

Volatile Products of Poly(ethylene terephthalate) Thermal Degradation in Nitrogen Atmosphere

MAŁGORZATA DZIĘCIOŁ, JERZY TRZESZCZYŃSKI

Institute of Fundamental Chemistry, Technical University of Szczecin, Al. Piastów 42, 71-065 Szczecin, Poland

Received 12 May 1999; accepted 23 October 1999

ABSTRACT: Thermal degradation of PET was studied in a nitrogen atmosphere at 200–700°C. The experiments were carried out in a tubular furnace under isothermal conditions. The volatile substances evolved from PET were identified and quantified. Weight losses of PET during the thermal degradation in different temperatures were determined. The results are presented on plots as a function of the degradation temperature. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1894–1901, 2000

Key words: poly(ethylene terephthalate) thermal degradation; volatile substances evolved from poly(ethylene terephthalate); plastics thermal degradation

INTRODUCTION

Thermal degradation of plastics can be performed for different purposes in following processes:^{1–8}

- Pyrolysis—conversion of plastics to useful materials, for example, fuels and monomers (400–900°C, in nitrogen or other inert gas);
- Combustion—utilization and energy recovery from plastics (600–2000°C, in air);
- Hydrocracking—degradation of plastics to liquid and gas hydrocarbons (300–500°C, under hydrogen pressure);
- Gasification—conversion of plastics into synthesis gas (1300–1600°C in oxygen–steam or air–steam mixtures);
- Carbonization—production of activated carbons from plastics (400–600°C in nitrogen, carbon dioxide, or other atmosphere).

Plastics thermal degradation can also take a place in noncontrolled conditions, for example, during fires or open-air burning. The substances

emitted during noncontrolled plastics thermal degradation may create a serious hazard for human health and for the environment. The temperatures used during the production and processing of polymers may also cause degradation reactions and the emission of toxic substances.^{9–11}

Poly(ethylene terephthalate) (PET) is the most widely used thermoplastic polyester. In recent years, the use of this polymer has grown rapidly in packaging, textiles, audiovideo tapes, and other applications. During production, processing, and material recycling, PET is subjected to temperatures in the range 200–300°C in a vacuum, nitrogen, or air. These conditions result in degradation reactions, which may lead to changing of polymer properties (e.g., reduction of molecular weight and intrinsic viscosity, discoloration) and the emission of volatile substances. Studies^{11–15} have shown that at these temperatures acetaldehyde and formaldehyde are the main substances evolved from PET. Thermal degradation of PET at higher temperatures was studied by several authors, mostly by means of pyrolysis–gas chromatography (Py–GC)^{16–19} or direct pyrolysis mass spectrometry (Py–MS).^{20–22} The other techniques used in the studies of PET thermal-degradation products were thermal volatil-

Correspondence to: M. Dzięcioł.

Journal of Applied Polymer Science, Vol. 77, 1894–1901 (2000)
© 2000 John Wiley & Sons, Inc.

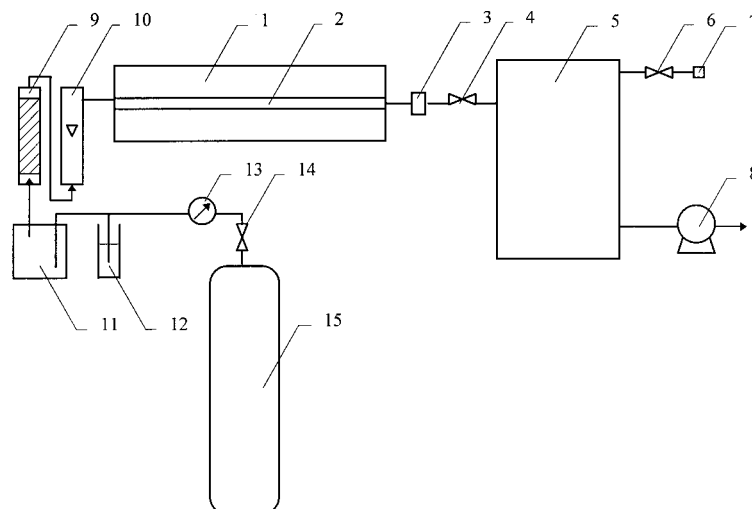


Figure 1 Scheme of apparatus used for the thermal degradation studies of materials in a nitrogen atmosphere: (1) flow tubular furnace; (2) ceramic tube; (3) glass fiber filter; (4) needle valve; (5) vacuum container; (6) glass cock; (7) septum; (8) vacuum pump; (9) nitrogen cleaning filter; (10) flowmeter; (11) buffer container; (12) hydraulic regulator of pressure; (13) manometer; (14) pressure reducing valve; (15) compressed nitrogen container.

ization analysis (TVA)²³ and thermogravimetric and differential thermal analysis connected with Fourier transform infrared spectroscopy (TG-DTA/FTIR).^{24,25} Different products of PET thermal degradation were observed, depending on the degradation temperature, atmosphere, and technique used. In Py-GC and direct Py-MS, the residence time of plastic in a hot zone is very short and the primary degradation products can be observed, which may differ from those obtained in the real thermal degradation processes. During processing, thermal recycling, or fire, the time of the temperature effect on plastics is much longer and secondary products of further degradation are observed.

There is not much data in the literature concerning the amounts of substances emitted during the thermal degradation of PET at different temperatures. In our earlier studies, we examined the temperature influence on the composition and concentrations of the volatile substances emitted during the thermal degradation of PET in air.²⁶ This article reports the results of our studies on the composition and amounts of the volatile substances evolved from PET during thermal degradation in nitrogen at several different temperatures for 20 min. The aim of this work was to identify and quantify the substances evolved and to examine the temperature effect on both the amount and type of compounds formed.

EXPERIMENTAL

The PET granulate for bottle processing Polyclear-T 86 of Hoechst (Frankfurt/Main, Germany) was tested. According to the producer's information, the granulate is a pure polymer which does not contain any additives. The experiments were carried out under isothermal conditions at the temperatures of 200, 300, 400, 500, 600, and 700°C for 20 min in a nitrogen atmosphere. The scheme of the apparatus used for the experiments is shown in Figure 1. Before the beginning of the experiment, the vacuum container was washed several times with nitrogen and evacuated using a vacuum pump. The PET samples (0.1 g) in the ceramic boat were placed in the ceramic tube heated to the given temperature. During the experiment, the rate of the nitrogen flow through the tubular furnace was kept at 0.025 m³/h and controlled using a flowmeter. The delivered nitrogen was cleaned using filters with silica gel and 4 Å molecular sieves. At the outlet of the tube, a fiber glass filter was placed to trap nonvolatile thermal degradation products. The volatile substances were collected in a 0.0127 m³-volume glass container.

The composition and concentrations of the volatile thermal degradation products were determined using gas chromatographic and colorimetric methods. The identification of the particular

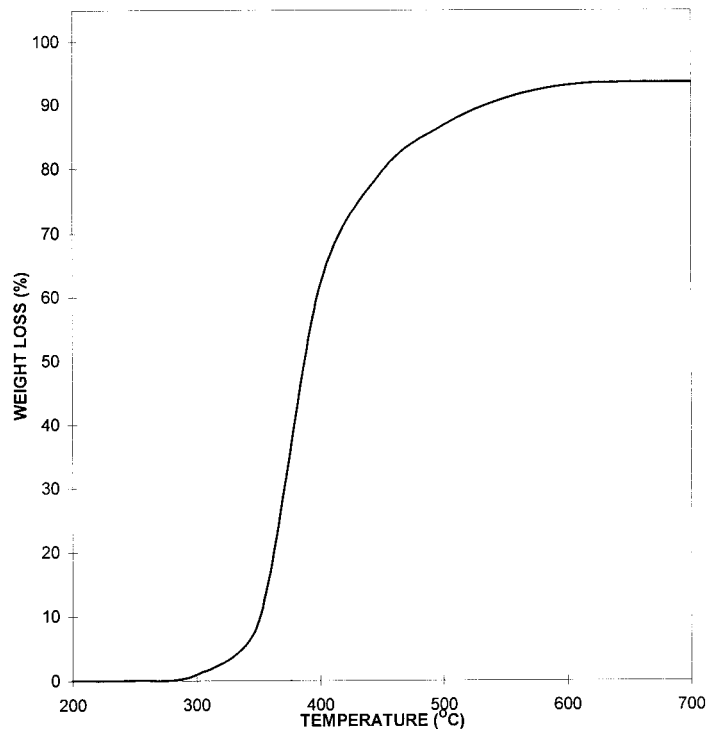


Figure 2 Weight-loss changes of PET (Polyclear-T 86) in a nitrogen atmosphere as a function of degradation temperature.

compounds was carried out by comparison of their retention times with the retention times of standards on two chromatographic columns with differ-

ent polarity. To determine the concentrations of the substances evolved from PET, the gas mixtures of standards were prepared in the same

Table I Volatile Thermal Degradation Products of PET (Polyclear-T 86) in Nitrogen Atmosphere

Substance	Temperature (°C)					
	200	300	400	500	600	700
Acetaldehyde	0.2	0.9	143.4	352.2	385.2	117.8
Formaldehyde	0.04	0.08	0.72	1.45	2.39	3.09
Benzaldehyde	<0.5	<0.5	<0.5	2.5	3.3	4.7
Aliphatic C ₁ -C ₄ hydrocarbons	<0.1	<0.1	5.4	34.0	70.4	107.2
Benzene	<0.1	0.1	2.5	12.9	42.2	106.6
Toluene	<0.1	<0.1	0.2	3.1	6.6	20.9
Ethylbenzene	<0.2	<0.2	<0.2	0.5	1.3	8.3
Styrene	<0.2	<0.2	0.8	2.0	2.8	11.9
Acetophenone	<0.5	<0.5	<0.5	2.1	12.1	142.0
Vinyl benzoate	<0.5	<0.5	4.9	54.4	64.2	<0.5
Methyl acetate	<0.5	<0.5	1.4	3.0	3.7	7.2
Methyl alcohol	<0.2	<0.2	2.2	5.5	2.5	0.9
2-Methyl-1,3-dioxolane	<0.2	<0.2	0.9	0.9	1.2	3.0
Carbon monoxide	<5	<5	1024	1424	1579	1581
Carbon dioxide	<50	86	456	906	1402	1883

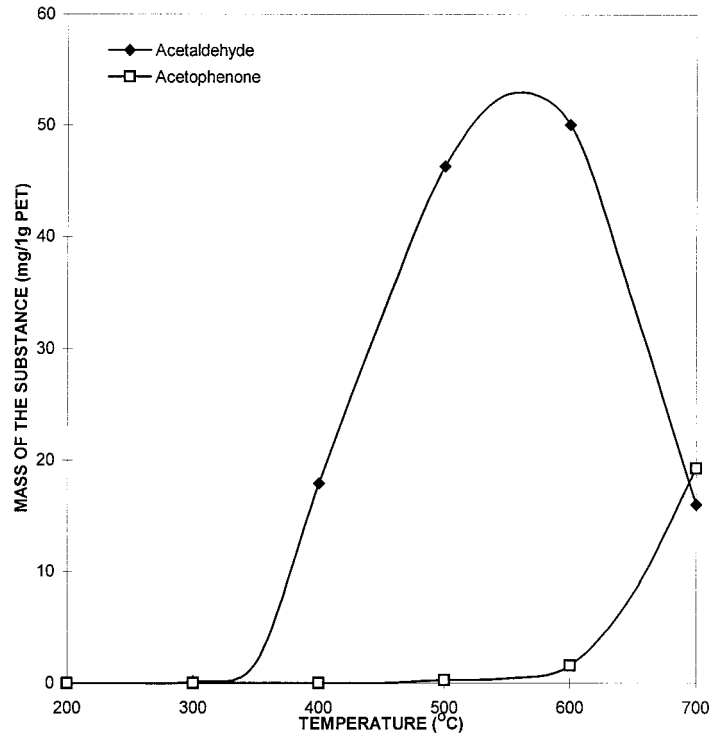


Figure 3 Mass changes of acetaldehyde and acetophenone evolved from PET (Polyclear-T 86) as a function of degradation temperature.

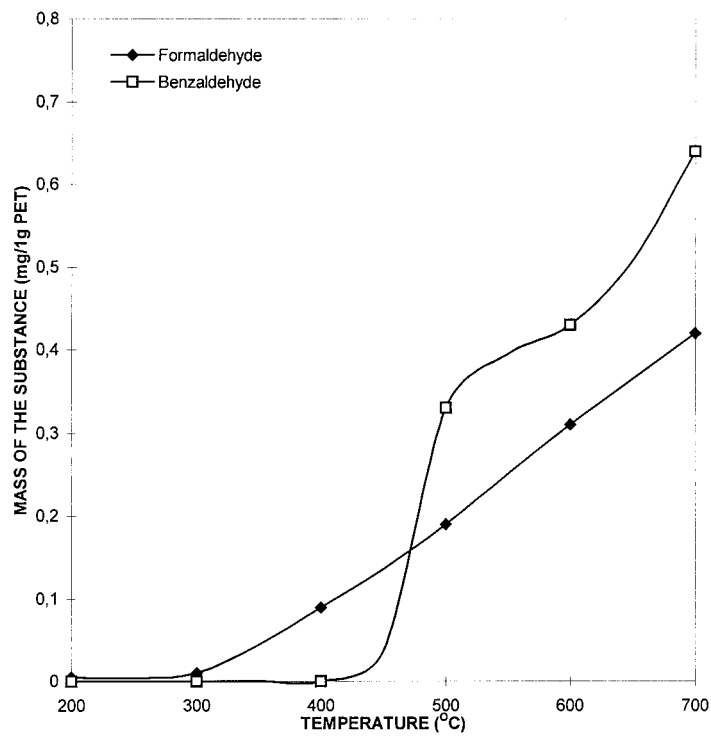


Figure 4 Mass changes of formaldehyde and benzaldehyde evolved from PET (Polyclear-T 86) as a function of degradation temperature.

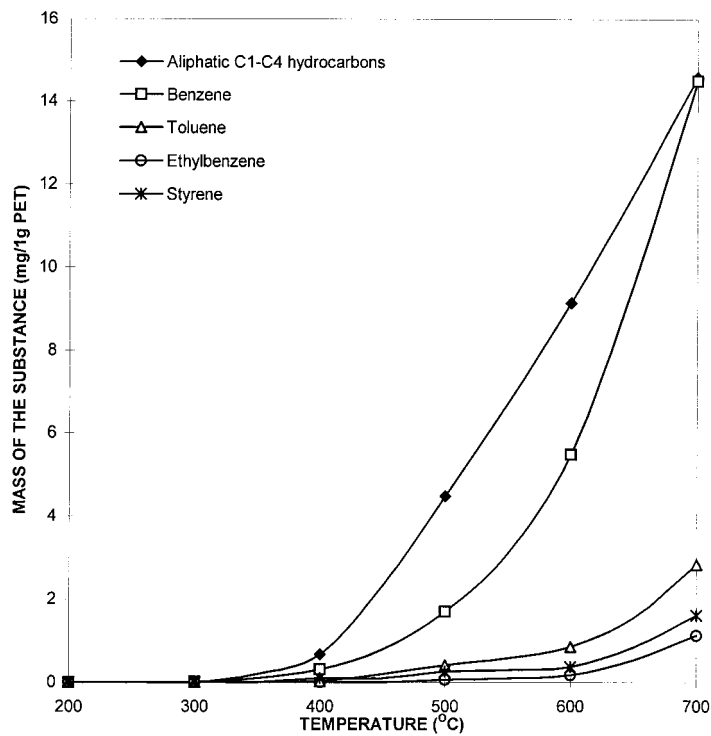


Figure 5 Mass changes of hydrocarbons evolved from PET (Polyclear-T 86) as a function of degradation temperature.

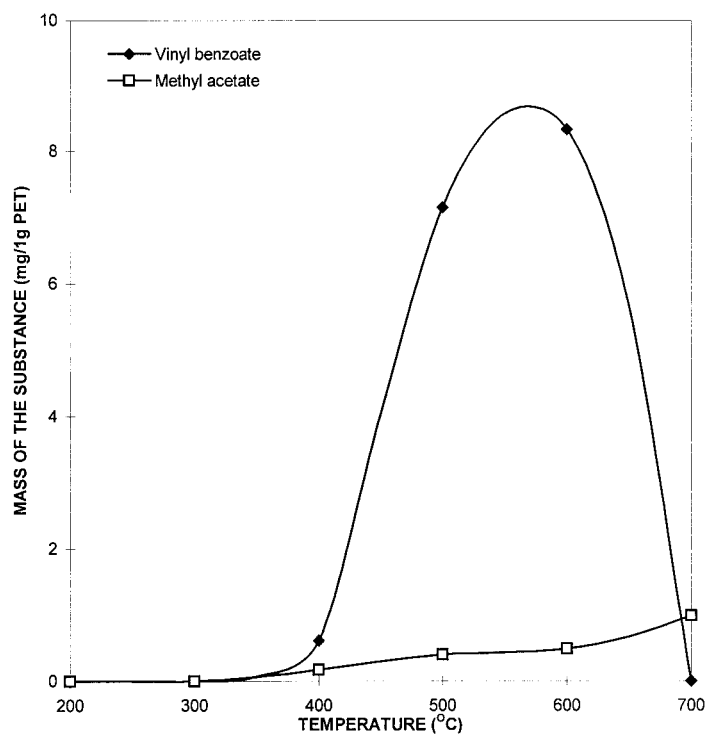


Figure 6 Mass changes of esters evolved from PET (Polyclear-T 86) as a function of degradation temperature.

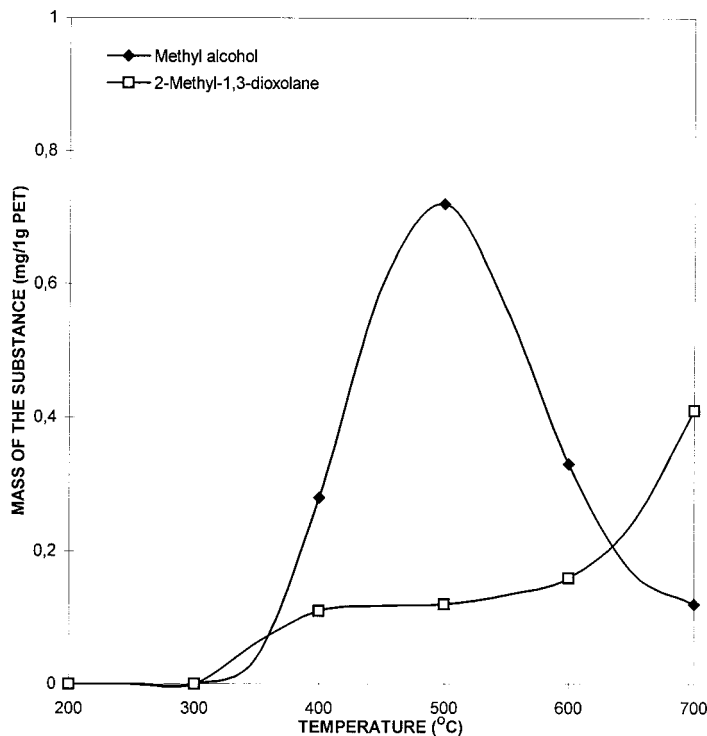


Figure 7 Mass changes of methyl alcohol and 2-methyl-1,3-dioxolane evolved from PET (Polyclear-T 86) as a function of degradation temperature.

apparatus and conditions which were used for the degradation experiments. For each of the compounds, the calibration plot was prepared and used for the quantitative analyses. Collecting and processing of the chromatographic data was performed by means of computer using the CHROMED program. Most of the substances were analyzed using a Chrom 5 gas chromatograph with an FID detector and the following packed columns: SE 30 (10%) + Carbowax 20 M (0.3%) on a Chromosorb W NAW, 60–80 mesh, and XE 60 (8%) + Carbowax 20 M (0.3%) on a Chromosorb W NAW, 60–80 mesh. A gas chromatograph ELPO N-504 with a TCD detector and column packed with silicagel of 50–100 mesh were used for carbon dioxide analyses. Carbon monoxide was analyzed using Dräger tubes. Formaldehyde was absorbed in water and analyzed colorimetrically as a complex with chromotropic acid.¹⁰

RESULTS

After completing the thermal-degradation experiments, the weight losses of PET were evaluated. At lower temperatures (200–300°C), the

weight losses were very small (respectively, 0.1% and 0.7%). The greatest changes of the sample weights were observed at 300–500°C. At higher temperatures (600–700°C), the sample decomposed almost 94%. The percentage of the PET weight loss as a function of the degradation temperature is shown in Figure 2.

Analyses showed that volatile substances emitted during the thermal degradation of PET consist of carbon oxides, aldehydes (acetaldehyde, formaldehyde, benzaldehyde), aliphatic C₁–C₄ hydrocarbons, aromatic hydrocarbons (benzene, toluene, ethylbenzene, styrene), esters (vinyl benzoate, methyl acetate), acetophenone, methyl alcohol, and 2-methyl-1,3-dioxolane. The concentrations of the determined compounds are given in Table I. For each of the substances, the mass evolved from 1 g of PET was calculated.²⁶ The dependence of the evolved substances masses on the degradation temperature is shown in Figures 3–8.

CONCLUSIONS

The main volatile substances evolved from PET during the thermal degradation in a nitrogen at-

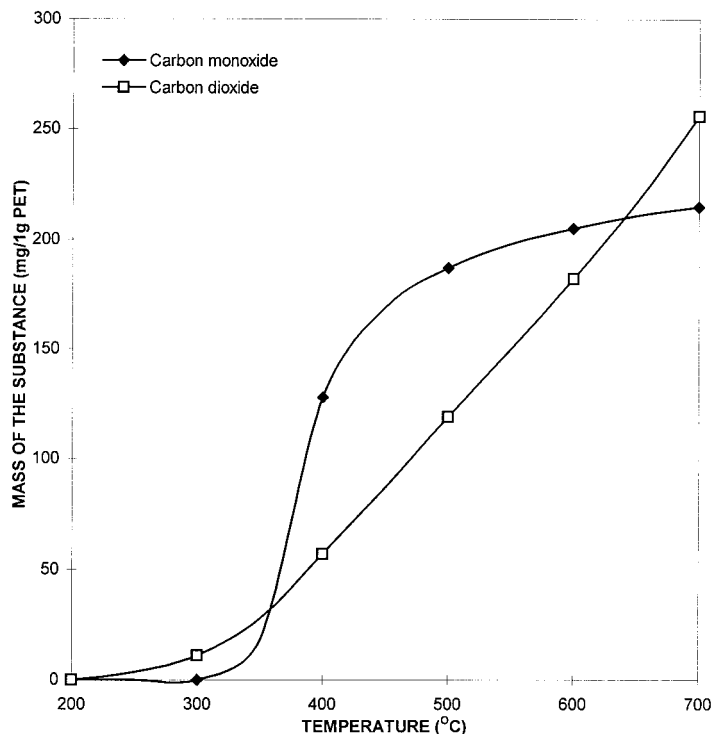


Figure 8 Mass changes of carbon oxides evolved from PET (Polyclear-T 86) as a function of degradation temperature.

mosphere were carbon monoxide, carbon dioxide, acetaldehyde, acetophenone, aliphatic C_1 – C_4 hydrocarbons, and benzene. Within the temperature range 200–300°C, only acetaldehyde and formaldehyde were detected. At higher temperatures, the mixtures of volatile decomposition products of PET became more complex. With the temperature increase, the concentrations of carbon oxides, aromatic and aliphatic hydrocarbons, acetophenone, methyl acetate, and 2-methyl-1,3-dioxolane increased. The maximum yields of acetaldehyde and vinyl benzoate were observed at 600°C. Methyl alcohol reached a maximum at about 500°C.

During the thermal degradation of PET in nitrogen, considerably smaller amounts of carbon oxides and formaldehyde were formed than in an air atmosphere. The yield of aliphatic C_1 – C_4 hydrocarbons in nitrogen was about twice greater, whereas the yields of aromatic hydrocarbons were similar. The maximum yield of acetaldehyde was observed in nitrogen at a higher temperature than in air (400°C).²⁶

REFERENCES

1. Schnabel, W. *Polymer Degradation*; Carl Hanser: Munich, 1981.
2. Buekens, A. G.; Schoeters, J. G. *Conserv Recycl* 1986, 9, 253.
3. Kaminsky, W. *Makromol Chem Macromol Symp* 1991, 48/49, 381.
4. Kaminsky, W. *Makromol Chem Macromol Symp* 1992, 57, 145.
5. Wanjek, H.; Stabel, U. *Kunststoffe* 1994, 84, 109.
6. Mark, F. E. *Polym Recycl* 1995, 1, 115.
7. R'95-Recovery, Recycling, Reintegration, Collected Papers of the International Congress, Geneva, 1-3.02.1995, Vol. 5, Thermal Processes, Energy Recovery; Barrage, A.; Edelmann, X., Ed.; EMPA: Dübendorf, 1995.
8. Blazsó, M. *J Anal Appl Pyrolysis* 1997, 39, 1.
9. Aseeva, R. M.; Zaikov, G. E. *Combustion of Polymer Materials*; Hanser: Munich, 1986.
10. Trzeszczyński, J. *Investigations on Air Pollution by Toxic Substances Educed from Plastics*; Technical University of Szczecin: Szczecin, 1978.
11. Zimmermann, H. In *Developments in Polymer Degradation*; Grassie, N., Ed.; Applied Science: London, 1984; Vol. 5, p 79.
12. Buxbaum, L. *Angew Chem* 1968, 80, 225.

13. Kovarskaya, B. M.; Levantovskaya, I. I.; Blumenfeld, A. B.; Draluk, G. V. *Plast Massy* 1968, 5, 42.
14. Villain, F.; Coudane, J.; Vert, M. *Polym Degrad Stab* 1994, 43, 431.
15. Villain, F.; Coudane, J.; Vert, M. *Polym Degrad Stab* 1995, 49, 393.
16. Sugimura, Y.; Tsuge, S. *J Chromatogr Sci* 1979, 17, 269.
17. Bednas, M. E.; Day, M.; Ho, K.; Sander, R.; Wiles, D. M. *J Appl Polym Sci* 1981, 26, 277.
18. Ohtani, H.; Kimura, T.; Tsuge, S. *Anal Sci* 1986, 2, 179.
19. Ohtani, H.; Tsuge, S. In *Applied Pyrolysis Handbook*; Wampler, T. P., Ed.; Marcel Dekker: New York, 1995; p 97.
20. Lüderwald, I.; Urrutia, H. *Makromol Chem* 1976, 177, 2079.
21. Adams, R. E. *J Polym Sci Polym Chem Ed* 1982, 20, 119.
22. Montaudo, G.; Puglisi, C.; Samperi, F. *Polym Degrad Stab* 1993, 42, 13.
23. McNeill, I. C.; Bounekhel, M. *Polym Degrad Stab* 1991, 34, 187.
24. Kinoshita, R.; Teramoto, Y.; Nakano, T.; Yoshida, H. *J Therm Anal* 1992, 38, 1891.
25. Kinoshita, R.; Teramoto, Y.; Yoshida, H. *J Therm Anal* 1993, 40, 605.
26. Dzięcioł, M.; Trzeszczyński, J. *J Appl Polym Sci* 1998, 69, 2377.