# Solid-state modification of poly(butylene terephthalate): Design of process from calorimetric methods for catalyst investigation to reactive extrusion

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## ARTICLE INFO

## ABSTRACT

The production of plastics has been increasing for more than half a century and the problem with significant growth is the waste associated with this activity. At this time, polymers are mainly recycled by classical pathway (e.g., mechanical or chemical recycling) but at the moment these techniques still present several issues (e.g., obtaining unclean material, etc.). In this study, it is proposed to reuse the materials to give them a second life by solid-state modification (SSM). This paper reports the design of a new process based on SSM technique of polyesters from batch into a continuous process. Poly(butylene terephthalate) (PBT) and 1,12-dodecanediol (DDO) are used as model compounds. At first, a calorimetric method is developed to investigate the main features of the reaction at small scale and make the proper choice of catalyst with the help of differential scanning calorimetry (DSC). At the second step, a qualitative kinetic discussion confirms our calorimetric results and the influence of the reaction time on the molecular and thermal characteristics of the copolymers obtained. The optimized conditions are then transferred to a gram-scale batch reactor and finally tested in reactive extrusion (REx) continuous process allowing to decrease the reaction time as much as possible and to test the shear forces in the SSM framework. This study therefore encompasses the design of a new process for recycling polymeric materials and offers the possibility of making polymers more sustainable.

## 1. Introduction

The global waste crisis, related to plastic production, consumption, and disposal, forces science and industry to undertake rapid actions in waste management via plastic reuse, recycling or upcycling [1]. Traditional mechanical, or chemical re(up)cycling provide possibilities but rise significant environmental concerns [2]. Here, polymer upcycling (i. e., "the process of selectively converting discarded plastics into chemicals, fuels, or materials of higher value") [3], via post-synthetic solid-state modification (SSM) of polyesters is considered to provide a low-energy and minimized environmental impact compared with traditional methods, related with the absence of undesirable organic solvents [4,5].

The SSM represents an easy-to-use tool to specifically affect the amorphous part of any semi-crystalline polymer, thus preserving its initial mechanical properties related with crystalline phase [4]. Although rarely used in fundamental research, the method has proven to

be of industrial relevance [6]. Indeed, the parent technique called solid-state polymerization (SSP) is already used as a post-synthesis technique to increase the molecular weights of some semi-crystalline polymers by limiting side reactions using lower reaction temperatures. This technique has also been implemented in the recycling of PET bottles for example [7,8]. In particular, the basic principle of SSM consists in heating the starting semi-crystalline polymer, together with a (co) monomer in a range between the glass transition ($T_g$) and the melting temperature ($T_m$) through an inert atmosphere or under vacuum, and induce multiple exchange reactions (repeating scissions - recombinations) mainly in the mobile amorphous zone [6,9]. This technique differs from conventional melt or solid-state polymerization and brings new desired properties to the initial polymer that are often difficult or impossible to obtain otherwise [10]. Many parameters can influence solid-state reactions, such as temperature and reaction time or the initial composition of the mixture as well as the type and gas flow [6,9]. However, one of the main parameters that could have an

important impact during these syntheses and has not yet been addressed in the literature is the influence of catalysts. Indeed, for many years, a large number of studies on the influence of catalysts in polymer synthesis have been carried out and have shown a very important interest, e.g., for the build-up of molecular weights or the limitation of by-products formed but nothing about SSM [11,12].

The few studies on SSM proposed by the research groups of C. Koning and S. Muñoz-Guerra show only examples involving poly(butylene terephthalate) (PBT) and biobased monomers, e.g., sugar or fatty acid derivatives [4,10,13]. Polyesters are of interest in many fields of research and more particularly poly(butylene terephthalate) [14–16]. This is a semi-crystalline thermoplastic polymer – the results of the melt polycondensation between terephthalic acid or dimethyl terephthalate and 1,4-butanediol catalyzed by an organotitanate (e.g., titanium tetrabutoxide) [17,18]. This polyester has excellent properties such as a high degree of crystallinity (40–50%) as well as a good mechanical resistance, thermal stability, excellent processability and finds applications in automotive industry, and electronic devices [19,20]. The PBT-related studies involving SSM focused on the microstructure of the obtained copolyesters and their morphology with an emphasis on the influence of structures and compositions on crystallinity [5].

In this work, calorimetric investigations are first conducted to investigate the impact of transesterification catalysts on SSM. Specifically, a small-scale reaction is realized through differential scanning calorimetry (DSC) technique to determine the most appropriate catalyst to use in the case of the PBT/1,12-dodecanediol (DDO) as model system. It enabled us to demonstrate the influence of the reaction time on the molecular and thermal characteristics of the copolymers obtained via this kinetic discussion. Once the experimental conditions are determined by the DSC experiments, they are validated in a batch process and finally transposed to reactive extrusion (REx) to vary the process by using the shear forces of this technique and thus counter the mass and heat transfer problems encountered in the batch process.

## 2. Experimental section

### 2.1. Materials

The PBT (Ultradur® B4520, BASF AG, $M_n$ from the supplier is 13,000 g/mol, $M_n$ determined by SEC is 6700 g/mol, $M_n$ calculated by ^{1}H NMR is 7400 g/mol, $T_g = 45\ °C$ and $T_m = 225\ °C$) is used as received. 1,12-dodecanediol (99%), dibutyltin (IV) oxide (DBTO, 99%), lanthanum (III) acetylacetonate hydrate (La(acac)$_3$·H$_2$O, > 99%), cobalt (II) acetylacetonate (Co(acac)$_2$, 97%) and titanium (IV) butoxide (TBT, 97%) are purchased from Sigma-Aldrich and used as received. Lead (II) acetate trihydrate (Pb(CH$_3$CO$_2$)$_2$·3H$_2$O, ≥ 99%) is purchased from Alfa aesar and used as received. Methanol (≥ 98.5%) and toluene (> 98%) used are of analytical grade and purchased respectively from Merck and VWR.

### 2.2. Solid-state preparation of PBT/DDO mixtures

DDO (2 g, 9.9 mol) and different catalysts in different amounts are first solubilized in methanol with a few drops of toluene and then left to evaporate overnight. In parallel, PBT pellets are milled beforehand in an IKA™ analytical mill to obtain a large granulometry powder. Then, a PBT/DDO 60:40 w/w mixture is ground with a Retsch CryoMill; an auto pre-cooling cycle takes place to reach the temperature of −196 °C, followed by two grinding cycles with a frequency of 30 s$^{-1}$ for 2 min with four stainless steel balls (15 mm diameter). The size of the powder obtained after grinding is 250 μm, evaluated by a vibratory sieve shaker AS 200 Digit. PBT/DDO mixtures are carried out in a 60:40 ratio as the amorphous part of PBT is about 40%. Each mixture is pre-dried before undergoing the different treatments proposed below (DSC, batch or REx SSM).

### 2.3. DSC investigations in the SSM

The calorimetric measurements are carried out by DSC (Q200, TA instruments, Zellik, Belgium) and the sample weight is about 10 mg. The program consists of an isotherm of different time (120, 240, 360 and 480 min) at 190 °C followed by a temperature ramp of 10 °C/min from −80 °C to 250 °C. No preheating cycle is performed before the described DSC experimentation.

### 2.4. Batch solid-state modification of PBT with 1,12-dodecanediol

Solid-state modification of PBT is performed using a specially designed Inox Autoclave-France reactor. Typically, 5 g of a powder PBT/DDO mixture is placed in the reactor. The catalyst is then added. The reaction is carried out at 190 °C during 6 h under a 0.4 bar flow of N$_2$ with a stirring speed of 40 rpm. The batch products are purified by Soxhlet extraction in chloroform to remove unreacted DDO.

### 2.5. Reactive extrusion between PBT and 1,12-dodecanediol

Reactive extrusion (REx) is tested into a 15 cm$^3$ twin-screw DSM micro compounder (Xplore Instruments BV, Sittard, The Netherlands) at 190 °C and 40 rpm under nitrogen flow. Premixing of PBT and DDO is realized in a Retsch CryoMill under the same conditions as explained before, and the milled polymer is fed into the micro compounder. The resulting product is finally recovered at 100 rpm. The REx products are purified by Soxhlet extraction in chloroform to remove unreacted DDO.

### 2.6. General methods

The ^{1}H NMR spectra are collected with a Bruker AMX-500 at a frequency of 500 MHz in a mixture of deuterated chloroform (CDCl$_3$)/trifluoroacetic acid (TFA) (90:10 w/w) and tetramethylsilane (TMS) as an internal reference. The concentration of each sample solution is of about 10 mg/ml and the number of scans is of 512.

The molecular weight of the polyesters is determined by gel permeation chromatography (GPC). The polymers are dissolved in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) with 0.019% NaTFA salt. The sample for the GPC measurement is prepared by dissolving 5.0 mg of polymer in 1.5 ml of solvent. The solutions are filtered through a 0.2 μm PTFE syringe filter before injection. The GPC instrument is calibrated with poly(methyl methacrylate) standards. Two microcolumns of combined GPC media with a particle size of 7 μm (4.6 × 250 mm, separation range 100–1,000,000 Da) and a precolumn of combined GPC media with a particle size of 7 μm (4.6 × 30 mm) are used in combination with a refractive index (RI) detector to determine molecular weights and dispersities.

The thermal investigations are recorded with differential scanning calorimetry (DSC) on a Q200 thermal analyzer (TA instruments, Zellik, Belgium) calibrated with high purity indium and operating under N$_2$ flow. The reported thermal transition values, $T_g$ (glass transition temperature) and $T_m$ (melting temperature), are defined as the midpoints of the sigmoidal curve, minima of the exotherms, and maxima of the endotherms, respectively.

The thermal decomposition behavior is recorded with thermogravimetric analysis (TGA) on a Q500 thermal analyzer (TA instruments, Zellik, Belgium), under N$_2$ or air flow. The weight loss is recorded upon heating the samples (having initial masses of ca. 7 mg) at 20 °C/minute from room temperature to 800 °C. The referred temperature of maximum degradation rate ($T_{max}$) is taken as the inflection point of the sigmoidal steps (i.e., the maxima of the first-derivative curve).

Viscosity measurements are performed with a Schott AVS 350/Ubbelohde automatic capillary viscometer. The viscosity of the polymers is determined at 30 °C. The samples are dissolved in a 9:1 v/v chloroform/trifluoroacetic acid solvent mixture at different concentrations.

## 3. Results and discussions

### 3.1. Effect of catalysts on transesterification reaction – DSC investigation

#### 3.1.1. Effect of different catalysts

The present study about the catalytic effect on SSM is carried out on a model system based on PBT and DDO. This monomer is chosen for its ease of carrying out these exchange reactions, as well as for its thermal properties allowing it not to sublimate or degrade at the SSM reaction temperature as can be seen from the TGA analysis presented in Supporting Information (Fig. S1).

The choice of the different catalysts is made according to the literature; some catalysts, e.g., DBTO, have already been proven in SSM [11,21] while the others are used mainly in polycondensation and more particularly in transesterifications [22-24].

PBT/DDO mixtures with different catalysts (Fig. 1) are investigated using calorimetry analysis (DSC), after a solid grind preparation with a CryoMill. This method of preparation is preferred above a solvent mixing route mainly because PBT has a very limited solubility in conventional organic solvents, requiring the use of toxic and expensive solvents such as phenols [19,25]. The use of the CryoMill eliminates the need for these numerous solvent mixtures and the preparation mixture is thus a greener method. All compounds are dried prior to the different reactive treatments to avoid any hydrolysis problems that could be encountered due to the presence of residual water during SSM.

SSM reactions can be divided into two stages: first exchange reactions, transesterification, alcoholysis in this case, between a difunctional monomer, i.e., DDO and the polyester at a temperature above its $T_g$ and below its $T_m$. Then, recombination reactions take place to re-form the chains. In the case of PBT, the operating SSM temperature is 190 °C. Indeed, this temperature allows to obtain a sufficient mobility of the chains to achieve the exchange reactions between the polymer and the added monomer while losing butanediol units (Fig. 2) [26].

There are already a couple of publications using the calorimetric technique to study the catalytic activity during transesterifications, in particular by observing the differences in melting temperatures between the obtained copolymer and the initial mixture [27,28]. The objective of this research is thus to mimic SSM reaction conditions using the DSC investigations. At the first sight, a 6 h-isotherm at the SSM temperature is chosen to get enough time for the exchange reactions as well as for the chain-recombination to take place and is then followed by a classical temperature ramp.

To compare the selectivity of the different catalysts, it is necessary to keep the reaction time and temperature as well as the catalyst ratio constant (in this case 300 ppm). Both the catalytic activity and the elimination of small molecules (butanediol in this case) during polycondensation are accordingly considered. Such studies have already been performed by other groups on polyester modifications and more particularly on poly(ethylene terephthalate) to choose the most appropriate catalyst [27,29].

The residues recovered from the pans at the end of the DSC analyses are first investigated by $^1H$ NMR analyses and the results are shown in Figs. 3 and 4 with the values reported in Table 1 [30]. Only the NMR analysis about DBTO is represented here, the other spectra being similar in terms of chemical shifts. The spectra of PBT and DDO alone are present in Supporting Information (Figs. S2 and S3 respectively). A similar treatment is performed on PBT itself to ensure that its properties are maintained in the absence of DDO and catalysts.

For the spectrum before DSC treatment at 190 °C (Fig. 3B), the $^1H$ chemical shifts at $\delta$ 2.02, 4.50 and 8.12 ppm are ascribed, respectively, to the $OCH_2CH_2$, $OCH_2CH_2$ and the aromatic $CH$ of the PBT. Those appearing at 1.29, 1.74 and 4.37 ppm are related to the different protons of DDO, as presented in Fig. 3. The chemical structure after DSC is shown in Fig. 3A. New peaks are observed; the $^1H$ chemical shifts at $\delta$ 1.45, 1.82 and 4.40 ppm are assigned to $OCH_2CH_2CH_2$ (**c′**), $OCH_2CH_2CH_2$ (**d′**), $OCH_2CH_2CH_2$ (**e′**) from DDO repeating units, respectively. Those observed at 1.96 (**3′**) and 4.47 ppm (**2′**) are related to some trace of butanediol, which is released during the DSC analysis, as depicted in Scheme 1. These results show that transesterification reactions, especially here alcoholysis, take place between PBT and DDO during the DSC isotherm. These exchange reactions lead to the formation of a new repeating unit within the PBT, i.e., PDT unit.

The conversions are estimated using the relative intensities of the $OCH_2CH_2CH_2$ protons in free DDO (**d**) and in the PDT repeating unit (**d′**). The calculated values are indicated in Table 1. These calculations reveal that $Pb(CH_3COO)_2$ has the highest percentage of conversion. DBTO, $Co(acac)_2$ and $La(acac)_3$ follow it with percentages around 90%. In terms of thermal properties, knowing that the PBT alone used has a $T_m$ of about 220 °C, the most interesting catalysts seem to be $Pb(CH_3COO)_2$ and DBTO, which retain a melting point above 100 °C. The fact that these melting temperatures are so low may be related to molecular weight loss or a change to the crystal structure due to the presence of DDO. At this stage of the study, additional crystallographic analyses should be performed to answer this question. The $M_n$ calculated by NMR analyses are also presented in Table 1. These values show that the molecular weight build up is better in the case of $Pb(CH_3COO)_2$ and DBTO whereas, in the absence of a catalyst (entry 1), the weight loss is greater than in the case of all the various added catalysts. In this case, it is possible that the transesterifications occur without or with a very slow recombination step which demonstrates the benefit of a catalyst in solid-state modification reactions.

DBTO is already widely used for SSM [5]. Indeed, tin presents a major interest thanks to its capacity to extend its coordination number. It presents a classical mode of action as Lewis acid, where Sn gets coordinated with the ester group to activate the carbonyl carbon and to allow the nucleophilic attack of the alcohol [31]. However, another
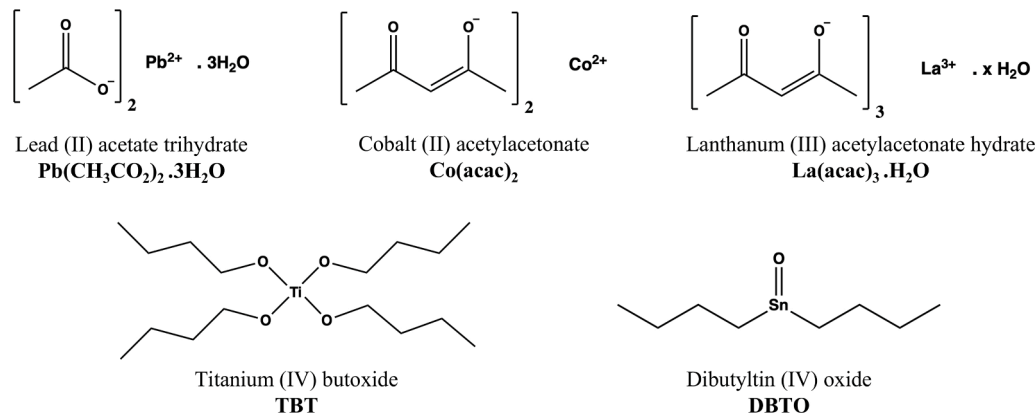


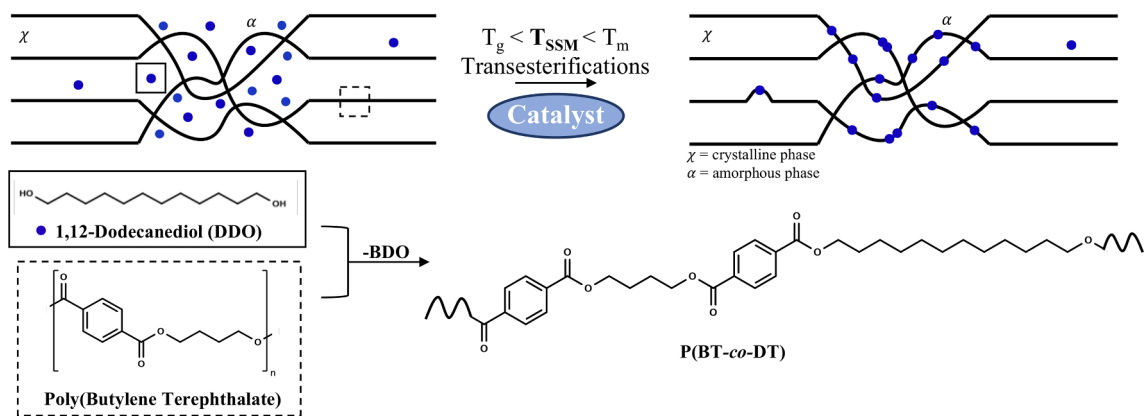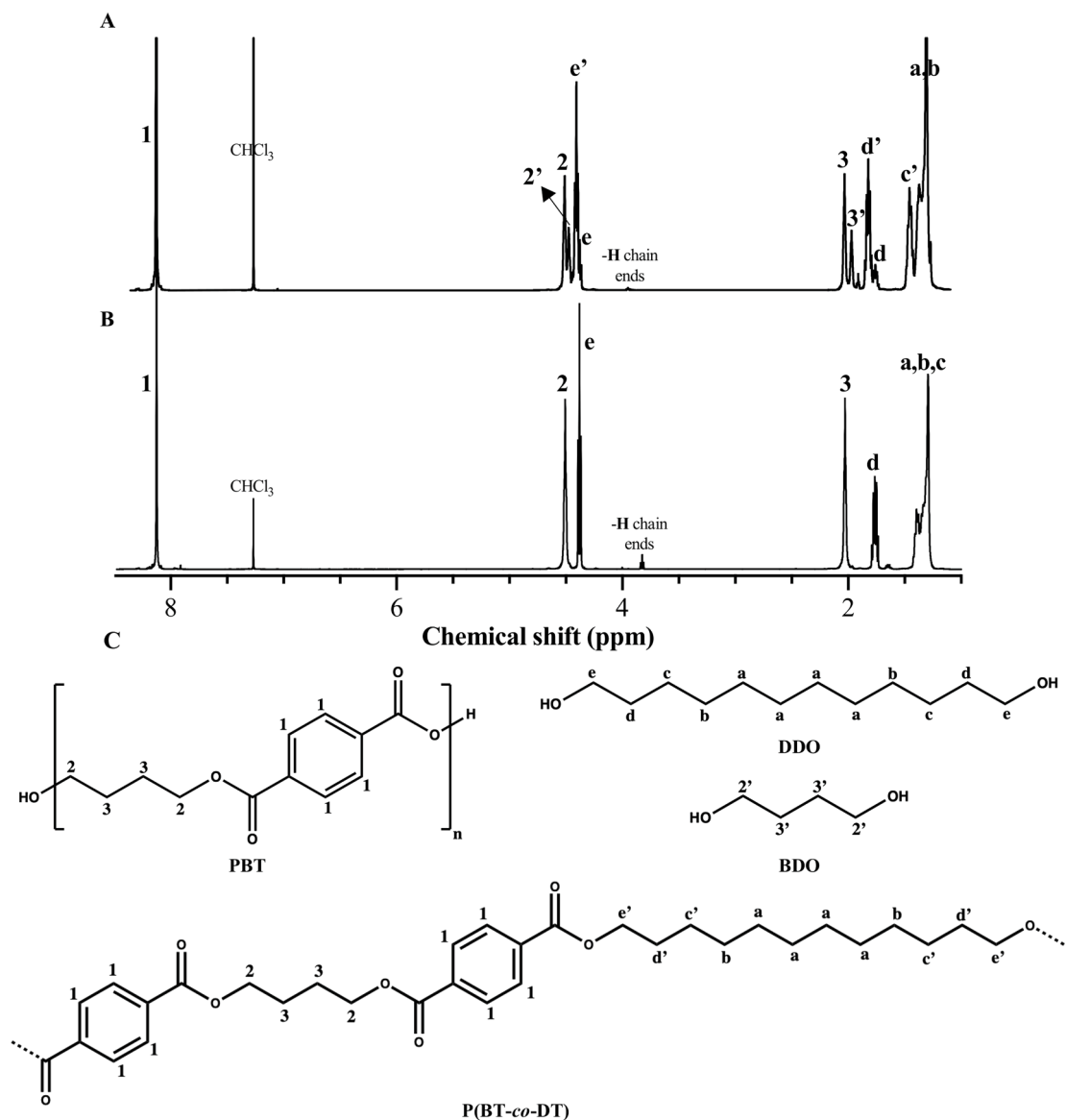Fig. 1. Scheme of the different catalysts used in this study.

**Fig. 2.** Schematic representation of the SSM between PBT and DDO.



**Fig. 3.** $^1$H NMR spectra of PBT/DDO/DBTO mixtures (A) after, (B) before DSC treatment at 190 °C (CDCl$_3$/TFA 9:1, 500 MHz) and (C) chemical structures of PBT, DDO, BDO and P(BT-co-DT) unit.
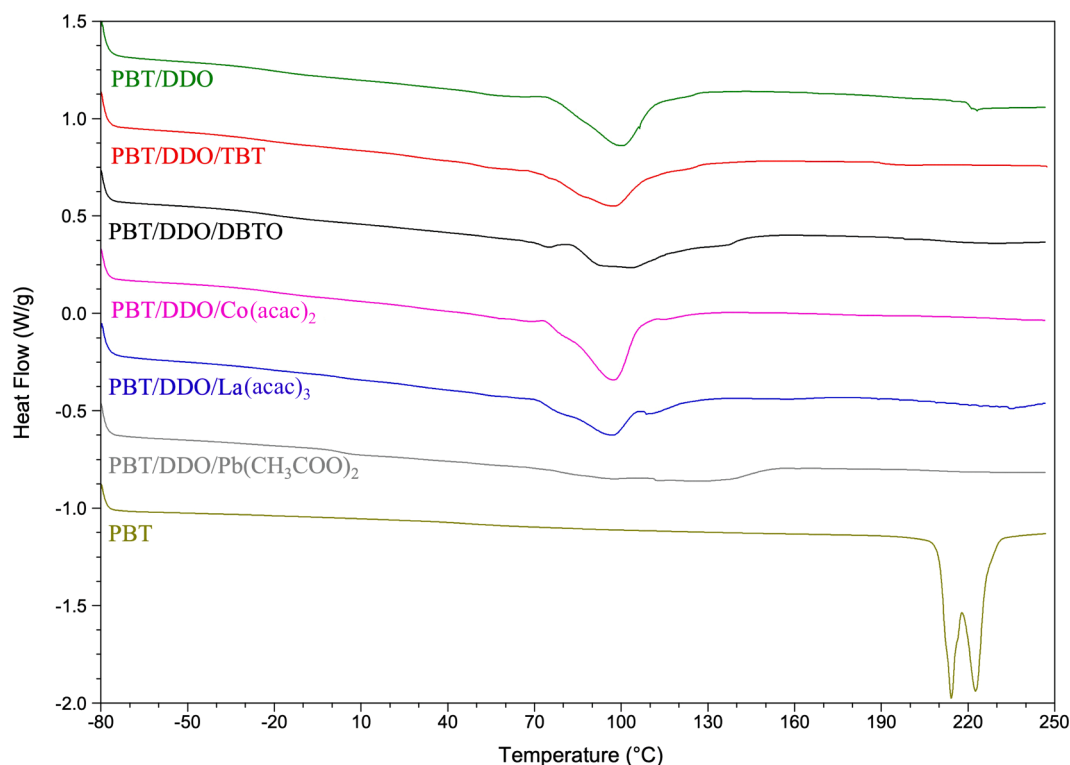
**Fig. 4.** DSC curves of PBT/DDO mixtures in absence and in presence of 300 ppm of the different catalysts after the DSC treatment at 190 °C.

**Table 1**
Thermal and molecular properties of PBT/DDO mixtures in absence (entry 1) and in presence of 300 ppm of the different catalysts.

| Entry | Catalyst | DSC[a] | | NMR[b] | | | | | SEC[g] |
|---|---|---|---|---|---|---|---|---|---|
| | | $T_m$ (°C) | $\Delta H_m$ (J/g) | $[DDO]_{mol}$[c] | | Conversion[d] (%) | $[BDO]_{mol}$[e] | | $M_n$[f] (g/mol) | Đ |
| | | | | $t_0$ | $t_f$ | | $t_0$ | $t_f$ | | |
| 1 | / | 101 | 35 | 0.67 | 0.08 | 88 | 1 | 0.46 | 4100 | 4.0 |
| 2 | TBT | 98 | 31 | 0.67 | 0.13 | 80 | 1 | 0.55 | 5400 | 4.2 |
| 3 | DBTO | 104 | 27 | 0.67 | 0.07 | 89 | 1 | 0.55 | 6900 | 4.4 |
| 4 | Co(acac)$_2$ | 98 | 33 | 0.67 | 0.07 | 89 | 1 | 0.52 | 6000 | 4.1 |
| 5 | La(acac)$_3$ | 97 | 27 | 0.67 | 0.07 | 90 | 1 | 0.40 | 6200 | 4.3 |
| 6 | Pb(CH$_3$COO)$_2$ | 112 | 23 | 0.67 | 0.02 | 97 | 1 | 0.48 | 9000 | 4.0 |

[a] Ramp of 10 °C/min. from −80 °C to 250 °C after a 6-hour isotherm at 190 °C.

[b] $^1$H NMR (CDCl$_3$/TFA 90:10, 500 MHz).

[c] $[DDO]_{mol}, t_0 = \frac{\int d}{\int 1}$.

[d] $Conversion(\%) = \frac{\int d'}{\int d + \int d'} x100$.

[e] $[BDO]_{mol}, t_0 = \frac{\int 3}{\int 1}$; $[BDO]_{mol}, t_f = \frac{\int 3 + \int 3'}{\int 1}$.

[f] $M_n = (FW_{PBT} \times n) + (FW_{PDT} \times n) + FW_{endgroups}$, n is the number of repeating units and FW is the molar fraction, $t_0$ and $t_f$ correspond respectively to before and after DSC treatment.

[g] Experimental dispersity obtained by SEC in HFIP, PMMA standards.

mechanism has already been identified, namely the exchange/insertion pathway. This pathway is often preferred when an exchange of ligand (ester function) with diol is less probable, as the literature shows [32,33]. The lead acetate trihydrate is also a Lewis acid and its mechanism is similar to that of DBTO.

In the GPC study, only the dispersities are presented herein because it is not possible to conclude anything from the molecular weights obtained by this technique due to their bimodal distribution (Fig. S4 in Supplementary Material). Pb(CH$_3$COO)$_2$ and DBTO are therefore preferred above the others for the remaining study.

An important parameter to be considered when studying the influence of catalysts is the amount of catalyst present [34]; as it will be discussed in the next section.

### 3.1.2. Effect of catalyst concentration

The selected catalysts are Pb(CH$_3$COO)$_2$ and DBTO and three concentrations are compared: 100, 300 and 500 ppm relative to the amount of PBT. The thermal and molecular characteristics are presented in Table 2.

Table 2 shows that increasing the amount of catalyst from 100 to

**Table 2**

Thermal and molecular properties of PBT/DDO mixtures with different catalyst quantities.

| Entry | Catalyst | Quantities (ppm) | DSC[a] | | NMR[b] | | | | | SEC[f] |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $T_m$ (°C) | $\Delta H_m$ (J/g) | [DDO]$_{mol}$[c] | | Conversion[d] (%) | [BDO]$_{mol}$[e] | | $M_n$ (g/mol) | Đ |
| | | | | | $t_0$ | $t_f$ | | $t_0$ | $t_f$ | | |
| 1 | / | / | 101 | 35 | 0.67 | 0.07 | 88 | 1 | 0.46 | 4100 | 4.0 |
| 2 | DBTO | 100 | 101 | 31 | 0.67 | 0.12 | 83 | 1 | 0.62 | 5900 | 4.2 |
| | | 300 | 104 | 27 | 0.67 | 0.07 | 89 | 1 | 0.55 | 6900 | 4.4 |
| | | 500 | 108* | 26* | 0.67 | 0.07 | 90 | 1 | 0.41 | 7000 | 5.0 |
| 3 | Pb(CH$_3$COO)$_2$[g] | 100 | 101 | 19 | 0.67 | 0.09 | 86 | 1 | 0.53 | 8100 | 4.2 |
| | | 300 | 112 | 23 | 0.67 | 0.02 | 97 | 1 | 0.48 | 9000 | 4.0 |
| | | 500 | 97* | 20* | 0.67 | 0.01 | 99 | 1 | 0.49 | 9100 | 4.0 |

[a] Ramp of 10 °C/min. from −80 °C to 250 °C after a 6-hour isotherm at 190 °C.

[b] H NMR (CDCl$_3$/TFA 90:10, 500 MHz).

[c] $[DDO]_{mol} = \dfrac{\int d}{\int 1}$.

[d] $Conversion(\%) = \dfrac{\int d'}{\int d + \int d'} \times 100$.

[e] $[BDO]_{mol}, t_0 = \dfrac{\int 3}{\int 1}$; $[BDO]_{mol}, t_f = \dfrac{\int 3 + \int 3'}{\int 1}$.

[f] $M_n = (FW_{PBT} \times n) + (FW_{PDT} \times n) + FW_{endgroups}$, n is the number of repeating units and FW is the molar fraction, $t_0$ and $t_f$ correspond respectively to before and after DSC treatment.

[g] Experimental dispersity obtained by SEC in HFIP, PMMA standards. * Large melting peak.

300 ppm results in better conversion for both the DBTO and the Pb(CH$_3$COO)$_2$ catalyst. This increase positively impacts on the molar mass building up. Above 300 ppm, a plateau is reached, and a higher amount of catalyst does not present any additional catalytic effect on conversion or molar mass building up. Similar conclusions can be drawn from the observation about their thermal transition. Indeed, the melting temperature increases between 100 and 300 ppm, without any real positive influence at 500 ppm catalyst. In addition, the DSC curves at 500 ppm present very wide fusion peaks, which can therefore impede the values taken. To summarize, a quantity of 300 ppm seems to be an optimal amount to combine high DDO conversion with sufficient mass building up.

Finally, DBTO is selected to avoid the major toxicity problems that lead-based catalysts brings and which are widely reported in the literature [35–37]. Notice that our lead-based catalyst also brings a pronounced color during our synthesis. In addition, DBTO is already widely used and known for transesterification and particularly in solid-state reactions [4,5,21].

### 3.1.3. Qualitative kinetic discussion - Effect of DBTO on PBT/DDO mixture in function of time

In this last section about the calorimetric investigation of the influence of catalysts, a qualitative kinetic discussion is carried out on the PBT/DDO mixture with 300 ppm of DBTO. For this study, different isothermal times (from 1 to 12 h) are realized by DSC [11]. Once again, the residues from the DSC analyses are analyzed by $^1$H NMR. These molecular and thermal characteristics are presented in Table S1 in Supplementary Material.

It shows that the conversion is higher than 80% after only one hour of isotherm and varies randomly according to the duration of the isotherm, likely linked to the integration error from our NMR analyses. These values are also in agreement with the [DDO]$_{mol}$ after DSC treatment (Table S1). Regarding the [BDO]$_{mol}$ calculated from the integration of aromatic **CH** and OCH$_2$**CH**$_2$ of the PBT, it is smaller after DSC treatment, which means that there is a loss of butanediol during the isotherm. $M_n$ values (Fig. 5) drop at the beginning, i.e., for short isotherm times, certainly related to the chain scission reactions that take place at the beginning, but $M_n$ increases with longer isothermal times. This indicates that the chains recombine once the transesterifications are
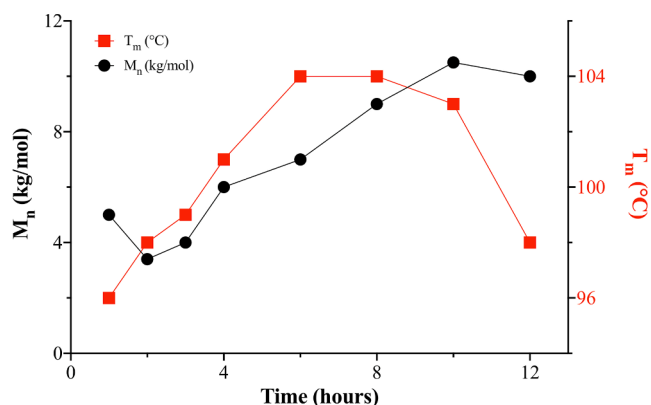


**Fig. 5.** Kinetic study of the influence of DBTO catalyst on PBT/DDO.

carried out. This increase in molar mass is widely visible up to 6 or 8 h of isothermal, after that a plateau seems to be reached. In addition, from entry 1 in Tables 1 and 2, it is clear that a catalyst is needed to achieve recombination.

The thermal properties shown in Table S1, obtained from the temperature ramp following the isotherm, reinforce the observations made for $M_n$. The $T_m$, shown in Fig. 5, increases continuously from 1 to 6 h isothermal treatment and reaches a plateau beyond that and it falls back upon subjection to 12 h of isothermal time. After 8 h, the $T_m$ will decrease which can probably be related to the incorporation of some DDO within the crystalline phases. To keep the properties linked to the crystalline phase, a good compromise can be found for 6 h of reaction which allows not to face too long residence time. Regarding the fusion enthalpies, they are higher in the case of very short isothermal periods and decrease almost by half after 6 h of treatment. This correlation between high melting temperature and better mass building up is often represented in the literature [38].

This kinetic discussion demonstrates the influence of time on the thermal and molecular properties of the copolymers obtained after the DSC treatment. It shows that 6 h of isothermal time seems to be an optimum time for combining sufficient molecular and thermal properties.

## 3.2. Process validation

### 3.2.1. Reactor scale results – Batch process

Once the optimized synthesis parameters are obtained by calorimetry, similar conditions can be validated via a batch experiment to design the complete process. To do so, a modification of PBT with DDO is accomplished by SSM in an Autoclave® reactor. The reaction is conducted at 190 °C for 6 h following the optimal conditions determined in the first part of this research with 300 ppm DBTO as catalyst and a $N_2$ continuous flow. The by-product, here butanediol, is eliminated by the $N_2$ flow ensuring the equilibrium shift towards the formation of the desired reaction products. Under these conditions, the crystalline phases of the PBT must be preserved due to mobility restrictions. The SSM then occur in two stages; first, transesterifications take place between the polymer and the monomer. It then follows a recombination of the chains to have a reconstruction of the molar masses. A catalyst-free SSM is also performed to prove the interest of the presence of a catalyst. The copolymers obtained are molecularly analyzed by ^{1}H NMR as shown in Fig. 6 and thermally by DSC analysis. All the values are reported in Table 3.

Table 3 shows the comparison between P(BT-co-DT)s synthesized by SSM with or without DBTO and the copolymers obtained after the DSC treatments. The first feature to be highlighted is that at the conversion level and thus the incorporation of the monomer into the PBT, the values are upgraded in both cases during batch SSM compared to DSC. This is due to the fact that both heat and mass-transfer are enhanced in the case of batch process, which allows a better incorporation and reaction between the polymer and the monomer [39]. Once again, the values in the table clearly show the interest of using catalyst with respect to the extent of the monomer incorporation, with a more significant conversion rate in the presence of DBTO as well as the construction of the molar masses. Knowing that the PBT used initially presents an $M_n$ of about 7400 g/mol

(calculated by ^{1}H NMR), the building up of the molar masses does not seem complete even in the presence of DBTO. A mass effect could be here at the origin of this gap between the DSC and the batch SSM. Indeed, the kinetics seem to be slower in the reactor, but the size of the vessel is much larger than the size of the pan used in DSC, allowing a more confined environment during reaction [6]. Therefore, it seems that the batch technique is effective by overcoming some of these mass transfer issues but is not enough when molar mass building up is considered. An effective method to solve them is reactive extrusion (REx). Indeed, for batch reactions, viscosity increases with the polymerization time and at a certain time, the material becomes unmanageable in terms of mixing and heat transfer. In the case of REx, the extruder creates a continuous thin surface layer and thus increases the degree of mixing due to the shear forces but also minimizes temperature gradients in the processed polymer [40,41]. This technique also makes it possible to reduce the residence time compared to a discontinuous reaction, thus reducing the prolonged exposure of the material to high temperatures that could cause degradation of the polymers [42]. The literature offers us polymer modification reactions with REx, e.g., grafting, but these syntheses have never been realized in a semi-solid state as proposed in this study [43–45].

### 3.2.2. Reactive extrusion – Proof of concept

The promising results presented above allow us to investigate the SSM of PBT in a continuous way using REx. This process is carried out under the same conditions as the batch tests, i.e., 190 °C with a $N_2$ continuous flow and 40 rpm at different reaction times. After a solid-state premix of PBT and DDO in a CryoMill as described before, the mixture is introduced for 5 min and left in the extruder for 20, 30 and 60 min. It is possible that due to viscous heating and low clearance between the screw and the barrel wall the polymer melts but to avoid this as much as possible the melt control function is used rather than the barrel
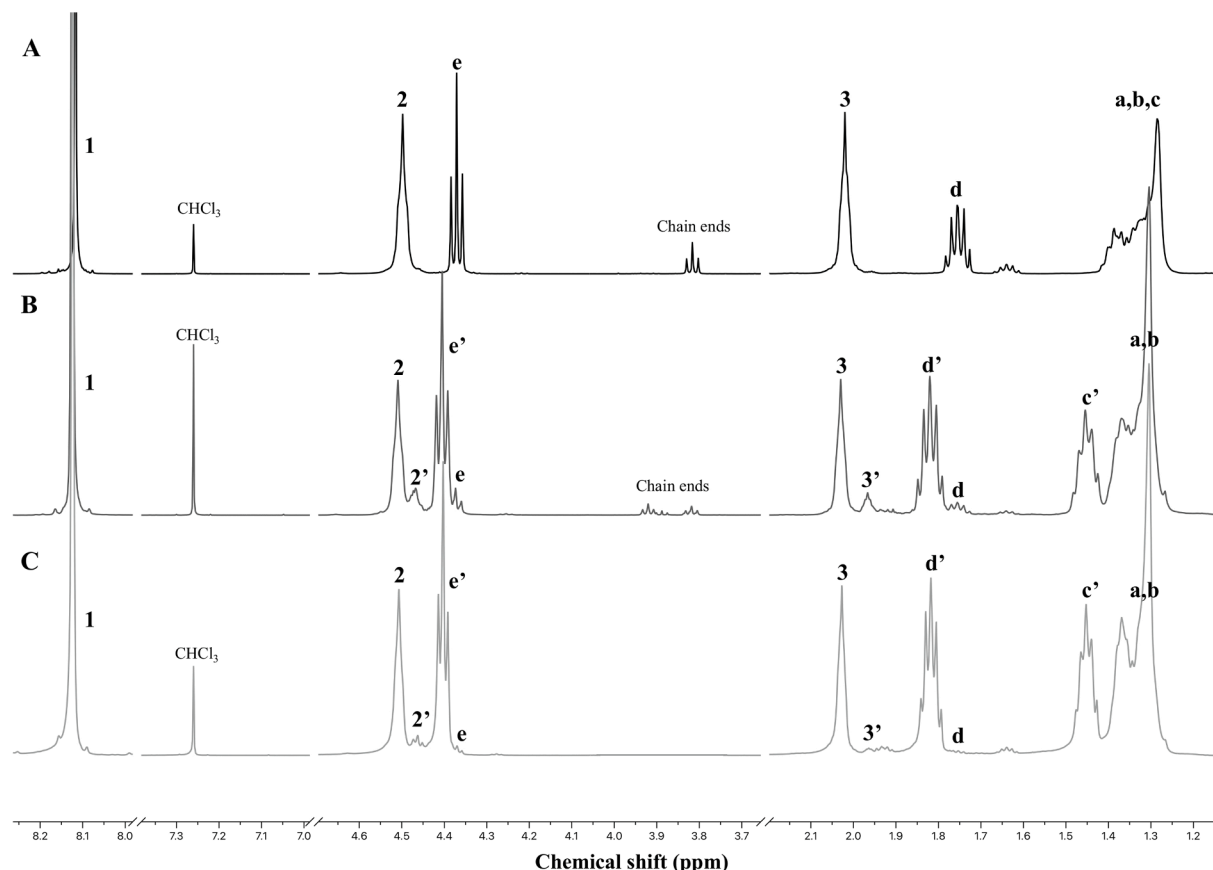


Fig. 6. ^{1}H NMR spectra of (A) PBT/DDO/DBTO mixture before SSM, (B) P(BT-co-DT) synthesized by SSM without and (C) with DBTO (CDCl$_3$/TFA 9:1, 500 MHz).

**Table 3**

Thermal and molecular characteristics of P(BT-co-DT) obtained by SSM in an Autoclave reactor.

| Composition | Treatment | DSC | | NMR[b] | | | | | | SEC[f] |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $T_m$ (°C) | $\Delta H_m$ (J/g) | $[DDO]_{mol}$[c] | | Conversion[d] (%) | $[BDO]_{mol}$[e] | | $M_n$ (g/mol) | Đ |
| | | | | $t_0$ | $t_f$ | | $t_0$ | $t_f$ | | |
| PBT$_{60}$DDO$_{40}$ w/o catalyst | 6 h DSC[a] | 101 | 35 | 0.67 | 0.07 | 88 | 1 | 0.46 | 4100 | 4.4 |
| | 6 h SSM | 110 | 35 | 0.67 | 0.04 | 93 | 1 | 0.4 | 2500 | 2.8 |
| PBT$_{60}$DDO$_{40}$DBTO$_{300ppm}$ | 6 h DSC[a] | 104 | 27 | 0.67 | 0.06 | 89 | 1 | 0.55 | 6900 | 4.0 |
| | 6 h SSM[g] | 117 | 40 | 0.67 | 0.02 | 96 | 1 | 0.48 | 4300 | 4.0 |

[a] Ramp of 10 °C/minute from −80 °C to 250 °C after a 6-hour isotherm at 190 °C.

[b] $^1$H NMR (CDCl$_3$/TFA 90:10, 500 MHz).

[c] $[DDO]_{mol} = \dfrac{\int d}{\int 1}$.

[d] $Conversion(\%) = \dfrac{\int d'}{\int d + \int d'} x100$.

[e] $[BDO]_{mol}, t_0 = \dfrac{\int 3}{\int 1}$; $[BDO]_{mol}, t_f = \dfrac{\int 3 + \int 3'}{\int 1}$.

[f] $M_n = (FW_{PBT} \times n) + (FW_{PDT} \times n) + FW_{endgroups}$, n is the number of repeating units and FW is the molar fraction, $t_0$ and $t_f$ correspond respectively to before and after SSM treatment.

[g] Experimental dispersity obtained by SEC in HFIP, PMMA standards.

control. The successful execution of the REx and in particular the exchange reactions during this extrusion is evaluated by $^1$H NMR (Fig. 7 and Table 4).

This technique appears to be very effective with respect to the exchange reactions between PBT and DDO. Conversion rates of about 65%, 80% and 90% can be achieved after only 20, 30 and 60 min, respectively. This shows that during SSM, transesterification reactions, in this case alcoholysis, and thus chain breaks occur rapidly. What can also be

observed is that the PBT/PDT ratio gets inverted as the reaction time increases. Indeed, when the **2-2′**, **3-3′**, **e-e'** and **d-d'** peak pairs are observed, the trend is reversed with a higher proportion of PBT-related peaks for short reaction times. In contrast, for 60 min of reaction, the PDT peaks are predominant. This is reinforced by the values in Table 4, especially with the $[DDO]_{mol}$ which decrease for longer REx times.

The major problem comes from the rebuilding of the chains and thus from the construction of the molecular weights. In fact, after 60 min in
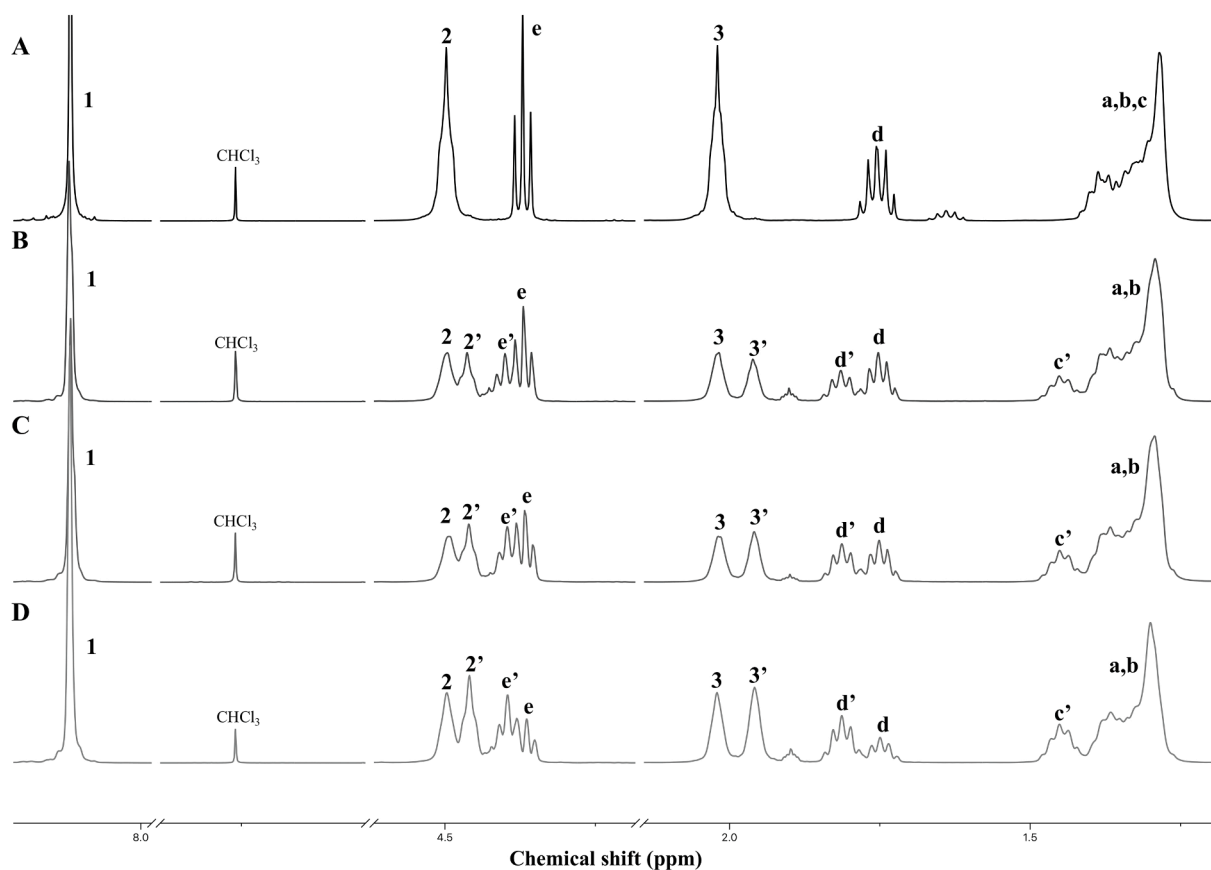


**Fig. 7.** $^1$H NMR spectra of (A) PBT/DDO/DBTO mixture before SSM, (B) P(BT-co-DT) synthesized by REx after 20 min, (C) 30 min and (D) 60 min (CDCl$_3$/TFA 9:1, 500 MHz).

**Table 4**

Thermal and molecular characteristics of P(BT-co-DT) obtained by REx at different reaction times.

| Entry | Time$_{REx}$ (minutes) | DSC | | NMR[a] | | | | | SEC[f] |
|---|---|---|---|---|---|---|---|---|---|
| | | T$_m$ (°C) | ΔH$_m$ (J/g) | [DDO]$_{mol}$[b] | | Conversion[c] (%) | [BDO]$_{mol}$[d] | | M$_n$ (g/mol) | Đ |
| | | | | t$_0$ | t$_f$ | | t$_0$ | t$_f$ | | |
| 1 | 20 | 93 | 16 | 0.67 | 0.24 | 65 | 1 | 0.88 | 2900 | n.r. |
| 2 | 30 | 93 | 47 | 0.67 | 0.14 | 80 | 1 | 0.7 | 2700 | 4.7 |
| 3 | 60 [e] | 88 | 16 | 0.67 | 0.07 | 90 | 1 | 0.82 | 1300 | n.r. |

[a] $^1$H NMR (CDCl$_3$/TFA 90:10, 500 MHz).

[b] $[DDO]_{mol} = \frac{\int d}{\int 1}$.

[c] $Conversion(\%) = \frac{\int d'}{\int d + \int d'} x100$.

[d] $[BDO]_{mol},t_0 = \frac{\int 3}{\int 1}$ ; $[BDO]_{mol},t_f = \frac{\int 3 + \int 3'}{\int 1}$.

[e] $M_n = (FW_{PBT} \times n) + (FW_{PDT} \times n) + FW_{endgroups}$, n is the number of repeating units and FW is the molar fraction, t$_0$ and t$_f$ correspond respectively to before and after REx treatment.

[f] Experimental dispersity obtained by SEC in HFIP, PMMA standards.

REx, the visual aspect of the recovered material suggests a more important degradation of the material than in case of the reaction done in the Autoclave®. Monitoring these reactions is also carried out by observing the evolution of the torque which showed a constant decrease during the course of the reaction once the totality of the material introduced until reaching zero. No increase is observed, meaning that the chains do not recombine afterwards. The calculated M$_n$ present in Table 4 show a higher loss for a longer extrusion time. At the beginning of the treatment, DDO acts as a plasticizer which certainly helps the exchange reaction. However, after a long residence time, the shear is such that it causes the melting of the mixture, which can lead to the loss of the semi-solid state, i.e., a loss of crystallinity. It is possible that the (micro)structure obtained by SSM as well as the conservation of the parameters related to the crystallinity of the polymer is lost in this case.

These results suggest that REx between a polyester and a diol monomer is achievable, but an additional vacuum step should be added to boost the chains building up. Indeed, as a reminder, during classical melt polycondensation, there are two steps. A first one of transesterification which is used to form small oligomers and a second one of polycondensation which is used to build the masses. This step is associated with a high vacuum to eliminate the by-products produced during the condensation reactions. It is therefore decided to transpose this to the SSM by adding a vacuum step.

The application of high vacuum ($\simeq 10^{-2}$ mbar) is then considered. In this respect, a 4-hour vacuum step under stirring is then applied on the sample having undergone the SSM in the reactor as well as to this obtained by REx (30 min, DBTO). The influence of this step is evaluated by DSC and viscosity measurements (Table 5). The figure showing the viscosity measurements is present in the SUPPORTING INFORMATION

(Fig. S5). As previously mentioned, the GPC measurements are irrelevant in this study due to their bimodal distribution. Moreover, the insolubility of the obtained copolymers in conventional solvents used in GPC (e.g., HFIP) restrict its use here. Viscosity measurements are then preferred to study the influence of these vacuum steps on the evolution of the molecular masses [46]. Intrinsic viscosity [η] is used to draw the trends.

As might be seen in Table 5, improvements are visible in terms of thermal properties. Specifically, in terms of T$_g$, this increases especially in the case of REx. This is certainly due to longer chains after the vacuum step. T$_m$ rises also of about 25 °C in the case of the copolymer obtained by REx, possibly related to the modification of the crystallinity. The change in the melting peak can also be due to annealing of the copolymer during the vacuum step.

Regarding the viscosity, it increases significantly after the post-treatment vacuum step as shown in Table 5 and in Fig. S5. This increase in viscosity is certainly related to an increase in molecular weights and these values confirm the T$_g$ values obtained.

This post-processing step shows its real interest in the reconstruction of the molar masses. This step could be directly applied at the end of solid-state modification to have an almost continuous process, the equipment should just be adapted for that.

## 4. Conclusions

In conclusion, a first example of SSM is developed for PBT with a difunctional monomer starting from DSC investigations which are translated to a continuous process. First, a detailed study using calorimetry allowed to evaluate the effect of different catalysts on SSM reactions. In this study, various catalysts are tested in different proportions and DBTO is found to be the most suitable one after studying the variations in the melting temperature obtained by DSC and the conversions from NMR analyses. Then, a qualitative kinetic discussion has reinforced this investigation by evaluating the influence of the reaction time on the molecular and thermal characteristics of the copolymers obtained. The identified conditions are then validated in batch process, and this has proven to be a method of choice in terms of conversion but also demonstrated the interest of catalysts in the case of solid-state modifications. Finally, REx proved to be an interesting method to overcome the mass transfer problems encountered during batch SSM. With this technique, it is possible to obtain high conversion percentage of DDO after only 30 min, but for the moment with low molecular weights and a liquid-like appearance. This may signify structural degradation. The vacuum post-processing step has shown a real interest in the

**Table 5**

Thermal and molecular characteristics of P(BT-co-DT) obtained by SSM before and after vacuum step.

| Sample | Treatment | DSC | | | Intrinsic viscosity [η] (l/g) |
|---|---|---|---|---|---|
| | | T$_g$ (°C) | T$_m$ (°C) | ΔH$_m$ (J/g) | |
| P(BT-co-DT)$_{SSM}$ | Before post-vacuum | 0 | 117 | 40 | 0.321 |
| | After post-vacuum | 3 | 120 | 25 | 1.097 |
| P(BT-co-DT)$_{REx}$ | Before post-vacuum | −20 | 93 | 47 | 0.035 |
| | After post-vacuum | 3 | 118 | 18 | 0.717 |

reconstruction of masses with increasing viscosity. Some technical adaptations could then allow to perform these steps directly at the end of the modification and thus the whole process would be almost continuous. A significant advantage of our process is the possibility to extend these results to a wide range of monomers and polymers to improve specific properties, such as its flammability in the case of PBT. Current studies are carried out in the case of the SSM of PBT using biobased derivatives, such as sugar derivatives for example. This technique of SSM in a continuous process could also be applied on other polymeric matrices, e.g., biobased polyesters as poly(ethylene furanoate).

This study could therefore bring a more sustainable character to some polymeric matrices by combining different points, for example the process, the end of life of materials, the feedstocks, etc.

## Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

## CRediT authorship contribution statement

**Carolane Gerbehaye:** Investigation, Writing – original draft, Visualization, Conceptualization. **Katrien V. Bernaerts:** Investigation, Writing – review & editing. **Rosica Mincheva:** Writing – review & editing, Supervision, Conceptualization. **Jean-Marie Raquez:** Writing – review & editing, Supervision, Conceptualization.

## 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.

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## Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2022.111010.

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