

# Thermal Stability of Native Polybutylene Terephthalate

V. N. Shelgaev,<sup>1</sup> A. K. Mikitaev,<sup>1</sup> S. M. Lomakin,<sup>1,2</sup> G. E. Zaikov,<sup>1,2</sup> E. V. Koverzanova<sup>1,3</sup>

<sup>1</sup>GNU "Center on Composite Materials" of Ministry of Education of RF, 9 Miusskaya Pl, 125047 Moscow, Russia

<sup>2</sup>N. M. Emanuel Institute of Biochemical Physics, HAS, 4 Kosygin Street, 119991 Moscow, Russia

<sup>3</sup>N. N. Semenov Institute of Chemical Physics, RAS, 4 Kosygin Street, 119991 Moscow, Russia

Received 1 April 2003; accepted 27 October 2003

**ABSTRACT:** The thermal and thermooxidative stability of polybutylene terephthalate (PBTP), synthesized in the presence of the optimal stabilizing system, has been investigated. The basic products of PBTP degradation and the regularities of their formation in the temperature regime close to the temperature regimes of its processing were determined. The investigations conducted allowed recommendations to be

made on the temperature regimes of PBTP processing because even a small excess of the chosen temperature (265°C) leads to polymer chain fragmentation. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2351–2356, 2004

**Key words:** degradation; stability; polybutylene terephthalate; processing; regulation; oxidation; products of reactions

## INTRODUCTION

As reported earlier,<sup>1</sup> we have developed a new way to synthesize polybutylene terephthalate (PBTP) in the presence of stabilizing systems. The PBTP synthesized in such conditions had high physical and chemical characteristics, including enhanced thermal stability.

At the same time, it is known that the wide use of the native PBTP will be limited without careful physicochemical investigation. Because of this, the study of the PBTP thermal and thermooxidative stability is one of the priority tasks. The actuality of this problem is especially important when the material or composites based on it is supposed to be used in the fields where the thermal stability is the main criterion. Special attention in this work was paid to the PBTP transformations in conditions close to the ones of the polymer processing.

We assumed that the understanding of the basic processes taking place at thermal and thermooxidative polymer destruction in these conditions will allow the development of more effective stabilizing systems for PBTP.

## EXPERIMENTAL

As the object for investigation, we used the polybutylene terephthalate (PBTP) type MAKOOJI, synthesized in the presence of the catalytic system containing Irganox-1010, trinonylphenylphosphine, and sodium

hypophosphite taken in the ratio 0.3 : 0.1 : 0.05 mass %, correspondingly. The polymer had the highest physicochemical properties from the PBTP synthesized by us before.<sup>1</sup>

The polymer samples were investigated both in the range of temperatures close to the PBTP processing temperatures (250–260°C) and at temperatures at which the PBTP decomposition occurs at a significant rate (340–500°C).

The PBTP sample pyrolysis was conducted in the pipe pyrolytic cell under air flow (consumption 40 ml/min). The gaseous pyrolysis products were trapped by passing them through hexane cooled in an icy bath. The dry residue after evaporating hexane was dissolved in tetrahydrofuran. The products underwent esterification according to the procedure<sup>2</sup> to form the acid derivatives. After that, they were analyzed.

The screening analysis of the pyrolysis products was conducted by using a gas chromatograph LjBer-500M equipped with an electron trap detector. To separate the destruction products, we used the glass-filled column length 4 m with an inner diameter 3 mm. The stable phase was phenylmethylsilicon OV-17; the column and ejector temperatures were 230°C, and the detector temperature was 290°C. The gas-carrier was nitrogen; the consumption was 25 ml/min. The probe volume was 2.0  $\mu$ l.

The complex chromatomass-spectrometric analysis was conducted by using a gas chromatograph Varian 3300 with the mass-spectrometric detector, the ionic trap Finnigan VAT ITD 800. The product separation was conducted on the quartz capillary with a column length of 30 m, inner diameter of 0.32 mm with the stable phase DB-5 (phenylmethylsili-

Correspondence to: G. E. Zaikov (chembio@sky.chph.ras.ru).

con, film thickness, 0.25  $\mu\text{m}$ ). In the course of analysis, the column temperature rose from 100 to 270°C at a rate of 10°C/min. The injector temperature was 200°C. As gas carrier, helium was used. The gas pressure at the entrance was 0.1 MPa. The probe in an amount of 1.0  $\mu\text{l}$  was incorporated into the chromatograph (without the stream division). The time to the probe incorporation was 30 s. The mass spectra were registered at ionization by the electron strike with the energy 70 eV; the scanning rate was 1 mass-spectrum/min; the scanning diapason was 40–650 a.e.m.

## RESULTS AND DISCUSSION

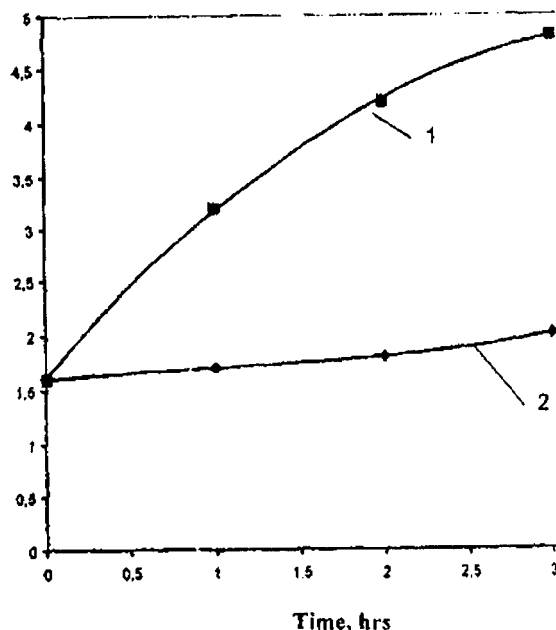
The data in Figure 1 show the yield of some oxygen-containing gaseous products forming in the process of the PBTP thermooxidative destruction.

The data in Figure 1 also show the yield of the analogous products formed in the process of PBTP destruction in the helium atmosphere. As seen, in the presence of oxygen, the yield of all destruction products is significantly increased. Besides, carbon monoxide is formed, which was absent at PBTP destruction in helium.

The noticeable destruction rate increase in the presence of oxygen can also be observed on the fast accumulation of carboxyl groups in the polymer (Fig. 2, curve 1).

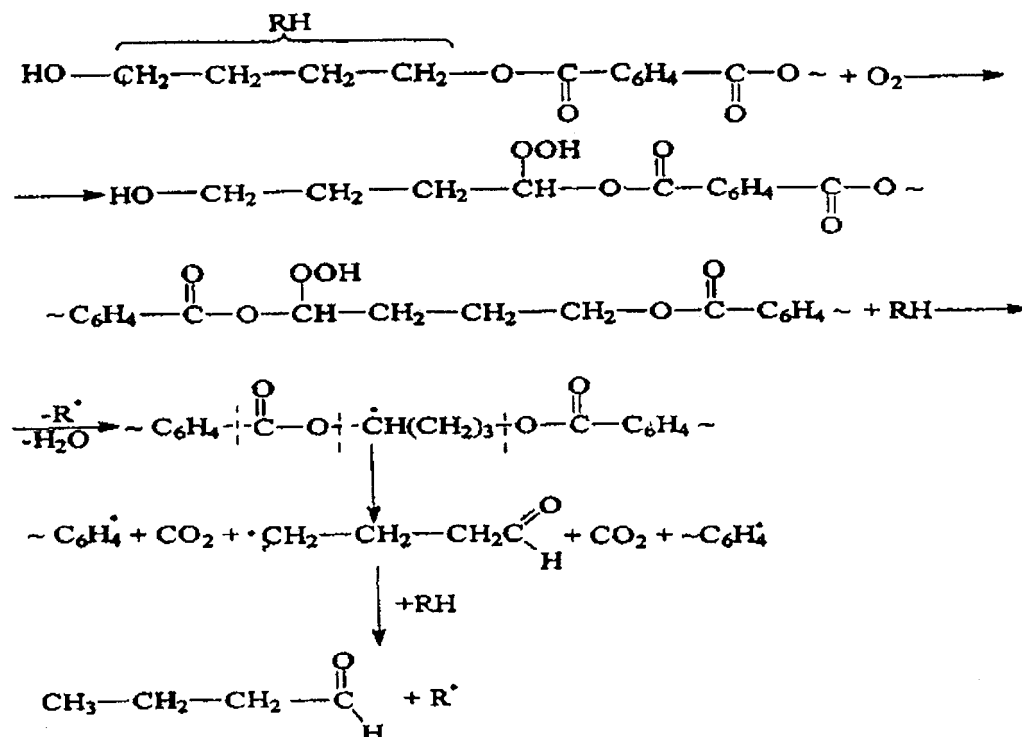
It follows from the obtained data that the thermooxidative destruction of PBTP probably occurs

$\text{COOH} \cdot 10^6 \text{ g}\cdot\text{eq./g}$



**Figure 1** Kinetics of oxygen absorption (curve 1) and gaseous products separation at thermooxidation (curves 2–5) and the thermal destruction of polybutylene terephthalate (curves 2' and 4') in helium. 1, O<sub>2</sub>; 2, 2', CO; 3, CO; 4, 4', H<sub>2</sub>O; 5, CH<sub>3</sub>O.  $P_{\text{O}_2} = 40 \text{ kPa}$ ;  $T = 270^\circ\text{C}$ .

through the stage of hydroperoxides formation. This is confirmed by the water yield increase in the presence of oxygen. The absorption of a significant amount of oxygen (Fig. 1, curve 1) at the PBTP



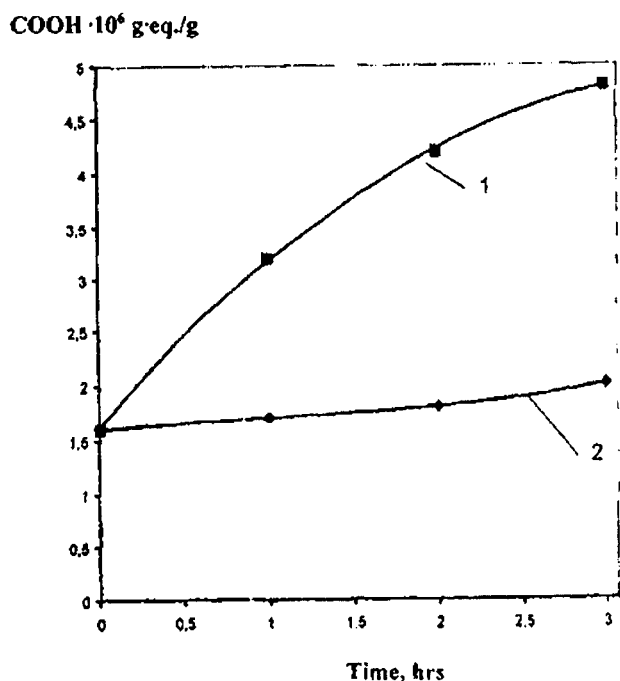
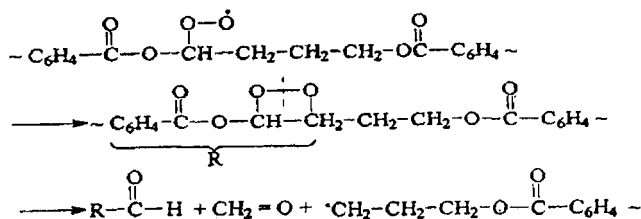


Figure 2 Change of the COOH groups amount with time at heating of polybutylene terephthalate in different gaseous media (270°C, 3 h). 1, in oxygen,  $P_0 = 40$  kPa; 2, in vacuum.

oxidation witnesses the oxygen participation not only in the initiation but also in the further stages of the radical chain process. The thermooxidative destruction of PBTP occurs probably in accordance with the same mechanism as the liquid-phase oxidation of the low molecular hydrocarbons.<sup>3</sup>

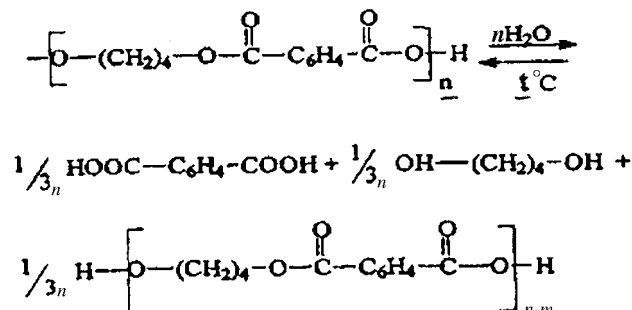
The initiation of the radical chain process starts as the result of interaction of oxygen atoms with the atoms of hydrogen of the polymer chain methylene fragments, formation of hydroperoxide, its decomposition, and the consecutive fragmentation of the polymer chain. This is accompanied by separation of the gaseous and liquid products.

It is probable that along with the hydroperoxide formation, the isomerization of the peroxide radical with a consecutive decomposition on the bond  $\text{—O—O—}$  takes place. This will lead to the formation of aldehyde.<sup>4</sup>



As the PBTP thermooxidative destruction proceeds, the mechanism of the process becomes more complicated, the variability of the active centers, and the intermediate and the end products increase.

Along with the radical chain process, the hydrolytic process take place. They are accelerated by the formed acidic decomposition products in the course of the thermooxidation process



where  $m \geq 1$ .

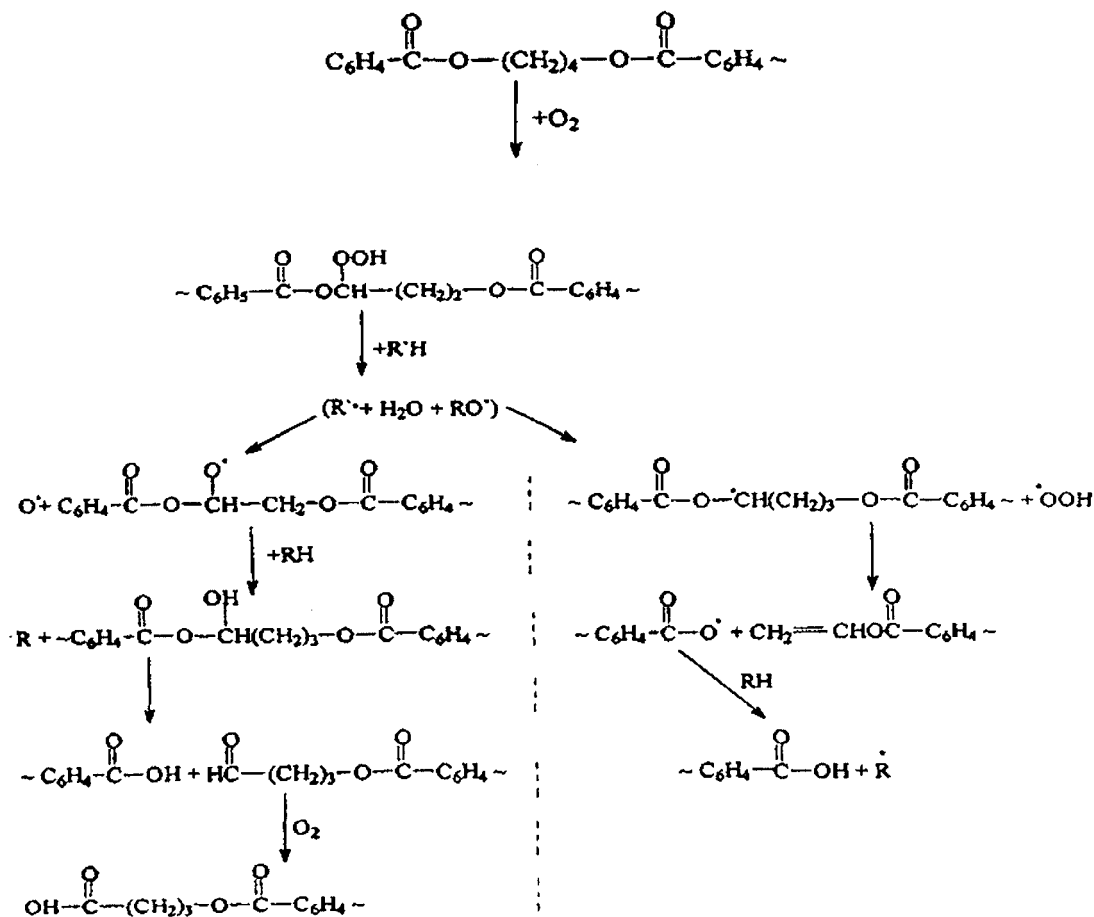
The formation of various acidic products can occur also at the hydroperoxide decomposition as in the case published in ref. [5].

Thus, in the process of PBTP thermooxidative destruction at moderate temperatures, the following products are formed: water, aldehydes, and others. The products at elevated temperatures at synthesis and in the melt on the stages of processing can cause the hydrolysis of the ester bonds that will negatively affect the molecular mass value, and, as a result, the polymer properties. This was the reason to conduct PBTP synthesis in the presence of the stabilizing systems.

In this case, when the PBTP thermooxidative destruction occurs at the enhanced pyrolysis temperatures, the composition of the decomposition products and their amount is noticeably changing. The data in Table I show the composition of the PBTP destruction products formed at thermooxidation at 340 and 520°C. At these temperatures, there is a mass PBTP decomposition according to the data of the thermogravimetric analysis.

As seen from the data, at the PBTP thermooxidative destruction at 340°C, the basic products are terephthalic acid, 4-(pentanoyl) benzoic acid, and also 4-hydroxybutyl-4-acetyl benzoate, 3-butenyl-4-formyl benzoate, 1-(4-hydroxybutyl)-4-methyl terephthalate, and 4-benzocarboxy-4-[(3-butenyloxy) carbonyl]-1-benzocarboxy anhydride. By increasing the pyrolysis temperature to 520°C, two new compounds appear: benzaldehyde and 1-(S-butenyl) benzene. At the same time, the concentration of 4-hydroxybutyl-acetyl benzoate and 3-butenyl-4-formyl benzoate decrease approximately three times. The concentration of 1-(4-hydroxybutyl)-4-methyl terephthalate decreases 1.5–2.0 times. The ratio between 4-(pentanoyl) benzoic and terephthalic acids was also changed.

It is possible that at conditions of the heat wave in air, the simultaneously occurring processes take place: the radical chain reactions of oxidation and the occa-

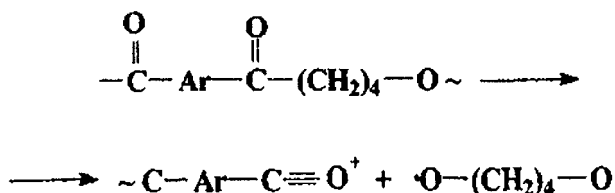


Structure 4

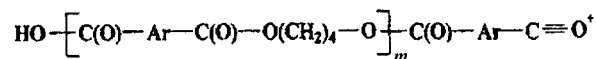
sional homolytic decomposition of polymer chains. From that position, it is possible to explain the existence of such a wide range of various products.

We have also investigated the kinetics of the thermal PBTP destruction at relatively low temperatures close to the processing temperatures. By using the method of the pyrolytic mass spectrometry, it was shown that thermal destruction of PBTP in the temperature range 250–350°C is accompanied by the formation of carbon oxides, water, hydrocarbons (predominantly butadiene), and benzoic and terephthalic acids. Besides, the mixture of oligomeric ethers is also formed.

The appearance in the mass-spectra ions with high molecular mass at the PBTP pyrolysis, is probably related, as in the case of PET,<sup>6</sup> with the rupture of the 8-bonds in the ester fragment of the macrochain:



In the mass spectrum, the intense peaks of ions were found

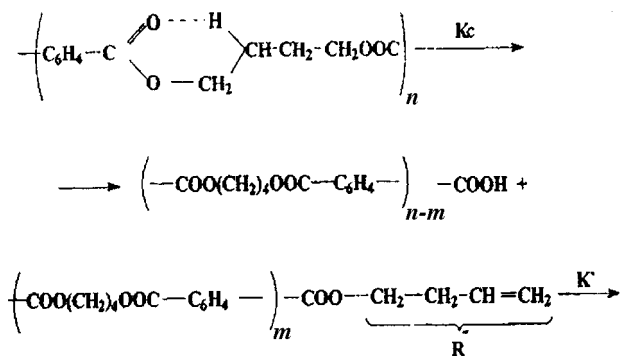


The ions are formed at the destruction products ionization. The destruction of the carboxyl-containing products of decomposition leads to the appearance of carbon dioxide in the gaseous phase.

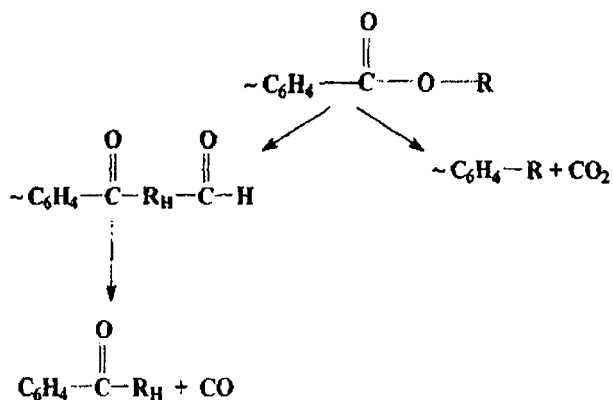
The data in Figure 2 and the kinetic curves prepared from the experimental data show the character of the change of the number-average state of polymerization and the change of the end carboxyl groups content at different temperatures. The linear character of the values dependency witnesses that the PBTP destruction occurs randomly. It is possible that, as in the case of polyethylene terephthalate, the PBTP thermal decomposition on the stage of initiation is originally accompanied by formation of the cyclic transitional state in an occasional spot of the polymer chain with its consecutive decomposition.<sup>7</sup>

TABLE I  
Products of the PBTP Thermooxidative Destruction at Temperatures of 340 and 520°C

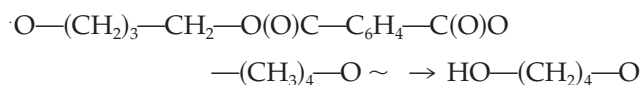
Compound name	Separation time (mm)	Hexane extract		Products dissolving in THF		Methyl derivatives	
		Peak intensity	%	Peak intensity	%	Peak intensity	%
340°C							
Methyl ether of benzoic acid	4 : 16	—	—	—	—	1119	0.4
Methyl ether of terephthalic acid	6 : 23	—	—	—	—	1227	0.5
Benzaldehyde	7 : 11	933	4.6	1875	0.5	163	0.1
4-[(Butenylloxy)carbonyl]-benzoic acid	8 : 43	—	—	1465	0.4	207	0.1
Dimethyl ether of terephthalic acid	9 : 04	—	—	1152	0.3	134,571	51.1
4-Hydroxybutyl-4-formyl benzoate	11 : 53	1119	5.1	2858	0.8	819	0.3
Methyl-4-(4-pentanoyl) benzoate	12 : 17	—	—	—	—	109,687	41.6
1-Phenyl-1-pentanone	12 : 45	715	3.6	3910	1.0	1230	0.5
Terephthalaldehyde acid	12 : 59	—	—	4501	1.2	—	—
4-Hydroxybutyl-4-acetyl benzoate	13 : 11	2033	10.1	14,266	3.7	1925	0.7
1-benzocarboxy-4-methoxy-1-benzocarboxy anhydride	13 : 57	418	2.1	2854	0.8	—	—
3-Butenyl-4-formyl benzoate	15 : 13	3930	19.6	147,510	38.8	1907	0.7
1-Benzocarboxy-4-pentanoyl-1-benzocarboxy anhydride	15 : 19	1005	5.0	11,730	3.1	—	—
4-Benzocarboxy-4-[(3-butenyloxy)-carbonyl]-1-benzenecarboxy anhydride	15 : 50	4417	22.0	86,666	22.8	4371	1.7
1-(4-Hydroxybutyl)-4-methyl terephthalate	16 : 04	2136	10.6	45,576	12.0	2362	0.9
Nonidentified compounds	—	3493	17.4	56,118	14.7	3786	1.5
		20,099	100	380,481	100	263,374	100
520°C							
1-(3-Butenyl) benzene	5 : 05	—	—	47,457	17.3	—	—
Benzaldehyde	7 : 13	6886	63.6	14,465	5.3	289	0.5
Dimethyl ether of terephthalic acid	9 : 04	—	—	—	—	39,491	63.6
Diphenyl ketone	10 : 49	—	—	1209	0.4	135	0.2
4-Hydroxybutyl-4-formyl benzoate	11 : 56	213	2.0	3330	1.2	262	0.4
Methyl-4-(4-pentanoyl) benzoate	12 : 18	—	—	—	—	13,326	21.5
1-Phenyl-1-pentanone	12 : 45	168	1.6	3441	1.3	481	0.8
Terephthalaldehyde acid	12 : 55	213	2.0	3330	1.2	113	0.2
4-Hydroxybutyl 4-acetyl-benzoate	13 : 11	420	3.9	15,086	5.5	745	1.2
1-Benzocarboxy-4-methoxy-1-benzocarboxy anhydride	13 : 58	—	—	2289	0.8	146	0.2
3-Butenyl 4-formyl benzoate	15 : 15	—	—	33,398	12.2	436	0.7
1-Benzocarboxy-4-pentanoyl-1-benzocarboxy anhydride	15 : 21	—	—	6031	2.2	238	0.4
4-Benzocarboxy-4-[(3-butenyloxy)-carbonyl]-1-benzenecarboxy anhydride	15 : 50	716	6.6	78,092	28.5	2104	3.4
1-(4-Hydroxybutyl)-4-methyl terephthalate	16 : 04	500	4.6	22,182	8.1	966	1.6
Nonidentified compounds	—	1708	15.8	43,558	16.0	3390	5.6
		10,824	100	273,898	100	62,122	100



At higher temperatures, the destruction of butene-ether end groups is observed.



One of the ways of the PBTP thermal decomposition can be the rupture of the ether bonds with formation of the hydroxyl group caused by the migration of the methylene group hydrogen atom. This way of the reaction probably occurs at enhanced temperatures (above 300°C):



This is supported by a significant amount of the hydroxyl-containing compounds formed at high-temperature PBTP pyrolysis (Table I).

## CONCLUSION

The thermal and thermooxidative stability of PBTP, synthesized in the presence of the optimal stabilizing system, has been investigated. The basic products of the PBTP destruction and the regularities of their formation in the temperature regime close to the temperature regimes of its processing were determined.

The thermooxidative PBTP destruction has radical-chain character. It starts from the oxidative decomposition of the aliphatic part of polymer. Parallel to the process, there are thermohydrolytic processes. The thermal destruction of polybutylene terephthalate occurs randomly.

The conducted investigations allowed recommendations to be made on the temperature regimes of PBTP processing because even a small excess of the chosen temperatures ( $\sim 265^\circ\text{C}$ ) leads to the polymer chain fragmentation.

## References

1. Mikitaey, A. K.; Storozhuk, I. P.; Shelgaev; Alakaeva, Z. T. *Plast Massy (Russ)*, 2001, 4, 47.
2. Lurie A. A. *Chromatographic Materials (Russ)*; M. Khimiya: 1978, p 273.
3. *Polymer Encyclopedia (Russ)*, Sovetskaya Enzyklopedia; Vol. 3; 1977; pp. 624-626.
4. Kovarskaya, B. M.; Blumenfeld, A. B.; Levantovskaya, L. L. *Thermalstability of Heterocyclic Polymers (Russ)*; Khimiya; 1977; p. 74.
5. Buxbaum, I. N. *Am Chem Soc, Poly Prep* 1967, 8, 552-557.
6. Ludenvald, J.; Urrutia, H. *Macromol Chem* 1999, 177, 2079.
7. Passalama, V. *Polymer* 1976, 17, 1044.