BULGARIAN ACADEMY OF SCIENCES

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eng. SIMONA MIROSLAVOVA ZAHOVA

Preparation of phosphor-containing products with added value based on PET waste

DISSERTATION ABSTRACT

presented for acquisition of

the Educational and scientific degree "DOCTOR"

Scientific supervisors:

Assoc. Prof. Violeta Mitova, PhD

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The dissertation was discussed and admitted to defense at a meeting of the Colloquium of the Institute of Polymers – BAS.

The dissertation is presented on 118 pages, and includes 37 figures. 306 references are used. The results are reported in 2 publications and 7 science forums.

The defense of the dissertation will take place on February 28, 2025 at 2 pm in the meeting room of the Institute of Polymers - BAS at a meeting of the scientific jury.

The defense materials are available to the interested ones in the office of the Institute of Polymers - BAS; Sofia, Akad. G. Bonchev St., Bl. 103B.

Autor: eng. Simona Miroslavova Zahova

Dissertation title: Producing of phosphor-containing substances with added value based on PET waste

I would like to express my gratitude to my scientific supervisor Assoc. Prof. Violeta Mitova, PhD for the expert guidance during my doctoral studies. Thank you for the chance and most of all for the trust she gave me! Thank you for the priceless knowledge and advice I received, for the unreserved support and understanding, for the constructive criticism, for the comprehensive and invaluable help. Thank you for your patience! Thank you for never stopping believing in me and my capabilities! Thank you for everything you taught me!

I would like to express special thanks to Prof. Kolio Troev and Prof. Neli Koseva, for being always available to solve scientific problems and practical issues related to my work.

Thanks to my colleagues Assoc. Prof. Ivelina Tsacheva, PhD and Asst.prof. Zornitsa Todorova, PhD for the help they provided me with the laboratory work, for the comments they made on the text of the dissertation and of course for their friendly support.

My thankfulness to the whole staff of the "Phosphorus-containing Monomers and Polymers" laboratory at IP-BAS for being wonderful colleagues and I could always relay on them.

I thank the management and employees of the Institute of Polymers for the opportunity to work in a pleasant creative atmosphere, for the administrative assistance provided at all stages of my studies at the educational and scientific degree "Doctor".

Thanks to my family!

List of abbreviations

BHET - bis(2-hydroxyethyl) terephthalate

DMT - dimethyl terephthalate

EG – ethylene glycol

CR – carbon residue

DP- degradation product

DP/PPD – product obtained by the reaction of a degradation product of the glycolysis of PET and PPD

DP/TMP – product obtained by the interaction of a degraded product of glycolysis of PET and TMP

DSC - differential scanning calorimeter

FT-IR- Fourier transform infrared spectroscopy

GPC – gel permeation chromatography

M_n- number average molecular weight

M_w- weight average molecular weight

MW heating – microwave heating

NMR – nuclear magnetic resonance

PDI – polydispersy index

PET - polyethylene terephthalate

PPD - phenylphosphonic dichloride

TGA – thermogravimetric analysis

TA - terephthalic acid

TEA – triethylamine

TEA.HCl - triethylamine hydrochloride

TEP - triethyl phosphate

TiP – titanium(IV)phosphate catalyst

TMP - trimethyl phosphate

THF - tetrahydrofuran

UV- vis - ultraviolet–visible spectroscopy

XRD – X-ray diffractal analysis

I. INTRODUCTION

During the last years, the protection of the environment and life in ecosystems has been a priority in the research and development of scientists from all over the world. The pollution of the planet with waste products from various productions for household and industrial needs is increasing and threatens the natural ecological balance. The increased consumption of plastic materials, which have high atmospheric resistance and low biodegradability, increasingly necessitates the development of technologies that will ensure the reduction of accumulated plastic waste.

Polyethylene terephthalate (PET) is among the most widely used polymers in two main application areas - textile and packaging industries. Many of the polymer's applications are for the production of disposable products that have a short life, quickly turn into waste, thus creating economic and environmental problems. The main methods for recycling PET are primary (processing of technological waste), mechanical, chemical and enzymatic degradation, as well as pyrolysis. The mechanical recycling method does not solve the problem of recycling PET waste, but refers to its mechanical grinding and obtaining various products by reprocessing the material. Enzymatic hydrolysis of polyester has serious limitations for application on an industrial scale, and pyrolysis is applicable to plastic waste that cannot be recycled by any other method.

Of particular importance for the recovery of PET is its chemical recycling by solvolysis. The method involves the solvolysis of the polyester in excess of reagents such as water (hydrolysis), alcohols (alcohololysis), glycols (glycolysis), amines (aminolysis) and ammonia (ammonolysis). The mechanism of glycolysis essentially represents the cleavage of ester bonds under the action of glycol, resulting in bis(2-hydroxyethyl) terephthalate (BHET) and oligomers. The development and application of highly efficient catalysts, the optimization of various reaction conditions, such as reaction time, PET:catalyst ratio, PET:glycol, application of microwave heating and others lead to effective degradation under relatively mild conditions, complete conversion of PET and achieving a high yield of monomer. Through easily feasible procedures such as water extraction and crystallization, it can be isolated from the resulting degraded mixture and included both in the synthesis of a new polymer (PET) and in the composition of a wide variety of other polymer products with high added value such as polyurethanes, unsaturated polyesters, vinyl esters and many others, including biopolymers.

The plastics waste can be part of the circular economy by transforming them into useful products. This dissertation presents the development of a method to solve the problem of PET waste through their chemical degradation and repolymerization into high value added products (the so called "upcycling" process).

II. AIM AND OBJECTIVES OF THE DISSERTATION

***The aim of the present dissertation work is to obtain phosphorus-containing products with added value based on PET waste.***

To achieve this aim, the following tasks were formed:

1) Synthesis and characterization of an effective catalyst for conducting glycolysis of PET.

2) Chemical degradation of waste bottles through glycolysis and determination of optimal conditions for the process.

   2.1) Glycolysis of PET waste in the presence of a catalyst under conventional heating;

   2.2) Glycolysis of PET waste in the presence of a catalyst under MW heating;

   2.3) Characterization of the degradation products and proof of their structure;

3) Preparation and characterization of phosphorus-containing products based on the product obtained from the glycolysis of PET.

   3.1) Preparation and characterization of polyphosphonates;

   3.2) Preparation and characterization of polyphosphates;

4) Determining the area of application of the obtained materials.

III. RESULTS AND DISSCUTION

1. Synthesis and characterization of TiP catalyst

The first task of the present work is the synthesis of TiP catalyst. It was obtained by the reaction of titanium (IV) chloride and TEP at a molar ratio of 1:5 (Scheme 1). The content of Ti and P in the catalyst composition was determined by wave-dispersed X-ray fluorescence analysis, which established a ratio between Ti:P=1:2, which corresponds to the structure presented in Scheme 1. From the wide-angle X-ray diffraction pattern (Figure 1) it is evident that the material is amorphous displaying a broad peak centered around $2\Theta=22.5$ [1].
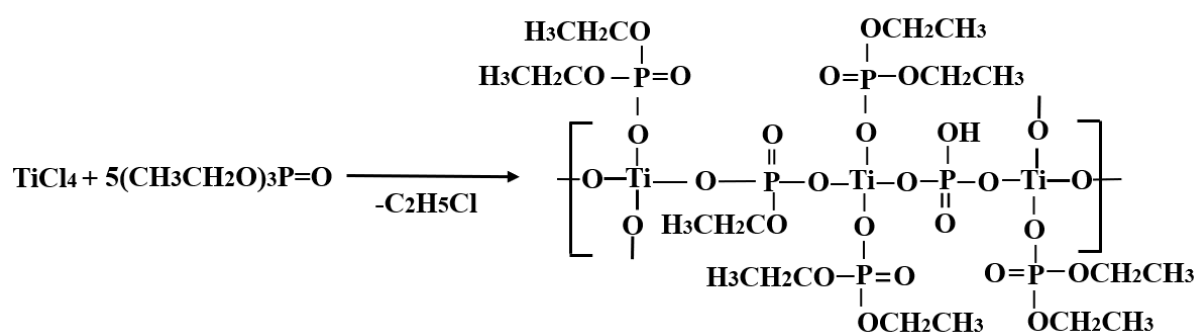
Scheme 1. Synthesis of TiP catalyst.
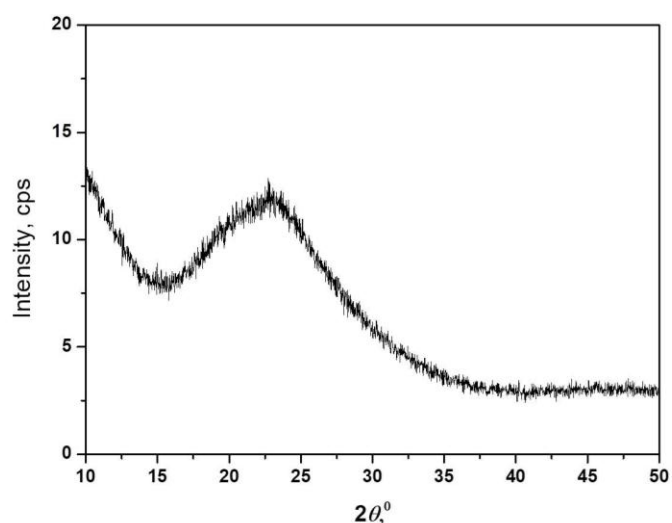
Figure 1. Wide angle X-ray patten of TiP.

The structure of TiP was confirmed by FT-IR spectroscopy. In the FT-IR spectrum of TiP (Figure 2) a band was observed at 684 cm^{-1} which can be assigned to the Ti-O stretching. It is in the spectral region where the characteristic absorption of TiO_2 appears [1]. The peaks at 817 and 783 cm^{-1} are attributed to Ti-O-Ti bonds [2,3]. The absorptions in the range 980-1207 cm^{-1} can be assigned to $P = O$, P-O-C and P-O-Ti bonds [4-7].
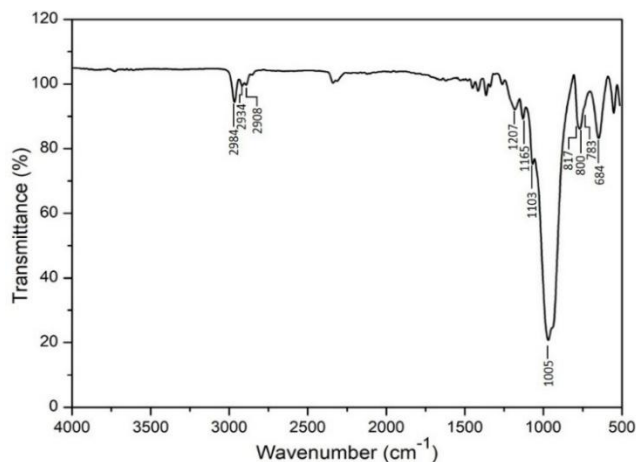

Figure 2. FT-IR spectrum of TiP.

The ^{1}H NMR spectrum of TiP reveals two signals assigned to the presence of -POCH$_2$CH$_3$ segments in the catalyst structure: a triplet at 1.29 ppm with $^3J(P,H) = 7$ Hz, which is characteristic for the methyl protons and at 4.00–4.07 ppm, a multiplet due to the methylene hydrogens.

The obtained catalyst was characterized by ^{31}P{H} and ^{31}P NMR analyzes (Figure 3a and 3b). In the ^{31}P {H} NMR spectrum (Figure 3a) there are signals for three types of phosphorus atoms at 1.19, - 0.92 and - 13.12 ppm. In the ^{31}P NMR spectrum (Figure 3b) the signal at 1.19 ppm represents a quintet, which can be assigned to phosphorus atom with the following sub stituents –TiO(O)P(OCH$_2$CH$_3$)$_2$. The signal at - 0.92 ppm represents a triplet which is determined by the phosphorus of the following structure -Ti-O-P-(O)(OCH$_2$CH$_3$)-O-Ti-. The third signal is a singlet at - 13.12 ppm that can be assigned to the phosphorus atom in the structure -Ti-O-P-O(O)(OH)-O-Ti- probably formed via reaction of dealkylation of ethoxy group [8]. The content of this fragment is less than 8%. The NMR data confirmed the presence of the structural fragments depicted in Scheme 2. The ratio of the integral intensities of the signals display similar content of the three structural fragments in the catalyst composition as presented in Scheme 2.

The results of the analyzes give us reason to assume that a heterochain catalyst with a well-defined structure and composition has been obtained.
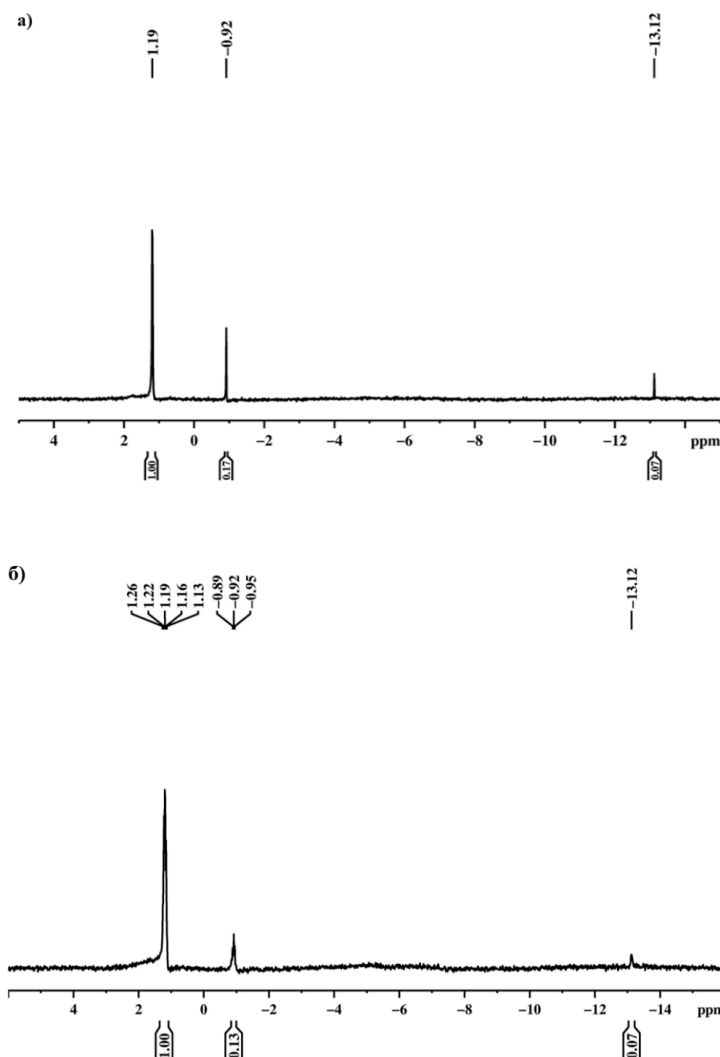

Figure 3. ^{31}P{H} NMR (a) and ^{31}P NMR (b) spectra of TiP catalyst in CDCl$_3$.

2. PET glycolysis with conventional and MW heating

2.1. Effect of reaction conditions of the degradation process and analysis of the glycolysed products

The glycolysis process involves partial or complete depolymerization where the high molecular weight polymer reacts with glycol most often EG. There are several factors which affect the achievement of high monomer yield - considerable excess of EG, reaction time and catalyst concentration. The aim of the present investigation is the optimization of the process

of glycolysis to full decomposition of PET into basic products. The complete degradation of the PET flakes is taken as an indicator of the end of the reaction. In order to avoid recovering of big amounts of EG, the glycolysis process was carried out at a molar ratio of PET/EG=1:2.77, i.e. the mass of the added EG was 90% of the that of the polymer. EG was used as a reagent and as a solvent.

In order to reduce the degradation time, MW heating was applied. It is known that by applying MW heating the necessary temperature for carrying out a given reaction is reached in a shorter time. Loss factor (tan δ) of ethylene glycol as a solvent is 1.35 [9]. This means that ethylene glycol can absorb enough energy to reach a "thermal" microwave effect, temperature of 200 ∘C at which glycolysis was carried out without susceptor (heat transfer Teflon disc). Thus, EG played a triple role – as a reagent, a solvent and also as a MW absorber in PET degradation. For comparison, degradation was also conducted under conventional heating. The conditions under which the experiments were performed are presented in Table 1 and Table 2.

Table 1. *Glycolysis of PET by conventional heating with different amounts of TiP catalyst at molar ratio EG:PET repeating units=2.77 and temperature 200 ℃.*

Sample code	TiP (wt. %) [*]	Reaction time (min)
1	-	540
2	0.05	215
3	0.1	195
4	0.2	170
5	0.3	155
6	0.5	165

*based on PET weight

Table 2. *Glycolysis of PET under MW heating and at different amount of TiP catalyst, molar ratio EG:PET repeating units=2.77 and temperature 200 ∘C.*

Sample code	TiP (wt. %)[*]	Power (W)	Reaction time (min)
7	-	350	410
8	-	450	320
9	-	500	225
10	0.05	450	65
11	0.1	450	50
12	0.2	450	45
13	0.2	500	41
14	0.2	600	38
15	0.3	450	42
16	0.5	450	45

*based on PET weight

In order to compare the influence of the TiP catalyst, initial degradation was carried out in the absence of a catalyst at a temperature of 200 °C by applying conventional and MW heating, respectively. It was found that by applying conventional heating, complete degradation of PET flakes was achieved after 9 hours. The application of MW heating led to a significant reduction in the reaction time (up to 2 times), but without a significant increase in the amount of monomer in the resulting degraded product (samples 7-9, Table 4). These experimental results could be explained by the fact that microwaves do not affect the activation energy of the reaction, but provide heating throughout the volume of the mixture, which helps to complete the reaction quickly. Futuremore, the glycolysis of PET is an equilibrium reverse reaction and the reverse reaction begins polycondensation. As the depolymerization process progresses, a polycondensation process also occurs, which leads to a decrease in the yield of monomer. These observations clearly indicate the need to use a catalyst when conducting glycolysis of PET.

To determine the efficiency of the catalyst, a series of experiments were conducted at a constant ratio of PET:EG=1:2.77 and a temperature of 200 °C. The amount of catalyst was varied (0.05 wt %, 0.1 wt %, 0.2 wt %, 0.3 wt % and 0.5 wt % based on PET weight). Glycolysis catalyzed by TiP was carried out by applying conventional (samples 2-6, Table 1) or MW heating (samples 10-16, Table 2), and the influence of its content is shown in Figure 4. It was found that the addition of even a minimal amount of catalyst (from 0.05 wt %) has a positive effect on the BHET content in the degradation product (Tables 3 and 4), both under conventional as well as MW heating. Figure 4 presents the dependence of the ratio of BHET in the degradation product on the amount of TiP used. For the conventional glycolysis the highest level of BHET content in the reaction product (67.1%) was achieved using 0.3% TiP and a reaction time of 155 min. For MW assisted reaction the optimal degradation resulting in 61.7% monomer content was obtained using 0.2% catalyst for 45 min.
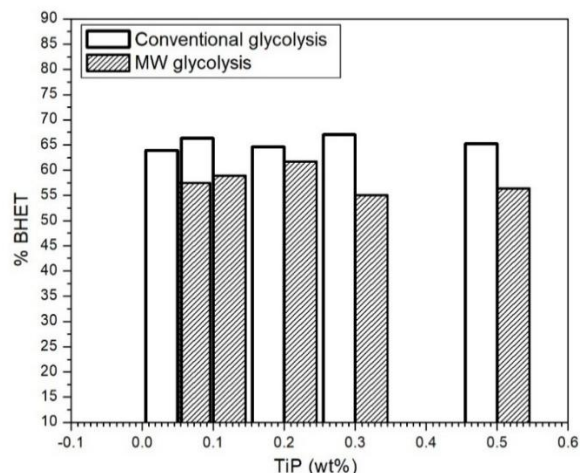
Figure 4. Content of BHET in the glycolysis crude product obtained applying different amounts of TiP under conventional and MW assisted heating.

To confirm the structure of the products of PET glycolysis NMR and FTIR analysis were performed. The ^{1}H NMR spectra of the glycolysis product is shown in Figure 5. The signal at 8.06 ppm indicates the presence of the 4 aromatic protons of the terephthalic residue. The signal for the protons in the hydroxyl groups of EG and degradation products is at 2.00 ppm. The triplets at 3.92 and 4.43 ppm are assigned to the methylene protons of CH_2–OH and COO–CH_2, respectively. The additional signals at 4.64 ppm are attributed to the methylene pro tons in diester segments [–C(O)O–CH_2–CH_2–OC(O)] which are due to the presence of dimers and trimers in the glycolysis product.
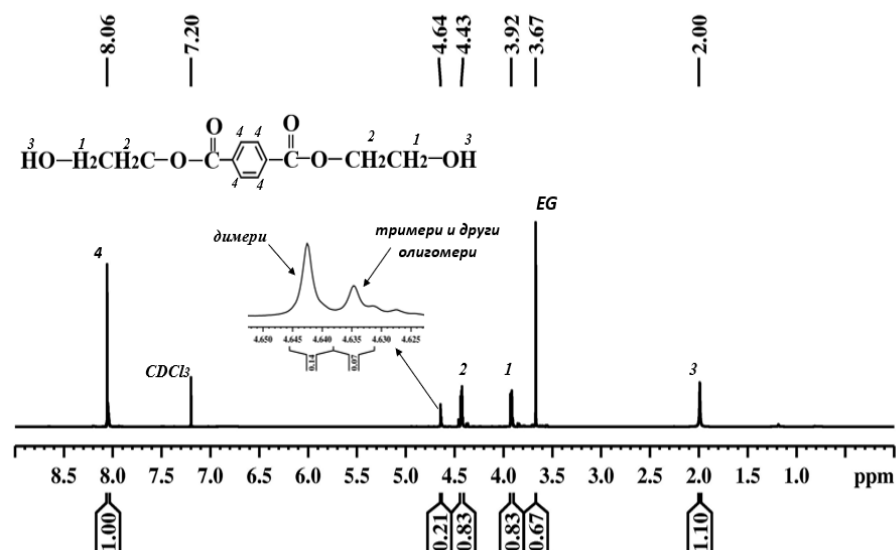
Figure 5. ^{1}H NMR spectrum of the glycolysis product in CDCl₃.

Based on the integral intensities of these signals a quantitative analysis of the composition of the main degradation products was done. The amount of dimers and trimers in the degradation mixture for samples (codes 1, 5, 8 and 12) obtained at different conditions of glycolysis process are presented in Table 5. The results are comparable with those of GPC analyses. The GPC and NMR results confirmed that the BHET, dimer and trimers are predominant components in the degradation product. It was observed that under different conditions of glycolysis (type of heating and amounts of catalyst) keeping constants EG:PET molar ratio, the amount of BHET in glycolysis product was almost the same. However, a significant reduction (12 times) in reaction time was observed - from 540 min at conventional heating without catalyst to 45 min using MW heating and 0.2 wt % TiP catalyst.

The content of BHET in degradation products 1, 5, 8 and 12 was also determined by UV spectroscopy. The obtained results (Table 5) are in very good agreement with the results of GPC and NMR analyses. The results unequivocally showed the effectiveness of the glycolysis process carried out under microwave irradiation. In addition to the significant reduction in reaction time, it was also found that the content of BHET was comparable to that obtained with conventional heating (~60%). Performing glycolysis using MW heating leads to a significant reduction in the reaction time, both in the presence and absence of a catalyst. The combination of MW heating and the presence of TiP allowed for a reduction in the reaction time to 45 minutes and the production of BHET in a high yield of over 75% (Table 6).

Table 3. *Composition of products obtained from PET conventional glycolysis according to GPC analysis.*

Sample code	GPC analysis of glycolyzed products			
	BHET %	dimer %	trimer %	tetramer (and others) %
1	59	29	10	2
2	64	27	7	2
3	67	25	7	1
4	65	26	8	1
5	67	25	7	1
6	65	26	8	1

Table 4. *Composition of products obtained from PET MW glycolysis according to GPC analysis.*

Sample code	GPC analysis of glycolyzed products			
	BHET %	dimer %	trimer %	tetramer (and others)
7	45	33	16	6
8	49	29	13	9
9	48	39	13	-
10	58	28	10	4
11	59	28	10	3
12	62	28	8	2
13	52	29	12	7
14	56	29	11	4
15	55	29	12	4
16	57	28	11	4

Table 5. *Composition of the products of PET glycolysis according to GPC, NMR and UV analysis*

Sample code	BHET %				dimers %			tetramer (and others) %		
	NMR[a]	NMR[b]	GPC[a]	UV[b]	NMR[a]	NMR[b]	GPC[a]	NMR[a]	NMR[b]	GPC[a]
1	64	52	59	62	24	20	29	12	10	12
5	61	53	67	64	28	24	25	11	10	8
8	47	37	49	48	34	27	29	19	15	22
12	61	49	62	58	26	21	28	13	11	10

a-without considering the amount of EG in the DP; b – with considering the amount of EG in the DP

Table 6. *BHET yields in the glycolysis of PET according to NMR and UV analysis.*

Sample code	Type of heating	TiP (wt %) [*]	Reaction time (min)	Yeild, %	
				NMR[b]	UV[b]
1	conventional	-	540	74	90
5	conventional	0.3	155	71	88
8	MW	-	320	53	67
12	MW	0.2	45	75	83

[*]based on PET weight; b - with considering the amount of EG in the DP

The FT-IR spectrum of the product is shown in Figure 6. The peaks at 3443 and 1130 cm^{-1} denotes the existence of hydroxyl groups. The band at 1713 cm^{-1} is due to C=O stretching, peaks at 1250 and 1070 cm^{-1} refer to, C–O ester bond asymmetric vibration, and C–O ester bond symmetric vibration, respectively. Peaks at 2871 and 2963 cm^{-1} are related to the C–H bonds stretching. The signals between 898 and 670 cm^{-1} are attributed to the vibration of C–H in the aromatic residues [10].

From the TGA curve of the degradation product (Figure 7) it is evident that the thermal decomposition of the product takes place in two stages: at 230 ˚C which refers to weight loss of around 44% due to the thermal decomposition of the components of degradation product (BHET, EG, dimers and trimers). The next stage, at 420 ˚C the loss is around 46% and is associated with the thermal degradation of PET obtained via repolymerization during the heating process of TGA [10,11]. The remaining residue at 600 ˚C is about 10%.
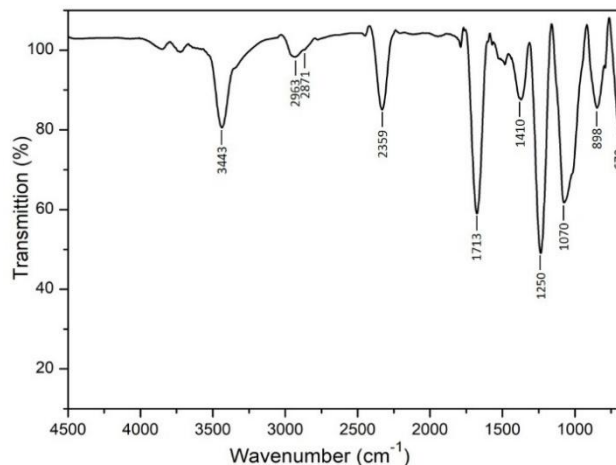
Figure 6. FTIR analysis of the degradation product.
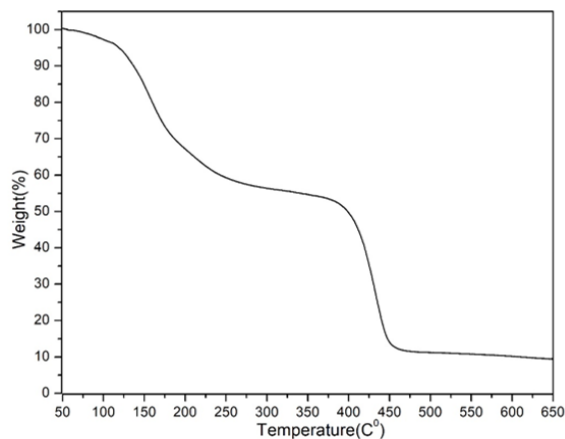
Figure 7. TGA curve of the glycolysis product.

2.2. Characterization of purified BHET monomer from the product of degradation

In order to confirm the production of BHET, as the main product of the glycolysis, a simple separation of the degradation product was carried out. The solid-liquid separation and recrystallization of the crude glycolysis product in water affords pure BHET. In the ^{1}H NMR spectrum of the purified BHET (Figure 8a) the signal at 8.15 ppm indicated the presence of the 4 aromatic protons of the aromatic ring. Signals at 4.52 ppm and 4.01 ppm are characteristic for the methylene protons of COO–CH_2 and CH_2–OH, the signal at 1.93 ppm refers to the hydroxyl groups. The ^{1}H NMR spectrum accords with the that of BHET reported in the literature [12].

The ^{13}C NMR data of the purified product (Figure 8b) indicate a characteristic signals of carbonyl group at 166.06 ppm, aromatic carbon atoms at 133.85 ppm and 129.72 ppm. Resonance at 61.30 ppm (-O-CH_2–CH_2–OH) and 67.07 ppm (-O-CH_2–CH_2–OH) were also observed, which confirmed that the isolated product is the BHET monomer.

The formation of BHET was also verified by DSC analysis. The sharp endothermic peak at 110 ˚C in the thermogram (Figure 9) was an indication that pure monomer was successfully obtained via glycolysis of PET waste. This result agrees with the melting point of BHET reported in the literature [13] and it can be compared with DSC of a commercial monomer (Figure 9).
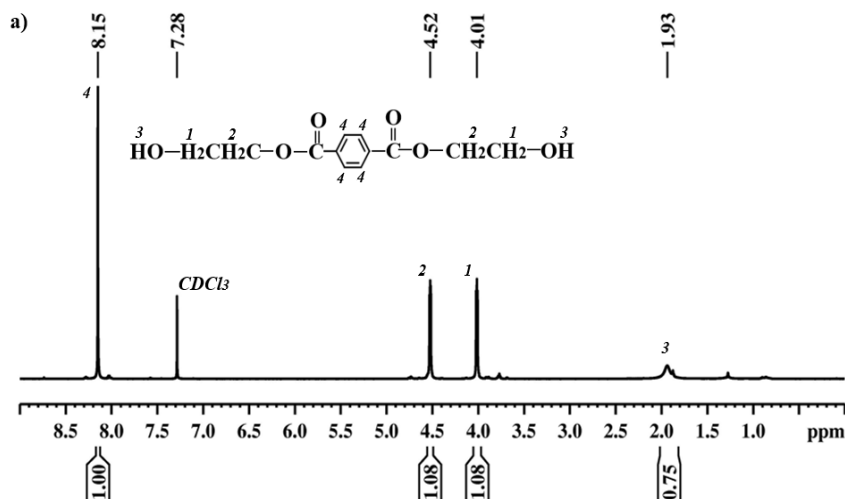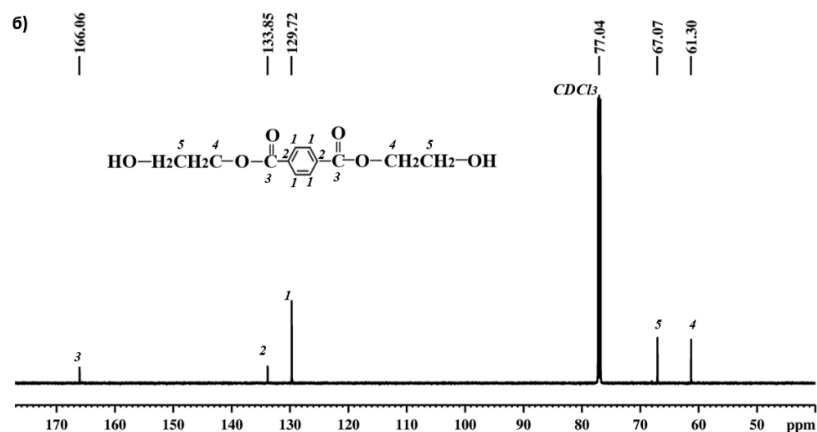
Figure 8. ^1H NMR (a) and ^{13}C NMR (b) spectra of the recrystallized BHET in CDCl$_3$.
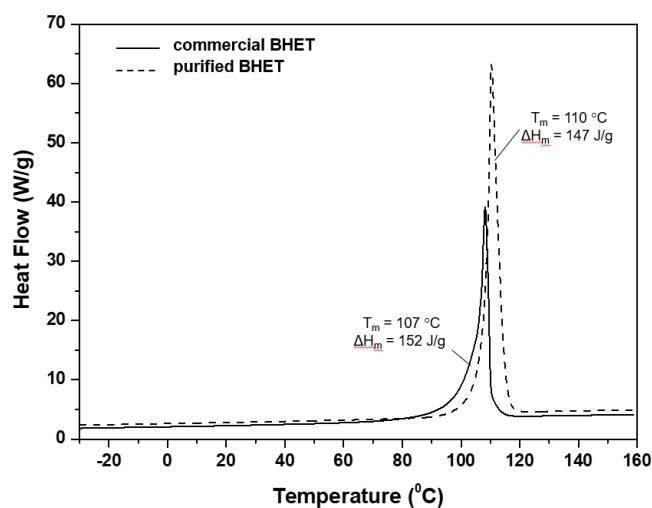

Figure 9. Comparative DSC profiles of commercial BHET and BHET
from glycolysis.

Conclusion:

The application of MW heating in the glycolysis of PET allows the decreasing of the time to complete depolymerization without having a negative effect on the monomer yield. The time required to degrade the PET flakes using MW heating and 0.2 wt % TiP was reduced 12 times compared to that using conventional heating (without using a catalyst). In addition, in accordance with the concept of "green chemistry", based on minimal solvent use, the reaction is carried out with a small excess of EG, at a molar ratio of PET:EG=1:2.77. Based on the power of the heat sources used - a magnetic stirrer (600W) and a microwave reactor (450 W), as well as the time required to carry out the degradation, it is calculated that the energy used to carry out glycolysis

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when applying conventional heating (~1.55 kW/h) significantly exceeds that required for the process when applying MW heating (~0.34 kW/h), i.e. in this way ~22% of energy savings can be achieved. The resulting degradation product is a well-defined mixture of monomers, dimers, trimers (and other oligomers) and low content of EG. This allows for subsequent use of the glycolysis product without the need for subsequent separation and purification procedures of the main products which further optimizing the recycling process.

3. Production of phosphorus-containing value added products based on PET waste

Crucial to the utilization of plastic waste is its efficient conversion into new raw materials. Therefore, one of the main goals of this dissertation work is to create new value added products from the well-defined product obtained from the degradation of PET, which can be used as flame retardant additives for polymers.

3.1. Preparation of phosphorus-containing products based on the degradation product of PET glycolysis and PPD

3.1.1. The model reactions- interaction between BHET (commercial product) and PPD

In the literature there are no ^{31}P NMR data for the phosphorus atoms with surroundings as the expected reaction products obtained from interaction of PPD and the products of PET glycolysis. The analysis of the degradation product revealed that approximately 50 wt % of its composition is BHET (the rest of its composition is respectively: ~20 wt % dimer, ~10 wt % trimer and other oligomers and ~20 wt % EG). Based on this and for the purpose of signals assignment, two model reactions between BHET (commercial product) and PPD were performed at molar ratio BHET:PPD=1:1 and =2:1 (Scheme 2).
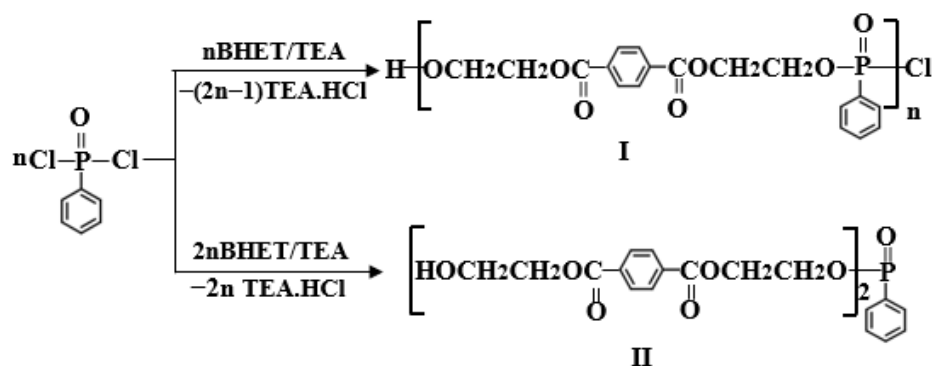
Scheme 2. Interaction between BHET and PPD at molar ratios 1:1 and 2:1.

In the ^{31}P{H} NMR spectrum of the reaction product (BPClTEA) obtained at molar ratio 1:1 (Figure 10a) there are signals at 20.69 ppm, 20.20 ppm, 11.03 ppm, 10.85 ppm and -5.45 ppm with integral intensities 0.03, 1.00, 0.08 and 0.02, respectively. The signals at 20.69 ppm and 20.20 ppm are characteristic for the mono and diesters of phenylphosphonic acid [14,15]. The signals at 11.03 ppm and -5.45 ppm should be attributed to the phenylphosphonic acid [16] and pyrophosphonate structures [16] respectively. ^{31}P{H} NMR spectrum of the reaction product (2BPClTEA) obtained at molar ratio 2:1 (Figure 10b) showed a signal at 20.02 ppm. Signals at 20.20 ppm (molar ratio 1:1) and 20.02 ppm (molar ratio 2:1) are with a significantly stronger integral intensity, which gives us reason to attribute it to the phosphorus atom in the repeating unit of **I** and in di[bis(2-hydroxyethylterephthalate)] phenylphosphonate **II**. The phosphorus atoms in both products have the same surroundings.
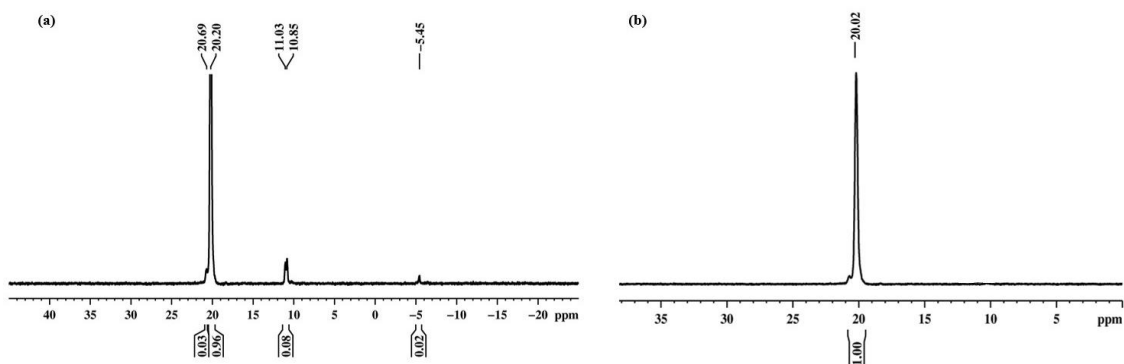
Figure 10. ^{31}P{H} NMR spectra of the reaction product at molar ratio (a) 1:1 (BPClTEA) and (b) 2:1 (2BPClTEA).

In ^{1}H NMR spectrum of BPClTEA (Figure 11) the signal at 3.89 ppm, a triplet with a coupling constant $^3J(H, H)$= 4 Hz, refers to HOCH_2CH$_2$-; the triplet at 4.44 ppm relates to methylene protons of HOCH$_2$CH_2-OC(O); at the range 7.29-8.02 ppm aromatic protons which should be attributed to the hydrogen atoms of BHET and of the aromatic nucleus of PPD. Signals in region 4.34-4.24 ppm, representing multiplets, should be referred to -CH$_2$CH$_2$O-P(O)-OCH$_2$CH$_2$- protons. The signal at 3.03 ppm for the proton of HO-CH$_2$CH$_2$- was also observed. The same characteristic signals occur in the ^{1}H NMR spectrum of product 2BPClTEA.

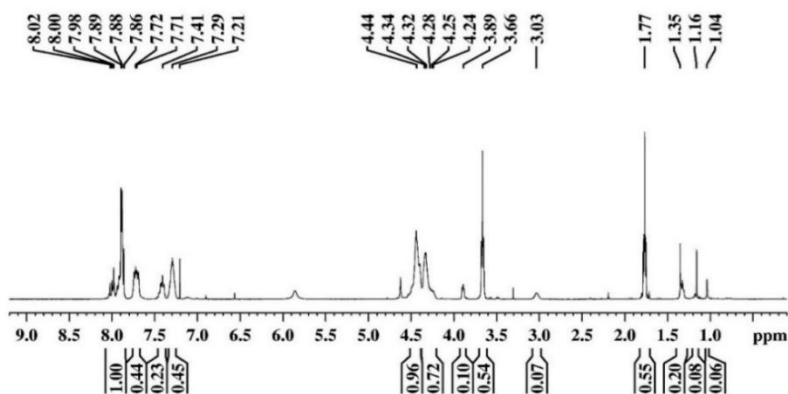Figure 11. ^{1}H NMR spectrum of BPClTEA.

The ^{13}C NMR data of BPClTEA (Figure 12) indicate characteristic signals at 59.86 ppm (HO*C*H$_2$CH$_2$-), 66.95 ppm (HOCH$_2$*C*H$_2$-) and for aromatic carbon atoms of BHET and PPD in the range 125.01-132.52 ppm. Resonances at 164.84 ppm and 164.25 ppm, for the carbonyl group were also observed. A new signals appear at 62.98 ppm, a doublet with a coupling constant ^{3}J(P, C)= 6 Hz, typical for -*C*H$_2$CH$_2$O-P(O)- carbon atom and at 66.05 ppm for -*C*H$_2$CH$_2$O-P(O)-. Based on NMR (^{1}H, ^{13}C, ^{31}P{H}) database we suggest that the product of interaction between BHET and PPD at molar ratio 1:1 has a structure coincides with the presented on Scheme 2 (Scheme 2, product I).

The above results give us a reason to assume that if the signal at 20.20 ppm (integral intensity 0.96) in the ^{31}P NMR spectrum is for the phosphorus atom in the repeating units, and that at 20.69 ppm (integral intensity 0.03) for the phosphorus atom in the of the end unit, then the molecular mass (W$_n$) of polyphenylphosphonate is ~12000 g/mol (n=32, molecular weight of the repeating unit 376).
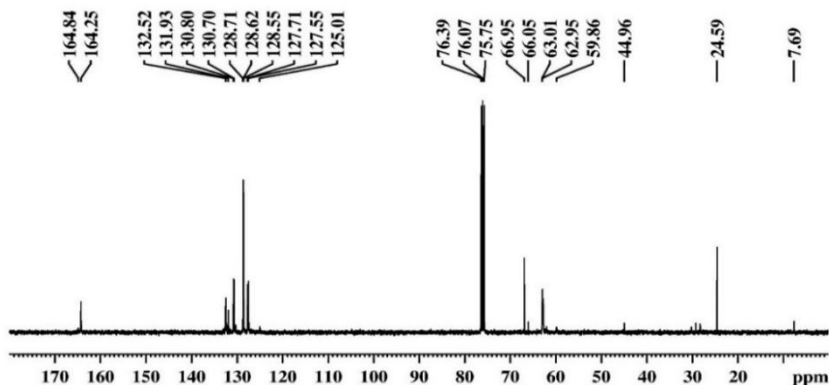

Figure 11. ^{13}C NMR spectrum of BPClTEA.

3.1.2. Preparation of value added products based on degradation product and PPD at molar ratio 1:1

10.000 g PG-PET including 48.78 % (0.0192 mol) BHET; 20.89 % (0.0047 mol) dimer; 10.96 % (0.0017 mol) trimer; 19.37 % (0.0312 mol) EG. With the highest molar content are EG, 0.0312 mol and BHET, 0.0192 mol, while the dimer and trimer are one order of magnitude lower. This gives us a reason to assume that the following two main reactions occur simultaneously (Scheme 3).

A) Interaction between EG and PPD.
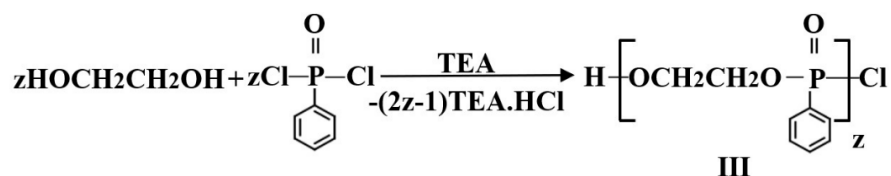
B) Interaction between BHET and PPD.
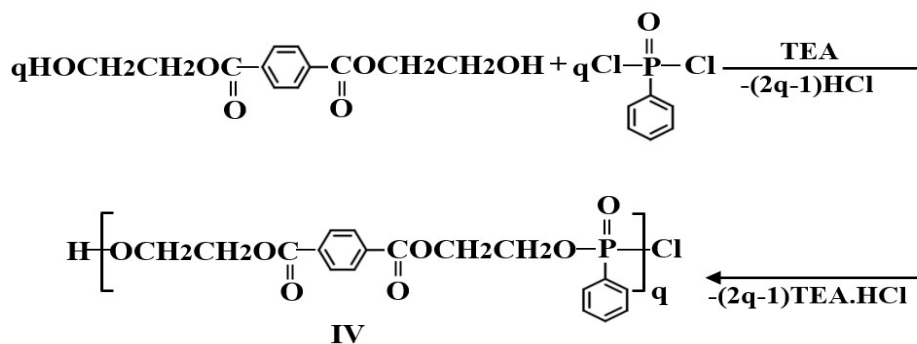
Scheme 3. Interaction between: A) EG and PPD; B) BHET and PPD.

The interaction between products with structure III and IV leads to the formation of copolymer VI (scheme 5). The total molar content of EG and BHET is 88.70% of the molar content of the degradation product. Products III and IV, obtained on the basis of BHET and EG, are approximately 90% of the mass of the product, i.e. these are the primary products obtained from the interaction between the degradation product and PPD. The ^{1}H NMR spectrum of the reaction product, DP/PPD (Figure 13) showed signal at 10.97 ppm which is characteristic for P-OH protons. Signal at 8.02 ppm characteristic for aromatic protons of PET. The aromatic protons of PPD are in rage 7.33-7.94 ppm. The additional signals at 4.63 ppm are attributed to the methylene protons in the segments -C(O)O-CH$_2$-CH$_2$-OCO- which are due to the presence of dimers and trimers in the degradation

mixture. The signals at 3.88 ppm and 4.43 ppm are assigned to the methylene protons adjacent to the hydroxyl group in BHET unit -CH_2-OH and C(O)O-CH_2. Multiplets at 4.38-4.19 ppm can be referred to the methylene protons of P(O)O-CH$_2$CH$_2$ and P(O)O-CH$_2$CH$_2$. At 3.00 ppm there is a signal for the proton of HOCH$_2$-CH$_2$ structure.
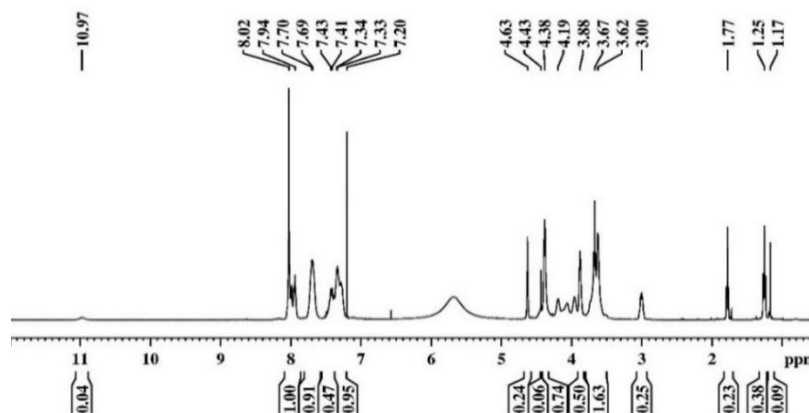

Figure 13. ^{1}H NMR spectrum of DP/PPD.

In ^{31}P{H}NMR spectrum (Figure 14) of the reaction product there are signals at: 19.73, 20.28, and 21.10 ppm with integral intensity 5.11, 1.43 and 1.00, respectively. Three types of phosphorus atoms must exist, namely, the phosphorus atom in the repeating unit of product **III**, in the repeating unit of product **IV**, and in the terminal unit. Based on the literature data [14,15] can be assumed that the signal at 19.73 ppm and 20.28 ppm can be assigned to the phosphorus atom in the repeating units, while those one at 21.10 ppm for phosphorus atom in the terminal unit. The quantitative composition of the degradation product suggests that the signal at 19.73 ppm should be attributed to the phosphorus atom in the repeating units of product **III**, and that at 20.28 ppm to the phosphorus atom in the repeating unit of product **IV**. The number average molecular mass of the phosphorylated product, calculated on the basis of the data from the ^{31}P{H}NMR spectrum, is ~ 1450 g/mol.
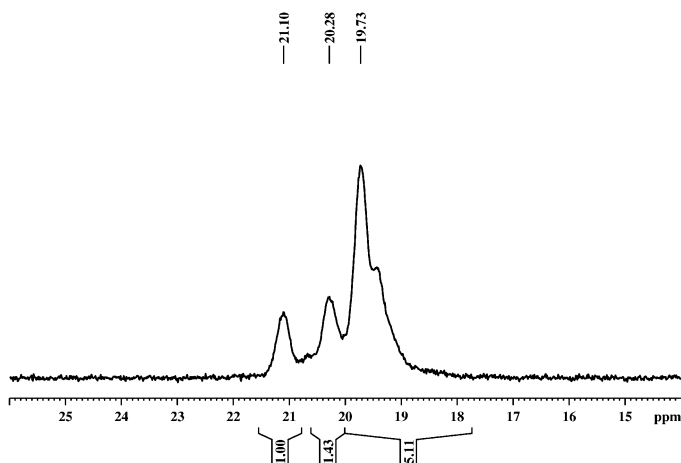
Figure 14. $^{31}P\{H\}$ NMR spectrum of DP/PPD.

In ^{13}C NMR spectrum of reaction product (Figure 15) there are signals at: 67.97 ppm for - OH-*CH$_2$*CH$_2$O-; 60.90 ppm for OH-*CH$_2$*CH$_2$O-. The signals at 63.00 ppm for -C(O)O-CH$_2$-CH$_2$-OCO- which are due to the presence of dimers and trimers in the product; at 133.99-128.40 ppm for the aromatic carbon atoms of BHET and PPD; at 165.55 ppm and 166.03 ppm for C=O carbon atoms. New signals appear at 66.90 ppm for -P(O)O-CH$_2$*CH$_2$*-O(O)C-; and a doublet at 63.57 ppm with ^{2}J(P,C) = 5.7 Hz, characteristic for -CH$_2$*CH$_2$*O(O)P- carbon atom.
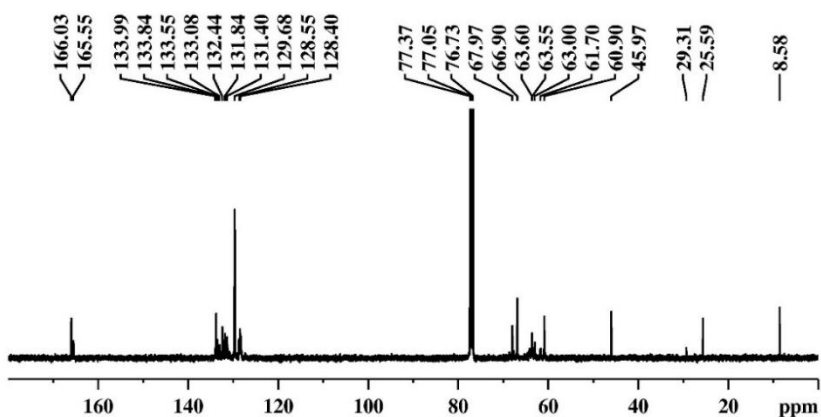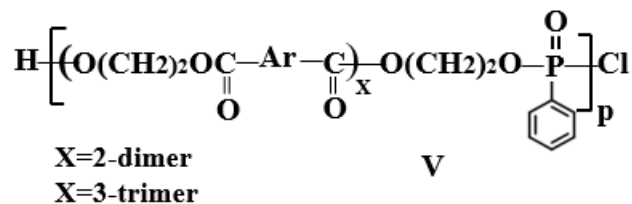

Figure 15. ^{13}C NMR spectrum of DP/PPD.

The NMR data for reaction products of dimer and trimer with PPD (Scheme 4, product 5) will be the same as those for products **III** and **IV** (Scheme 5) because the substituents attached to the phosphorus atom are the same. Data from NMR spectroscopy confirm the proposed structures.

X=2-dimer
X=3-trimer

V

Scheme 4. Products obtained from the interaction of dimers and trimers with PPD.

VI

−HCl

VII
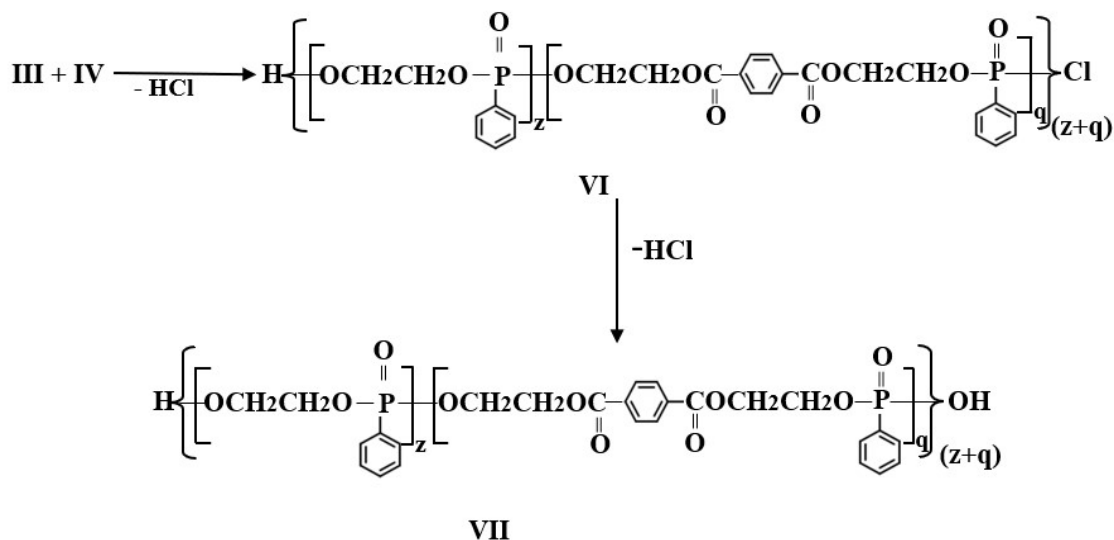
Scheme 5. Interaction between III and IV.

3.2. Production of value-added products based on degradation product and TMP at molar ratio 1:1

In addition to using PPD, reactions were carried out in which PPD was replaced with TMP for interaction with a degradation product of PET glycolysis.

3.2.1. The model reaction- transesterification of TMP with BHET (commercial product)

Again, there is no information in the literature on signal shifts in the ^{31}P NMR spectrum for a product obtained from the interaction of TMP and PET degradation products or for similar structures. In order to assign the signals in the ^{31}P NMR spectra to the resulting products and the lack of data on similar phosphate structures in the literature, a product obtained by the interaction of commercial BHET and TMP was synthesized. The reaction was carried out at a molar ratio of BHET:TMP=1:2, at a temperature of 190 °C and reaction time of 5 hours (product BTMP5). The resulting product was heated for an additional 4 hours at the same temperature (product BTMP9).

In the ^{31}P{H} NMR spectrum of the reaction product obtained after 5 h of heating, BTMP5 (Figure 16) there are signals (δ, ppm/integral intensity) at: 2.63 (1.00), 2.30 (2.48), 1.48 (0.48), 1.17 (0.75) and 0.05 (0.30) which are characteristic of phosphate structures. The main signals are at 2.63 ppm and 2.30 ppm in a ratio of 1:2.48 (28.70 %, 71.30 %).

In ^{31}P NMR spectrum of the product (Figure 17), the signals represent multiplets of nine lines ([3]J (P, H) = 11.38 Hz), which gives information about the phosphorus surrounding atoms.
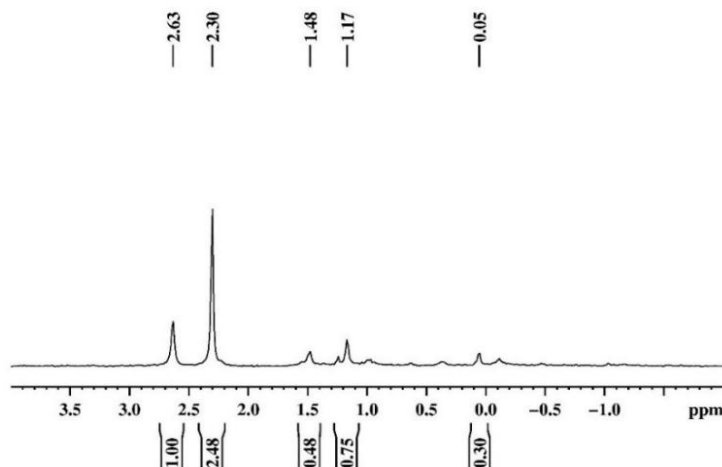

Figure 16. ^{31}P{H} NMR spectrum of BTMP5.
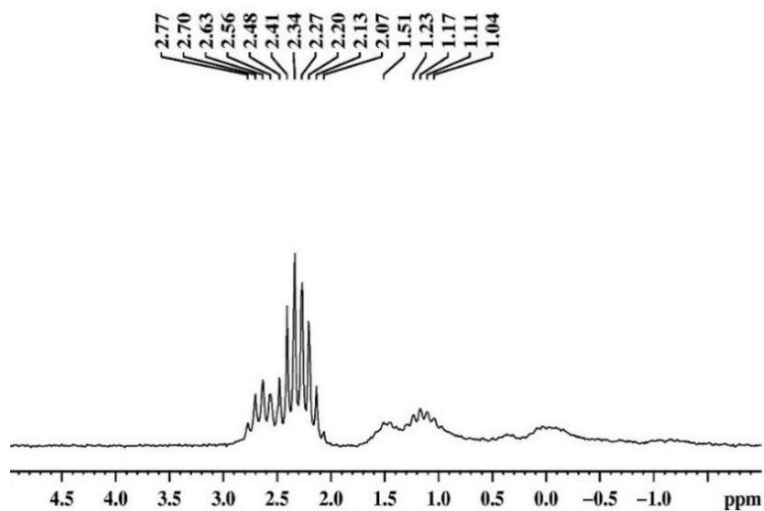

Figure 17. ^{31}P NMR spectrum of BTMP5.

In the ^{31}P{H} NMR spectrum of the reaction product obtained after 9 h of heating, BTMP9 (Figure 18) the signals are at 2.70 ppm and 2.29 ppm in ratio 1.00:2.32 (30.10 %, 69.90 %). From

^{31}P NMR analysis of the same product (Figure 19) it is clear that the signals are multiplets from nine lines with the coupling constant ^3J (P, H) = 11.74 Hz.
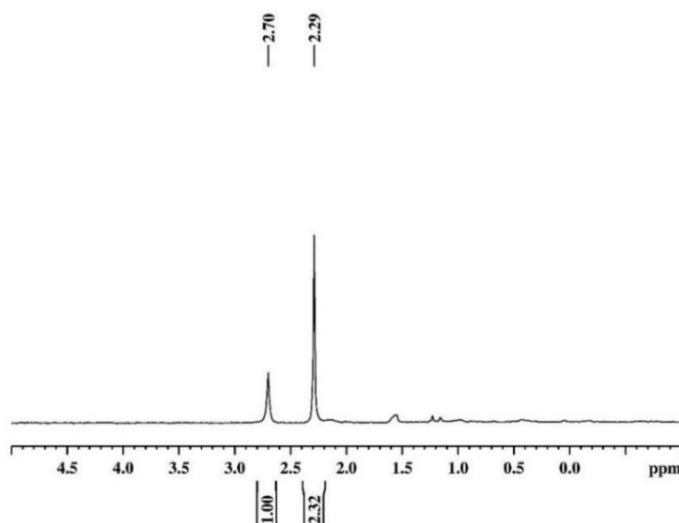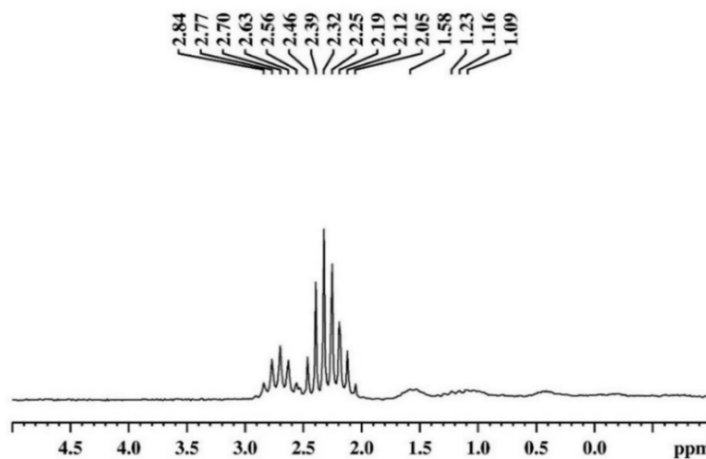

Figure 18. $^{31}P\{H\}$ NMR spectrum of BTMP9.

Figure 19. ^{31}P NMR spectrum of BTMP9.

The data from $^{31}P\{H\}$ NMR analysis show that the additional increasing of the reaction time does not lead to the significant changes in the content of the reaction products. The signal intensity at 2.70 ppm from 28.70 % increase up to 30.10 %. The presents of two signals gives us a reason to assume that in the reaction mixture there are two phosphorus-containing compounds with very similar structure of substituents of phosphorus atom but with different amounts.

In ^1H NMR spectrum of BTMP5 (Figure 20) the signal at 3.34 ppm should be attributed to the proton of OH group (*H*OCH$_2$-CH$_2$- structure). The doublets at 3.66 ppm and 3.69 ppm with ^3J(P,H)

= 12 Hz are characteristic of POCH_3 protons with integral intensities 1.42 and 3.50 respectively, in a ratio of 1.00:2.47, which is the same as the ratio of integral intensities for phosphorus atoms 1.00:2.48.
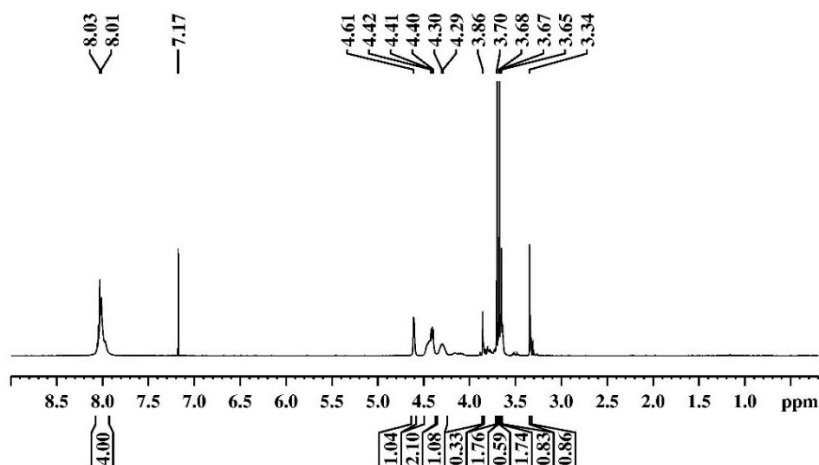

Figure 20. ^{1}H NMR spectrum of BTMP5.

Signals in the region 4.29-4.42 ppm should be attributed to –C(O)OCH_2- and P(O)OCH_2- protons; the signals at 8.01 ppm and 8.03 ppm are assigned to the aromatic protons. In the ^{1}H NMR spectrum there is a new signal at 3.86 ppm, a singlet, which is characteristic of methyl protons of the ester group CH_3OC(O)-Ar-. Reason for assigning this signal to these protons is the fact that in the starting compounds, BHET and TMP, there are no protons whose signals are singlets in this region. Additionally, the signal for methyl protons of dimethyl terephthalate is at 3.94 ppm [17]. In ^{1}H NMR spectrum of BTMP9 (Figure 21) there are the same signals as for the 5 h heating product. The ratio of integral intensities for POCH_3 protons is almost the same, from 1:2.48 to 1:2.45.
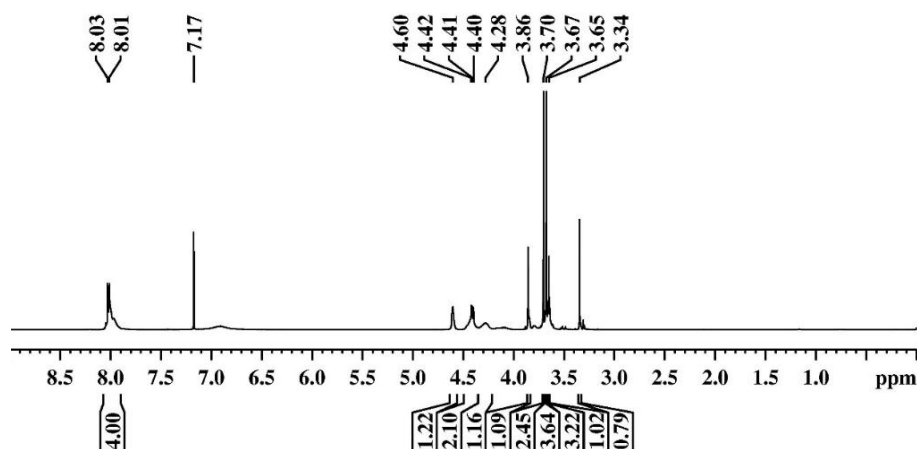

Figure 21. ^{1}H NMR spectrum of BTMP9.

In ^{13}C NMR spectrum of BTMP9 (Figure 22) there are signals at: 52.42 ppm, a singlet; 54.12 ppm, d,^{2}J(P,C) = 6.0 Hz and 54.46 ppm, d, ^{3}J(P,C) = 6.0 Hz which should be reported to P-OCH$_3$ carbon atoms; 59.04 ppm for HOCH$_2$ carbon atoms; 63.81 ppm d, ^{2}J(P,C) = 5.7 Hz which can be assigned to P(O)OCH$_2$ carbon atoms, 70.41 ppm for C(O)OCH$_2$- carbon atoms; at 133.70 ppm and 129.65 ppm are for aromatic carbon atoms. There are also two signals for the carbonyl carbon atom at 165.43 and 166.16 ppm (C=O carbon atoms). ^{13}C NMR spectrum shows the presence of two types of P-OCH$_3$ carbon atoms, which is in agreement with the results of ^{1}H NMR and ^{31}P NMR spectroscopy. The singlet at 52.42 ppm can be attributed to the carbon atom of the methyl ester group CH$_3$OC(O)-, since the signal for this carbon atom of dimethyl terephthalate is at 52.39 ppm [17].
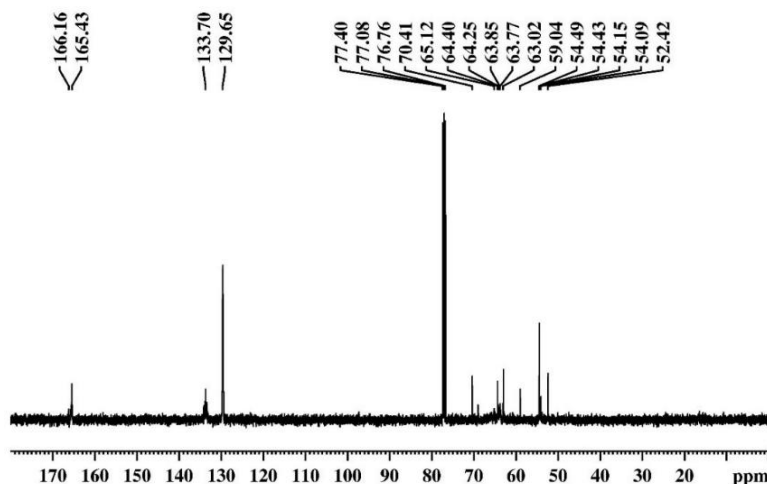

Figure 22. ^{13}C NMR spectrum of BTMP9.

A phosphorus atom whose signal in ^{31}P NMR spectrum is a multiplet of nine lines can be obtained as a result of a transesterification reaction of TMP and BHET, and also as a result of an exchange reaction between the ester group of BHET and the methoxy group of TMP. The signals for the phosphorus atoms of the products of transesterification (compounds **I** and **II**, Scheme 6) should be at the same shift in spectrum because its surrounding is the same. The signal for the phosphorus atom of dimethyl(2-hydroxyethyl) phosphate **III** (Scheme 6) should not coincide whit that of compound **I** and **II**, since there is a difference in the substituents – in dimethyl(2-hydroxyethyl) phosphate **III** the substituent is OCH$_2$CH$_2$OH and in **I** and **II** is OCH$_2$CH$_2$OC(O)-Ar-C(O)OCH$_2$CH$_2$OH. A methyl ester group - CH$_3$OC(O)- is formed as a result of the exchange reaction. It is known that the alkoxy groups of the H-phosphonic and the phosphoric acids

participate is exchange reactions with the amide [18], the urethane [19] and the carbonate [20] groups. We assume that the reaction between BHET and TMP proceeds according to the following reaction scheme (Scheme 6).
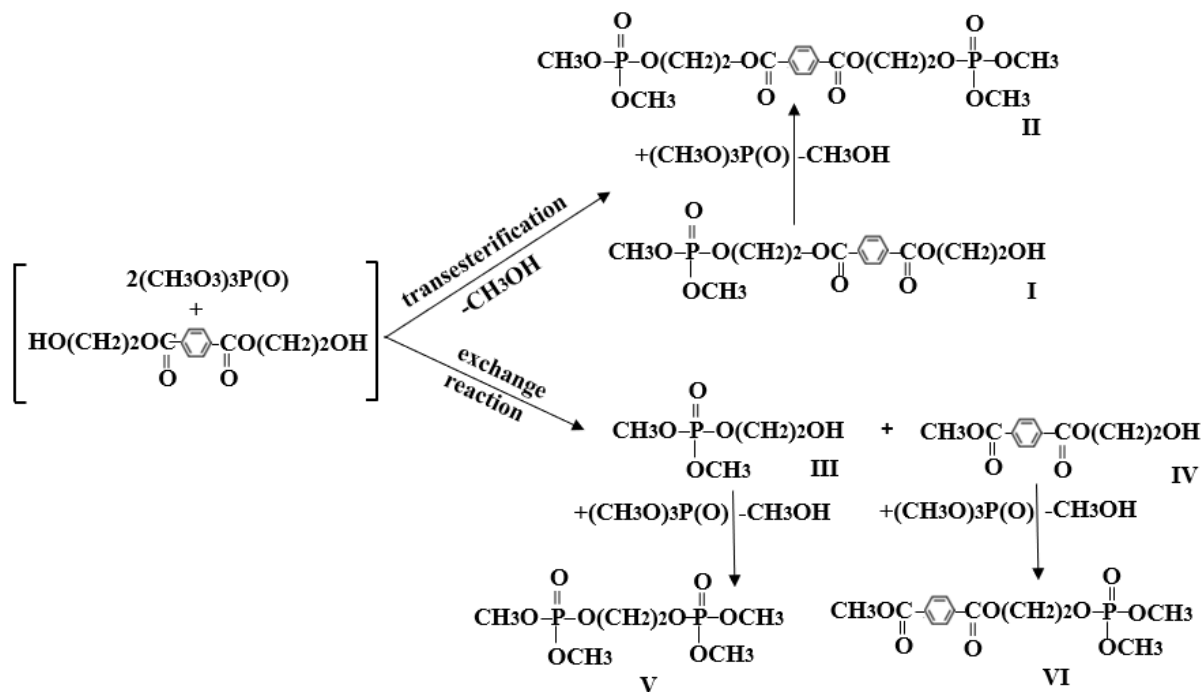
Scheme 6. Interaction between BHET and TMP.

Under these reaction conditions, two reactions take place simultaneously: transesterification between TMP with BHET and an exchange reaction between TMP and BHET. At the first stage of transesterification, a product **I** is formed, which at the second stage is converted into a product **II**. Since the exchange reaction proceeds at a lower rate compared to the transesterification reaction [18-20] it should be assumed that the signal at 2.29 ppm (Figure 18) should be relate to the phosphorus atom in the product **II**, and that at 2.70 ppm to the phosphorus atom in dimethyl(2-hydroxyethyl) phosphate **III**. Its content based on ^{31}P{H} NMR is 30.10 %. The content of methyl (2-hydroxyethyl) terephthalate **IV** is the same. Transesterification of TMP with dimethyl(2-hydroxyethyl) phosphate **III** and methyl (2-hydroxyethyl) terephthalate **IV** leads to the formation of compounds **V** and **VI** (Scheme 6). The NMR data suggest that the main products of the reaction of BHET (commercial product) with TMP are **II** with content of 70 %, **V** and **VI** with a content of 30 %.

3.2.2. Production of value-added products based on degraded product and TMP at a molar ratio of 1:2

It was found that the content of DP is BHET, 48.78 %; dimer, 20.89 %; trimer, 10.96 % and EG, 19.37 %. A reaction between DP and TMP was carried out at temperature of 190 °C for 3h at molar ratio 1:2. The data from ^{1}H and ^{13}C NMR analysis (Figures 23 and 24) are similar to these of the reaction product of the interaction of commercial BHET and TMP. The presence of signals at 3.88 ppm in ^{1}H NMR spectrum and 52.42 ppm at ^{13}C NMR spectrum confirms the assumption that an exchange reaction takes place in this interaction as well.
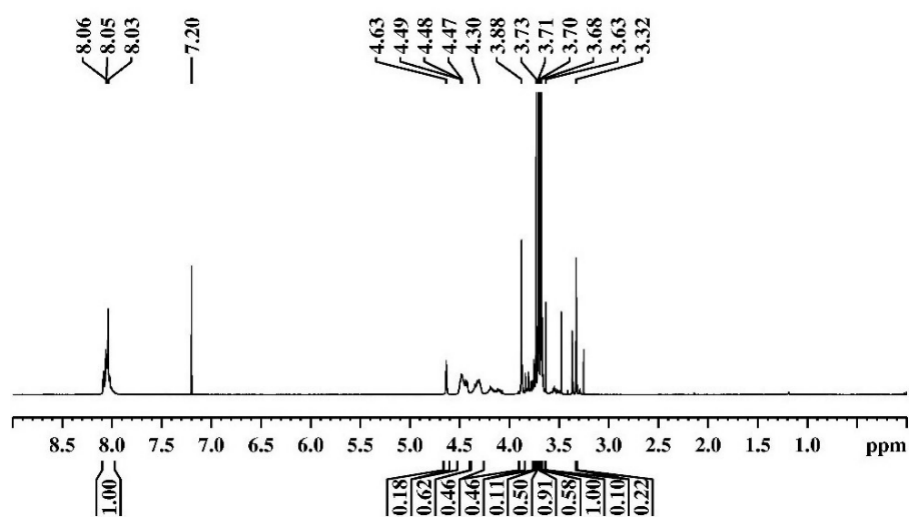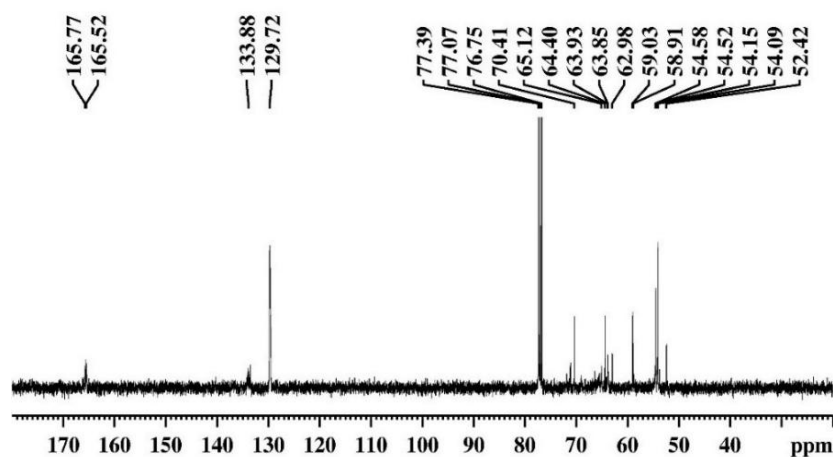

Figure 23. ^{1}H NMR spectrum of DP/TMP.

Figure 24. ^{13}C NMR spectrum of DP/TMP.

In $^{31}P\{H\}$ NMR spectrum of DP/TMP (Figure 25) the main signals (δ, ppm/integral intensity) are at: 2.48 (1.00) and 2.16 (0.59). In the ^{31}P NMR spectrum of DP/TMP (Figure 26) the signals represent multiplets of nine lines with a coupling constant $^{3}J(P,H) = 11.34$ Hz.
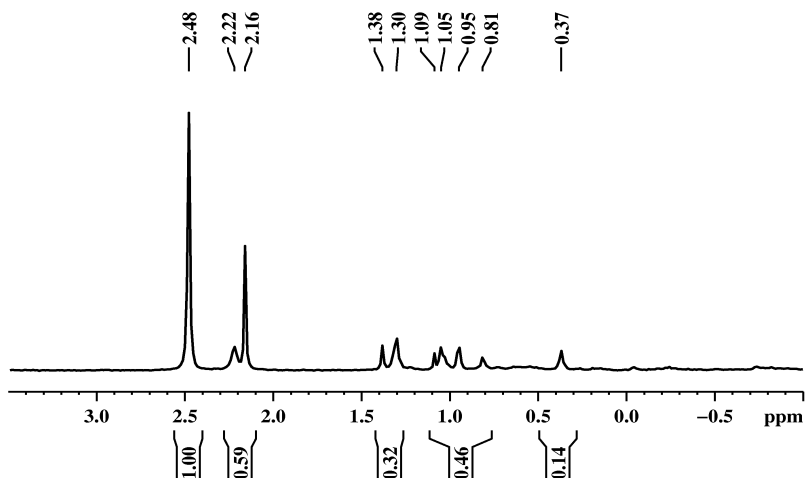
Figure 25. $^{31}P\{H\}$ NMR spectrum of DP/TMP.
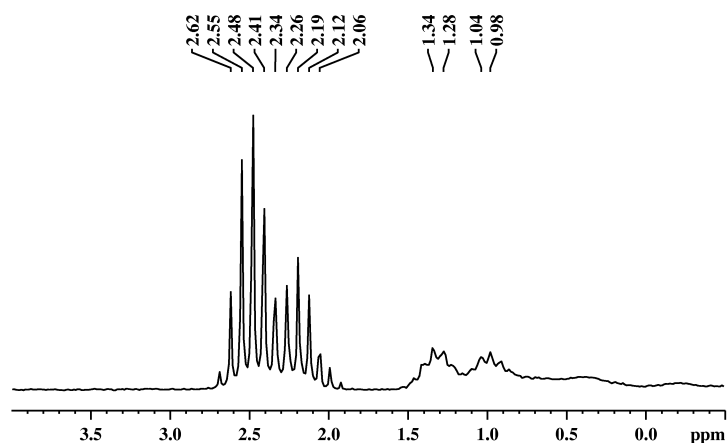
Figure 26. ^{31}P NMR spectrum of DP/TMP.

The content of 10.000 g DP is: BHET (0.0192 mol), dimer (0.0047 mol), trimer (0.0017 mol), EG (0.0312 mol). The molar content of EG is the highest – 1.6 times higher than that of BHET, 6.6 times higher than that of the dimer, and 18 times higher than that of the trimer. The GPC analysis (Figure 27) shows that the reaction mixture (DP/TMP) contained products with a molecular weight (Mw) of 220, 300, 430, 630, 835. With this ratio between the molar concentrations of the

components of the glycolysis product and TMP we propose the following reaction scheme for the interaction of DP and TMP (Scheme 7).
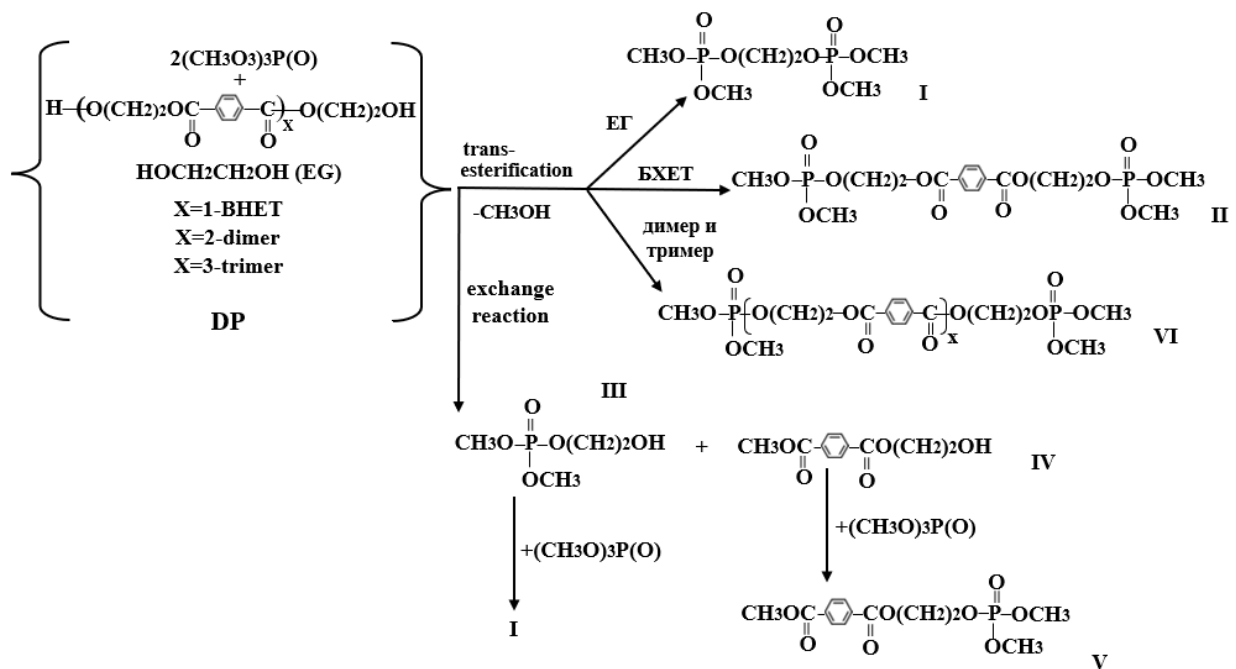
Scheme 7. Interaction between DP and TMP.

Figure 27. Molecular weight distribution curve of product DP/TMP, according to GPC analysis.

According to the proposed reaction scheme (Scheme 7), two reactions occur simultaneously in this interaction: a transesterification reaction whose products are **I, II, V** and **VI** and an exchange reaction whose products are **III** and **IV**.
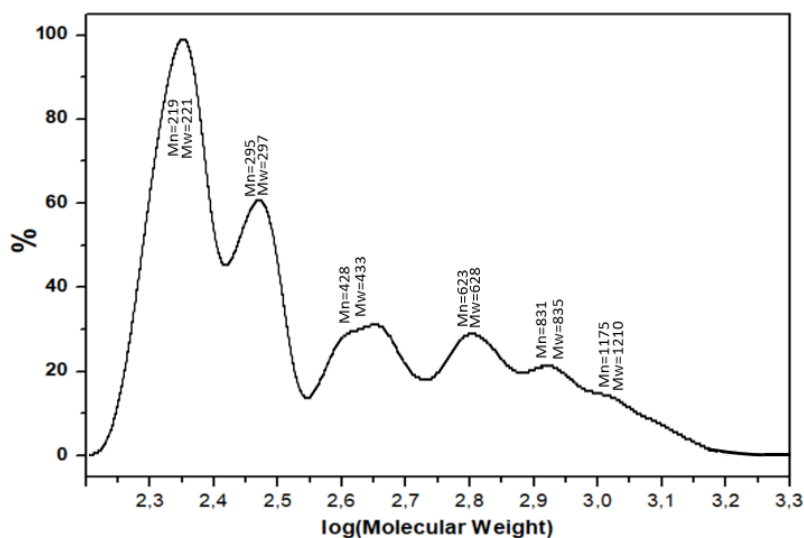
The GPC analysis indicates that DP/TMP contained products with a molecular weight (Mw) of 220, 300, 430, 630 and 835. The molecular mass 220 should be attributed to product **IV** (Mw=224) which confirms the progress of the exchange reaction. The molecular weight of 300 can be assisted to product **I** (Mw= 278) and the molecular weight 430 should be assigned to product **II** (Mw= 470). The molecular weights 630 and 835 should be attributed to the products **VIa** (x=2) (Mw = 662) and **VIb** (x=3) (Mw = 856).

Table 7 summarizing the molecular weights (Mn and Mw) and polydispersy index (PDI) of the products from the interaction between DP and TMP.

Table 7. *Molecular weights and PDI for the resulting products from the interaction between DP and TMP.*

продукт	Mn, Da	Mw, Da	PDI
I	290	300	1
II	430	430	1
IV	220	220	1
VIa	620	630	1
VIb	830	835	1

Product numbers are described relative to Scheme 7

4.Determination of thermal stability of the obtained phosphorylated products

Molecules containing phosphorus atom in its structure (inorganic phosphate and organophosphorus) are used as flames retardants. These elements support the formation of an inhibitory layer on the surface of the polymeric matrix during combustion and reduce the contact area between the polymer and oxidizing agents. During combustion, a solid layer of carbon mass – char residue (CR) is formed through a pyrolysis reaction. Decomposition of the phosphorus-containing compounds release radicals of PO·, P_2 and P· that have the ability to capture the radicals of H·, O· and HO·. These phenomena allow the formation of high amounts of the CR after the thermal decomposition, at high temperatures even in an inert atmosphere [21]. It is well known that the CR is a very important characteristic for the determining their ability as flame retardant additive since CR can favor an intumescent effect in the polymeric matrix and create a physical barrier to oxygen therein [22]. The amount of CR obtained after thermal decomposition in an inert atmosphere of various phosphorylated products ranges from 11 wt % to ~ 25 wt % [23-25].

From the TGA curve of the product BPClTEA (Figure 28) it can be seen that the decomposition of the sample proceeds in three steps: the first stage of degradation from about 90 °C to 200 °C the

weight lost is about 9%, in the second stage from 200 °C to 390 °C the decomposition rate is higher – 31 %. At the third stage from 390 °C to 500 °C the weight lost is about 43 %. At 800 °C the carbonized residue is about 17 %.
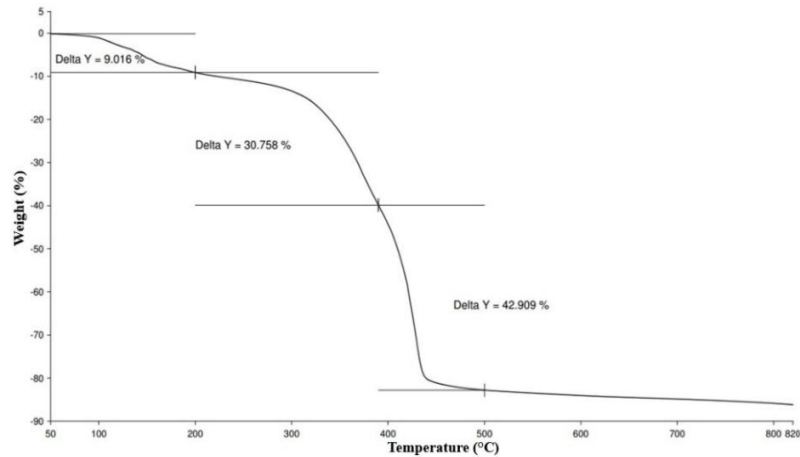
Figure 28. TGA curve of BPClTEA.

From TGA analyses of BTMP9 (Figure 29) it is evident that the degradation of the material takes place in three stages: at 350 °C which refers to the weight loss of around 57 %; in the second (at 450 °C) and the third (at 700 °C) stages the losses of material are around 28 %. The CR at 800 °C is nearly 15 %.

Figure 29. TGA curve of BTMP9.

From the TGA data of the reaction product from the interaction between DP with TMP (Figure 30) it is obvious that the decomposition of the sample proceeds in three stages: at 360 °C which

refers to the weight loss of 62 %; in the second (at 500 °C) and third (at 700 °C) stage, the losses are around 25 %. The remaining residue at 800 °C is about 13 %.
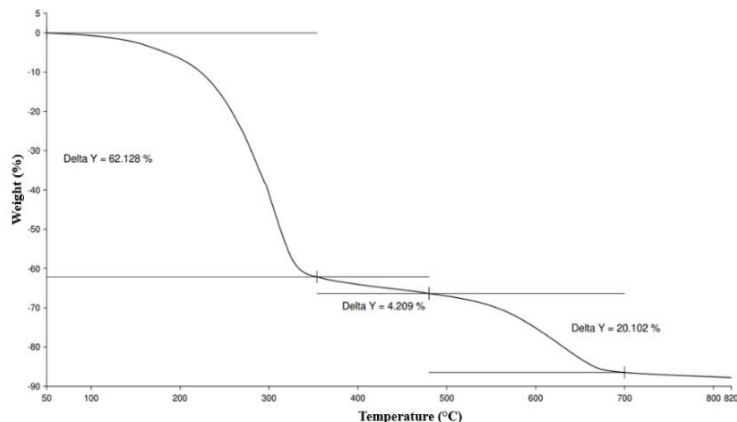
Figure 30. TGA curve of DP/TMP.

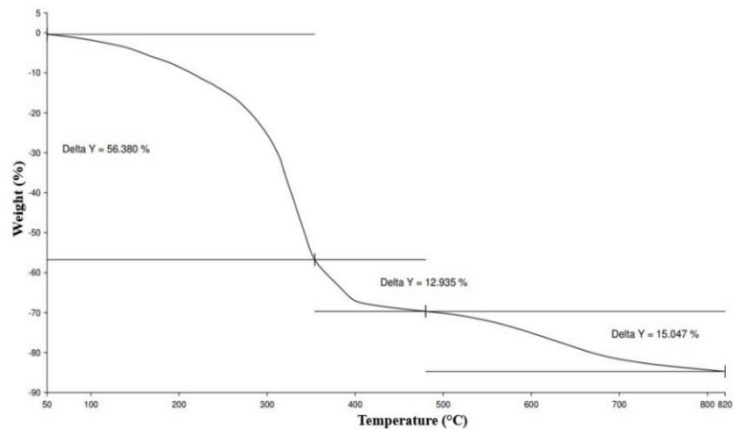From the TGA curve of product DP/PPD with is established that the thermal degradation takes place at three stages. In the first one was observed insignificant losses (~3.5 %) at a temperature of about 200 °C. In the next two phases from 250 °C to 400 °C and from 400 °C to 600 °C the losses of material (nearly 80 %) indicating the thermal decomposition of the phosphor-containing product. The thermogram also shows that the amount of CR after heating to 800 °C it is approximately 17 %.
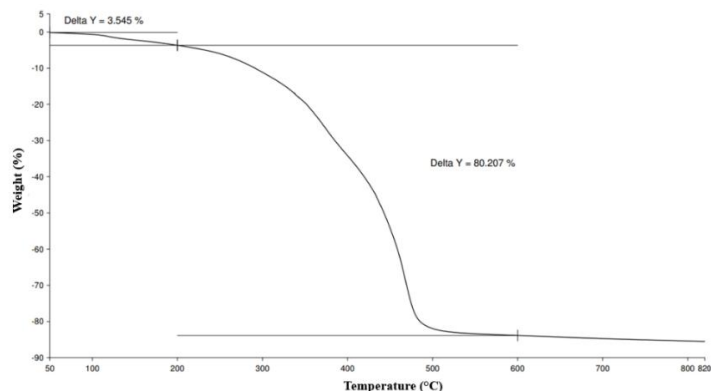
Figure 30. TGA curve of DP/PPD.

The amount of char residue obtained from TGA analyses of the newly obtained products after glycolysis of PET is similar to that of other phosphorus-containing materials used as flame retardant additives for polymers. The CR values of DP/PPD and DP/TMP are compared with those of phosphorylated materials reported in the literature [22-25]. This determines the potential application of the obtained products as flame retardant additives for polymers.

Conclusion:

For the first time, the obtained degraded product was used directly for the synthesis of new phosphorus-containing products via polycondensation reaction with PPD or transesterification with TMP without the need for additional purification or processing. Products were obtained from the interaction between a degraded product and PPD. The structure of the resulting oligomeric product contains a phosphorus atom and an aromatic group, which determine its increased resistance to combustion. TG analysis of DP/PPD showed an amount of charred residue of ~ 17%, which suggests the possibility of its application as an additive - flame retardant for polymers (polyurethanes, PET). The interaction between the PET degradation product and TMP leads to the production of triesters of phosphoric acid, which, in addition to being used as thermal stabilizers for polymer materials or lithium-ion cells, can be part of the composition of flame retardant additives for polymers. This is confirmed by the amount of charred residue obtained after TG analysis (~ 13 %).

IV. CONCLUTIONS

1. A catalyst, titanium (IV) phosphate (TiP), was synthesized and applied in the glycolysis process of PET flakes (obtained from waste bottles), showing a good catalytic effect, both when conducting glycolysis under conventional heating and when applying MW heating.

2. Conducting glycolysis with MW heating in the presence of a TiP catalyst is an effective way to degrade PET waste at relatively mild conditions and significantly reduce the reaction time (more than three times). It was found that using 0.2 wt % TiP catalyst for 45 min., a BHET yield of 75 % was achieved. A BHET yield of 71 % was achieved with conventional heating (0.3 wt %) for 155 min.

3. The obtained degraded product was used directly, without the need for additional purification or processing, for the synthesis of new phosphorus-containing products by polycondensation reaction with PPD or transesterification with TMP. Phosphorus-containing oligomeric products (DP/PPD and DP/TMP) were obtained with potential application as additives, giving desired properties to polymers.

V. DISERTATION CONTRIBUTIONS

➢ For the first time, a TiP catalyst has been used to degrade PET, through a glycolysis process with MW heating.

➢ For the first time, value added products have been obtained by directly using the degraded product obtained from the glycolysis of PET without the need for its additional processing, isolation or purification.

➢ For the first time, a method has been described for increasing the value of products obtained from the glycolysis of waste PET by phosphorylating with PPD and TMP to obtain new materials that have the potential to be applied as flame retardant additives for polymers.

List of scientific papers and presentations

The dissertation summarizes the results reported in the following publications and scientific presentations:

1. **Simona Zahova,** Ivelina Tsacheva, Kolio Troev, Violeta Mitova, ***"Conventional and MW assisted PET glycolysis promoted by titanium based catalyst",*** *Polymer degradation and stability,* **2023**, *212, 110353*, (IF 5.9) Q1 – noted **8** citation.

2. **Simona Zahova,** Pencho Tuleshkov, Kolio Troev, Violeta Mitova ***"Value-Added Products Derived from Poly(ethylene terephalate) Glycolysis ",*** *Molecules*, **2024**, *29, 4261.* (IF 4.2) Q1

Scientific presentations:

- 09.10.**2020 -** Third scientific and technical conference "Packaging - trends in development and application", Simona Zahova, Violeta Mitova: Methods for recycling polyethylene terephthalate and application of the obtained materials - **report** (included for publication in a collection with ISSN 2603- 4743).
- 03.06.**2021** - Twelfth scientific session "Young scientists in the world of polymers", Simona Zahova, Ivelina Tsacheva, Kolio Troev, Violeta Mitova: Study of the glycolysis process of waste PET in a microwave reactor - **poster**;

- 08.10.**2021** - Fourth scientific and technical conference "Packaging - trends in development and application", Simona Zahova, Ivelina Tsacheva, Kolio Troev, Violeta Mitova: Glycolysis of waste PET under conventional and microwave heating in the presence of titanium (IV) phosphate catalyst-**report**

- 20.10.**2021** - Scientific and practical conference "Trends in food and beverage packaging - safety, quality, ecology and regulatory framework", Simona Zahova, Ivelina Tsacheva, Kolio Troev, Violeta Mitova: Glycolysis of waste PET under conventional and microwave heating in the presence of a titanium(IV) phosphate catalyst-**report**

- 02.06.**2022** - Thirteenth scientific session "Young scientists in the world of polymers", Simona Zahova, Ivelina Tsacheva, Kolio Troev, Violeta Mitova: Preparation of phosphorus-containing polymer additives based on recycled PET - **poster;**

- 05-08.07.**2022** – 20th Symposium POLYMERS 2022, Simona Zahova Ivelina Tsacheva, Kolio Troev, Violeta Mitova*: Preparation of phosphorus-containing polymer additives based on recycled PET* – **poster**;

- 30.09.**2022** - Fifth scientific and technical conference "Packaging - trends in development and application", Simona Zakhova, Ivelina Tsacheva, Kolio Troev, Violeta Mitova: Preparation of phosphorus-containing polymer additives based on recycled PET-**report**

- Most significant scientific applied achievement for **2023 -** Glycolysis of PET waste under conventional and microwave heating; project manager Assoc. Prof. Violeta Mitova, PhD; The results are published in 1 article with authors:
  Simona Zahova, Ivelina Tsacheva, Kolio Troev, Violeta Mitova; Conventional and MW assisted PET glycolysis promoted by titanium based catalyst, Polymer Degradation and Stability 2023, 212,110353. **IF 5.9, Q1**.

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