



## Invention Article

# A novel process for recovery and exploitation of polyesters and polyamides from waste polymeric artifacts

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## ABSTRACT

Plastic waste is one of the world's biggest sources of pollution. Despite the growing trend towards recycling, there are currently no effective technologies to offset the continuous increase in plastic production. Polyesters and polyamides are among the most widely produced single-use plastics, mainly used in the manufacture of textiles and soft drink bottles. Currently, only a small proportion of these polymers can be effectively recycled. The two primary methods employed for this purpose are mechanical and chemical recycling. Presently, mechanical recycling remains the more widely adopted process within the industrial sector. However, the treatment process is limited to a narrow range of waste materials as it is impossible to remove dyes and the mechanical properties deteriorate due to incompatibility between different plastic materials. Another critical limit of this recycling technology is the limited number of recycling loops that can be done due to the thermal degradation that occurs during the extrusion process. The alternative option is chemical recycling, which allows the depolymerization of the original product to recover the monomers directly. The main drawbacks are the long reaction times and the many solvents needed to achieve high-purity products. As a result, chemical recycling is only economically feasible for large companies that can produce the virgin polymer *in situ*. In this work, a new technology has been patented. This process consists of three main steps. The first one is the distillation-assisted cyclodepolymerization (DA-CDP), introduced as a modification of the CDP process. In this unit, cyclic oligomers together with high molecular weight compounds are produced. Then, after polymer purification, it is possible to achieve the same molecular weight as the initial polymer in less than 30 min, exploiting the ring-opening polymerization (ROP) of the next step.

## Specifications Table

<b>Subject code</b>	1508 – Process Chemistry and Technology
<b>Specific subject area</b>	The patented technology refers to the circular synthesis of polyesters and polyamides with high commercial value, enhancing waste that is currently irrecoverable.
<b>Industry code</b>	C08J: WORKING-UP; GENERAL PROCESSES OF COMPOUNDING; AFTER-TREATMENT NOT COVERED BY SUBCLASSES C08B, C08C, C08F, C08G or C08H
<b>Details of inventors</b>	Flavio Tollini ( <a href="mailto:flavio.tollini@polimi.it">flavio.tollini@polimi.it</a> ; Politecnico di Milano - CMIC Department "Giulio Natta") Massimo Morbidelli ( <a href="mailto:massimo.morbidelli@polimi.it">massimo.morbidelli@polimi.it</a> ; Politecnico di Milano - CMIC Department "Giulio Natta") Giuseppe Storti ( <a href="mailto:giuseppe.storti@polimi.it">giuseppe.storti@polimi.it</a> ; Politecnico di Milano - CMIC Department "Giulio Natta")

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<b>Dates of invention</b>	Natta) Davide Moscatelli ( <a href="mailto:davide.moscatelli@polimi.it">davide.moscatelli@polimi.it</a> ; Politecnico di Milano - CMIC Department "Giulio Natta") Conception: 2019 Disclosure: The patent application has been publicly disclosed in patent databases.
<b>Patent details (only if patented)</b>	Date patent filed: 9 June 2021 (the Italian patent application No. 102021000015005 was granted on July 11th 2023); an international patent application was filed on June 7th 2022, with the No. PCT/IB2022/055289 and published on December 15th, 2022, with the No. WO 202/259142 A1; at the end of the international phase Politecnico entered the US national phase and the EP regional phase (filing No. 21782818.5) on

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	October 23rd December. Patent owner: Politecnico di Milano Patent attorney or agent: Raffaella Asensio (Perani & Partners) Contact for service: Massimo Barbieri (Technology Transfer Office – Politecnico di Milano) Link to patent: <a href="https://worldwide.espacenet.com/patent/search/family/077627300/publication/WO2022259142A1?q=pm%3DWO2022259142A1">https://worldwide.espacenet.com/patent/search/family/077627300/publication/WO2022259142A1?q=pm%3DWO2022259142A1</a>
Intended use	The intellectual property rights of all patent family members have been transferred to a startup company.
Related research article	None
Related other sources: (datasets, software, diagrams, plans, etc.)	None

## 1. Value of the invention

- The patented process allows for the complete recycling of polyesters, polyamides, cotton textiles and packaging via a simpler, cost-effective, and safer process than existing recycling technologies.
- The patented process enables the recycling of waste materials that are currently incinerated. Moreover, this technology can enhance the value of the initial waste, achieving actual upcycling.
- The patented process allows for the complete removal of heavy and light contaminants, regardless of the source material and colour, without any degradation of the polymer.
- The technology's modular configuration enables easy integration with the current recycling system, facilitating the extension of

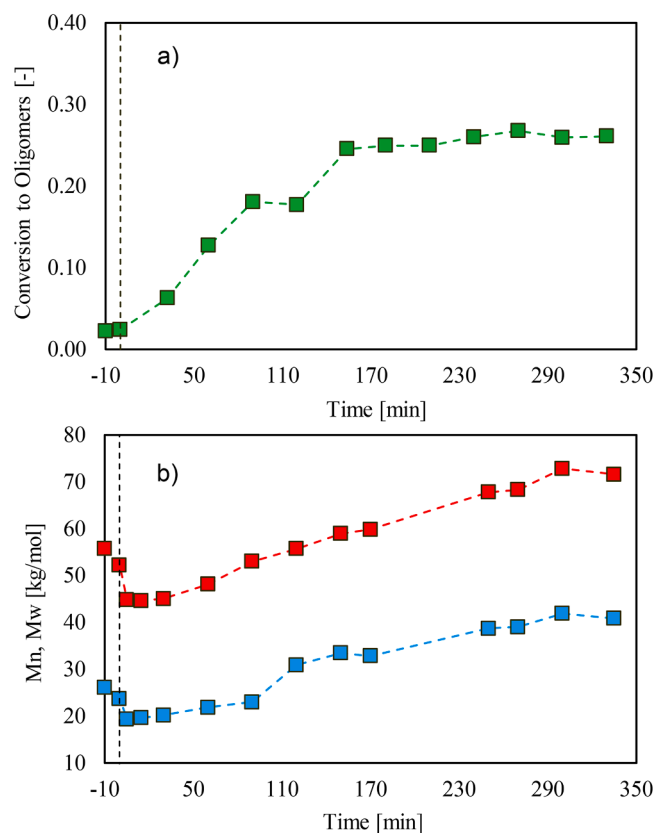


Fig. 1. (a) ■ Oligomer Conversion vs time; (b) ■ Number average ( $M_n$ ) and ■ weight average ( $M_w$ ) molecular weight vs time.

current processes into new feed streams and increasing the value of the resulting products.

## 2. Invention description

The invention is focused on recycling polyesters and polyamides via a process of partially depolymerizing the waste polymer, which is immediately followed by a ring-opening polymerization (ROP) step. The process consists of three stages: (1) recovering the polymer, (2) purifying it, (3) Re-polymerizing it.

The modular technology consists of three primary units. In the first one, the polymer undergoes partial depolymerization exploiting the advantages of the distillation-assisted cyclo-depolymerization (DA-CDP). This reaction enables the production of a fraction of oligomers (within the range of 0–40 %) and an increase in the average molecular weight of the residual polymer. This step can be performed under different operating conditions, depending on the feed conditions. The reaction takes place at the boiling point of the mixture, within the pressure range of 200-1000 mbar, and requires a time scale of 0–6 h.

Butyltin(IV) oxide and tin(II) ethylhexanoate have been used as catalysts in a molar concentration ranging from 0.01 % to 1 %.

The starting polymer/solvent ratio can be exploited in the range between 50 and 350 g/L. The reaction is assisted by a continuous distillation which aims to remove a fraction of solvents and by-products in a weight amount ranging from 0 to 10 % hourly. Moreover, this distillation process enables the removal of low-boiling contaminants.

The aim of the DA-CDP is to partially depolymerize the starting waste, enabling the removal of light contaminants concurrent with the distillation. The recycling of polyesters and polyamides has proven to be successful in these conditions. PET high molecular weight flakes, obtained from bottles, are presented as an illustrative example. The chemical equilibrium of the main species involved in the reaction is represented by the following equations Eqs. (1)–(12). Focusing on the kinetic scheme, linear species can undergo three different polycondensation reactions depending on both the end-groups and the by-products.



The same considerations can be applied for end-biting reactions:



And for the back-biting reactions:

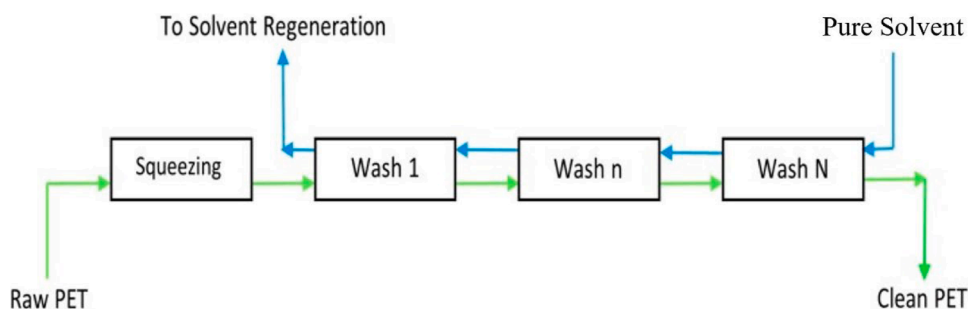


Fig. 2. DA-CDP product purification exploiting a counter-current configuration through the dirty PET and the pure solvent.

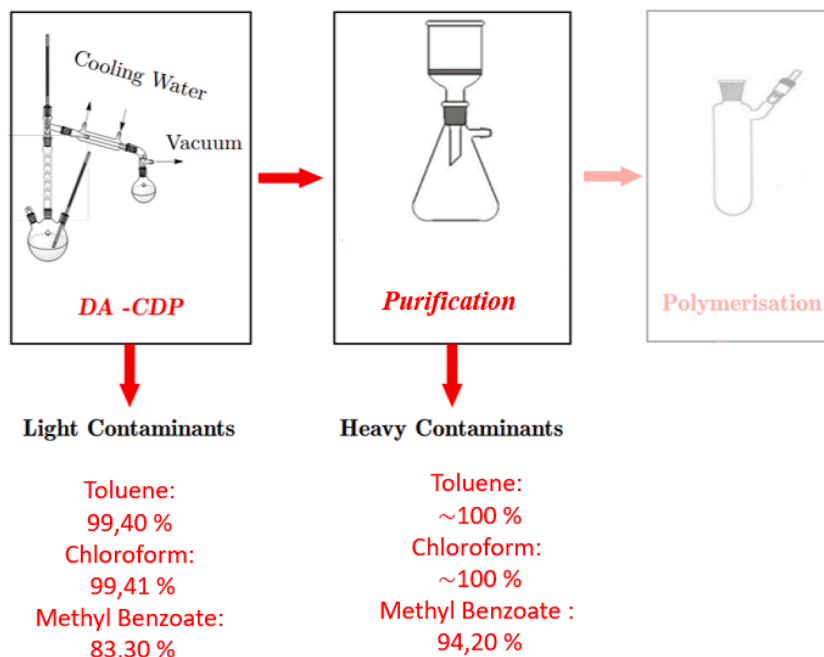


Fig. 3. Contaminants removal after DA-CDP and purification step. The contaminants have been chosen as surrogates, able to simulate some of the most representative additives.



Where  $L_n^{Acid}$ ,  $L_n^{Acid}$ , and  $L_n^{EG}$  are the PET linear chains acid/EG-, acid/acid-, or EG/EG-terminated, with n-length;  $C_n$  are the cyclic species with n-length and EG,  $H_2O$ , and TPA are the by-products.

By diluting the system, the reaction equilibrium shifts from a high molecular weight polymer to cyclic and linear oligomers (cyPET and linPET) due to the advantages of thermodynamic equilibria and the Le Châtelier Principle. Conversion to cyclic oligomers increases until a plateau is reached. However, increasing the concentration and removing by-products enhances the formation of high molecular weight chains. Through vaporisation, the solvent is removed together with EG and  $H_2O$ . At higher concentrations, the generation of high molecular weight chains is favoured due to polycondensations being second-order reactions. Therefore, the production of oligomers is relevant until a certain concentration (until the system is sufficiently diluted) and high molecular weight chains at increasing concentration. This latter phenomenon

becomes prevalent once a substantial amount of solvent is removed. The DA-CDP method enables the production of both high molecular weight chains and cyclic oligomers (cyPET). This step has, also, the advantage of removing volatile contaminants and pigments, ending with a polymer that is as pure as possible (Fig. 3).

Finally, the profiles of conversion to oligomers (mainly cyPET) and the average molecular weights (including both number-average and weight-average) have been represented in Fig. 1.

After completing the reaction, the final solution is cooled down, precipitated, and then purified. The solid is washed with clean solvent to remove dyes, additives, and heavy contaminants present in the waste polymer (Fig. 2). The countercurrent configuration has been identified as the most effective method for washing and squeezing the final solid, resulting in a purified pre-polymer.

The scheme presented below provides a conclusive assessment of the contaminants, pigments, and additives that have been removed (Fig. 3):

In the final stage of the process, the ultimate objective is to produce high molecular weight r-PET (bottle grade). Fast ring-opening polymerisation ensures the attainment of this final technical grade. To achieve this goal, the pre-polymer produced from DA-CDP is purified and subsequently fed into the reactor. The system is then heated to a temperature between 250°C and 300°C, under vacuum conditions. Thanks to the fast ROP, the initial molecular weight can be regained within 30 min, allowing an increase in molecular weight of less than an hour

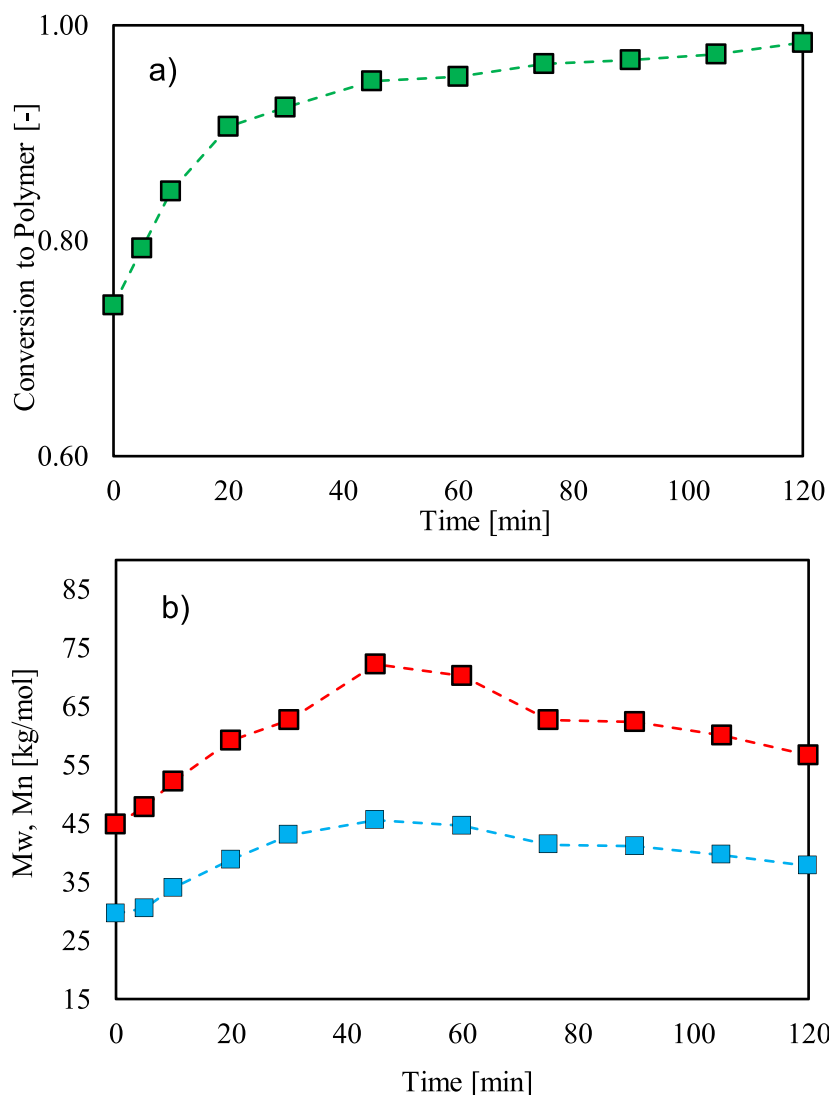


Fig. 4. (a) ■ Conversion to Polymer vs time; (b) ■ Number average ( $M_n$ ) and ■ weight average ( $M_w$ ) molecular weight vs time.

leading to the final technical grade (bottle grade PET). The same kinetic mechanism provided for the DA-CDP can be ensured in the ROP step. The differences arise from the distinct temperature, pressure, and concentration levels in the system. Due to the high temperature and concentrated nature of the system, the opening of the cyclic oligomers, together with the polycondensations reactions are favoured, resulting in the generation of a high linear molecular weight polymer.

Inside the whole process, polymer degradation is avoided due to oligomer formation, temperature, and time control. These oligomers can then be re-polymerised together with the linear polymer, thereby increasing the polymer's molecular weight in a very short time, as shown in Fig. 4.

The waste solvent from each unit is collected and regenerated, ensuring the system's circularity. The resulting recycled polymer possesses a high technical grade and is recovered at the end of the process.

### 3. Background

To date, there are three leading recycling technologies for plastics: (1) Chemical recycling. (2) Mechanical recycling. (3) Energy recovery. One of the main challenges today is the recycling systems and the inability to treat complex polymeric fillers at an acceptable cost to ensure closed-loop recycling and without polymer degradation. The objective of the proposed technology is to allow the circular synthesis of

Table 1

List of IPC classification symbols assigned to the Italian patent application No. 102021000015005.

IPC code (subgroup level)	Definition
C08G63/78	Macromolecular compounds obtained by reactions forming a carboxylic ester link in the main chain of the macromolecule • <b>Preparation processes</b>
C08J11/22	Recovery or working-up of waste materials•••• by <b>treatment with organic oxygen-containing compounds</b>
C08G63/81	Macromolecular compounds obtained by reactions forming a carboxylic ester link in the main chain of the macromolecule • <b>using solvents</b>
C08G63/91	Macromolecular compounds obtained by reactions forming a carboxylic ester link in the main chain of the macromolecule • <b>Polymers modified by chemical after-treatment</b>

polyesters and polyamides (about 20 % of the polymer market) with high commercial value, valorising waste that is currently not recoverable.

The patented process provides several technical advantages over the prior art. It employs a partial cyclodepolymerization associated with a simultaneous solvent distillation, effectively removing most of the by-products and contaminants.

The technique only partially decomposes polymers, resulting in the production of cyclic oligomers exclusively.

In comparison to conventional chemical processes, a complete depolymerization is unnecessary.

The EPO classified and evaluated the Italian patent application based on the IPC system (refer to Table 1) and conducted a patentability search in the technical fields of C08G and C08J.

The Search Report obtained from the UIBM via EPO lists four background documents.:

D1: Cyclo-depolymerization of poly(propylene terephthalate): some ring-opening polymerizations of the cyclic oligomers produced [1]

D2: EP 3778744 A1 [2]

D3: Cyclodepolymerization as a method for the synthesis of macrocyclic oligomers [3]

D4: EP 3606980A1 [4]

The cited references were deemed to be background art by the examiner (classified under the A category) and all claims were considered both novel and inventive over the cited prior art in the Written Opinion. Therefore, the patent application was granted in Italy.

EP and US applications are under examination.

#### 4. Application potential

The global size of the plastics market was valued at 593 billion U.S. dollars in 2021. It is predicted to grow in the coming years to reach a value of 811 billion U.S. dollars by 2028, registering a CAGR of 3.7 % during the forecast period of 2022 to 2030 [5].

The worldwide market for recycled market was valued at 47.6 billion U.S. dollars in 2022. It is expected to grow at a CAGR of 4.8 % within the period of 2022 to 2030.

The production of plastics globally surged to 390.7 Mt in 2021, with 90.2 % being fossil-based. [6] This market is expected to grow at a CAGR of 5.2 % between 2022 and 2030.

To meet the expected increase in demand for recycled PET (polyethylene terephthalate), at least 430 new plants will have to be built in the coming years, resulting in a potential 1.5-billion-euro market for plant sales.

This technology addresses both manufacturing and recycling companies, aiming to be modular and configurable according to customer needs. It provides a significant advantage over current processes that are not flexible at all.

The patented process allows contaminants to be easily removed from PET, unlike mechanical processes, whilst preserving their straightforwardness. Additionally, the rapid ROP system can be utilized to perform polymerization directly within the extruder, eliminating the need for a dedicated reactor as required in traditional processes. The modular solution enables configuration of the recycling system in a complementary way to the technologies already employed, thereby granting a tailored

solution to specific requests.

#### Ethics statements

No specific ethics statement.

#### CRedit authorship contribution statement

**Massimo Barbieri:** Data curation, Writing – review & editing. **Edoardo Terreni:** Conceptualization, Investigation, Supervision, Data curation, Writing – original draft. **Flavio Tollini:** Conceptualization, Investigation, Supervision, Data curation, Writing – original draft. **Giuseppe Storti:** Supervision. **Davide Moscatelli:** 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.

#### Acknowledgments

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A special thanks to **Thomas Worden** (Technology Transfer Office of Politecnico di Milano) for his revision of the text in English language.

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