Composition dependence of thermal properties of poly(trimethylene-co-ethylene terephthalate)

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Recently, poly(trimethylene terephthalate) (PTT) has been introduced to the same family of polyesters as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) [1]. Owing to its outstanding characteristics such as high elastic recovery, chemical resistance and resilience [2, 3], PTT has attracted increasing attention. Like PET and PBT, the applicability and processing condition of PTT are determined by its thermal properties, such as crystallization, melting, etc. Much work has concentrated on this topic recently [4–7]. Moreover, copolymerization using several amounts of a second glycol or diacid comonomer is an approach frequently used to attain new linear thermoplastic polyesters with modified thermal properties. But to our knowledge, the detailed study of thermal properties of poly(trimethylene-co-ethylene terephthalate) (PTET) has not been reported in spite of its potential industrial and academic values. In this study, copolyesters based on different molar ratios of polytrimethylene terephthalate to polyethylene terephthalate have been synthesized. The effects of the copolyester composition on thermal properties have been discussed herein. The crystallization was examined by Wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC), and glass transition temperatures (T_g) were explored by DSC.

Different molar ratios of 1,3-propanediol (1,3-PDO) to ethylene glycol (EG) and equivalence of terephthalic acid were mechanically stirred and the mixture was kept in the range of 453–513 K catalyzed by tetrabutyl titanate for 3 hr; then the mixture was heated up to 543 K and kept for 3.5 hr with reduced pressure so that polyesters with different molar ratios of PTT to PET could be prepared. The ratio of 1,3-PDO to EG will be used to denote the copolyesters, e.g., PTET100/0 and PTET0/100 are used to refer to PTT and PET homopolymers, respectively. The intrinsic viscosities of them measured in the solution of 1:1 (w/w) 1,1,2,2-tetrachloroethane/phenol at 298 K, are in the range of 0.0677–0.0823 m^3/kg.

Compositions of the copolyesters synthesized were analyzed by ^{1}H NMR spectrometry (Bruker AM 500). The samples were dissolved in a mixture of $CDCl_3/CF_3COOD$. Tetramethylsilane was used as an internal standard.

DSC experiments were performed on a Perkin–Elmer Pyris 1 instrument calibrated with In and Pb. Samples were heated at 50 K above their respective melting temperatures (PTET43/57 was heated at 543 K) for 3 min, then cooled by liquid nitrogen to 273 K. The second heating and cooling runs were recorded and the scanning rates were mentioned in the specified circumstances.

The specimens for WAXD measurements were prepared by melt pressing with the thickness of 300 μ. The melts were cooled rapidly to 403 K and crystallized at that temperature for 1 hr, then cooled to room temperature. WAXD measurements were carried out with a Rigaku D/max-ra diffractometer using graphite monochromatized Cu K_α radiation ($\lambda = 0.1542$ nm; 40 kV; 80 mA; 2 kcps).

For a series of PTET copolyesters synthesized, chemical compositions were determined by ^{1}H NMR spectroscopy. As shown in Fig. 1, the molar ratio of the 1,3-PDO and EG units on the polymer backbone was estimated from integrations of their specific chemical shifts. The results are summarized in Table I. Table I also lists the number average molecular weights ($\bar{M}_n$'s) of the copolyesters which are calculated from the measured intrinsic viscosities using the Mark–Hauwink equation with constants a and k determined previously for PTT homopolymer [8]. As PET homopolymer has different values of constants a and k, the calculated $\bar{M}_n$'s of the copolyesters can only be deemed to estimated values. However, it seems that all the copolyesters were synthesized in reasonably high molecular weight.

Fig. 2 illustrates WAXD patterns of the copolyesters crystallized from melt. It is easily seen that the PTET copolyesters with PET less than 57% show crystalline peaks. The relevant crystalline positions (2θ) remain the same, taking after those of PTT homopolymer. As a consequence, we can infer that the crystals come from PTT homopolymer. In present work, PTET with PET no more than 57% were denoted to PTT copolyesters, PET copolyesters refer to those with PET more than 57%. The copolyester with 57% PET becomes amorphous. The result confirms that the PTT copolyester becomes less crystallizable with involvement of PET. On the contrary, for PET copolyesters the crystalline

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TABLE I Compositions, intrinsic viscosities and number average molecular weights of PTET copolyesters

Sample designation	Feed ratio[a] (1,3-PDO/EG)	Copolyester composition[b] (1,3-PDO/EG)	η (m^3/kg)	$\bar{M}_n^c$
PTET0/100	0/100	0/100	0.0602	35 390
PTET13/87	10/90	13.2/86.8	0.0679	42 840
PTET22/78	20/80	22.1/77.9	0.0565	26 860
PTET33/67	30/70	32.6/67.4	0.0726	47 640
PTET43/57	40/60	43.1/56.9	0.0677	42 640
PTET55/45	50/50	55.4/44.6	0.0770	52 300
PTET62/38	60/40	62.3/37.7	0.0803	55 900
PTET71/29	70/30	71.3/28.7	0.0781	53 500
PTET83/17	80/20	82.8/17.2	0.0807	56 350
PTET90/10	90/10	90.5/9.5	0.0801	55 690
PTET100/0	100/0	100/0	0.0823	58 130

[a] Molar ratio of 1,3-PDO and EG fed in the polymerization.
[b] Measured by ^{1}H NMR spectroscopy.
[c] Estimated from the measured intrinsic viscosities.

diffraction peaks match those of the PET crystal structure, indicating that the crystalline phase present is that of PET homopolymer. Similarly, we found PET copolyester became less crystallizable with the involvement of PTT.

Similar results have been given by DSC, however a nonuniform conclusion is reached because of the difference between the two characterization methods. Fig. 3 presents examples of DSC diagrams of the copolyesters. PTET22/78 revealed no crystallization exotherms at heating or cooling rate of 10 K/min, though its WAXD pattern exhibited crystallization peaks in Fig. 2. However, when the cooling rate was reduced to 3 K/min, PTET22/78 showed a very weak crystallization exotherm.

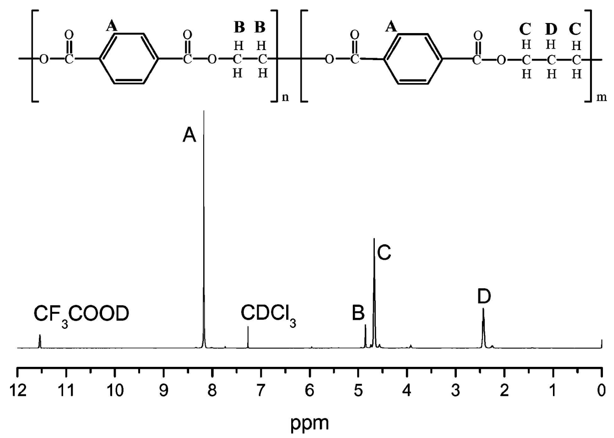

Figure 1 ^{1}H NMR spectroscopy of PTET22/78 dissolved in a mixture of CDCl$_3$ and CF$_3$COOD.

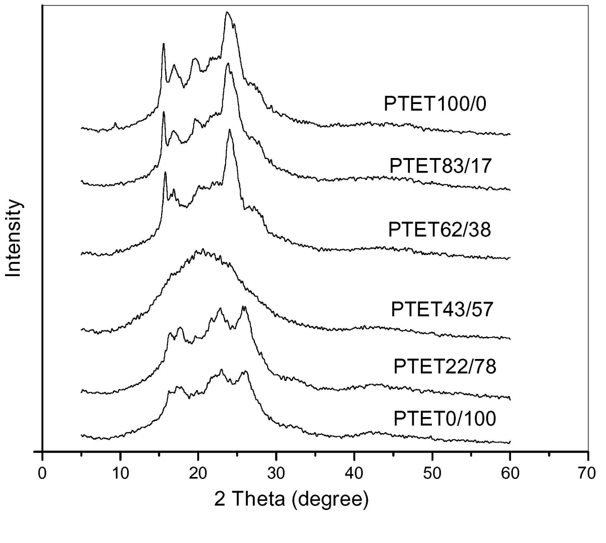

Figure 2 WAXD patterns for PTET copolyesters.

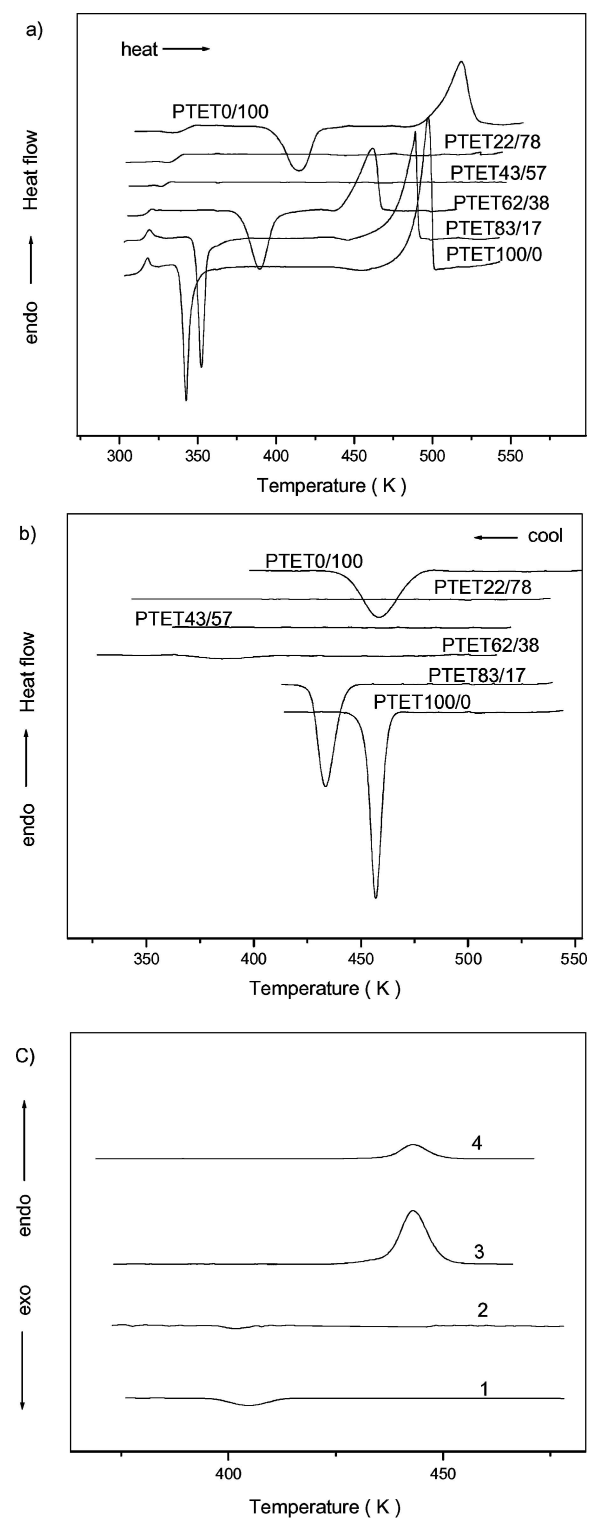

Figure 3 DSC thermograms of PTET copolyesters: (a) heating and (b) cooling rates are 10 K/min, (c) indicates slow heating and cooling runs of PTET 22/78. Runs 1 and 2 show DSC thermograms during cooling at the rate of 3 and 5 K/min, respectively. Runs 3 and 4 represent DSC thermograms during heating at the rate of 5 K/min, following 1 and 2, runs respectively).

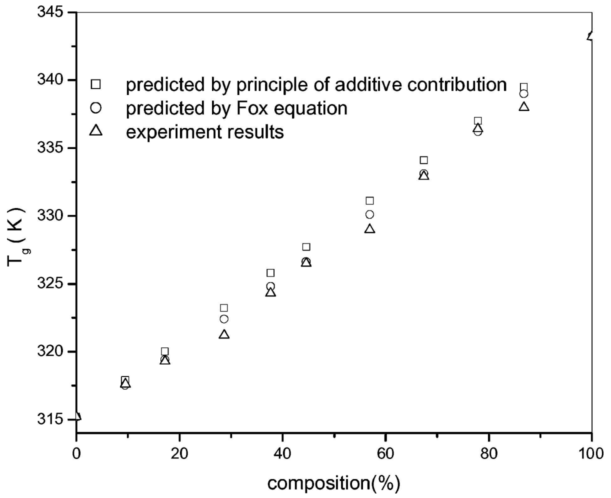

Figure 4 Correlation between T_g and the composition of PET.

When heated at a rate of 5 K/min, melting processes were detected for PTET22/78, even when it had been crystallized at a cooling rate higher than 3 K/min (e.g., 5 K/min as shown in Fig. 3c). Here it is proposed that during relatively slow heating, molecular motions result in rearrangement so that the crystals may be produced.

T_c and ΔH_c are crystallization temperature and heat of crystallization during cooling runs. T_m and ΔH_m refer to melting temperature and heat of fusion during heating runs. For PTT coplyesters, both T_c and T_m decrease with increasing the composition of PET. This suggests that the crystals grow imperfectly, as the composition of PET increases. Meanwhile, both ΔH_c and ΔH_m decrease when the composition of PET is up. As for PET copolyesters, the crystals grow more imperfectly when the composition of PTT increases.

It is a fact that PET shows higher glass transition temperature compared to that of PTT, due to less flexibility of the PET chain. Fig. 4 shows dependence of glass transition temperature on the composition of PET. Both the additive principle [9] and the Fox equation [10] can predict the relation between T_g and the composition, however, the Fox equation is better to describe the effect of PET content on T_g. The glass transition temperature of the copolyesters increases with the composition of PET.

Usually, the copolymer crystallization behavior was investigated with a copolymer content lower than 20% [11–14]. In present work, although the PTT copolyesters had high PET contents, their crystallization was still observed. The reason could be attributed to the similar chemical structures of 1,3-PDO and EG. However, the results presented in this study proved that only one type of unit is able to crystallize in PTET coplyesters. Detailed studies of crystallization and melting behavior of crystallizable PTET copolyesters are in progress and will be published shortly.

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