The concept of environmental sustainability is increasingly used in connection with international standards. Basically, sustainability means working and interacting in ways that do not affect the living systems and the natural resources. The main components of the concept are elimination of wastes, removal of toxic emissions, and finding renewable sources opposed to classical feedstocks.

Polyethylene terephthalate (PET) is an aromatic polyester with excellent thermal and mechanical resistance and outstanding chemical properties, which is used mainly for fibers and packing. Widespread application and non-biodegradability of PET creates huge amounts of waste and, consequently, induces a great interest for recycling this material. Therefore, a key issue nowadays is the PET conversion into reusable products [1]. PET recycling is also important for conservation of oil resources, reduction of greenhouse effect, and energy preservation [2].

According to the principles of sustainable development, chemical recycling is the most acceptable technique for PET because it gives both parent raw materials and secondary value-added products. The chemical structure of PET backbone can be modified using suitable comonomers conferring to the resulting copolyesters targeted properties [6,7].

Various methods for PET recycling were proposed. Among them, chemical recycling can be accomplished by hydrolysis, methanalysis and glycolysis. Using renewable resources as an alternative to standard petrochemicals, comes in the pregnant worldwide trend for manufacture of materials based on biological products [1,2]. The development of biobased chemicals has the potential to reduce the amount of petroleum consumed in the chemical industry and to open new markets to agriculture; 1,4:3,6-dianhydrohexitols are examples of such chemicals. The use of 1,4:3,6-dianhydroisorbitol (isosorbide, IS) in polymers, and more specifically polycondensates, can be motivated by several features: they are rigid molecules, chiral and non-toxic [3]. For this reasons, there are expectations that polymers with high glass transition temperature and/or special optical properties can be synthesized. Isosorbide has been incorporated as a monomer into aliphatic and aromatic polyesters. Copolymers containing isosorbide moieties, ethylene glycol moieties and terephthaloyl moieties have been reported only rarely. They were made by reacting terephthaloyl dichloride in solution with the diol monomers or by melt polycondensation of dimethyl terephthalate, ethylene glycol and isosorbide [4,5].

Significant improvements of copolyesters physicochemical and thermal properties could be achieved by introducing certain amounts of isosorbide moieties along the hydrocarbon chain [3]. In this way, isosorbide derived from renewable resources has become a valuable diol component to be used in synthesis of polyesters suitable for engineering applications. Most probably, the low reactivity of the secondary hydroxyl groups in 1,4:3,6-dianhydrohexitols, prevented so far the approach of PET glycolysis with IS.

Our work presents the results on PET wastes destruction using isosorbide, in comparison with common diols such as EG and PG.

In this study we describe the glycolysis of polyethylene terephthalate (PET) waste with Isosorbide (IS) and we characterize the isolated products. The results are discussed in correlation with glycolysis products achieved using common glycols, such as Ethyleneglycol (EG) and 1,2-Propyleneglycol (PG). It is revealed that oligomer α–ω-bishydroxy-glycolterephthalates are the main products resulting from PET glycolysis process. These were characterized by means of proton nuclear magnetic resonance spectroscopy (1H-NMR), infrared spectroscopy (FTIR) and size exclusion chromatography (SEC). The products resulting from glycolysis experiments were similar and consist in mixtures of glycols (EG together with the glycol involved in destruction) and bishydroxy oligoesters (symmetrical and nonsymmetrical chain ends). Chromatography of acetylated products allowed separation of some products or product clusters.

Keywords: PET waste, glycolysis, renewable resources, isosorbide

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Our work presents the results on PET wastes destruction using isosorbide, in comparison with common diols such as EG and PG.
Experimental part

**Materials**

PET from waste-bottles was used for the degradation process. They were cut in flakes of 6-8 mm, washed with clean water and dried at 100°C in vacuum overnight, reaching a moisture content < 0.2%. The intrinsic viscosity determined (according to ASTM D4603) was of 0.77 dL/g, melting range 254-260°C, lam 2.5-3 mg KOH/g.

Ethylenglycol (EG), Propylyenglycol (PG), Isosorbide (IS), Methylen Chloride (MC), Ethyl Ether (EE), Petroleum Ether (PE), Titanium (IV) butoxyde (TBT) (catalyst) were reagents of reagent grade and were used as received without further purification.

Thin Layer Chromatography (TLC) was performed on Aluminium plates layered with silicagel 60 F254. For column chromatography, silicagel 60 (60 – 200 mesh) from Merck was used.

**Apparatus**

Melting points were measured with a heated plate Boetzius apparatus and the values are not corrected. 1H-NMR spectra were recorded on a Varian Gemini 300BB spectrometer operating at 300 MHz for 1H, using CDCl3 as solvent, at room temperature. Fourier Transform Infrared (FTIR) spectra were recorded with a Bruker: Vertex-70 FTIR, in solid with ATR. Molecular weight distribution of oligoesters was determined by SEC in THF at 25°C.

PET Glycolysis procedure

A round bottom, two necked flask of 250 mL, equipped with a reflux condenser and a nitrogen inlet, was introduced in a thermoregulated heating bath filled with silicon oil and filled with 50 mmol (9.6 g) of PET flakes, 50 or 500 mmol of glycol and 0.25μmol (85 mg) of TBT catalyst. PET destruction took place under continuous magnetically stirring at 210°C, over a period of 8-20 h.

Free glycols removal was performed in two ways:

- by vacuum distillation, at 1-2 mm Hg in case of EG and PG and under 0.1 mm Hg for IS, under nitrogen. In order to avoid any possible repolymerization of the glycolysates, the temperature of the bath did not exceed 130°C. Olygomeric compounds with a residual content of 3-4% glycols were obtained this way. This product crystallizes over time and could be isolated by trituration with ethyl ether and filtration.

- by hot water extraction: this procedure was realized by dropping water into the reaction mass cooled to the 130°C, then by pouring the reaction mass into water, under constant stirring. Monomeric compounds, such as glycolterephthalic acid - glycol, which crystallized on cooling, are obtained, besides free glycols.

Derivatization with acetic anhydride or with p-nitrobenzoyl chloride was performed as follows:

- the acetylation was realized by dissolving about 1g of product in 10 mL methylene chloride, followed by addition of 1 mL of acetic anhydride and 2 mL triethylamine. The mixture was stirred overnight at room temperature, then it was decomposed with 10 mL of water and the layers were separated. The aqueous layer was extracted twice with 10 mL methylene chloride. The organic solutions were washed with a saturated solution of sodium bicarbonate, until neutral reaction, then with brine. The yields varied between 55 and 100%.

- the p-nitrobenzoates were prepared in a similar way, using p-nitrobenzoyl chloride instead of acetic anhydride.

Chromatography of the acetylated glycolysates

The acetylated product (about 1g) dissolved in ethyl ether or methylene chloride was laid down on a double amount of silicagel (about 2g). The column was prepared from 10g silicagel in petroleum ether, then the laid down probe was deposited on top of the column and eluted with gradient mixtures of PE/EE then EE/MC. The first eluted are the glycols acetates, then the olygoesters acetates, in order of increasing their molecular weight. Each fraction was analysed by 1H-NMR.

**Isolation and characterization of the glycolysis products**

The following products were isolated from PET glycolysis in EG and PG:

- **Bis-hydroxyterephthalate, BHET**. (1, n=1): white crystals, melting point 110-111°C (lit. m.p. 110°C) [9]; isolated by hot water extraction from the PET glycolysis in excess EG (10:1).

- **1H-NMR (CDCl3): 8.12 (s, 4H, T-H); 4.49 (m, 4H, CH-OT); 3.98 (m, 4H, CH2-OH); 2.40 (bs, 2H, -OH).**

- **Bis-hydroxyterephthalate acetate, BHET-Ac**. 1H-NMR (CDCl3): 8.06 (s, 4H, T-H); 4.56 (m, 4H, CH2-OAc); 4.46 (m, 4H, CH2-OCH2); 2.02 (s, 6H, -CO-CH3).

- **Ethane-1,2-diy bis(2-hydroxyethyl) diterephthalate, 1, n=2;** white crystals, melting point 160-164°C, obtained by hot water extraction from the PET glycolyse with EG, at low molecular ratio (1:5).

- **Ethane-1,2-diy bis(2-acetoxyethyl) diterephthalate, 2,** white crystals, melting point 16-120°C; 1H-NMR (CDCl3): 8.12 (s, 8H, T-H); 4.71 (s, 4H, -CH2-CO- - interchain); 4.54 (m, 4H, CH2-OAc); 4.42 (m, 4H, CH2-OAc); 2.09 (s, 6H, -CO-CH3).

- **Bis-(2-hydroxypropyl) terephthalate, 3,** white crystals, melting point 121-123°C; 1H-NMR (CDCl3): 8.10 (s, 4H, T-H); 4.51 (m, 2H, CH2); 4.37 (m, 4H, -CH2-OH); 1.45 (d, J = 6.1 Hz, 6H, -CH3).

- **1-(Hydroxypropan-2-y1) (2-hydroxypropyl) terephthalate, 4,** white crystals, melting point 149-150°C; 1H-NMR (CDCl3): 8.07 (s, 4H, T-H); 5.41 (m, 1H, CH2); 4.60 (m, 1H, CH2); 4.36 (m, 2H, -CH2-CH2-CO-); 4.12, 3.94 (m, 2H, -CH2-OH); 1.53 (d, J = 6.3 Hz, 3H, -CH3); 1.44 (d, J = 6.1 Hz, -CH3).

The PET glycolysis in IS was followed by acetylation (EE : PE in ratio 1:1) consisted in three components which were isolated by distillation:

- **Ethyleneglycol diacetate;** b.p. 110-111°C / 60 - 70 mm Hg; 1H-NMR (CDCl3): 4.26 (s, 4H, -CO-CH2-CH2-); 1.95 (s, 6H, -CO-CH3).

- **Isosorbide diacetate;** b.p. 157 - 165°C / 0.5 mm Hg; m.p. 55 - 60°C; 1H-NMR (CDCl3): 4.95 - 5.05 (m, 2H, -CH2-O); 4.64 (m, 1H, -CH2-CH2-); 3.41 (m, 1H, -CH2-OCH2); 3.79 (bs, 2H, -CH2); 3.79 - 3.77, 3.57 - 3.63 (m, 2H, CH2); 1.97 (s, 3H, -CO-CH3); 1.93 (s, 3H, -CO-CH3).

The residue consists mainly in BHET.

From the second eluted fraction (with EE), two compounds were isolated by preparative TLC:

- **4-(6-acetoxy-hexahydro-furo[3,2-b]-furan-3-yl) terephthalate, 5,** viscous oil; 1H-NMR (CDCl3): 8.05, 8.03 (two singlets, 4H, T-H); 5.32 - 5.40 (m, 1H, -CH2-OT); 5.04 - 5.16 (m, 1H, -CH2-OAc); 4.85 - 4.93 (m, 1H, -CH2-CH2-OAc); 4.46 (m, 2H, -CH2-OT); 4.41 (m, 1H, -CH2-OAc); 4.36 (m, 2H, -CH2-CH2-OAc); 1.90 (s, 6H, -CO-CH3).

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Bis-(6-acetoxy-hexahydro-furo[3,2-b]furan-3-yl)terephthalate, 8, viscous oil; \(^1\)H-NMR (CDCl\(_3\)): 8.05, 8.09 \((\text{two singlets, 4H, T-H})\); 5.32 - 5.40 \((\text{m, 1H, -C\(_\text{H}\)-OT})\); 5.15 - 5.25 \((\text{m, 2H, -C\(_\text{H}\)-OAc})\); 4.87 - 4.93 \((\text{m, 2H, -C\(_\text{H}\)})\); 4.41 \((\text{d, 2H, -C\(_\text{H}\)})\); 3.75 - 4.10 \((\text{m, 8H, -C\(_\text{H}\_2\)})\); 2.13 \((\text{s, 3H, -CO-C\(_\text{H}\_3\)})\); 2.06 \((\text{s, 3H, -CO-C\(_\text{H}\_3\)})\).

Results and discussion

The reactions took place at atmospheric pressure under nitrogen, at 190-210°C, during 8 and 20 h, respectively, at mole ratios PET / Diol: 1/1.5 and 1/10, using 0.5 % mol (based on the weight of PET) TTB as transesterification catalyst. While 1/1.5 mole ratio is obviously most appropriate for practical applications, the 1/10 ratio pursued to acquire lower molar mass glycolyse products, which are easier to analyze or isolate.

The glycolysed products have been analyzed by \(^1\)H-NMR and FTIR. After derivatization by acetylation, attempts have been made to isolate the key products and characterize them independently. The hydroxyl and acidity number have also been determined. SEC analysis was performed, in order to separate the oligomers and determine their molecular mass.

Identification of glycolysis products by \(^1\)H-NMR

In order to better understand the complex processes that occur during the glycolysis of PET with isosorbide as diol component, two other glycolysis reactions with simple diols, namely EG and PG, were simultaneously investigated. Model p-nitrobenzoate isosorbide compounds have been prepared.

Glycolysis of PET with EG

The glycolysis of PET with EG has been intensely studied \([10-12]\). By performing the glycolysis in the previously described conditions, we have obtained a crystallized glycolysate, hardly soluble in common organic solvents, even after acetylation. Oligoesters \(1 \,(n=1, 2)\) have been isolated and oligoester \(1 \,(n=3)\) has been identified. Besides these compounds, similar products derived from DEG appear.

Spectral parameters of the chemical destruction products of PET have been determined and labelled as: end chain (ec), inter chain (ic) and free glycols (f).

The chemical shifts in the \(^1\)H-NMR spectra of the identified products are presented in table 1; the data refer to aliphatic subspectra. Aromatic protons appear around 8 ppm; the signal is splitted and the higher values are ascribed to lower oligomers. The protons of OH groups, as well as those of acetyl groups, appear around 2 ppm; the former protons produce broad signals, the latter sharp signals.

In the aliphatic region, independent absorptions for three types of protons were observed:
- free glycols EG and DEG. The corresponding acetates present higher chemical shifts values;
- the dissymmetrical glycols in the end chain position present a double number of signals, the more deshielded being assigned to those in the proximity of terephthaloyl groups;
- the glycols between the terephthaloyl units (interchain) present the most deshielded signals of the aliphatic group. This signal of EG is splitted for the compounds \(1 \,(n=2, 3)\), corresponding to dimeric and trimeric structures, respectively.

The results of the glycolyses are shown in table 2. We noticed that a ratio EG/PET =1.5 leads to a glycolysate with a high molecular weight, which being insoluble, could be only partially characterized. On increasing the EG excess from 1.5 to 10, the monomer became prevailing product.

Glycolysis of PET with PG

PET glycolysis with PG, although intensely studied \([14-16]\), generated controversies in regard to the molecular weights of the products; no structural elements by NMR data were presented. By destructing PET in the above

Table 1

<table>
<thead>
<tr>
<th>Formula</th>
<th>X=(\text{H}^a)</th>
<th>X=(\text{Ac}^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XO-CH(_3)-CH(_2)-OX</td>
<td>3.70</td>
<td>4.26</td>
</tr>
<tr>
<td>T-O-CH(_2)-CH(_2)-OX</td>
<td>4.5</td>
<td>4.0</td>
</tr>
<tr>
<td>T-O-CH(_2)-CH(_2)-OT</td>
<td>4.71</td>
<td>4.71</td>
</tr>
<tr>
<td>XO-CH(_3)-CH(_2)-O-CH(_3)-CH(_2)-OX</td>
<td>3.58</td>
<td>3.75</td>
</tr>
<tr>
<td>T-O-CH(_2)-CH(_2)-O-CH(_2)-CH(_2)-OX</td>
<td>3.75</td>
<td>3.65</td>
</tr>
<tr>
<td>T-O-CH(_2)-CH(_2)-O-CH(_2)-CH(_2)-OT</td>
<td>3.95</td>
<td>4.53</td>
</tr>
</tbody>
</table>

\(^a\)reported in lit. [13], \(^b\)values in the present work

Table 2

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Reaction time (h)</th>
<th>Glycol composition, % mol</th>
<th>EG:DEG</th>
<th>Product composition</th>
<th>Table 2</th>
<th>COMPOSITION OF THE GLYCOLYSED PET WITH EG AT DIFFERENT MOLAR RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1*</td>
<td>1.5</td>
<td>20</td>
<td>38.2</td>
<td>11.9, 49.8</td>
<td>95.6 : 4.3</td>
<td>59.0</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>20</td>
<td>73.9</td>
<td>0.8, 25.2</td>
<td>95.8 :4.1</td>
<td>83.9</td>
</tr>
</tbody>
</table>

\(*\)the analysed product represents about 80% of the glycolysate
conditions, we have obtained, with excellent yields soluble products, which crystallized in time. The 'H-NMR spectra of a glycolysed PET with PG at a molecular ratio of 1:1.5 is shown in figure 1.

The aromatic protons appear at about 8 ppm, the signals being strongly splitted. In the aliphatic region, we differentiated two groups of signals:

- the 3.25-5.6 ppm group, which gives information about the way of the bonding EG and PG moieties. The following assignments were made for EG: 4.69 and 3.70 ppm (interchain EG); 3.98 and 4.47 ppm (end-chain EG). For PG the assignments used in calculation of products composition were the following: 5.5 ppm (interchain PG); 5.25 ppm for CH-OT group.

- the 1.0-2.49 ppm group, assigned as follows: primary OH (1.79 ppm), secondary OH (2.3 ppm), free PG (doublet, 1.05 ppm), end-chain PG linked by CH-OT (doublet, 1.25 ppm), end-chain PG linked by CH-OT (doublet, 1.34 ppm) and interchain PG (doublet, 1.48 ppm).

Spectrum of the acetylated product, provide additional information as follows: all CH groups appeared in a detached zone of the spectrum: 5.6 ppm interchain PG, 5.4 ppm PG prim-T, sec-Ac, 5.35 ppm prim-Ac, sec-T, 5.1 ppm free PG diacetate. The deshielding of the signals (by 0.6 ppm) disclosed the ”etheric moiety” in DEG and probably in DPG. The acetyl groups appear at 2 ppm and the signals are strongly splitted. The above assignments were based on the individual spectrum of two monomeric products (compounds 2 and 3) which have been isolated through fractional crystallization.

In the destruction of PET with PG, we could highlight the fact that monomeric compounds result alongside with dimeric compounds. The two hydroxyl groups in PG have different reactivities, the selectivity of primary versus secondary OH being 1:3 (table 3).

The monomeric compounds have mainly terminal OH groups, which react slower than PG itself. The order of the chemical shifts assigned to methine groups is: interchain > sec-T, prim-Ac > prim-T, sec-Ac > Di-Ac.

Synthesis of the model compounds

Isosorbide was treated with p-nitrobenzoyl chloride (1:1 molar ratio) in pyridine, at low temperature. This reaction gave 4a, 5a and 6. Acetylation of 4a and 5a gave the model compounds: 4b and 5b (models for end-chain IS). For the interchain IS the model was the compound 6 (scheme 1).

![Scheme 1](image)

<table>
<thead>
<tr>
<th>Nr. Crt</th>
<th>Molecular ratio PET:PG</th>
<th>Glycol composition, % mol</th>
<th>PG / EG</th>
<th>Selectivity primary/secondary</th>
<th>Product composition, % mol</th>
<th>— n</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:1.5</td>
<td>24.3</td>
<td>19.3</td>
<td>56.3</td>
<td>32.6</td>
<td>13.2</td>
</tr>
<tr>
<td>2*</td>
<td>1:1.5</td>
<td>24.5</td>
<td>72.4</td>
<td>4.2</td>
<td>21.9</td>
<td>73.8</td>
</tr>
<tr>
<td>3*</td>
<td>1:10</td>
<td>11.4</td>
<td>88.5</td>
<td>6.3</td>
<td>3.3</td>
<td>90.2</td>
</tr>
</tbody>
</table>

* after removing the free glycols by distillation

Table 3

DISTRIBUTION OF GLYCOLS IN PET GLYCOLYSATES WITH PG IN A MOLECULAR RATIO OF 1:1.5 AND 1:10
The $^1$H-NMR spectra of the model compounds is shown in figure 2F. For compound 4b, in which the $p$-nitrobenzoyl group is linked to the exo-OH, we assign the NMR signals noted with M and for compound 5b in which the $p$-nitrobenzoyl group is linked to the endo-OH we assign the NMR signals noted with m, and the signals for compound 6 are noted di-. An endo/exo selectivity was calculated as being 1:4. The most deshielded (5.2-5.6 ppm) signal belongs to methine groups linked to $p$-nitrobenzoyl, and the next signals (5-5.3 ppm) belong to the methine groups linked to acetyl groups.

Glycolysis PET with IS

The literature data describe several synthesis of polyesters and copolyesters that use IS as diolic component [3]. So far, IS was not used for PET glycolysis. In this study, we submitted PET to glycolysis with IS, in different molar ratios: 1/1.5 and 1/10. The PET digestion takes place in 3-4 h; after 20 h, we revealed the dislodging of the EG group by IS, so that it becomes prevalent in the terephthalic esters compared to the experiment with EG. Figure 2 shows the NMR spectra of a PET glycolysate with IS at a ratio of 1/1.5 (A), the aromatic zone (B), the acetyl group (C) and the glycolic region (D), the chromatographic fraction (E) and the model compounds (F).

In the whole spectra we distinguish three types of signals: the 8.00-8.15 ppm signal of the aromatic protons; the 1.95-2.06 ppm signal, assigned to acetyl groups; the 3.4-5.6 ppm group of signals belonging to the free and bounded glycols arised from the glycolysate.

The aromatic protons are strongly splitted, showing that PET suffered an advanced depolymerization. The protons of the acetyl groups give multiple signals, proving that the OH groups are not equivalent.
The assignment of the signals in the 3.4-5.6 ppm group is deduced through the similarity with the PET glycolysates with EG and PG, as well as by analysis of the spectra of the model compounds. The presence of EG in the mixture is revealed by the following signals (see Table 1): 4.27 ppm, singlet for free EG (in the glycolysate of PET with EG, this signal appears at 4.26 ppm); 4.72 ppm, singlet, chain EG (in the glycolysate with EG this signal is at 4.71 ppm); 4.44 and 4.56 ppm, two multiplets (at partially overlapped), assigned for end-chain EG (values comparable with those at 4.45 and 4.56 ppm in Table 1).

The signals of IS were identified by comparing the spectra in figures 2D and 2F. The following observations were made:

- the 3.4 - 4.2 ppm signals group belongs to methylene protons in the etheric moiety and has no analytical value since presents many overlappings;
- the 4.4 - 5.6 ppm signals group belongs to methine protons. The deshielded signals correspond to esteric groups; bridge-head protons appear as four triplets and four doublets;
- free IS presents the following signals: at 5.1 - 5.25 ppm appear the protons of the two CH-OAc groups, overlapped with end-chain CH-OAc groups; the bridge-head proton in acetylated isosorbide appears as triplet at 4.84 ppm, whereas the other bridge-head proton appears as doublet at 4.5 ppm. These values are in good agreement with those of the corresponding protons in PG;
- the data for interchain IS are the following: 5.40 - 5.55 ppm, signals partly overlapped with those of end-chain CH-O-T; 5.18 - 5.13 ppm complex signal assigned to one bridge-head proton (H3) (the one giving a triplet in free and end-chain IS). This signal is measurable; 4.72 ppm, doublet, assigned to the second bridge-head proton (H4);
- the end-chain IS was identified by the following signals: 5.40 - 5.55 ppm, belonging to methine protons in the proximity of the terephthalic acid, overlapped with similar protons in the interchain IS; 5.1 - 5.25 ppm signal assigned to acetylated side of isosorbide moiety (H' or H") overlapped with that belonging to similar protons in free IS; the signals at 4.9 - 5.05 ppm, two partly resolved triplets, are assigned to end-chain protons. Stereochemical information may be get from these signals, namely the exo / endo linkage of IS to terephthalic acid. In our case, the exo / endo selectivity was very low; two doublets appear 4.56 and 4.68 ppm (assigned to H3), the last one being partly overlapped with the end-chain EG signal. These signals are also indicative for endo / exo stereochemistry.

From the experiment of glycolysis with IS, we have isolated ethyleneglycol diacetate (EG-Ac) and isosorbide diacetate (IS-Ac), as well as three monomeric compunds: BHET-Ac, disymmetrically substituted terephtalate 7 and symmetricaly substituted terephtalate 8, as mixture of steric isomers (scheme 2).

The nature of these compounds indicates that the reaction goes by partial elimination of ethylene glycol and balancing the glycols in terephthalate.

The functionalization of the products from PET glycolysis with IS by treatment with p-nitrobenzoyl chloride simplifies the 1H-NMR spectra and enables the highlighting of secondary products. Figure 3 presents the 1H-NMR spectra of a PET glycolysate with IS after the removal of the free glycols (A) and after treating with p-nitrobenzoyl chloride (B). The simplified spectra correspond to that of a IS polymer with terephthalic acid described in the literature [3]. From the data of table 1, we identified as a byproduct diethylene glycol, a compound that appears in all the PET glycolysis products described by us.

The results of the PET glycolysis with IS in various molar ratios are shown in table 4. We noticed that the ratio IS / EG is higher than 1 in all cases, EG being dislodged by IS. The low reactivity of IS after polycondensation leads to compounds with small molecular mass. In the reaction with high IS / PET ratio, total dislodgement of EG occurred.

![Scheme 2](image)

**Fig. 3.** The 1H-NMR spectra of a PET glycosate with IS after the removal of the free glycols (A) and after treatment with p-nitrobenzoyl chloride (B)

<table>
<thead>
<tr>
<th>Nr.</th>
<th>IS / PET</th>
<th>Reaction time (h)</th>
<th>Glycol composition, % mol</th>
<th>IS / EG</th>
<th>Product composition, % mol</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>f-EG g-EG e-EG f-IS g-IS e-IS</td>
<td></td>
<td>glycol   mono  di</td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>8</td>
<td>7.2 47.3 45.4 40.1 11.1 48.7</td>
<td>1.2</td>
<td>40.6 16.5 42.8 1.7</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>20</td>
<td>6.8 44.6 48.4 40.2 13.0 46.7</td>
<td>1.4</td>
<td>41.7 16.8 41.3 1.7</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>20</td>
<td>11.1 41.6 47.2 44.7 10.5 44.7</td>
<td>2.1</td>
<td>50.6 18.6 30.6 1.6</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>20</td>
<td>- 6.6 93.7 9.6 big 15.6 69.4 14.8 1.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a after 68.7% of glycols were removed by distillation*

Table 4

THE COMPOSITION IN PET GLYCOLYSIS WITH IS FOR VARIOUS MOLAR RATIOS
Identification of glycolysis products by FTIR

The FTIR spectra of the PET glycolysates with EG (A), PG (B) and IS (C) after removal of free glycols is presented in figure 4. The glycolysates show intense broad bands between 3000 and 3600 cm⁻¹, characteristic of the stretching frequencies of hydroxyl groups. Stretching frequencies for CH₂ and CH₃ groups may stand at 2850-3000 cm⁻¹. The sharp bands at 1700-1715 cm⁻¹ are due to stretching frequencies of esteric C=O groups. The frequencies 1100 cm⁻¹ and 600-900 cm⁻¹ may stand for etheric linkage and for the aromatic nuclei, respectively.

In this way, the FTIR spectra reveal that in all cases we deal with compounds of similar structures, namely aromatic hydroxyesters.

Determination of molecular weights
Size Exclusion Chromatography (SEC)

SEC chromatograms of PET glycolysates with IS (A) and with PG (B) are shown in figure 5. We noticed that the column resolution is poorer than that described in [14] for a PET glycolysate with PG, but the number of the detected oligomers is the same.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Characteristics</th>
<th>Hydroxyl value with remaining free glycols mg KOH/g</th>
<th>Hydroxyl value after removal of free glycols mg KOH/g</th>
<th>M_cal. From I₉O₉</th>
<th>MSEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>IS 1/10</td>
<td>679</td>
<td>320</td>
<td>350</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>IS 1/1.5</td>
<td>409</td>
<td>139</td>
<td>806</td>
<td>742</td>
<td>742</td>
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<tr>
<td>PG 1/10</td>
<td>1179</td>
<td>494</td>
<td>226</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PG 1/1.5</td>
<td>550</td>
<td>175</td>
<td>642</td>
<td>590</td>
<td>590</td>
</tr>
</tbody>
</table>
The chromatograms show 4 and 5 peaks respectively, indicating the same number of oligomers. The smallest detected masses are 590 for PG glycolysate and 742 for IS glycolysate. They correspond in both cases to dimers, in contradiction with the NMR results that indicated a substantial amount of monomeric compounds (some of them were isolated from the reaction mixture).

**Determination of hydroxyl value**

The molecular weights of the PET glycolysates with PG and IS were calculated also by determining the hydroxyl values of the glycolysed products through the classical method of pyridine/acetic anhydride [17] after removing the free glycols. The results are shown in table 5, in comparison with values obtained by SEC.

**Conclusions**

Products of PET wastes glycolysis with isosorbide have been obtained under usual conditions of glycolysis procedure. The products have been processed by derivatization with acetic anhydride, followed by chromatographic separation (column chromatography and TLC) and were analysed by ^1H-NMR, FTIR and SEC techniques. The results were compared with those in PET glycolysis experiments using common diols EG and PG, conducted and evaluated in similar manner. The assignment of the ^1H-NMR signals was based on analogy with glycolysates of PET with EG and PG, as well as the NMR analysis of model compounds. The model compounds have been obtained by isosorbide acylation with p-nitrobenzoyl chloride.

The results certify that PET glycolysates with isosorbide have a similar composition with the PET glycolysates with EG and PG, namely a mixture of free glycols and terephthalic oligoesters, but have a significantly higher content of inferior oligomers. Therefore, one may assert that the investigated procedure could be an attractive route for preparation of terephthalic copolysteres containing isosorbide units, compounds well-known for their physico-chemical and thermal outstanding properties and, concurrently, a way to recover one of the most problematic and voluminous polymer waste.

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