

Thermal Stability of Poly(ethylene-*co*-trimethylene terephthalate)s

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ABSTRACT: The thermal stability of poly(ethylene-*co*-trimethylene terephthalate) was first studied by thermogravimetry under nitrogen atmosphere at different heating rates. The results showed that the thermal behavior of the copolyester had a strong dependence on the chemical composition. The average activation energy from Ozawa technique increases with the concentration of EG units in the polyester, and a greater TG concentration in the copolyesters would decrease the onset degradation temperature. These phenomena may be attributed to the presence of one more

methylene of TG unit than of EG in the copolymer. It is also noted that the yield of solid residue increases with the concentration of EG units in the polymer chain at any heating rate, which may be associated with the content of aromatic ring in the polymer chain. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3330–3335, 2006

Key words: copolymerization; polyesters; thermogravimetric analysis (TGA); poly(ethylene-*co*-trimethylene terephthalate); Ozawa technique

INTRODUCTION

Poly(trimethylene terephthalate) (PTT), as a member of the aromatic polyester polymers, has attracted more and more attention from polymer chemists and manufacturers during the past decade because it is a high-performance polymer with numerous potential engineering applications. Most of aspects concerning PTT, such as synthetic technique,^{1–7} spinning technology,^{8–11} morphological structure and properties of fiber,^{12–17} and crystallization behaviors,^{18–22} have been widely investigated. Many studies have been made on PTT to understand the relationships between structure and property as well as to find applications. In comparison with poly(ethylene terephthalate) (PET), which is widely used as synthetic fibers, PTT fiber overcomes the strong rigidity,²³ poor dyeability²⁴ and slow crystallization behaviors²⁵ because of its chemical structure, i.e., three methylene flexible segments per repeating unit. On the other hand, it is also noted that PTT is inferior to PET in thermal stability.²⁶

Copolymerization is commonly an important technique to make better the polymers because it may mold their components advantageous properties to-

gether into one polymer system and thereby improve their disadvantageous properties. Lee et al.²⁷ first reported the nonisothermal crystallization characteristic of the poly(ethylene-*co*-trimethylene terephthalate) (PETT) from the *trans*-esterification of dimethyl terephthalate (DMT) with ethylene glycol (EG) and trimethylene glycol (TG). Wu and Lin²⁵ investigated systematically the crystallization behavior and morphology of PETT, and found the relationship between crystallization behavior and components of the copolymers.

It is well known that thermal property is very important to the processability of the polymer materials. In 2000, thermal properties of PTT was studied in detail by Wang et al.²⁶ using thermogravimetric analysis, and subsequently Son et al.²⁸ investigated the thermal properties of PTT/PET blends by differential scanning calorimetry (DSC). However, to the best of our knowledge, there is no report involving the thermal stability of PETT to date.

In this study, we report the thermal property of PETT with different content of TG units. PETT samples were synthesized by the polycondensation of terephthalate (TPA) with EG and TG, and the chemical compositions of the copolymers were determined by ¹H nuclear magnetic resonance (¹H-NMR) spectra. The thermostability of PETT under nitrogen was studied by the aid of thermogravimetry analyzer (TGA), and the thermal decomposition kinetic parameters were calculated by Ozawa technique.

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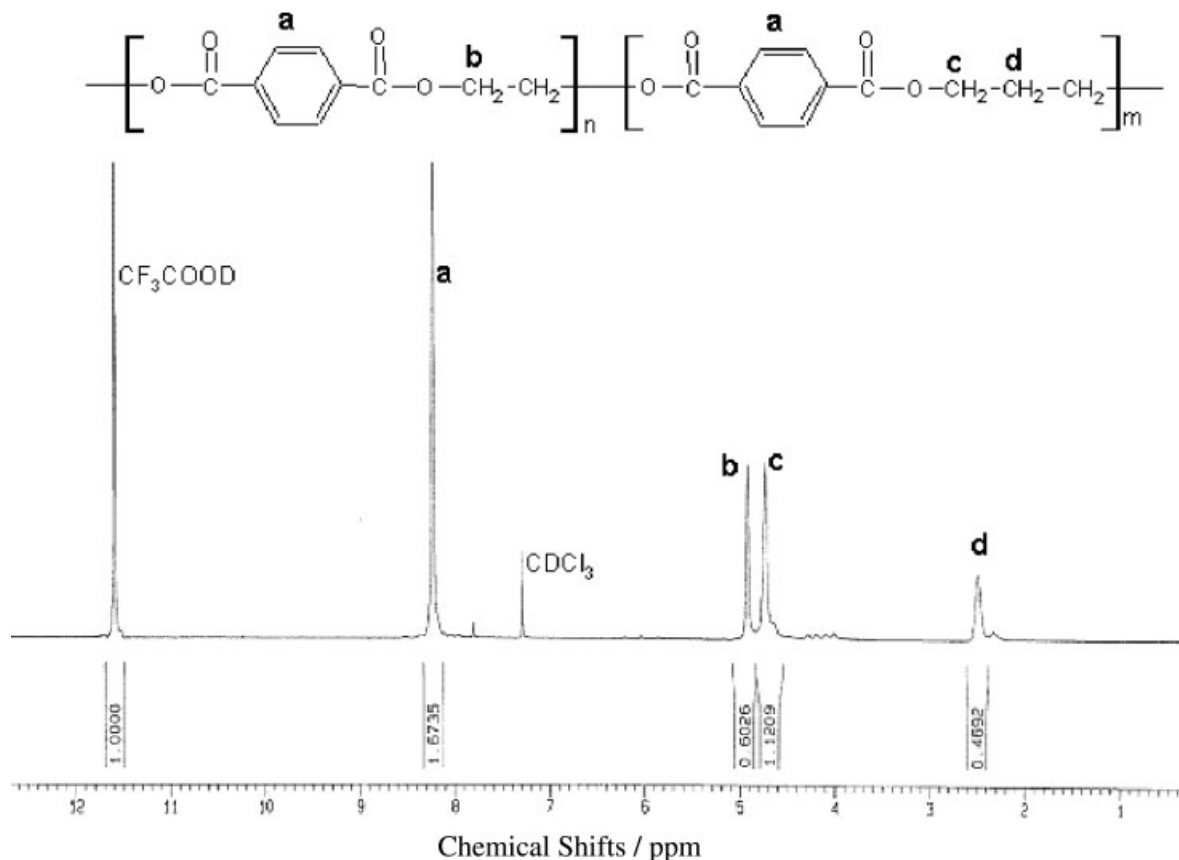


Figure 1 $^1\text{H-NMR}$ spectrum of the PETT50 copolymer dissolved in a mixed solvent at 300 MHz.

EXPERIMENTAL

Materials and polymerization

PET was kindly supplied by Yizheng Chemical Fibers Co., China. PTT and PETT samples were synthesized from the direct esterification of various ratios of EG (Yangzi Petrochemical, China) and TG (Shell, USA) with respect to TPA (Yizheng Chemical Fibers Co., China).

60 mol mixed diol (EG and TG), 30 mol PTA and 0.0075 mol antimony triacetate (Yizheng Chemical Fibers Co.) were put into a 20 L reactor vessel. The reactor was pressurized to 0.1 Mpa with nitrogen and heated to a temperature of 220°C. The direct esterification reaction was finished when the esterification rate was above 98%, calculated according to the amount of the water distilled off. Then, the prescribed amounts of tetrabutyl titanate (Shanghai Chemical Reagents, China) and triphenyl phosphate (Shanghai Chemical Reagents) were added, and the mixture was subjected to polycondensation. The temperature was increased from 220 to 270°C, and the diol (i.e., EG and TG) was distilled off under reduced pressure. The molecular weight of the polymer is approximately proportional to the torque of the stirring under the same reaction conditions such as final temperature,

vacuum and stirring rate. Therefore, the molecular weight of the polymer can be controlled with a prescribed final stirring torque. The chemical compositions of these copolyesters were determined by $^1\text{H-NMR}$ spectra.

Characterization

The intrinsic viscosity (IV) of PETT was measured in 1,1,2,2-tetrachloroethane/phenol (2 : 3 (w/w)) at $(25 \pm 0.1)^\circ\text{C}$ using an Ubbelohde viscometer. $^1\text{H-NMR}$ spectra were obtained on a Bruker ASPECT-300 instrument with a mixture of CF_3COOD and CDCl_3 (3 : 1 in volume) as the solvent.

Molecular weight were determined by Waters Alliance GPCV2000 gel permeation chromatography (GPC) using a 2690 pump, a differential refractometer detector, and two Waters GPC columns (7.5 mm ID, and 300 mm length). The PET or PETT sample (10 mg) was first dissolved in 1 mL of 2-chlorophenol at 100°C, and then diluted by CHCl_3 (9 mL). After filtered, 300 μL of the solution was injected. CHCl_3 was used as the eluent at a flow rate of 1.0 mL/min at 40°C. All molecular weights are reported relative to the calibration with polystyrene standard.

TABLE I
Composition and Intrinsic Viscosity for the Polymers

Polymer	Feed ratio of diols in the polymerization (TG mol %)	Composition in the polymer (TG mol %) ^a	IV (dL/g) ^b	M_w (g/mol) ^c
PET	0	0	0.637	35,100
PETT10	10	19.58	0.655	60,600
PETT20	20	28.69	0.662	64,300
PETT30	30	41.45	0.687	68,400
PETT40	40	49.52	0.701	69,700
PETT50	50	65.04	0.719	73,400
PETT60	60	70.58	0.741	75,700
PETT70	70	82.09	0.765	78,200
PETT80	80	87.37	0.744	64,100
PETT90	90	94.42	0.766	73,100
PTT	100	100	0.771	76,200

^aCalculated according to ¹H NMR spectra.

^bMeasured by Ubbelohde viscometer.

^cThe weight-average molecular weight was determined by GPC.

Thermal analysis of polymer samples was conducted using thermogravimetry analyzer in a Perkin-Elmer model 7 thermal analyzer over a temperature

range from ambient to about 650°C under nitrogen atmosphere at the heating rate of 2.5, 5.0, 10.0, 20.0, and 40.0 K/min, respectively.

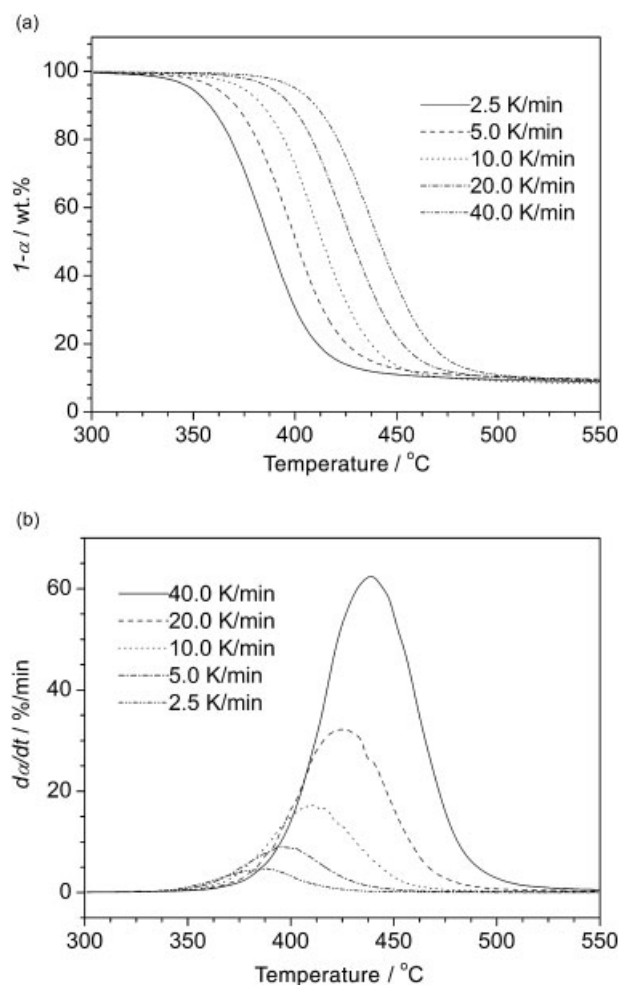


Figure 2 Dynamic (a) TGA and (b) DTG curves of PETT50 at various heating rates under nitrogen atmosphere.

RESULTS AND DISCUSSION

PETT and PTT samples were synthesized by the direct esterification method with various ratios of EG and TG with respect to TPA, and the chemical compositions of the polymers were determined by ¹H-NMR spectra. Figure 1 shows a typical ¹H-NMR spectrum for the PETT50 copolyester. This copolymer was characterized by 65.04 mol % TG units and 34.96 mol % EG units according to the integrations of its specific chemical shifts shown in Figure 1. The intrinsic viscosity and molecular weight were determined by an Ubbelohde viscometer and GPC, respectively. All the other polymers were characterized in the same manner. The results all listed in Table I. It can be clearly seen that

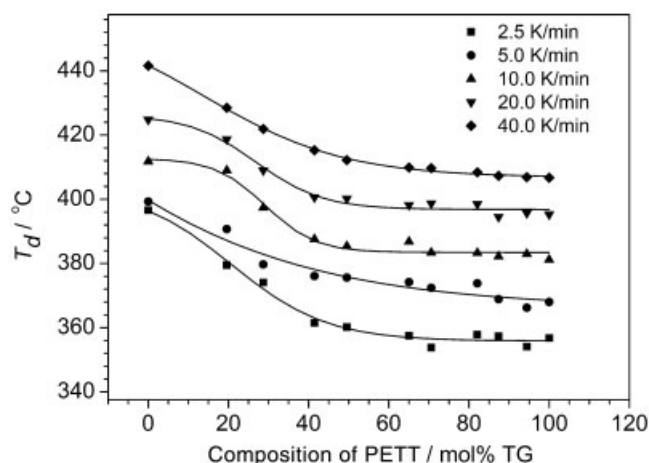


Figure 3 Effects of polyester composition and heating rate on decomposition temperature.

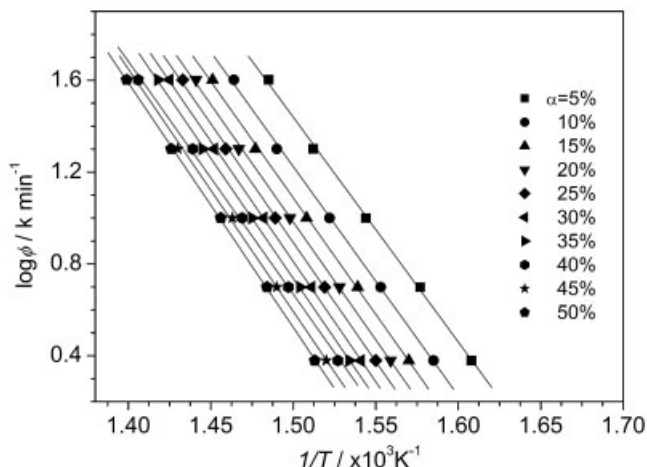


Figure 4 Plots of $\log \phi$ versus $1/T$ for PETT50 at various weight loss.

the amount of TG units incorporated into the polymer always exceeded that fed into the polymerization, which is consistent with those reported by Wu and Lin²⁵ and Lee et al.²⁷ The probable reasons are the relatively strong electronegative donating ability and the higher boiling point of TG than EG.

The polymer sample of 1.0 ± 0.1 mg was loaded into a platinum crucible, which was heated from ambient to about 650°C under nitrogen atmosphere at the heating rate of 2.5, 5.0, 10.0, 20.0, and 40.0 K/min, respectively. A typical TGA and differential thermogravimetry (DTG) traces for PETT50 at different heating rates are shown in Figure 2, and the onset degradation temperatures (T_d) of all the polymers at different heating rates are depicted in Figure 3. It is evident from Figure 2 and 3 that for the same polymer, as the heating rate increases, the degradation begins at a higher temperature and exhibits higher weight-loss rate; At the same heating rate, a greater TG concentration in the copolyesters would decrease the onset degradation temperature.

The thermal decomposition kinetics of the copolymer could be analyzed with the following kinetic equation:²⁹

$$\frac{d\alpha}{dt} = A \exp\left[\frac{-E}{RT}\right] (1 - \alpha)^n \quad (1)$$

where, α is the weight loss of the polymer undergoing degradation at time t , $d\alpha/dt$ denotes weight-loss rate, A is the frequency factor, n represents the decomposition reaction order, E stands for the activation energy of thermal decomposition, R is the gas constant, and T symbolizes the absolute temperature. For nonisothermal thermogravimetry, if the heating rate is ϕ , i.e. dT/dt , eq. (1) should be modified as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\phi} \exp\left[\frac{-E}{RT}\right] (1 - \alpha)^n \quad (2)$$

Ozawa technique³⁰ is a multiple heating-rate treatment method for TGA and DTG curves to obtain the kinetic parameters of thermal decomposition. The equation, which is from the integration of eq. (2), is as follows:

$$\log \phi = \log \frac{AE}{RF(\alpha)} - 2.315 - 0.4567 \frac{E}{RT} \quad (3)$$

where $F(\alpha) = \int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n}$. Therefore, from a plot of $\log \phi$ against $1/T$, the value of E could be determined from the slope. Figure 4 shows the typical plots for PETT50 at various weight loss (5–50%). Activation energy of the different polyester at various weight loss had been obtained according to Ozawa technique, the data listed in Table II. The results indicated that a somehow increasing trend of activation energy with the larger weight loss for the same polyester.

TABLE II
Dependence of Activation Energy (E) of the Polyesters Upon Weight Loss (α)

Polymer	E (kJ/mol)									
	$\alpha = 5\%$	$\alpha = 10\%$	$\alpha = 15\%$	$\alpha = 20\%$	$\alpha = 25\%$	$\alpha = 30\%$	$\alpha = 35\%$	$\alpha = 40\%$	$\alpha = 45\%$	$\alpha = 50\%$
PET	198.7	203.0	203.0	205.2	206.1	203.7	204.6	206.2	204.9	206.9
PETT10	192.0	197.6	200.6	204.4	206.6	208.0	208.9	208.0	208.0	209.4
PETT20	187.2	188.8	191.5	194.4	198.5	199.3	200.7	200.7	201.2	200.7
PETT30	184.7	187.7	190.5	192.5	194.7	196.7	198.1	200.2	200.2	201.7
PETT40	180.1	184.0	187.1	187.9	190.6	200.6	192.6	195.3	195.3	196.7
PETT50	178.2	181.7	184.7	186.6	186.6	190.6	190.6	184.7	192.3	192.3
PETT60	171.0	174.3	178.0	182.3	182.5	183.9	185.0	187.0	187.0	186.5
PETT70	174.4	181.6	182.9	184.7	186.0	188.0	188.6	193.1	189.9	190.6
PETT80	170.9	176.3	180.5	182.2	185.4	185.9	187.2	187.8	190.5	189.9
PETT90	173.4	178.5	182.2	181.7	185.9	187.1	189.0	189.8	190.5	192.5
PTT	174.2	179.9	183.5	186.6	186.7	188.6	189.3	192.5	191.2	191.8

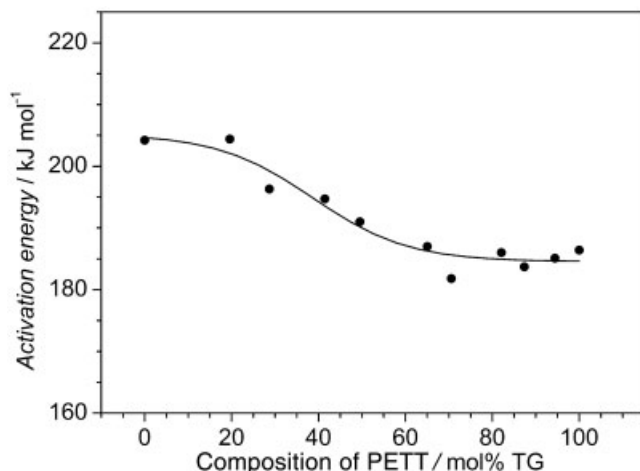
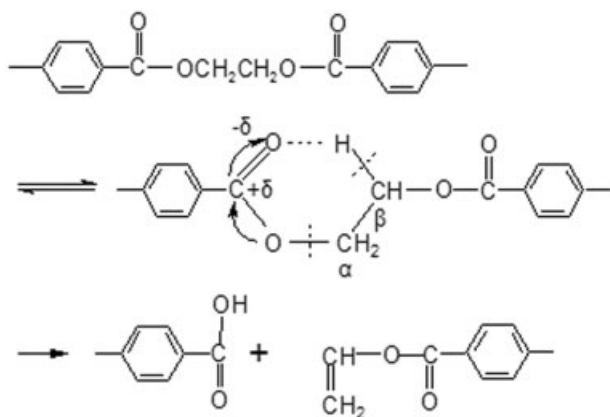


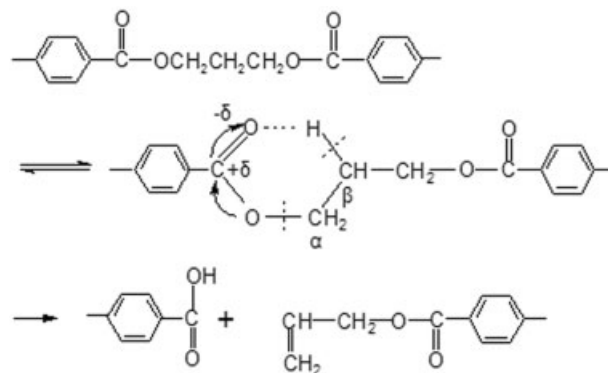
Figure 5 Dependence of average activation energy upon chemical composition of polyester.

The dependence of average activation energy upon chemical composition of polyester is depicted in Figure 5. It is obvious that the activation energy depends strongly on the content of the comonomer in PETT. As described in Figure 5, the average activation energy of the decomposition increases with the concentration of EG units in the polyester, which characterizes the improvement of thermostability with increase in the content of EG units in the copolyester.

Regarding the degradation mechanism of the polyester, Pohl³¹ and Day et al.³² proposed that it should involve considerable main chain cracking at the weak O—CH₂ bonds via a cyclic intramolecular rearrangement (Scheme 1). The chemical structure of PTT, which contains three methylene flexible segments per repeating unit, is similar to that of PET, which has two methylene moieties per repeating unit. The similar reaction may occur in PTT system (Scheme 2). The thermal behavior of the copolyester shows the strong dependence on the chemical composition, such as the



Scheme 1 Proposed mechanism of PET pyrolysis.



Scheme 2 Probable mechanism of PTT pyrolysis.

onset degradation temperature (Fig. 3) and average activation energy (Fig. 5), probably because the presence of one more methylene of TG unit than of EG, which is relatively strong electronegative to promote the homolysis of the weak O—CH₂ bond.

In addition, it is also noted that the yield of solid residue increases with the concentration of EG units in the polymer chain at any heating rate (Figs. 6 and 7). The cause for the phenomenon may be associated with the content of aromatic hydrogen of polymer chain. Lewis³³ and Yang et al.³⁴ believed that the chemical composition plays an important role in the carbonization behavior. For PETT, the more the aryl ring, the more stability, which leads to the more carbonization residue.

CONCLUSIONS

PETT and PTT samples were synthesized by the direct-esterification method with various ratios of EG and TG with respect to TPA. The chemical compositions, intrinsic viscosity, and molecular weight were

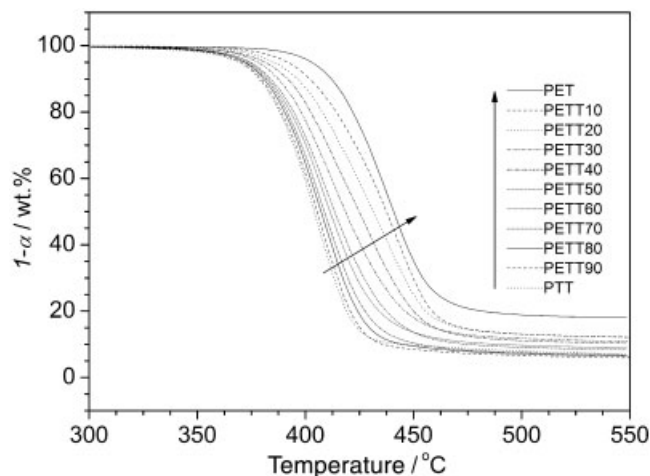


Figure 6 TG curves for the polyesters at the heating rate of 10.0 K/min.

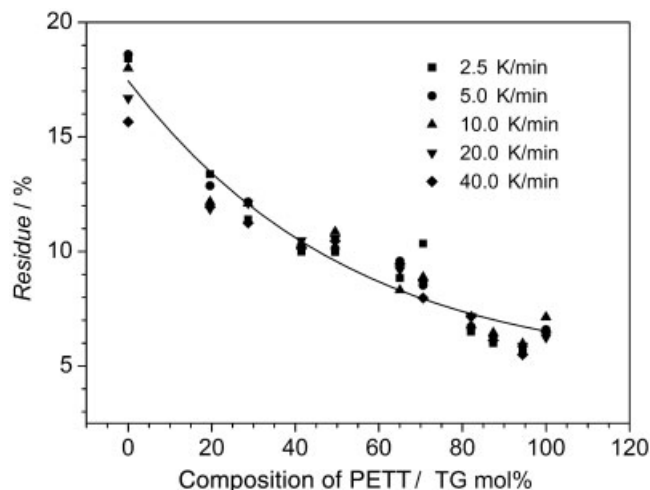


Figure 7 Effects of polyester composition on carbonization residue at 550°C.

determined. The thermal stability of PETT was studied under nitrogen atmosphere at the heating rate of 2.5, 5.0, 10.0, 20.0, and 40.0 K/min, respectively. The activation energy of thermal decomposition was calculated according to Ozawa technique. The results showed that the thermal behavior of the copolyester had a strong dependence on the chemical composition. The average activation energy of the decomposition increases with the concentration of EG units in the polyester, and a greater TG concentration in the copolyesters would decrease the onset degradation temperature. These phenomena may be attributed to the presence of one more methylene of TG unit than of EG in the copolymer. It is also noted that the yield of solid residue increases with the concentration of EG units in the polymer chain at any heating rate, which may be associated with the content of aromatic ring in the polymer chain. To our knowledge, this is the first to report the thermal stability of PETT by the aid of TGA.

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