Glycolytic Depolymerization of Polyethylene Terephtalate (PET) Wastes

Organic *vs.* metal-catalysis

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An improved synthetic protocol for glycolytic depolymerization of of poly(ethylene terephthalate) (PET) from various PET wastes is described. This has been established by a screening of commercially available organocatalysts in order to determine the most efficient catalytic system for PET depolymerisation. The main products of the glycolytic reaction were found to be bis(hydroxyethyl) terephthalate (BHET) and its oligomers or unsymmetrically substituted terephtalates depending on the glycol involved in the destruction. The monitoring of the catalytic reaction and the characterization of both, PET waste and glycolyzed products were performed by ^{1}H-NMR spectroscopy. Cyclic amidine are the most effective catalysts for the glycolytic destruction of PET with ethylene glycol, whereas guanidine – based catalyst perform better the glycolysis of PET with longer-chain diols. Outstanding catalytic activity for both 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD) was observed for glycolytic reaction of PET with ethylene glycol – isosorbide mixture.

Keywords: poly(ethylene terephthalate); organocatalysis; PET wastes; NMR spectroscopy; glycolysis reaction

Polyethylene terephtalate (PET) is a thermoplastic polyester which experienced a tremendous use in fibers and molding resins. This is based upon its superior properties from which, it is worth mentioning here: chemical and thermal stability, light weight and transparency[1,2]. Owing to the increase demand for textile application and in food packaging as well as bottle markets for replacement of glass, enormous volume of PET is produced[3,4]. The driving consumption of PET is given also by the fact that it is environmentally friendly, but because it is not biodegradable it must be recycled[5]. Recycled PET is mainly used in the production of fibers where the low production cost combined with the excellent properties of the material makes it an ideal substitution for cotton or other man-made fibers[6]. Industrial application of PET –fibers includes also other market textile ranging from high-tech industrial yarns to carpets, ropes, filters, conveyer belts and tire cords[7]. Moreover, owing to the controlled crystallization rate process, PET found application in the fabrication of photographic and magnetic films or as dielectric film in capacitors[8]. PET resin is the second largest application of polyethylene terephtalate and it is expected to continue to grow more and more due to its use in beverage packaging, mainly carbonated and non-carbonated soft drinks and water. Based on the excellent price-to-performance ratio of PET, coated high-barrier or multilayer PET bottles are currently used for commercialization of beer. PET containers are also increasingly used for a number of large non-food items, like for example cosmetics and other beauty products. Thus, the effective recycling of PET wastes both for the preservation of natural resources and for protection of the environment has received considerable attention lately [9]. The recycling of PET results in the following advantages: i) conservation of raw materials by reducing the need for virgin petrochemical feedstock; ii) less energy is required when converting recycled PET to a virgin equivalent, whether flake or pellet and as a consequence of this iii) less greenhouse gas emissions [10].

The recycling methods of PET waste are classified in four categories: primary, secondary, tertiary and quaternary[11]. The primary recycling method, also called the "in-plant" procedure deals with uncontaminated PET scrap materials and is performed only with single-type waste, reason why although the cheapest it is not a popular choice for PET recycling [12]. The secondary recycling is also known as mechanical recycling and includes sorting and separation of waste[13]. This methodology consists in grinding PET bottles into powder using physical means, extrusion by heat and reforming. Because PET is degraded through physical treatment, the resulting powder does not share the same quality properties as virgin PET, especially the gray colour resulting from the different colour of the wastes[14,15]. Therefore, mechanically recycled PET cannot be reused in fabrication of beverage packaging, instead, these recycled products are commercially used as fibers with applications varying from clothing to carpeting[16]. Tertiary recycling, commonly known as chemical recycling provides an alternative method of degrading PET into its monomeric form, which can then be used for the reproduction of PET or as building blocks for a variety of high-value materials [17]. The polymer can be cleaved at strategic points generally using methanolysis,

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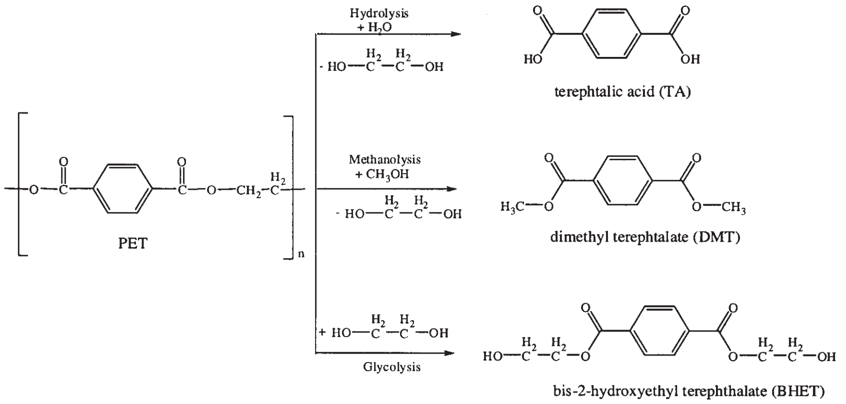

Fig. 1. Schematic representation of the tertiary recycling of polyethylene terephtalate wastes.

glycolysis, or hydrolysis leading to dimethylterephtalate (DMT), bis-2-hydroxyethyl terephthalate (BHET) or terephthalic acid (TA), compounds that can be re-used for the production of polyethylene terephtalate (fig. 1)[18]. Hydrolysis supposes the depolymerization of PET to terephtalic acid (TA) and ethylene glycol (EG) through reaction with water in acidic, basic or neutral conditions [19-21]. The big disadvantage of the hydrolytic process is given by the harsh reaction conditions (high temperature and pressure) owing to the weakest nucleophilic character of the water reagent along with corrosion and pollution problems [22]. Methanolysis is the degradation of PET to dimethyl terephtalate (DMT) and ethylene glycol by methanol [23]. The method implies high cost due to the difficult separation and recovering of the reaction products. Also, if water perturbs the process, it poisons the catalyst and forms various azeotropes [24]. Glycolysis is the most attractive methods, being used on a commercial scale and involves the molecular degradation of PET polymer by glycols, in the presence of trans-esterification catalysts, mainly metal acetates or titanates [25]. Glycolysis by ethylene glycol (EG) leads to the bis-2-hydroxyethyl terephthalate (BHET) monomer which can be used for PET synthesis and other PET glycolyzates [26]. The glycolyzed PET can also be used to manufacture polyurethane foams, copolyesters, acrylic coatings and hydrophobic dyes. Ethylene glycol or superior glycols (propylene glycol or dipropylene glycol) can also be used as diols for PET glycolysis. Therefore, much attention has been devoted to the glycolysis of PET and the research is focused now on developing more efficient catalysts [27-29].

Quaternary recycling of PET wastes involves the incineration of the waste with the recovery of the energy, but ecologically unacceptable due to the potential health risks from the burned substances. This method is a reliable solution when the sorting and separation of the plastic waste is difficult to be done and/or the waste is toxic and hazardous to handle.

From all these methodologies, PET glycolysis is considered as future recycling method of plastic waste being economically viable in terms of cost and application. The reaction itself follows a transesterification mechanism in the presence of a catalyst, commonly metal-based catalysts[30,31]. In the case of metal oxides, even modified on silica nanoparticles, the PET glycolysis occurred at temperature that exceeds 245°C with low conversion into glycolyzed products [32]. Acetates proved to be the best metal-based catalyst, [33,34] the glycolysis occurring between 190 – 200°C within 3 to 6 h, with the order of activity as follows: $Zn^{2+}>Mn^{2+}>Co^{2+}>Pb^{2+}$[35]. Improvement of the catalyst efficiency was reported for titanium salts when, the reaction time was reduced to 2.5 – 3 hours at 200 °C in the case of the phoshpate salts [36]. Although metal salts are effective in increasing the PET glycolysis rate, the reaction is promoted at high temperature and in addition, traces of heavy metals with negative impact on the environment, are always accompanying the glycolyzed products. Thus, the catalysts could not be recycled and reused, and the purity as well as application fields of the depolymerization products is seriously threatened.

The alternative to the metal-catalyzed glycolytic depolymerization is given by the organic superbases and ionic liquids catalysts which are intensively studied lately[37-40]. Using pyridine molecule as a basic model, researchers strategically developed tailored pyridine-based compounds with significant catalytic activity for the transeterification reaction [41,42]. Amidine based organocatalysts are representative examples of neutral bases capable to polarize the C=O double bond of the polyethylene terephtalate polymer, favoring glycolysis and/ or aminolysis reaction [43]. Further on, bifuctional catalysts were also introduced in PET glycolysis based on their efficiency in a related reaction, namely the ring opening polimerization (ROP) of lactides[44]. Because of their acid-base character, they activate both, the ester carbonyl group through their nucleophile component and the reactants (alcohols or amines) through their acid component [45]. The most popular is a guanidine-based catalyst, bicyclic 1,5,7-triazabiciclo [4,4,0] dec-ene (TBD) which mediates the cleavage of the ester bonds from PET in mild conditions while the amount of by-products from polymer degradation is seriously minimized [46]. Other effective type of organocatalyst is represented by ionic liquids which perform the glycolysis reaction around 180°C within 3 to 8 hours, depending on the substitution of the ionic liquid [47,48]. The high catalytic performance of this class of organic catalyst is given by their recycling capability and further by their possible transformation in N-heterocyclic carbenes. Structurally, N-heterocyclic carbenes (NHCs) offer more potential for higher reactivity due to the increased nucleophilicity compared to older organo-catalysts. Indeed, NHCs demonstrated relatively high yields for the transesterification of carboxylic esters with primary alcohols at 70 - 80°C in a shorter period of time [49,50]. However, the main draw back of using NHCs as organocatalysts for PET depolymerization is given by their unstable nature both in presence of air and humidity. This survey of the literature reports clearly shows the superior catalytic activity of the organanocatalytic systems over the metal-based salts and highlights the possible industrial application in the near future. The main advantage of this type of catalysts over conventional metal salts is given by the simpler purification of the glycolysis products and the mild reaction conditions, especially the reaction temperature which not exceed 200 °C.

Based on our previous report on metal-catalyzed glycolysis of PET waste [51], we propose to realize a preliminary screening of the commercially available organic catalysts in the glycolysis reaction of PET wastes of different provenience. Our aim is to establish a protocol for the synthesis of polyester polyols from PET wastes, adequate for production of rigid polyurethane foams using rigid diols as depolymerization reagent.

Experimental part

Methods and techniques

Melting points: Koehler Automatic Melting Point Range Apparatus (K90190). Elemental analyses: Perkin Elmer CHN 240B. NMR spectra in $CDCl_3$: Varian 300 (^1H: 300 MHz, ^{13}C: 75 MHz) spectrometer; chemical shifts (δ) are expressed in ppm. Ethylene glycol (EG), 1,2 propylene glycol (PG), 1,3-propylene glycol (1,3-PG), diethylene glycol (DEG) and isosorbide (IS) were purchased from Sigma Aldrich and freshly distilled before used. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazobicyclo [4.3.0]non-5-ene (DBN), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 4-dimethylaminopyridine (DMAP), 1,4-diazabicyclo[2.2.2]octane (DABCO) and imidazole (ImA) were purchased from Sigma Aldrich and used as received. PET wastes (bottles, textile and post-consumer materials) were carefully cut with scissors, washed with detergent and water, skimmed with benzene and dried in the laboratory oven at 80°C for 12 h. The powder was obtained by grinding after freezing the wastes with carbonic ice.

General procedure glycolysis of PET waste using organic catalyst

50 mL round-bottom three-necked flask equipped with a thermometer and a reflux condenser was loaded with 1.92 g of PET (10 mmol) and ethylene glycol (100 mmol) followed by addition of certain amount of organocatalyst (0.5 or 1.0 mmol). The flask was immersed in an oil bath preheated at a specified temperature and the glycolysis reaction continued until the PET waste disappeared and a clear mixture was formed. The excess of glycol was distilled at reduced pressure (2 - 3 mmHg) or decomposed by addition of water when a crystalline precipitate is formed after cooling overnight, filtered and dried. The precipitate or the viscous oil, representing 70-75% of PET, consists of bis-2-hydroxyethyl terephthalate (BHET) and its dimer (di-BHET). After water distillation, the filtrate consists of excess EG and BHET; and in some cases the catalyst. The glycolysis products were subject to NMR spectroscopy, the results being listed in table 1. The ^1H-NMR spectra of the BEHET monomer through glycolysis were compared with standard compound commercially available.

Characterization of the glycolyzed products

Bis-hydroxyethylterephthalate, (BHET): isolated by organocatalytic glycolysis of PET with EG: ^1H-NMR ($CDCl_3$-TFA): 8.10 (s, 4H, ar-H); 4.49 (m, 4H, CH_2-OCO); 3.98 (m, 4H, CH_2-OH); 2.40 (bs, 2H, -OH).

1-(Hydroxypropan-2-yl) (2-hydroxypropyl) terephthalate, isolated by organocatalytic glycolysis of PET with PEG: ^1H-NMR ($CDCl_3$): 8.07 (s, 4H, ar-H); 5.41 (m, 1H, CH_2); 4.60 (m, 1H, CH_2); 4.36 (m, 2H, -CH_2); 4.12-3.94 (m, 2H, -CH_2-OH); 1.53 (d, J = 6.3 Hz, 3H, –CH_3); 1.44(d, J = 6.1 Hz, 3H, -CH_3).

Bis(2-hydroxypropyl) terephthalate, isolated by organocatalytic glycolysis of PET with PEG: ^1H-NMR ($CDCl_3$): 8.10 (s, 4H, ar-H); 4.51 (m, 2H, CH); 4.37 (m, 4H, -CH_2-OCO); 1.45 (d, J = 6.1 Hz, 6H, -CH_3).

Glycolyzed PET with ethylene glycol/isosorbide: ^1H-NMR ($CDCl_3$): 8.07 (s, 4H, ar-H); 5.45 (br. 1H, CH-IS), 5.28-5.38 (m, 1H, CH-IS), 4.97-4.95 (m, 1H, CH-IS), 4.73-4.62 (m, 2H, CH_2-IS); 4.46-4.41 (m, 1H, -CH-IS); 4.37-4.31 (m, CH_2-IS), 4.19-4.08 (m, CH_2-IS), 3.98-3.89 (m, 4H, CH_2-IS), 3.85 (br, OH), 3.63-3.58 (m, 1H, CH-IS), 2.80 (br, OH).

Results and discussions

Spectroscopic analysis of PET wastes

The main sources of PET waste are food industry, especially packaging waste and textile industry where PET fiber is used either alone or in mixture with natural fibers, i.e. cotton and wool. They were subject to glycolytic recycling in the mentioned order. The chemical analysis of PET waste is important because contaminants will determine the properties of the recycled product. We and others have reported that the glycolyzed products can be analyzed by ^1H-NMR, but less efforts were put into NMR characterization of the PET waste itself. We report herein, the ^1H-NMR spectra of various type of PET wastes in order to asses the structural characterization of these materials. There were analyzed various samples and they are abbreviated as follows:

-post-consumer beverage bottles: opac flakes-PET I, compact glossy transparent - PET II, granules virgin PET - PET III, visibly contaminated with foreign material- PET IV, slightly colored - PET V, or deeply blue colored –PET VI

-two textile waste, white curtain – PETVII and PET-cotton blend (33/67) as PET VIII.

The ^1H-NMR spectra were recorded in deuterated chloroform ($CDCl_3$) and trifluoroacetic acid. In the case of ^{13}C-NMR, concentrated samples were prepared containing 20 – 30 mg / 0.5 mL, complete dissolution being achieved using ultrasonic hot bath. In figure 2 there are shown representative ^1H-NMR spectra for three representative types of PET: PET I, PET II and PET VII. The spectrum contains characteristic chemical shifts for terephthalate moiety around 8.10 ppm and the alkyl signals due to ethylene glycol at 4.7 ppm, respectively. The ratio of the integrals of these signals is 1: 1, corresponding to repeating units in the polymer. In addition, depending on the waste provenience two multiplets centered at 4.0 and 4.5 ppm are observed, assigned to inter-chain diethylene glycol (DEG) with a corresponding terephthalic signal in the aromatic area at 8.05 ppm. Sporadically, in the spectra appear other two signals at 1.27 and 2.33 ppm, simultaneously or only one, in varying ratios. ^{13}C-APT experiments have shown that the signal at 1.27 ppm corresponds to a methylene group due to the corresponding even number of H-atoms in the ^{13}C-APT spectrum, whereas the signal at 2.27 ppm comes from methyl groups - odd number of protons according to ^{13}C-APT spectrum. Other contaminants are either precipitating in the chosen conditions or are considered inorganic pigments like in the case of post-consumer white colored bottles. In conclusion, the post-consumer PET wastes contain two components EG and DEG, while the textile waste contains only EG. As can be seen these impurities do not interfere with the fingerprint signals of the polyethylene terephtalate skeleton.

Selection of the organic catalysts

It is well known that the glycolytic depolymerisation of PET waste is very slow in the absence of a catalyst and the rate of the reaction depends on many parameters, including particle size and shape. Therefore, the PET waste is used as fine powder obtained by grinding frosen PET flakes or plates in carbonic ice. We have previously reported that, proton nuclear magnetic resonance spectroscopy (^1H-

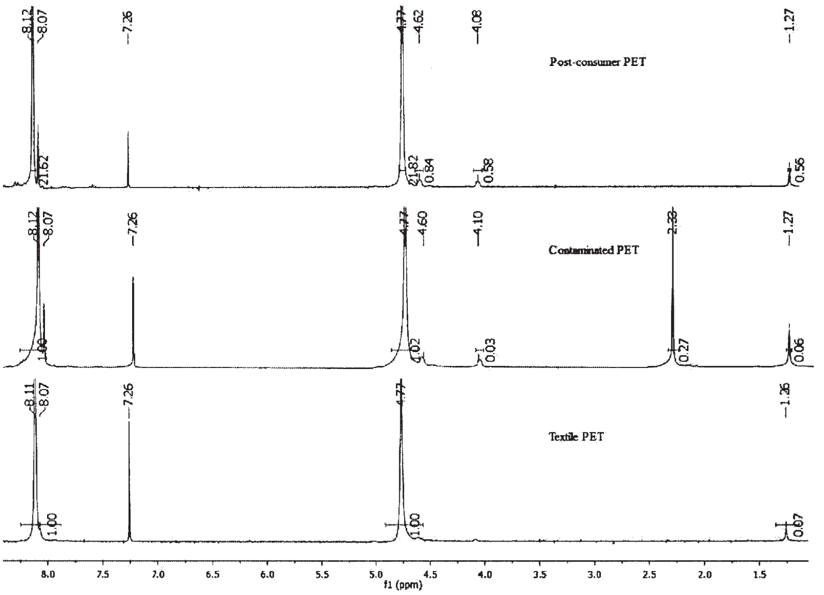

Fig. 2. Overlay of the ^{1}H-NMR spectra of different PET wastes.

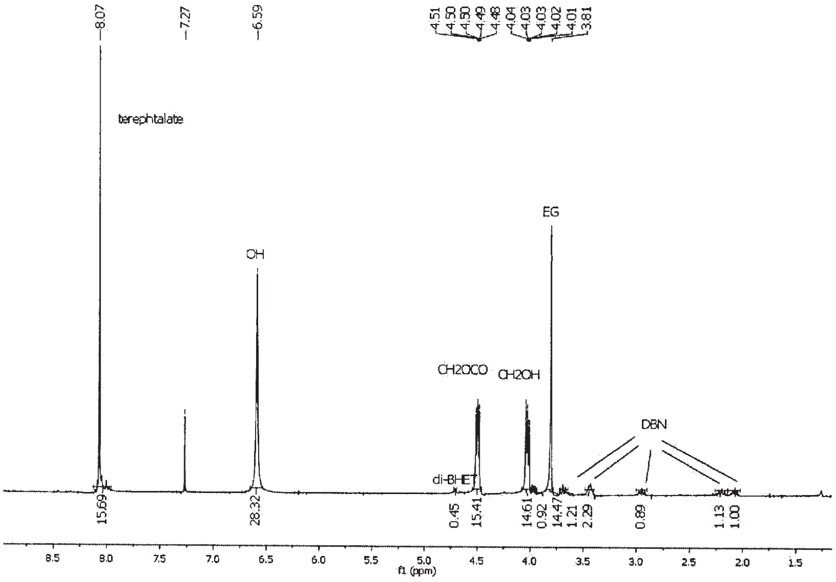

Fig. 3. ^{1}H-NMR spectrum of glycolytic mixture of post-consumer PET waste.

NMR) is an adequate tool to characterize the glycolyzed products in a laboratory scale [51]. The resonances of the catalysts does not affect the fingerprint signals of the polyethylene terephtalate fragment, therefore the reaction mixtures are easily investigated by NMR spectroscopy. The PET glycolysis was performed in the absence of a classical organic solvent, using instead excess of EG and 5-10 % molar loading of organocatalyst at temperature reaching maximum 190 °C. The catalytic activity was evaluated by the amount of generated bis-2-hydroxyethyl terephthalate (BHET) monomer. A representative example of glycolyzed products is shown in figure 3.

In all cases the reaction was monitored by NMR spectroscopy and compared with ^{1}H-NMR spectrum of standard BHET compound. The signal at 8.15 ppm indicates the presence of the four aromatic protons of the benzene ring, whereas the signals at 4.4 and 3.9 ppm are characteristic of the methylene protons of COO–CH$_2$ and CH$_2$–OH, pattern characteristic of the protons of the BHET monomer. Figure 2 shows the ^{1}H-NMR spectrum of the glycolyzed PET waste, indicating that the main product was BHET accompanied by chemical shifts of the organocatalysts.

The screening of commercially available organic catalysts on glycolytic depolymerization of PET wastes (fig. 4) was performed with 10% catalyst loading based on the PET content for PET / EG molar ratio of 1/15 at 190 ° C. The catalysts that were used belong to different classes of nitrogen bases. The obtained data are presented in table 1, conversions being calculated from ^{1}H-NMR spectra.

Detailed analysis of these data shows that organocatalysts with amidine skeleton (DBU and DBN) are the most effective, the reaction taking place in a short period of time with high selectivity in BHET. It is worth noting that unsubstituted imidazole, which was not tested until now for trans-esterification reactions is very effective for the glycolytic depolymerization of PET wastes. This is a promising result, since imidazole is an inexpensive catalyst and the glycolysis reactions occurs within 2 h with a high selectivity in **bis**-2-hydroxyethyl terephthalate (BHET) (~ 91%). However, the disadvantage of this catalyst appears from the fact that unlike others, it can not be recovered and reused, being solubilized in water used during the work-up procedure.

The obtained results are grouped by the destruction temperature: the amidinic bases and TBD have a shorter destruction time than the other three nitrogen bases, while the BHET content destruction time differs substantially (entry 1 compared with entry 2 and 3).

The other three bases lead to the same content of BHET, but the destruction time differs substantially (Entry 4-6). The colour of the obtained product is affected by the catalysts. In the presence of DMAP the precipitate is withe coloured, in the case of ImA the product is white-off colour,

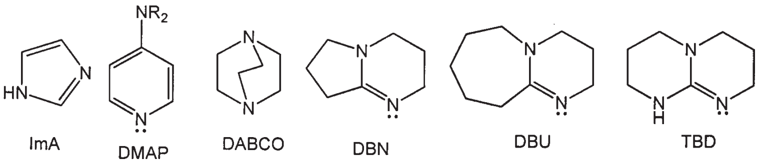

Fig. 4. Various nitrogen bases screened for glycolytic depolymerization of PET.

Table 1
GLYCOLYSIS WITH EG OF PET WASTE USING DIFFERENT NITROGEN BASES IN 10 % LOADING

Entry	Catalyst	Reaction time (min)	BHET conversion (%)	Oligomers (%)
1	TBD	30	89.5	10.5
2	DBU	13	97.9	2.1
3	DBN	14	97.2	2.8
4	DMAP	60	91.9	8.1
5	DABCO	80	91.3	8.7
6	ImA	120	90.5	9.5

for DBN, DBU and TBD the compound presented a beige colour and a dark brown colour when DABCO catalyzed the glycolysis reaction.

Other parameters dependence of PET glycolysis reaction

There were first investigated the effects of PET/EG molar ratio on the glycolytic conversion and selectivity in BHET using 5% 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) as catalyst in order to determine an optimum working protocol (table 2). Thus, with a very small excess of EG, the depolymerization occurs with around 50% conversion in *bis*-2-hydroxyethyl terephthalate (BHET), in more than 4 h (table 2, entry 1). Increasing the amount of EG lead to a decrease of reaction time accompanied by increasing conversion in BHET monomer with quantitative transformation in less than an hour when a large excess of glycolytic agent is used (table 2, entry 5). The selectivity of BHET formation for a PET/EG ratio of 1/10 is considered as an optimum ratio, since the monomer formation is around 90 % for a reaction time of 1 h. A prolonged reaction time is not desirable because BHET can further polymerize into dimmer or higher oligomers in the presence of excess of ethylene glycol.

Further, it was investigated the influence of the reaction temperature on the efficiency of the organic catalyst for the established PET / EG molar ratio of 1/10 in the presence of 5% organic catalyst, 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), respectively (table 3). Analysis of the data reveals that by decreasing the reaction temperature, longer period of time is required for glycolytic depolymerization. This decrease, however, is not parallel in the two studied cases; if amidine catalyst is used, namely DBU, the conversion decrease is slower than for TBD-catalyzed reactions. Thus, amidine-based organic catalysts showed higher performance than guanidine-based catalyst in glycolysis of PET wastes. However, comparison with metal-catalyzed glycolysis of PET highlights the significant improvement of the catalytic efficiency, since titanium(IV) isopropoxide catalyzed the depolymerisation of PET at 220°C in minimum 3 h of reaction time [51].

Further on, comparative studies on various type of PET wastes were carried out using two commercial catalysts: 1,5-diazabicyclo [4.3.0] non-5-ene (DBN) and 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD). In all cases, the reaction was monitored by NMR spectroscopy, the results of this screening conducted on different types of PET wastes are presented in table 4.

For a better assessment of organic catalyst efficiency the glycolysis of PET waste was performed with various glycols. Analysis of these data (table 5) highlights the versatility of the organocatalytic system for various glycols.

Table 2
DEPENDENCE OF PET GLYCOLYSIS ON PET/EG RATIO USING 5 % 1,8-DIAZABICYCLO [5.4.0] UNDEC-7-ENE (DBU) CATALYST.

Entry.	PET/EG ratio	Time (hours)	BHET (%)
1.	1/1.5	4.25	50
2.	1/5.0	2.50	80
3.	1/10	1.00	90
4.	1/15	0.75	95
5.	1/20	0.90	98

Table 3
TEMPERATURE DEPENDENCE OF PET GLYCOLYSIS WITH 5 % CATALYST LOADING

Temp (°C)	Reaction time (minutes)	
	TBD	DBU
190	60	25
180	150	45
170	350	80

Table 4
GLYCOLYSIS WITH EG OF VARIOUS TYPE OF PET WASTES SCREENED BY ORGANOCATALYSIS

Nr.	Type of PET waste	Catalyst	Time (min)	BHET[c] %	Work-up procedure
1	PET-I flakes$_a$	0.5 % $Ti(OiPr)_4$	180	92/92	EG distilation[d];85/130°C/2h
2	PET-II powder[a]	5 % TBD	60	90	-
3	PET-III powder[a]	5 % TBD	660	90	-
4	PET-V flakes[a]	10 % DBN	300	95/60	EG distilation[d]; 85/130°C / 3h
5	PET-IV flakes[a]	10 % DBN	200	95/80	EG distilation[d]; 85/130°C / 2h
6	PET-I flakes[a]	10 % DBU	50	97/90	EG distilation[d];85/110°C / 2h
7	PET-I flakes[a]	10 % DBN	60	95/93	1.washing with H_2O; 2. filtration[e]
8	PET-I flakes[a]	10 % DBU	50	97/93	1.washing with H_2O[f]; 2. filtration[e]
9	PET-I flakes[a]	10 % DMAP	120	88/86	1.washing with H_2O[f]; 2. filtration[e]
10	PET-I flakes[a]	10 % DABCO	180	88/86	1.washing with H_2O[f]; 2. filtration[e]
11	PET-I flakes[a]	10 % ImA	210	88/86	1.washing with H_2O[f]; 2. filtration[e]
12	PET-VII[b]	10 % DBN	180	95/85	1.filtration[g];2.distilation[d]85/110°C
13	PET- VIII[b]	10 % DBN	180	99	1.filtration[h];2.distilation 85/110°C

[a] PET/EG = 10/1; [b] PET/EG = 50/1; [c]determined by NMR/before/after workup; [d]b.p./bath temperature/ EG at 2 mmHg; [e]yield 70-75 %; [f]contains only BHET; [g] about 10 % inorganic solid; [h] qauntitative recovery of cotton/80% recovery of PET content

Table 5
ORGANOCATALYZED DEPOLYMERIZATION OF PET WASTE WITH VARIOUS GLYCOLS

Glycol	PET/glycol	Catalyst	Reaction time (hours)
1,2 propilen glicol	1/15	10 % DBU	1.0
1,3 propilen glicol	1/15	10 % DBU	1.5
dietilen glicol	1/10	10 % DBU	0.5
isosorbid	1/10	10 % DBU	1.0
isosorbid	1/1a	10 % DBU	2.0
isosorbid	1/2b	5 % TBD	3.0

[a] embedded IS 80%, [b] embedded IS about 50%.

The reaction time necessary to obtain the glycolyzed products decreases with increasing the molecular weight of glycol.

As polyester polyols are desired based on isosorbide, the glycolysis reaction was performed also with isosorbid using an amidine based catalyst - 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU). Because our final goal is to obtain polyester polyols with rigid structure for polyurethane foams, we involve isosorbide diol in the repolymerisation process. In order to use no excess of isosorbide (IS), the PET was previously glycolyzed with EG and then transesterified with IS. The reaction was performed under vacuum distillation and the temperature increased gradually from 130 to 190°C. If the molar ratio of PET/IS is 1:1 the IS is better embedded in the polymeric structure and the reaction product is favoured while for a ratio of 1:2 the reaction is accompanied by repolymerization of the terephthalate. This last method is preferred because it is avoided the use of excess of glycols which due to high boiling points are difficult to be removed during the working process.

Conclusions

Several nitrogen-based organic catalysts were screened for the glycolytic depolymerisation of various types of PET waste. In general, using short-chain diols for the glycolysis, amidine based catalysts proved to be the best choice. For example, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) performed the glycolytic depolymerization with outstanding selectivity in bis-2-hydroxyethyl terephthalate (BHET) for a PET/EG molar ratio of 1/10 at 190°C in less than 3 h. It is worth noting that unsubstituted imidazole, which was not tested until now for trans-esterification reactions is very effective for the glycolytic depolymerization of PET wastes. This is a promising result, since imidazole is an inexpensive catalyst and the glycolysis reactions occurs within 2 h with a high selectivity in bis-2-hydroxyethyl terephthalate (BHET) (~ 91%). In all cases, the organic catalysts are more efficient than the metal salts, the glycolytic depolymerization of PET being accomplished in a shorter period of time at much lower temperature.

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