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Published in:
European Polymer Journal

DOI:
[10.1016/j.eurpolymj.2018.04.040](https://doi.org/10.1016/j.eurpolymj.2018.04.040)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2018

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Flores, O., Demarteau, J., Mueller, A. J., Etxeberria, A., Irusta, L., Bergman, F., Koning, C., & Sardon, H. (2018). Screening of different organocatalysts for the sustainable synthesis of PET. *European Polymer Journal*, 104, 170-176. <https://doi.org/10.1016/j.eurpolymj.2018.04.040>

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Screening of different organocatalysts for the sustainable synthesis of PET

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A B S T R A C T

Industrially, poly(ethylene terephthalate) (PET) is produced using organometallic catalysts which have shown excellent ability to promote the polymerization at elevated temperatures. However, the catalysts remain permanently in the fabricated item because their removal is very difficult both from a technical and economical point of view. In this work, several organocatalysts have been evaluated as alternative to the industrially applied organometallic catalysts for the bulk polymerization of PET from dimethyl terephthalate (DMT) and ethylene glycol (EG) at high temperatures. The effectiveness of the organic catalysts in PET synthesis is evaluated by SEC, DSC, TGA, ¹H NMR and FTIR spectroscopy. After screening various organocatalyst families, our results demonstrate that the catalytic activity of 1,8-Diazabicyclo[5.4.0]undec-7-ene: benzoic acid salt (DBU:BA) is competitive in comparison with the conventional organometallic-based catalyst employed in PET synthesis. This ionic salt combines the excellent catalytic ability of organic compounds with the thermal stability of metal-based catalysts, resisting degradation up to > 250 °C which is close to the industrial polymerization temperature of PET. Moreover, the dimerization degree of ethyleneglycol in the presence of DBU:BA is significantly reduced in comparison to organometallic catalysts which enhances the thermal properties of the synthesized PET using DBU:BA. Thus, organic salts have shown to be promising catalyst for the bulk polymerization of PET and in addition may be a viable option to obtain metal-free PET.

1. Introduction

The extraordinary development of polymers in various fields has resulted in several decades of their intensive application for several uses in our daily life. Poly(ethylene terephthalate) (PET) is one of the most relevant polymers in the world, because of its high durability, excellent mechanical properties, transparency, recyclability and good processability. Moreover, this versatile material keeps a good balance of useful functional properties and low cost. As a consequence of the above, PET has a wide demand in the manufacture of products like textiles, packaging films, packaging products and beverage bottles. This has led to an increase in the production of this polyester, e.g., the Global PET production reached a capacity of 27.8 million tons in 2015 [1].

PET can be prepared by a) the polyesterification of terephthalic acid with ethylene glycol or b) by transesterification of dimethyl terephthalate with ethylene glycol, or by c) direct polycondensation of bis(hydroxyethyl) terephthalate [2–5]. The use of catalysts and harsh

polymerization conditions, being high vacuum in combination with high temperatures, are key factor in producing polymers with high molecular weights and good mechanical properties. The majority of catalysts used in the polymerization of PET are organometallic such as antimony, germanium, titanium and other compounds, where antimony trioxide is currently the most employed in the production of PET [2,3,6–11]. In spite of having high catalytic activities to synthesize high molecular weight PET, they also have some disadvantages such as their non-biodegradability, in some cases their high toxicity to the human health and environment and, most importantly, the difficulty to be removed from the resulting polymer [12]. Consequently, as the catalyst remains in the fabricated item, during the secondary melt fabrication process or mechanical recycling, side reactions may happen leading to significant property deterioration. Therefore, frequently mechanically-recycled PET generally ends up in secondary products [13,14].

In the last decade, extensive attempts have been carried out to reduce the toxicity of organometallic catalysts using more benign catalyst

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systems. In this regard, the utilization of fully organic compounds to promote step growth polymerizations is gaining a lot of attention. While organocatalysis has demonstrated its utility in ring-opening, anionic, zwitterionic, step growth and group-transfer polymerizations, the use of organocatalysis in polymerization reactions such as step-growth polymerizations remain less explored in comparison to more traditional metal-based polymerizations. A key reason for shifting to organocatalysts in polymerization reactions is their ability to be effectively removed from resultant polymers [15–20].

Several organocatalysts have shown to be effective to catalyze transesterification reactions such as 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). Although these catalysts have been reported in the literature for the depolymerization of PET [21–26], as far as we know the use of TBD and DBU in the polymerization of PET has not been described.

One of the main limitations for the utilization of organocatalysts is their poor thermal stability at temperatures that would be practical for PET polymerization and therefore full or partial thermal degradation of the catalyst may occur during the polymerization [27]. Recently, ionic compounds have emerged as an interesting alternative for carrying out polymerizations at high temperatures. For instance, Peruch et al. prepared some DMAP-based protic ionic compounds to mediate the ROP of L-LA at elevated temperatures [28]. Similarly, Fradet et al. and Sardon et al. utilized some Brønsted acid ionic liquid to promote polyesterification and ring opening polymerizations, respectively [29,30]. Similarly, we recently demonstrated the ability of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD): methane sulfonic acid (MSA) protic ionic compound to catalyze PET depolymerization [31].

In this work, several organocatalysts have been evaluated as alternatives to organometal-based catalyst for the bulk polymerization of poly(ethylene terephthalate) from dimethyl terephthalate (DMT) and ethylene glycol (EG) at high temperatures. Not only conventional organocatalyst such as DMAP, DBU, TBD or p-TSA have been screened but also some ionic compounds, such as 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate (Brønsted acid ionic liquid) or DBU:MSA and TBD:MSA protic ionic compounds, have been investigated and compared to titanium tetrabutoxide catalyst. This organometallic catalyst is widely used in the polymerization of Polybutylene terephthalate (PBT), but also has been studied as an alternative to reduce environmental impact in the synthesis of PET replacing the highly toxic antimony-based catalysts [6]. The effectiveness of the organic catalysts in PET synthesis is evaluated by SEC, DSC, TGA, ^1H NMR and FTIR spectroscopy.

2. Experimental

2.1. Materials

Dimethyl terephthalate (DMT, $\geq 99\%$), ethylene glycol (EG, 99.8%), titanium (IV) butoxide (TiBut, $\geq 99\%$), 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 98%), benzoic acid (BA, 99.5%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%), p-toluenesulfonic acid monohydrate (p-TSA, 98.5%), trifluoroacetic acid (TFA, 99%) and methanesulfonic acid (MSA, $\geq 99.5\%$) were purchased from Sigma-Aldrich. 4-Dimethylaminopyridine (DMAP, 99%) and Tetrahydrofuran (THF, 99.9%, Extra Dry) were supplied by Acros. 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate (BAIL, 98%) was obtained from Solvionic. Methanol (CH_3OH , 99.5%) and chloroform (CHCl_3 , 99.9%) were purchased from Fisher Scientific. Water was removed from the p-TSA before use.

The DBU:BA catalyst at molar ratio of base to acid (1:1) was prepared following the procedure reported by Hedrick [32]. TBD and MSA at molar ratio of base to acid (1:1), were mixed to obtain a TBD:MSA catalyst due to its ability to form PET from Bis(2-Hydroxyethyl) terephthalate [31].

2.2. Screening of different catalysts for PET synthesis

The catalysts tested for PET polymerization were: TiBut, DBU:BA (1:1), DMAP, TBD, DBU, p-TSA, BAIL and TBD:MSA (1:1). PET was obtained by reacting DMT (1 equiv., 0.015 mol, 3.0 g) with EG (1.4 equiv., 0.021, 1.3 g) in the presence of 5 mol% of catalyst (with respect to DMT). The reaction was performed in a tubular Schlenk flask with glass key and equipped with a magnetic stirrer and the flask was heated in a molten salt bath. This procedure was the same for each catalyst employed.

The polymerization reaction was carried out at 200 °C for 24 h at atmospheric pressure, followed by 24 h under vacuum. The polymer obtained was diluted in a mixture of chloroform and trifluoroacetic acid (8:1), precipitated an excess of methanol and collected by centrifugation. Finally, the material was dried under vacuum and analyzed by ^1H NMR, SEC, DSC and FTIR. The formation of PET was confirmed by NMR. ^1H NMR (δ ppm, CDCl_3/TFA , 300 MHz): 8.12 (4H, Ar-CH), 4.78 (4H, $\text{COO-CH}_2\text{-CH}_2\text{-OCO}$, internal group), 4.63 (4H, $\text{COO-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-OCO}$, dimer)/ (2H, $\text{COO-CH}_2\text{-CH}_2\text{-OH}$, end group), 4.18 (2H, $\text{COO-CH}_2\text{-CH}_2\text{-OH}$, end group), 4.10 (4H $\text{COO-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-OCO}$, dimer) and 4.02 (3H, COO-CH_3 , end group).

2.3. Optimized PET polymerization

Following the procedure described previously for PET synthesis, but in order to optimize the polymerization, DBU:BA (1:1) was used as catalyst in two reactions, the first reaction was carried out at 240 °C for 24 h under atmospheric pressure followed by 24 h under vacuum. The second reaction was carried out at 200 °C under atmospheric pressure for 24 h and then the temperature was increased to 250 °C and vacuum was applied for 4 h.

To complete the study, other reactions were carried out at 250 °C for 1 h under atmospheric pressure and 4 h under vacuum. In this case, the catalysts employed were: DBU:BA (1:1) and TBD:MSA (1:1). The same procedure than in the *Screening of different catalysts for PET Synthesis* section was applied to the purification and characterization of PET.

A complementary study has been made under the latter conditions but using 500 ppm of catalysts, being TiBut, DBU:BA and TBD:MSA. In this purpose, a stock solution (in dried THF) of 100 mg of the catalyst was realized for higher precision and the corresponding quantity of 500 ppm mol% of this solution was added to DMT and EG.

2.4. Characterization

2.4.1. NMR spectroscopy

^1H NMR spectra were recorded on a Bruker DPX300 spectrometer. For NMR analysis, polymers were dissolved in a mixture of deuterated chloroform (CDCl_3) and trifluoroacetic acid (TFA) (8:1, v/v), and spectra were referenced to CDCl_3 . About 10 mg of sample in 0.6 mL of solvent were used for ^1H NMR.

2.4.2. FTIR spectroscopy

Samples were taken from the tubular Schlenk flask at different reaction times and the obtained solids were analyzed by FTIR spectroscopy. A Nicolet 6700 spectrometer (Thermo Scientific) was used with golden gate single reflection ATR with a resolution of 4 cm^{-1} and a crystal diamond was employed.

2.4.3. Differential scanning calorimetry (DSC)

The thermal behavior of the polymers was analyzed by differential scanning calorimetry (DSC), employing a DSC 8500 (PerkinElmer). The DSC scans were collected employing 4.5–5.5 mg samples at heating and cooling rates of 20 °C/min from -20 to 270 °C under a nitrogen flow of 20 mL/min. The instrument was calibrated with indium and tin standards. The peak melting temperatures (T_m) and the latent heats of melting (ΔH_m) reported in the results section were taken from the

second heating scans. The glass transition temperatures were determined with a heating rate of 40 °C/min after rapidly quenching the sample (ballistic cooling).

2.4.4. Thermogravimetric analysis (TGA)

Weight loss as a function of temperature was examined by a TGA Q500 (TA instrument) under nitrogen atmosphere. Samples of 5–10 mg were heated from 40 to 600 °C at a rate of 10 °C/min.

2.4.5. Size exclusion chromatography (SEC)

Size exclusion chromatography was performed at 40 °C by an Agilent equipment provided with a refractive index detector and equipped with a precolumn HFIP-LG and two HFIP 804 and HFIP 803 columns from Shodex packed with polystyrene-divinylbenzene. The samples were chromatographed with a flow of 0.5 mL·min⁻¹ using 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) as solvent.

3. Results and discussion

3.1. Screening of different catalysts for PET synthesis

Organocatalyzed Polymerization of PET was carried out after mixing dimethyl terephthalate (DMT) (1 equiv., 0.015 mol, 3.0 g) and ethylene glycol (EG) (1.4 equiv., 0.021, 1.3 g) in a tubular Schlenk flask in the presence of 5 mol% of catalyst (Scheme 1a). The polymerization was performed in two steps. In the first step, the transesterification between dimethyl terephthalate and ethylene glycol was performed at 200 °C for 24 h obtaining oligomers. During the second step, the temperature was maintained and solid state polymerization was continued applying high vacuum and removing the excess of ethylene glycol and methanol, in order to obtain high molecular weights. Different organic catalysts, such as organic acids, *p*-toluenesulfonic acid (PTSA) and 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate (BAIL) and commercial organic bases such as diazabicyclo-[5.4.0]undec-7-ene (DBU) or 1,5,7 triazabicyclo[4.4.0]dec-5-ene (TBD) and nucleophilic activator such as 4-Dimethylaminopyridine (DMAP) and some ionic salts such as DBU:BA and TBD:MSA, have been screened in the polymerization (Scheme 1b). All these catalysts have been successfully used in transesterification reactions of cyclic esters [33–35], and therefore have been selected for our PET synthesis. For comparative purposes TiBut was also included as polymerization control along with an uncatalyzed reaction.

The polymerization was monitored by FTIR as shown in Fig. 1

Fig. 1. Infrared Spectra showing the evolution of PET formation at 200 °C employing TBD:MSA as catalyst.

where the infrared spectra of the samples obtained at different reaction times using TBD:MSA (1:1) as catalyst are shown. As can be seen the absorbance of the band centered at 1430 cm⁻¹ [36], assigned to the asymmetric bending (δas) of the methyl groups attached to terephthalate units decreases its intensity with the reaction and a new band assigned to the symmetric bending (δsi) of the methylene groups attached to terephthalate units appears at 1340 cm⁻¹ confirming the advance in the polymerization.

The monomer conversion was determined using the relative area of this band centered at 1430 cm⁻¹ vs. time for each polymerization using various catalysts. The reaction with TiBut and the uncatalyzed reaction were included as reference to evaluate the effectiveness of organic catalysts (Fig. 2). We observed that the rate of polymerization was

Scheme 1. (a) Organocatalyzed synthesis of PET from DMT and EG (the main condensate is CH₃OH in step 1 and excess EG in the step 2) and (b) Catalysts employed in the Screening Process.

Fig. 2. Conversion to PET at 200 °C monitored by FTIR.

found to be highly catalyst dependent. Without a catalyst, monomer conversion was less than 50% after 48 h and full conversion was not achieved. Conversely, DBU, DMAP and the salts of DBU:BA exhibited conversions exceeding 90% after 5 h of reaction time, obtaining a conversion of > 98% after 48 h. This was a very favorable result compared to the conversions obtained from TiBut (83% after 5 h and > 98% after 48 h). TBD also catalyzed the PET polymerization (84% after 5 h), with final conversion > 97% after 48 h. The TBD:MSA (1:1) catalyst yields a conversion of 53% after 5 h and the final conversion was slightly lower (93% after 48 h). Organic acids (p-TSA and BAIL) were found ineffective and gave rather low final conversions of 52 and 38%, respectively, after 48 h. These results demonstrate that the catalyst plays an important role in the polymerization and that the polymerization rate seems to be higher when using DBU, DMAP and DBU:BA (1:1) rather than TiBut to prepare PET.

To further confirm the PET synthesis, ^1H NMR was performed. Fig. 3 shows ^1H NMR of both monomers, viz. ethylene glycol (EG) and dimethyl terephthalate (DMT), and the ^1H NMR of PET after 48 h of synthesis using DBU:BA catalyst [37]. As expected, when the polymerization was completed, the characteristic peaks of the ethylene glycol and DMT had disappeared while new peaks assigned to PET at 8.12 ppm (Ar-CH, peak 1) and 4.78 (COO-CH₂-CH₂-OCO, peak 2) appeared, confirming the PET synthesis. Together with the signals associated with PET some low intensity signals attributed to dimerization of EG during the polymerization at 4.63 ppm and 4.10 ppm (COO-CH₂-CH₂-O-CH₂-CH₂-OCO dimer) and some others attributed to PET chain ends at 4.63 ppm and 4.18 ppm (COO-CH₂-CH₂-OH) and 4.02 ppm for the CH₃ (COO-CH₃) were observed [37,38].

To more precisely compare catalytic activities, kinetic studies were performed for each catalyst. The reaction proceeded with overall second order kinetics with respect to the monomers – $d[M]/dt = k[DMT][EG]$, as confirmed by the linear relationship between time, t and $1/(1 - p)$, where p is the fraction of monomer converted to polymer. Rate constants were obtained for each catalyst (Fig. 4). The organocatalysts DMAP, TBD and DBU:BA (1:1) showed higher rate constants than the reference metal catalyst.

The high catalytic activity of organocatalysts for PET polymerization is clearly demonstrated (Fig. 4). Nevertheless, the molecular weights calculated by NMR (SI section) and measured by SEC (Table 1) show that the final molecular weights obtained with organic catalysts are lower than those obtained with the reference metal catalyst after 48 h, at least at 200 °C, while the conversions were similar (Table 1). A factor that may influence the molecular weight is the reaction temperature. For PET synthesis, it has been reported that temperatures above the melting temperature of PET (> 250 °C) are required to obtain decent molecular weights [39,40]. With this in mind, we investigated if

using higher temperature we could reach higher molecular weights.

It is well known that one of the limitations of organocatalysts is their stability at high temperatures [27]. As seen in Fig. 5, when running the polymerization in the presence of TBD, DMAP and DBU, the polymers were colored. Ionic compounds could offer an interesting alternative due to their strong internal ionic interactions, which increases their thermal stability [34,41]. In this sense, we assume a higher thermal stability for the two ionic compounds DBU:BA and TBD:MSA rather than DBU, TBD or DMAP, which is confirmed by the absence of color after polymerization in the presence of these two catalysts (Fig. 5).

To further confirm the thermal stability and the absence of volatiles of these two ionic compounds during polymerization, TGA analysis was performed for all catalysts. In Fig. 6, it can be observed that DBU:BA and TBD:MSA are stable above 200 °C, and therefore they were selected to continue with the screening and to perform the PET polymerization at higher temperatures in order to try to increase the molecular weights.

3.2. Optimized polymerization of PET

After screening some polymerization conditions, we found that the best results in terms of molecular weight and conversion were obtained running the polymerization in two steps, mimicking the strategy used in the commercial synthesis of PET. In the first step dimethyl terephthalate (DMT) (1 equiv., 0.015 mol, 3.0 g) and ethylene glycol (EG) (1.4 equiv., 0.021 mol, 1.3 g) were mixed in a tubular Schlenk flask in the presence of 5 mol% of catalyst (Scheme 1a) and the polymerization was run for 1 h at 250 °C. In this first step PET oligomers were obtained by transesterification. In the second step, high vacuum was applied for 4 h to push the conversion to higher values and to increase the molecular weight by polycondensation. Using these polymerization conditions the two most stable catalysts DBU:BA and TBD:MSA were tested for PET polymerization and compared with TiBut. Although the catalyst TBD:MSA (1:1) gives lower conversion and catalytic activity than DBU:BA (1:1), it is thermally more stable at high temperatures and therefore this compound was also investigated in the polymerization.

As in the previous case NMR measurements were performed to confirm the polymerization and to calculate the molecular weight of PET. Fig. 7 shows a ^1H NMR spectrum of the PET sample synthesized with DBU:BA (1:1) as catalyst at 200 °C (a) versus the PET spectrum synthesized at 250 °C using the same catalyst (b). It can be seen that the intensity of the signal corresponding to the protons of the end groups (4.18 ppm for the COO-CH₂-CH₂-OH and 4.02 ppm for COO-CH₃), decreases when PET is synthesized at 250 °C (b), which indicates that the chains formed are longer and therefore the number of end groups decreases. Also, the molecular weight of PET synthesized at 250 °C is higher than that of PET synthesized at 200 °C.

From the NMR spectra the molecular weight was calculated. The results are shown in Table 2. In all cases, the molecular weight was greater when increasing the temperature. With the TBD:MSA catalyst, the obtained NMR-based molecular weight (M_n = 6.7 kDa) is lower than that obtained with TiBut (M_n = 12 kDa). Conversely, the DBU:BA catalyst exhibits a molecular weight calculated by NMR (M_n = 18.6 kDa) greater than that obtained with TiBut. To further analyze molecular weights, SEC analysis was performed using hexafluoroisopropanol as eluent. The SEC-based number average molecular weight obtained with the TiBut catalyst (16.8 kDa) is higher than that obtained with DBU:BA (10.7 kDa). Nevertheless, the $\bar{D}$ value obtained with the TiBut catalyst is quite high (4.9) for a polycondensation reaction (Theoretical value without branching being $\bar{D} \approx 2$). We believe that this rather high $\bar{D}$ could be attributed to some side reactions during PET polymerization in the presence of TiBut. It was reported that TiBut catalyst possess strong affinity to coordinate with PET. Pilatti et al. assumed that this interaction leads to branching, called “quasi networks”, and consequently to an apparent increase of the molecular weight in the melt state which confirms also why the internal viscosity

Fig. 3. ^1H NMR spectrum of a synthesized PET at 200 °C using DBU:BA as catalyst, recorded in CDCl_3/TFA ; ^{13}C satellites (*).

Fig. 4. Linear plot of $1/(1-p)$ as a function of time for the catalyzed polycondensation (at 200 °C). K_0 was determined from the slope.

is higher in the case of TiBut [42]. This phenomenon could explain not only the high $\bar{D}$ obtained using TiBut but also the lower molecular weight calculated by NMR for TiBut. In addition, we found that in the presence of TiBut the dimerization rate was much higher (7%) than using both organocatalysts. As a consequence, the high content of diethylene glycol units in the polymers can act as a defect in the crystallization of the material and decrease the values in T_m and ΔH_m [43–45]. Basically, any chemical group (different than the PET repeating unit) that is inserted within the PET chains will interrupt the regularity of the PET macromolecules, constituting defects along the chains. Such defects will limit the extent of crystallinity and also the lamellar thickness that the crystals can achieve. As the lamellar

Table 1

Molecular weights, dispersities and degrees of conversion of synthesized PETs.

Catalyst	M_n NMR ^a (kDa)	M_n SEC ^b (kDa)	M_w SEC ^b (kDa)	$\bar{D}^b$	Conversion ^c (%)
None	1.8	1.3	2.3	1.8	49
TiBut	7.2	2.0	4.5	2.2	> 98
DBU:BA (1:1)	5.2	1.5	3.1	2.0	> 98
DMAP	3.8	1.4	2.9	2.1	97
TBD	4.2	1.1	3.1	2.8	97
DBU	4	1.2	3.2	2.5	> 98
p-TSA	0.5	0.7	4.3	5.7	52
BAIL	0.6	0.3	2.7	8.3	38
TBD:MSA (1:1)	1.6	1.1	2.3	2.1	93

PET obtained at 200 °C.

^a Calculated by NMR.

^b Measured by SEC in HFIP against PMMA standards.

^c Final conversion determined by FTIR.

thickness is directly proportional to the melting point, the thinner the crystals the lower the T_m values.

In order to minimize the catalyst loading and to be competitive with industrial PET preparation polymerizations were performed using 100 times less catalyst. As expected the molecular weights (Table S1) were lower as the catalyst loading was reduced. In spite of the decrease in the molecular weight, it should be noted that the results for DBU:BA and TiBut were comparable even at low catalyst loading.

Another important feature strongly determined by the quality of the produced PET is its thermal behavior. Hence, the thermal properties of the different produced PET samples were compared by DSC (Fig. 8) and TGA (SI section). Table 2 shows the T_m , T_g and ΔH_m values of the PET synthesized using the three different catalysts (TiBut, TBD:MSA and

Fig. 5. Pictures of PET synthesized with different catalysts.

Fig. 6. TGA of organocatalysts employed.

DBU:BA) and the two different applied polymerization temperatures. We found that the higher the polymerization temperature the higher the molecular weight of PET and consequently the higher the T_m and ΔH_m in all cases. Nevertheless, in the case of PET obtained using TiBut catalyst, for which the molecular weight is the highest, we found that both the T_m and the ΔH_m were relatively low. This effect was also observed by Pilati et al. [42] when using TiBut catalyst. They concluded that the observed branching could interrupt the linear crystallizable sequences of PET and accordingly the T_m and the heat of fusion (and concomitantly the degree of crystallinity). The melting point of the PET

obtained with the TBD:MSA (1:1) catalyst of 257.7°C is close to the melting point of commercial PET grades.

To further confirm the similar thermal characteristics of PET synthesized with organocatalysis, the thermal stability of the polymers was analyzed by TGA (SI section). These TGA results show that the thermal stability of the PET materials synthesized with organic catalysts is similar to that of the PET synthesized with a metal-based catalyst.[10]

4. Conclusions

In conclusion, the ability to synthesize PET using organocatalysis has been demonstrated. The protic ionic salt diazabicyclo-[5.4.0]undec-7-ene (DBU): benzoic acid (BA) was found to efficiently activate the polymerization of dimethyl terephthalate and ethylene glycol, while also producing high molecular weights, comparable to organometallic catalyst. Moreover, we found that although the molecular weight in the presence of DBU:BA ($M_n = 11$ kDa) was slightly lower than using TiBut ($M_n = 16$ kDa), the $\bar{D}$ obtained was greater in the case of TiBut than DBU:BA (4.9 and 2.9 respectively). We demonstrated that this high $\bar{D}$ could be attributed to the higher ability of TiBut to coordinate with PET. This interaction leads to branching and consequently to an apparent increase of the molecular weight. Besides affecting the $\bar{D}$, the branching considerably affected the crystallization of PET reducing the T_m and ΔH_m of PET. On the other hand, the degree of dimerization can also influence the value of T_m . In this sense, we found that in the presence of DBU:BA catalyst PET with higher crystallinity was produced. The data obtained in this study reveal that organic ionic compounds have potential for synthesizing metal free PET due to their thermal

Fig. 7. ^1H NMR spectra of (a) PET synthesized at 200°C and (b) PET synthesized at 250°C.

Table 2
Molecular weight and thermal properties of synthesized PETs.

Catalyst	M_n NMR ^a (kDa)	Dimerization ^a (%)	M_n SEC ^b (kDa)	$\bar{D}_{SEC}$ ^b	$I.V.$ ^b (dl/g)	T_m ^c (°C)	T_g ^c (°C)	ΔH_m ^c (J/g)
At 200 °C								
DBU:BA (1:1)	5.2	0.4	1.5	2	–	250.6	67	49
At 250 °C								
TiBut	12	7.6	16.8	4.9	0.35	236.1	70	35
TBD:MSA (1:1)	6.7	0.5	7.3	2.3	0.26	257.7	80	60
DBU:BA (1:1)	18.6	1.4	10.7	2.9	0.26	252.0	77	52

^a Calculated by NMR. The dimerization is the degree of ethylene glycol that dimerized before polymerization.

^b Measured by SEC in HFIP.

^c Determined by DSC.

Fig. 8. DSC second heating scans for PET samples obtained with optimized reaction conditions using different catalyst systems (250 °C).

stability and catalytic activity, and may facilitate the recyclability of PET.

Acknowledgment

The work was supported by EU through project SUSPOL-EJD 642671 and the Gobierno Vasco/Eusko Jaurlaritz (IT 999-16 and IT-618-13). Haritz Sardon gratefully acknowledges financial support from MINECO through project SUSPOL and FDI 16507. Irma Flores would like to acknowledge Conacyt (Mexico) for supporting her PhD studies with a scholarship.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.eurpolymj.2018.04.040>.

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