

Thermal Behavior of Poly(trimethylene-co-ethylene terephthalate)

Yong XU, Sheng Rong YE*, Jin Wen QIAN

Institute of Polymer Science, Zhejiang University, Hangzhou 310027

Abstract: Poly (trimethylene-co-ethylene terephthalate) with various compositions of diol has been synthesized. The crystallization of copolyesters with high comonomer content was observed by both wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC). It was found that the copolyesters become less crystallizable with the involvement of the comonomer, the crystals of crystallizable copolyesters come from PTT or PET homopolymers. The glass transition temperature (T_g) of the copolyester increases with increasing PET component in the copolyester, and the relationship between T_g and composition obey both Fox equation and additive law, the former is better in describing this relationship.

Keywords: Copolyester, polytrimethylene terephthalate, polyethylene terephthalate, thermal behavior.

Since the development for fibers and engineering thermoplastics in the 1990s¹, polytrimethylene terephthalate (PTT) has attracted much attention owing to its outstanding characteristics, such as high elastic recovery, chemical resistance and resilience^{2,3}. Like polyethylene terephthalate (PET) and polybutylene terephthalate (PBT), the applicability and processing condition of PTT are determined by its thermal behavior, such as crystallization, melting, *etc.*. Much work has been concentrated on this topic⁴⁻⁷. Moreover, copolymerization using several amounts of a second glycol or diacid comonomer usually is an approach for attaining new linear thermoplastic polyesters with modified thermal properties. But to our knowledge, the study of thermal behavior of poly(trimethylene-co-ethylene terephthalate) (PTET) rich with 1,3-propanediol (1,3 PDO) unit has not been reported in spite of its potential academic and industrial 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 behavior have been discussed herein. The crystallization was examined by WAXD and DSC, and the glass transition temperatures (T_g) were determined by DSC.

Experimental

Different molar ratios of 1,3 PDO to ethylene glycol (EG) and equivalence of terephthalic acid were mechanically stirred and the mixture was kept in the temperature

* E-mail: yeshr@zju.edu.cn

range of 180–240 °C catalyzed by tetrabutyl titanate for 3 h, then the mixture was heated up to 270 °C and kept for 3.5 h 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 (the number before the slash is the molar fraction of PTT content in the copolyesters; the number after the slash is the molar fraction of PET content in the copolyesters) are used to refer to PTT and PET homopolymers, respectively. The intrinsic viscosities of PTET measured in the solution of 1:1 (w/w) 1,1,2,2-tetrachloroethane/phenol at 25 °C, are in the range of 0.677–0.823 dl/g.

DSC experiments were performed on a Perkin–Elmer Pyris 1 instrument calibrated with In and Pb. The samples were heated at 50°C (above their respective melting temperatures, PTET40/60 were heated at 270 °C) for 3 min, then cooled by liquid nitrogen to 0°C. The second heating and cooling runs were recorded and the scanning rates were mentioned in the specified circumstances.

The specimens with the thickness of 300 µm for WAXD measurements were prepared by melt pressing. The melts were cooled rapidly to 130°C and crystallized at that temperature for 60 min, 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 K cps).

Results and Discussion

Figure 1 illustrates WAXD patterns of the copolyesters crystallized from melt. It is easily seen that the PTET copolyesters with PET less than 60% show crystalline peaks. The relevant crystalline positions (2θ) remain the same, taking after those of PTT homopolymer. So we can infer that the crystals come from PTT homopolymer. In the present work, PTET with PET no more than 60% were denoted to PTT copolyesters, PET copolyesters refer to those with PET more than 60%. The copolyester with 60% PET become amorphous. The result confirms that the PTT copolyester becomes less crystallizable with involvement of PET. On the contrary, for PET copolyesters the crystalline diffraction peaks match with those of the PET crystal structure, indicating that the present crystalline phase is that of PET homopolymer. Similarly, we found PET copolyester becomes less crystallizable with involvement of PTT.

Similar results have been given by DSC, however a non-uniform conclusion is reached because of the difference between the two characterization methods. **Figure 2** presents examples of DSC diagrams of the copolyesters. PTET20/80 revealed no crystallization exotherms at heating or cooling rate of 10°C/min, though its WAXD pattern exhibited crystallization peaks in **Figure 1**. However, when the cooling rate was reduced to 3 °C/min, PTET20/80 showed a very weak crystallization exotherm.

When heated at a rate of 5 °C/min, melting processes were detected for PTET20/80, even when it had been crystallized at a cooling rate higher than 3 °C/min (*e.g.* 5 °C/min as shown in **Figure 2c**). Here it is proposed that during relatively slow heating, molecular motions result in rearrangement so that the crystals may be produced.

Figure 1 WAXD patterns for PTET copolyesters

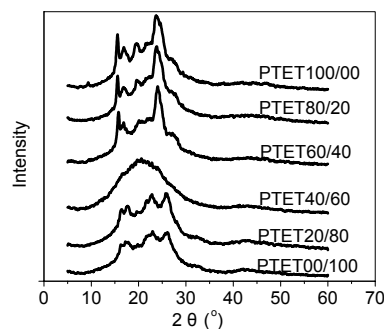
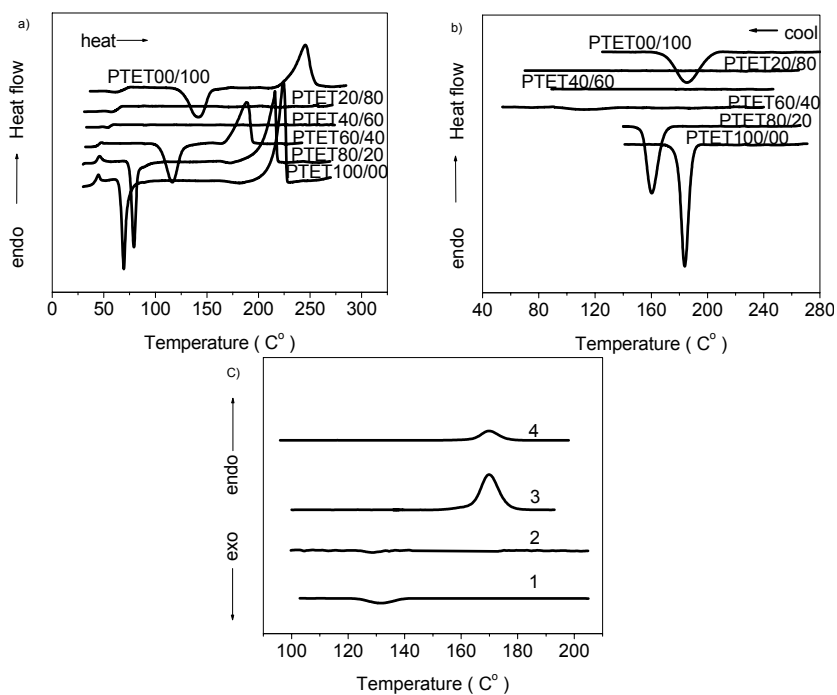
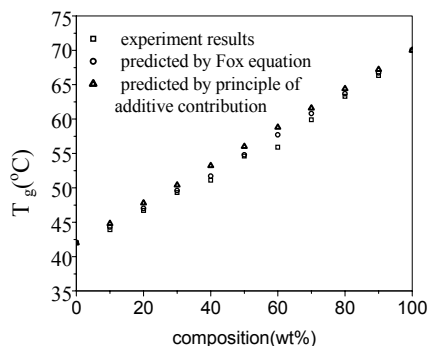


Figure 2 DSC thermograms of PTET copolyesters



(a) heating and (b) cooling rates are 10 °C/min, (c) indicates slow heating and cooling runs of PTET 20/80(1 and 2 runs show DSC thermograms during cooling at the rate of 3 and 5 °C/min, respectively. 3 and 4 runs represent DSC thermograms during heating at the rate of 5 °C/min, following 1 and 2 runs, respectively.)

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 copolyesters, both T_c and T_m decrease with increasing the composition of PET. This suggested that the crystals grow imperfectly, as the composition of PET increases. Meanwhile, both ΔH_c and ΔH_m decrease when the composition of PET increases. As for PET copolyesters, the crystals grow more imperfectly when the composition of PTT increases.

Figure 3 Correlation between T_g and the composition of PET.

It is the case that PET shows higher glass transition temperature, compared with that of PTT, due to less flexibility of the PET chain. **Figure 3** shows dependence of glass transition temperature on the composition of PET. Both the additive principle⁸ and the Fox equation⁹ 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 . T_g of the copolyesters increases with the composition of PET.

Usually, the copolymer crystallization behavior was investigated with a copolymer content lower than 20 %¹⁰⁻¹³. In the 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 copolyesters. Detailed studies of crystallization and melting behavior of crystallizable PTET copolyesters are in progress and will be published shortly.

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