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Effect of functional groups on the thermal degradation of phosphorus- and phosphorus/nitrogen-containing functional polymers

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Abstract

In the present study the thermal behavior of phosphorus- and phosphorus/nitrogen-containing functional polymers was studied. The polymers were synthesized *via* oxidative chlorophosphorylation reaction of butadiene rubber and were subsequently subjected to hydrolysis, aminolysis and/or alcoholysis in order to introduce appropriate functionalities. The successful modifications of the polymer and presences of functional groups were determined using Fourier Transform Infrared Spectroscopy. It was found that the product of hydrolysis of the modified butadiene rubber contains acidic groups in its structure, the products of aminolysis and alcoholysis contain both acidic and amine and/or an alcohol derived moieties. The kinetic analyses of the thermal decomposition reaction were evaluated using thermogravimetric analysis and subsequently Friedman and Ozawa-Flynn-Wall methods. It was shown that degradation of the cross-linked polymers depends on the attached functional groups. The mass loss and the overall kinetic parameters of degradation showed complex mechanisms which characterize these thermal reactions.

Key words: butadiene rubber, functional groups, thermal behavior, kinetic parameters of degradation

Introduction

1 Functional synthetic polymers (FSP) are increasingly prominent in many applications due to their
2 unique properties. The specific application fields of FSP are determined by the nature of functional
3 groups and their location and the structure of the polymer matrix [1, 2]. FSP with pendant
4 phosphorus-, phosphorus/nitrogen-containing groups and cross-linked matrix have been
5 successfully applied in nanotechnology, biotechnology and biomedical engineering, food industry,
6 hydrometallurgy, catalysis, purification of various industrial and waste water as a polymer supports,
7 adsorbents and ion exchange resins [3–8]. Most of these processes are carried out at relatively high
8 temperatures and are accompanied by some structural changes in the polymer matrix and functional
9 groups. Thus, gaining knowledge on physical and chemical properties with thermal stability
10 measurements seems to be crucial for successful applications of FSP [4, 9–12].

11 Many researchers have studied thermal stability of cross-linked FSP with different types of
12 pendant functional groups [13–22]. The thermal behavior of a series of commercial polymers
13 (Purolite C104, C105 and C106, Amberlite IRC 120, etc.) with carboxylic groups has been
14 investigated by Chambree et al [13,14]. The apparent kinetic parameters and the degradation
15 products depending on the sample properties (i.e. granulation, cross-linking degree, porosity and
16 physical form) were evaluated. The thermal stability of copolymer networks based on 4-
17 vinylpyridine/crotonic acid/divinylbenzene and their N-oxide derivatives have been investigated. As
18 a result was determined the influence of pyridine groups and its oxide forms to the thermal stability
19 of polymers with carboxyl groups. It has been found that the decomposition temperatures do not
20 depend on the 4-vinylpyridine content and the thermal stability of the copolymer networks were
21 decreased with the N-oxidation procedure [15]. In another works [16–18] thermal behavior of some
22 acrylamide, its amine derivatives and acrylonitrile cross-linked copolymers have been studied. It
23 was revealed that the decomposition characteristic were dependent on the nature and molar relations
24 of comonomers, attached functional groups, cross-linking degree, porosities and on the extent
25 conversion. These investigations show that cross-linked FSP with carboxylic groups and their
26 various derivatives have been explored in detail elsewhere [13–18]. The inspection of appropriate
27 works [19–21] point that the literature also gives enough information about thermal stability and
28 overall kinetic parameters of degradation process for polymers with sulfo groups, but in case of
29 polymers with phosphorus-containing groups, literature seems to offer relatively poor information
30 [22].

31 Over the past few years, our group developed the synthesis of polymers with different types
32 of phosphorus-containing functional groups by chemical modification (oxidative
33 chlorophosphorylation reaction) of industrial polymer – butadiene rubber (BR) [23]. It was
34 established that this reaction can be performed using readily available commercial reagents under

1 mild conditions and in simple equipment. The reaction scheme allows the synthesis of the
2 respective products with the active P–Cl bonds that can be further modified for obtaining FSP with
3 various functional groups. Thus, some phosphorus-(PCP) [23] and phosphorus/nitrogen-containing
4 (PNCP) [24, 25] polymers with different types of functional groups were synthesized by this
5 method. The mentioned polymers were successfully applied for the formation of nanocomposites
6 with magnetic nanoparticle [26], an adsorbent [27, 28] and an extractant for preconcentration of
7 metal ions by solid-phase extraction method [24–26]. Furthermore, it was indicated that the nature
8 of functional groups play an important role during the application process. Polymers containing
9 phosphoric acid groups were found to be effective and universal adsorbents for heavy metal ions
10 [27], while polymers with amine groups (instead of one hydroxyl moieties in the acidic groups) for
11 organic molecules [28].
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19 In the present study we investigate the thermal degradation behavior of ten polymers with
20 different types of functional groups, synthesized through chemical modification of BR. A kinetic
21 analysis of the thermogravimetric/differential thermogravimetric results by means of the Friedman
22 and Ozawa-Flynn-Wall (OFW) kinetic methods was also presented. The investigated effects of
23 functional groups on thermal behavior of the functional polymers may be used for improvement of
24 industrial processes in this field.
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30 It must be noted that our previous works included some preliminary information about only
31 three polymers from the group studied in this paper [23, 25, 28]. Therefore the detailed synthetic
32 procedures with interpretation of their chemical structures were also described in this paper.
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37 **Experimental**

38 **Materials**

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41 The functional polymers used in the study were synthesized on the base of BR. BR was purchased
42 from Voronezh Synthetic Rubber Manufactory (Russia). Phosphorus trichloride (PCl₃), Carbon
43 tetrachloride (CCl₄), sulfuric acid (H₂SO₄), monoethanolamine (MEtA), diethanolamine (DEtA),
44 diethylamine (DEA), triethylamine (TEA), 4-aminoantipyrine (AAP), o-phenyldiamine (PhDA),
45 phenylhydrazine (PhH), diphenylamine (DPhA), glycerol (Gly), p-xylene, chloroform and acetone
46 that were applied for chemical modification of BR and their purification/washing were used without
47 any further purification (Gorex Analyt GmbH). Oxygen was supplied to the reaction medium by
48 purging through the concentrated H₂SO₄.
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57 **Methods**

58 **Preparation of polymers**

1 All the polymers were synthesized in several steps (see Scheme 1). The first step was common for
2 all the samples and consisted of treatment of BR by PCl_3 leading to phosphochlorinated rubber
3 (PChBR). In the second step, depending on introduced functional groups, PChBR underwent either
4 hydrolysis or aminolysis or alcoholysis reactions. The final chemical structure of some samples was
5 obtained after water treatment. The synthesized polymers were abbreviated as P1–P10, respectively.

6 **Chemical modification of BR (oxidative chlorophosphorylation reaction).** A 5 % solution of BR
7 in CCl_4 was prepared. After that PCl_3 was added to the reaction mixture at a ratio of 1:5 (BR: PCl_3 ,
8 w/w) and the reaction system was purged with oxygen at a rate 7 L h^{-1} . The reaction was conducted
9 for 8 hours, and after its completion, p-xylene was added dropwise under continues evaporation of
10 the liquid phase (containing CCl_4 , the POCl_3 intermediate and the unreacted PCl_3). After that the
11 obtained suspension containing PChBR and p-xylene was purged with nitrogen.

12 **Synthesis of P1.** P1 was synthesized *via* hydrolysis of PChBR. The hydrolysis process was carried
13 out at $50 \text{ }^\circ\text{C}$ for 4 h under continuous stirring. Then the product was filtered, washed with distilled
14 water up to neutral pH, and then with acetone. The product was initially dried in air and then in the
15 vacuum, at $40 \text{ }^\circ\text{C}$.

16 **Synthesis of P2.** P2 was synthesized by aminolysis of PChBR by MEtA. MEtA (2 mmol) was
17 added to the suspension (PChBR in p-xylene, 1 mmol) in equimolar amount to functional groups.
18 The reaction was conducted at $45 \text{ }^\circ\text{C}$ for 4 h under continuous stirring. The product was purified in
19 the same way as for P1.

20 P3–P5 compounds were synthesized using the same procedure as described above for P2.
21 DEtA, DEA, TEA were used respectively as amines.

22 **Synthesis of P6.** The solution of AAP in chloroform/acetone solvent mixture was added to
23 suspension of PChBR and p-xylene. The reaction mixture was stirred at a $45 \text{ }^\circ\text{C}$ for 4 h. The
24 product was purified in the same way as P1.

25 The samples P7–P9 were synthesized using the same procedure. PhDA, PhH and DPhA were
26 used respectively as amines.

27 **Synthesis of P10.** Gly (2 mmol) was added to the suspension of PChBR (1 mmol) in p-xylene. The
28 reaction mixture was stirred at $45 \text{ }^\circ\text{C}$ for 4h. The purification procedure was the same as previously
29 for P1.

30 The colors of the obtained polymers changed from light brown to dark brown depending on
31 type of samples. The obtained polymers before use were scuffed in agathic vessel up to disperse
32 state (35–50 mesh).

33 **Fourier Transform Infrared Spectroscopy analysis**

1 The synthesized PCP and PNCP were characterized by Fourier Transform Infrared Spectroscopy
2 (FTIR) using a Thermo Nicolet iS10 FTIR spectrometer (Thermo Scientific) with ATR equipment
3 (SMART iTX). Samples before the measurements were dried in vacuum. The obtained spectra were
4 baseline corrected using Omnic v9.0 software (Thermo Scientific).
5

6 **Thermogravimetric analyses**

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8 Thermogravimetric (TG) analyses were performed using NETZSCH TG 209/cell Thermal Analysis
9 System between 20 and 850 °C using Al₂O₃ crucibles. The measurements were carried out under
10 nitrogen flow (35 mL min⁻¹) at three different heating rates ($\beta=1, 5$ and 10 °C min⁻¹) for granulated
11 samples. The sample masses were 4.400 ± 0.430 mg.
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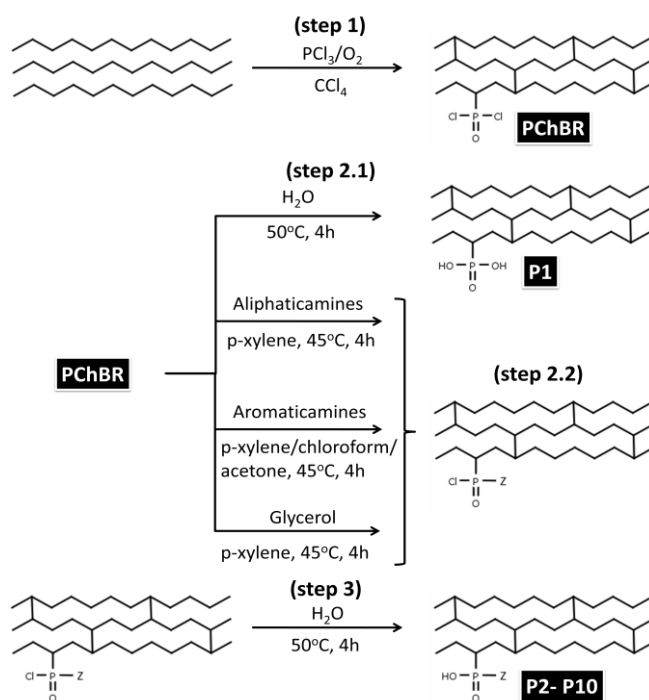
16 **Differential Scanning Calorimetric analyses**

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18 Differential scanning calorimetric (DSC) analyses was carried out on DSC 1, Fa (Mettler Toledo)
19 between 30 and 500 °C using Al crucibles. The measurements were done under nitrogen flow (20
20 mL min⁻¹) at 10 °C min⁻¹ heating rate. The samples amount were *ca.*2.300 ± 0.400 mg.
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28 **RESULTS AND DISCUSSION**

29 **Synthesis and characterization of the polymers**

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31 The general synthetic procedure is shown in Scheme 1. Chemical modification of BR was carried
32 out by oxidative chlorophosphorylation reaction with PCl₃ in the presence of oxygen leading to the
33 formation of PChBR (Step 1 in Scheme 1). The reaction procedure was described elsewhere in
34 details [23–28]. It was emphasized that during the modification reaction of the polymer cross-
35 linking process occurred between macromolecular chains. As a results we obtained cross-linked
36 products with different functional groups such as: –P(O)Cl₂ (phosphonyldichloride) and –OP(O)Cl₂
37 (phosphoryldichloride) [23–28].
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Scheme 1 Synthetic procedure for modification of BR and synthesis of phosphorus- and phosphorus/nitrogen-containing polymers

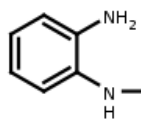
During the hydrolysis reaction (Step 2.1) phosphonyldichloride and phosphoryldichloride groups were transformed to phosphonate ($-\text{P}(\text{O})(\text{OH})_2$) and phosphate ($-\text{OP}(\text{O})(\text{OH})_2$) groups respectively (sample P1). The nature and distribution of functional groups in the polymer matrix, as well as the nature of the spatial network in polymer P1 was studied before by means of NMR spectroscopy in solid phase [23].

After aminolysis and alcoholysis of PChBR an intermediate compound (PChBR-Z, Step 2.2) was obtained. In the third step P2-P10 ($-\text{P}(\text{O})(\text{OH})(\text{Z})$, Step 3) polymers were formed after washing with water. Table 1 present the formulas of Z groups attached to particular synthesized polymers.

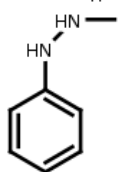
Table 1 Structures of Z groups attached to particular polymers

Polymer number	Nature of the Z group
P2	$-\text{HN}-(\text{CH}_2)_2\text{OH}$
P3	$-\text{N}(\text{C}_2\text{H}_4\text{OH})_2$
P4	$-\text{N}(\text{C}_2\text{H}_5)_2$
P5	$-\text{N}^+(\text{C}_2\text{H}_5)_3$
P6	

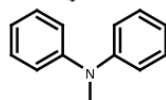
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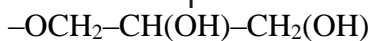
P8



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P10



The expected structures of the samples were confirmed by FTIR spectroscopy. The FTIR spectrum of P1 is shown in Fig. 1 and the spectra of P2–P10 are shown in Fig. S1 (Supplementary material).

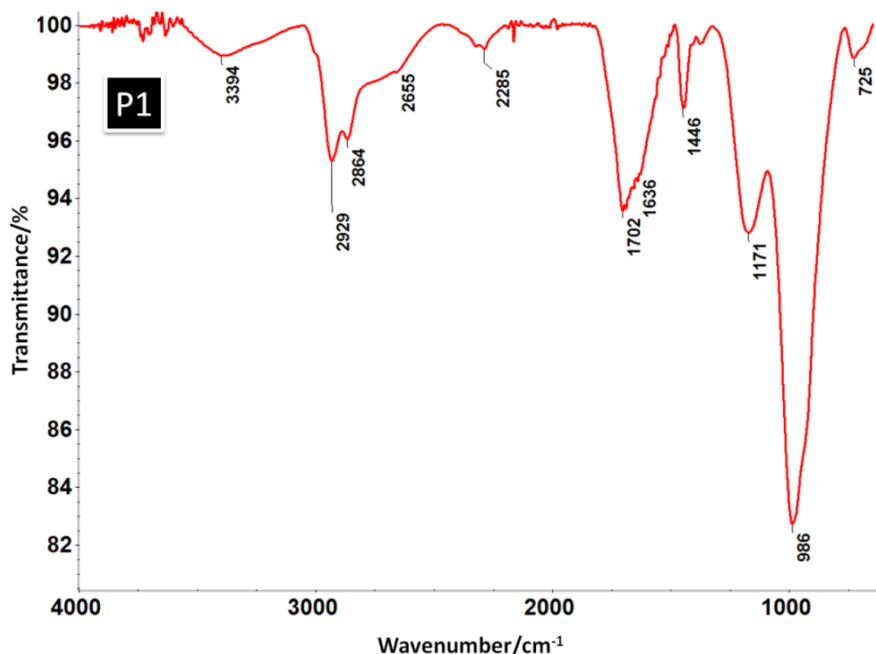


Fig.1 FTIR spectrum of the polymer P1

Bands appearing in 1200–1150 cm^{-1} region can be assigned to vibrations of P=O groups. The IR bands at 1702, 2864 and 3394 cm^{-1} are attributed to OH vibration in $-\text{PO}(\text{OH})_2$ groups. IR band at 986 cm^{-1} , corresponding to C–O–P bond, indicates the attachment of $-\text{PO}(\text{OH})_2$ group to the polymer chain *via* oxygen.

When comparing the spectra of P2 and P1 it is clearly seen that new characteristic bands assigned to secondary amines N–H: 3256 cm^{-1} (stretching vibrations) and 1633 cm^{-1} (bending vibrations) appeared. Furthermore, the band for C–O–P bonds was splitted (1000-1100 cm^{-1}). Overlapping of characteristic bands of P=O and C–N groups was observed in the region between 1100–1200 cm^{-1} . In general, the largest changes were observed in the region between of 900–1750

1 cm⁻¹. Very significant changes were also observed for the samples P3 and P4 when compare to the
2 spectra of P1 indicating successful modification of the polymer. This observation can be explained
3 taking into account that in the selected reaction conditions, aliphatic amines are in liquid state and
4 they can easily reach the reaction sites (groups with P-Cl bonds). Although TEA is also in liquid
5 state the degree of substitution of PChBR by this amine (P5) seems to be lower than for P3 and P4
6 (compare the FTIR spectra for P1 and P3, P4, P5) likely due to larger sterical hindrance in the
7 tertiary amines compare to the secondary ones. The results of the FTIR analyses show that the
8 PChBR with P-Cl bonds can also be modified with aromatic amines (during experiments the amine
9 solutions in p-xylene/chloroform/acetone solvent mixtures were used). When comparing the spectra
10 of polymers P6-P9 with the spectrum of polymer P1 the differences in the region of 900-1200;
11 1400-1700 and 3000-3400 cm⁻¹ are due to different types of amines used. It proves the presence of
12 aromatic moieties in the functional groups of polymers P6-P9. Thus, despite the fact that for the
13 syntheses of polymers P6 and P9 aromatic amines were used in solution (in the reaction conditions,
14 aromatic amines are in solid state), they can reach the reaction sites and be used for preparation of
15 functional polymers.
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26 Finally, the spectra of polymers P1 and P10 were compared. As it may be observed for the
27 spectrum of polymer P10 the IR bands at about 950-1000 cm⁻¹ (C-O-P) and 3000-3500 cm⁻¹ (O-
28 H) became more intense. This confirms successful reaction between PChBR and Gly and
29 attachment of alcohol moieties to the polymer.
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33 The overall results of FTIR measurements indicate that in P2-P10 were indeed introduced
34 appropriate functional groups (e.g. amines, hydroxyl) in addition to P-OH groups that were obtained
35 by hydrolyses of P-Cl groups.
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40 **Identification of thermal decompositions steps**

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42 TG analyses have been widely used for evaluating the thermal stability of polymers. This kind of
43 measurement is fast and requires only very small amount of a sample.
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46 TG and DTG curves, characteristic for the polymers are presented in Fig. 2 (for P1 and P2)
47 and Fig. S2 (for P3-P10). The degradation stages and the mass loss at various heating rate, derived
48 from the TG curves are listed in Table 2.
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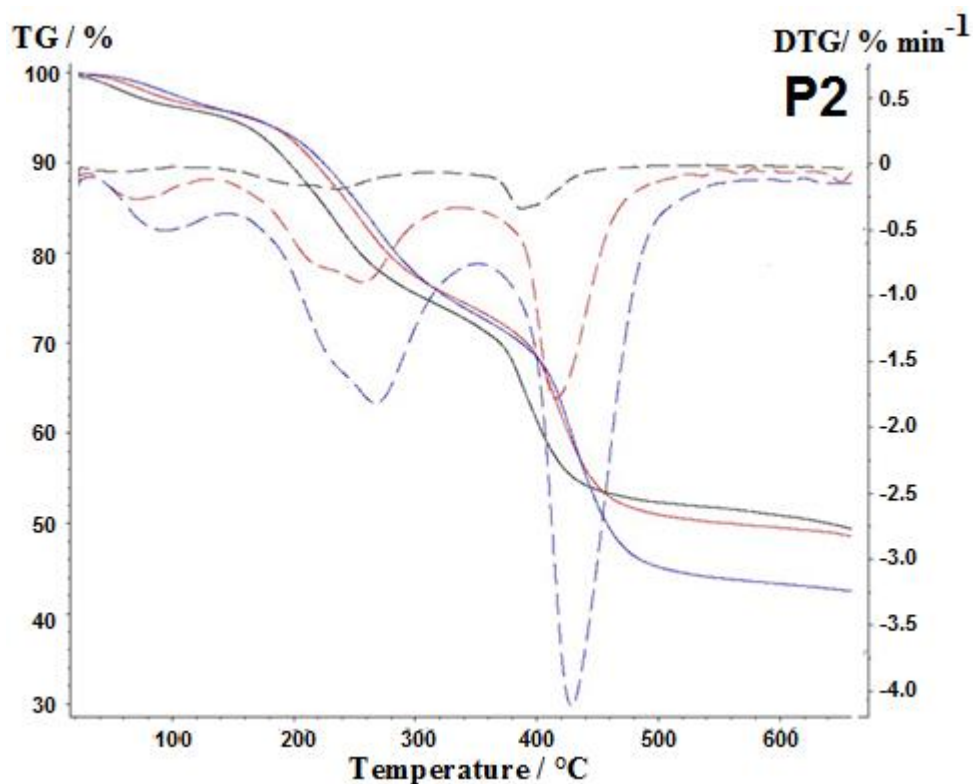
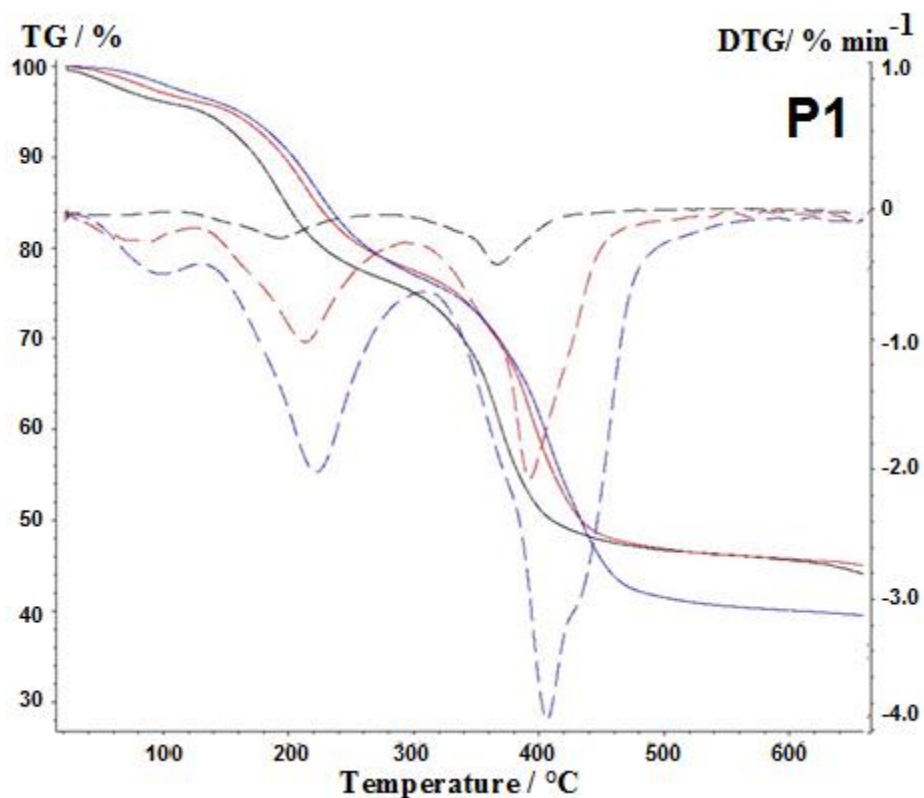


Fig. 2 TG and DTG curves of the polymers P1 and P2 with different heating rate: black line – 1 °C min⁻¹; red line – 5 °C min⁻¹; blue line – 10 °C min⁻¹

Table 2 Mass changes and characteristic temperatures of thermal degradation for the polymers at different heating rates.

Polymers	Heating rate/ $^{\circ}\text{C min}^{-1}$	First step				Second step				Third step				Residue at $850^{\circ}\text{C}/\%$
		T_i	T_m	T_f	$\Delta m/\%$	T_i	T_m	T_f	$\Delta m/\%$	T_i	T_m	T_f	$\Delta m/\%$	
P1	1	24	59	110	4	110	193	274	19	274	367	540	30	27
	5	24	88	124	4	124	213	293	18	293	393	550	32	34
	10	30	98	131	3	131	222	311	20	311	407	588	36	35
P2	1	24	53	100	3	100	235	319	22	319	388	551	23	30
	5	27	71	128	4	128	256	333	21	333	416	598	25	34
	10	31	94	146	4	146	267	346	22	346	429	608	30	33
P3	1	27	60	104	3	104	234	314	19	314	391	560	20	45
	5	27	90	133	3	133	257	344	19	344	420	601	25	43
	10	36	94	117	2	117	264	356	20	356	436	620	22	50
P4	1	24	36	71	1	71	178	304	36	304	376	540	24	23
	5	29	56	84	1	84	210	325	34	325	410	586	28	27
	10	30	72	98	1	98	231	343	35	343	426	597	30	28
P5	1	24	45	74	1	74	206	301	24	301	382	592	30	27
	5	29	88	107	2	107	229	318	22	318	416	619	35	30
	10	33	37	116	2	116	246	335	24	335	432	643	37	32
P6	1	24	45	97	2	97	232	287	17	287	406	551	22	33
	5	29	66	113	2	113	249	316	18	316	422	593	22	39
	10	29	73	125	3	125	259	318	18	318	435	617	29	42
P7	1	25	44	92	1	92	208	270	19	270	390	475	22	30
	5	27	64	102	1	102	222	306	20	306	426	594	26	36
	10	31	75	116	1	116	231	320	20	320	440	609	31	40
P8	1	24	45	81	1	81	170	284	23	284	390	546	22	30
	5	27	65	98	1	98	184	302	24	302	408	580	25	31
	10	30	77	103	1	103	190	317	25	317	425	623	28	35
P9	1	24	56	101	2	101	206	283	15	283	389	549	32	35
	5	28	88	120	3	120	223	304	16	304	412	602	37	34
	10	34	100	130	2	130	235	315	16	315	427	632	41	34
P10	1	24	68	101	2	101	257	298	24	298	385	606	29	36
	5	31	90	121	3	121	279	319	24	319	417	637	32	34
	10	34	106	130	3	130	288	332	25	332	433	639	35	32

T_i – Initial degradation temperature, $^{\circ}\text{C}$

T_m – The temperature corresponding to the maximum rate of degradation (based on DTG curves), $^{\circ}\text{C}$

T_f – The final degradation temperature, °C

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2 It can be seen that the degradation of the polymers proceeds in three stages (Fig. 2, S2, Table
3 2) irrespective to the nature of functional groups. However the characteristic temperatures for
4 particular samples are different. The characteristic temperatures of decomposition steps were shifted
5 to the lower values with decrease of the heating rate and each stage was found to be more clearly
6 separated from other stages. In general, three-stage thermal degradation process are common for
7 various polymer with functional groups [17, 29], including some phosphorus-, phosphorus/nitrogen-
8 containing polymers [30, 31].
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11 The obtained plots for all the studied polymers show very similar shape of TG and DTG
12 curves for the first decomposition step. Based on experimental condition (synthesis, pre-treatment
13 procedure) and structure of the polymers (porous and cross-linked), it seems that mass loss in this
14 stage is due to the elimination of physically adsorbed water, existing in the pores, and water
15 hydrogen-bonded with the functional groups.
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17
18 According to the literature [13] the values of mass loss in the first stage assigned to
19 evaporation of physically adsorbed water were different (between 4 and 22 %) for cross-linked
20 polymers. It depends on several factors. In work [13] series of commercial polymers with
21 carboxylic groups, based on methacrylic–divinylbenzene matrix were investigated. The authors
22 showed that in the same polymer matrix important role play the form of functional groups (acidic or
23 sodium salt), the size of granulated samples, its microstructure and heating rate. The results
24 obtained in the current study (Table 2) show that temperature characteristic of this first stage lie in
25 the range between 20 and 150 °C and the relatively small mass loss vary between 1 and 4 %.
26 Considering that the investigated polymers have the same polymeric matrix, degree of cross-linking
27 and size of the granules the reported differences may be explained by the nature of the functional
28 groups and their hygroscopicity.
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31 The second degradation stages (see Fig. 2 and S2) differ more significantly among the studied
32 polymers. It was observed (Table 2) that the value of mass loss also varies in a fairly wide range
33 (17-36%) and for all the samples the second decomposition stage is characterized by relatively
34 higher values of the mass losses than for the first stage. In this stage, the mass loss is the result of
35 the conversion/decomposition of the functional groups. The process starts with the reaction of
36 dehydration of phosphonate and phosphate groups in the polymer P1. As it can be seen in Fig. 2 and
37 S2 the DTG curves have a bit more complex shapes as compare to the one of P1 and show a wider
38 temperature range in which the mentioned conversion/decomposition occurs (relatively more
39 pronounced for P2, P3, P8 and P10). This can be explained by the fact that these polymers have
40 both the acidic groups (phosphonate and phosphate) and other types of groups (amines and
41

hydroxyl). Therefore, in this stage in addition to dehydration of the acid groups other types of parallel/consecutive reactions may take place. The conversion reactions of the fragments of aliphatic (dehydration processes for P2 and P3, and other reactions for P4, P5) and aromatic amines (for P6–P9) and alcohols (P10) can be referred to these reactions. As a result of these reactions values of T_m were generally shifted to the higher ones as compared to the one measured for P1 (222 °C at heating rate: 10 °C min⁻¹). The highest value of T_m (288 °C at heating rate: 10 °C min⁻¹) was obtained for P10, which can be attributed to more complex intramolecular reactions of Gly moieties that may turn into more stable connections.

The value of mass loss depends on the molecular mass of the products of the degradation process and possibility of their release from the reaction medium that could not be explained only on the basis of the TG results. But, the highest value of mass loss for the sample P4 (Table 2) may be attributed to higher degree of substitution obtained for this sample as compared to the other ones. (Scheme 1, step 2.2). It may be explained by higher rate of aminolysis for the aliphatic and less bulky amine used for the synthesis of P4 compare to other modification reactions. It was additionally confirmed by FT-IR results (see above).

The third stage of decomposition is also characterized by significant mass loss (between 20 and 37 %). This stage can be attributed to side group elimination from polymer chain, random depolymerization and detachment of large organic molecules, formed in the second stage. In this stage reactions such as cracking and gasification processes characteristic for these high temperatures occur as well. The mass loss varied from 30 to 36 % for the polymer P1. For majority of amine derivatives of P1 the amount of the mass loss is decreased to the level about 20–30 %. For P5 and P10 the mass losses are similar to the one measured for P1. The nature of functional groups also influences the temperature characteristics in this stage. In particular, the values of T_m for samples P2–P10 were increased by ca. 10 - 40 °C as compared to P1.

Finally, the residual amounts of the polymers were compared. As it was revealed, the nature of the functional groups in some way affect this value as well. The largest value was observed for P3 while the smallest for P4. For the others polymers the values were moderate and similar. Totally, the values of residues were in the range of 20 and 50 % that are typical for cross-linked functional polymers [13–22].

It is well-known that the thermal degradation of cross-linked polymers at non-isothermal conditions is a very complicated heterogeneous process. The main steps of the heterogeneous degradation reactions of the solid materials are as follows: (i) reactants and heat transfer to the separation surface of phases, (ii) rearrangement of interfaces with the consumption of solid reactant, (iii) transport of volatile products from the reaction space [18]. Unequivocally, we can say that the nature of functional groups influences the abovementioned steps of heterogeneous process. In

generally, thermal stability of the polymers studied here can be compared to the stability of other commercial and in laboratory-synthesized functional polymers using appropriate characteristic temperatures [13–22].

Thermal degradation kinetics of polymers

According to non-isothermal kinetic theory, thermal degradation of polymers can be described by the following function

$$\frac{d\alpha}{dT} = \frac{1}{\beta} A e^{\frac{-E_a}{RT}} f(\alpha) \quad (1)$$

where $f(\alpha)$ is a differential expression of a kinetic model function, α is a fractional mass loss, β is a heating rate, E_a is an activation energy, A is a pre-exponential factor for a given decomposition reaction, T is temperature, and R is the general gas constant. The fractional mass loss ranges from 0 and 1 and expresses the reaction progress as a function of time or temperature. For non-isothermal TG analysis, the fractional mass loss at any time is:

$$\alpha = \frac{m_0 - m_T}{m_0 - m_\infty} \quad (2)$$

where, m_0 is the initial sample mass, m_T is the sample mass at temperature T and m_∞ is the final sample mass.

In our study for evaluation of kinetic parameters (E_a , A) Ozawa–Flynn–Wall (OFW) [32–34] and Friedman [35] methods were chosen. These methods could be used to study polymer thermal degradation kinetics, without any prior knowledge of the reaction mechanism. The kinetic parameters were calculated using Netzsch Thermo kinetics Software [36]. The mean values of E_a and A for all the samples are presented in Table 3.

It is clearly seen from Table 3, that the values of E_a calculated by the two methods for the first degradation stage are similar for all the studied polymers. The overall E_a of the first degradation stage varied between 50.0 and 96.0 kJ/mol. Polymer P8 has the highest E_a while polymers P2, P5 the lowest. If one compares the values of E_a with the corresponding values of mass loss some discrepancy can be observed. It can be explained by variations of removal of physically adsorbed water from the samples due to various surface morphologies and porosities [25, 26]. Also similar values of E_a for some commercial cross-linked polymers based on methacrylic–divinylbenzene copolymer with carboxyl groups were described elsewhere [13, 14].

Table 3 The kinetics parameters obtained by Friedman and OFW methods for polymers

Polymers	Step I				Step II				Step III			
	$E_a / \text{kJ mol}^{-1}$		A / s^{-1}		$E_a / \text{kJ mol}^{-1}$		A / s^{-1}		$E_a / \text{kJ mol}^{-1}$		A / s^{-1}	
	Fried man	OFW	Fried man	OFW	Fried man	OFW	Fried man	OFW	Fried man	OFW	Fried man	OFW
P1	82.2	75.8	$2.24 \cdot 10^9$	$5.01 \cdot 10^8$	140.2	142.3	$2.04 \cdot 10^{12}$	$9.77 \cdot 10^{12}$	195.7	193.1	$3.24 \cdot 10^{12}$	$4.17 \cdot 10^{12}$
P2	55.5	60.5	$3.39 \cdot 10^5$	$2.88 \cdot 10^6$	156.0	147.1	$5.13 \cdot 10^{12}$	$2.00 \cdot 10^{12}$	240.5	236.9	$2.04 \cdot 10^{15}$	$2.19 \cdot 10^{15}$
P3	79.8	79.2	$1.32 \cdot 10^9$	$2.00 \cdot 10^9$	124.7	122.5	$5.01 \cdot 10^9$	$8.51 \cdot 10^9$	211.6	207.5	$1.32 \cdot 10^{13}$	$9.33 \cdot 10^{12}$
P4	73.5	84.9	$1.32 \cdot 10^9$	$1.41 \cdot 10^{11}$	107.1	103.5	$3.02 \cdot 10^8$	$3.24 \cdot 10^8$	169.5	170.0	$1.58 \cdot 10^{10}$	$2.34 \cdot 10^{10}$
P5	52.3	62.2	$2.34 \cdot 10^5$	$9.77 \cdot 10^6$	125.4	118.1	$9.12 \cdot 10^9$	$4.68 \cdot 10^9$	177.9	177.5	$5.13 \cdot 10^{10}$	$7.76 \cdot 10^{10}$
P6	80.0	87.6	$4.07 \cdot 10^9$	$1.48 \cdot 10^{11}$	164.7	162.9	$1.07 \cdot 10^{14}$	$2.04 \cdot 10^{14}$	232.5	220.9	$7.24 \cdot 10^{14}$	$2.57 \cdot 10^{14}$
P7	71.4	79.7	$2.88 \cdot 10^8$	$9.33 \cdot 10^9$	158.8	164.2	$1.48 \cdot 10^{14}$	$1.51 \cdot 10^{15}$	140.5	121.9	$6.17 \cdot 10^7$	$3.09 \cdot 10^6$
P8	91.3	95.6	$3.39 \cdot 10^{11}$	$3.24 \cdot 10^{12}$	137.4	137.0	$1.08 \cdot 10^{12}$	$3.09 \cdot 10^{12}$	254.6	241.1	$3.72 \cdot 10^{16}$	$1.00 \cdot 10^{16}$
P9	67.8	67.6	$2.29 \cdot 10^7$	$3.63 \cdot 10^7$	143.0	142.1	$2.29 \cdot 10^{12}$	$5.25 \cdot 10^{12}$	221.5	219.7	$1.17 \cdot 10^{14}$	$1.51 \cdot 10^{14}$
P10	77.7	76.5	$5.01 \cdot 10^8$	$5.62 \cdot 10^8$	150.0	147.9	$2.63 \cdot 10^{12}$	$4.47 \cdot 10^{12}$	244.6	225.2	$5.25 \cdot 10^{15}$	$4.17 \cdot 10^{14}$

Kinetic parameters value's of the second thermal degradation stage are higher than for the previous stage. The overall E_a of the second stage varied between approximately 100 and 165 kJ mol⁻¹. From the results (Table 3) we can see that the lower value of E_a is characterized for P4, which contains moieties of DEA groups and may undergo easier conversion. Such results were not observed for other polymers with aliphatic fragments (P2, P3 and P5) due to the low degree of aminolysis. Relatively higher values of E_a were obtained for samples P6 and P7, which comprise fragments of aromatic amines with more complicated structure.

The third stage of thermal degradation is characterized by the highest mass loss values approximately 120 and 260 kJ mol⁻¹ (Table 3). The exception of this trend is polymer P7 with PhDA moieties in the structure. Probably the diamine fragments lead to additional cross-linking between macromolecules during the aminolysis reaction (Scheme 1, step 2.2) and so change the ratio values of E_a in the second and third stage of degradation.

The values of the pre-exponential factor calculated by the two methods (Table 3) differ a little bit for some samples that could be explained by different mathematical approach of the used methods.

Generally, the polymers are characterized by substantial mass loss in the second and the third stage. In order to obtain the wider image of the thermal behavior of the studied polymers, the variations of E_a vs. α (fractional mass loss) during the main degradation stages were plotted in Figs. 3–6.

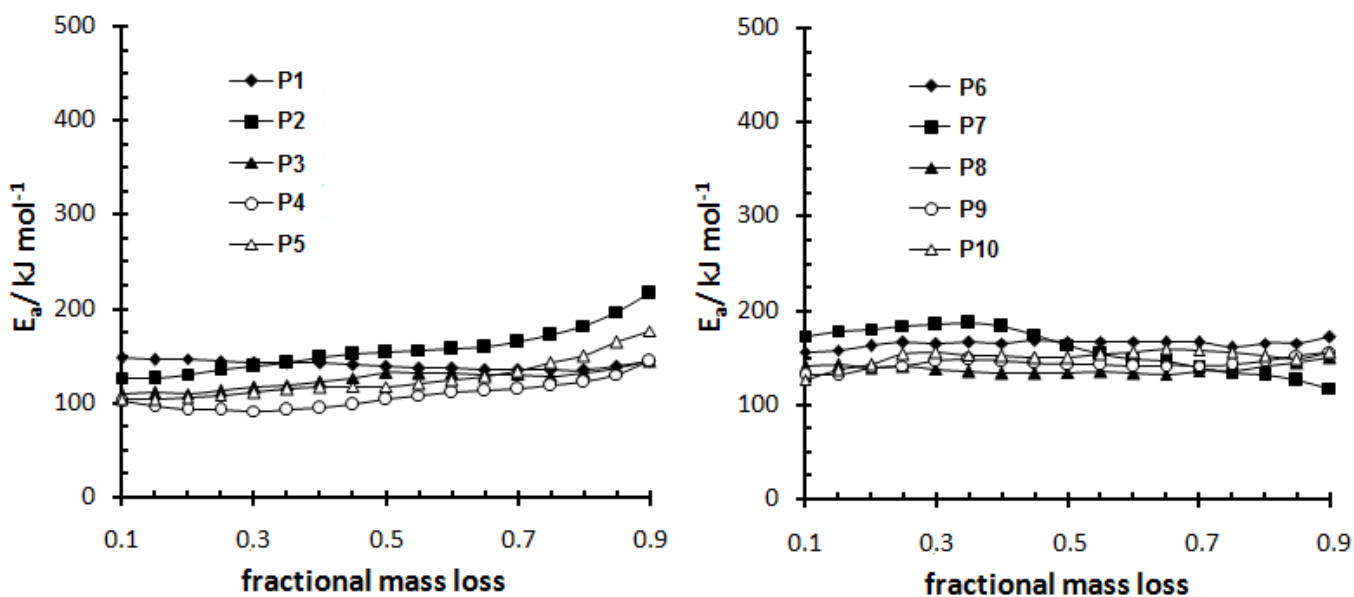


Fig. 3 Variation of E_a versus fractional mass loss (α) for the second degradation stage of polymers P1–P10 based on Friedman method

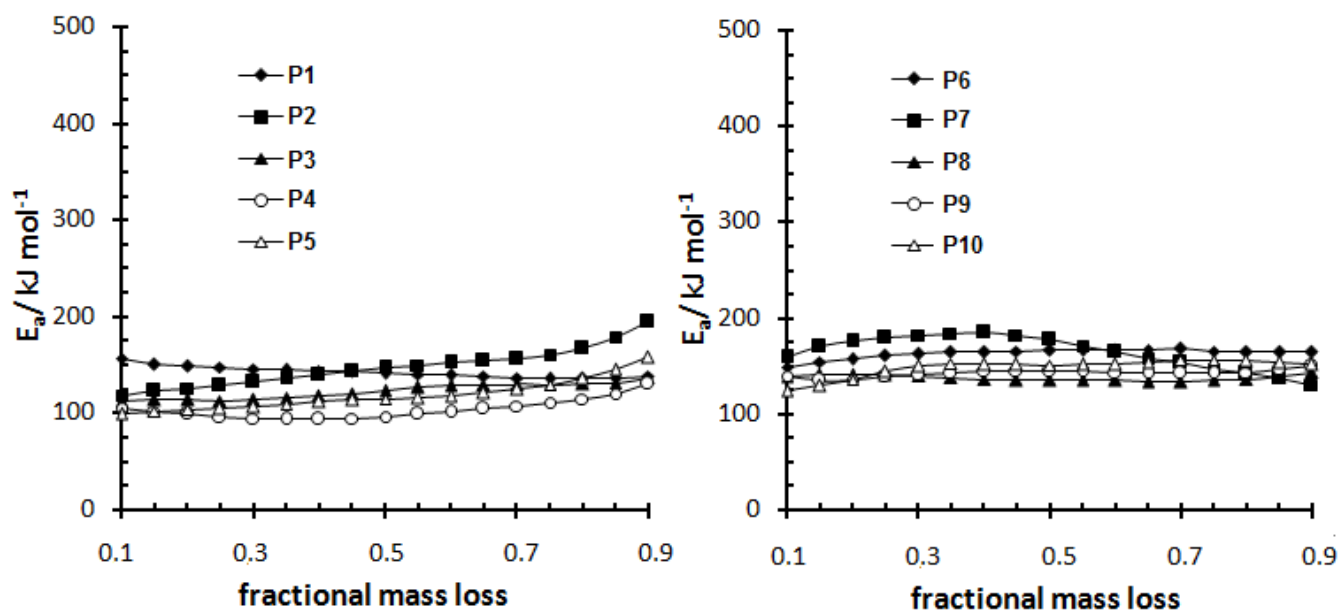


Fig. 4 Variation of E_a versus fractional mass loss (α) for the second degradation stage of polymers P1–P10 based on OFW method

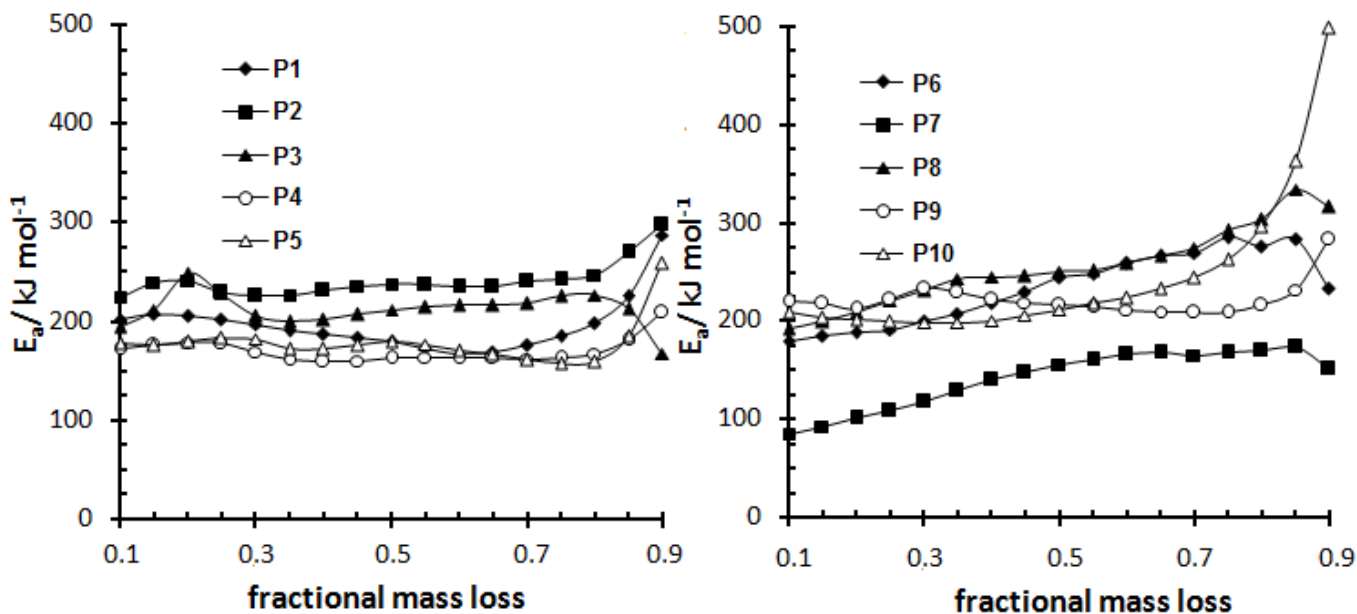


Fig. 5 Variation of E_a versus fractional mass loss (α) for the third degradation stage of polymers P1–P10 based on Friedman method

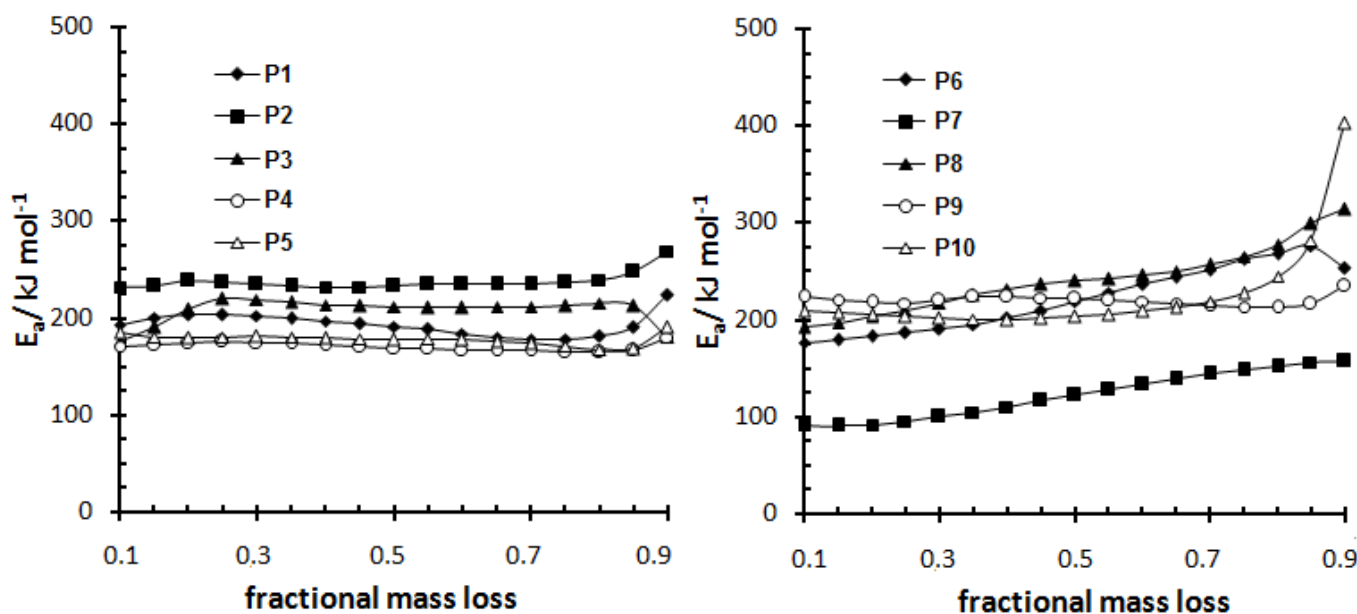


Fig. 6 Variation of E_a versus fractional mass loss (α) for the third degradation stage of polymers P1–P10 based on OFW method

The E_a - α plot in Fig. 3 indicates that generally, the second stage is the one of the main degradation process for the polymers because this process is non-stationary in non-isothermal conditions. Increase of temperature has different effects on the activation energy depending on the type of the functional groups. As shown for polymer P1 with increasing temperature, the E_a decreases gradually. For polymers P2–P5, which are products of modifications of PChBR by aliphatic amines, E_a increases with temperature (the curves are similar). It is also clear from that for

1 P6, P8 and P9, as product of modifications of PChBR with aromatic amines, E_a varies only a little
2 with temperature and approximately constant values of E_a was found for $0.2 < \alpha < 0.8$. Here an
3 exception is polymer P7, where values of E_a was higher in the range of α between 0.2 and 0.5. This
4 confirms once more that the polymer P7 differs from other samples not only by chemical
5 composition of functional groups but also by nature of cross-linked bonds (see above).
6

7 As it can be seen in Figure 4 OFW method similarly describes the mechanisms of the second
8 degradation stages of the measured polymers.
9

10 For much more complicated degradation processes E_a varies non-linearly with α and reflects
11 the modification of either the reaction mechanism or the rate determining step. The E_a variations vs.
12 α for the polymers in their third degradation stage are plotted in Fig. 5 and 6. The E_a values for all
13 the polymers show some variations with increasing of α indicating many changes in the degradation
14 pathway. In this degradation stage, the decrease of E_a could be also caused by the mass loss of the
15 evaluated compounds caused by the degradation of functional groups attached to the polymer
16 backbone. This variation of E_a characterized by a dramatic increase or decrease as a function of α
17 could be assigned either to some competitive processes or to the depolymerization in non-stationary
18 conditions. The effect is particularly pronounced for P10. This can be explained by the fact that the
19 polymer contains the Gly moieties, which during the conversion process in the second degradation
20 stage may participate in the formation of additionally cross-linking bonds (C–C or C–O–C) for
21 rupture of which more energy is required. It usually occurs in high temperature range, which is
22 compliant with high values of α , above 0.8.
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38 **DSC measurements**

39 DSC analysis is an important and often used analysis tool in order to evaluate thermal stability of
40 many different structural functional polymers [37–39].
41

42 The DSC curves of functional polymers are presented in Fig. 7 (for P1 and P3) and Fig. S3
43 (for P2, P4–P10), which also shows some differences in the thermal behavior of the polymers
44 studied. In the range of 88–150 °C for most of samples, a distinct endothermic effect corresponding
45 to the process of moisture vaporization from the polymers are observed (exception is the samples
46 P1 and P5). Definitely, there are effects corresponding to the samples P1 and P5, but they are
47 invisible. Probably they have a relatively small value.
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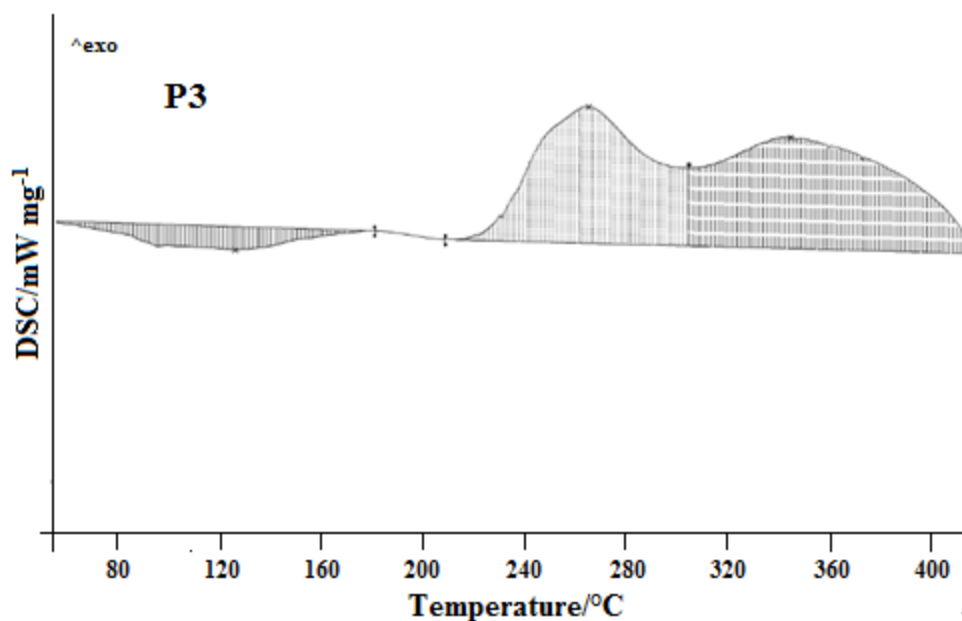
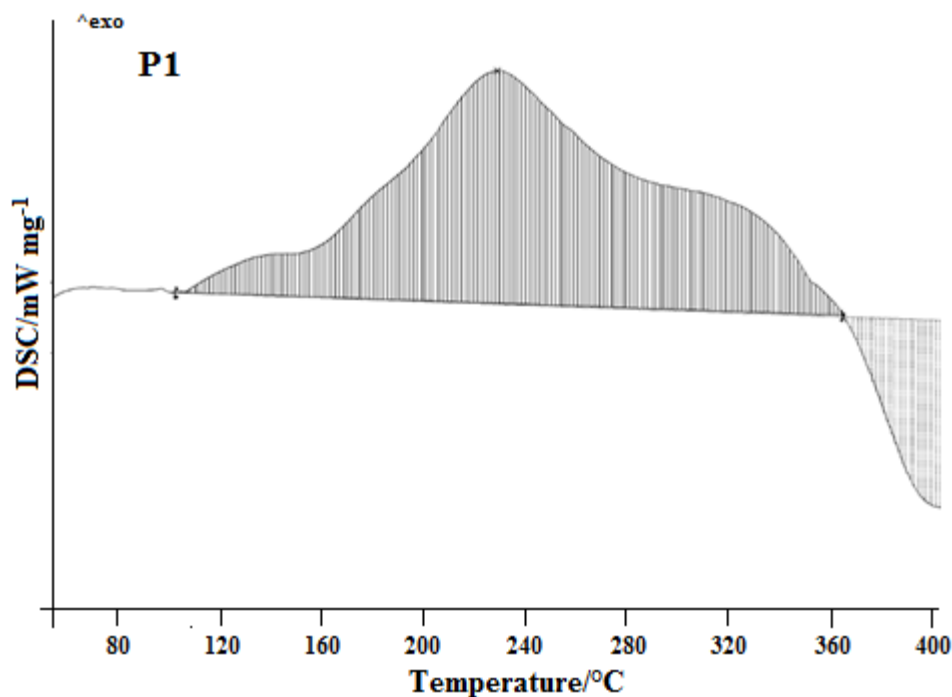


Fig. 7 DSC curves of the functional polymers P1 and P3

The temperature area between 100 and 400 °C may be noted as the second interval of the process. In this region occurs conversion/decomposition of the functional groups as discussed above. The curves clearly show that these regions are quite complex and including exothermic and/or endothermic effects. In case of polymer P1, a relatively simple and more visible exothermic peak at 216 °C is present, which corresponds to the dehydration of phosphorus-containing acidic groups. The similar effect (an exothermal effect) with relatively complex views were also observed for samples P7 ($T_{\text{peak}}=273$ °C), P9 ($T_{\text{peak}}=232$ °C) and P10 ($T_{\text{peak}}=257$ °C). The position of those

1 peaks approximately close to the results obtained in the TG/DTG analysis. In these regions two
2 exothermic effects were observed for samples P2, P3, P5 and P8. And the most complex character
3 of the observed thermal effects was detected for polymers P4 (one exothermic and two
4 endothermic) and P6 (one exothermic and one endothermic). The appearance of the endothermic
5 peaks for some samples (P4, P6) is a result of the decomposition of functional groups.
6

7 An endothermic peak (not shown in Fig.) is present in the curve above ~400 °C for all
8 samples. This reflects the thermal degradation of the polymer chain and their crosslinked parts.
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10 11 12 13 **Conclusions**

14 Thermal behavior of some phosphorus- and phosphorus/nitrogen-containing functional polymers
15 synthesized by either hydrolysis or aminolysis and alcoholysis reaction of PChBR was investigated
16 in this work. PChBR was synthesized *via* oxidative chlorophosphorylation reaction of butadiene
17 rubber, BR. The modification process was confirmed *via* FTIR spectroscopy.
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20 It was indicated that thermal degradation of the polymers depends on the nature of the
21 functional groups attached to BR. The obtained DTG curves clearly showed the presence of three
22 degradation stages for all the polymers. During the first stage elimination of physically adsorbed
23 water existing in the pores and hydrogen-bonded water with the functional groups takes place. In
24 the second degradation stages the mass loss is the result of the conversion/decomposition of the
25 functional groups. The third stage of decomposition is characterized by significant mass loss
26 (between 20 and 37 %). This stage can be attributed to side group elimination from polymer chain,
27 random depolymerization and detachment of large organic molecules, formed in the second stage.
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30 Kinetic parameters, such as E_a and A value's were calculated according to Friedman and
31 OFW methods. The overall E_a of the third thermal degradation stage was higher than for the second
32 stage. The exception was polymer P7 with PhDA moieties in the structure that may take part in
33 additional cross-linking of the macromolecules during the aminolysis steps of synthesis reaction.
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36 Based on DSC measurements, in thermal behavior of functional polymers were observed
37 some differences, especially in the range of 100–400 °C, where occur conversion/decomposition of
38 the functional groups.
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40 Generally, thermal stability of the studied polymers can be compared, using the proposed
41 above parameters, with other functional polymers especially the ones containing the functional
42 groups applied in this studies.
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