doi.org/10.1080/03602550802188680.

[15] S. Poulin-Dandurand, S. Pérez, J.F. Revol, F. Brisse, The crystal structure of poly(trimethylene terephthalate) by X-ray and electron diffraction, Polymer (Guildf). 20 (1979) 419–426. https://doi.org/10.1016/0032-3861(79)90064-8.

[16] J. Liu, S.G. Bian, M. Xiao, S.J. Wang, Y.Z. Meng, Thermal degradation and isothermal crystalline behavior of poly(trimethylene terephthalate), Chinese Chem. Lett. 20 (2009) 487–491. https://doi.org/10.1016/j.cclet.2008.11.035.

[17] A. Sanz, A. Nogales, T.A. Ezquerra, M. Soccio, A. Munari, N. Lotti, Cold crystallization of poly(trimethylene terephthalate) as revealed by simultaneous WAXS, SAXS, and dielectric spectroscopy, Macromolecules. 43 (2010) 671–679. https://doi.org/10.1021/ma902188c.

[18] C. Sarathchandran, C.H. Chan, S.R. Abdul Karim, S. Thomas, Poly(Trimethylene terephthalate)-the new generation of engineering thermoplastic polyester, Phys. Chem. Macromol. Macro to Nanoscales. (2014)

573–618. https://doi.org/10.1201/b16706-22.

[19] H.K. Yip, H.L. Williams, Transitions and relaxations of linear polyesters related to poly(ethylene terephthalate). I. Melting, J. Appl. Polym. Sci. 20 (1976) 1209–1215. https://doi.org/10.1002/app.1976.070200507.

[20] Polyethylene terephthalate (PET): Production, Price, Market and its Properties, Plast. Insight. (2020) 1. https://www.plasticsinsight.com/resin-intelligence/resin-prices/polyethylene-terephthalate/ (accessed November 19, 2020).

[21] F. Welle, The Facts about PET, 2018.

[22] B. Gantillon, R. Spitz, T.F. McKenna, The Solid State Postcondensation of PET, 1: A Review of the Physical and Chemical Processes Taking Place in the Solid State, Macromol. Mater. Eng. 289 (2004) 88–105. https://doi.org/10.1002/mame.200300289.

[23] M.E. Nichols, R.E. Robertson, The multiple melting endotherms from poly(butylene terephthalate), J. Polym. Sci. Part B Polym. Phys. 30 (1992) 755–768. https://doi.org/10.1002/polb.1992.090300713.

[24] Omnexus, Complete Guide on Polybutylene Terephthalate (PBT), 2019. https://omnexus.specialchem.com/selection-guide/polybutylene-terephthalate-pbt-plastic.

[25] M. Soccio, A. Nogales, T.A. Ezquerra, N. Lotti, A. Munari, Effect of copolymerization in the dynamics of poly(trimethylene terephthalate), Macromolecules. 45 (2012) 180–188. https://doi.org/10.1021/ma202361r.

[26] M. Soccio, N. Lotti, L. Finelli, M. Gazzano, A. Munari, Neopenthyl Glycol Containing Poly(propylene terephthalate)s: Structure–Properties Relationships, J. Polym. Sci. Part B Polym. Phys. 46 (2007) 170–181. https://doi.org/10.1002/polb.

[27] R.K. Saxena, P. Anand, S. Saran, J. Isar, Microbial production of 1,3-propanediol: Recent developments and emerging opportunities, Biotechnol. Adv. 27 (2009) 895–913. https://doi.org/10.1016/j.biotechadv.2009.07.003.

[28] C. Hwo, T. Forschner, R. Lowtan, D. Gwyn, B. Cristea, Poly(Trimethylene Phthalates or Naphthalate) and Copolymers: New Opportunities in Film and Packaging Applications, J. Plast. Film Sheeting. 15 (1999) 219–234. https://doi.org/10.1177/875608799901500305.

[29] H.H. Chuah, Poly(trimethylene terephthalate), Encycl. Polym. Sci. Technol. 3 (2001) 544–558. https://doi.org/10.1002/0471440264.pst292.

[30] J. Zhang, Study of Poly(trimethylene terephthalate) as an Engineering Thermoplastics Material, J. Appl. Polym. Sci. 91 (2004) 1657–1666.

[31] J.M. Howell, W. Tung, F. Werny, Carpets made from poly(trimethylene terephthalate) bulked continuous filaments, US Patent 6552980, 1997.

[32] E.M. Woo, G. Lugito, C.E. Yang, S.M. Chang, Atomic-force microscopy analyses on dislocation in extinction bands of poly(Dodecamethylene terephthalate) spherulites solely packed of single-crystal-like lamellae, Crystals. 7 (2017). https://doi.org/10.3390/cryst7090274.

[33] K.C. Yen, E.M. Woo, K. Tashiro, Six types of spherulite morphologies with polymorphic crystals in poly(heptamethylene terephthalate), Polymer (Guildf). 51 (2010) 5592–5603. https://doi.org/10.1016/j.polymer.2010.09.031.

[34] G. Lugito, E.M. Woo, S.M. Chang, Periodic extinction bands composed of all flat-on lamellae in poly(dodecamethylene terephthalate) thin films crystallized at high temperatures, J. Polym. Sci. Part B Polym. Phys. 55 (2017) 601–611. https://doi.org/10.1002/polb.24304.

[35] E.M. Woo, G. Lugito, S.M. Chang, Three-dimensional interior analyses on periodically banded spherulites of poly(dodecamethylene terephthalate), CrystEngComm. 20 (2018) 1935–1944. https://doi.org/10.1039/c7ce02226c.

[36] K.C. Yen, E.M. Woo, K. Tashiro, Amorphous phase and crystalline morphology in blend of two polymorphic polyesters: Poly(hexamethylene terephthalate) and poly(heptamethylene terephthalate), Polymer (Guildf). 50 (2009) 6312–6322. https://doi.org/10.1016/j.polymer.2009.10.066.

[37] J. Lu, L. Zhou, H. Xie, L. Wu, B.G. Li, Biobased flexible aromatic polyester poly(1,5-pentylene terephthalate) (PPeT): Revisiting melt crystallization behaviors and thermo-mechanical properties, Eur. Polym. J. 110 (2019) 168–175. https://doi.org/10.1016/j.eurpolymj.2018.11.029.

[38] D.R. Kelsey, K.S. Kiibler, P.N. Tutunjian, Thermal stability of poly(trimethylene terephthalate), Polymer (Guildf). 46 (2005) 8937–8946. https://doi.org/10.1016/j.polymer.2005.07.015.

[39] K. Pang, R. Kotek, A. Tonelli, Review of conventional and novel polymerization processes for polyesters, Prog. Polym. Sci. 31 (2006) 1009–1037. https://doi.org/10.1016/j.progpolymsci.2006.08.008.

[40] P. Schlack, Bobingen, A.-G. für Textil-Faser, Ger. Patent 922255, 1955.

[41] R.J. Sheehan, Terephthalic Acid, Dimethyl Terephthalate, and Isophthalic acid, in: Ullmann's Encycl. Ind. Chem., 2012: p. 12. https://doi.org/DOI: 10.1002/14356007.a26_193.pub2.

[42] N.A.M. Fadzil, M.H.A. Rahim, G.P. Maniam, A brief review of para-xylene oxidation to terephthalic acid as a model of primary C-H bond activation, Cuihua Xuebao/Chinese J. Catal. 35 (2014) 1641–1652. https://doi.org/10.1016/S1872-2067(14)60193-5.

[43] E.F. Aransiola, M.O. Daramola, T. V. Ojumu, Xylenes: Production technologies and uses, in: Xylenes Synth. Charact. Physicochem. Prop., 2013: pp. 1–12.

[44] R.M. Steyerberg, J.P. Düren, A.S. Witten, R.W. Niederkassel, Process for the production of dimethyl terephthalate from p-xylene and methanol, US Patent 4642369, 1987.

[45] S. Rebsdat, D. Mayer, Ethylene glycol, in: Ullmann's Encycl. Ind. Chem., 2012: pp. 531–547. https://doi.org/10.1016/B978-0-12-804239-7.00042-1.

[46] P. Magnussen, L. Kniel, O. Winter, K. Stork, Ethylene-Keystone to the Petrochemical Industry, Chem. Industiies Ser. 2 (1980). https://doi.org/https://doi.org/10.1002/cite.330530212.

[47] S.F. Bosen, W.A. Bowles, E.A. Ford, B.D. Perlson, Antifreezes, in: Ullmann's Encycl. Ind. Chem., 2012: pp. 1–8. https://doi.org/10.1002/14356007.a03.

[48] S. Cammas, M.M. Béar, L. Moine, R. Escalup, G. Ponchel, K. Kataoka, P. Guérin, Polymers of malic acid and 3-alkylmalic acid as synthetic PHAs in the design of biocompatible hydrolyzable devices, Int. J. Biol. Macromol. 25 (1999) 273–282. https://doi.org/10.1016/S0141-8130(99)00042-2.

[49] J.W. Lee, M.S. Han, S. Choi, J. Yi, T.W. Lee, S.Y. Lee, Organic Acids: Succinic and Malic Acids, Compr. Biotechnol. Second Ed. 3 (2011) 149–161. https://doi.org/10.1016/B978-0-08-088504-9.00183-5.

[50] B. Kamm, P.R. Gruber, M. Kamm, Biorefineries-Industrial Processes and Products: Status Quo and Future Directions, 2005. https://doi.org/10.1002/9783527619849.

[51] H. Gräfje, W. Körnig, H.-M. Weitz, W. Reiß, G. Steffan, H. Diehl, H. Bosche, K. Schneider, H. Kieczka, R. Pinkos, Butanediols, Butenediol, and Butynediol, Ullmann's Encycl. Ind. Chem. (2019) 1–12. https://doi.org/10.1002/14356007.a04_455.pub2.

[52] A. Cukalovic, C.V. Stevens, Feasibility of production methods for succinic acid derivatives: a marriage of renewable resources and chemical technology, Biofuels, Bioprod. Biorefining. (2008) 505–529. https://doi.org/10.1002/bbb.105.

[53] G. Kaur, A.K. Srivastava, S. Chand, Advances in biotechnological production of 1,3-propanediol, Biochem. Eng. J. 64 (2012) 106–118. https://doi.org/10.1016/j.bej.2012.03.002.

[54] T. Haas, G. Böhme, D. Arntz, Process for the Preparation of 3-Hydroxyalkanals, US Patent 5284979, 1994.

[55] J.B. Powell, S.B. Mullin, P.R. Weider, D.C. Eubanks, J.P. Arhancet, Process for Preparing 1,3-Propanediol, US Patent 5770776, 1998.

[56] T. Haas, B. Jaeger, R. Weber, S.F. Mitchell, C.F. King, New diol processes: 1,3-propanediol and 1,4-butanediol, Appl. Catal. A Gen. 280 (2005) 83–88. https://doi.org/10.1016/j.apcata.2004.08.027.

[57] G.A. Kraus, Synthetic methods for the preparation of 1,3-propanediol, Clean. 36 (2008) 648–651. https://doi.org/10.1002/clen.200800084.

[58] T. Haas, N. Wiegand, D. Arntz, Process for the production of 1,3-propanediol, US Patent 5334778, 1994.

[59] J.F. Knifton, T.G. James, K.D. Allen, P.R. Weider, J.B. Powell, L.H. Slaugh, One-step production of 1,3-propanediol from ethylene oxide and syngas with a catalyst with a phospholanoalkane ligand, US Patent 6576802 B2, 2003.

[60] M. Parthiban, PTT-An innovative polymer and its versatile application in textiles, Fibre2fashion.Com. (2008) 1. https://www.fibre2fashion.com/industry-article/3261/ptt-an-innovative-polymer (accessed November 19, 2020).

[61] T. Ohishi, H. Otsuka, PET (Poly(ethylene terephthalate)) and PTT (Poly(trimethylene terephthalate)), Encycl. Polym. Nanomater. (2014) 9–13. https://doi.org/10.1007/978-3-642-36199-9.

[62] DuPont, The Sorona Story, (2020). http://sorona.com/our-story/ (accessed May 11, 2020).

[63] A. Raab, Sorona celebrates 20th anniversary of first commercial run, (2020) 1. http://sorona.com/press-release/soronar-celebrates-20th-anniversary-of-first-commercial-run/ (accessed November 19, 2020).

[64] S. Muñoz-Guerra, C. Lavilla, C. Japu, A. Martínez De Ilarduya, Renewable terephthalate polyesters from carbohydrate-based bicyclic monomers, Green Chem. 16 (2014) 1716–1739. https://doi.org/10.1039/c3gc42394h.

[65] X. Lu, G. Ji, H. Zong, B. Zhuge, The role of budABC on 1,3-propanediol and 2,3-butanediol production from glycerol in Klebsiella pneumoniae CICIM B0057, Bioengineered. 7 (2016) 439–444. https://doi.org/10.1080/21655979.2016.1169355.

[66] H.W. Wijaya, T. Kojima, T. Hara, N. Ichikuni, S. Shimazu, Synthesis of 1,5-Pentanediol by Hydrogenolysis of Furfuryl Alcohol over Ni–Y2O3 Composite Catalyst, ChemCatChem. 9 (2017) 2869–2874. https://doi.org/10.1002/cctc.201700066.

[67] E. Soghrati, C. Choong, C.K. Poh, S. Kawi, A. Borgna, Single-Pot Conversion of Tetrahydrofurfuryl Alcohol into Tetrahydropyran over a Ni/HZSM-5 Catalyst under Aqueous-Phase Conditions, ChemCatChem. 9 (2017) 1402–1408. https://doi.org/10.1002/cctc.201601708.

[68] K. Huang, Z.J. Brentzel, K.J. Barnett, J.A. Dumesic, G.W. Huber, C.T. Maravelias, Conversion of Furfural to 1,5-Pentanediol: Process Synthesis and Analysis, ACS Sustain. Chem. Eng. 5 (2017) 4699–4706. https://doi.org/10.1021/acssuschemeng.7b00059.

[69] H. Liu, Z. Huang, H. Kang, C. Xia, J. Chen, Selective hydrogenolysis of biomass-derived furfuryl alcohol into 1,2- and 1,5-pentanediol over highly dispersed Cu-Al2O3 catalysts, Chinese J. Catal. 37 (2016) 700–710. https://doi.org/10.1016/S1872-2067(15)61080-4.

[70] Z. Wang, B. Pholjaroen, M. Li, W. Dong, N. Li, A. Wang, X. Wang, Y. Cong, T. Zhang, Chemoselective hydrogenolysis of tetrahydrofurfuryl alcohol to 1,5-pentanediol over Ir-MoOx/SiO2 catalyst, J. Energy Chem. 23 (2014) 427–434. https://doi.org/10.1016/S2095-4956(14)60168-6.

[71] W. Xu, H. Wang, X. Liu, J. Ren, Y. Wang, G. Lu, Direct catalytic conversion of furfural to 1,5-pentanediol by hydrogenolysis of the furan ring under mild conditions over Pt/Co2AlO4 catalyst, Chem. Commun. 47 (2011) 3924–3926. https://doi.org/10.1039/c0cc05775d.

[72] S. Liu, Y. Amada, M. Tamura, Y. Nakagawa, K. Tomishige, Performance and characterization of rhenium-modified Rh-Ir alloy catalyst for one-pot conversion of furfural into 1,5-pentanediol, Catal. Sci. Technol. 4 (2014) 2535–2549. https://doi.org/10.1039/c4cy00161c.

[73] H. Mutlu, M.A.R. Meier, Castor oil as a renewable resource for the chemical industry, Eur. J. Lipid Sci. Technol. 112 (2010) 10–30. https://doi.org/10.1002/ejlt.200900138.

[74] J. Devroede, R. Duchateau, C.E. Koning, J. Meuldijk, The Synthesis of Poly(butylene terephthalate) from Terephthalic Acid, Part I: The Influence of Terephthalic Acid on the Tetrahydrofuran Formation, J. Appl. Polym. Sci. 116 (2009) 2658–2667. https://doi.org/10.1002/app.

[75] T.H. NG, H.L. Williams, Thermomechanical analysis of linear aromatic polyesters, Macromol. Chem. 182 (1981) 3323–3330. https://doi.org/10.1002/macp.1981.021821135.

[76] D.J. Brunelle, Cyclic oligomer chemistry, J. Polym. Sci. Part A Polym. Chem. 46 (2008) 1151–1164. https://doi.org/10.1002/pola.22526.

[77] N. González-Vidal, A.M. De Ilarduya, V. Herrera, S. Muñoz-Guerra, Poly(hexamethylene terephthalate-

co-caprolactone) copolyesters obtained by ring-opening polymerization, Macromolecules. 41 (2008) 4136–4146. https://doi.org/10.1021/ma702464k.

[78] W.A. MacDonald, New advances in poly(ethylene terephthalate) polymerization and degradation, Polym. Int. 51 (2002) 923–930. https://doi.org/10.1002/pi.917.

[79] S. V. Vinogradova, V. V. Korshak, Heterochain polyesters-XXIII. The effect of the structure of the polyester unit on the polyester melting point, Polym. Sci. U.S.S.R. 2 (1961) 10–19. https://doi.org/10.1016/0032-3950(61)90004-1.

[80] J. Bateman, R.E. Richards, G. Farrow, I.M. Ward, Molecular Motion in Polyethylene Terephthalate and other Glycol Terephthalate Polymers, Polymer (Guildf). 1 (1960) 63–71. https://doi.org/10.1016/0032-3861(60)90008-2.

[81] M. Tasaki, H. Yamamoto, T. Yoshioka, M. Hanesaka, T.H. Ninh, K. Tashiro, H.J. Jeon, K.B. Choi, H.S. Jeong, H.H. Song, M.H. Ree, Microscopically-viewed relationship between the chain conformation and ultimate Young's modulus of a series of arylate polyesters with long methylene segments, Polymer (Guildf). 55 (2014) 1799–1808. https://doi.org/10.1016/j.polymer.2014.01.058.

[82] Archna, V. Moses, S. Sagar, V. Shivraj, S. Chetan, A Review on processing of waste PET (Polyethylene Terephthalate) plastics, Int. J. Polym. Sci. Eng. 1 (2015) 1–13. https://doi.org/https://doi.org/10.37628/ijpse.v1i1-2.120.

[83] I. Flores, A. Martínez de Ilarduya, H. Sardon, A.J. Müller, S. Muñoz-Guerra, Synthesis of Aromatic–Aliphatic Polyesters by Enzymatic Ring Opening Polymerization of Cyclic Oligoesters and their Cyclodepolymerization for a Circular Economy, ACS Appl. Polym. Mater. 1 (2019) 321–325. https://doi.org/10.1021/acsapm.8b00265.

[84] A. Lodha, R.S. Ghadage, S. Ponrathnam, Polycondensation reaction kinetics of wholly aromatic polyesters, Polymer (Guildf). 38 (1997) 6167–6174. https://doi.org/10.1016/S0032-3861(97)00183-3.

[85] L. Hu, L. Wu, F. Song, B.G. Li, Kinetics and modeling of melt polycondensation for synthesis of poly[(butylene succinate)-co-(butylene terephthalate)], 1 - esterification, Macromol. React. Eng. 4 (2010) 621–632. https://doi.org/10.1002/mren.201000021.

[86] I. Flores, J. Demarteau, A.J. Müller, A. Etxeberria, L. Irusta, F. Bergman, C. Koning, H. Sardon, Screening of different organocatalysts for the sustainable synthesis of PET, Eur. Polym. J. 104 (2018) 170–176. https://doi.org/10.1016/j.eurpolymj.2018.04.040.

[87] E.M. Aghaee, M. Alimohammadi, R. Nabizadeh, G.J. Khaniki, S. Naseri, A.H. Mahvi, K. Yaghmaeian, H. Aslani, S. Nazmara, B. Mahmoudi, M. Ghani, Effects of storage time and temperature on the antimony and some trace element release from polyethylene terephthalate (PET) into the bottled drinking water, J. Environ. Heal. Sci. Eng. 12 (2014) 1–7. https://doi.org/10.1186/s40201-014-0133-3.

[88] X. Zhang, M. Fevre, G.O. Jones, R.M. Waymouth, Catalysis as an Enabling Science for Sustainable Polymers, Chem. Rev. 118 (2018) 839–885. https://doi.org/10.1021/acs.chemrev.7b00329.

[89] D.W.C. Macmillan, The advent and development of organocatalysis, Nature. 455 (2008) 304–308. https://doi.org/10.1038/nature07367.

[90] K. Fukushima, K. Nozaki, Organocatalysis: A Paradigm Shift in the Synthesis of Aliphatic Polyesters and Polycarbonates, Macromolecules. 53 (2020) 5018–5022. https://doi.org/10.1021/acs.macromol.0c00582.

[91] S.L. Kwolek, P.W. Morgan, Preparation of polyamides, polyurethanes, polysulfonamides, and polyesters by low temperature solution polycondensation, J. Polym. Sci. Part A Gen. Pap. 2 (1964) 2693–2703. https://doi.org/10.1002/pol.1964.100020619.

[92] D.J. Liaw, J.J. Hsu, B.Y. Liaw, Synthesis and characterization of new soluble cardo polyesters derived from 1,1-bis-[4-(4-chlorocarboxyphenoxy)phenyl]-4-tert-butylcyclohexane with various bisphenols by solution polycondensation, J. Polym. Sci. Part A Polym. Chem. 39 (2001) 2951–2956. https://doi.org/10.1002/pola.1276.

[93] H. Hirano, M. Tanaka, Linear polymers with sulfur in the main chain , I, Die Angew. Makromol. Chemie. 267 (1999) 57–62. https://doi.org/https://doi.org/10.1002/(SICI)1522-9505(19990601)267:1<57::AID-

APMC57>3.0.CO;2-T.

[94] J.A. Pawlak, Solution polycondensation method, US Patent 4049629, 1977.

[95] A.M.A. Youssef, Solution and Bulk Polymerization, 2019. https://doi.org/10.13140/RG.2.2.16472.96001/2.

[96] K. Grodowska, A. Parczewski, Organic solvents in the pharmaceutical industry, Polish Pharm. Soc. 67 (2010) 3–12.

[97] A. Conix, Thermoplastic Polyesters from Bisphenols, Ind. Eng. Chem. 51 (1959) 147–150. https://doi.org/https://doi.org/10.1021/ie50590a035.

[98] S. Yasuda, G.C. Wu, H. Tanaka, K. Sanui, N. Ogata, Synthesis of polyester by direct polycondensation with triphenylphosphine, Polym. J. 13 (1983) 989–991. https://doi.org/10.1002/pol.1983.170210901.

[99] E.D. Giol, P. Dubruel, S. Van Vlierberghe, Use of poly(alkylene terephthatales) and methods for their preparation, US Patent 0031824 A1, 2019.

[100] C. Dell, O. Soizic, L. Buu, D. Russell, Effect of modification of cyclic butylene terephthalate on crystallinity and properties after ring-opening polymerisation, J. Mater. Sci. 50 (2015) 8073–8088. https://doi.org/10.1007/s10853-015-9375-4.

[101] R.J. Young, P.A. Lovell, Introduction to polymers: Third Edition, CRC Press, 2011.

[102] Odian, Ring-opening polymerization, in: Princ. Polym., 2004: pp. 544–618.

[103] A.C. Albertsson, Advances in polymer science: degradable aliphatic polyesters, Springer, 2002.

[104] H. Zahn, J.F. Repin, Synthese einer homologen Reihe von cyclischen Äthylenterephthalaten, Chem. Ber. 103 (1970) 3041–3049. https://doi.org/10.1002/cber.19701031006.

[105] E. Meraskentis, H. Zahn, Darstellung cyclischer Ester aus Terephthalsäure und Diolen, Chem. Ber. 103 (1970) 3034–3040. https://doi.org/10.1002/cber.19701031005.

[106] G. Montaudo, C. Puglisi, F. Samperi, Primary thermal degradation mechanisms of PET and PBT, Polym. Degrad. Stab. 42 (1993) 13–28. https://doi.org/10.1016/0141-3910(93)90021-A.

[107] G.C. East, A.M. Girshab, Cyclic oligomers in poly(1,4-butylene terephthalate), Polym. Commun. 23 (1982) 323–324. https://doi.org/https://doi.org/10.1016/0032-3861(82)90325-1.

[108] I. Goodman, B.F. Nesbitt, The structures and reversible polymerization of cyclic oligomers from poly(ethylene terephthalate), J. Polym. Sci. 48 (1960) 423–433. https://doi.org/10.1002/pol.1960.1204815042.

[109] H. Repin, E. Papanikolau, synthesis and properties of cyclic di(ethylene terephthalate), J. Polym. Sci. Part A-1. 7 (1969) 3426–3427. https://doi.org/10.1017/CBO9781107415324.004.

[110] S.D. Ross, E.R. Coburn, W.A. Leach, W.B. Robinson, Isolation of a cycle trimer from polyethylene terephthalate film, J. Polym. Sci. 13 (1954) 406–407. https://doi.org/10.1002/pol.1954.120137012.

[111] L.H. Peebles, M.W. Huffman, C.T. Ablett, Isolation and identification of the linear and cyclic oligomers of poly(ethylene terephthalate) and the mechanism of cyclic oligomer formation, J. Polym. Sci. Part A-1 Polym. Chem. 7 (1969) 479–496. https://doi.org/10.1002/pol.1969.150070207.

[112] D.J. Brunelle, J.E. Bradt, J. Serth-Guzzo, T. Takekoshi, T.L. Evans, E.J. Pearce, P.R. Wilson, Semicrystalline polymers via ring-opening polymerization: Preparation and polymerization of alkylene phthalate cyclic oligomers, Macromolecules. 31 (1998) 4782–4790. https://doi.org/10.1021/ma971491j.

[113] N. González-Vidal, A. Martínez de Ilarduya, S. Muñoz-Guerra, Poly(hexamethylene terephthalate-co-caprolactone) copolymers: Influence of cycle size on ring-opening polymerization, Eur. Polym. J. 46 (2010) 792–803. https://doi.org/10.1016/j.eurpolymj.2009.12.016.

[114] C. Zhang, H. Zhang, J. Yang, Z. Liu, Study on depolymerisation of poly(trimethylene terephthalate) in supercritical methanol by GPC-HPLC-IR, Polym. Degrad. Stab. 86 (2004) 461–466. https://doi.org/10.1016/j.polymdegradstab.2004.05.018.

[115] J. Gao, Z. Jin, Z. Pan, Depolymerization of poly(trimethylene terephthalate) in hot compressed water at

240-320 °C, Polym. Degrad. Stab. 97 (2012) 1838–1843. https://doi.org/10.1016/j.polymdegradstab.2012.05.015.

[116] T. Rieckmann, S. Völker, Poly(Ethylene Terephthalate) Polymerization– Mechanism, Catalysis, Kinetics, Mass Transfer and Reactor Design, 2004. https://doi.org/10.1002/0470090685.ch2.

[117] J. Li-Na, Study on preparation process and properties of polyethylene terephthalate (PET), Appl. Mech. Mater. 312 (2013) 406–410. https://doi.org/10.4028/www.scientific.net/AMM.312.406.

[118] J.H. Kim, J.J. Lee, J.Y. Yoon, W.S. Lyoo, R. Kotek, Alkaline depolymerization of poly(trimethylene terephthalate), J. Appl. Polym. Sci. 82 (2001) 99–107. https://doi.org/10.1002/app.1828.

[119] J. Wang, Depolymerization of Waste Polybutylene Terephthalate in Hot Compressed Water in a Fused Silica Capillary Reactor and an Autoclave Reactor: Monomer Phase Behavior, Stability, and Mechanism, (2013) 1–8. https://doi.org/10.1002/pen.

[120] T. Sako, T. Sugeta, K. Otake, N. Nakazawa, M. Sato, K. Namiki, M. Tsugumi, Depolymerization of polyethylene terephthalate to monomers with supercritical methanol, J. Chem. Eng. Japan. 30 (1997) 342–349. https://doi.org/10.1252/jcej.30.342.

[121] B.F.S. Nunes, M.C. Oliveira, A.C. Fernandes, Dioxomolybdenum complex as an efficient and cheap catalyst for the reductive depolymerization of plastic waste into value-added compounds and fuels, Green Chem. 22 (2020) 2419–2425. https://doi.org/10.1039/c9gc04206g.

[122] M. Okada, Chemical syntheses of biodegradable polymers, Prog. Polym. Sci. 27 (2002) 87–133. https://doi.org/10.1016/S0079-6700(01)00039-9.

[123] D. Goldberg, A review of the biodegradability and utility of poly(caprolactone), J. Environ. Polym. Degrad. 3 (1995) 61–67. https://doi.org/10.1007/BF02067481.

[124] C. David, X. Lefèbvre, C. Lefèvre, W. Demarteau, J.M. Loutz, Thermal behaviour of polyesters of hexanediol with terephthalic and isophthalic acids, Prog. Org. Coatings. 35 (1999) 45–54. https://doi.org/10.1016/S0300-9440(99)00016-8.

[125] Y. Jiang, A.J.J. Woortman, G.O.R. Alberda Van Ekenstein, K. Loos, A biocatalytic approach towards sustainable furanic-aliphatic polyesters, Polym. Chem. 6 (2015) 5198–5211. https://doi.org/10.1039/c5py00629e.

[126] P. Fleckenstein, J.G. Rosenboom, G. Storti, M. Morbidelli, Synthesis of Cyclic (Ethylene Furanoate) Oligomers via Cyclodepolymerization, Macromol. React. Eng. 12 (2018) 1–14. https://doi.org/10.1002/mren.201800018.

[127] A. Ben-Haida, L. Conzatti, P. Hodge, B. Manzini, P. Stagnaro, An introduction to entropically-driven ring-opening polymerizations, Macromol. Symp. 297 (2010) 6–17. https://doi.org/10.1002/masy.200900109.

[128] J.N. Hoskins, S.M. Grayson, Cyclic polyesters: Synthetic approaches and potential applications, Polym. Chem. 2 (2011) 289–299. https://doi.org/10.1039/c0py00102c.

[129] D.J. Brunelle, Cyclic oligomers of polycarbonates and polyesters, in: Cycl. Polym., 2000: pp. 185–228.

[130] R. Hajiraissi, M. Parvinzadeh, Preparation of polybutylene terephthalate/silica nanocomposites by melt compounding: Evaluation of surface properties, Appl. Surf. Sci. 257 (2011) 8443–8450. https://doi.org/10.1016/j.apsusc.2011.04.127.

[131] J. V. Kurian, A new polymer platform for the future - Sorona® from corn derived 1,3-propanediol, J. Polym. Environ. 13 (2005) 159–167. https://doi.org/10.1007/s10924-005-2947-7.

[132] B. Demirel, A. Yaras, H. Elçiçek, Crystallisation behaviour of PET material, BAÜ Fen Bil. Enst. Derg. Cilt. 13 (2011) 26–35.

[133] R.M.R. Wellen, E.L. Canedo, On the Kissinger equation and the estimate of activation energies for non-isothermal cold crystallization of PET, Polym. Test. 40 (2014) 33–38. https://doi.org/10.1016/j.polymertesting.2014.08.008.

[134] X.L. Jiang, S.J. Luo, K. Sun, X.D. Chen, Effect of nucleating agents on crystallization kinetics of PET, Express Polym. Lett. 1 (2007) 245–251. https://doi.org/10.3144/expresspolymlett.2007.37.

[135] C. Wu, Synthesis and Characterization of Poly(trimethylene terephthalate) Nanocomposites Incorporating Multi-Walled Carbon Nanotubes, J. Appl. Polym. Sci. 114 (2009) 2658–2667. https://doi.org/10.1002/app.

[136] A. Szymczyk, Z. Roslaniec, M. Zenker, M.C. García-Gutiérrez, J.J. Hernández, D.R. Rueda, A. Nogales, T.A. Ezquerra, Preparation and characterization of nanocomposites based on COOH functionalized multi-walled carbon nanotubes and on poly(trimethylene terephthalate), Express Polym. Lett. 5 (2011) 977–995. https://doi.org/10.3144/expresspolymlett.2011.96.

[137] A. Gupta, V. Choudhary, Effect of Multiwall Carbon Nanotubes on Thermomechanical and Electrical Properties of Poly(trimethylene terephthalate), J. Appl. Polym. Sci. 123 (2012) 1548–1556. https://doi.org/10.1002/app.

[138] G.Z. Papageorgiou, D.G. Papageorgiou, V. Tsanaktsis, D.N. Bikiaris, Synthesis of the bio-based polyester poly(propylene 2,5-furan dicarboxylate). Comparison of thermal behavior and solid state structure with its terephthalate and naphthalate homologues, Polymer (Guildf). 62 (2015) 28–38. https://doi.org/10.1016/j.polymer.2015.01.080.

[139] G. Mathew, J.P. Hong, J.M. Rhee, H.S. Lee, C. Nah, Preparation and characterization of properties of electrospun poly(butylene terephthalate) nanofibers filled with carbon nanotubes, Polym. Test. 24 (2005) 712–717. https://doi.org/10.1016/j.polymertesting.2005.05.002.

[140] N. González-Vidal, A.M. de Ilarduya, S. Muñoz-Guerra, P. Castell, M.T. Martínez, Synthesis and properties of poly(hexamethylene terephthalate)/multiwall carbon nanotubes nanocomposites, Compos. Sci. Technol. 70 (2010) 789–796. https://doi.org/10.1016/j.compscitech.2010.01.014.

[141] D. Serbezeanu, T. Vlad-bubulac, C. Hamciuc, M. Aflori, Structure and Properties of Phosphorous-Containing Thermotropic Liquid-Crystalline Aliphatic–Aromatic Copolyesters, Macromol. Chem. Phys. 211 (2010) 1460–1471. https://doi.org/10.1002/macp.201000050.

[142] K.C. Yen, E.M. Woo, K. Tashiro, Microscopic fourier transform infrared characterization on two types of spherulite with polymorphic crystals in poly(heptamethylene terephthalate), Macromol. Rapid Commun. 31 (2010) 1343–1347. https://doi.org/10.1002/marc.201000054.

[143] E.M. Woo, S. Nurkhamidah, Surface nanopatterns of two types of banded spherulites in poly(nonamethylene terephthalate) thin films, J. Phys. Chem. B. 116 (2012) 5071–5079. https://doi.org/10.1021/jp301108d.

[144] PerkinElmer, Thermogravimetric Analysis (TGA): A Beginner's Guide This, (2010). https://doi.org/10.5860/choice.47-6310.

[145] S. Montava-Jordà, S. Torres-Giner, S. Ferrandiz-Bou, L. Quiles-Carrillo, N. Montanes, Development of sustainable and cost-competitive injection-molded pieces of partially bio-based polyethylene terephthalate through the valorization of cotton textile waste, Int. J. Mol. Sci. 20 (2019) 1–19. https://doi.org/10.3390/ijms20061378.

[146] M. Bautista, A. Martínez De Ilarduya, A. Alla, S. Muñoz-Guerra, Sulfonated poly(hexamethylene terephthalate) copolyesters: Enhanced thermal and mechanical properties, J. Appl. Polym. Sci. 129 (2013) 3527–3535. https://doi.org/10.1002/app.39108.

[147] S. V. Levchik, E.D. Weil, A review on thermal decomposition and combustion of thermoplastic polyesters, Polym. Adv. Technol. 15 (2004) 691–700. https://doi.org/10.1002/pat.526.

[148] V. Passalacqua, F. Pilati, V. Zamboni, B. Fortunato, P. Manaresi, Thermal degradation of poly(butylene terephthalate), Polymer (Guildf). 17 (1976) 1044–1048. https://doi.org/10.1016/0032-3861(76)90004-5.

[149] T.Y. Kim, S.A. Jabarin, Solid-state polymerization of poly(ethylene terephthalate). III. Thermal stabilities in terms of the vinyl ester end group and acetaldehyde, J. Appl. Polym. Sci. 89 (2003) 228–237. https://doi.org/10.1002/app.11905.

[150] V.S. Mahesh, K. Tharpa, N.S. Gadigone, B.F. Al-Farhood, F.H. Al-Mutairi, A. Kumar, Mechanism of acetaldehyde formation in polyethylene terephthalate resin—A new insight, Polym. Eng. Sci. 61 (2021) 362–366. https://doi.org/10.1002/pen.25579.

[151] S.R. Shukla, E.A. Lofgren, S.A. Jabarin, Effects of injection-molding processing parameters on

acetaldehyde generation and degradation of poly(ethylene terephthalate), Polym. Int. 54 (2005) 946–955. https://doi.org/10.1002/pi.1794.

[152] F. Villain, J. Coudane, M. Vert, Thermal degradation of poly(ethylene terephthalate) and the estimation of volatile degradation products, Polym. Degrad. Stab. 43 (1994) 431–440. https://doi.org/10.1016/0141-3910(94)90016-7.

[153] K. Banik, G. Mennig, Influence of the injection molding process on the creep behavior of semicrystalline PBT during aging below its glass transition temperature, Mech. Time-Dependent Mater. 9 (2005) 247–257. https://doi.org/10.1007/s11043-005-9003-9.

[154] R.S. Stein, A. Misra, Morphological Studies on Polybutylene Terephthalate., J. Polym. Sci. Part A-2, Polym. Phys. 18 (1980) 327–342. https://doi.org/10.1002/pol.1980.180180215.

[155] M. Pyda, E. Nowak-Pyda, J. Mays, B. Wunderlich, Heat capacity of poly(butylene terephthalate), J. Polym. Sci. Part B Polym. Phys. 42 (2004) 4401–4411. https://doi.org/10.1002/polb.20286.

[156] P. Nicholas, P.D. Cheremisinoff, Condensed Encyclopedia of Polymer Engineering Terms, 2001. https://doi.org/10.1016/B978-0-08-050282-3.50021-4.

[157] Y. Kong, J.N. Hay, Multiple melting behaviour of poly(ethylene terephthalate), Polymer (Guildf). 44 (2002) 623–633. https://doi.org/10.1016/S0032-3861(02)00814-5.

[158] J.T. Yeh, J. Runt, Multiple melting in annealed poly(butlene terephthalate), J. Polym. Sci. Part B Polym. Phys. 27 (1989) 1543–1550. https://doi.org/10.1002/polb.1989.090270714.

[159] S.Y. Hobbs, C.F. Pratt, Multiple melting in poly(butylene terephthalate), Polymer (Guildf). 16 (1975) 462–464. https://doi.org/10.1016/0032-3861(75)90258-X.

[160] J. Kim, M.E. Nichols, R.E. Robertson, The annealing and thermal analysis of poly(butylene terephthalate), J. Polym. Sci. Part B Polym. Phys. 32 (1994) 887–899. https://doi.org/10.1002/polb.1994.090320512.

[161] I. Goodman, Neue Erkenntnisse in der Chemie des Terylene und verwandter Polyester, Angew. Chem. 74 (1962) 606–612. https://doi.org/https://doi.org/10.1002/ange.19620741603.

[162] M. Tasaki, H. Yamamoto, T. Yoshioka, M. Hanesaka, T.H. Ninh, K. Tashiro, H.J. Jeon, K.B. Choi, H.S. Jeong, H.H. Song, M.H. Ree, Crystal structure analyses of arylate polyesters with long methylene segments and their model compounds on the basis of 2-D X-ray diffractions and infrared progression bands, Polymer (Guildf). 55 (2014) 1228–1248. https://doi.org/10.1016/j.polymer.2014.01.024.

[163] M. Xuelin, H. Farong, Study on the properties of poly(pentamethylene terephthalate), Acta Polym. Sin. (2004).

[164] Young’s Modulus - Tensile and Yield Strength for common Materials, (n.d.). https://www.engineeringtoolbox.com/young-modulus-d_417.html (accessed May 7, 2020).

[165] Overview of materials for Polyethylene Terephthalate (PET), Unreinforced, (n.d.). http://www.matweb.com/search/DataSheet.aspx?MatGUID=a696bdcdff6f41dd98f8eec3599eaa20&ckck=1 (accessed May 7, 2020).

[166] T.H. Ng, L. Williams, Stress-Strain Properties of Linear Aromatic Polyesters in the Nonlinear Viscoelastic Range, J. Appl. Polym. Sci. 32 (1986) 4883–4896. https://doi.org/https://doi.org/10.1002/app.1986.070320511.

[167] I.M. Ward, M.A. Wilding, H. Brody, The Mechanical Properties and Structure of Poly(m-methylene Terephthate) Fibers, J Polym Sci Part A-2 Polym Phys. 14 (1976) 263–274. https://doi.org/10.1002/pol.1976.180140206.

[168] D.S. Achilias, G.Z. Papageorgiou, G.P. Karayannidis, Isothermal and nonisothermal crystallization kinetics of polypropylene terephthalate, J. Polym. Sci. Part B Polym. Phys. 42 (2004) 3775–3796. https://doi.org/10.1002/polb.20239.

[169] M. Li, Y.G. Jeong, Poly(ethylene terephthalate)/exfoliated graphite nanocomposites with improved thermal stability, mechanical and electrical properties, Compos. Part A Appl. Sci. Manuf. 42 (2011) 560–566. https://doi.org/10.1016/j.compositesa.2011.01.015.

[170] I.M. Inuwa, R. Arjmandi, A.N. Ibrahim, M.K.M. Haafiz, S.L. Wong, K. Majeed, A. Hassan, Enhanced

mechanical and thermal properties of hybrid graphene nanoplatelets/multiwall carbon nanotubes reinforced polyethylene terephthalate nanocomposites, Fibers Polym. 17 (2016) 1657–1666. https://doi.org/10.1007/s12221-016-6238-9.

[171] B.A. Alshammari, F.S. Al-Mubaddel, M.R. Karim, M. Hossain, A.S. Al-Mutairi, A.N. Wilkinson, Addition of graphite filler to enhance electrical, morphological, thermal, and mechanical properties in poly (ethylene terephthalate): Experimental characterization and material modeling, Polymers (Basel). 11 (2019) 1–20. https://doi.org/10.3390/polym11091411.

[172] W.J. Cantwell, Fracture behavior of glass fiber/recycled PET composites, J. Reinf. Plast. Compos. 18 (1999) 373–387. https://doi.org/10.1177/073168449901800406.

[173] F. Laoutid, L. Ferry, J.M. Lopez-Cuesta, A. Crespy, Red phosphorus/aluminium oxide compositions as flame retardants in recycled poly(ethylene terephthalate), Polym. Degrad. Stab. 82 (2003) 357–363. https://doi.org/10.1016/S0141-3910(03)00213-1.

[174] V. V. Dubrovsky, V.A. Shapovalov, V.N. Aderikha, S.S. Pesetskii, Effect of hybrid filling with short glass fibers and expanded graphite on structure, rheological and mechanical properties of poly(ethylene terephthalate), Mater. Today Commun. 17 (2018) 15–23. https://doi.org/10.1016/j.mtcomm.2018.08.002.

[175] K. Anoop Anand, U.S. Argarwal, R. Jospeh, Carbon Nanotubes-Reinforced PET Nanocomposite by Melt-Compounding, J. Appl. Polym. Sci. 104 (2007) 3090–3095. https://doi.org/https://doi.org/10.1002/app.25674.

[176] A. Gupta, V. Choudhary, Electrical conductivity and shielding effectiveness of poly(trimethylene terephthalate)/multiwalled carbon nanotube composites, J. Mater. Sci. 46 (2011) 6416–6423. https://doi.org/10.1007/s10853-011-5591-8.

[177] S. Jacob, M. Misra, A.K. Mohanty, Novel biocomposites from poly(trimethylene terephthalate) and recycled carbon fibres, J. Mater. Sci. 47 (2012) 6056–6065. https://doi.org/10.1007/s10853-012-6514-z.

[178] X. Hu, A.J. Lesser, Effect of a silicate filler on the crystal morphology of poly(trimethylene terephthalate)/clay nanocomposites, J. Polym. Sci. Part B Polym. Phys. 41 (2003) 2275–2289. https://doi.org/10.1002/polb.10592.

[179] F. Wang, H. Wang, K. Zheng, L. Chen, X. Zhang, X. Tian, Isothermal crystallization kinetics and mechanical properties of poly(butylene terephthalate)/attapulgite nanocomposites, Colloid Polym. Sci. 292 (2014) 953–963. https://doi.org/10.1007/s00396-013-3142-3.

[180] D. Wu, T. Shi, T. Yang, Y. Sun, L. Zhai, W. Zhou, M. Zhang, J. Zhang, Electrospinning of poly(trimethylene terephthalate)/carbon nanotube composites, Eur. Polym. J. 47 (2011) 284–293. https://doi.org/10.1016/j.eurpolymj.2010.12.006.

[181] D.S. Varma, R. Agarwal, I.K. Varma, Poly (ethylene Terephthalate)/ Poly (alkylene Terephthalate) Copolyester Fibers: Sorption and Dyeability, Text. Res. J. 56 (1986) 438–441. https://doi.org/https://doi.org/10.1177/004051758605600707.

[182] S. Xu, F. Wu, Z. Li, X. Zhu, X. Li, L. Wang, Y. Li, Y. Tu, A green cascade polymerization method for the facile synthesis of sustainable poly(butylene-co-decylene terephthalate) copolymers, Polymer (Guildf). 178 (2019) 121591. https://doi.org/10.1016/j.polymer.2019.121591.

[183] Y. Chebbi, N. Kasmi, M. Majdoub, P. Cerruti, G. Scarinzi, M. Malinconico, G. Dal Poggetto, G.Z. Papageorgiou, D.N. Bikiaris, Synthesis, Characterization, and Biodegradability of Novel Fully Biobased Poly(decamethylene- co-isosorbide 2,5-furandicarboxylate) Copolyesters with Enhanced Mechanical Properties, ACS Sustain. Chem. Eng. 7 (2019) 5501–5514. https://doi.org/10.1021/acssuschemeng.8b06796.

[184] S.J. Chiu, Y.S. Wu, A comparative study on thermal and catalytic degradation of polybutylene terephthalate, J. Anal. Appl. Pyrolysis. 86 (2009) 22–27. https://doi.org/10.1016/j.jaap.2009.03.003.

[185] A.L. Andrady, Microplastics in the marine environment, Mar. Pollut. Bull. 62 (2011) 1596–1605. https://doi.org/10.1016/j.marpolbul.2011.05.030.

[186] M. Eriksen, L.C.M. Lebreton, H.S. Carson, M. Thiel, C.J. Moore, J.C. Borerro, F. Galgani, P.G. Ryan, J.

Reisser, Plastic Pollution in the World's Oceans: More than 5 Trillion Plastic Pieces Weighing over 250,000 Tons Afloat at Sea, PLoS One. 9 (2014) 1–15. https://doi.org/10.1371/journal.pone.0111913.

[187] G. Suaria, C.G. Avio, A. Mineo, G.L. Lattin, M.G. Magaldi, G. Belmonte, C.J. Moore, F. Regoli, S. Aliani, The Mediterranean Plastic Soup : synthetic polymers in Mediterranean surface waters, Nat. Publ. Gr. (2016) 1–10. https://doi.org/10.1038/srep37551.

[188] V.M. Pathak, Navneet, Review on the current status of polymer degradation: a microbial approach, Bioresour. Bioprocess. 4 (2017). https://doi.org/10.1186/s40643-017-0145-9.

[189] WEF, The New Plastics Economy: Rethinking the future of plastics, Ellen MacArthur Found. (2016) 120. https://www.ellenmacarthurfoundation.org/assets/downloads/publications/NPEC-Hybrid_English_22-11-17_Digital.pdf.

[190] D.E. Nikles, M.S. Farahat, New motivation for the depolymerization products derived from poly(ethylene terephthalate) (PET) waste: A review, Macromol. Mater. Eng. 290 (2005) 13–30. https://doi.org/10.1002/mame.200400186.

[191] N. Malik, P. Kumar, S. Shrivastava, S.B. Ghosh, An overview on PET waste recycling for application in packaging, Int. J. Plast. Technol. 21 (2017) 1–24. https://doi.org/10.1007/s12588-016-9164-1.

[192] Y. Yang, J. Yang, L. Jiang, A bacterium that degrades and assimilates poly(ethylene terephthalate), Science (80-.). 351 (2016) 759. https://doi.org/10.1126/science.aaf8305.

[193] D. Tillier, H. Lefebvre, M. Tessier, J.C. Blais, A. Fradet, High temperature bulk reaction between poly(ethylene terephtalate) and lac tones: 1H NMR and SEC/MALDI-TOF MS study, Macromol. Chem. Phys. 205 (2004) 581–592. https://doi.org/10.1002/macp.200300053.

[194] S.M. Al-Salem, P. Lettieri, J. Baeyens, Recycling and recovery routes of plastic solid waste (PSW): A review, Waste Manag. 29 (2009) 2625–2643. https://doi.org/10.1016/j.wasman.2009.06.004.

[195] H. Shent, R.J. Pugh, E. Forssberg, A review of plastics waste recycling and the flotation of plastics, Resour. Conserv. Recycl. 25 (1999) 85–109. https://doi.org/10.1016/S0921-3449(98)00017-2.

[196] F. Awaja, D. Pavel, Recycling of PET, Eur. Polym. J. 41 (2005) 1453–1477. https://doi.org/10.1016/j.eurpolymj.2005.02.005.

[197] Z.O.G. Schyns, M.P. Shaver, Mechanical Recycling of Packaging Plastics: A Review, Macromol. Rapid Commun. 42 (2021) 1–27. https://doi.org/10.1002/marc.202000415.

[198] M.N. Siddiqui, H.H. Redhwi, A.A. Al-Arfaj, D.S. Achilias, Chemical recycling of PET in the presence of the bio-based polymers, PLA, PHB and PEF: A review, Sustain. 13 (2021). https://doi.org/10.3390/su131910528.

[199] A.B. Raheem, Z.Z. Noor, A. Hassan, M.K. Abd Hamid, S.A. Samsudin, A.H. Sabeen, Current developments in chemical recycling of post-consumer polyethylene terephthalate wastes for new materials production: A review, J. Clean. Prod. 225 (2019) 1052–1064. https://doi.org/10.1016/j.jclepro.2019.04.019.

[200] A. Carniel, V. de A. Waldow, A.M. de Castro, A comprehensive and critical review on key elements to implement enzymatic PET depolymerization for recycling purposes, Biotechnol. Adv. 52 (2021) 107811. https://doi.org/10.1016/j.biotechadv.2021.107811.

[201] O. Sato, K. Arai, M. Shirai, Hydrolysis of poly(ethylene terephthalate) and poly(ethylene 2,6-naphthalene dicarboxylate) using water at high temperature: Effect of proton on low ethylene glycol yield, Catal. Today. 111 (2006) 297–301. https://doi.org/10.1016/j.cattod.2005.10.040.

[202] T. Adschiri, O. Sato, K. Machida, N. Saito, K. Arai, Recovery of terephthalic acid by decomposition of PET in supercritical water, Kagaku Kogaku Ronbunshu. 23 (1997) 368. https://doi.org/https://doi.org/10.1252/kakoronbunshu.23.505.

[203] S. Baliga, W.T. Wong, Depolymerization of poly(ethylene terephthalate) recycled from post-consumer soft-drink bottles, J. Polym. Sci. Part A Polym. Chem. 27 (1989) 2071–2082. https://doi.org/10.1002/pola.1989.080270625.

[204] J.Y. Chen, C.F. Ou, Y.C. Hu, C.C. Lin, Depolymerization of poly(ethylene terephthalate) resin under pressure, J. Appl. Polym. Sci. 42 (1991) 1501–1507. https://doi.org/10.1002/app.1991.070420603.

[205] V. Jankauskait, G. Macijauskas, R. Lygaitis, Polyethylene Terephthalate Waste Recycling and Application Possibilities : a Review NA PL of recycling O Metal content SO NA, Mater. Sci. 14 (2008). http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.557.3593&rep=rep1&type=pdf.

[206] V. Sinha, M.R. Patel, J. V. Patel, Pet waste management by chemical recycling: A review, J. Polym. Environ. 18 (2010) 8–25. https://doi.org/10.1007/s10924-008-0106-7.

[207] H.H. Zhang, H.W. Xiang, Y. Yang, Y.Y. Xu, Y.W. Li, Depolymerization of Poly(trimethylene terephthalate) in Supercritical Methanol, J. Appl. Polym. Sci. 92 (2004) 2363–2368. https://doi.org/10.1002/app.13713.

[208] C. Zhang, L. Xu, H. Zhang, J. Yang, J. Du, Z. Liu, Determination of solid products from the de-polymerization of poly(trimethylene terephthalate) in supercritical methanol, J. Chromatogr. A. 1055 (2004) 115–121. https://doi.org/10.1016/j.chroma.2004.08.146.

[209] F. Kawai, T. Kawabata, M. Oda, Current knowledge on enzymatic PET degradation and its possible application to waste stream management and other fields, Appl. Microbiol. Biotechnol. 103 (2019) 4253–4268.

[210] N.A. Samak, Y. Jia, M.M. Sharshar, T. Mu, M. Yang, S. Peh, J. Xing, Recent advances in biocatalysts engineering for polyethylene terephthalate plastic waste green recycling, Environ. Int. 145 (2020) 106144. https://doi.org/10.1016/j.envint.2020.106144.

[211] R. Koshti, L. Mehta, N. Samarth, Biological Recycling of Polyethylene Terephthalate: A Mini-Review, J. Polym. Environ. 26 (2018) 3520–3529. https://doi.org/10.1007/s10924-018-1214-7.

[212] T. Sang, C.J. Wallis, G. Hill, G.J.P. Britovsek, Polyethylene terephthalate degradation under natural and accelerated weathering conditions, Eur. Polym. J. 136 (2020) 109873. https://doi.org/10.1016/j.eurpolymj.2020.109873.

[213] A.R. Othman, H.A. Hasan, M.H. Muhamad, N. ’Izzati Ismail, S.R.S. Abdullah, Microbial degradation of microplastics by enzymatic processes: a review, Environ. Chem. Lett. 19 (2021) 3057–3073. https://doi.org/10.1007/s10311-021-01197-9.

[214] I. Kleeberg, K. Welzel, J. VandenHeuvel, R.J. Müller, W.D. Deckwer, Characterization of a New Extracellular Hydrolase from Thermobifida fusca Degrading Aliphatic-Aromatic Copolyesters, Biomacromolecules. 6 (2005) 262–270. https://doi.org/10.1021/bm049582t.

[215] I. Kleeberg, C. Hetz, R.M. Kroppenstedt, R.J. Müller, W.D. Deckwer, Biodegradation of Aliphatic-Aromatic Copolyesters by Thermomonospora fusca and Other Thermophilic Compost Isolates, Appl. Environ. Microbiol. 64 (1998) 1731–1735. https://doi.org/10.1128/aem.64.5.1731-1735.1998.

[216] A. Eberl, S. Heumann, R. Kotek, F. Kaufmann, S. Mitsche, A. Cavaco-Paulo, G.M. Gübitz, Enzymatic hydrolysis of PTT polymers and oligomers, J. Biotechnol. 135 (2008) 45–51. https://doi.org/10.1016/j.jbiotec.2008.02.015.

[217] R.J. Müller, H. Schrader, J. Profe, K. Dresler, W.D. Deckwer, Enzymatic degradation of poly(ethylene terephthalate): Rapid hydrolyse using a hydrolase from T. fusca, Macromol. Rapid Commun. 26 (2005) 1400–1405. https://doi.org/10.1002/marc.200500410.

[218] A. Eberl, S. Heumann, T. Brückner, R. Araujo, A. Cavaco-Paulo, F. Kaufmann, W. Kroutil, G.M. Guebitz, Enzymatic surface hydrolysis of poly(ethylene terephthalate) and bis(benzoyloxyethyl) terephthalate by lipase and cutinase in the presence of surface active molecules, J. Biotechnol. 143 (2009) 207–212. https://doi.org/10.1016/j.jbiotec.2009.07.008.

[219] K. Janczak, G.B. Dąbrowska, A. Raszkowska-Kaczor, D. Kaczor, K. Hrynkiewicz, A. Richert, Biodegradation of the plastics PLA and PET in cultivated soil with the participation of microorganisms and plants, Int. Biodeterior. Biodegrad. 155 (2020). https://doi.org/10.1016/j.ibiod.2020.105087.

[220] L. Espino-Rammer, D. Ribitsch, A. Przylucka, A. Marold, K.J. Greimel, E.H. Acero, G.M. Guebitz, C.P. Kubicek, I.S. Druzhinina, Two Novel Class II Hydrophobins from Trichoderma spp. Stimulate Enzymatic Hydrolysis of Poly(Ethylene Terephthalate) when Expressed as Fusion Proteins, Appl. Environ. Microbiol. 79 (2013) 4230–4238. https://doi.org/10.1128/AEM.01132-13.

[221] R. Wei, W. Zimmermann, Biocatalysis as a green route for recycling the recalcitrant plastic polyethylene terephthalate, Microb. Biotechnol. 10 (2017) 1302–1307. https://doi.org/10.1111/1751-7915.12714.

[222] A.M. Al-Sabagh, F.Z. Yehia, G. Eshaq, A.M. Rabie, A.E. ElMetwally, Greener routes for recycling of polyethylene terephthalate, Egypt. J. Pet. 25 (2016) 53–64. https://doi.org/10.1016/j.ejpe.2015.03.001.

[223] J. Scheirs, Polymer recycling: Science, Technology and Applications, Wiley, 1998.

[224] J.S. Lee, J. Leisen, R.P. Choudhury, R.M. Kriegel, H.W. Beckham, W.J. Koros, Antiplasticization-based enhancement of poly(ethylene terephthalate) barrier properties, Polymer (Guildf). 53 (2012) 213–222. https://doi.org/10.1016/j.polymer.2011.11.006.

[225] E.L.V. Lewis, R.A. Duckett, I.M. Ward, J.P.A. Fairclough, A.J. Ryan, The barrier properties of polyethylene terephthalate to mixtures of oxygen, carbon dioxide and nitrogen, Polymer (Guildf). 44 (2003) 1631–1640. https://doi.org/10.1016/S0032-3861(02)00933-3.

[226] C. Dombre, S. Marais, C. Chappey, C. Lixon-Buquet, P. Chalier, The behaviour of wine aroma compounds related to structure and barrier properties of virgin, recycled and active PET membranes, J. Memb. Sci. 463 (2014) 215–225. https://doi.org/10.1016/j.memsci.2014.03.066.

[227] M.R. Galdi, L. Incarnato, Influence of Composition on Structure and Barrier Properties of Active PET Films for Food Packaging Applications, Packag. Technol. Sci. 24 (2010) 89–102. https://doi.org/10.1002/pts.

[228] R. Nisticò, Polyethylene terephthalate (PET) in the packaging industry, Polym. Test. 90 (2020). https://doi.org/10.1016/j.polymertesting.2020.106707.

[229] S. Manshoven, A. Smeets, M. Arnold, L. Mortensen, Plastic in textiles: potentials for circularity and reduced environmental and climate impacts, 2021.

[230] A. Majumdar, S. Shukla, A.A. Singh, S. Arora, Circular fashion: Properties of fabrics made from mechanically recycled poly-ethylene terephthalate (PET) bottles, Resour. Conserv. Recycl. 161 (2020). https://doi.org/10.1016/j.resconrec.2020.104915.

[231] M. Wang, X. Luo, X. Zhang, D. Ma, Shape memory properties in poly(ethylene oxide)-Poly(ethylene terephthalate) copolymers, Polym. Adv. Technol. 8 (1997) 136–139. https://doi.org/10.1002/(SICI)1099-1581(199703)8:3<136::AID-PAT621>3.0.CO;2-I.

[232] D.P.R. Kint, S. Munoz-Guerra, Modification of the thermal properties and crystallization behaviour of poly(ethylene terephthalate) by copolymerization, Polym. Int. 52 (2003) 321–336. https://doi.org/10.1002/pi.1175.

[233] M. Nagata, Biodegradability of Poly (ethylene terephthalate) Copolymers with Poly (ethylene glycol) s and Poly (tetramethylene glycol), Polym. Int. 39 (1996) 83–89. https://doi.org/https://doi.org/10.1002/(SICI)1097-0126(199602)39:2<83::AID-PI475>3.0.CO;2-C.

[234] D.K. Gilding, A.M. Reed, Biodegradable polymers for use in surgery - poly(ethylene oxide)/poly(ethylene terephthalate) (PEO/PET) copolymers: 2. In vitro degradation, Polymer (Guildf). 20 (1979) 1454–1458. https://doi.org/10.1016/0032-3861(81)90169-5.

[235] Dupont, Dupont SORONA, (2020). http://sorona.com/ (accessed May 10, 2020).

[236] K.L. Hatch, The use of classification systems and production methods in identifying manufactured textile fibers, in: M. Houck (Ed.), Identif. Text. Fibers, Woodhead Publishing Series in Textiles, 2009: pp. 111–130. https://doi.org/10.1533/9781845695651.1.111.

[237] Polymer Properties Database - triexta fiber (polytrimethylene terephthalate), (n.d.). https://polymerdatabase.com/Fibers/PTT.html (accessed October 5, 2021).

[238] Swicofil - PTT, (n.d.). https://www.swicofil.com/commerce/products/ptt/179/introduction (accessed October 5, 2021).

[239] J.M. Kim, I. Lee, J.Y. Park, K.T. Hwang, H.J. Park, Applicability of biaxially oriented poly (trimethylene terephthalate) films using bio-based 1,3-propanediol in retort pouches, J. Appl. Polym. Sci. 46251 (2018) 1–9. https://doi.org/10.1002/app.46251.

[240] E. Diederichs, M. Picard, B.P. Chang, M. Misra, A. Mohanty, Extrusion Based 3D Printing of Sustainable Biocomposites from biocarbon and Poly(trimethylene terephthalate), Molecules. 26 (2021) 14.

[241] DuPont, Crastin - Polybuthylene Terephthalate Resin For Industrial Applications, (n.d.). https://www.dupont.com/products/crastin.html (accessed October 5, 2021).

[242] LanXess, Pocan - Engineering Plastics made from PBT, (n.d.). https://lanxess.com/en/Products-and-Solutions/Brands/Pocan (accessed October 5, 2021).

[243] Dupont, Crastin, (2020). https://www.dupont.com/products/crastin.html#DelrinSolutions (accessed May 11, 2020).

[244] Rebling, polybutylene terephthalate, (n.d.). https://rebling.com/custom-molding/thermoplastic-materials/pbt/ (accessed May 11, 2020).

[245] A. Ganguly, P. Channe, R. Jha, S. Mitra, S. Saha, Review on transesterification in polycarbonate – poly (butylene terephthalate) blend, Polym. Eng. Sci. 61 (2021) 650–661. https://doi.org/10.1002/pen.25652.

[246] T. Standau, B. Hädelt, M. Fafara, V. Altstädt, Development of a bead foam based on the engineering polymer polybutylene terephthalate, AIP Conf. Proc. 2055 (2019). https://doi.org/10.1063/1.5084836.

[247] M. Felix de Andrade, I. Diego de Lima Silva, G. Alves da Silva, P.V. David Cavalcante, F. Thayse da Silva, Y.M. Bastos de Almeida, G.M. Vinhas, L. Hecker de Carvalho, A study of poly (butylene adipate-co-terephthalate)/orange essential oil films for application in active antimicrobial packaging, Lwt. 125 (2020) 109148. https://doi.org/10.1016/j.lwt.2020.109148.

[248] W. Zhang, C. Zheng, Y. Zhang, W. Guo, Preparation and characterization of flame-retarded poly(butylene terephthalate)/poly(ethylene terephthalate) blends: Effect of content and type of flame retardant, Polymers (Basel). 11 (2019). https://doi.org/10.3390/polym11111784.

[249] C. Lefèvre, D. Villers, M.H.J. Koch, C. David, Synthesis and thermal characterization of crystallizable poly(caprolactone)/poly(hexamethylene terephthalate) block copolymer, Polymer (Guildf). 42 (2001) 8769–8777. https://doi.org/10.1016/S0032-3861(01)00362-7.

[250] E. Cenni, G. Ciapetti, L. Savarino, S. Stea, D. Cavedagna, G. Falsone, G. Mari, A. Pizzoferrato, Cytotoxicity and capability of activating hemocoagulation of polybutyleneterephthalate filters, Clin. Mater. 14 (1993) 191–198. https://doi.org/10.1016/0267-6605(93)90002-O.

[251] K.G. Dahmen, N. Maurin, H.A. Richter, C. Mittermayer, Screening of biomedical polymer biocompatibility in NMRI-mice peritoneal cavity. A comparison between ultra-high-molecular-weight polyethylene (UHMW-PE) and polyethyleneterephthalate (PET), J. Mater. Sci. Mater. Med. 8 (1997) 239–245. https://doi.org/10.1023/A:1018595825048.

[252] A.J.A. Klomp, G.H.M. Engbers, J. Mol, J.G.A. Terlingen, J. Feijen, Adsorption of proteins from plasma at polyester non-wovens, Biomaterials. 20 (1999) 1203–1211. https://doi.org/10.1016/S0142-9612(99)00009-5.

[253] D. V. Kilpadi, M.S. Johnston, D.E. Ferguson, T.D. Estridge, D.S. Feldman, The effect of solvent extraction and sterilization procedure on the tissue response to Dacron® velour, Biomaterials. 20 (1999) 129–136. https://doi.org/10.1016/S0142-9612(98)90132-6.

[254] D. Radakovic, J. Reboredo, M. Helm, T. Weigel, S. Schürlein, E. Kupczyk, R.G. Leyh, H. Walles, J. Hansmann, A multilayered electrospun graft as vascular access for hemodialysis, PLoS One. 12 (2017) 1–21. https://doi.org/10.1371/journal.pone.0185916.

[255] K.D. Andrews, P. Feugier, R.A. Black, J.A. Hunt, Vascular Prostheses: Performance Related to Cell-Shear Responses, J. Surg. Res. 149 (2008) 39–46. https://doi.org/10.1016/j.jss.2007.08.030.

[256] S. Venkatraman, F. Boey, L.L. Lao, Implanted cardiovascular polymers: Natural, synthetic and bio-inspired, Prog. Polym. Sci. 33 (2008) 853–874. https://doi.org/10.1016/j.progpolymsci.2008.07.001.

[257] M. Desai, A.M. Seifalian, G. Hamilton, Role of prosthetic conduits in coronary artery bypass grafting, Eur. J. Cardio-Thoracic Surg. 40 (2011) 394–398. https://doi.org/10.1016/j.ejcts.2010.11.050.

[258] A. Subramaniam, S. Sethuraman, Biomedical Applications of Nondegradable Polymers, Elsevier Inc., 2014. https://doi.org/10.1016/B978-0-12-396983-5.00019-3.

[259] L. Xue, H.P. Greisler, Biomaterials in the development and future of vascular grafts, J. Vasc. Surg. (2003). https://doi.org/10.1067/mva.2003.88.

[260] E.D. Giol, Novel biomaterials intended for vascular tissue engineering. Surface modification of PET and synthesis of PET-like polyesters, University of Ghent, 2016.

[261] B. Van de Voorde, L. Benmeridja, E.-D. Giol, L. Van der Meeren, L. Van Damme, Z. Liu, A. Toncheva, J.-M. Raquez, N. Van den Brande, A. Skirtach, H. Declercq, P. Dubruel, S. Van Vlierberghe, Potential of poly(alkylene terephthalate)s to control endothelial cell adhesion and viability, 2021.

[262] S. Park, J.P. Bearinger, E.P. Lautenschlager, D.G. Castner, K.E. Healy, Surface modification of poly(ethylene terephthalate) angioplasty balloons with a hydrophilic poly(acrylamide-co-ethylene glycol) interpenetrating polymer network coating, J. Biomed. Mater. Res. 53 (2000) 568–576. https://doi.org/10.1002/1097-4636(200009)53:5<568::AID-JBM17>3.0.CO;2-8.

[263] H. Becker, B. Raton, Self supporting and forming breast implant and method for forming and supporting an implant in a human body, US Patent 0226352 A1, 2012.

[264] I. Ul Ahad, A. Bartnik, H. Fiedorowicz, J. Kostecki, B. Korczyc, T. Ciach, D. Brabazon, Surface modification of polymers for biocompatibility via exposure to extreme ultraviolet radiation, J. Biomed. Mater. Res. - Part A. 102 (2014) 3298–3310. https://doi.org/10.1002/jbm.a.34958.

[265] J.P. Eiberg, O. Røder, M. Stahl-Madsen, N. Eldrup, P. Qvarfordt, A. Laursen, M. Greve, T. Flörenes, O.M. Nielsen, C. Seidelin, T. Vestergaard-Andersen, T. V. Schroeder, Fluoropolymer-coated Dacron Versus PTFE Grafts for Femorofemoral Crossover Bypass: Randomised Trial, Eur. J. Vasc. Endovasc. Surg. 32 (2006) 431–438. https://doi.org/10.1016/j.ejvs.2006.04.018.

[266] H. Pärsson, W. Jundzill, T. Jonung, L. Norgren, K. Johansson, Healing characteristics of polymer-coated or collagen-treated dacron grafts: An experimental porcine study, Vascular. 2 (1994) 242–248. https://doi.org/10.1177/096721099400200221.

[267] J.M.A. Van Der Bas, P.H.A. Quax, A.C. Van Den Berg, M.J.T. Visser, E. Van Der Linden, J.H. Van Bockel, Ingrowth of aorta wall into stent grafts impregnated with basic fibroblast growth factor: A porcine in vivo study of blood vessel prosthesis healing, J. Vasc. Surg. 39 (2004) 850–858. https://doi.org/10.1016/j.jvs.2003.11.045.

[268] U. Hake, H. Gabbert, S. Iversen, E. Al., Evaluation of the healing of precoated vascular dacron prostheses, Langenbecks Arch Chir. 376 (1991) 323–329. https://doi.org/doi:10.1007/BF00186423.

[269] H. Li, S. Chen, Biomedical coatings on polyethylene terephthalate artificial ligaments, J. Biomed. Mater. Res. - Part A. 103 (2015) 839–845. https://doi.org/10.1002/jbm.a.35218.

[270] J.R. Smith, D.A. Lamprou, Polymer coatings for biomedical applications: A review, Trans. Inst. Met. Finish. 92 (2014) 9–19. https://doi.org/10.1179/0020296713Z.000000000157.

[271] I. Martín-Fabiani, E. Rebollar, S. Pérez, D.R. Rueda, M.C. García-Gutiérrez, A. Szymczyk, Z. Roslaniec, M. Castillejo, T.A. Ezquerra, Laser-induced periodic surface structures nanofabricated on poly(trimethylene terephthalate) spin-coated films, Langmuir. 28 (2012) 7938–7945. https://doi.org/10.1021/la300833x.

[272] T. Çaykara, M.G. Sande, N. Azoia, L.R. Rodrigues, C.J. Silva, Exploring the potential of polyethylene terephthalate in the design of antibacterial surfaces, Med. Microbiol. Immunol. (2020). https://doi.org/10.1007/s00430-020-00660-8.

[273] G.J. Meijer, A. Van Dooren, M.L. Gaillard, R. Dalmeijer, C. De Putter, R. Koole, C.A. Van Blitterswijk, Polyactive® as a bone-filler in a beagle dog model, Int. J. Oral Maxillofac. Surg. 25 (1996) 210–216. https://doi.org/10.1016/S0901-5027(96)80033-6.

[274] G.J. Meijer, M.S. Cune, M. Van Dooren, C. De Putter, C.A. Van Blitterswijk, A comparative study of flexible (Polyactive®) versus rigid (hydroxylapatite) permucosal dental implants. I. Clinical aspects, J. Oral Rehabil. 24 (1997) 85–92.

[275] S. Grande, P. Cools, M. Asadian, J. Van Guyse, I. Onyshchenko, H. Declercq, R. Morent, R. Hoogenboom, N. De Geyter, Fabrication of PEOT/PBT Nanofibers by Atmospheric Pressure Plasma Jet Treatment of Electrospinning Solutions for Tissue Engineering, Macromol. Biosci. 18 (2018) 1–17. https://doi.org/10.1002/mabi.201800309.

[276] M.B. Claase, M.B.O. Riekerink, J.D. de Bruijn, D.W. Grijpma, G.H.M. Engbers, J. Feijen, Enhanced bone marrow stromal cell adhesion and growth on segmented poly(ether ester)s based on poly(ethylene oxide) and poly(butylene terephthalate), Biomacromolecules. 4 (2003) 57–63. https://doi.org/10.1021/bm0256045.

[277] R. Dijkhuizen-Radersma, F.L.A.M.A. Péters, N.A. Stienstra, D.W. Grijpma, Control of vitamin B 12 release from poly (ethylene glycol)/ poly(butylene terephthalate) multiblock copolymers, Biomaterials. 23 (2002) 1527–1536.

[278] A.K. Gaharwar, S.M. Mihaila, A.A. Kulkarni, A. Patel, A. Di Luca, R.L. Reis, M.E. Gomes, C. Van Blitterswijk, L. Moroni, A. Khademhosseini, Amphiphilic beads as depots for sustained drug release integrated into fibrillar scaffolds, J. Control. Release. 187 (2014) 66–73. https://doi.org/10.1016/j.jconrel.2014.04.035.

[279] A.A. Deschamps, A.A. Van Apeldoorn, J.D. De Bruijn, D.W. Grijpma, J. Feijen, Poly(ether ester amide)s for tissue engineering, Biomaterials. 24 (2003) 2643–2652. https://doi.org/10.1016/S0142-9612(03)00054-1.

[280] J.M. Bezemer, R. Radersma, D.W. Grijpma, P.J. Dijkstra, J. Feijen, C.A. Van Blitterswijk, Zero-order release of lysozyme from poly(ethylene glycol)/poly(butylene terephthalate) matrices, J. Control. Release. 64 (2000) 179–192. https://doi.org/10.1016/S0168-3659(99)00127-3.

[281] A.M. Radder, H. Leenders, C.A. Van Blitterswijk, Application of porous PEO/PBT copolymers for bone replacement, J. Biomed. Mater. Res. 30 (1996) 341–351. https://doi.org/10.1002/(SICI)1097-4636(199603)30:3<341::AID-JBM8>3.0.CO;2-Q.

[282] G.J. Beumer, C.A. van Blitterswijk, M. Ponec, Biocompatibility of a biodegradable matrix used as a skin substitute: An in vivo evaluation, J. Biomed. Mater. Res. 28 (1994) 545–552. https://doi.org/10.1002/jbm.820280504.

[283] E.J. Kim, G.D. Yeo, C.M. Pai, I.K. Kang, Preparation of surface-modified poly(butylene terephthalate) nonwovens and their application as leukocyte removal filters, J. Biomed. Mater. Res. - Part B Appl. Biomater. 90 B (2009) 849–856. https://doi.org/10.1002/jbm.b.31354.

[284] S.M. Kenny, M. Buggy, Bone cements and fillers: A review, J. Mater. Sci. Mater. Med. 14 (2003) 923–938. https://doi.org/10.1023/A:1026394530192.

[285] M. Risbud, D.N. Saheb, J. Jog, R. Bhonde, Preparation , characterization and in vitro biocompatibility evaluation of poly(butylene terephthalate)/ wollastonite composites, Biomaterials. 22 (2001) 1591–1597.

[286] DuPont, Polymer for better injection devices, (n.d.). https://www.dupont.com/knowledge/injector-pen-materials.html (accessed October 5, 2021).