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THERMAL DEGRADATION OF POLYESTERS BY SIMULTANEOUS TG-DTA/FT-IR ANALYSIS

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A combination system of thermogravimetric/differential thermal analysis (TG-DTA) and Fourier-transform infrared absorption spectroscopy (FT-IR) was described. This simultaneous TG-DTA/FT-IR technique gave spectroscopic and weight loss information about the thermal degradation process of engineering polyesters; poly(ethylene terephthalate)(PET) and poly(butylene terephthalate)(PBT). The evolved gases from PET were benzoic acid, carbon dioxide and carbon monoxide, while those from PBT were terephthalic acid esters and benzoic acid esters.

Keywords: polymers, TG-DTA / FT-IR

Introduction

Thermogravimetry (TG) is well established as an analytical tool which gives weight loss information of materials heated under various atmospheric conditions. Recently, the simultaneous techniques such as TG/gas chromatography (GC), TG/mass spectrometry (MS) and TG/infrared absorption spectrometry (IR) were developed to identify the evolved gases [1–5]. GC is a highly sensitive tool, however, quantitative analysis is difficult because of the need for many standard materials. With the MS, due to the complex nature of the MS spectrum of mixed gases, it is difficult to analyze quantitatively. In addition, the ionization process has a possibility of introducing the chemical reaction of evolved gases and the successive decomposition of higher boiling point gases.

Fourier Transform IR (FT-IR) method has a high sensitivity for trace component detection and identification. Since spectrum data are collected within 5 sec by FT-IR, TG-DTA and FT-IR analyses are carried out in real time. TG-

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DTA/FT-IR technique has been used to perform analysis on a wide range of evolved gases, both qualitatively and quantitatively. Simple evolved gases, such as oxides of carbon, nitrogen, and sulfur, are easily identified by FT-IR, even if they are evolved together. Mixtures of more complex products such as esters and ethers are not always totally identifiable [6], but the observed group frequencies are often enough to define the types of products. TG/FT-IR studies were reported for pharmaceutical samples [6], thermal degradation products of various polymers [7, 8] and combustion products from coals [9].

Polymer samples produce several types of evolved gases through thermal degradation under various atmospheres. Sometimes the evolved gases from polymeric samples contain higher boiling point materials. In this study, the possibility of application of simultaneous TG-DTA/FT-IR method to analyze the thermal degradation process of polyesters were discussed.

Experimental

Samples

Calcium oxalate, a standard sample for weight loss calibration of TG-DTA was used without purification. Two kinds of commercial grade polyesters; poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) supplied from Polyplastics Co. Ltd., Shizuoka, Japan were used.

Measurements

Seiko SSC5200H thermal analysis system with the Seiko thermogravimetry/differential thermal analysis module TG/DTA220 was connected with the Bio-Rad FTS 40 Fourier-transform infrared spectrometer using the Bio/Rad TG/IR interface to create an integrated simultaneous TG-DTA/FT-IR system. A standard deuterated triglycine sulfate was used as a detector. The evolved gases were introduced to a gas cell in the TG-DTA/FT-IR interface from the furnace tube of TG-DTA through a heated transfer line (inside diameter; 0.7 mm, length; 1500 mm) with a glass-coated inside-surface. Figure 1 shows the schematic diagram of the integrated TG-DTA/FT-IR system. The TG-DTA furnace tube, a transfer line and the gas cell were temperature-controlled in order to prevent condensation of evolved gases. A small furnace volume and very low transfer line volume gives good gas flow characteristics and low dilution of the evolved gases for maximum sensitivity.

TG-DTA measurements were carried out using 5–15 mg samples in platinum sample containers at 20 K/min under a dry nitrogen gas flow. The flow rate of dry nitrogen gas was varied from 50 ml/min to 500 ml/min. Calcium oxalate was heated from 30° to 230°C. PET and PBT were heated from room temperature to 900°C.

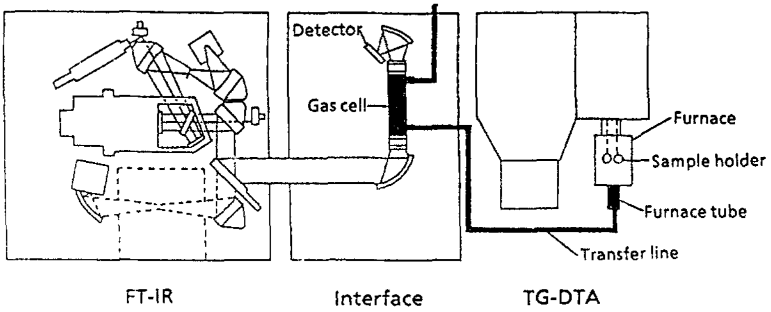

Fig. 1 Schematic diagram of the integrated TG-DTA/FT-IR system

All spectroscopic data were collected at 8 cm^{-1} resolution, corresponding to 2 scans per spectrum which provided a time resolution of approximately 1.7 sec. The collected spectra were identified referring the EPA vapor phase library (approximately 3.300 spectra) supplied by the Bio-Rad FT-IR spectra data base. A form of target factor analysis [6] was used to identify possible components of the evolved gas mixture.

Results and discussion

In order to determine the optimum measuring condition of the integrated TG-DTA/FT-IR system, the dehydration process of calcium oxalate was measured under various gas flow rates. Figure 2 shows the gas flow rate dependence of time lag between the peak time of the differential TG curve and the peak time of the specific gas profile at 2200–1150 cm^{-1} corresponding to the absorption bands of water. When dry nitrogen gas flowed at rate above 200 ml/min, time lag was within about 2 sec and the signal-to-noise ratio (S/N) on the spectra became low with the increasing gas flow rate. The optimum gas flow rate was 200 ml/min in this TG-DTA/FT-IR system.

The temperature of a heated transfer line is an important measurement condition used to ensure that no cold spots exist to condense higher boiling gases, and to prevent further extra chemical reaction or thermal decomposition. FT-IR spectra of evolved gases from PET at 451°C were shown in Fig. 3 as a function of transfer line temperature. The absorption intensity was normalized by the intensity at 2350 cm^{-1} which band was identified to carbon dioxide. By increasing the transfer line temperature, the absorption intensities at 1762, 1181 and 1087 cm^{-1}, which were the absorption bands identified to benzoic acid and benzoic acid esters, increased slightly. These facts suggested that some of the evolved benzoic acid and/or benzoic acid esters were trapped in the transfer line at 200°C . However, the maximum temperature of the transfer line is limited by the thermal degradation temperature of the evolved gases. The separate measurement of DSC

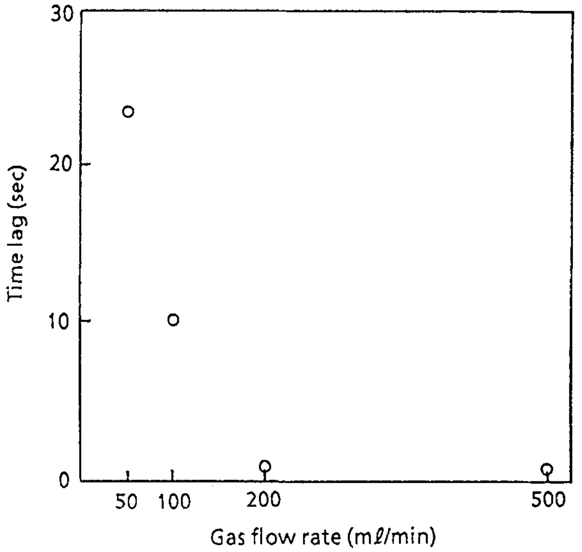

Fig. 2 Relationship between nitrogen gas flow rate and time lag from TG-DTA furnace to IR gas cell

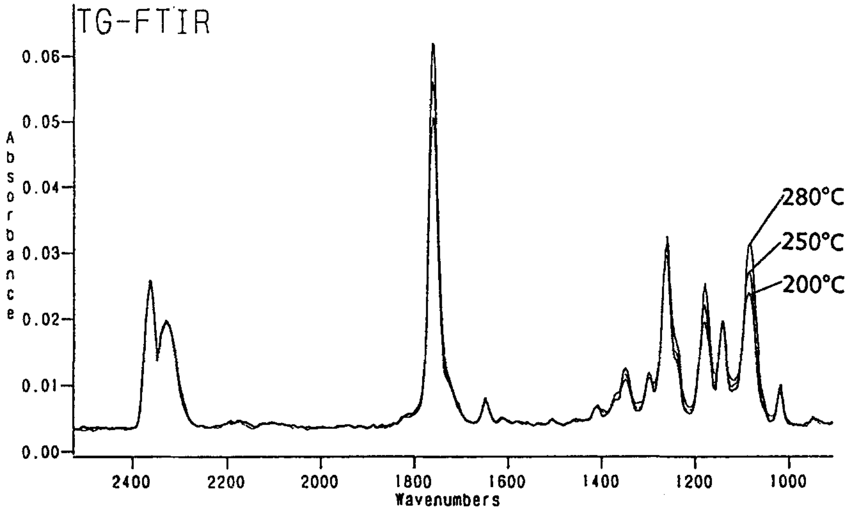

Fig. 3 Influence of transfer line temperature on FT-IR spectra of evolved gases from PETY at 451°C

with hermetic sealed container indicated that the thermal degradation of benzoic acid ethyl ester started around 250°C. TG-DTA/FT-IR measurement of benzoic acid ethyl ester was carried out under the condition of a transfer line temperature of 280°C. Benzoic acid ethyl ester was sublimed at a temperature below 200°C.

Since FT-IR spectra of the evolved gases matched the spectrum of benzoic acid ethyl ester, the evolved benzoic acid ethyl ester did not decompose while passing through a heated transfer line, controlled at 280°C. The temperatures of the transfer line and gas cell in the TG-DTA/FT-IR interface were controlled at 280°C in this study.

Figure 4 shows TG-DTA curves of PET (*a*) and PBT (*b*). A single weight loss due to thermal decomposition was observed for both polyesters in the experimental temperature range. The weight loss started at 360°C and approached a constant value at 550°C for PET. The weight loss of PBT started at lower temperature (320°C) and stopped at 450°C. The residues at 800°C were about 10% and 5% of the starting materials for PET and PBT, respectively.

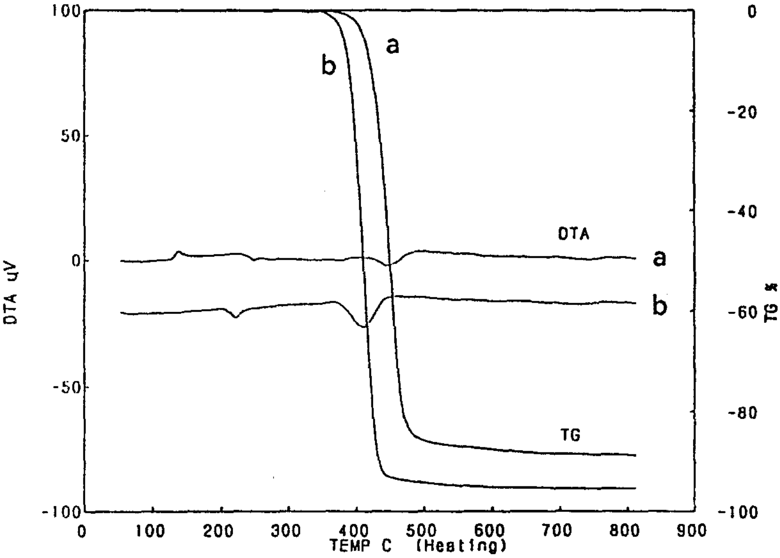

Fig. 4 TG-DTA curves for PET and PBT

FT-IR spectra of evolved gases at various temperatures from PET and PBT were shown in Figs 5 and 6, respectively. The difference between both spectra was observed at around 3000 cm^{-1}, 2350 cm^{-1}, 1700 cm^{-1}, 1300–1000 cm^{-1} and 700 cm^{-1}. Since the absorption band at 2350 cm^{-1} was due to carbon dioxide, PET produced a much larger amount of carbon dioxide during thermal decomposition than PBT. The spectra of PBT showed the separated double absorption peaks at 1760 and 1740 cm^{-1}, while the spectra of PET showed single peak at 1760 cm^{-1}. The absorption band at 1740 cm^{-1} was assigned to aromatic esters, therefore, the evolved gases from PBT contained a much larger amount of aromatic esters than those from PET.

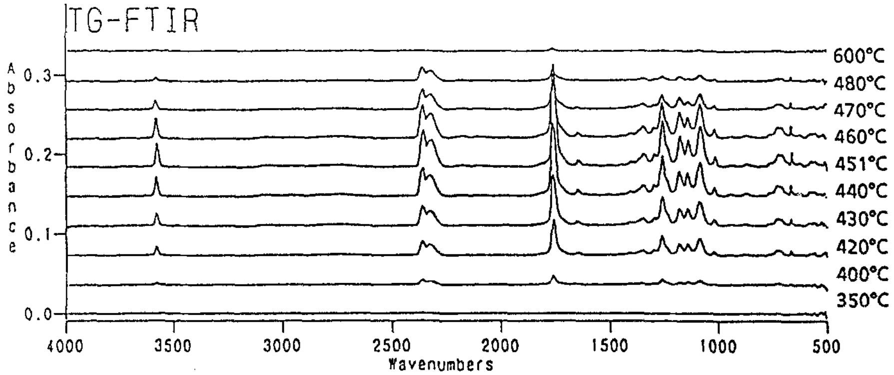

Fig. 5 FT-IR spectra of mixed gases evolved from PET at various temperature

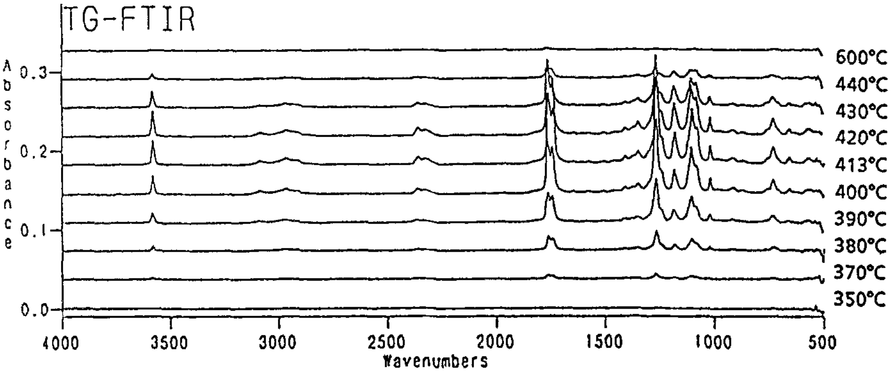

Fig. 6 FT-IR spectra of mixed gases evolved from PBT at various temperature

Tables 1 and 2 list the target spectra selected from the library search according to their residual values. The Hit Quality Index (HQI) was a measure of the difference between the unknown spectrum and the library spectrum. The value of HQI was calculated by the following equation,

$$(\mathrm{HQI})^2 = \sum_{w} \left(\frac{U_w}{|U|} - \frac{L_{iw}}{|L_i|} \right)^2 \tag{1}$$

In the above equation, U_w is an unknown spectrum (w indexes wave number) and L_{iw} is library spectrum i. The bottom equation defines U, the normalization constant for the unknown. The normalization constant for a library spectrum, L_i, is defined similarly. As shown in Table 1, the evolved gases from PET at 451°C included benzoic acid, carbon dioxide, carbon monoxide and benzoic acid derivatives. The main evolved gases from PET were benzoic acid and carbon dioxide. The evolved gases from PBT at 413°C listed in Table 2 contained benzoic acid

Table 1 Target factor analysis results for the evolved gases from PET at 451°C using the EPA vapor phase library

Name	HQI
Carbon dioxide	
Carbon monoxide	
Benzoic acid	0.52
p-toluic acid	0.55
m-toluic acid	0.57
Fumaric acid, methyl-,	0.59
Benzoic acid, 3, 4-dimethyl-,	0.59
Benxoic acid, p-tert-butyl-,	0.62
Benxoic acid, p-hydroxy-,	0.64

esters, terephthalic acid esters, carbon dioxide, and halogenide. The main evolved gases from PBT were benzoic acid esters and terephthalic acid esters. These facts suggested that ether linkages and ethylene linkages were cleaved during the thermal degradation of PET, and that ether linkages were cleaved selectively in the case of PBT. The evolved gases from PBT contained several types of halogenide products, while the evolved gases from PET contained a trace amount of halogenide. This fact suggests that a commercial PBT contains more halogen materials as anti-combustion agents than PET.

Table 2 Target factor analysis results for the evolved gases from PBT at 413°C using the EPA vapor phase library

Name	HQI
Carbon dioxide	
Benzoic acid, 3, 5-dichloropentyl ester	0.38
Benzoic acid, benzyl ester	0.41
Terephthalic acid, diallyl ester	0.43
Terephthalic acid, dibutyl ester	0.43
Terephthalic acid, dimethyl ester	0.44
Benzoic acid, propyl ester	0.46
Benzoic acid, butyl ester	0.47
Benzoic acid, ethyl ester	0.48
Phthalic acid, diethyl ester	0.48
Benzoic acid, isobutyl ester	0.48
Benzoic acid, p-bromo-, ethyl ester	0.48

FT-IR spectra obtained through spectral windows, wave number range at 3630–3550 cm^{-1}, 2245–2015 cm^{-1}, 2400–2250 cm^{-1}, 1870–1680 cm^{-1}, and

1500–840 cm^{-1} for the evolved gases from PET and PBT were shown in Figs 7 and 8, respectively. These figures show the specific gas profiles, which are measurements of the integrated IR absorbance in the spectra as a function of temperature. These windows can be defined, each monitors the evolution of a particular gas. Figures 7 and 8 show the specific gas profiles for aromatic carboxylic acid such as benzoic acid (3630–3550 cm^{-1}), carbon dioxide (2400–2250 cm^{-1}), aromatic carboxylic acid and aromatic esters (1870– 1680 cm^{-1}, 1500–840 cm^{-1}) and carbon monoxide (2245–2015 cm^{-1}).

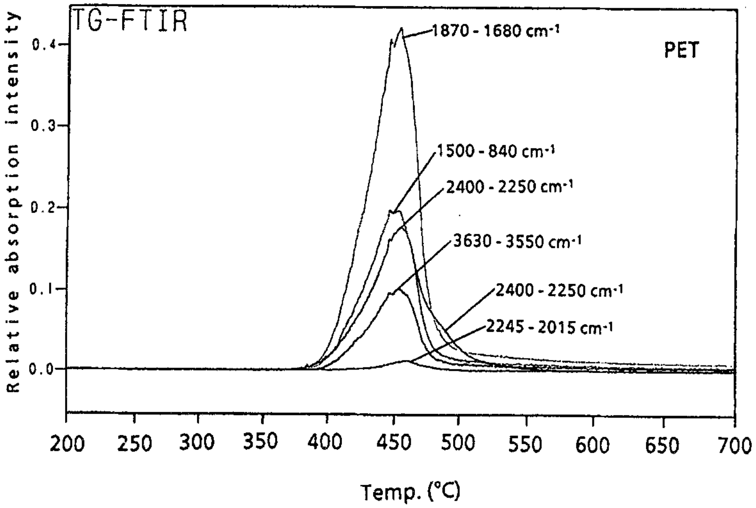

Fig. 7 Absorption intensity changes of specific gas profiles at 3630–3550 cm^{-1}, 2245–2015 cm^{-1}, 2400–2250 cm^{-1}, 1870–1680 cm^{-1} and 1500–840 cm^{-1} for PET as a function of temperature

In the case of PET, carbon dioxide and aromatic esters were detected in the initial stage of decomposition. When the spectra of PET at 400° and 420°C were compared, the ratio of carbon dioxide in relation to the total amount of gas evolved was higher at 400° than at 420°C. The substract spectrum, which was obtained by subtracting the spectrum at 400°C from the spectrum at 500°C, suggested that a greater ratio of benzoic acid existed in the evolved gases at 500°C than the gases evolved in the initial stage of the decomposition. On the contrary, the subtract spectrum obtained by subtracting the spectrum at 500° from 400°C showed the existence of phthalic acid dimethyl ester and terephthalic acid diethyl ester. In addition to aromatic acid dimethyl esters, the subtract spectrum showed the characteristic absorption bands at 1650 cm^{-1} and at 1144 cm^{-1}, which were due to alkyl vinyl esters. Alkyl vinyl esters may be produced by thermal degradation of plasticizer in PET.

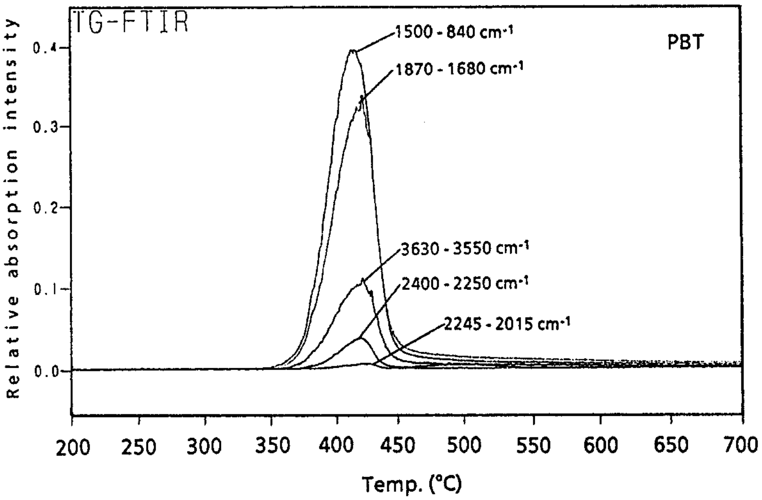

Fig. 8 Absorption intensity changes of specific gas profiles at 3630–3550 cm^{-1}, 2245–2015 cm^{-1}, 2400–2250 cm^{-1}, 1870–1680 cm^{-1} and 1500–840 cm^{-1} for PBT as a function of temperature

The specific gas profiles for PBT shown in Fig. 8 suggested that aromatic esters evolved from the initial stage to the final period of decomposition, and that a small amount of carbon dioxide evolved at the midrange of decomposition. The specific gas profile of carbon dioxide from PBT showed two peaks as shown in

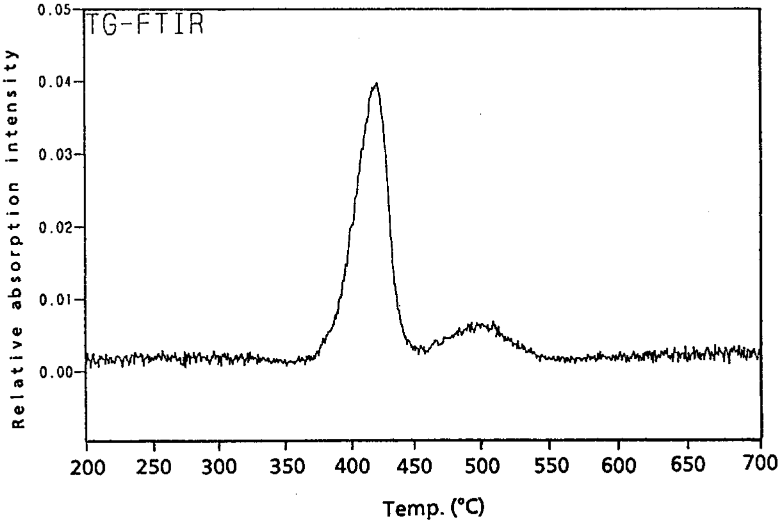

Fig. 9 Absorption intensity changes of specific gas profiles at 2400–2250 cm^{-1} for PBT as a function of temperature

Fig. 9, the large peak at 416°C and a small peak at 498°C. The former temperature was the midpoint of decomposition and the latter was the final stage of decomposition. The subtract spectrum which was obtained by subtracting the spectrum at 420°C from the spectrum at 400°C suggested that terephthalic dibutyl ester evolved at the initial stage of decomposition.

Conclusion

Thermal decomposition process of PET and PBT were investigated by the integrated TG-DTA/FT-IR simultaneous analysis. The main evolved gases from PET were benzoic acid and carbon dioxide. Since carbon dioxide evolved in the initial stage of decomposition of PET, the ether linkages and the ethylene linkages were cleaved at first. In the initial stage of decomposition of PBT, the ether linkages were cleaved selectively.

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Zusammenfassung — Es wird ein kombiniertes System aus TG-DTA und FT-IR beschrieben. Mit dieser simultanen TG-DTA/FT-IR-Technik wurden spektroskopische und Massenverlustangaben über die thermische Zersetzung technisch wichtiger Polyester, namentlich von Poly(ethylenterephthalat) (PET) und Poly(Butylenterephthalat) (PBT) ermittelt. Die aus PET freigesetzten Gase waren Benzoesäure, Kohlendioxid und Kohlenmonoxid, die aus PBT freigesetzten Gase hingegen Terephthalsäureester und Benzoesäureester.