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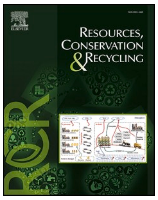

Full length article

# Open-loop recycling of post-consumer PET to closed-loop chemically recyclable high-performance polyimines

Nejib Kasmi, Eva Bäckström, Minna Hakkarainen *

*Department of Fibre and Polymer Technology, School of Engineering Sciences in Chemistry, Biotechnology and Health, KTH Royal Institute of Technology, Teknikringen 56-58, Stockholm, SE-100 44, Sweden*

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ABSTRACT

Intriguing high-performance polyimines (PI) were designed from diamines recovered by open-loop recycling of postconsumer PET bottles by microwave-assisted aminolysis. These new PIs had excellent thermal properties ($T_m$ = 226–286 °C, $T_g$ = 88–148 °C, heat resistance up to 327 °C) and super-high toughness and strength with Young's modulus of 4.02–4.93 GPa and tensile strength of 237–467 MPa, both significantly higher compared with common engineering plastics. The synthesized PIs also demonstrated recyclability "on demand" to original building blocks via mild and ultrafast acetic acid catalysed hydrolysis (70 °C for 10 min). Furthermore, the recovered monomer mixture was directly repolymerizable providing attractive closed-loop polymer-to-polymer recyclability under extremely mild conditions. These high performance thermoplastics, with easily tunable properties by selection of diamine used for aminolysis, in combination with closed-loop chemical recyclability have great promise as next-generation circular materials, designed from recycled plastics waste, for a wide property and application range.

## 1. Introduction

Plastics are an integral part of modern life and are exceptionally useful materials for a myriad of practical applications, but poorly managed plastic waste escalates adverse environmental impacts on all ecosystems when they reach the end of the use phase. Poly(ethylene terephthalate) — PET, the fourth largest produced polymer in the world, is an important industrial polymer which is widely used in food packaging, textile fibers, soft drink bottles, thermoformed trays, films, etc. (Sousa et al., 2021). The cumulative demand for PET packaging in the EU from 2020 to 2030 is forecasted to reach 63 million tons, with annual consumption increasing from 5.1 million tons in 2020 to 6.9 million tons in 2030 (Andreasi Bassi et al., 2022). However, this material is not readily biodegradable and once thrown in nature it is predicted to persist in lands, oceans and landfills for centuries as it is hardly attacked by water and/or microorganisms (Majumdar et al., 2020). Therefore, the development of new recycling approaches for this engineered material is imperative to improve circular plastic economy. Mechanical recycling plays a prominent role in PET waste management. However, the overall performance of mechanically recycled thermoplastics is typically hampered by the deterioration of mechanical properties and molecular weight decay after a number of repeated processing cycles due to thermal degradation and possible contamination (Agostinho et al., 2022; Bäckström et al., 2021; Fredi et al., 2021; Khan et al., 2022; Majumdar et al., 2020). Solid state polymerization (SSP) has numerous potential advantages and a strong industrial interest to overcome these limitations of post-consumer mechanically recycled PET (Crus et al., 2006; Kasmi et al., 2018; Pinter et al., 2021). This well-known technique has been successfully employed to produce high molecular weight recycled PET with improved properties, and thus extend its shelf life (Molnar et al., 2019; Pinter et al., 2021). In fact, such shortcomings lead to lower quality and less profitable materials, which in worse cases ends up in aquatic/terrestrial environments in the form of non-degradable terephthalic microplastic debris.

Chemical recycling by depolymerization is an important future end-of-life option for turning post-consumer plastics highly resistant to biodegradation into a portfolio of useful chemicals (Mendiburu-Valor et al., 2022; Meys et al., 2020; van der Hulst et al., 2022). It can provide solutions when mechanical recycling is not possible (Thiyagarajan et al., 2022). Aminolysis is one potential chemical recycling pathway for polyesters (Thiyagarajan et al., 2022) offering an open-loop recycling route for commercial polyesters supporting a circular plastics economy

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* Corresponding author.
*E-mail address:* minna@kth.se (M. Hakkarainen).

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(Thiyagarajan et al., 2022). This chemical process involves breaking down the waste polyester to useful value-added chemicals, which can then be re-introducible in the polymer value chain and re-used for polymerization of new high-quality plastics. It has already been used as an innovative solution to develop a waste-management strategy for post-consumer PET via an aminolytic chain cleavage that yields terephthalic diamides. The recovered PET aminolyzed products obtained by using a wide range of amines have been successfully tested in different applications. Indeed, they have been evaluated as plasticizers, adhesion promoters on metal/glass surfaces and resin components in UV-curable formulations, antibacterial drugs against various bacterial and fungal strains, as textile dyes on polyester and nylon fabrics, and as corrosion inhibitors in the anticorrosive paint formulations, among others (Bäckström et al., 2021; George et al., 2014; Merkel et al., 2020; Teotia et al., 2020). Recycled terephthalamide products have therefore been shown to have potential value for a wide variety of promising practical applications. The aminolysis process was also used to recycle waste polycarbonate (PC) and PET materials into versatile intermediates which were then converted into new polymers such as "biodegradable" polyurethanes (Mir Mohamad Sadeghi et al., 2011; Wu et al., 2018).

One bottleneck for chemical recycling by depolymerization is typically energy-intensive process, which often requires long reaction times and is therefore not economically viable (Agostinho et al., 2022). There is need for new innovative technologies and processes that could lead to possible substantial energy savings. Microwave (MW) irradiation has been successfully employed in the chemical recycling of plastics (Alberti et al., 2021). Catalysis also plays a crucial role in ensuring efficient MW-assisted chemical recycling of post-consumer plastics, including PET (Ellis et al., 2021; Kang et al., 2020). In this context, it was found that a variety of catalysts allow solvolysis reactions to occur in shorter times and at a lower reaction temperature (Barnard et al., 2021; Ellis et al., 2021; Zangana et al., 2022). A major benefit of using MW activation is to speed up chemical processes, resulting in shorter reaction times, milder reaction conditions and excellent yields. For instance, MW-assisted depolymerization of end-of-life poly(ethylene furanoate) (PEF), the fully renewable counterpart of PET, via methanolysis into dimethyl furanoate with high yield of 98% yield in 60 min has been reported (Alberti et al., 2021). MW-assisted chemical recycling has also been applied to PC (hydrolysis) and PET (glycolysis, hydrolysis, aminolysis) (Fredi et al., 2021;Ghosal et al., 2022; Tsintzou et al., 2012). MW-assisted aminolysis could be a promising waste-management solution for end-of-life polymers to reduce plastic pollution by producing value-added monomers.

During recent years dynamic covalent chemistry (DCC) has arisen as a promising tool to improve the mechanical recyclability of thermoplastics collected for recycling (Röttger et al., 2017) or to achieve reprocessable thermosets through covalent adaptable networks (van Zee et al., 2020). Schiff base (i.e. imine chemistry) involving a reaction between an aldehyde or ketone and primary amine, is an example of promising reversible DCC chemistry (Liguori et al., 2022; Xu et al., 2020).

We hypothesized that aminolysis of PET by different diamines could provide attractive aromatic building blocks with two primary amine-groups that could be reacted with dialdehydes for fabrication of aromatic polyimines (PIs). The incorporation of imine-functionalities could further provide thermoplastics with build-in chemically recyclability under mild conditions. At the same time the aromatic-building blocks in combination with amide functionalities, providing possibility for intermolecular hydrogen bonding, were expected to lead to high performance in terms of thermal and mechanical properties. Therefore, we utilized a rapid microwave-assisted aminolysis pathway to turn post-consumer PET bottles, into value-added recycled terephthalate diamines and we further developed a facile synthesis route for turning them into novel value-added PIs. The thermal properties, heat resistance and mechanical performance of fabricated PIs designed from recycled were investigated in detail and correlated to the structure of the diamines. Last but not least the closed-loop circularity of the new PIs was demonstrated by mild de-and repolymerization reactions.

## 2. Experimental

### 2.1. Materials

The post-consumer poly(ethylene terephthalate) PET used for the recycling experiments was Aqua d'Or PET bottles. 1,6-hexanediamine (1,6-HMDA, purum 99%), 1,8-octanediamine (1,8-OCDA, purum 98%), and 1,12-dodecanediamine (1,12-DODA, purum 98%) reagents were purchased from Sigma-Aldrich Merck, terephthalaldehyde (TPA-CHO, purum >98%) was purchased from TCI chemicals. Acetic acid-$d_4$ (99.5% atom D) for NMR analysis was from Thermo Scientific™. All other solvents used for purification were of analytical grade.

### 2.2. Microwave-assisted open-loop chemical recycling (aminolysis) of PET bottles

Before chemical recycling through catalyst-free microwave-assisted aminolysis, the post-consumer PET bottle was washed with water and cut into small flakes by installing a 7 mm sieve on the SHR3D IT shredder from 3devo. In order to optimize the conditions of the recycling process and thus to reduce the reaction time and improve the yield; different reaction temperatures, ramp and run times were tested. The optimal conditions were found to be: a predetermined amount of PET flakes (1 eq = 4.2 mmol) was placed in a FlexiWave Teflon vial equipped with a magnetic stirrer with an excess (50.4 mmol) of biobased aliphatic diamine —i.e. 1,6-HMDA, 1,8-OCDA or 1,12-DODA — as reaction media for aminolysis. The vials were placed in a FlexiWave microwave from Milestone (Sorisole, Italy) with a maximum power of 1500 W. The reaction temperature was followed by a probe inserted into one of the reaction vials and the power was automatically adjusted to keep the selected reaction temperature. After the ramp time of 15 min (i.e. heating time to the reaction temperature), the mixture was heated for 1.5 h at 200 °C. After cooling down to room temperature, the target recycled diamines were recovered by filtration followed by precipitation in water (for PET-HMDA and PET-OCDA) or in ethanol (for PET-DODA) and drying in a vacuum oven. The yield of PET-HMDA, PET-OCDA, and PET-DODA diamines was calculated using the following equation:

$$Yield\ (\%) = \frac{weight\ of\ the\ obtained\ product}{maximum\ theoretical\ weight\ of\ the\ product} x\ 100$$

### 2.3. Synthesis of polyimines

A series consisting of three new aliphatic-aromatic PIs were synthesized via imine polycondensation procedure as follows: A predetermined amount (1 eq= 4 mmol) of the recycled diamine (PET-HMDA, PET-OCDA or PET-DODA) produced by recycling of PET bottles and TPACHO with a molar ratio of diamine:dialdehyde of 1:1.05 were charged in a round bottom flask with acetic acid as catalyst (10–15 drops). Ethanol absolute (70 mL) was chosen as reaction solvent. The mixture was heated under $N_2$ flow for 18 h at 45 °C. At last, after the polymerization of targeted PIs was completed, the mixture was cooled to ambient temperature. The resulting PIs were purified by precipitating in water, washed with EtOH and then dried in a vacuum oven. The PIs were named according to the number of carbon atoms in the diamines, i.e. PI6, PI8 and PI12).

### 2.4. Closed-loop chemical recycling of PIs by acidic hydrolysis

To determine the chemical recyclability of the synthesized PIs under extremely mild conditions by acid-catalysed hydrolysis, the following experiment was performed. 0.5 g of each PI sample was put in 10 mL of acetic acid in a round bottom flask equipped with a magnetic stirrer. The mixture was then heated for 10 min at 70 °C under atmospheric pressure to investigate the closed-loop chemical recyclability. All the PIs materials were completely degraded within a very short time (10 min) and the solutions turned pale yellow colour.

### *2.5. In-situ repolymerization of the recovered monomers by acidic hydrolysis of PI6*

The mixture of the depolymerized products (PET-HMDA + TPACHO dialdehyde) in acetic acid (10 mL), resulting from the acid hydrolysis of PI6, was introduced into a flask with ethanol absolute as solvent (80 mL). The reaction temperature was heated to 45 °C and was left to proceed for 18 h under nitrogen flow and continuous stirring with a magnetic stirrer. At last, after cooling to ambient temperature, the recycled polyimine rPI6 was purified following the same procedure described for the virgin PI6 (by precipitation in water, washing with EtOH then drying in a vacuum oven).

### *2.6. Nuclear magnetic resonance (NMR) spectroscopy*

The $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra of terephthalate diamines (PET-HMDA, PET-OCDA, and PET-DODA) obtained by aminolysis of PET and the recovered products obtained from the chemical recycling of the synthesized PIs (PI6, PI8, and PI12) were recorded on an Avance 400 (Bruker, U.S.A.) spectrometer (400 MHz), using acetic acid-$d_4$ as a solvent for all the samples.

### *2.7. Fourier transformed-infrared (FTIR) spectroscopy*

Infrared spectra of PIs were recorded on a Perkin-Elmer Spectrum 2000 Fourier transform infrared (FTIR) spectrometer (Norwalk, CT), in the wavenumber range from 750 to 4000 cm$^{-1}$ and in transmittance mode. The FTIR spectra were registered at a resolution of 4 cm$^{-1}$.

### *2.8. Differential scanning calorimetry (DSC)*

The thermal behaviour of the prepared terephthalate diamines and their corresponding PIs was studied by means of a Mettler Toledo DSC820. The terephthalate diamine monomers and PI samples, sealed in an aluminum pan, were heated up/cooled down under nitrogen flow (50 mL/min) from 30 to 210 °C and 30 to 310 °C, respectively, at a heating rate of 10 °C/min and maintained at these temperatures for 2 min to erase any thermal history. Two heating scans and one cooling scan were performed.

### *2.9. Thermogravimetric analysis (TGA)*

To investigate the thermal stability of the terephthalate diamine monomers produced by aminolysis of PET and PIs synthesized from these monomers, thermogravimetric (TGA) analysis was carried out under nitrogen atmosphere with a TGA/SDTA851e (Mettler Toledo, U.S.A.). The samples with a weight around 10 mg were inserted in 70 μL ceramic crucibles and heated at constant heating rate of 10 °C/min from 30 °C to 600 °C.

### *2.10. Mechanical properties*

Mechanical properties, i.e. Young's Modulus, stress at break and strain at break, of the prepared PIs were investigated by means of an Instron 5944 universal testing machine equipped with a 500 N load cell, at a crosshead speed of 5 mm/min and effective gauge length of 15 mm. The PIs were compression molded (210 °C for 25 min, force 240 kN and cooling to room temperature) to films with length: 20 mm × width: 5 mm × average thickness ~ 0.3 mm. Thickness for each analyzed PI sample was considered as the mean value of 4 different measurements performed along the specimen's length. The samples were conditioned in an environmental chamber at 22 °C and 40% relative humidity for 48 h prior to testing. The reported data are the average of 4 determinations.

## 3. Results and discussion

### *3.1. Microwave-assisted aminolysis of PET and structural characterization of produced terephthalate diamines*

Three novel terephthalate diamines, PET-HDMA, PET-OCDA, and PET-DODA were designed and successfully produced from post-consumer PET bottle by solvent and catalyst-free MW-assisted aminolysis approach as shown in Fig. 1A.

After optimization of the recycling process of PET-HMDA diamine monomer, in which different temperatures (200 °C, 210 °C and 220 °C), ramp and run times (1.5 h, 1 h 45 min, and 2 h) were tested (see Table S1), the optimal conditions were found as following: PET flakes and an excess of aliphatic diamine 1,6-HMDA with the molar ratio of PET repeating unit/diamine of 1:6 were introduced. The aminolysis reaction was performed under catalyst and solvent-free conditions at 200 °C for 1.5 h. In more details, as shown in Table S1, it has been observed that the longer the reaction time, the lower the yield. The results also showed a systematic decrease in the yield of PET-HMDA upon increasing the reaction temperature. The same procedure optimized for the synthesis of PET-HMDA (200 °C, reaction time of 1.5 h and a molar ratio of PET repeating unit/diamine of 1:6) was applied to the aminolysis reaction of PET using longer chain aliphatic diamines consisting of 8 (1,8-OCDA) or 12 (1,12-DODA) methylene units. At last, after completion of depolymerization, the obtained crude products, PET-HMDA and PET-OCDA, were cooled to room temperature and distilled water was added under stirring. PET-DODA with 12 methylene units was purified by precipitation in ethanol. The target diamines were recovered in very high yields (97%, 95% and 96% for PET-HMDA, PET-OCDA and PET-DODA, respectively) by filtration and dried in a vacuum oven. The three terephthalate diamine monomers obtained were soluble in acetic acid, but had high solvent resistance to other common organic solvents (e.g. DMSO, chloroform, methanol, ethanol, acetone, DMF).

$^1$H and $^{13}$C NMR spectroscopies were used to ascertain the chemical structures of the recycled diamines PET-HMDA, PET-OCDA and PET-DODA, therefore confirming the completion of PET depolymerization through aminolysis route. The $^1$H and $^{13}$C NMR spectra of PET-DODA, presented in Fig. 1, are shown as an example for the detailed proton and carbon peaks assignments. The corresponding NMR spectra of PET-HMDA and PET-OCDA are placed in the Supplementary materials (Figure S1-S2). The complete aminolysis of PET was demonstrated by the disappearance of the resonances at about 4.5 ppm ($^1$H NMR) and around 60 ppm ($^{13}$C NMR) typical of ethylene glycol protons of PET. The recorded $^1$H and $^{13}$C NMR spectra of the terephthalate diamines are in excellent accordance with the expected structures and the observed NMR peaks can be attributed to the different protons and carbons in the monomer structures.

In the $^1$H NMR spectrum of PET-DODA (Fig. 1B), the resonances appearing within the 1.3–1.7 ppm range were associated with the inner and middle methylene protons (d, e, f, g, h, i, j, k, l, and m) in the dodecamethylene segment, overlapped with (n) protons of the amine function. The peaks of the outer CH$_2$ groups (b) and (c) were observed at 3.48 and 3.17 ppm, respectively. The aromatic protons of the terephthalic moiety tagged as (a) were detected as a singlet signal at 7.98 ppm. The PET-DODA monomer was also scrutinized by $^{13}$C NMR to confirm its chemical constitution (Fig. 1C). The twelve CH$_2$ groups in the dodecamethylene segment exhibited discernible resonances at 26.06, 26.73, 26.94, 28.84, 28.96, 29.12, 29.19, 29.31, 29.36, 29.39, 39.86, and 40.18 ppm. The aromatic carbons in the terephthalic ring split into two signals (a) and (b) at 127.46 and 136.79 ppm, respectively. The most deshielded chemical shift appearing at 168.22 ppm is characteristic of the carbonyl carbon of the amide group. The detailed assignments for PET-HMDA and PET-OCDA are given in supplementary material. To sum

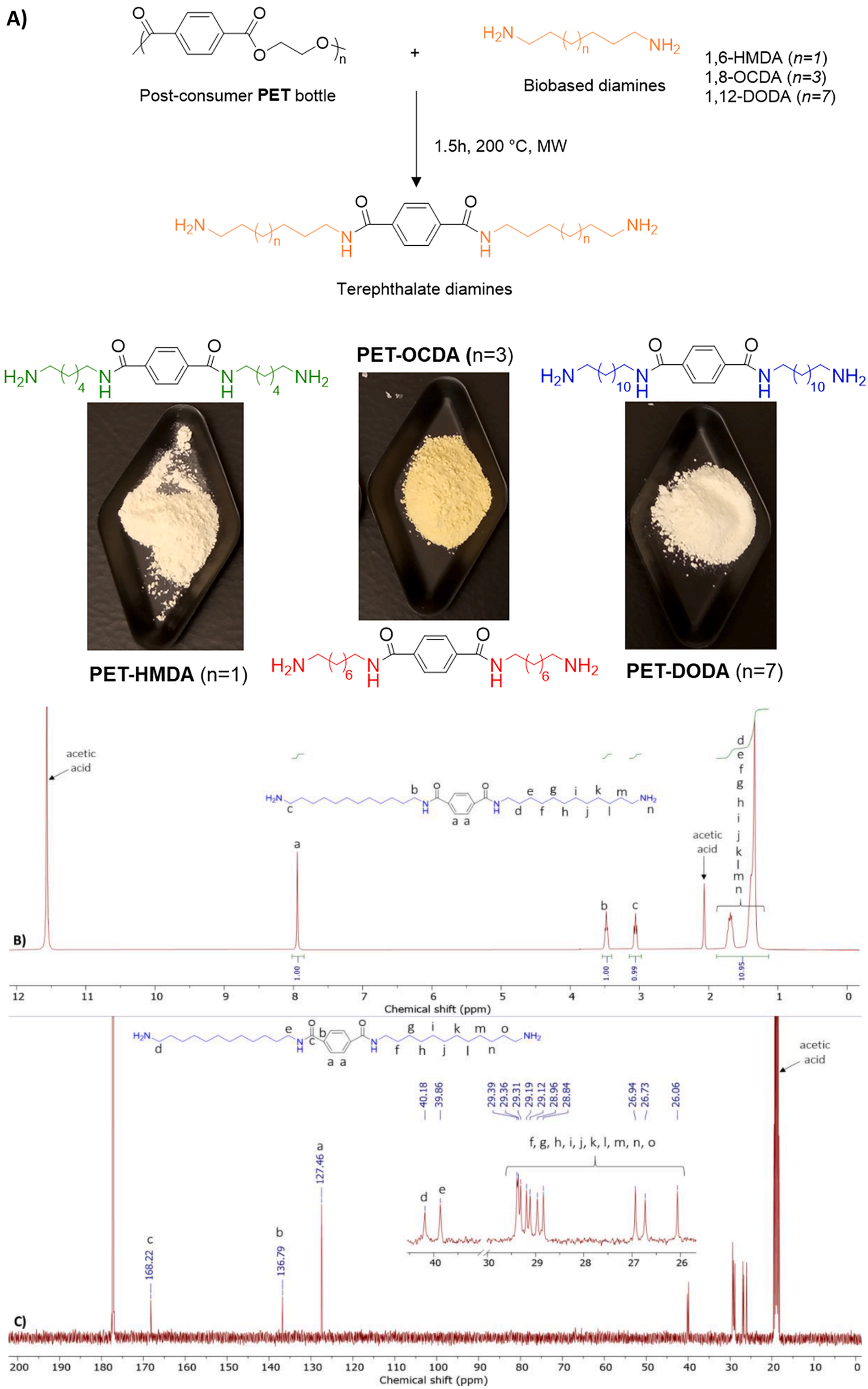

**Fig. 1.** A) Production of terephthalate diamines through MW-assisted aminolysis of post-consumer PET, B) $^{1}$H NMR and C) $^{13}$C NMR spectra of PET-DODA diamine (registered in acetic acid-$d_4$).

up, the NMR data of the three terephthalate diamines did not reveal any additional peak indicative of the presence of impurities, thus confirming their successful synthesis by aminolysis of post-consumer PET bottle waste. The chemical structure of recycled diamines from PET aminolysis was further assessed by FT-IR spectroscopy. The obtained data, used as supportive and complementary evidence for the $^{1}$H and $^{13}$C NMR results, is depicted in Figure S3. For all the terephthalate diamine monomers, the conversion of terephthalate ester to terephthalamide group was confirmed by the shifting of carbonyl stretching band ($C = O$) of ester at around 1720 $cm^{-1}$ to 1623 $cm^{-1}$ of amide, indicating successful completion of PET aminolysis. Other characteristic bands attributed to -NH of the primary amine group and -CO—N of the amide moiety were observed at ca 3310 $cm^{-1}$ and ca 1536 $cm^{-1}$, respectively. HPLC-ESI-MS is another technique that can be used to assess the product purity. However, due to the solubility issues of the synthesized aminolysis products, only the diamine PET-HMDA slightly soluble in methanol was analysed by ESI-MS. The obtained ESI-MS data shown in Fig. S4 revealed the appearance of a major peak at $m/z$ 363.58, confirming the synthesis product.

### 3.2. *Thermal properties of terephthalate diamines from PET aminolysis*

The thermal behaviour of the obtained terephthalate diamines was characterized by DSC. During the heating process, as shown in Fig. 2A, melting points ($T_m$) of the targeted monomers are evident in the 167–176 °C range. These high values are mainly associated with the rigid structure of the diamines prompted by the presence of stiff building blocks, i.e. terephthalate units and amide bonds and expected strong secondary interaction between amide and amine groups. The cooling scans (Fig. 2B) showed that PET-HMDA, PET-OCDA, and PET-DODA monomers possess remarkable exothermic crystallization ($T_c$) at 144, 151, and 156 °C, respectively. This indicates that these new building blocks have good crystallization ability from the melt, likely thanks to the presence of longer aliphatic units (C6, C8 and C12) in the monomers. It is worthy to note that discernible trends in $T_m$ and $T_c$ values were observed as a function of the length of these aliphatic units. In more detail, monomers with shorter aliphatic carbon chains displayed higher $T_m$ values. Contrariwise, $T_c$ follows the opposite trend, that is, upon decreasing the length of the aliphatic unit from C12 to C6, $T_c$ steadily decreased from 156 to 144 °C.

The thermal degradation behaviour and stability of the resulting diamine monomers were assessed by TGA analysis under nitrogen atmosphere. The typical profiles are shown in Fig. 2C and the degradation temperatures at 5% and 10% weight loss as well as the residue at 500 °C are gathered in Table S2. The synthesized terephthalate diamines revealed satisfactory thermal stability with onset decomposition temperatures ($T_{d,5\%}$) oscillating from 185 to 239 °C depending on the aliphatic diamine involved. The amount of formed residual weight upon heating to 500 °C for these monomers ranged between 0.6 to 4%. The derivative thermogravimetric (dTG) traces recorded for the

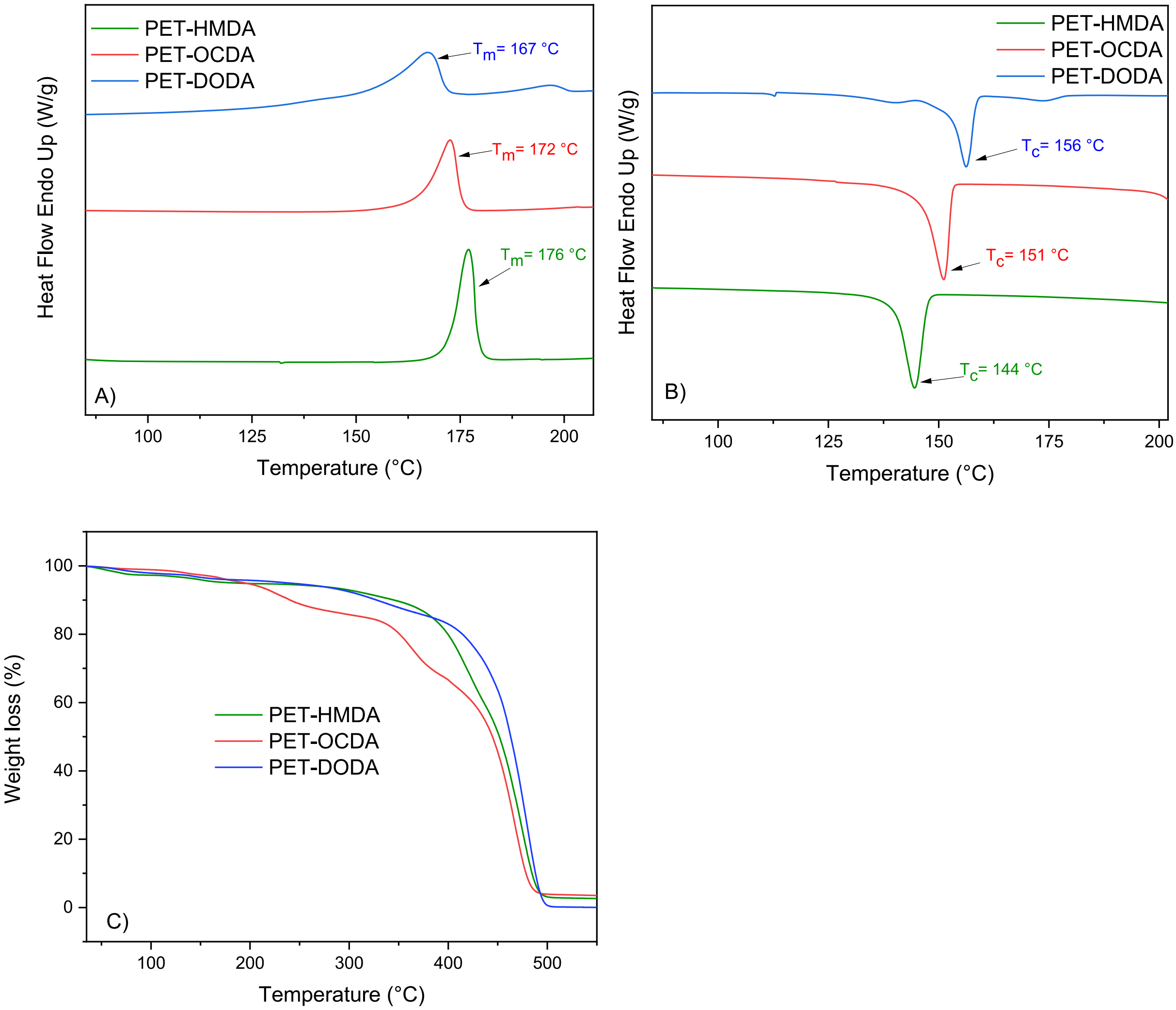

**Fig. 2.** Thermal properties of the purified recycled terephthalate diamines, PET-HMDA, PET-OCDA and PET-DODA: A) Second DSC heating scan, B) DSC cooling scan, C) TGA thermograms.

terephthalate diamine monomers in the 30–600 °C range are comparatively depicted in Fig. S5. The dTG curve of PET-HMDA shows two well-defined decomposition steps with the peaks at 421.4 and 474.2 °C. The decomposition profile of PET-DODA essentially undergoes one major single stage with maximum degradation temperature ($T_{max}$) of 479 °C, while the degradation of PET-OCDA took place in different stages.

### 3.3. Synthesis of polyimines

The synthesis of three new PIs was successfully performed via imine polycondensation procedure as shown in Fig. 3A. Predetermined amounts of the recycled diamines, designed from post-consumer PET bottle, and TPACHO with a molar ratio of diamine:dialdehyde of 1:1.05 were subjected to the polymerization. Acetic acid was utilized as catalyst and ethanol as reaction solvent. The reaction was left to proceed under nitrogen atmosphere for 18 h at moderate temperature of 45 °C. The resulting PIs were found to be highly resistant to organic solvents. Unlike PI8 and PI12 which are completely insoluble in any solvent, PI6 with 6 methylene units as aliphatic spacer group was slightly soluble in DMSO. Thus, it was characterized by $^{13}$C NMR. The recorded spectrum confirms polymerization as demonstrated by the appearance of a deshielded peak at 167 ppm typical of imine (C = N) carbon. The spectrum did not reveal any additional peak indicative of the presence of impurities and was perfectly consistent with the expected structure, where all signals are correctly attributed to the different carbons in the expected PI chain, as displayed in Fig. 3B. Due to the solubility issue of the synthesized PIs, FTIR spectroscopy was utilized to support the successful polymerization of PI6, PI8 and PI12. The FTIR spectra demonstrated the disappearance of the vibration band characteristics of aldehyde bond at 1683 cm$^{-1}$ and the appearance of the vibration band of the imine bond at 1625 cm$^{-1}$ (Fig. 3C) indicating successful synthesis of the targeted PIs.

The thermal properties of the three PIs, synthesized from diamine monomers from aminolysis of PET, were investigated by DSC and the thermograms are presented in Fig. 4A and 4B. PI6, PI8 and PI12 all exhibited extremely high $T_g$ value of 148, 131 and 88 °C, respectively. The much higher $T_g$ value of PI6 could be mainly ascribed to the use of terephthalate diamine (PET-HMDA) with shorter aliphatic-chains. This affords more rigid chemical structure by reduction the chain mobility of the resulting polymer and, thereby, a strikingly high $T_g$ value is spotted. Obvious trends were observed in the thermal behaviour of these PIs as a function of their chemical compositions. As clearly shown in Fig. S7A, the tunable thermal parameters of the developed PIs mainly depend on the length of the flexible aliphatic unit within their molecular chain. In this context, an increase in the length of the aliphatic bridges in PIs from 6 to 12 methylene units gradually decrease the $T_m$ and $T_g$ from 286 to 261 °C and from 148 to 88 °C, respectively.

To get an idea of the potential application domains of the synthesized PIs, it is important to assess their thermal degradation behaviour and stability. Therefore, TGA analysis was carried out to assess the thermal stability of PI6, PI8 and PI12. Their TGA thermogram in the temperature range from 30 to 600 °C are depicted in Figs. 4C and S6. The most representative degradation parameters, such as 5% and 10% weight loss-temperatures ($T_{d,5\%}$ and $T_{d,10\%}$), decomposition rate maximum ($T_{d,max}$), and the char yields at 500 °C are listed in Table S2.

It was found that $T_{d,5\%}$ and remaining residue at 500 °C ($R_{500\ °C}$) of the PIs follow the same trend as was observed for $T_m$ and $T_g$; the longer the aliphatic chain, the lower the $T_{d,5\%}$ and $R_{500\ °C}$ (Fig. S7B). Indeed, PI6, PI8 and PI12 all revealed excellent thermal stability with $T_{d,5\%}$ appearing at 348, 332 and 328 °C, respectively. This finding is understandable as stiffer chains with higher aromatic content are typically less vulnerable to thermal degradation. To sum up, the aliphatic chain length of recycled diamine monomers incorporated into the PIs backbone can be utilized as a key control parameter to tailor the thermal behaviour and stability of this new class of PIs derived from open-loop recycled PET. The decomposition profiles of the PIs illustrate that they undergo one major degradation step, leaving approximately 9–20% of degradation residues upon heating to 500 °C. This is reasonable owing to the presence of rigid aromatic segments, provided by terephthalate units, typically resulting in high carbon-forming properties. The demonstrated superior resistance to heat ensures good thermal stability at temperatures much higher than the glass transition and melting temperatures. This provides a thermal processing window up to 60–100 °C above respective $T_m$, thereby enabling high-temperature processing.

### 3.4. Mechanical properties of the PIs

The mechanical performance of the prepared PIs is crucial for their potential applications. The mechanical properties of compression molded PI films investigated by tensile testing are illustrated in Fig. 5. The stress-strain curves of these novel polymers are shown in Fig. 5A, while their main tensile properties are summarized in Table S3. The PIs developed here possess exceptional mechanical performance combining super-high strength and ultra-high toughness. The Young's moduli ($E$) and tensile strength ($\sigma$) appeared in the 4.0–4.9 GPa and 237–467 MPa range, respectively. Such high mechanical properties are likely explained by the multiple interchain hydrogen-bonding interactions that can be formed between the two electronegative oxygen and nitrogen atoms of the amide function with the hydrogen sandwiched in between (see Scheme S2). Similar outcomes were recently reported for other polymers (Song et al., 2019; Wu et al., 2021), where the presence of similar noncovalent interactions dramatically improved the mechanical strength of the resulting polymers. In more detail, it was found that the modulus progressively decreased with increasing length of the diamine chain incorporated into PIs backbone (Table S3). This discernible trend could be mainly attributed to increased chain mobility going from diamine with 6 $CH_2$ groups (PI6) to the longer diamines consisting of 8 (PI8) or 12 (PI12) methylene units. In contrast, the tensile strength and elongation at break ($\varepsilon$) of the synthesized PIs followed the opposite trend, that is, upon increasing the diamine chain length from C6 to C12, the tensile strength and $\varepsilon$ increased steadily from 237 to 467 MPa and from 7 to 17%, respectively. These findings confirmed that structural control by tailoring the length of the aliphatic chain in terephthalate diamine can be used as a practical parameter to effectively "on demand" tune the mechanical properties of the final materials.

As can be observed from Fig. 5C and 5D, the prepared PIs exhibited significantly higher Young's modulus and tensile strength than other polyimines reported in the literature (e.g. bio-PI3, bio-PI4, bio-PI5 and bio-PI6) (Tachibana et al., 2018) or common commercially available engineering and commodity plastics such as aliphatic and aromatic polyesters (Su et al., 2020), e.g., polylactic acid (PLA) (Niu et al., 2020), poly(ethylene terephthalate) (PET) (Ahmed et al., 2021) and poly (ethylene furanoate) (PEF) (Fei et al., 2022), polycarbonates (PC) (Choi et al., 2019), polyurethanes (PU) (Phua et al., 2012), polyamide-6 (PA6) (Attar et al., 2022), poly(vinyl chloride) (PVC) (Su et al., 2020), polypropylene (PP) (Su et al., 2020), and high-density polyethylene (HDPE) (Su et al., 2020). To sum up, the impressive mechanical performance of the produced PIs, including stiffness, high mechanical strength and robustness, as well as their high heat resistance, could cement their position as a promising new class of super-high-performance polymers. The mechanical performance of the produced PIs was demonstrated superior to a wide range of common commercial engineering plastics.

### 3.5. Chemical recycling of PIs by acidic hydrolysis

Next generation materials must all be circular to further reduce their environmental impacts when they reach the end of the use phase. To higher degree recover and recycle post-consumer materials, many technological advances have been made in recycling processes. Solvolysis has emerged as a promising chemical recycling route to both closed-loop and open-loop recycling of disposed plastics waste (Arena et al., 2022). In this context, we wanted to develop an easy-to-implement

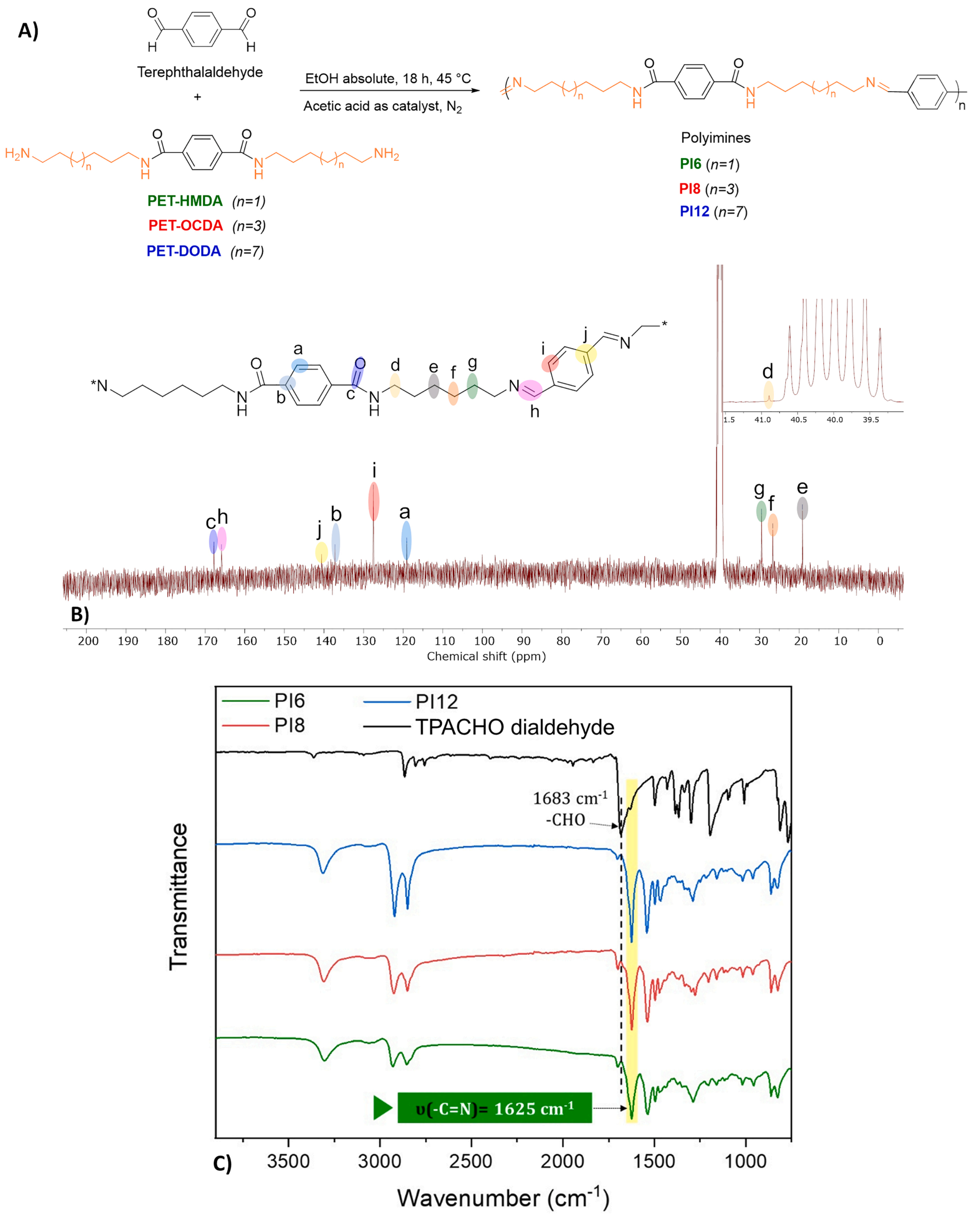

**Fig. 3.** A) Synthesis of polyimines from recycled building blocks, B) $^{13}$C NMR spectrum of PI6 (registered in DMSO-$d_6$), and C) FTIR spectra of all prepared PIs.

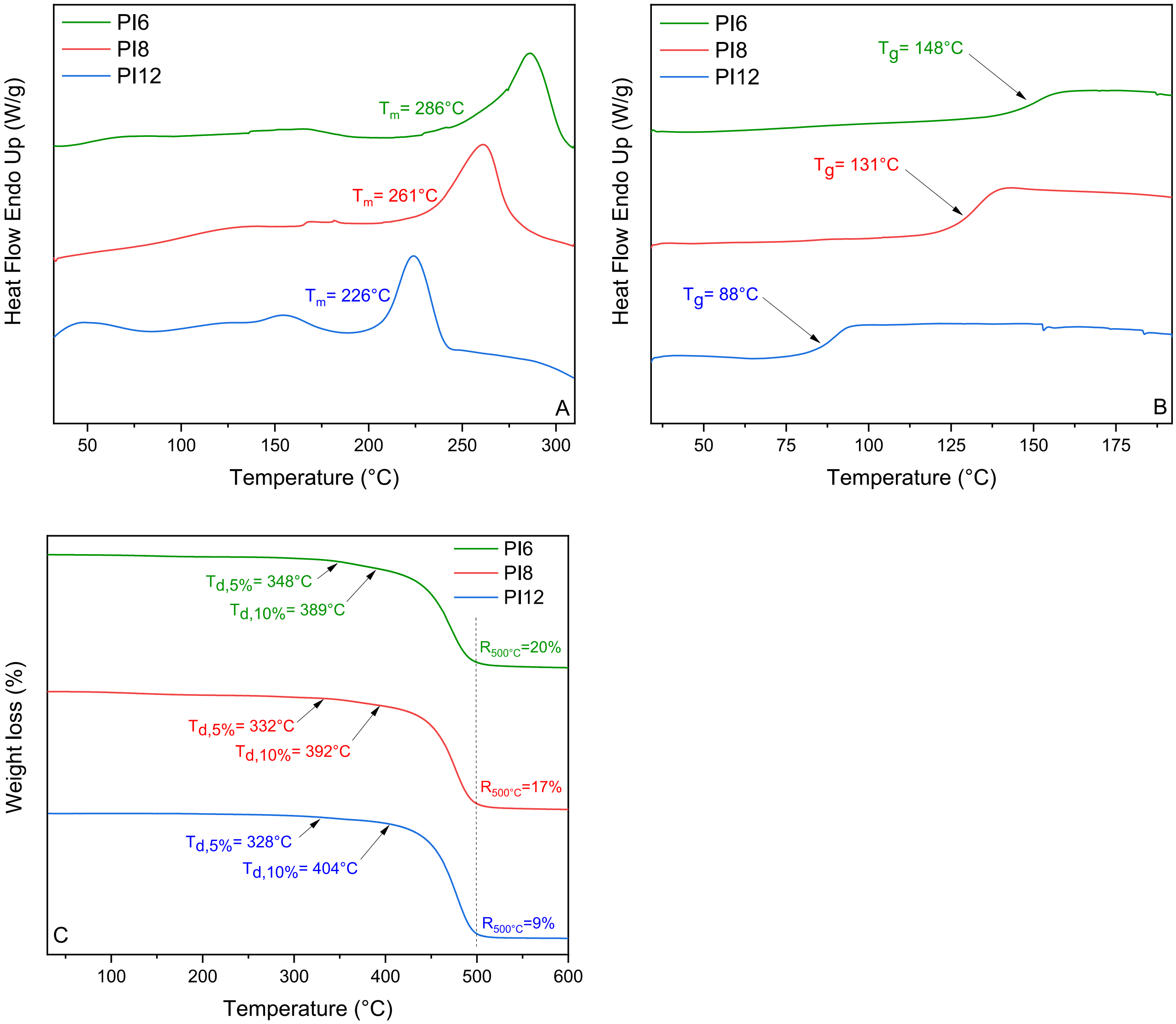

**Fig. 4.** DSC thermograms of synthesized polyimines: A) First heating scans of the purified samples, B) Second heating scans (by 10 °C.min$^{-1}$), and C) TGA thermograms of PIs.

closed-loop process for the new PIs developed herein (Scheme S1), thus unlocking their circularity at the end of their useful life.

Given the susceptibility of the dynamic imine bonds in the main chain of the developed PIs to acid catalysed hydrolysis (Zhou et al., 2020), potential recyclability under mild conditions could further expand the horizons of these new high-performance materials in terms of repeated recyclability and sustainability. Acidic hydrolysis using acetic acid was carried out on the synthesized PIs under mild conditions (70 °C for 10 min under atmospheric pressure) aiming to break down the synthesized PIs into their original monomers. This would allow the production of new PIs with same virgin quality in closed-loop.

After hydrolysis, the purity and the chemical structure of the obtained monomers, that is, terephthalaldehyde and diamines originating from PET recycling, were verified by $^{1}$H and $^{13}$C NMR using deuterated acetic acid as a solvent. The obtained spectra did not reveal any additional peaks indicative of the presence of impurities and they were perfectly consistent with the expected structures. In more detail, apart from the proton and carbon peaks arising from the three prepared diamines already illustrated above (Figs. 1, S1 and S2), additional new signals associated with recovered terephthalaldehyde were observed for all PIs at the same chemical shifts. The NMR spectra of depolymerized polyimine PI6 is shown as an illustrative example (Fig. 6), while the $^{1}$H/$^{13}$C NMR data for depolymerized PI8 and PI12 were placed in the SI file (Figs. S8-S9). In the $^{1}$H NMR spectrum of PI6 shown in Fig. 6A, the two resonances appearing as singlets at 8.17 and 10.24 ppm are assigned to the aromatic protons of terephthalic unit and aldehyde protons, respectively. In the $^{13}$C NMR spectrum (Fig. 6B), the signals of the carbonyl group carbons labelled as (n) and the two aromatic carbons (m) and (l) characteristic of terephthalaldehyde are visible at 192.72 ppm, 140.16 and 130.03 ppm, respectively. To sum up, $^{1}$H/$^{13}$C NMR spectroscopy corroborates unambiguously the successful complete depolymerization of the three PIs by acidic hydrolysis, where all signals are correctly attributed to the different protons and carbons in the molecular chain of the recovered building blocks (dialdehyde + diamine).

From an economical perspective, the low operating temperature (70 °C) and the very short reaction time required (10 min) for PIs hydrolysis is beneficial due to low energy consumption, and it might make this depolymerization approach a viable and cost-effective route in the future for recycling this new class of robust materials. Due to the difficulty of separating the recovered building blocks obtained by hydrolysis, we adopted another innovative and easy-to-implement strategy aiming at repolymerizing the recovered monomers (diamine + dialdehyde) *in-situ* to reproduce new polymer aiming at same virgin PI quality than the original PI material, thus avoiding any additional separation process of

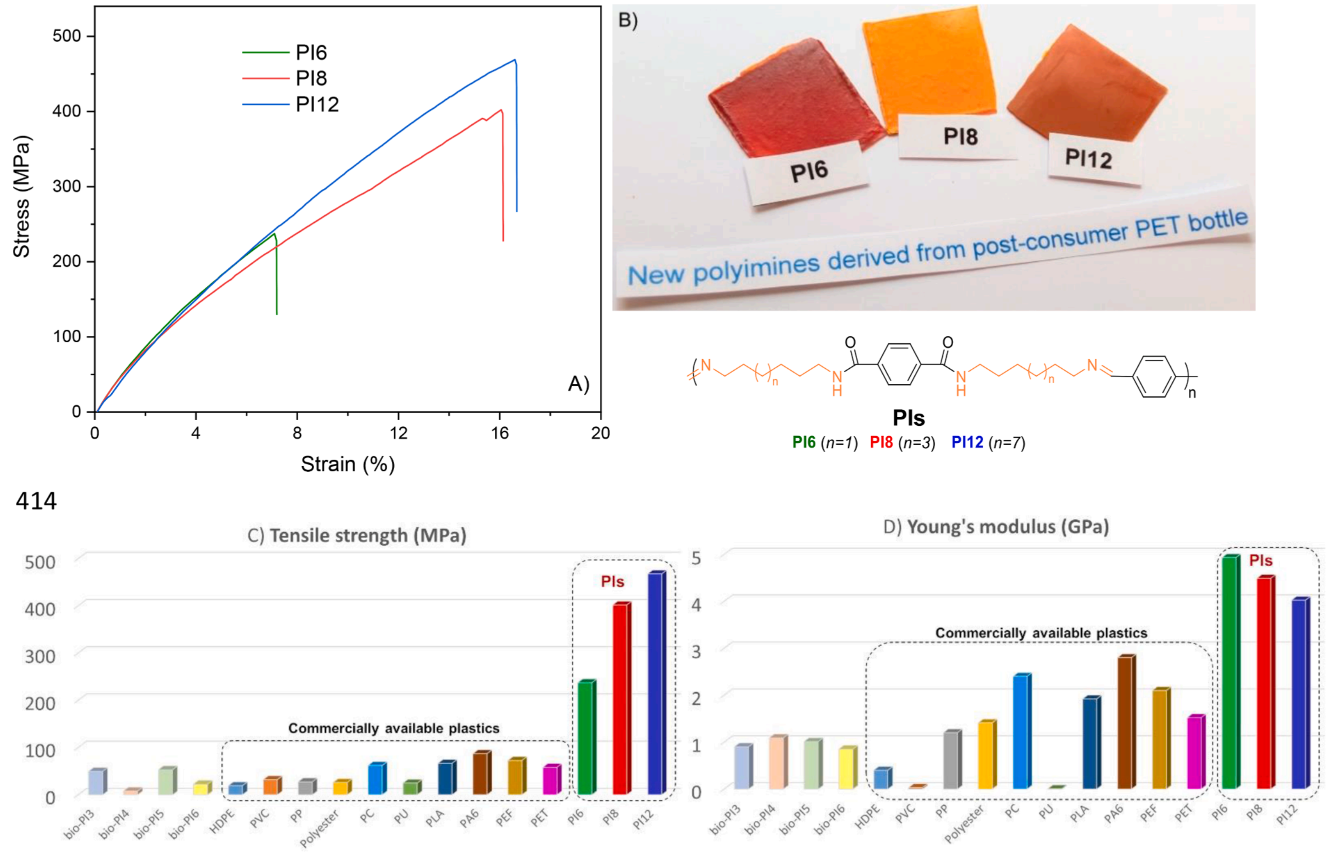

**Fig. 5.** A) Stress-strain curves of the synthesized PIs, B) photos of the PI films derived from aminolyzed post-consumer PET bottles, C) comparison of tensile strength of the synthesized PIs with other polyimines and typical values for common commercial plastics, and D) comparison of Young's modulus of the synthesized PIs with other polyimines and typical values for common commercial plastics (Ahmed et al., 2021; Attar et al., 2022; Choi et al., 2019; Fei et al., 2022; Niu et al., 2020; Phua et al., 2012; Su et al., 2020).

the recycled products. This would also give favourable environmental and economic impact.

Due to the great similarity in physicochemical properties of the PIs, PI6 was taken as an example to assess the feasibility of the *in-situ* repolymerization process. The recycled diamine PET-HMDA and terephthalaldehyde were mixed after adding ethanol as a solvent to prepare the new recycled polyimine rPI6. The imine condensation reaction took place at low temperature of 45 °C for 18 h. The successful *in-situ* repolymerization of the recovered products (PET-HMDA diamine and dialdehyde) was confirmed by FTIR spectroscopy (Fig. 6D). The spectrum illustrates no remaining -CHO band of the free dialdehyde (1683 $cm^{-1}$), but instead imine -C = N stretching (1625 $cm^{-1}$) is shown, proving that repolymerization has occurred. DSC thermogram of the purified rPI6 sample, obtained from the second heating scan, is depicted in Fig. 6C and compared to that of virgin PI6. Results showed that the original PI6 and recycled rPI6 exhibited very similar high $T_g$ values (148 *vs.* 142 °C). This demonstrates that the dynamic exchange nature of the imine bonds in PI6 provided a robust material that can be depolymerized and repolymerized through simple and green process without the need to separate the recovered building blocks before repolymerization. To recap, acidic hydrolysis provides a sustainable solution for end-of-life PIs, enabling closed-loop lifecycles perfectly fitting the circular economy (from PI to rPI) and contributing to sustainable development goals.

## 4. Conclusions

We disclose an innovative open-loop recycling of post-consumer PET bottles to closed-loop recyclable value-added polyimines. In this vein, an efficient and facile end-of-life option of PET waste by chemical recycling was developed. PET bottle waste was successfully recycled to value-added products by catalyst- and solvent-free MW-assisted aminolysis into three new diamines with very high melting points (>166 °C). Three potentially bio-based aliphatic diamines with different chain lengths of 6, 8 and 12 carbons, were utilized in this back-to-monomer chemical recycling aminolysis pathway. The recovered terephthalate diamines were then polymerized via imine condensation to three novel high-performance PIs. The latter exhibited very high $T_g$ and $T_m$ values in the range of 88–148 °C and 226–286 °C, respectively, while preserving an excellent thermal stability up to 200 °C and 100 °C above their $T_g$ and $T_m$, respectively. More importantly, the resulting PIs materials demonstrated exceptional mechanical performance with tensile strength and Young's modulus in the range of 237–467 MPa and 4.02–4.93 GPa, respectively, significantly outperforming most of available commodity plastics in the market. Furthermore, acidic hydrolysis in acetic acid under mild conditions (a very short reaction time of 10 min, at ambient pressure and low temperature of 70 °C) was found to be suitable for efficient selective depolymerization of synthesized PIs back to original high-purity building blocks. Last but not least these building blocks could be directly repolymerized back to PIs with similar properties to the original PIs. We thus successfully demonstrated open-loop recycling of postconsumer PET waste into new mechanically and thermally high performing materials, that are open-loop recyclable under mild de-and repolymerization conditions. This innovative solution provides value to waste to fuel the recycling rates of common plastic packaging.

## CRediT authorship contribution statement

**Nejib Kasmi:** Conceptualization, Formal analysis, Investigation,

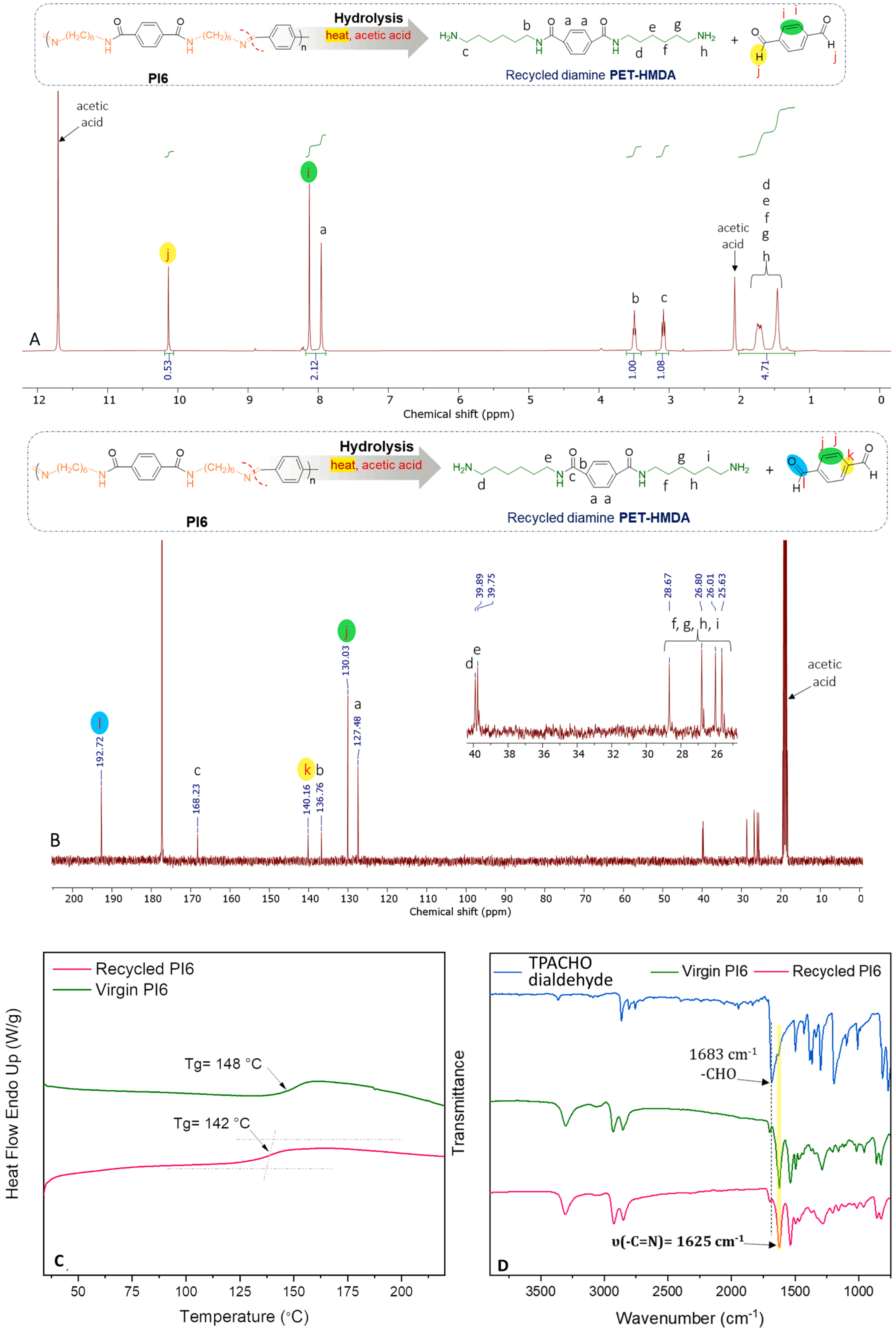

**Fig. 6.** A) $^1$H and B) $^{13}$C NMR spectra of the recycled terephthalate diamine PET-HMDA via acid hydrolysis (recorded in acetic acid-$d_4$ at room temperature), C) DSC thermogram, and D) FTIR spectrum of recycled PI6 after in-situ repolymerization.

Methodology, Visualization, Writing – original draft. **Eva Bäckström:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Writing – review & editing. **Minna Hakkarainen:** Conceptualization, Formal analysis, Funding acquisition, Methodology, Supervision, Writing – review & editing.

## Declaration of Competing Interest

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

## Data availability

Data will be made available on request.

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.resconrec.2023.106974.

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