

# Pyrolysis of an Amorphous Copolyester

Aifang Yu, Xiang'an Huang

State Key Laboratory for the Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai, People's Republic of China, 200051

Received 20 July 2003; accepted 4 March 2005

DOI 10.1002/app.22415

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The pyrolysis of the amorphous copolyester poly(ethylene glycol-co-cyclohexane 1,4-dimethanol terephthalate) (PETG) was investigated. The applied technique was thermogravimetry/differential scanning calorimetry/mass spectrometry analysis. The pyrolysis products of PETG were ascertained. The results showed that the PETG mass loss was 90.36% from room temperature to 650°C, its thermal decomposition was mainly completed in one step at

425.2°C, and the aliphatic backbone of PETG played a dominant role in controlling the behavior of the pyrolysis. The pyrolysis mechanism was also examined. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2793–2797, 2006

**Key words:** amorphous; polycondensation; polyesters; pyrolysis; thermogravimetric analysis (TGA)

## INTRODUCTION

Many polymeric materials exist in our surroundings, and there is not one day that they are not seen. The purpose of a polymeric material is to be light, provide good construction, low-cost, and so forth. On the other hand, the burning material has faults such as difficulty in calculating the fatigue life. Its characteristics, especially with respect to low flame resistance, comes into question with the possibility of its involvement in a fire. Therefore, to control the combustion of a polymeric material, conducting pyrolysis research becomes important.

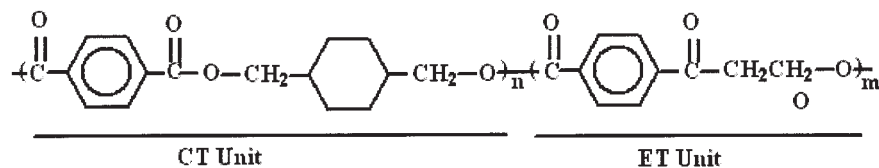
Although flaming combustion has received more attention, the study of smoldering combustion is important because it is the combustion mechanism when no flame exists. Smoldering often precedes flaming conditions with solid materials. Therefore, fundamental studies of the subject are needed in order to make desirable changes.

Smoldering combustion proceeds by a process of pyrolysis, producing volatile products and a solid char; then, the solid char oxidizes with diffusing oxygen to produce the heat that keeps the whole process self-sustaining. The pyrolysis is a complex series of events producing basically all the volatile products with the exception of carbon oxides and water. The aim of this work is to evaluate the processes and mechanisms of pyrolysis involved in the smoldering combustion of the amorphous polyester poly(ethylene

glycol-co-cyclohexane 1,4-dimethanol terephthalate) (PETG).

PETG is a copolyester with optical clarity, good low-temperature toughness, a lower glass-transition temperature, and resistance to hydrocarbons. The amorphous property allows the polymer to provide active bonding with little or no effect on the overall appearance of the material. PETG's lack of crystallinity provides sheets with the greatest clarity, lowest haze, greatest ease of formation, and highest impact strength, though with a lower modulus. PETG combines good toughness (even at low temperatures) with film clarity and melt strength. A considerable amount of literature has been written on PETG and its blends. Samios and Kalfoglou<sup>1</sup> investigated the compatibility behavior of melt-mixed blends of copolyester PETG with polycarbonate (PC). Papadopoulou and Kalfoglou<sup>2,3</sup> reported the compatibility behavior of melt-mixed binary blends of copolyester PETG with poly(butylene terephthalate) and poly(ethylene terephthalate) (PET) successively over the complete composition range. The *in situ* compatibilization via the catalyzed transesterification of PETG/poly(ethylene-co-vinyl acetate) (EVA) was examined by Legros et al.<sup>4</sup> using mechanical, rheological, and morphological characterization techniques. The properties of PETG/EVA blends were investigated by Lacroix and coworkers.<sup>5,6</sup> Bass<sup>7</sup> studied PETG polyester fibers for nonwovens. Both virgin PET and 100% recycled PET as replacements for a PETG packaging tray were evaluated and compared with PETG sheets by Griffin.<sup>8</sup> However, no publication has reported PETG's pyrolysis behavior.

Correspondence to: X. Huang (hxa@dhu.edu.cn).



Structure 1 Structural formula of PETG.

## EXPERIMENTAL

### Materials

The PETG investigated in this study (PETG 6763) was an amorphous copolyester obtained from Eastman Kodak Chemical Co. (Kingsport, TN). It was synthesized from a mixture of cyclohexane dimethanol, ethylene glycol, and terephthalic acid in a molar ratio of approximately 1/2/3.<sup>9</sup> Its molecular weight was 26,000 g/mol. Because of the introduction of the cyclic diol moiety, the crystallinity of PETG is hampered in comparison with that of PET. The latter is obtained simply from terephthalate acid and ethylene glycol polycondensation and has a more regular chemical structure. Although PET is semicrystalline, PETG is essentially amorphous, and the structural formula of PETG is shown in Structure 1.

### Thermogravimetry/differential scanning calorimetry/mass spectrometry (TG-DSC-MS) measurements

A Netzsch STA 449C thermogravimetry/differential scanning calorimetry (TG-DSC) device (Selb, Babaria, Germany) coupled with a Balzers Thermostar quadrupole mass spectrometer (Brügg, Switzerland) was used in the experiments. A quartz capillary tube was used as the interface between the thermal analyzer and the quadrupole. The mass of PETG was 10.4 mg. Argon gas (5 mL/min) was used for the protective gas of the TG-DSC furnace. Helium gas with a flow speed of 40 mL/min was used as the carrying gas. The vacuum for the system of the quadrupole was  $10^{-4}$  Pa. All the procedures were controlled according to a proposed program.

The TG-DSC program was operated first. The temperature region was room temperature to 650°C. The heating rate was 10°C/min. The mass spectrometry (MS) program was operated second. The calculations and data treatment were in progress after the proposed programs were completed.

## RESULTS AND DISCUSSION

Thermal analysis using TG-DSC-MS is a very useful technique for studying pyrolysis events performed in an inert atmosphere such as helium and oxidation events performed in an oxygen atmosphere. Small

samples and controlled heating minimize the effects of heat and mass transfer and allow better elucidation of the principal chemical reactions. Pyrolysis starts with the vaporization of volatile materials, and then the primary decomposition of nonvolatile components produces a solid char. Depending on the availability of oxygen, the char may undergo secondary higher temperature pyrolysis before or concurrent with oxidation. The primary pyrolytic decomposition produces a large number of tars and gases. The secondary high-temperature pyrolysis of the solid char is a source of many of the hydrocarbons and aromatic compounds found in the final volatile products. The amount and reactivity of the char formed determine how well the smoldering process will continue or spread. Above 300°C, pyrolysis and oxidation can occur simultaneously. The TG-DSC-MS results are plotted in Figures 1-4.

The thermogravimetry (TG) curves in Figure 1 show the mass loss: 90.36% (room temperature to 650°C). There basically should be no mass loss over 700°C. Differential scanning calorimetry (DSC) in Figure 1 shows a small endothermic peak at 86.7°C, two small exothermic peaks at 365 and 399.1°C, and a big endothermic peak at 425.2°C. Some of the MS results are shown in Figures 2-4.

### Glass-transition temperature

Because the glass-transition temperature is a function of end-group activity, an endothermic peak at 85.7°C

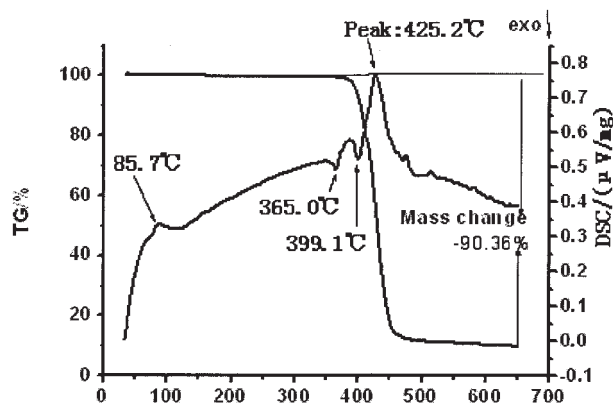
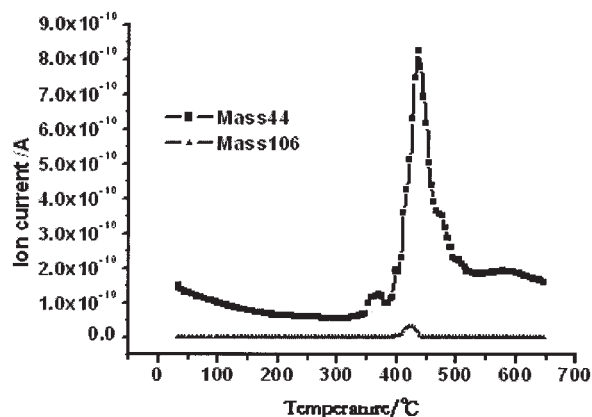


Figure 1 TG-DSC curves for PETG.

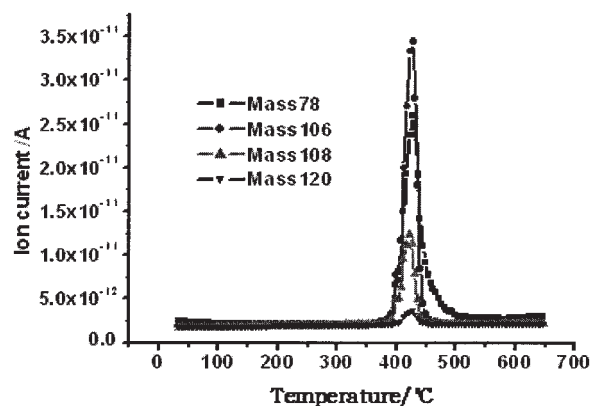


**Figure 2** MS spectra for PETG/ $[\text{CO}_2]^+$  or  $[\text{CH}_3\text{CHO}]^+$  ( $m/z = 44$ ) and  $[\text{C}_6\text{H}_5\text{OH}]^+$  or  $[\text{C}_8\text{H}_{10}]^+$  ( $m/z = 106$ ).

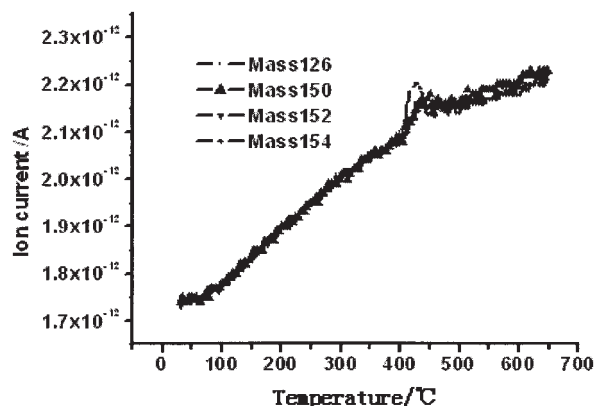
appears. The fact that PETG is amorphous is the reason for the disappearance of a true melting point in the DSC curve.

### Exothermic peaks

The exothermic peaks indicate that the oxidation species formed in the ethylene terephthalate (ET) units are efficiently fragmented during the temperature-increase conditions. This confirms the efficient hydroperoxidation of ethylene glycol units in the PETG copolymer in the thermal degradation. The thermal degradation of polymers in the presence of oxygen gives the formation of oxidative species that are located in sensitive sites of their structure. As mentioned earlier, in the first stage, radicals ( $\text{R}\cdot$ ) are formed, which readily react with oxygen, giving peroxides as primary oxidation species. The exothermic termination of two alkylperoxy radicals produces an excited carbonyl state, which is deactivated by chemiluminescence to its ground state.<sup>10</sup>



**Figure 3** MS spectra for PETG/ $[\text{C}_6\text{H}_6]^+$  ( $m/z = 78$ ),  $[\text{C}_6\text{H}_5\text{OH}]^+$  or  $[\text{C}_8\text{H}_{10}]^+$  ( $m/z = 106$ ),  $[\text{C}_8\text{H}_{12}]^+$  ( $m/z = 108$ ), and  $[\text{C}_8\text{H}_8\text{O}]^+$  ( $m/z = 120$ ).



**Figure 4** MS spectra for PETG/ $[\text{C}_8\text{H}_{14}\text{O}]^+$  ( $m/z = 126$ ),  $[\text{C}_9\text{H}_{10}\text{O}_2]^+$  or  $[\text{C}_{12}\text{H}_8]^+$  ( $m/z = 150$ ),  $[\text{C}_{12}\text{H}_{10}]^+$  ( $m/z = 152$ ), and  $[\text{C}_{12}\text{H}_{10}]^+$  ( $m/z = 154$ ).

Corresponding to the small exothermic peaks of DSC, only the positive-ion mass of  $m/z = 44$  has another peak at a certain lower temperature. Therefore, it can be said that the oxidative species acetaldehyde is generated with increasing temperature.

### Endothermic peak

Corresponding to the big endothermic peak of DSC, the MS spectra for PETG are presented in Figures 2–4; which show the positive-ion mass spectra peaks of  $m/z = 44, 78, 106, 108, 120, 126, 150, 152$ , and  $154$  at  $425.2^\circ\text{C}$ . The ion current intensities and the formed positive-ion mass spectra are listed in Table I. The peaks are related to the pyrolysis of PETG. PETG generates many kinds of pyrolysis products. The main products are acetaldehyde, carbon dioxide, benzene, benzoic acid, 1,4-bis(methylene)-cyclohexane, 4-methylbenzaldehyde, and 4-methylene-cyclohexanemethanol. The pyrolysis mechanism of PETG is presumed from the aforementioned results, and it is shown in Figure 5.

The positive-ion mass spectra of  $\text{CO}_2^+$  or  $\text{CH}_3\text{CHO}^+$ ,  $\text{C}_6\text{H}_6^+$ ,  $\text{C}_8\text{H}_{12}^+$ ,  $\text{C}_8\text{H}_8\text{O}^+$ ,  $\text{C}_8\text{H}_{14}\text{O}^+$ ,  $\text{C}_9\text{H}_{10}\text{O}_2^+$ , and  $\text{C}_{12}\text{H}_{10}^+$  ( $m/z = 44, 78, 108, 120, 126, 150$ , and  $154$ ) are

**TABLE I**  
Ion Current Intensities at  $425.2^\circ\text{C}$

$m/z$	Expected positive-ion mass spectra	Ion current intensities (A)
44	$\text{CO}_2^+$ or $\text{CH}_3\text{CHO}^+$	$6.29 \times 10^{-10}$
78	$\text{C}_6\text{H}_6^+$	$2.6 \times 10^{-11}$
106	$\text{C}_6\text{H}_5\text{OH}^+$ or $\text{C}_8\text{H}_{10}^+$	$3.45 \times 10^{-11}$
108	$\text{C}_8\text{H}_{12}^+$	$1.13 \times 10^{-11}$
120	$\text{C}_8\text{H}_8\text{O}^+$	$3.66 \times 10^{-12}$
126	$\text{C}_8\text{H}_{14}\text{O}^+$	$2.21 \times 10^{-12}$
150	$\text{C}_9\text{H}_{10}\text{O}_2^+$ or $\text{C}_{12}\text{H}_8^+$	$2.15 \times 10^{-12}$
152	$\text{C}_{12}\text{H}_{10}^+$	$2.16 \times 10^{-12}$
154	$\text{C}_{12}\text{H}_{10}^+$	$2.14 \times 10^{-12}$

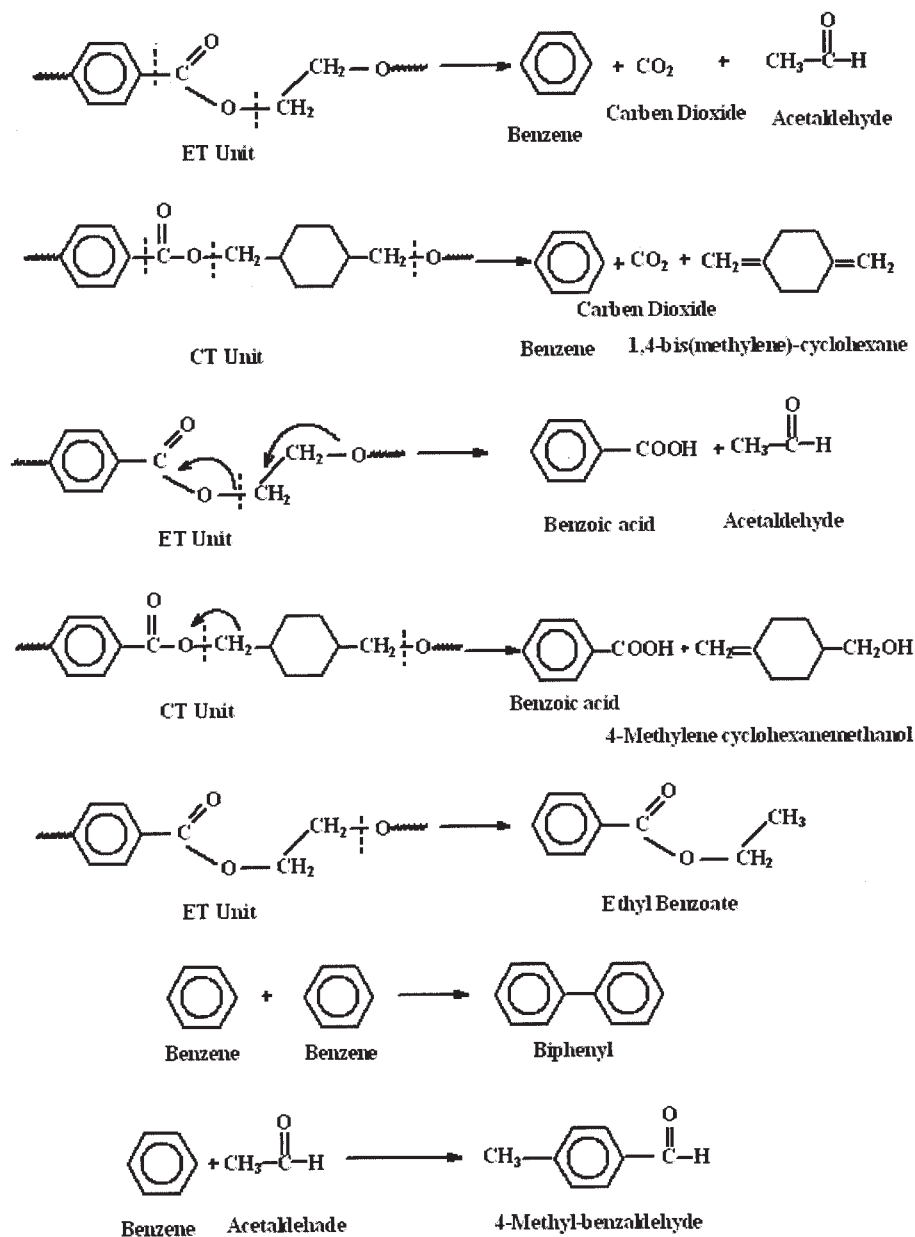


Figure 5 Pyrolysis mechanism of PETG. CT is the repeat unit of poly(1,4-cyclohexylene dimethylene terephthalate) (PCT).

the molecular ion peaks of acetaldehyde or carbon dioxide, benzene, 1,4-bis(methylene)-cyclohexane, 4-methyl-benzaldehyde, 4-methylene-cyclohexanemethanol, ethyl benzoate, and biphenyl, respectively. The ion mass spectrum of  $C_6H_6^+$  ( $m/z = 78$ ) also belongs to the fragment of biphenyl, ethyl benzoate, 4-methylene-cyclohexanemethanol, 1,4-bis(methylene)-cyclohexane, or benzoic acid. The ion mass spectrum of  $C_6H_5OH^+$  or  $C_8H_{10}^+$  ( $m/z = 106$ ) is the fragment of ethyl benzoate, 4-methylene-cyclohexanemethanol, 1,4-bis(methylene)-cyclohexane, or benzoic acid. The ion mass spectrum of  $C_8H_{12}^+$  ( $m/z = 108$ ) also belongs to the fragment of 4-methylene-cyclohexanemethanol. The ion mass spectrum of  $C_{12}H_{10}^+$  ( $m/z = 152$ ) is the fragment of biphenyl.

## CONCLUSIONS

Through TG-DSC-MS measurements, the pyrolysis products of the copolyester PETG have been ascertained. The results show that the PETG mass loss is 90.36% from room temperature to 650°C, its thermal decomposition is mainly completed in one step at 425.2°C, and the aliphatic backbone in PETG plays a dominant role in controlling the behavior of the pyrolysis. 4-Methylene-cyclohexanemethanol, 1,4-bis(methylene)-cyclohexane, and benzoic acid are characteristic heat decomposition products. The pyrolysis products of PETG are characteristic of the PETG composition and can be used to determine the polymer chemical structure.

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