Available online at www.sciencedirect.com

ScienceDirect

Chinese Chemical Letters 20 (2009) 487–491

CHINESE
CHEMICAL
LETTERS

www.elsevier.com/locate/cclet

# Thermal degradation and isothermal crystalline behavior of poly(trimethylene terephthalate)

Jian Liu [a], Shu Guang Bian [b], Min Xiao [a,*], Shuan Jin Wang [a], Yue Zhong Meng [a,*]

[a] *State Key Laboratory of Optoelectronic Materials and Technologies/Institute of Optoelectronic and Functional Composite Materials,*
*Sun Yat-Sen University, Guangzhou 510275, PR China*
[b] *High Technology R & D Center MOST, Beijing 100044, PR China*

Received 2 September 2008

---

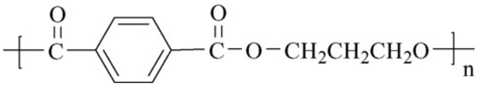
## Abstract

Poly(trimethylene terephthalate) (PTT) is an excellent fiber material. Its thermal degradation and isothermal crystalline behaviors were in this study investigated using thermogravimetric analysis (TGA), thermogravimetric analysis–Fourier transform infrared spectroscopy (TGA–FTIR) analysis, differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The thermal degradation mechanism of PTT follows Mclafferty rearrangement principle. The PTT with intrinsic viscosity (IV) of 0.74 dl/g has a maximum crystallinity of about 55% at 190 °C, as demonstrated by DSC and XRD measurements consistently.

*Keywords:* Poly(trimethylene terephthalate); Thermal degradation; Isothermal crystallization

---

Poly(trimethylene terephthalate) is aromatic polyester from terephthalic acid and 1,3-propanediol, its molecular structure is illustrated as following:



It is a promising material for engineering plastic and textile fiber because it combines many excellent performances of nylons and other polyesters [1,2]. In 1941, Calico Printers Ass Company [3] obtained PTT successfully via polycondensation of terephthalic acid (TPA) and 1,3-propanediol (PDO), but PTT could not be obtained at large scale till the 1990s due to expensive PDO. In the 1990s, the successful synthesis of low cost PDO has been reported by many companies such as Shell [4], Dupont [5] and Degussa [6] using different techniques. These techniques may make it possible to commercialize PTT product, and finally join the polyester family like poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). Ward and Wilding [7] found that PTT exhibited better elastic recovery than PET and PBT. Owing to excellent comprehensive properties as fiber material, PTT has been widely studied recently [8–14].

Generally, the synthesis of PTT is performed under high-temperature, high-vacuum and presence of effective catalyst conditions. At high-temperature, PTT is degraded easily. Understanding the mechanism of thermal

---

* Corresponding author.
*E-mail address:* mengyzh@mail.sysu.edu.cn (Y.Z. Meng).

1001-8417/$ – see front matter © 2008 Yue Zhong Meng. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.
doi:10.1016/j.cclet.2008.11.035

degradation of PTT is beneficial for obtaining high molecular weight PTT. PTT is semi-crystalline polyester. The crystallization behavior of PTT will affect its processing and mechanical properties. So, in this letter, we report the thermal degradation and isothermal crystalline behaviors of the PTT with intrinsic viscosity (IV) of 0.74 dl/g or weight average molecular weight ($\overline{M}w$) of 49,197 [15].

## 1. Experimental

PTT was obtained by conventional synthesis procedures [16]. Intrinsic viscosity of PTT was determined by a Ubbelohde viscometer (model 1835) at 25 °C. The concentration of the sample is 0.5 g/dl in 1:1 (w/w) of phenol:1,1,2,2-tetrachloroethane. Decomposition temperature of the PTT was evaluated by a thermogravimetric analysis (TGA) (TA instrument, Mode 2950) with about 6 mg of the sample. The sample was heated from ambient temperature to 600 °C at rate of 10 °C/min. TGA–FTIR was performed using about 10 mg of the samples under nitrogen flow (40 ml/min) on Cahn TG 131 instrument that was connected to Mattson Research grade FTIR through heated stainless steel tubing. The rate of heating was maintained at 10 °C/min and the final temperature was 600 °C. The evolved decomposition products were introduced to the IR chamber through the heated stainless steel tubing and analyzed by in situ vapor phase FTIR. Differential scanning calorimetry (DSC) experiment was performed on a NETZSCH 204 DSC in a nitrogen atmosphere. Each sample was heated from room temperature to 270 °C at a heating rate of 80 °C/min and held for a period of 5 min to ensure complete melting of the samples. After this period, each sample was rapidly cooled by liquid nitrogen (i.e. at a cooling rate of about 90 °C/min) from 270 °C to a desired crystallization temperature $T_c$ ranging from 185 to 210 °C, where it was held until the crystallizations were considered fully (i.e. no significant change in the heat flow as a function of time was further observed). All of the subsequent melting endotherms were recorded for analysis. The crystallinity $X_C$ of the samples was calculated by $X_C = \Delta H_c/\Delta H_0$, where $\Delta H_0 = 145$ J/g [17,18] was the heat of fusion for 100% crystalline PTT and $\Delta H_c$ was the measured heat of fusion for the PPT samples. XRD patterns of PTT were recorded on a D/max-IIIA diffractometer (rigaku corporation, Japan) with a copper target as radiation source ($\lambda = 1.54056$ Å). The diffractometer was operated at 35 kV and 25 mA. Scanning profiles were recorded at 12° ($2\theta$) per minute from 5° to 65°. Prior to the XRD test, PTT was treated by isothermal crystalline at 190 °C as the sample done for its DSC measurement but subsequently rapidly cooled by liquid nitrogen to room temperature at a cooling rate of about 90 °C/min.

## 2. Results and discussion

The starting degradation temperature of PTT was ~374 °C as indicated by TGA measurements, which is consistent with the results in literature [19]. The TGA–FTIR spectra of the PTT samples are presented in Fig. 1. The strongest absorption band in the range of 1750–1600 $\text{cm}^{-1}$ corresponds to the combination of stretching vibration mode of benzene ring skeleton and carbonyl group. While ~1450 $\text{cm}^{-1}$ band is assigned as another stretching vibration mode

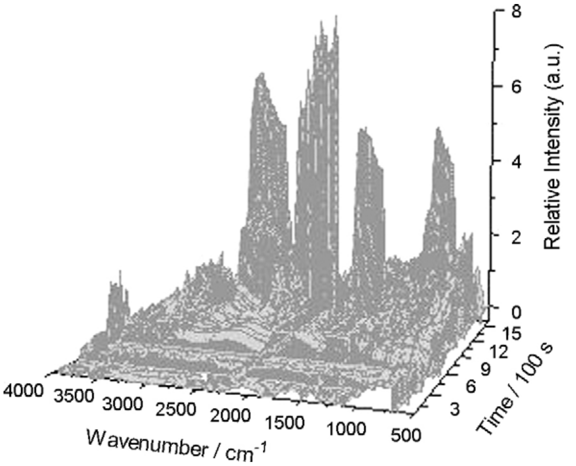


Fig. 1. TG-FTIR spectra of PTT thermal decomposition.