Katrina Knauer*, Cody Higginson, Yuanzhe Liang and Minjung Lee

Circular plastics technologies: depolymerization of polymers into parent monomers

Abstract: While most commodity plastics were not designed to easily depolymerize, some common plastics can be broken down into their parent monomers in the presence of heat, pressure, catalysts, and/or solvent. Here, we provide a high-level overview of the depolymerization technologies that have been studied and/or scaled as promising monomer-loop recycling processes for selective plastic waste streams. Namely, commodity plastics that are considered unzippable/depolymerizable include polyethylene terephthalate, polyamides, polymethyl methacrylate, and polystyrene. Monomer-loop recycling technologies are one of several pathways toward a circular economy for plastics.

Keywords: Depolymerization; recycling; solvolysis; unzipping; circularity; plastics.

1 Introduction

In contrast to the pyrolysis of plastic waste to produce fuel, naphtha, and other chemicals (Section 1) along the molecular recycling loop, some plastics can be depolymerized or "unzipped" to recover monomers directly in the so-called monomer recycling loop [1]. These monomers can be purified to remove additives, fillers, and pigments present in the plastic waste and used to resynthesize the parent polymer. In a sense, this is an idealized representation of a circular material – one that can be cycled through monomer and polymer repeatedly (Figure 1).

Not all plastics are amenable to this kind of depolymerization. Most plastics manufactured today were designed for the "take-make-waste" model, based on a linear economy framework that does not adequately address materials' end-of-life issues. In principle, any polymer could be rendered "depolymerizable" by manipulating the thermodynamic equilibrium of the polymerization and depolymerization by modifying temperature, pressure, concentration, state, etc. [3]. A thermodynamic measure of depolymerizability, or how easily a polymer can unzip to its parent monomers, can be

***Corresponding author: Katrina Knauer**, National Renewable Energy Laboratory, 15013 Denver W Pkwy, Golden, CO, 80401-3393, USA, E-mail: katrina.knauer@nrel.gov. https://orcid.org/0000-0002-0125-7532
Cody Higginson, Menlo Park, CA, USA
Yuanzhe Liang, National Renewable Energy Laboratory, Golden, CO, USA
Minjung Lee, Bioenergy Science and Technology, National Renewable Energy Laboratory, 15013 Denver W Pkwy, Golden, CO, 80401, USA. https://orcid.org/0000-0003-1687-897X

https://doi.org/10.1515/psr-2023-0014

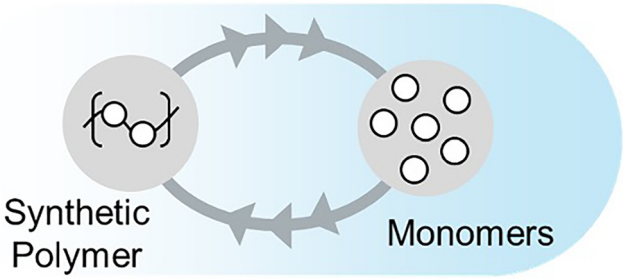

Figure 1: Simplified schematic of the monomer loop for plastics recycling as defined by the Ellen McArthur Foundation (EMF), figure adapted from Ellis *et al.* [2].

measured by the ceiling temperature (T_c) of the polymer [4]. The T_c is defined as the temperature at which the polymerization and depolymerization reactions reach an equilibrium state. In other words, depolymerization will occur at temperatures above the T_c of the polymer. However, most commodity plastics have a T_c at or near the carbon degradation temperature and undergo random chain scission and crosslinking rather than an "unzipping" mechanism to monomer. Unzipping occurs when the bonds break at the polymer chain end (i.e., chain-end scission) to release the monomer in a systematic mechanism rather than random fragmentation along the backbone (Figure 2).

Some commodity plastics can be broken down into one or more of their constituent monomers in sufficiently high yield and purity to be used to produce new polymers with properties comparable to the original material. For some condensation polymers like polyethylene terephthalate (PET), this depolymerization process requires the input of stoichiometric reactants and catalysts, while other materials, such as polystyrene (PS) or polymethyl methacrylate (PMMA), can be coaxed under appropriate conditions to unzip

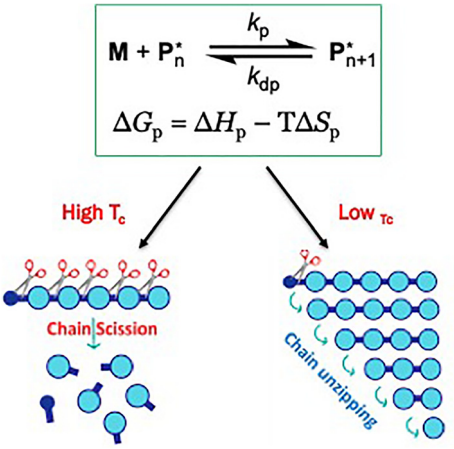

Figure 2: Simplified representation of T_c and random chain scission verses chain-end unzipping mechanisms in polymer depolymerization.

predominantly into their component monomers (styrene and methyl methacrylate, respectively). We categorize these depolymerization routes into two general branches: solvolysis and pyrolytic depolymerization ("unzipping"). Selected examples of plastics for which depolymerization is being explored as a means of chemical recycling, and the methods used to accomplish this are surveyed in this chapter. The conditions and processes described are not exhaustive, but are intended to be representative of chemical recycling strategies for the various classes of materials discussed herein [5].

2 Technical scope

2.1 Solvolysis

Solvolysis is the depolymerization of a polymer by reaction with the chosen solvent, such as water, methanol, or ethylene glycol. Solvolysis is particularly suited for the breakdown of condensation polymers containing functional groups cleaved by hydrolysis and alcoholysis, and to some extent phosphorolysis and aminolysis, including polyesters, polyamides, polyurethanes, and polyethers. The primary goal behind the solvolysis chemistries discussed in this section is to collect monomers that can be purified and re-polymerized into their parent materials in an infinite cyclic process.

2.1.1 Polyethylene terephthalate

PET, the condensation polymer of terephthalic acid (TA) and ethylene glycol (EG), is the third most produced thermoplastic (following polyethylene and polypropylene, respectively), and the most common thermoplastic polyester produced today. It is used in a wide range of applications such as textile fibers, thermoforming in manufacturing, and food, drink, and storage containers. Most of the demand for PET is for textile fibers, while beverage bottles constitute the second largest source of demand for PET. While mechanical recycling of PET is currently widespread, the mechanical, thermal, and rheological properties of the recycled plastic weaken over repeated processing cycles compared to virgin resin [6]. Furthermore, most mechanical recyclers will only take rigid, clear PET bottle flake as feedstock and other PET form factors (textiles, clam shells, film, etc.) are landfilled. It is perhaps for this reason that significant research efforts have focused on the chemical recycling of PET to recover virgin-like quality monomers, and headway has been made in the commercialization of several PET depolymerization strategies [7, 8]. Multiple reagents exists that can cleave ester bonds in PET backbones, but the primary strategies that enable recovery of chemicals useful for the synthesis of virgin-grade PET are hydrolysis, methanolysis, and glycolysis (Figure 3).

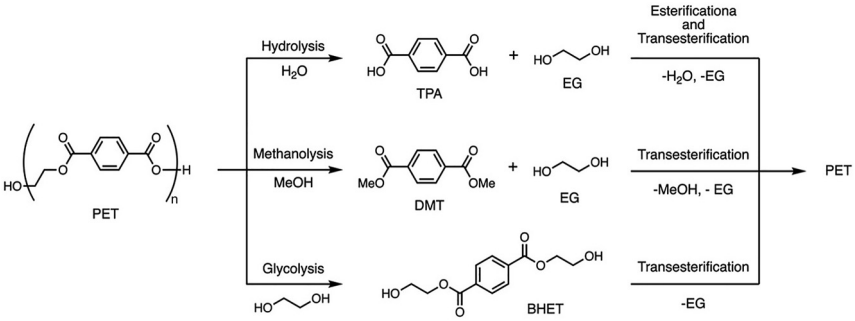

Figure 3: Solvolytic routes for chemical depolymerization of PET into monomers TA, DMT, BHET, and EG.

2.1.1.1 Hydrolysis

Hydrolysis of PET involves reacting the polymer with water at elevated temperatures to cleave the ester bonds, usually in the presence of a catalyst [8], the products of which are TPA and EG, and has been reviewed extensively in the academic literature [8–14]. The reaction can take place under acidic, alkaline, or neutral conditions, and research related to enzymatic hydrolysis of PET has also gained considerable momentum in recent years, as outlined below [8, 11, 15–18].

2.1.1.1.1 Acidic hydrolysis. Acidic hydrolysis of PET can be carried out with concentrated mineral acids serving as catalyst, including nitric acid and phosphoric acid [11, 19]. However, the most common acid used in this process is sulfuric acid, as outlined in the following examples [8, 11, 20–22]. Brown and O'Brien described a process in 1976 employing at least 87 % sulfuric acid for the hydrolysis of PET [23]. In this case, the depolymerization was carried out at 100 °C for 5 min at atmospheric pressure, after which near-theoretical yields of TPA and EG were obtained in crude form. Thereafter, the crude hydrolysate was treated with sodium hydroxide to neutralize the sulfuric acid and TA (pH 7.5–9.0), forming soluble sodium terephthalate. The mixture was filtered to remove insoluble residues and passed through an ion exchange decolorizing column. The solution containing ethylene glycol, sodium sulfate, sodium hydroxide, and sodium terephthalate was acidified to pH 2.5–3.0 by addition of sulfuric acid to precipitate terephthalic acid, which was collected by centrifugation and found to be of 99+% purity after washing with water. The ethylene glycol in the aqueous centrifuge mother liquor was extracted with trichloroethylene and recovered at 99+% purity by distillation.

In 1982, Pusztaszeri described a lower temperature process employing concentrated sulfuric acid to depolymerize PET scrap [21]. In the process, PET solid is stirred with water and concentrated sulfuric acid (volume ratio of 2:13 to 8.5:13) at room temperature for 5–30 min at atmospheric pressure to produce a fully liquified crude product. Crude TPA, having solubility in water of 0.0017 g/100 g of solvent, is precipitated by the addition of an equivalent volume of cold water and collected by filtration [23]. In this case, the filtrate

containing aqueous ethylene glycol, excess sulfuric acid, and other impurities is discarded as waste. The use of less concentrated sulfuric acid to depolymerize PET for recovery of TA and EG has been described by Yoshioka, et al. [22] However, the process requires higher temperatures (150–190 °C) and pressures than the preceding two examples to obtain comparable yields of TA, and reaction times of up to 12 h were reported. While the reaction efficiency and yield of TA and EG from acidic hydrolysis of PET are typically high, there are several shortcomings of this method that make it somewhat unattractive for industrialization. These include the use of large volumes of strong acids and the generation of copious aqueous and inorganic salt waste [11].

2.1.1.1.2 Alkaline hydrolysis. The hydrolysis of PET in basic media is usually performed with aqueous sodium hydroxide solutions of 4–20 weight percent (wt%) to produce sodium terephthalate and ethylene glycol in good yield [11]. Furthermore, nearly complete conversion of PET is possible. On the other hand, alkaline hydrolysis is typically slower than acidic hydrolysis with conventional heating methods, and is often performed at high temperatures (in some cases greater than 200 °C) and elevated pressure (1.4–2 MPa) [11]. The process can be carried out in aqueous solution, or in non-aqueous co-solvents employing a phase transfer catalyst [11, 24, 25]. TA monomer can be recovered by neutralization of the hyrolysate with strong mineral acids (typically sulfuric acid or hydrochloric acid) and precipitation, while the EG product generated can be recovered by distillation or “salting out” from the filtrate. Such a process was patented as early as 1959; Pitat and colleagues reported the alkaline hydrolysis of PET in 18 wt% aqueous sodium hydroxide solution at 100 °C for 2 h, at which point the majority of the sodium terephthalate product formed precipitates from the reaction mixture [26]. The terephthalate salt is collected by filtration and redissolved to form a nearly saturated solution to which sulfuric acid is added to provide TPA as a filterable precipitate in 94 % yield. The filtrate containing EG hydrolysis product is recharged with NaOH and recycled into subsequent rounds of hydrolysis to accumulate EG, which is later recovered by distillation. Overall, the process requires approximately 0.8 kg of solid sodium hydroxide per kilogram of terephthalic acid recovered.

In a more recent example of alkaline hydrolysis, Loop Industries patented their first-generation process in 2017 wherein an organic co-solvent, preferably dichloromethane (DCM), is used to swell the PET and accelerate depolymerization in a solution of C1–C4 alcohol and potassium or sodium hydroxide [27]. The organic solvent is present at 3–5 volume percent relative to the alcohol (preferably methanol) containing dissolved potassium or sodium hydroxide. In contrast to the other examples of alkaline hydrolysis presented above, the exothermic depolymerization occurs at atmospheric pressure without additional external heating. The process enables recovery of TA and other TA derivatives such as 4-(methoxycarbonyl)benzoic acid) after dissolution of salts formed in the depolymerization with water, followed by acidification with sulfuric acid and collection of the precipitated TA. Ethylene glycol, in addition to dichloromethane and methanol used in the depolymerization, are recovered by a distillation process.

Alkaline hydrolysis is not without drawbacks; as in acidic hydrolysis, separation processes required to obtain pure monomers can be energy intensive, and these methods still generate large amounts of inorganic salt wastes. One apparatus and method proposed in a 2013 patent application by Parravicini and colleagues from the Swiss recycling company Gr3n aims to increase the depolymerization efficiency and reduce the waste generated in the process [28]. The DEMETO method (depolymerization by microwave technology) utilizes a continuous reactor to carry out hydroglycolysis of PET, described as hydrolysis by alkaline hydroxide salts in an ethylene glycol solvolytic mixture, and is purportedly tolerant of contaminants present in the PET feedstock. The approach may also be applicable to polyamides (*vide infra*). The method involves co-feeding ground PET via an Archimedean screw system and solvolytic reagents (sodium or potassium hydroxide salts in ethylene glycol) via a separate feed line into an elongated horizontal microwave reaction chamber (Figure 4, upper left). The heterogeneous reaction mixture is carried through the reaction chamber and into a separation unit consisting of filtration and distillation modules. EG is distilled from terephthalate salts and can be reused in the solvolytic mixture and for synthesis of new PET resin. The terephthalate salts are acidified with hydrochloric acid to yield TA precipitate for new PET synthesis (Figure 4, right). The proposed handling of waste salts in the DEMETO process differs from other examples presented in this section. Namely the sodium or potassium chloride salts from the TA precipitation step are electrolyzed to regenerate NaOH (or KOH) reagents, and hydrogen and chlorine gas (Figure 4, bottom left). Hydrogen and chlorine are photochemically recombined to regenerate the hydrochloric acid used in precipitation of TA. While the Gr3n process has yet to be demonstrated at commercial scale, the consideration in the process design for addressing common waste streams in PET hydrolysis is noteworthy.

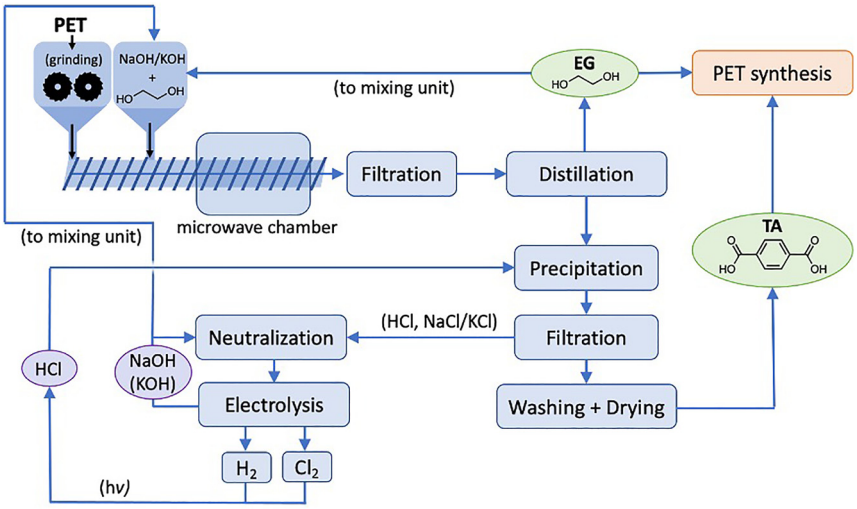

Figure 4: Hydroglycolysis unit proposed by Gr3n for scalable chemical recycling of PET [29].

2.1.1.1.3 Neutral hydrolysis. PET hydrolysis under neutral conditions is performed with water or steam, typically at elevated pressures (1–4 MPa) and temperatures in the range of 200–300 °C, with a ratio of PET to water from 1:2 to 1:12 [11]. The neutral hydrolysis process occurs substantially faster when performed with a PET melt rather than the solid, leading to a preference for conditions above 245 °C [30]. While neutral hydrolysis can be conducted without additional catalysts, common transesterification catalysts can also be employed, including alkali-metal acetates, as well as acetates of zinc, calcium, and manganese [11]. Campanelli and colleagues report that addition of zinc acetate to neutral depolymerization reactions at 250–265 °C increases the rate constant by approximately 20 % compared to the uncatalyzed system [31]. Key benefits of performing PET hydrolysis under neutral conditions as described above compared to acidic and alkaline conditions are the avoidance of highly corrosive reaction conditions, simplifying apparatus maintenance, and the lack of large quantities of waste inorganic salts formed as process byproducts. Despite these advantages, a key drawback is the typically lower purity of the TA product due to contamination by other insoluble impurities and fillers that may be present in the parent polymer, thus requiring more complex purification approaches that negate some of the benefits of neutral hydrolysis. Furthermore, neutral hydrolysis of PET is typically slower than either acidic or basic hydrolysis processes. A strategy for the neutral hydrolysis of PET was described by Tustin and colleagues in a now-expired patent issued to Eastman Chemical Company [32]. In the process, PET is first heated with water at 200–280 °C and pressures greater than 1.7 MPa for 2 h to provide a crude TA precipitate upon cooling. EG could be isolated by a two-stage distillation of the filtrate. The crude TA was purified by heating in the presence of a flow of steam to produce a vapor composed of water and TA. The TA was collected as a solid deposit after cooling and was found to be 95.7 wt% pure by HPLC. The isolated TA could be used to resynthesize PET, but this was only demonstrated after diluting with virgin-grade TA such that the TA recovered from the neutral hydrolysis was only 36 wt% of the total TA feed. Few major industrial chemical recycling efforts for PET today seem to rely on the neutral hydrolysis strategy, likely because of the challenges associated with the lower purity of TA obtained from the method.

2.1.1.1.4 Enzymatic hydrolysis. An approach for PET hydrolysis that is gaining momentum is the use of esterase enzymes to facilitate depolymerization into TPA, EG, as well as bis(2-hydroxylethyl) terephthalate (BHET), and mono(2-hydroxyethyl) terephthalate (MHET) [5, 16–18]. Ester degrading enzymes (i.e., esterase) have been identified and studied in nature for decades. PET is an excellent candidate for esterase degradation given the high concentration of ester bonds in the polymer backbone. As a result, PET biodegradation via enzymatic hydrolysis has been studied for nearly two decades [33–40]. One of the most notable findings were those reported by Yoshida et al. in 2016 where they characterized the soil bacterium, *Ideonella sakaiensis* 201-F6, which employs a two-enzyme system to depolymerize PET to TPA and EG [41]. The first enzyme was named PETase which performs the initial attack on the PET backbone cleaving the ester bonds to form BHET, MHET, and TPA

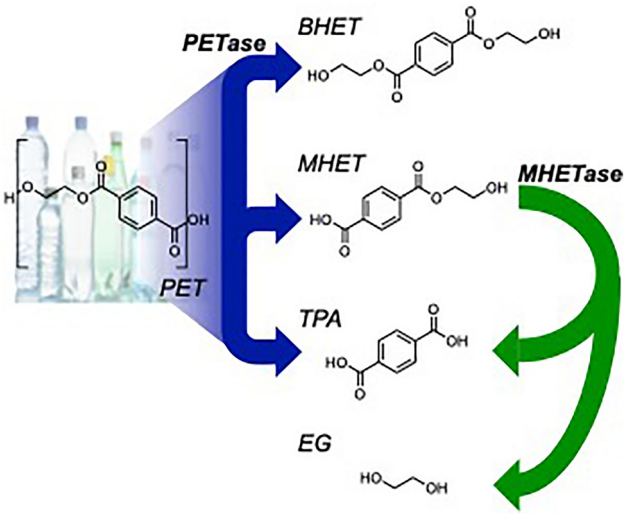

Figure 5: Scheme demonstrating PETase depolymerization of PET to BHET, MHET, and TPA. MHETase converts MHET to TPA and EG, adapted from Austin et al. [46].

(Figure 5). The PETase activity will also cleave the resulting BHET to yield MHET and EG. The second enzyme is called MHETase which further hydrolyzes the MHET to produce TPA and EG [41]. The structure, mechanism of hydrolysis, the evolution products, and engineering of the two-enzyme system for PET depolymerization have been reported in detail by Knott et al. [42]. The enzymatic recycling of actual PET waste was modeled and analyzed based on techno-economic analysis (TEA) and life cycle impacts by Singh et al. (Figure 6) [5]. The process involves first pretreating post-consumer polyester flakes to reduce the crystallinity. This is required since PETase does not demonstrate significant activity on crystalline substrates and will only attack amorphous domains. Most PET waste is ~30–40 % crystalline, thus an amorphization step is required prior to enzymatic recycling. This is done by extruding the PET flake and cryo-grinding the extruded material into an amorphous powder. Following pre-treatment, the PET is enzymatically depolymerized in a bioreactor containing both PETase and MHETase. The gradual addition of sodium hydroxide (or a neutralizing base) is required to maintain the pH. Most enzymes are only active within a specific pH window and as PET is depolymerized, the pH gradually decreases due to the formation of TPA. To maintain the activity of the PETase and MHETase, the reaction requires pH control. Following depolymerization, the recycled TPA and EG are recovered via downstream processes. Costs and energy inputs of this process are dominated by the cost of the PET feedstock and the energy requirements for the PET flake pretreatment (i.e., cryo-grinding). Uekert et al. conducted a life cycle assessment (LCA) of this process and reported that enzymatic hydrolysis currently performs 1.2 to 17 times worse than virgin TPA and PET production across most impact categories, excepting ecotoxicity and fossil fuel depletion

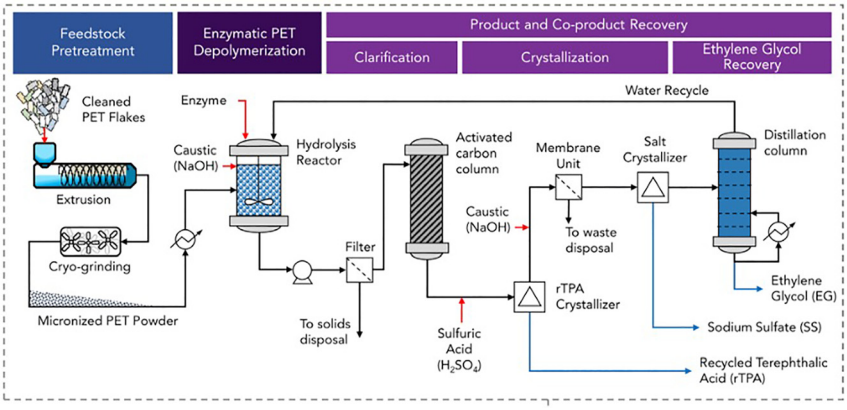

Figure 6: Simplified process flow diagram of the PET enzymatic depolymerization process from Singh et al. [5].

[43]. The top contributors to these impacts include post-consumer PET collection and the required pretreatment, sodium hydroxide usage for pH control, and electricity inputs [43]. As a result, current studies are focused on discovering and engineering enzymes that are active on crystalline substrates and in wider pH windows [44, 45].

Carbios is a France based startup company founded in 2011 that is actively scaling a PETase based recycling technology for PET waste. The Carbios technology was published by Tournier et al. in 2020 [18]. The Carbios enzyme is only effective on amorphous PET and requires a amorphization pretreatment as well as the pH control reported previously in this text. Carbios claims 90 % amorphous PET depolymerization into target monomers in under 10 h [18]. In 2021, Carbios launched an industrial demonstration plant in Clermont-Ferrand, France to validate the efficiency of their enzymatic process. The demonstration plant includes a 20-cubic-meter depolymerization reactor capable of processing two metric tons of PET per cycle. Carbios intends to scale this process to a fully industrial scale in 2023 [47].

2.1.1.2 Methanolysis into DMT and EG

In the methanolysis of PET, methanol (MeOH) deconstructs the PET backbone via a transesterification reaction at the ester bond resulting in the methyl-ester analogue of TPA, DMT, and EG. Methanolysis has several advantages over other solvolysis processes such as higher robustness to contamination [48], existing infrastructure [49], and the insolubility of DMT in water allowing for easier separations and purification than TPA. Additionally, conventional PET manufacturing processes require the conversion of TPA to DMT for transesterification with EG to produce high molecular weight PET products. Thus, methanolysis products are ideal for immediate reuse in PET manufacturing. However, new trends for PET production processes are using TPA instead of DMT as the raw material [50]. This creates vulnerability in the economic model for methanolysis as the conversion of the DMT to TPA by hydrolysis adds considerable costs to the

methanolysis process [51]. The methanolysis of PET waste has been studied for decades and several types of methanolysis processes have been explored with the primary pathways falling under liquid methanolysis, vapor methanolysis, and super critical methanolysis.

2.1.1.2.1 Liquid methanolysis. Liquid methanolysis is a catalytic process that involves high temperature (180–280 °C) and pressure (20–40 atm) to fully depolymerize the PET backbone. High temperatures are required to fully melt the PET and allow for full penetration of the methanol into the bulk of the polymer and high pressure is required to keep the MeOH in the liquid state at temperatures above the boiling point. Typical transesterification catalysts used for PET polymerization can also be used for liquid methanolysis such as zinc acetate (the most commonly used catalyst for methanolysis) [50], magnesium acetate, cobalt acetate, or titanium-based transesterification catalyst. Liquid methanolysis can be operated as a batch or continuous process. However, the high-pressure operation renders continuous mode challenging and expensive to operate and most processes at pilot or industrial scale are done in batch mode.

Several efforts have been made to reduce the temperature and pressure required for complete methanolysis of PET to DMT and EG and improve the LCA metrics. These efforts typically include the addition of co-solvents (to better solubilize the PET and improve contact with the methanol), novel catalysts, or both. For example, Liu et al. reported that aromatic solvents assisted in the dissolution of PET due to intermolecular interactions and improved the depolymerization efficiency of PET in solvolysis processes [52]. Ionic liquids have also been explored as cosolvents to improve the yields and energy requirements for methanolysis [53], but have significant cost limitations when applied to PET recycling and the value of the DMT products are not sufficient to justify the use of ionic liquids. Pham et al. recently reported a low-energy catalytic PET methanolysis process using potassium carbonate. This study reported yields of DMT of 93.1 % at 25 °C in 24 h [54]. Yang et al. recently reported a study applying liquid methanolysis, with a toluene cosolvent, with zinc bis[bis(trimethylsilyl)amide] as the catalyst to depolymerize a mixture of polyesters including PET at temperatures below 120 °C and DMT yields >80 % (Figure 7) [55]. These results are particularly impactful as this demonstrates that other relatively common polyesters can be depolymerized into their parent monomers in the same pot as PET such as polylactic acid (PLA) and polybutylene adipate terephthalate (PBAT).

Recently, Loop Industries pivoted from hydrolysis of PET to liquid methanolysis and filed a patent for a low-temperature, liquid methanolysis process to depolymerize PET (Figure 8) [56]. In the Loop process, stoichiometric (or sub-stoichiometric) amounts of alkali methoxides and co-solvents are used as active ingredients to depolymerize PET at temperatures less than 60 °C.

2.1.1.2.2 Vapor methanolysis. Vapor methanolysis is another method to depolymerize PET which uses super-heated vapor instead of liquid methanol. Vapor methanolysis is usually

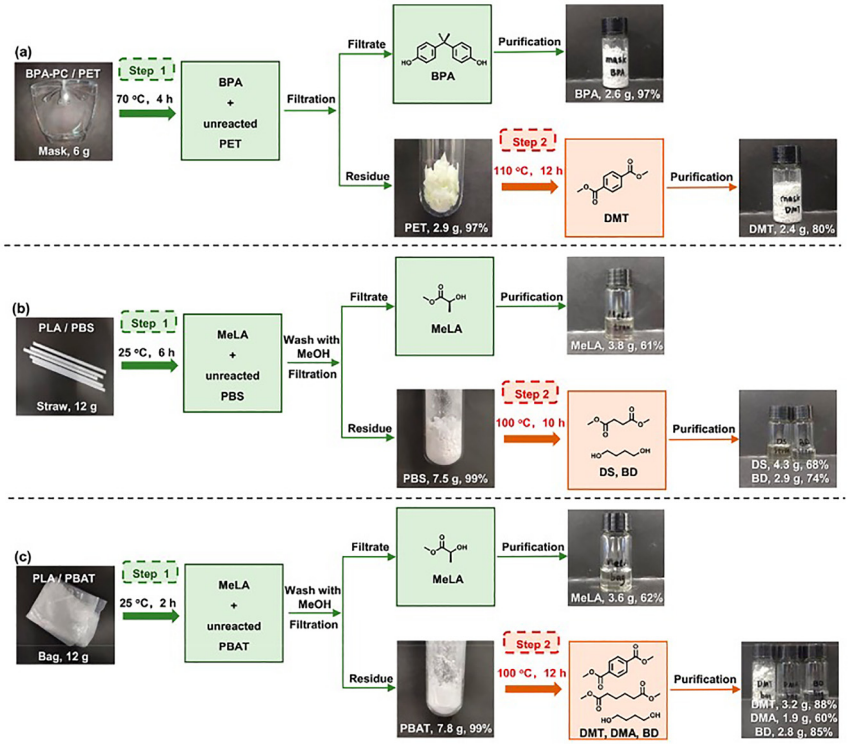

Figure 7: Graphical results from Yang et al. applying liquid methanolysis on mixed polyester substrates. Substrates in this study were (a) BPA-PC/PET mask, (b) PLA/PBS straw, and (c) PLA/PBAT bag [55].

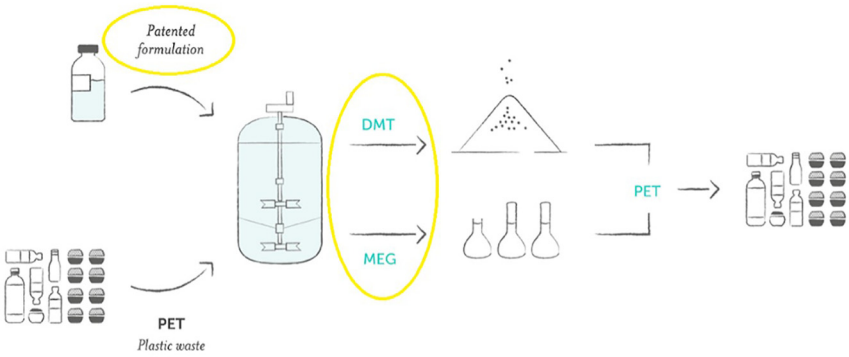

Figure 8: Depiction of the Loop Industry methanolysis process to yield DMT and monoethylene glycol (MEG), taken from the Loop website [56].

conducted at temperatures above 250 °C. Since it is not required to keep the methanol in a liquid state, vapor methanolysis does not need the high pressures used in liquid methanolysis. In the vapor methanolysis reactor, the PET exists in a melt phase and the methanol gas is passed through the PET melt. The influence of temperature on the gas–liquid interactions in vapor methanolysis is more complex than liquid methanolysis and high agitation is required to ensure good contact between the gas bubbles and the PET melt [48]. Some benefits of vapor methanolysis, when compared to liquid methanolysis, are the lower pressure which allow for easier removal of the DMT product as a vapor. Since products can be removed *in-situ* via vapor removal, the reaction equilibrium is also shifted promoting higher conversions. Thus, vapor methanolysis typically results in higher yields than liquid methanolysis [57], but the reaction rate is much slower.

In the 1990s, Eastman-Kodak developed and patented an integrated methanolysis process with their plant in Kingsport, TN to produce high purity DMT from PET [58]. Since then, the company, now only Eastman, has revitalized the technology and is currently performing feasibility tests to commercialize a methanolysis facility to recycle PET waste [49].

2.1.1.2.3 Supercritical methanolysis. Efforts have been made to improve product yields and economics for methanolysis of PET via the use of supercritical methanol. As discussed in Section 1, the high density and ionic product of supercritical fluids (SCFs) promotes the solvation of compounds. Depolymerization under a supercritical state of methanol allows for high conversion of PET and an improved DMT yield (up to 95 %) within 1 h under optimal reaction conditions (260–270 °C, 9–11 MPa) [59, 60]. Additionally, Sako et al. reported up to 100 % yields of DMT from PET in 30 min under super critical methanol conditions [61]. While the conversion rates in supercritical methanolysis are significantly faster than liquid or vapor methanolysis, the reaction must be conducted at a higher temperatures and pressure, and thus, high capital and operating costs are the primary disadvantages. Additionally, the high pressures render continuous processing of PET very difficult as noted for liquid methanolysis. Nevertheless, reports of successfully applying supercritical methanolysis, or other SCFs, to deconstruct PET are released regularly [57, 62].

2.1.1.3 Glycolysis into BHET

Glycolysis of PET involves transesterification with excessive glycol to generate BHET and EG as products. The reaction can take place with or without catalysts. Chen et al. reported in 1991 that PET was depolymerized at high temperature (200–240 °C) and pressure (2–6 bar) in the absence of a catalyst, but the monomer yield remained low [63]. The glycolysis product was quenched to room temperature in the protection of nitrogen gas at the end of the reaction. Next, a large amount of water was used to wash the solid contents to remove the unreacted EG, followed by filtration to obtain the insoluble products. The final products were then transferred to boiling water, where BHETwas extracted from the suspension.

Factors that influence the non-catalytic PET glycolysis include the reaction temperature, pressure and concentration ratio of EG to PET. Increasing pressure or temperature can accelerate the reaction rates. At a constant temperature, pressure and PET concentration, the glycolysis rate of PET is proportional to the square of EG concentration. It indicates that EG acts as both a reactant and catalyst in glycolysis. Furthermore, the system quickly reaches an equilibrium between BHET and PET oligomers (e.g., dimer and trimer) at a higher ratio of EG/PET, whereas the depolymerization ends incompletely with higher molecular weight oligomers at a lower ratio of EG/PET.

Various types of catalysts were discovered to improve the PET glycolysis kinetics, conversion, and reaction conditions. Güçlü et al. reported the first employment of metal acetates as a PET glycolysis catalyst in 1989. In their experiment, xylene was used to form a multiphase reaction in zinc-acetate-catalyzed glycolysis of PET with EG at 170–245 °C. BHET was extracted constantly from the xylene layer to shift the equilibrium of the PET depolymerization, yielding ~80 % monomer conversion [64]. Chen et al. found that manganese acetate could depolymerize ~100 % PET into BHET and dimers at 190 °C after 1.5 h [65]. Light metal salts were reported to catalyze PET glycolysis by Troev et al. In their reaction, titanium phosphate successfully depolymerized PET into BHET up to 97 % selectivity at 190 °C after 2.5 h [66]. Fang et al. reported that polyoxometalates could achieve 85 % yield of BHET at 190 °C for 40 min [67]. Ionic liquids (ILs) were first used as PET glycolysis catalysts in 2009 by Wang et al., who found the ILs could achieve full conversion of PET to BHET at 180 °C at ambient pressure after 8 h [68]. Another attempt was made by Yue et al. to use basic ILs to catalyze glycolysis of PET into BHET with a yield of 71 % at 190 °C for 2 h [69]. Similar to ILs, deep eutectic solvents (DESs) were chosen for PET glycolysis-catalysts because of low cost, low toxicity and simple chemistry. In 2015, Wang et al. reported the first employment of DESs to catalyze PET glycolysis. Their optimal reaction condition took place at 170 °C for 30 min, achieving 83 % yield of BHET [70]. Sert et al. discovered that an effective DES made from potassium carbonate and EG was able to achieve BHET yield of ~88 % at 180 °C after 2 h [71]. Organocatalytic PET glycolysis was discovered as the catalyst using the amine base 1,5,7-triazabicyclo[4.4.0] dec-5-ene (TBD) by Fukushima et al. in 2011. In this case, BHET yield reached 78 % at 190 °C and 1 atmospheric pressure after 3.5 h [72]. Jehanno et al. utilized a methanesulfonic acid and salt derived from TBD as a PET glycolysis catalyst, yielding 91 % BHET conversion at 180 °C after 2 h [73]. Emerging techniques, such as, microwave-assisted PET glycolysis can reduce energy consumption in conventional heating reaction conditions. Pingale et al. reported the first microwave irradiation study on PET glycolysis in 2008. In their reaction, microwave heating shortened the depolymerization timespan by 16 times, while providing the same yield of BHET [74]. Recently, Parrott patented a microwave-assisted PET glycolysis technique, which can achieve 94 % BHET yield with 0.1 wt% zinc acetate as a catalyst in 5 min of irradiation at 250 °C [75]. Last but not least, a variety of heterogeneous catalysts have been found to assist PET glycolysis. For example, 3 nm cobalt nanoparticles were reported as reusable catalysts for PET glycolysis by Veregue et al. The

conversion of BHET reached 77 % at 180 °C after 3 h [76]. Wang et al. used a colloidal catalyst based on graphitic carbon nitride to catalyze PET glycolysis, achieving 80 % BHET yield in 30 min at 196 °C [77].

In addition to various lab practices, glycolysis is one of the most widely used industrial PET chemical recycling methods. Eastman Chemical Company patented their glycolysis process for recycling post-consumer or scrap polyester in 1995. In the first stage of the process, the polyesters are mixed with EG in a ratio of EG to dicarboxylic acid component in the polyester between 2 to 6 [78]. Then the reaction takes place between 180 °C to 240 °C for up to 4 h to produce an oligomeric material with salts of metals (e.g., Zn, Sb, Ti, Sn, Mn, or Ge) as catalysts. The second stage of the process involves dissolving the glycolysis products in a hot solvent (e.g., water, alcohols, ethers, nitriles, chlorinated hydrocarbons, aromatic hydrocarbons, or ketones). The hot stream is then treated with adsorbents (e.g., activated carbon, activated clay, silica, and alumina), followed by hot microfiltration to remove insoluble impurities, such as pigments and trace metals. The product will precipitate out when cooling the hot permeate to room temperature, and then the product is extracted through filtration or centrifugation.

Ioniqa's technology offers a closed-loop solution for PET recycling via a patented glycolysis process [79]. Their process involves using a combination of a catalyst complex, heat, and pressure to break down PET under the glycolysis condition using ethanediol. The catalyst comprises butylmethylimidazolim ($bmim^+$) and $FeCl^{4-}$, the bridging moiety is triethoxysilylpropyl, and the nanoparticle is magnetite/maghemite. The preferred combination of catalyst loading, temperature, pressure and reaction time is 2–5 wt%, 180 °C, 60 kPa and 1.5 h. The process also involves recovering the catalyst and retrieving trimers, dimers and/or monomers. In the first step of retrieving, water is added to dissolve monomers and solvent, whereas catalyst complex can be recovered in a separate phase under influence of an external electro-magnetic field gradient (e.g., 1T). The second step of retrieving involves crystallization of monomers. As Ioniqa stated in their patent, the degradation product is ready to be used without further need of purification.

Jeplan's glycolysis technology can break down PET plastic that has been contaminated with other materials, e.g., food residue or labels [80]. In the first step of the glycolysis process, PET is heated together with bis(β-hydroxylethyl) terephthalate (BHET) to pre-decompose the PET at 200–245 °C, under normal or increase pressure for up to 1.5 h. Then a reaction between pre-decomposition products with EG (3–5 wt%) takes place at 200–220 °C under normal or increase pressure for up to 2.5 h for BHET conversation. An ester exchange reaction catalyst (e.g., sodium and magnesium methylates, fatty acid salts and carbonates of Zn, Cd, Mn, Co, Ca, and Ba such as zinc borate and zinc acetate, metal Na and Mg, and oxides) can be added to the depolymerization reaction to facilitate smooth reaction. In the second step, the glycolysis product is brought into contact with activated carbon for decoloring treatment and then cation and/or anion exchange resins at 30–70 °C for deionization treatment. In the third step, BHET is recovered by distillation or evaporation to distill off the compounds with a boiling point lower than that of BHET. The

temperature and pressure in this step are selected to be 100–150 °C at 70–300 Pa. The BHET obtained from Jeplan's glycolysis process can be used to produce high-quality PET fibers, films, and bottles.

IBM-VolCat developed a glycolysis method of depolymerizing polyesters from post-consumer products, e.g., beverage bottles, to produce a high purity BHET [81]. The depolymerization reaction takes place with an alcohol of 25 carbons and an amine organocatalyst at 150–250 °C. The selection of an organocatalyst with a boiling point significantly lower than the boiling point of the alcohol allows for the easy recycling of the amine catalyst. Increasing the reaction temperature and pressure above the boiling point of alcohols can accelerate depolymerization rates and catalyst recovery. Upon completion of the depolymerization reaction, the product undergoes direct filtration to remove insoluble contaminations and unreacted polymers, then treatment with activated carbon to remove additional impurities including dyes, and treatment with ion exchange resins to remove catalyst residues. Lastly, a combination of crystallization and distillation is used to recover BHET and EG. In an exemplar application, VolCat demonstrated that the proposed glycolytic depolymerization of PET can close the loop in the PET bottle industry, i.e., depolymerization of post-consumer beverage bottles to product high purity BHET and then production of high-quality bottle grade PET from the recovered BHET.

2.1.2 Polyamides

Polyamides are another class of polymers that contain cleavable heteroatoms in the backbone and are suitable for chemical depolymerization routes. The most common polyamide plastics found in municipal solid waste (MSW) are polyamide 6 (PA6) and polyamide 66 (PA66). The amide groups are stable enough to render PAs as highly useful materials in many high-performance applications such as fibers in carpets and textiles, automotive and aerospace applications, electronics, and building and construction materials. The amide bonds in PAs offer a point of attack for various degradation agents that can depolymerize the polymer to parent monomers via pyrolysis, hydrolysis, ammonolysis, or by applying supercritical fluids or ionic liquids. In Section 1, we discussed the thermal unzipping of PA6 (also known as Nylon 6) to its parent monomer, cyclic ε-caprolactam (CPL), under pyrolysis conditions. Studies have shown that PA6 will depolymerize to CPL in >80 % yields at temperatures 330–400 °C [82]. BASF patented a catalytic pyrolysis technology for depolymerizing PA6 (from carpet waste) into CPL in 1991 but is not practicing the technology today [83].

The amide bonds in PAs offer a point of attack for various degradation agents that can depolymerize the polymer to parent monomers using similar solvolytic approaches applied to PET such as hydrolysis, aminolysis, and methanolysis, albeit under different conditions [84]. PAs are associated with high glass transition temperatures (T_g), high melt temperatures (T_m), and high concentrations of hydrogen bonding. Thus, for complete depolymerization of these materials, more extreme conditions are often required then for PET. Most studies have focused on depolymerization of PA6. This is likely due to the

lower crystallinity, lower T_m, and lower resistance to chemicals and acids than PA66 which makes it easier to break down chemo-catalytically. However, high operational temperatures (>250 °C), 13, 16 high pressures 16 and strong acidic or basic conditions often entail high energy input and operational difficulties that limit the applicability.

Chemical recycling of PA66, on the other hand, is even more challenging, because PA66 polymer chains interact more strongly with one another since each secondary amide bond participates in two strong hydrogen bonds [85]. As a result, PA66 possesses a rigid semi-crystalline polymer structure, which translates into a higher tensile strength and higher melting point compared to PA6 on a macroscopic scale [86]. Both the intrinsic strength of the secondary amide bond and the resulting semi-crystalline polymer matrix pose severe challenges for the chemical recycling of PA66, which is typically tackled by applying high temperatures (>275 °C) [87–90], high pressures [91–93], supercritical fluids [94, 95], and/or strong acidic [84] or alkaline conditions [90, 96].

A process for depolymerizing PA6 scrap using high pressure steam was patented by AlliedSignal [97]. In the AlliedSignal process, PA6 was dissolved in high-pressure steam at 125–130 psi and 175–180 °C for 0.5 h in a batch process and then continuously hydrolyzed with super-heated steam at 35 °C and 100 psi (790 kPa) to yield 98 % CPT. The recovered monomer could be repolymerized without additional purification. Braun et al. 1999 reported the depolymerization of nylon 6 carpet in a small laboratory apparatus with steam at 3400 °C and 1500 kPa for 3 h to obtain a 95 % yield of CPT [98]. Aquafil Econyl and gr3n are two other companies that are commercially operating technologies for depolymerizing PA 6 and PA 66 via solvolysis. These technologies focus mostly on recycling of used carpets or fishing gear.

2.2 Thermal unzipping into monomers

2.2.1 Polymethyl methacrylate

Polymethyl methacrylate (PMMA) is a widely used thermoplastic in various electronics, automotive, and building and construction applications. Notable products and tradenames for PMMA are Perspex®, Plexiglas® and Lucite® [99]. PMMA is one of the few commodity plastics that undergoes chain unzipping into the parent monomer, methyl methacrylate (MMA), using thermal of photochemical approaches [100, 101]. In a pyrolysis process, the liquid product from PMMA is comprised mostly of MMA that can be used to resynthesize PMMA products. Thermal pyrolysis of PMMA has been studied extensively [99, 100, 102, 103]. The effects of temperature, additives, fillers, and solids loading on the distribution of pyrolytic products were have been investigated [104, 105]. Studies have shown that PMMA thermal pyrolysis results in nearly 97 % recovery of MMA at relatively low temperatures at temperatures between 400 and 500 °C. In several papers it was reported that the liquid pyrolysis product was so pure that it could be polymerized again without any further

treatment [105–107]. As outlined in Section 1, this process can be aided/assisted by the use of microwaves or plasma to improve monomer yields and reduce energy inputs and residence time [108–111].

Even though PMMA depolymerization via pyrolysis is more facile than other commodities such as polyolefins (Figure 9), we have not seen widespread adoption of this recycling process. One significant limitation is likely feedstock reliability. Unlike PET and polyolefins, PMMA is not collected in curbside recycling bins since it is not a common household plastic. As a result, there is no widespread collection system for PMMA and this requires special collections or drop-offs. Some companies, such as CompuPoint USA, are collecting used electronics and separating PMMA components. In 2022, Sumitomo Chemical announced that they were piloting a pyrolysis technology for PMMA recycling [112]. The Japan Steelworks Co. developed a continuous, twin-screw extruder technology to pyrolyze PMMA to MMA and improve the economics and energy inputs for the process. A schematic of The Japan Steelworks Co. is presented in Figure 10 [113].

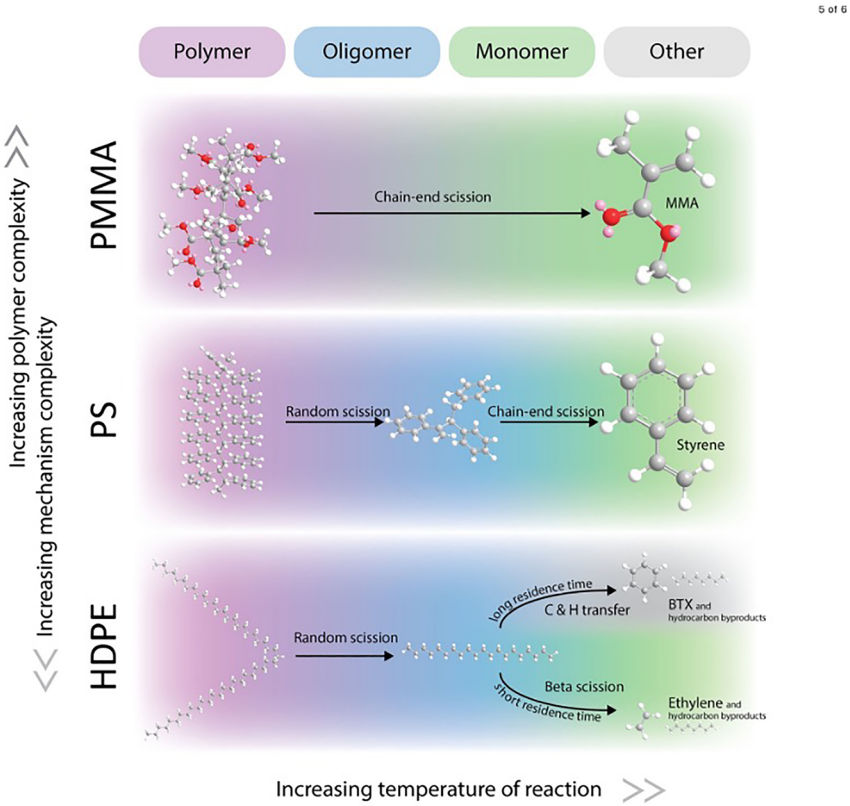

Figure 9: Comparison of unzipping mechanism of PMMA and PS to polyolefins from Vollmer et al. [8].

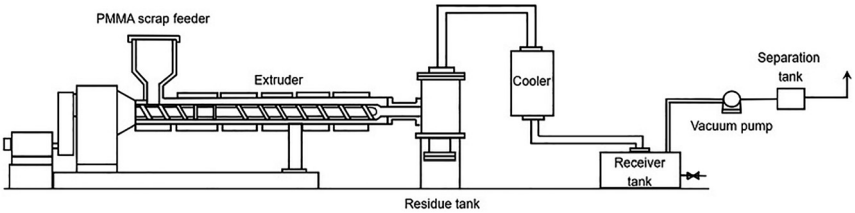

Figure 10: Schematic of twin-screw reactive extrusion design to depolymerize PMMA [113].

2.2.2 Polystyrene

Polystyrene (PS) is another important commodity plastic used in packaging applications. General-purpose PS is a transparent, hard, and somewhat brittle plastic. PS can also be easily foamed (i.e., Styrofoam), to yield a lightweight, waterproof packaging material. Expanded polystyrene (EPS) is another similar foam material, which has been used as insulation, life vests and rafts, and food containers. PS foam is notoriously challenging from a recycling perspective due to the low density and porosity (i.e., uptake of contaminants) of the foam waste. Additionally, PS foam has been identified as a major contributor to ocean plastic debris and easily breaks apart in the natural world yielding a formidable amount of microplastics. As a result, researchers, companies, and NGOs have focused significant effort towards the effective recovery and recycling of PS. Thermal or thermo-catalytic pyrolysis of PS to styrene monomer has been studied extensively [114–119]. However, unlike PMMA, PS will undergo random chain scission at mid-temperatures in pyrolysis (i.e., 300–400 °C) generating a liquid oil, consisting mainly of C6-C12 aromatic hydrocarbons, gasses, and solid residues. At higher temperatures (400–500 °C) chain-end scission becomes the primary mechanism and the pyrolysis product consists primarily of styrene monomer. However, this process is not perfect. Styrene and α-methylstyrene have poor thermal-oxidative stability, resulting in the formation on undesired side products in the pyrolysis process (Figure 11). This increases the costs and energy for downstream separations to recover the styrene monomer in high yields. The oil product is not suitable for automotive fuels due to the high content of aromatic hydrocarbons that can cause carbon formation problems in the engine. Several factors inhibit the formation of styrene: heat transfer problems due to the difficulty of establishing contact between PS and the heat transfer material causing uneven heat supply, and intensified side reactions at high temperatures and long contact times.

One approach to overcome the issues mentioned above is depolymerization with a temperature of less than 550 °C and a vapor resident time of less than 10 s in a uniform heat distributed fluidized bed reactor. Liu et al. have reported styrene yields of 72–79 % using this method [115]. Another approach is depolymerization in a hydrocarbon medium, which can avoid the heat transfer problem and side reactions mentioned above and achieve high styrene selectivity.

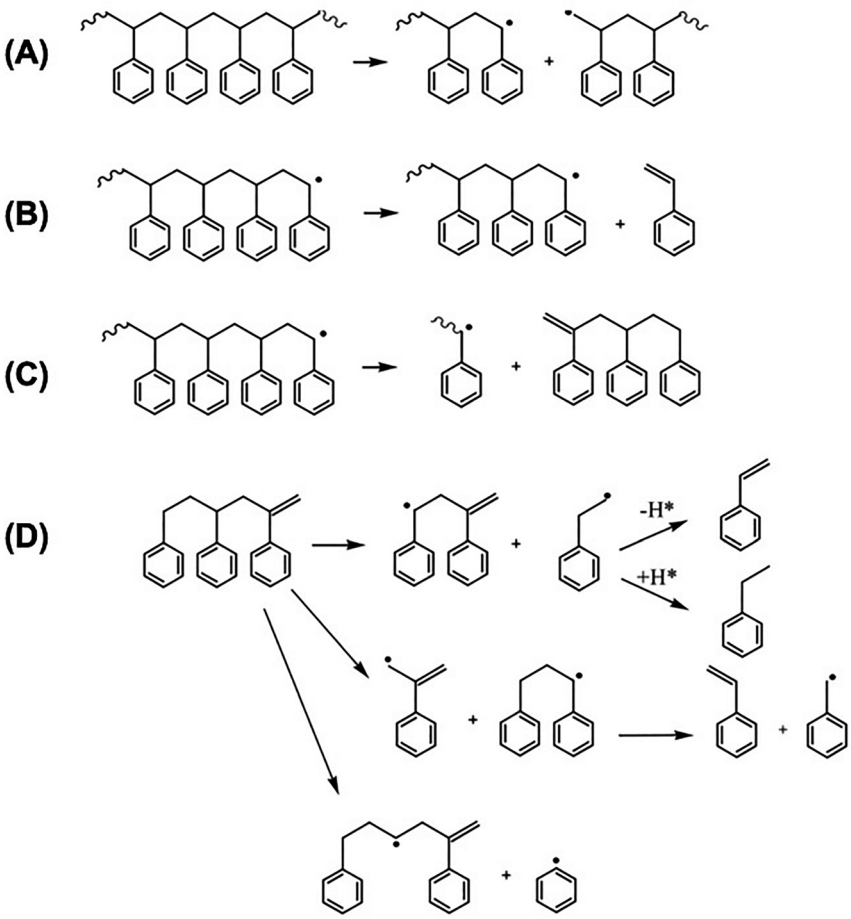

Figure 11: Scheme of pyrolysis reaction for PS and undesired side reactions. (A) Hemolytic cleavage of backbone C–C bond in PS, (B) beta-cleavage of the backbone C–C bond and formation of styrene monomer, (C) hydrogen transfer and formation of trimer, and (D) thermal cracking of the trimer.

Several companies have emerged in the last decade that are piloting thermal pyrolysis of PS to recover styrene monomer. Most notably is Agilyx, a startup company that has pioneered a pyrolysis technology to depolymerize PS waste (Figure 12), with an emphasis on PS foam [120]. Agilyx has demonstrated a pyrolysis technology at their facility in Tigard, Oregon, which has a capacity of 10 tons per day of PS waste, according the to the Agilyx website. Agilyx claims their core differentiator from other pyrolysis technologies is their novel styrene purification process using Technip Energies' process for purifying styrene monomer. The technology for the purification of Agilyx Styrene Oil has been pilot tested in Technip Energies' Research Center in Weymouth, MA, USA. Pyrowave is another company attempting to optimize and scale the pyrolysis of PS waste

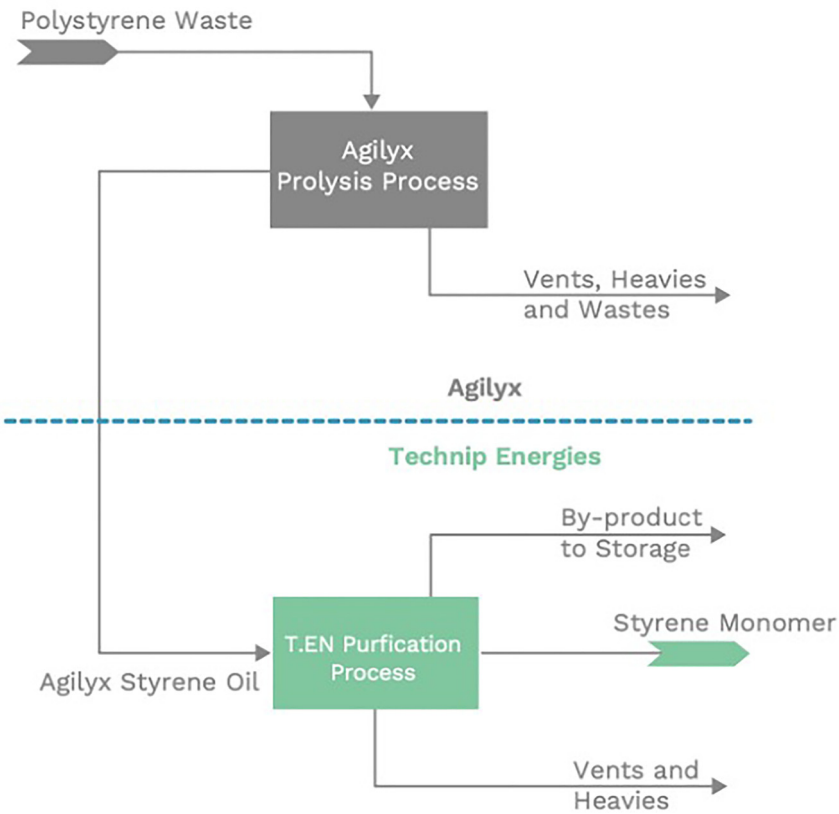

Figure 12: Schematic of Agilyx pyrolysis process for PS waste as shown on the Agilyx website [120].

to recover styrene monomer. Pyrowave is pioneering a microwave assisted pyrolysis process and claim their process is less energy intensive and polluting than conventional PS pyrolysis.

3 Summary and future outlooks

Monomer-loop recycling technologies are one of several pathways toward a circular economy for plastics. While most commodity plastics were not designed to easily depolymerize, some common plastics can be broken down into their parent monomers in the presence of heat, pressure, catalysts, and/or solvent. Here, we provided a high-level overview of the depolymerization technologies that have been studied and/or scaled as promising monomer-loop recycling processes for selective plastic waste streams. Namely, commodity plastics that are considered unzippable/depolymerizable include PET, PA6, PMMA, and PS. While several reports have demonstrated that these polymers

can be depolymerized to recover high monomer yields, many gaps and challenges still exist before these technologies can achieve industrial reality. In a recent study by Uekert et al., the technical, economic, and environmental metrics of emerging closed-loop recycling processes were analyzed and compared against mechanical recycling [121]. Regardless of the high monomer yields and purity that can be achieved through these chemical depolymerization routes, mechanical recycling outperformed all other technologies, as well as virgin plastic production across economic and environmental considerations, but it exhibited lower material qualities and other technical metrics. Thus, chemists have their work cut out for them to continue to optimize and improve chemical depolymerization technologies and reduce the environmental impact of the proposed routes. However, the future is bright. In a recent Strategy for Plastics Innovation repot from the U.S. Department of Energy, chemical recycling was identified as a promising technology for mitigating plastic waste and highlighted as key area for innovation and optimization [122].

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: None declared.
Conflict of interest: The authors declare no conflicts of interest regarding this article.

References

1. Billiet S, Trenor SR. 100th anniversary of macromolecular science viewpoint: needs for plastics packaging circularity. ACS Macro Lett 2020;9:1376–90.
2. Ellis LD, Rorrer NA, Sullivan KP, Otto M, McGeehan JE, Román-Leshkov Y, et al. Chemical and biological catalysis for plastics recycling and upcycling. Nat Catal 2021;4:539–56.
3. Shi C, Reilly LT, Phani Kumar VS, Coile MW, Nicholson SR, Broadbelt LJ, et al. Design principles for intrinsically circular polymers with tunable properties. Chem 2021;7:2896–912.
4. Dainton FS, Ivin KJ. Reversibility of the propagation reaction in polymerization processes and its manifestation in the phenomenon of a 'ceiling temperature'. Nature 1948;162:705–7.
5. Singh A, Rorrer NA, Nicholson SR, Erickson E, DesVeaux JS, Avelino AFT, et al. Techno-economic, life-cycle, and socioeconomic impact analysis of enzymatic recycling of poly(ethylene terephthalate). Joule 2021;5: 2479–503.
6. López Md. MC, Ares Pernas AI, Abad López MJ, Latorre AL, López Vilariño JM, González Rodríguez MV. Assessing changes on poly(ethylene terephthalate) properties after recycling: mechanical recycling in laboratory versus postconsumer recycled material. Mater Chem Phys 2014;147:884–94.
7. Thiounn T, Smith RC. Advances and approaches for chemical recycling of plastic waste. J Polym Sci 2020; 58:1347–64.
8. Vollmer I, Jenks MJ, Roelands MC, White RJ, van Harmelen T, de Wild P, et al. Beyond mechanical recycling: giving new life to plastic waste. Angew Chem Int Ed 2020;59:15402–23.
9. Barnard E, Rubio Arias JJ, Thielemans W. Chemolytic depolymerisation of PET: a review. Green Chem 2021; 23:3765–89.
10. Datye KV, Raje HM, Sharma ND. Poly(ethylene terephthalate) waste and its utilisation: a review. Resour Conserv 1984;11:117–41.

11. George N, Kurian T. Recent developments in the chemical recycling of postconsumer poly(ethylene terephthalate) waste. Ind Eng Chem Res 2014;53:14185–98.
12. Karayannidis GP, Chatziavgoustis AP, Achilias DS. Poly(ethylene terephthalate) recycling and recovery of pure terephthalic acid by alkaline hydrolysis. Adv Polym Technol 2002;21:250–9.
13. Paszun D, Spychaj T. Chemical recycling of poly(ethylene terephthalate). Ind Eng Chem Res 1997;36: 1373–83.
14. Yoshioka T, Grause G. Feedstock recycling of PET. In: Feedstock recycling and pyrolysis of waste plastics. Edithvale, Australia: Wiley; 2006:641–61 pp.
15. Kawai F, Kawabata T, Oda M. Current knowledge on enzymatic PET degradation and its possible application to waste stream management and other fields. Appl Microbiol Biotechnol 2019;103:4253–68.
16. Kawai F, Kawabata T, Oda M. Current state and perspectives related to the polyethylene terephthalate hydrolases available for biorecycling. ACS Sustainable Chem Eng 2020;8:8894–908.
17. Maurya A, Bhattacharya A, Khare SK. Enzymatic remediation of polyethylene terephthalate (PET)–Based polymers for effective management of plastic wastes: an overview. Front Bioeng Biotechnol 2020;8:1–13.
18. Tournier V, Topham CM, Gilles A, David B, Folgoas C, Moya-Leclair E, et al. An engineered PET depolymerase to break down and recycle plastic bottles. Nature 2020;580:216–9.
19. Yoshioka T, Okayama N, Okuwaki A. Kinetics of hydrolysis of PET powder in nitric acid by a modified shrinking-core model. Ind Eng Chem Res 1998;37:336–40.
20. Brown GE, Jr, O'brien RC. Method for recovering terephthalic acid and ethylene glycol from polyester materials. US3952053A, 1976.
21. Pusztaszeri SF. Method for recovery of terephthalic acid from polyester scrap. US4355175A, 1982.
22. Yoshioka T, Motoki T, Okuwaki A. Kinetics of hydrolysis of poly(ethylene terephthalate) powder in sulfuric acid by a modified shrinking-core model. Ind Eng Chem Res 2001;40:75–9.
23. Sheehan JR. Terephthalic acid, dimethyl terephthalate, and isophthalic acid. In: Ullmann's Encyclopedia of Industrial Chemistry; 2000, vol 35. Available from: https://onlinelibrary.wiley.com/doi/abs/10.1002/14356007.a26_193.pub2.
24. Kosmidis VA, Achilias DS, Karayannidis GP. Poly(ethylene terephthalate) recycling and recovery of pure terephthalic acid. Kinetics of a phase transfer catalyzed alkaline hydrolysis. Macromol Mater Eng 2001; 286:640–7.
25. Oku A, Hu L-C, Yamada E. Alkali decomposition of poly(ethylene terephthalate) with sodium hydroxide in nonaqueous ethylene glycol: a study on recycling of terephthalic acid and ethylene glycol. J Appl Polym Sci 1997;63:595–601.
26. Pitat J, Holcik V, Bacak M. A method of processing waste of polyethylene terephthalate by hydrolysis. GB822834A, 1959.
27. Essaddam H. Polyethylene terephthalate depolymerization. WO2017007965A1, 2017.
28. Parravicini M, Crippa M, Vittorio Bertele M. Method and apparatus for the recycling of polymeric materials via depolymerization process. WO2013014650A129, 2013.
29. Available from: https://gr3n-recycling.com [Accessed 5 Sep 2022].
30. Campanelli JR, Kamal MR, Cooper DG. A kinetic study of the hydrolytic degradation of polyethylene terephthalate at high temperatures. J Appl Polym Sci 1993;48:443–51.
31. Campanelli JR, Cooper DG, Kamal MR. Catalyzed hydrolysis of polyethylene terephthalate melts. J Appl Polym Sci 1994;53:985–91.
32. Tustin GC, Pell TM Jr, Jenkins DA, Jernigan MT. Process for the recovery of terephthalic acid and ethylene glycol from poly (ethylene terephthalate). US5413681A51. Rijeka, Coratia: InTech; 1995.
33. Araújo R, Silva C, O'Neill A, Micaelo N, Guebitz G, Soares CM, et al. Tailoring cutinase activity towards polyethylene terephthalate and polyamide 6,6 fibers. J Biotechnol 2007;128:849–57.
34. de Castro AM, Carniel A, Nicomedes Junior J, da Conceição Gomes A, Valoni É. Screening of commercial enzymes for poly(ethylene terephthalate) (PET) hydrolysis and synergy studies on different substrate sources. J Ind Microbiol Biotechnol 2017;44:835–44.

35. Herrero Acero E, Ribitsch D, Steinkellner G, Gruber K, Greimel K, Eiteljoerg I, et al. Enzymatic surface hydrolysis of PET: effect of structural diversity on kinetic properties of cutinases from thermobifida. Macromolecules 2011;44:4632–40.
36. Ribitsch D, Herrero Acero E, Przylucka A, Zitzenbacher S, Marold A, Gamerith C, et al. Enhanced cutinase-catalyzed hydrolysis of polyethylene terephthalate by covalent fusion to hydrophobins. Appl Environ Microbiol 2015;81:3586–92.
37. Ribitsch D, Yebra AO, Zitzenbacher S, Wu J, Nowitsch S, Steinkellner G, et al. Fusion of binding domains to thermobifida cellulosilytica cutinase to tune sorption characteristics and enhancing PET hydrolysis. Biomacromolecules 2013;14:1769–76.
38. Ronkvist ÅM, Xie W, Lu W, Gross RA. Cutinase-catalyzed hydrolysis of poly(ethylene terephthalate). Macromolecules 2009;42:5128–38.
39. Roth C, Wei R, Oeser T, Then J, Föllner C, Zimmermann W, et al. Structural and functional studies on a thermostable polyethylene terephthalate degrading hydrolase from Thermobifida fusca. Appl Microbiol Biotechnol 2014;98:7815–23.
40. Sulaiman S, Yamato S, Kanaya E, Kim JJ, Koga Y, Takano K, et al. Isolation of a novel cutinase homolog with polyethylene terephthalate-degrading activity from leaf-branch compost by using a metagenomic approach. Appl Environ Microbiol 2012;78:1556–62.
41. Yoshida S, Hiraga K, Takehana T, Taniguchi I, Yamaji H, Maeda Y, et al. A bacterium that degrades and assimilates poly(ethylene terephthalate). Science 2016;351:1196–9.
42. Knott BC, Erickson E, Allen MD, Gado JE, Graham R, Kearns FL, et al. Characterization and engineering of a two-enzyme system for plastics depolymerization. Proc Natl Acad Sci USA 2020;117:25476–85.
43. Uekert T, DesVeaux JS, Singh A, Nicholson SR, Lamers P, Ghosh T, et al. Life cycle assessment of enzymatic poly(ethylene terephthalate) recycling. Green Chem 2022;24:6531–43.
44. Erickson E, Gado JE, Avilán L, Bratti F, Brizendine RK, Cox PA, et al. Sourcing thermotolerant poly(ethylene terephthalate) hydrolase scaffolds from natural diversity. Nat Commun 2022;13:7850.
45. Deng B, Yue Y, Yang J, Yang M, Xing Q, Peng H, et al. Improving the activity and thermostability of PETase from Ideonella sakaiensis through modulating its post-translational glycan modification. Commun Biol 2023;6:39.
46. Austin HP, Allen MD, Donohoe BS, Rorrer NA, Kearns FL, Silveira RL, et al. Characterization and engineering of a plastic-degrading aromatic polyesterase. Proc Natl Acad Sci USA 2018;115:E4350–7.
47. Enzymatic recycling: removing the constraints of current processes. Available from: https://www.carbios.com/en/enzymatic-recycling/.
48. Han M. 5 - depolymerization of PET bottle via methanolysis and hydrolysis. In: Thomas S, Rane A, Kanny K, Abitha VK, Thomas MG, editors Recycling of polyethylene terephthalate bottles. William Andrew Publishing; 2019. pp. 85–108.
49. Eastman's polyester renewal technology. Available from: https://www.eastman.com/Company/Circular-Economy/Solutions/Pages/Polyester-Renewal.aspx [Accessed 1 Feb 2023].
50. Sinha V, Patel MR, Patel JV. Pet waste management by chemical recycling: a review. J Polym Environ 2010; 18:8–25.
51. Achilias DS, Andriotis L, Koutsidis IA, Louka D, Nianias N, Siafaka PI, et al. Recent Advances in the Chemical Recycling of Polymers (PP, PS, LDPE, HDPE, PVC, PC, Nylon, PMMA). Rijeka, Coratia: InTech; 2012.
52. Liu B, Lu X, Ju Z, Sun P, Xin J, Yao X, et al. Ultrafast homogeneous glycolysis of waste polyethylene terephthalate via a dissolution-degradation strategy. Ind Eng Chem Res 2018;57:16239–45.
53. Jiang Z, Yan D, Xin J, Li F, Guo M, Zhou Q, et al. Poly(ionic liquid)s as efficient and recyclable catalysts for methanolysis of PET. Polym Degrad Stabil 2022;199:109905.
54. Pham DD, Cho J. Low-energy catalytic methanolysis of poly(ethyleneterephthalate). Green Chem 2021;23: 511–25.

55. Yang R, Xu G, Dong B, Guo X, Wang Q. Selective, sequential, and “one-pot” depolymerization strategies for chemical recycling of commercial plastics and mixed plastics. ACS Sustainable Chem Eng 2022;10: 9860–71.
56. Loop Industry - REVOLUTIONARY, SUSTAINABLE TECHNOLOGY. Available from: https://www.loopindustries.com/en/technology [Accessed 10 Feb 2023].
57. Lozano-Martinez P, Torres-Zapata T, Martin-Sanchez N. Directing depolymerization of PET with subcritical and supercritical ethanol to different monomers through changes in operation conditions. ACS Sustainable Chem Eng 2021;9:9846–53.
58. Gamble WJ. Process of recovering components from scrap polyester. EP0599309A2, 1993.
59. Genta M, Iwaya T, Sasaki M, Goto M. Supercritical methanol for polyethylene terephthalate depolymerization: observation using simulator. Waste Manag 2007;27:1167–77.
60. Yang Y, Lu Y, Xiang H, Xu Y, Li Y. Study on methanolytic depolymerization of PET with supercritical methanol for chemical recycling. Polym Degrad Stabil 2002;75:185–91.
61. Sako T, Sugeta T, Otake K, Takebayashi Y, Kamizawa C, Tsugumi M, et al. Kinetic study on depolymerization of poly (ethylene terephthalate) with methanol at high temperature and pressure. Kobunshi Ronbunshu 1998;55:685–90.
62. Liu J, Yin J. Carbon dioxide synergistic enhancement of supercritical methanol on PET depolymerization for chemical recovery. Ind Eng Chem Res 2022;61:6813–9.
63. Chen JY, Ou CF, Hu YC, Lin CC. Depolymerization of poly(ethylene terephthalate) resin under pressure. J Appl Polym Sci 1991;42:1501–7.
64. Güçlü G, Kas¸göz A, Özbudak S, Özgümüs¸ S, Orbay M. Glycolysis of poly(ethylene terephthalate) wastes in xylene. J Appl Polym Sci 1998;69:2311–9.
65. Chen C-H. Study of glycolysis of poly(ethylene terephthalate) recycled from postconsumer soft-drink bottles. III. Further investigation. J Appl Polym Sci 2003;87:2004–10.
66. Troev K, Grancharov G, Tsevi R, Gitsov I. A novel catalyst for the glycolysis of poly(ethylene terephthalate). J Appl Polym Sci 2003;90:1148–52.
67. Fang P, Liu B, Xu J, Zhou Q, Zhang S, Ma J, et al. High-efficiency glycolysis of poly(ethylene terephthalate) by sandwich-structure polyoxometalate catalyst with two active sites. Polym Degrad Stabil 2018;156:22–31.
68. Wang H, Liu Y, Li Z, Zhang X, Zhang S, Zhang Y. Glycolysis of poly(ethylene terephthalate) catalyzed by ionic liquids. Eur Polym J 2009;45:1535–44.
69. Yue QF, Wang CX, Zhang LN, Ni Y, Jin YX. Glycolysis of poly(ethylene terephthalate) (PET) using basic ionic liquids as catalysts. Polym Degrad Stabil 2011;96:399–403.
70. Abbott AP, Ahmed EI, Harris RC, Ryder KS. Evaluating water miscible deep eutectic solvents (DESs) and ionic liquids as potential lubricants. Green Chem 2014;16:4156–61.
71. Sert E, Yılmaz E, Atalay FS. Chemical recycling of polyethlylene terephthalate by glycolysis using deep eutectic solvents. J Polym Environ 2019;27:2956–62.
72. Fukushima K, Coulembier O, Lecuyer JM, Almegren HA, Alabdulrahman AM, Alsewailem FD, et al. Organocatalytic depolymerization of poly(ethylene terephthalate). J Polym Sci Polym Chem 2011;49: 1273–81.
73. Jehanno C, Flores I, Dove AP, Müller AJ, Ruipérez F, Sardon H. Organocatalysed depolymerisation of PET in a fully sustainable cycle using thermally stable protic ionic salt. Green Chem 2018;20:1205–12.
74. Pingale ND, Shukla SR. Microwave assisted ecofriendly recycling of poly (ethylene terephthalate) bottle waste. Eur Polym J 2008;44:4151–6.
75. Parrott M. Chemical recycling of polyethylene terephthalate by microwave irradiation. US10508186B2, 2020.
76. Veregue FR, Pereira da Silva CT, Moisés MP, Meneguin JG, Guilherme MR, Arroyo PA, et al. Ultrasmall cobalt nanoparticles as a catalyst for PET glycolysis: a green protocol for pure hydroxyethyl terephthalate precipitation without water. ACS Sustainable Chem Eng 2018;6:12017–24.

77. Wang Z, Wang Y, Xu S, Jin Y, Tang Z, Xiao G, et al. A pseudo-homogeneous system for PET glycolysis using a colloidal catalyst of graphite carbon nitride in ethylene glycol. Polym Degrad Stabil 2021;190:109638.
78. Ekart MP. Process including glycolysis and subsequent purification for recycling polyester materials. US5635584A, 1996.
79. Artigas MP. Polymer degradation. WO2016105200A1, 2014.
80. Shuji I. Bis-β-hydroxyethyl terephthalate production process and purification process. CN1511821A, 2007.
81. Allen RA. Methods and materials for depolymerizing polyesters. US20160060419A1, 2014.
82. Czernik S, Elam CC, Evans RJ, Meglen RR, Moens L, Tatsumoto K. Catalytic pyrolysis of nylon-6 to recover caprolactam. J Anal Appl Pyrol 1998;46:51–64.
83. Corbin TF. Process for the recovery of epsilon-caprolactam from nylon 6 carpet. EP0522235A1, 1992.
84. Češarek U, Pahovnik D, Žagar E. Chemical recycling of aliphatic polyamides by microwave-assisted hydrolysis for efficient monomer recovery. ACS Sustainable Chem Eng 2020;8:16274–82.
85. Stuyck W, Janssens K, Denayer M, De Schouwer F, Coeck R, Bernaerts KV, et al. A sustainable way of recycling polyamides: dissolution and ammonolysis of polyamides to diamines and diamides using ammonia and biosourced glycerol. Green Chem 2022;24:6923–30.
86. Kohan MI, Mestemacher SA, Pagilagan RU, Redmond K. Polyamides. In: Ullmann's Encyclopedia of Industrial Chemistry; 2011.
87. Bonfield JH. Regeneration of e-caprolactam from polyamides. US3182055A, 1965.
88. McKinney RJ. Ammonolysis of nylon. US5302756A, 1993.
89. McKinney RJ. Lewis acid catalyzed ammonolysis of nylon. US5395974A, 1995.
90. Moran EF. Depolymerization of nylon 6,6 (and optionally) nylon 6 to obtain hexamethylene diamine (and caprolactam). WO1994008942A1, 1993.
91. Zhou W, Neumann P, Al Batal M, Rominger F, Hashmi ASK, Schaub T. Depolymerization of technical-grade polyamide 66 and polyurethane materials through hydrogenation. ChemSusChem 2021;14:4176–80.
92. Kumar A, von Wolff N, Rauch M, Zou Y-Q, Shmul G, Ben-David Y, et al. Hydrogenative depolymerization of nylons. J Am Chem Soc 2020;142:14267–75.
93. Fernandes AC. Reductive depolymerization as an efficient methodology for the conversion of plastic waste into value-added compounds. Green Chem 2021;23:7330–60.
94. Meng L, Zhang Y, Huang Y, Shibata M, Yosomiya R. Studies on the decomposition behavior of nylon-66 in supercritical water. Polym Degrad Stabil 2004;83:389–93.
95. Matsumoto H, Akinari Y, Kaiso K, Kamimura A. Efficient depolymerization and chemical conversion of polyamide 66 to 1,6-hexanediol. J Mater Cycles Waste Manag 2017;19:326–31.
96. Song S. A kind of alcoholysis recovery method of nylon 66 material. CN107056624B, 2017.
97. Sifniades S. Process for depolymerizing nylon-containing waste to form caprolactam. US5932724A, 1996.
98. Braun M, Levy AB, Sifniades S. Recycling nylon 6 carpet to caprolactam. Polym-Plast Technol Eng 1999;38: 471–84.
99. Godiya CB, Gabrielli S, Materazzi S, Pianesi MS, Stefanini N, Marcantoni E. Depolymerization of waste poly(methyl methacrylate) scraps and purification of depolymerized products. J Environ Manag 2019;231: 1012–20.
100. Braido RS, Borges LEP, Pinto JC. Chemical recycling of crosslinked poly(methyl methacrylate) and characterization of polymers produced with the recycled monomer. J Anal Appl Pyrol 2018;132:47–55.
101. Rahimi A, Garciá JM. Chemical recycling of waste plastics for new materials production. Nat Rev Chem 2017;1:1–11.
102. Achilias DS. Chemical recycling of poly(methyl methacrylate) by pyrolysis. Potential use of the liquid fraction as a raw material for the reproduction of the polymer. Eur Polym J 2007;43:2564–75.
103. Ferriol M, Gentilhomme A, Cochez M, Oget N, Mieloszynski JL. Thermal degradation of poly(methyl methacrylate) (PMMA): modelling of DTG and TG curves. Polym Degrad Stabil 2003;79:271–81.
104. Kaminsky W, Eger C. Pyrolysis of filled PMMA for monomer recovery. J Anal Appl Pyrol 2001;58–59:781–7.

105. Kaminsky W, Franck J. Monomer recovery by pyrolysis of poly(methyl methacrylate) (PMMA). J Anal Appl Pyrol 1991;19:311–8.
106. Kaminsky W, Predel M, Sadiki A. Feedstock recycling of polymers by pyrolysis in a fluidised bed. Polym Degrad Stabil 2004;85:1045–50.
107. Smolders K, Baeyens J. Thermal degradation of PMMA in fluidised beds. Waste Manag 2004;24:849–57.
108. Tsai T-L, Lin C-C, Guo G-L, Chu T-C. Chemical kinetics of polymethyl methacrylate (PMMA) decomposition assessed by a microwave-assisted digestion system. Ind Eng Chem Res 2008;47:2554–60.
109. Tsai T-L, Lin C-C, Guo G-L, Chu T-C. Effects of microwave-assisted digestion on decomposition behavior of polymethyl methacrylate (PMMA). Mater Chem Phys 2008;108:382–90.
110. Haque SM, Ardila-Rey JA, Umar Y, Rahman H, Mas'ud AA, Muhammad-Sukki F, et al. Polymeric materials for conversion of electromagnetic waves from the sun to electric power. Polymers 2018;10:307.
111. De Tommaso J, Dubois J-L. Risk analysis on PMMA recycling economics. Polymers 2021;13:2724.
112. Sumitomo Chemical to Construct Chemical Recycling Pilot Facility for Acrylic Resin to Reduce Impact on the Environment. Available from: https://www.sumitomo-chem.co.jp/english/news/detail/20210823e.html [Accessed 1 Mar 2023].
113. Method and apparatus for continuous regeneration of acrylic resin. WO2017048748A1, 1997.
114. Maafa IM. Pyrolysis of polystyrene waste: a review. Polymers 2021;13:225.
115. Liu Y, Qian J, Wang J. Pyrolysis of polystyrene waste in a fluidized-bed reactor to obtain styrene monomer and gasoline fraction. Fuel Process Technol 2000;63:45–55.
116. Hussain Z, Khan KM, Hussain K. Microwave–metal interaction pyrolysis of polystyrene. J Anal Appl Pyrol 2010;89:39–43.
117. Park K-B, Jeong Y-S, Guzelciftci B, Kim J-S. Two-stage pyrolysis of polystyrene: pyrolysis oil as a source of fuels or benzene, toluene, ethylbenzene, and xylenes. Appl Energy 2020;259:114240.
118. Fan S, Zhang Y, Liu T, Fu W, Li B. Microwave-assisted pyrolysis of polystyrene for aviation oil production. J Anal Appl Pyrol 2022;162:105425.
119. Lee T, Jung S, Park Y-K, Kim T, Wang H, Moon DH, et al. Catalytic pyrolysis of polystyrene over steel slag under CO2 environment. J Hazard Mater 2020;395:122576.
120. Recycling technology for a circular economy. Available from: https://www.agilyx.com [Accessed 1 Mar 2023].
121. Uekert T, Singh A, DesVeaux JS, Ghosh T, Bhatt A, Yadav G, et al. Technical, economic, and environmental Comparison of closed-loop recycling technologies for common plastics. ACS Sustainable Chem Eng 2023; 11:965–78.
122. Depart of Energy: Strategy for Plastics Innovation. Available from: https://www.energy.gov/entity%3Anode/4394292/strategy-plastics-innovation.