Mechanistic Investigations of the Organocatalytic Depolymerization of PET Waste with Isosorbide

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Glycolysis of PET waste with isosorbide, a biomass derived diol, was catalyzed by commercially available 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD) at temperature up to 190°C when low molecular weight oligomer containing at least one equivalent of isosorbide was obtained. The structural assignment of the oligomer product was established by NMR spectroscopy showing predominantly end-chain bonded isosorbide with exo/endo ratio of 55/45. Mechanistic considerations of the transesterification reaction of isosorbide with dimethylterephthalate (DMT) as model reaction revealed that the hydrogen bonding interaction of TBD with this diol is the favored mechanism pathway. This was established by corroborating solution NMR spectroscopy studies with DFT calculations at B3LYP level where it was observed that isosorbide is hydrogen bonded to TBD through both endo and exo hydroxyl groups. On the other hand, the TBD catalyst reacts with dimethylterephthalate at low temperature forming a stable, easy to handle covalently bonded adduct.

Keywords: PET waste; isosorbide; organocatalysis; transesterification

Polyethylene terephthalate (PET) is a thermoplastic polyester being one of the most commonly used consumer plastic in the world [1]. Due to the fact that it is not biodegradable, the increased consumption of PET led to a significant accumulation of waste into land field; thereby the recycling of PET waste represents a major concern for the scientific community. Among the different recycling techniques, chemical recycling is particularly interesting since it allows controlled cleavage of the polymer with isolation of the pure monomers that can be reused either in the PET manufacture or to obtain other valuable polymers for industrial applications [2-4]. Glycolysis is considered to be the versatile chemical method on the grounds that, besides monomer formation, oligomeric products such as aromatic polyester-polyols can be produced [3-5] which are starting materials in the polyurethane industry [6,7]. The glycolysis of PET is considered a transesterification reaction, reason why metal salts are often used as catalysts [1,8-12] with major drawbacks, such as harsh reaction conditions and metal contaminated final products [13]. The feasibility of the chemolytic depolymerization of PET waste was improved using organocatalysts that perform at lower temperature. For example, Wang et al. used urea as a green, low priced catalyst for the glycolysis of PET wastes under mild conditions [14], whereas ionic liquids have the potential to substitute the metal-catalysts for depolymerization of PET under lower pressure and temperature, with no emission of toxic substances [15-18]. Additionally, under special conditions, these latter mentioned organocatalysts can be converted into N-heterocyclic carbenes which are capable to perform the depolymerization of PET at 80 - 90°C [19]. Efficient glycolytic depolymerization of PET was also reported for guanidine catalysts, especially bifunctional guanidine-based organocatalysts [20].

The use of polymers and/or depolymerization agents derived from renewable resources makes the chemical recycling of polymeric materials even more attractive. Isosorbide is a chiral diol isolated from the cereals extracted starch *via* enzymatic reduction of glucose to sorbitol and subsequent dehydration [21]. The use of this diol in polymers synthesis is based upon its rigid structure, suitable for the preparation of polyester-polyols, precursors for production of polyurethane rigid foams [22]. The main problem that limits the use of isosorbide as depolymerizing agent is related to the low reactivity of the secondary alcohol groups [23]. The preparation of polyterephthalates containing isosorbide is less investigated and uses as starting materials terephthalic acid dichloride in order to compensate the low reactivity of the diol [24]. Instead, the esterification with dimethylterephthalate was reported to occur at 250 °C using $Ti(OBu)_4$ as catalyst, temperature at which isosorbide is coloured if exposed for long time [25].

We have previously reported on the use of isosorbide as glycolysis reagent of PET waste under both metal and organic catalysis [26,27]. Herein, we extended our research towards depolymerization of PET waste with isosorbide by mechanistic investigations of the reactivity of this diol with dimethylterephthalate (DMT), a monomer formed by chemical scission of the PET polymer. The binding mode of the diol was assigned by NMR spectroscopy where different resonances were attributed to varied structural content of the oligomers [28,29]. Further on, the transesterification reaction of dimethyl terephthalate with isosorbide was chosen as model reaction and investigated in solution and by DFT calculations. Through this mechanistic considerations it has been observed that a

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covalent-bonded adduct is formed during the catalytic reaction between the TBD catalyst and the ester (DMT); this adduct being the real catalyst of the depolymerization reaction.

Experimental part

Materials and instruments

The synthesis reactions were carried out under inert atmosphere. All reagents were used as received, except were specified. PET waste was obtained from post-consumer bottles and cut into small flakes and cleaned thoroughly by washing with water containing detergent and then with distilled water. The cleaned PET waste flakes were dried at 80 °C for several hours prior to use. 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), ethylene glycol (EG; anhydrous, 99.8%), and solvents were purchased from Sigma-Aldrich and used as received. All Nuclear Magnetic Resonance (^{1}H and ^{13}C NMR) measurements were recorded on Bruker 300 and 500 MHz spectrometers, at room temperature in deuterated solvents: benzene-d6 (C_6D_6), chloroform-d ($CDCl_3$), CD_3COOD and deuterated dimethylsulfoxide (DMSO-d_6). Mass spectrometry was performed using Varian 1200L Triple Quadrupole LC/MS/MS spectrometer by direct injection in ESI mode. Melting points were determined with Koehler Automatic Melting Point Range Apparatus (K90190). FTIR spectra were acquired with a Bruker Vertex 70 Spectrometer, with a horizontal device for attenuated reflectance and diamond crystal, on a spectral window ranging from 4000 to 400 cm^{-1}.

Glycolysis of PET with isosorbide (IS)

A two-necked round-bottom flask (25 mL) equipped with argon inlet, reflux condenser and drying tube was charged with finely cut PET waste (0.96 g, 5.0 mmol), TBD (69.5 mg, 0.5 mmol) and isosorbide (5.0 to 150.0 mmol). The resulting mixture was purged with argon and immersed in an oil bath heated at 190 °C and stirred for various time (fig. 1). The structural assignment of the resulting oligomers was established by NMR spectroscopy with isosorbide bonded predominantly as end-chain in *exo*/*endo* ratio of 55/45. The excess of isosorbide and the resulting ethylene glycol were removed by three successive extractions with boiling water resulting brown powder after drying (0.95 g, ~ 70 % yield). The washing water solutions were worked-up for possible catalyst recycling. Thus, after water removal under reduced pressure, 1.2 g of semisolid compound was separated containing isosorbide as major compound alongside with TBD and traces of terephthalate according to ^{1}H-NMR spectrum. This semisolid product is subsequently reacted with PET waste and additional amount of isosorbide for an established PET/IS ratio and the reaction runs as described above. By comparison to virgin catalyst, this reaction occurs much slower, the depolymerization of PET occurring in doubled reaction time.

Transesterification reaction of dimethylterephthalate (DMT) with isosorbide

In a 25 mL pear shaped flask equipped with oil bubbler and argon inlet there were introduced DMT (0.97 g, 5.0 mmol), TBD (69.5 mg, 0.5 mmol) and isosorbide (1 or 2 equivalents). The resulting mixture was purged with Argon and immersed in an oil bath heated at 190 °C with stirring. On the upper part of the reaction flask a white crystalline solid consisting of equimolecular amount of DMT and isosorbide (^{1}H-NMR analysis) is deposited. Thus, periodically with a spatula this solid is re-introduced in the reaction flask until four hours period is reached. The color of the reaction mixture is darkening and the resulting product is analyzed by NMR spectroscopy showing oligomers containing IS end-groups (40.7 %) and interchain bonded IS (20.5 %) with a conversion of 68.5 %.

^{1}H-NMR investigations of the hydrogen bonding interactions

Since isosorbide (IS) has a low solubility in C_6D_6, the concentrations of the reactants were established in accordance with the amount of IS brought in the solution. Thus, we prepared stock solutions by dissolving certain amounts of IS (7.3 mg, 0.05 mmol), TBD (7.0 mg, 0.05 mmol) and DMT (9.6 mg, 0.05 mmol) in C_6D_6 (1 mL). Then equimolar mixed samples (IS+TBD, DMT+TBD, and IS+TBD+DMT) combining 0.3 ml of each stock solution are formulated. The blank samples are prepared from 0.3 ml of the stock solution and 0.3 mL of C_6D_6.

Synthesis of covalently bonded TBD-DMT adduct- methyl 4-(2,3,4,6,7,8-hexahydro-1H-pyrimido[1,2-a]pyrimidine-1-carbonyl) benzoate, 1

To a solution of TBD (2.16 g, 15.54 mmol) in hot benzene (25 mL), DMT (3.01 g, 15.54 mmol) dissolved in hot benzene (25 mL) was added. The resulting mixture was stirred and sporadically heated for 30 minutes, then left at room temperature overnight. The white-crystalline formed compound is filtered off. There were obtained 3.92 g, ~ 84 %, m. p. 230-231 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.09 (d_{AB}, 2H, J = 6Hz, H^a), 8.01 (d_{AB}, 2H, J = 6 Hz, H^b), 3.89 (s, 3H, OCH_3), 3.35 (t, 4H, J = 6 Hz, CH_2^c), 3.25 (t, 4H, J = 6 Hz, CH_2^d), 1.99 (m, 4H, CH_2^e) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 173.42 (CO-OMe), 167.20 (CO-NH), 151.68 (Cq), 142.33 (Cq), 130.98 (Cq), 129,13 (C^a), 128.99 (C^b), 51.99 (CH_3), 46.86 (C^c), 37.59 (C^d), 20.94 (C^e) ppm; FT-IR (ATR) : ν = 2948 (m), 2870 (s), 2756 (w), 1712 (s; COOMe), 1652(s; amide), 1558 (m, C=N-guanidine), 1371 (s), 1277 (s) cm^{-1}; ESI-MS positive mode (m/z (%)): 340 (65) [M+K], 162 (20), 140 (100) [TBD$^+$], 112 (30).

Results and disscussions

Organocatalytic glycolysis of PET wastes with isosorbide at high temperature

We first performed the depolymerization reactions of PET waste with isosorbide (IS) using commercially available 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD) as catalyst. Based on previous reports on other glycols, the reaction was carried out under inert atmosphere and humidity protection at 190°C for different PET/IS molar ratios, using 10 mol % catalyst loading. Under these conditions, there were obtained coloured products for which the visual disappearance of the PET flakes could not be clearly observed. In addition, due to the lower reactivity of the secondary alcohol groups of isosorbide [30], the reaction protocol, i.e time and reagents ratio were established by successive runs performed at various period of time (fig. 1). The conversion was determined by dissolving the reaction product in chloroform, followed by filtration and drying of the residual PET.

For equimolar PET/IS reaction, the glycolysis of the polymer is achieved within 6 h at 190°C. Increasing the amount of isosorbide does not shorten the depolymerization reaction time, the complete conversion of PET polymers occurring within 7 - 8 h for 1/2 ratio or 10 h for 1/10 molar ratio (fig. 1). The conversion was calculated using the following equation:

$$\text{conversion (\%)} = (w_0\text{-}w)/w_0 \times 100\ \%$$

where w_0 is the initial weight of PET flakes and w is the recovered, unreacted PET.

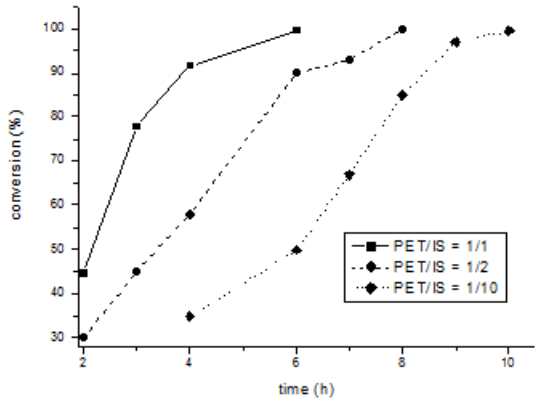
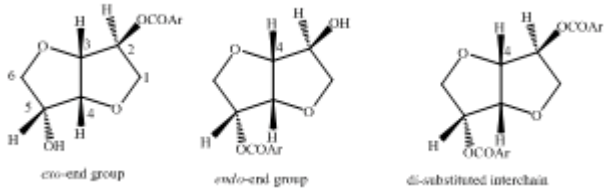


Fig. 1. Monitorization of the glycolysis of PET wastes with isosorbide

The isosorbide-mediated glycolysis of PET waste supposes the replacement of bonded ethylene glycol by isosorbide resulting in oligomers containing *exo* and *endo* IS at chain terminating positions, along side with interchain bonded and free IS. The structural assignment of the glycolizate was established by NMR spectroscopy and a detail of the aliphatic area of both ^{1}H and ^{13}C NMR spectra are shown in figure 2. For isosorbide (IS) (signals shown with ○ in fig. 2-top) bonding assignment (scheme 1), based on similar literature reports [28, 29], the following signals were carefully analyzed:



Scheme 1. Chemical structures of the exo, endo and di-substituted isosorbide

i) the protons at the position 4 are identified as three distinct, well resolved signals assigned as: 5.08 ppm for di-substituted IS; 4.97 ppm for *endo*-substituted IS and 4.72 ppm attributed to *exo*-bonded IS.

ii) the C*H*-OAr signals are observed at 5.39-5.47 ppm from which the proton in *endo*-substituted IS is well defined, whereas for *exo*- and di-substituted IS, the protons show overlay of the signals. The *exo*-substituted IS was determined by subtraction from these C*H*-OAr integrals the C*H*-4 protons of *endo*-substituted IS and twice the protons corresponding to the di-substituted IS, respectively. The free IS shows two distinctive signals at 4.3-4.2 and 3.5 ppm.

Moreover, the ethylene glycol (EG) signals (shown as □ in fig. 2-top) are as follows: 3.69 ppm corresponding to free EG, whereas the bonded EG resonate at 4.47 ppm for end-chain group and 4.69 ppm for interchain bonded EG. The bonded EG is determined by subtractions from the total integration area of aliphatic protons of the isosorbide signals and those of the free ethylene glycol signal.

All these assignments are supported by ^{13}C NMR spectroscopy (fig. 2 - bottom) where, the IS signals are well defined, especially for the 4 and 3 positions. Each bonding position gives four clear signals; from 88.3 to 85.55 ppm for the *exo*/*endo* at position 4 and 82.0 to 80.5 ppm

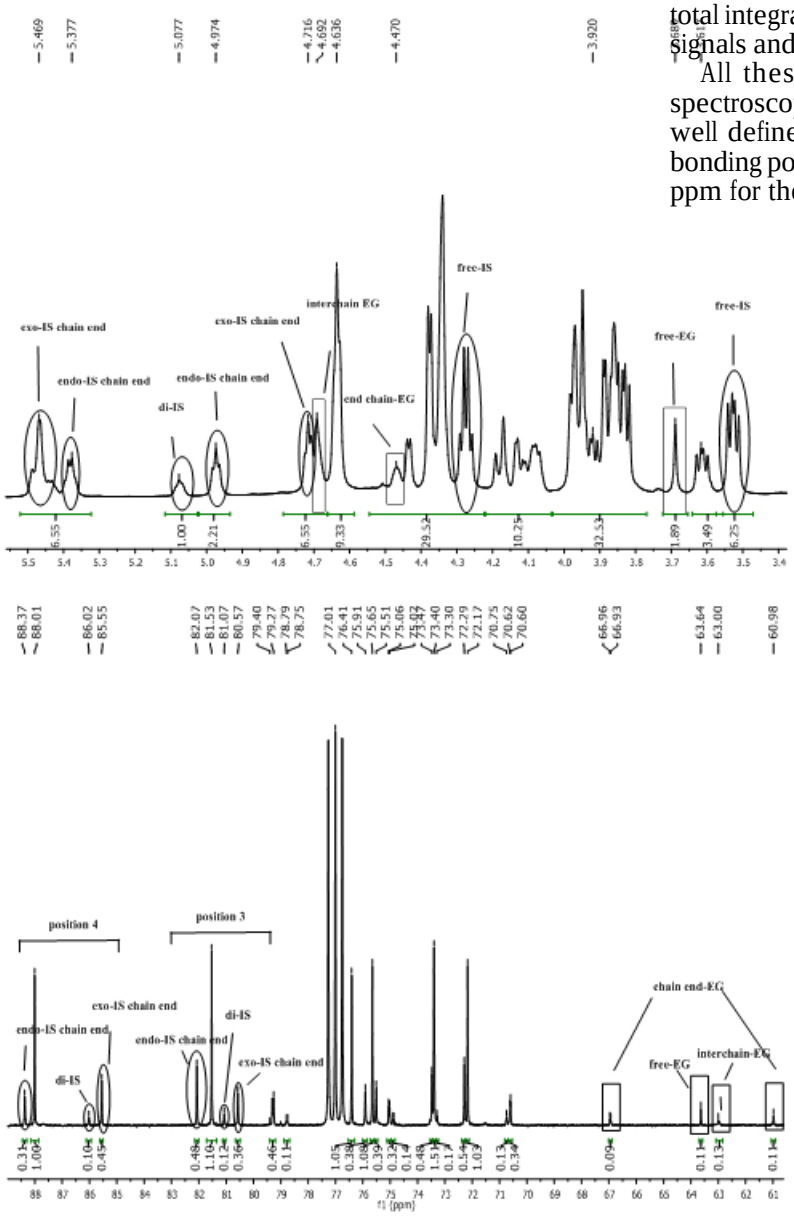


Fig. 2. ^{1}H-NMR (top) and ^{13}C-NMR (bottom) spectra of the oligomers formed by glycolysis of PET waste with isosorbide (detail of the aliphatic area)

for the position 3 of IS (signals marked with in figure 2 - bottom). The di-substituted IS shows signals at 86.0 and 81.5 ppm and the intense signals correspond to free IS. The EG signals are well defined in ^{13}C-NMR (marked with ¡% in figure 2-bottom) with the end-chain bonded EG signal appearing at 66.9 and 60.9 ppm, whereas interchain EG is at 63.0 ppm and free EG resonate at 63.6 ppm.

Next, in order to gain a deeper insight into the reaction mechanism, we performed the transesterification reaction of dimethylterephthalate (DMT) with isosorbide in 1/2 ratio using TBD as catalyst. The reaction needs special attention due to sublimation of the reagents which has to be kept in the reaction molten mixture during development. However, a conversion of 68.5% was recorded, the resulting oligomers containing IS end-groups (40.7 %) and interchain bonded IS (20.5 %). This reaction was used as model reaction for mechanistic investigations, both in solution and by DFT and it will be further discussed.

Transesterification reaction of dimethyl terephthalate with isosorbide

^{1}H-NMR investigation of the reaction at low temperature

Despite the numerous reports using guanidine-based catalysts [31-37], there have been few mechanistic studies dedicated to a deeper understanding of the activity of this compound in polymer science [20,35-37]. Two mechanism pathways were considered: i) covalent bonded ester to the catalyst, with subsequent breakage of the amide bound before addition of the alcohol and ii) hydrogen bonding interaction between the catalyst and the reactants. Later, Hedrick et al. reported the computational studied on the TBD-catalyzed methanolysis involving dimethylterephthalate [36] and the trans-esterification reaction of methyl acrylate with benzyl alcohol [37]. Depending on the nature of the ester and the alcohol, both or only one mechanism pathway was reported as possible.

The ^{1}H-NMR spectrum of the isosorbide contains signals characteristic to its –CH_2 and –CH protons in the expected region (fig. 3, top). For the OH groups, in accordance with their orientation, *exo* and *endo* respectively, two sets of doublets are observed. The *endo* hydroxyl group, involved in the strong intramolecular hydrogen bonding interaction resonates at 2.50 ppm with a coupling constant of 7.2 Hz. This is due to the *trans* orientation with respect to the C-O bond of the hydroxyl proton and the vicinal C-H proton. In the case of *exo* hydroxyl, the doublet is located at 0.82 ppm with a smaller coupling constant (4.2 Hz) owing to the random orientation of this proton. In a 1: 1 mixture with TBD (fig. 3, middle), the formation of the hydrogen bonded complex occurred. Specifically, a significant shift of the NH proton from 4.73 ppm in the free TBD to 4.04 ppm is observed in the hydrogen bonded adduct. This broad signal corresponds to 3H meaning that, the hydroxyl protons of isosorbide are also contained in the new signal that is upfield shifted upon formation of the hydrogen bonded adduct. This is also confirmed by the disappearance of the doublet signals observed at lower frequency in the ^{1}H-NMR spectrum of the free isosorbide. In addition, the CH_2- and CH- proton resonances of the isosorbide molecule also show a small degree of shielding as compared to their chemical shifts in the free diol (fig. 3).

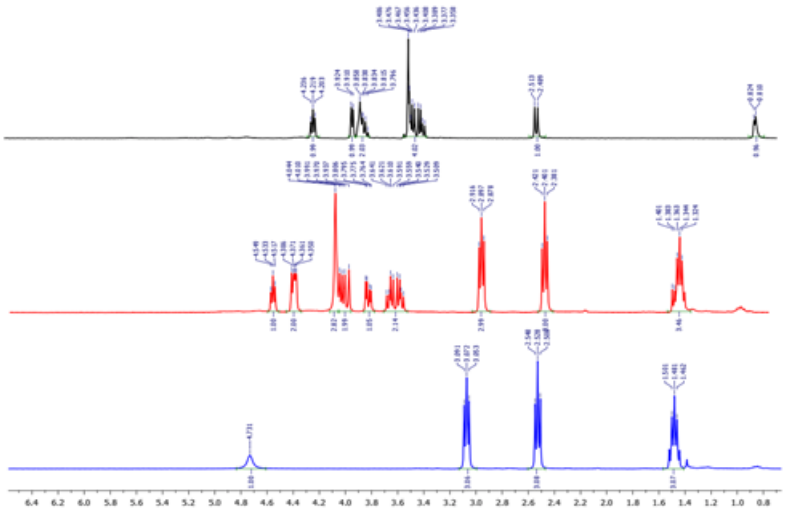


Fig.3. ^{1}H-NMR spectra of isosorbide (IS) (top); TBD: IS hydrogen bonded complex (middle); 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD) (bottom).

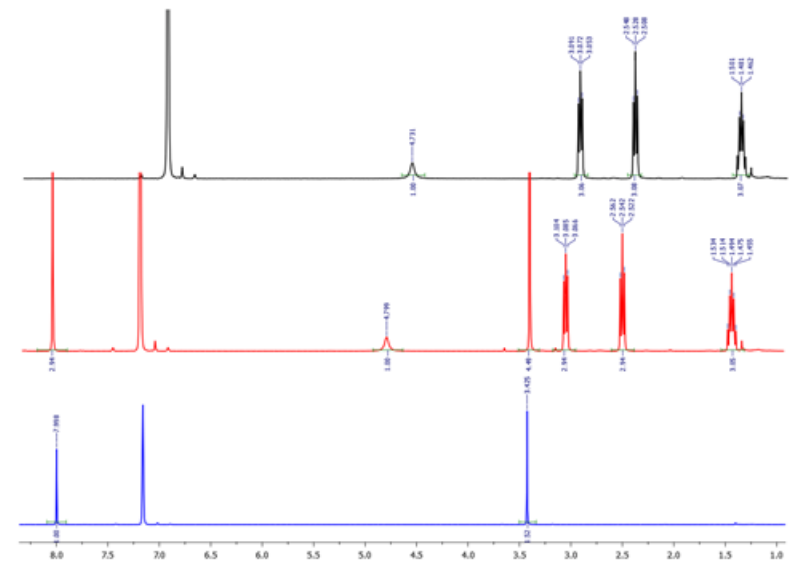
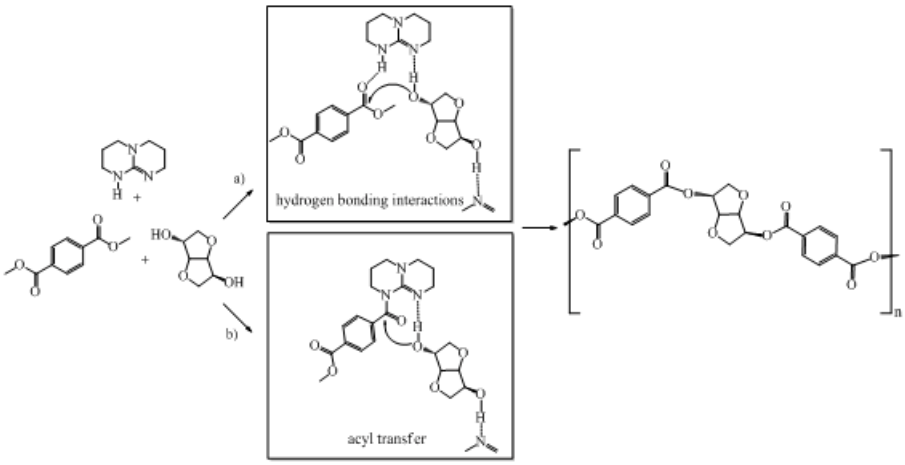


Fig. 4. ^{1}H-NMR spectra of TBD (top); TBD-DMT hydrogen bonded complex (middle); dimethylterephthalate (DMT) (bottom).



Scheme 2. Proposed mechanism pathways of the TBD-catalyzed transesterification reaction of dimethylterephthalate with isosorbide.

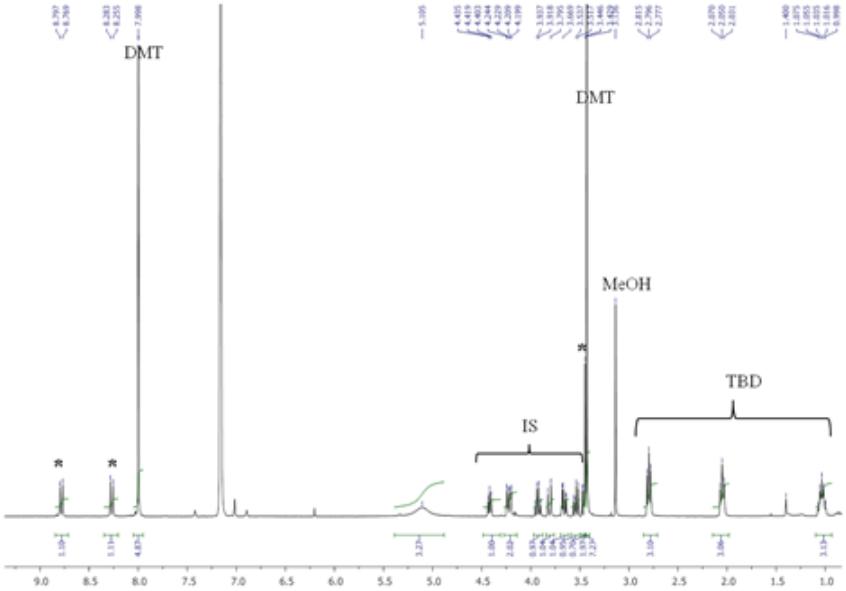
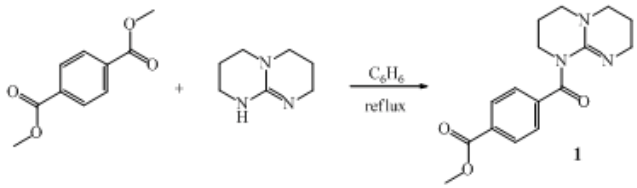


Fig. 5. ^{1}H-NMR spectrum of equimolecular mixture of isosorbide: dimethyl terephtalate: 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD) in C_6D_6 at room temperature recorded after 48 h; the new signals are marked with *

In the case of the second possible binary complex formation, the hydrogen bonding interaction between equimolecular amounts of TBD and DMT was firstly monitored at room temperature. The NH proton of the cyclic guanidine is only 0.07 ppm upfield shifted, whereas the aromatic and the alkyl protons of both reactants are not influenced by this weak association (fig. 4). Comparison of the two hydrogen bonded complexes reveals an activation of isosorbide by the catalyst which subsequently is labile for transesterification reaction with dimethyl-terephthalate (scheme 2, route a).

If the three components are mixed in deuterated benzene at room temperature, new signals are observed after 24 h at room. The ^{1}H-NMR spectrum of the ternary complex shows two new doublet signals in the aromatic region centered at 8.78 (J = 8.4 Hz) and 8.26 (J = 8.4 Hz) ppm (fig. 5) in around 22 % yield which is increasing at 31 % after other 48 h. Moreover, small shifts of the TBD were recorded alongside with the appearance of a singlet at 3.16 ppm assigned to the methyl protons of resulting methanol. Analysis of the ^{13}C-NMR spectrum of the ternary adduct after 48 hours revealed the splitting of the carbonyl group of DMT (initially observed at 165.9 ppm) into two new signals at 166.9 and 173.2 ppm. The structure of this new compound was attributed to the formation of the covalently bonded TBD-DMT adduct, **1** (scheme 3). In order to confirm this interpretation, we performed the reaction of DMT with TBD in refluxing benzene with continuous removal of the resulting methanol, when **1** is isolated in high yield (~ 84 %) (scheme 3).



Scheme 3. Synthesis of the monoamide-monoester (methyl 4-(2,3,4,6,7,8-hexahydro-1H-pyrimido[1,2-a]pyrimidine-1-carbonyl)benzoate), **1**

The ^{1}H-NMR spectrum in $CDCl_3$ is similar with the one discussed above, namely the terephthale protons as AB type quartet at 8.01 and 8.08 ppm, singlet signal characteristic for the methyl protons of the ester group at 3.98 ppm and TBD resonances as three multiplets at 1.99, 3.25 and 3.35 ppm. The NMR signals of this isolated covalently bonded compound are similar to the one formed in the NMR tube by mixing the three components, differing the chemical shift values due to different used deuterated solvents. Further on, the IR spectrum showed two stretching vibrations for the carbonyl group: one at 1712 (ester) and other at 1652 (amide) cm^{-1}, together with C=N guanidine vibration at 1558 cm^{-1}. The lack of the OH group stretching vibration in the IR spectrum confirms the ester-amide formation.

It can be summarized that, the NMR spectroscopy revealed the formation of two adducts involving hydrogen bonding interactions as well as covalent bonding. The TBD reacts through hydrogen bonding with IS diol as it was

expected, whereas the reaction with DMT occurs through covalent adduct formation even at room temperature and high dilution.

Computational results

To further support this proposed mechanism, we performed DFT calculations at the B3LYP/6-31G level of theory using Gaussian 09 and the PCM solvation model with benzene as a solvent in order to corroborate them with the experimental data. The results are presented in table 1. Molecular modelling of the most stable conformer of isosorbide (1,4:3,6-dianhydrohexitol) showed two *cis*-fused five-membered rings in *V*- form with a OCCO dihedral of 102^0. The hydroxyl at C-2 position is outside the wedge and it is *exo*, whereas the hydroxyl at C-6 position is inside of the wedge shape and is *endo*. The *endo* hydroxylic group is involved in a strong intramolecular hydrogen bonding interaction (fig. 6a), with a calculated H bond distance of 2.102 Å. The H bond energy was calculated from the energies of conformers in figures 6a and b and has a value of -5.84 kcal/mol. The TBD and DMT molecules were also optimized and used as starting points for the adduct descriptions.

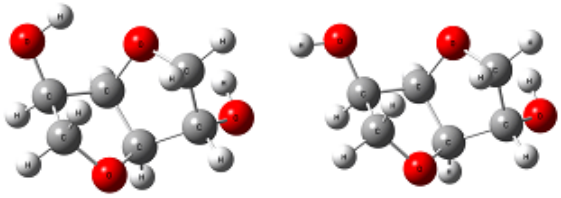


Fig. 6. Optimized geometry of the most stable conformer of isosorbide a) with and b) without the intramolecular H bond

The binary complex formed between isosorbide and TBD revealed that both hydroxyl groups of the diol may be involved in the hydrogen bonding interaction (fig. 7). Apart from this, an N-H…O hydrogen bond is formed, so the energies reported here comprise both these interactions and are calculated relatively to the isosorbide conformer that has not formed the intramolecular H bond (fig. 7b). The *exo* hydroxyl group forms a H bond of 1.568 Å, while the calculated H bond energy is -25.36 kcal/mol. Both values indicate a much stronger H bond than the intramolecular one. When the H bond is formed between TBD and the *endo* hydroxyl in position 6, the adduct formed is less stable by 2.54 kcal/mol, with a H bond energy of -22.81 kcal/mol and a H bond length of 1.585 Å. So the theoretical data show that both hydroxyl groups, *exo* and *endo*, are prone to strong H bond formation in presence of acceptors. From the relative energies of these two conformers, one can see that the most reactive is the *exo* hydroxyl group of isosorbide, which can form a stronger H bond.

Another type of adduct between isosorbide and TBD (noted as 2 in table 1) may be formed, in which the two hydrogens involved in H bonds, i.e. N-H and O-H, are quasi-equivalent and the hydroxyl hydrogen atom is transferred to the TBD molecule that has two NH groups, as can be seen in figure 8. In this case, the H bond distances (both of the type N-H…O) are even smaller, i.e. 1.582 Å (1.600 Å) for the *exo* adduct and 1.585 Å (1.619 Å) for the *endo* one. The overall H bond energies are -25.19 and -22.39 kcal/mol, respectively. Comparing the relative energies of all the isosorbide-TBD binary adducts, one can see that *exo* is more reactive in both types of adducts, with only 0.16 kcal/mol energy gap between them, meaning that an adduct in which both protons are quasi-equivalent (and as such could have the same chemical shift) is very probable.

We also modeled the DMT-TBD hydrogen bonded adduct and the covalent one as monoamide-monoester **1**, in order to have a clue on their energetics and on the

Table 1

CALCULATED H BOND ENERGIES AND RELATIVE ENERGIES (kcal/mol)

Molecule/adduct	**Interaction energy**	Relative energy
Isosorbide	-5.84	-
Isosorbide OH *exo* - TBD	-25.36	0.00
Isosorbide OH *endo*-TBD	-22.81	2.54
Isosorbide OH *exo* – TBD (2)	-25.19	0.16
Isosorbide OH *endo*-TBD (2)	-22.39	2.97
TBD-DMT	-7.84	0.00
1 + MeOH	-10.94	9.81
Isosorbide-TBD-DMT *exo*	-32.43	0.00
Isosorbide-TBD-DMT *endo*	-27.26	5.17
Acyl transfer adduct *exo* + MeOH	-16.45	28.90
Acyl transfer adduct *endo* + MeOH	-13.38	31.97

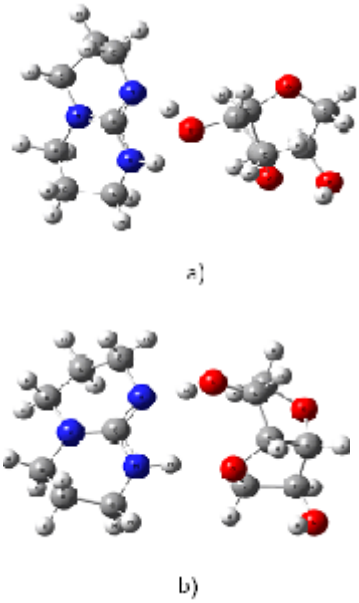


Fig. 7. Optimized geometries of adducts of isosorbide with TBD when a) *exo* and b) *endo* hydroxyl groups form an intermolecular H bond

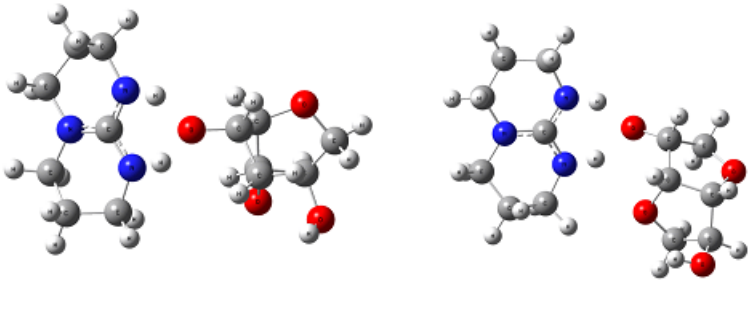


Fig. 8. Optimized geometries of adducts of isosorbide with TBD when a) *exo* and b) *endo* hydroxyl groups form an intermolecular H bond. The N-H and O-H hydrogens are quasi-equivalent.

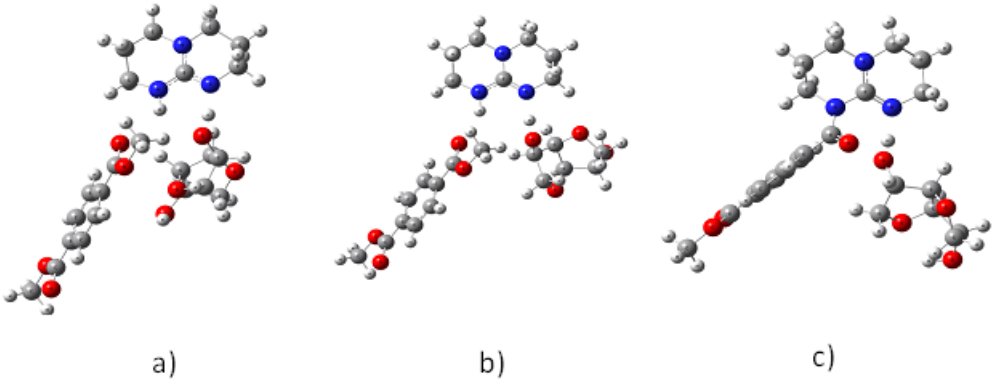


Fig. 9. Ternary isosorbide-TBD-DMT adducts in which the isosorbide OH forming the H bond is a) *exo*; b) *endo* and c) the most stable acyl transfer adduct

prevalence of the hydrogen bonding or acyl transfer mechanisms shown in scheme 2. The adduct between **1** and methanol is 9.81 kcal/mol higher in energy than the DMT-TBD hydrogen bonded adduct, favoring mechanism a) in scheme 2, as assumed on experimental grounds. Looking at scheme 2, one can see there are two alternative intermediates that form on mechanism a) and b), herein denoted as ternary adducts. In order to compare their energy, the energy of one methanol molecule must be added to the *acyl transfer* intermediate. For mechanism a), both OH *exo* and *endo* from isosorbide were considered as H bond donors, forming OH…N H bonds of 1.519 and 1.533 Å, respectively, while the NH…O one is 2.343 and 2.006 Å, respectively. The most stable ternary adduct corresponds to OH *exo* (fig. 9a), as can be seen from the relative energies in table 1. The most stable acyl transfer adduct (*exo* again), with the geometry in figure 9c, is no less than 28.90 kcal/mol higher in energy than the hydrogen bonding interactions adduct, meaning that mechanism a) is more probable than b) in agreement with the experimental observations.

Conclusions

The depolymerization of PET waste is effectively catalyzed by TBD at 190 °C forming isosorbide-containing aromatic polyester-polyol. Mechanistic investigations using NMR spectroscopy and theoretical studies reveal that TBD is involved in hydrogen bonding interaction with the isosorbide diol involving especially *exo* hydroxyl group of the diol. Instead, TBD reacts with the ester generating a covalently bonded adduct both at room temperature and in refluxing benzene. This interpretation was corroborated with DFT calculations when the acyl transfer adduct is higher in energy than the hydrogen bonding interactions adduct. This covalently-bonded adduct is considerably easy to handle, in contrast to commercially available TBD which is very hygroscopic and suffers ageing upon exposure to carbon dioxide from air. Further explorations of the catalytic potential of this amide-ester in the field of chemical depolymerization of PET wastes are ongoing in our research groups.

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