LETTER

Synthesis and crystallization behavior of poly(trimethylene terephthalate)–poly(ethylene glycol) segmented copolyesters

Yong Xu · Hong-Bing Jia · Sheng-Rong Ye · Jian Huang

Poly(trimethylene terephthalate) (PTT) is a relatively new linear aromatic polyester and has drawn more and more attention due to its outstanding characteristics such as high elastic recovery, chemical resistance and resilience[1–3]. As a typical semicrystalline polymeric material, the applicability and processing condition of PTT are determined by its thermal properties and crystallization behavior. Thus, many studies have focused on this topic [4–7]. In our previous work, the kinetics analysis of PTT crystallization including the secondary crystallization process was carried out by using a new mathematical model [7]. Furthermore, to improve the properties of polyester material, copolymerization using several amounts of a second glycol or diacid comonomer is an effective approach to attain new linear thermoplastic polyesters with modified thermal properties. Recently the authors reported investigations about the composition dependence of thermal properties of poly (trimethylene-co-ethylene terephthalate) and poly (trimethylene isophthalate-co-terephthalate) [8, 9]. However, so far there's been little reported on the modification of the thermal properties of PTT, which is copolymerized with a polyglycol to form a segmented copolyester in spite of its potential industrial and academic values. It was reported that the thermal properties of Poly(ethylene terephthalate)(PET) could be remarkably changed by copolymerization with poly(ethylene glycol)(PEG) and the copolyesters have been developed commercially as important thermolplastic co-poly(ether-ester) elastomers [10]. In this work, PTT-PEG segmented copolyesters with various PEG content and molecular weight were synthesized and the effects of the copolyester composition on crystallization behavior have been discussed herein. To our knowledge, it is the first time that the thermal properties of PTT-PEG segmented copolyesters (PTEG) has been presented.

The esterification of terephthalic acid (TPA) (166.13 g, 1.0 mol) with 1,3 propanediol (1,3 PDO) (106.53 g, 1.4 mol) in the presence of tetrabutyl titanate as a catalyst was performed in a four-necked round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a distillation column. The mixture of TPA, 1,3 PDO, and the catalyst was continuously stirred and kept in the range of 453–513 K for 3 h, then various amount of PEG2000 and PEG4000 (PEG with number-average molecular weight, $\overline{M}_n$s of 2000 and 4000, respectively) was added into the reaction mixture and mechanically stirred for 0.5 h. After esterification, mixtures were heated up to 543 K and kept for 3.5 h for polycondensation with reduced pressure and thus copolyesters with various PEG content could be prepared. The composition of the copolymers is denoted to PTEGa-b/c, in which 'a' is the starting PEG molecular weight, 'b', the weight percentage of PTT hard segments, 'c', the weight percentage of PEG soft segments. 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 0.0806–0.0835 m^3/kg. Compositions of the copolyesters synthesized were analyzed by ^{13}C-NMR spectrometry (Bruker AM 500). The samples were dissolved in a mixture of $CDCl_3$/CF_3COOD. Tetramethylsilane was used as an internal reference.

Y. Xu (✉) · H.-B. Jia
Department of Polymer Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, P.R. China
e-mail: xuyong@zuaa.zju.edu.cn

Y. Xu · S.-R. Ye
Institute of Polymer Science, Zhejiang University, Hangzhou 310027, P.R. China

J. Huang
Department of Chemistry, University of Texas at San Antonio, San Antonio, TX 78249-1644, USA

DSC measurements were performed on a Perkin Elmer DSC-7 instrument with samples about 5 mg. Temperature calibration was carried out using In, Pb and Zn standards. The specimens for WAXD measurements were prepared by melt pressing with the thickness of 300 μm. The melts were cooled rapidly to 403 K and crystallized at that temperature for 1 h, then cooled to room temperature (Another sample of PTEG2000-72.22/27.78 was cooled by liquid nitrogen from melt and vacuum dried, then the glassy film was heated rapidly to 308 K and crystallized at that temperature for 1 h). WAXD measurements were carried out with a Rigaku D/max-ra diffractometer using graphite monochromatized Cu K_{α} radiation (λ = 0.1542 nm; 40 kV; 80 mA; 2 K cps).

The depolarized light intensity (DLI) technique was used to follow the crystallization of samples. In the present work isothermal crystallization was carried out with a JJY-1A Instrument (designed by Institute of Chemistry, Chinese Academy of Science). The sample that had been made into thin film (thickness of about 150 μm) between two glass cover slips, was first heated at 553 K for 100 s in the melting oven and then immediately shot into the crystallization bath whose temperature (T_c) had already been selected. The intensity of depolarized transmittance I_t which was proportional to the fraction of crystal phase formed at time t, was recorded during the crystallization process. The relative crystallinity X_t can be expressed as:

$$X_t = (I_t - I_0)/(I_\infty - I_0) \tag{1}$$

where I_0, I_∞ are the intensity values of depolarized light before and after the crystallization transformation, respectively.

The chemical compositions of a series of PTEG copolyesters were determined by ^{13}C NMR spectroscopy. As shown in Fig. 1, the molar ratio of the 1,3 PDO, PEG and TPA units on the polymer backbone was calculated from integrations of their specific chemical shifts. The results are summarized in Table 1. The detailed sequence-length distributions of trimethylene and PEG sequences and randomness in the copolymers will be reported in another paper. Table 1 also listed the number average molecular weights ($\overline{M}_n$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 [11]. Because PEG homopolymer has different values of constants a and k, the calculated $\overline{M}_n$s of the copolyesters can only be deemed to estimated values. However, it seems that all the copolyesters were synthesized with reasonably high molecular weight.

Furthermore, the composition data in Table 1 indicates that almost all the PEG fed in the polymerization come into
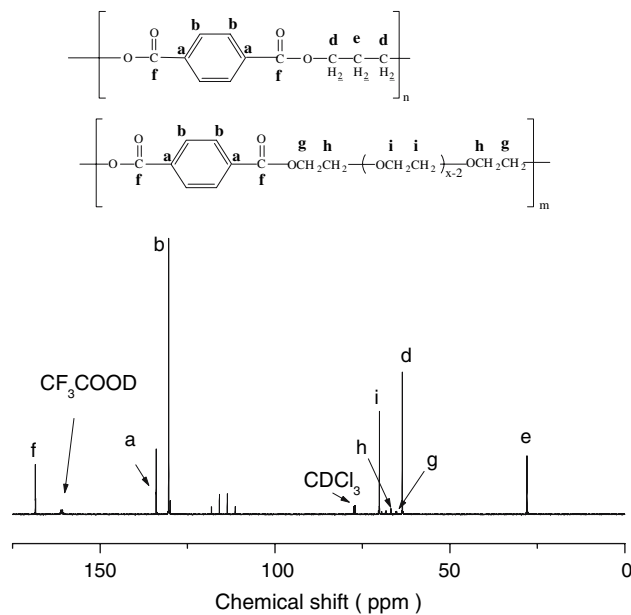

Fig 1 ^{13}C-NMR spectrum and chemical shifts assignment of PTEG2000-88.76/11.24

the resultant polymer, while the amount of 1,3 PDO unit incorporated into the resultant polymers is obviously smaller than that fed in the bulk polymerization. This should be attributed to the volatilization of the excessive 1,3 PDO during the polymerization process. 1,3 PDO is gaseous (the boiling point of 1,3 PDO is 487 K at atmospheric pressure) at the aforementioned polymerization condition and will escape at reduced pressure during the polycondensation, however, the PEG is in the melt state and will be almost totally incorporated into the copolymers finally.

The identification of the crystalline structure of the copolyesters was performed by using the wide-angle X-ray diffractometry technique. The diffraction curves for several PTEG copolyesters and neat PTT are reported in Fig. 2. It can be seen that all the PTEG copolyesters show crystalline peaks and the relevant crystalline positions (2 *Theta*) remain the same, taking after those of PTT homopolymer. As a consequence, we can infer that all the copolyesters are crystallizable and the crystals come from PTT homopolymer. Figure 3 illustrates WAXD patterns of copolyester with high PEG2000 content (PTEG2000-72.22/27.78) which has been annealed for 1 h from glassy state at the temperature of 308 K. It is easily seen that only an amorphous halo could be detected. However, it has been concluded that 308 K is very suitable for the molecular chains of PEG2000 to crystallize [12]. So here it is proposed that PEG2000 is not able to crystallize or co- crystallize with PTT in the PTEG copolyesters when the PEG2000 content is lower than 30 wt%.

Table 1 Compositions, intrinsic viscosities and number average molecular weights of PTEG copolyesters

Sample designation	Feed ratio[a] (1,3 PDO/PEG/TPA)	Copolyester composition[b] (1,3 PDO/PEG/TPA)	Mass fraction of PEG in copolyester (%)	$[\eta]$ (m^3/kg)	$\overline{M}_n$[c]
neat PTT	1.4/0/1	1.4/0/1	0	0.0823	58130
PTEG2000-97.39/2.61	1.4/0.00345/1	0.99702/ 0.00324/1	2.61	0.0831	59030
PTEG2000-94.54/5.46	1.4/ 0.00720/1	0.99346/ 0.00698/1	5.46	0.0806	56240
PTEG2000-91.64/8.36	1.4/0.01135/1	0.98943/0.01101/1	8.36	0.0822	58020
PTEG2000-88.76/11.24	1.4/ 0.01580/1	0.98602/ 0.01526/1	11.24	0.0835	59480
PTEG2000-82.22/17.78	1.4/0.02625/1	0.97445/ 0.02597/1	17.78	0.0820	57800
PTEG2000-72.22/27.78	1.4/0.04620/1	0.95567/0.04597/1	27.78	0.0819	57680
PTEG4000-82.24/17.76	1.4/0.01313/1	0.98719/0.01302/1	17.76	0.0807	56350

[a] Molar ratio of 1,3 PDO, PEG and TPA fed in the polymerization

[b] Measured by ^{13}C NMR spectroscopy

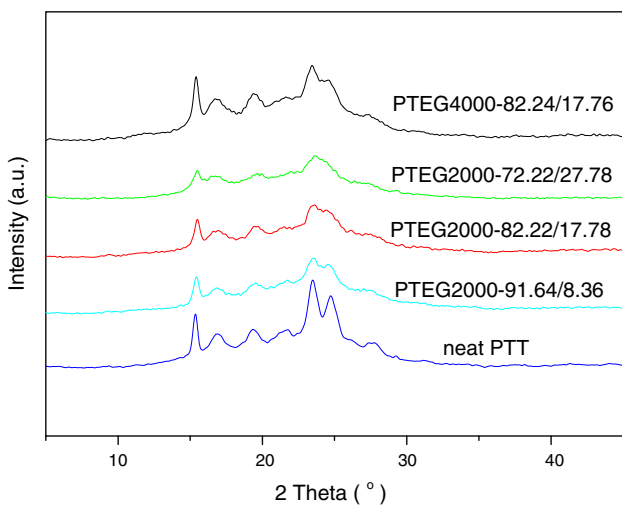[c] Estimated from the measured intrinsic viscosities

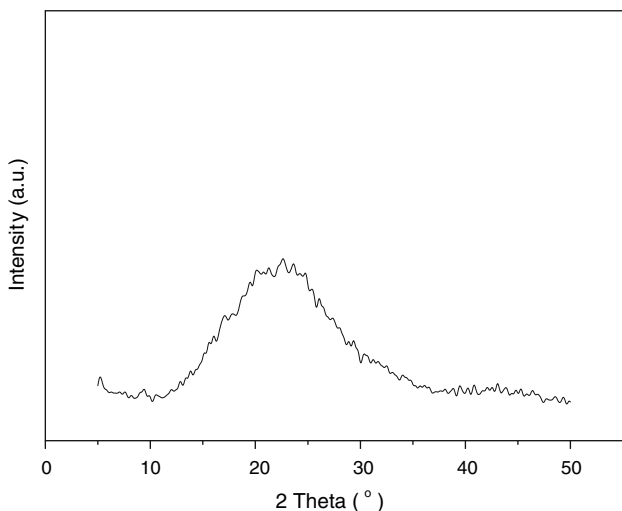**Fig 2** WAXD patterns of PTEG copolyesters

Fig 3 WAXD patterns of PTEG2000-72.22/27.78, the sample was crystallized at 308 K for 1 h from glassy state

Moreover, the degree of crystallinity decreases with the increasing PEG content and the amorphous portion of the patterns regularly grows. The result confirms that the PTEG copolyester obtains less favorable perfection of crystals with involvement of PEG. Meanwhile, we can find that the degree of crystallinity of PTEG4000-82.24/17.76 is higher than that of PTEG2000-82.22/17.78. This indicates that when the weight fraction of soft segment is kept and the PEG molecular weight is larger from 2000 to 4000, the copolyester becomes more crystallizable, which may because that the increasing molecular weight of PEG increases the molecular mobility and hence more favorable perfection of crystals were obtained.

Figure 4a shows heating scans at 10 K/min of PTEG copolyesters with various compositions after keeping their amorphous samples at 308 K for 1 h and then at 401 K for 1 h. 308 K and 401 K has been reported to be the appropriate temperature for PEG and PTT homopolymer to form crystals, respectively [12, 13]. It is clearly seen from Fig. 4a that only one endothermic peak (T_m) near 502 K (T_m for neat PTT) can be detected for all the copolyesters and we can not find melting transitions near the T_m of crystalline PEG (at about 324 K for PEG2000 and 332 K for PEG4000). These results are consistent with the WAXD study. Moreover, the melting transition of copolyesters with various compositions where the stating PEG molecular weight is kept constant (2000) continuously decreases from 501 K (neat PTT) to 489 K (PTEG2000-72.22/27.78) with increasing PEG2000. These results suggest that the mobility of polymer chains is increased while the crystal growth of PTT chains is decreased with the incorporation of the PEG chains. Besides, we found that T_m of PTEG4000-82.24/17.76 is higher than that of PTEG2000-82.22/17.78, which should be due to the more favorable perfection of crystals in the former copolyester.
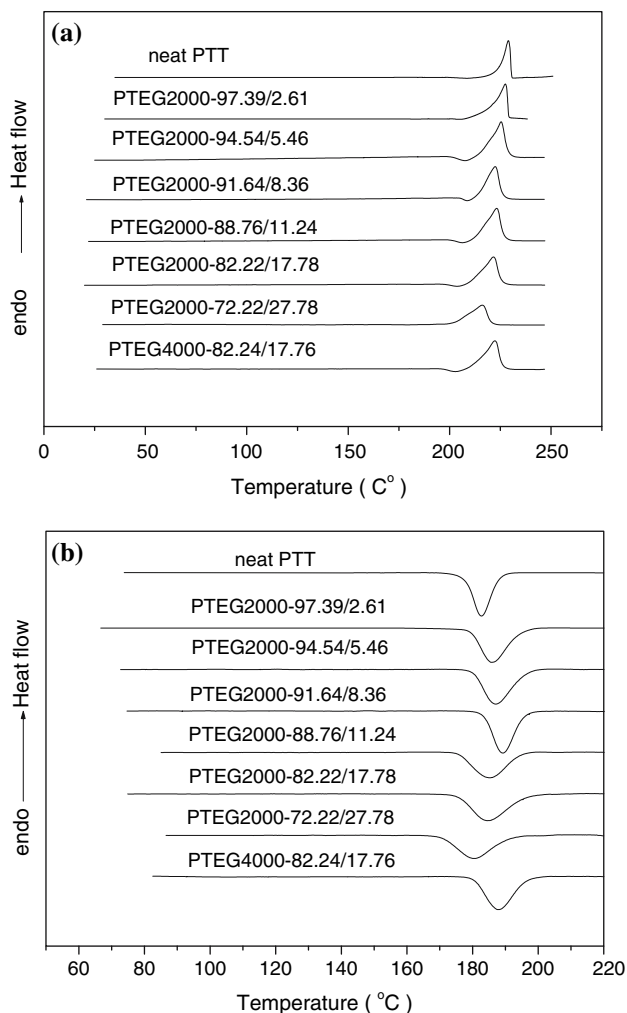
Fig 4 DSC thermograms of PTEG copolyesters: (**a**) heating and (**b**) cooling rates are 10 K/min

Fig 5 Crystallization half-times of PTEG copolyesters as a function of T_c

Figure 4b gives the DSC thermograms of PTEG copolyesters from melt after keeping them at 531 K for 3 min to erase their thermal history. It is interesting that when a small amount of PEG was incorporated into the PTT, the peak of the crystallization exothermic peak (T_c) of the copolyesters increases. The dynamic peak crystallization temperature during cooling from the melt was correlated with the nucleation density and the number of the nuclei per unit volume increased as the peak T_c increased [14, 15]. In the present study, 8.36 wt% of PEG2000 induces the earliest formation of PTT nuclei. When the amount of PEG in the copolyesters further increases, the T_cs of the copolyesters decrease from 463 K (PTEG2000-91.64/8.36) to 454 K (PTEG2000-72.22/27.78). This may be attributed to the decrease of the regularity of PTT molecular chains due to the incorporation of PEG. PTEG4000-82.24/17.76 has a higher T_c than that of PTEG2000-82.22/17.78, which suggests that the effect of the flexible chains on enhancing
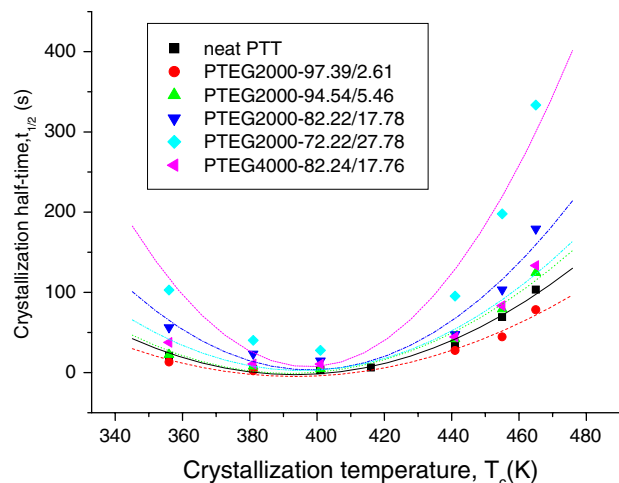
the nucleation ability of PTT is more important in PEG4000 than in PEG2000 due to the longer flexible chains of PEG4000.

The half-time of crystallization $t_{1/2}$, which is the time needed for half of isothermal crystallization to occur ($X_t = 0.5$), is taken as a measure of the overall rate of crystallization. Figure 5 shows the influence of temperature and co-unit content on the half-time. A high rate of crystallization corresponds to a low $t_{1/2}$ and maximum rates occur at minimum $t_{1/2}$ ($t_{1/2}^{min}$). Chuah [5] has studied the crystallization kinetics of PTT homopolymer by means of DSC, and gave the similar temperature dependence of half-times as neat PTT in present work does i.e. the rate of crystallization increases as the temperature decreases within the temperature range of 448–468 K. The study of crystallization behavior of PTT homopolymer at both low and high degrees of undercooling has been reported in a separate paper [13]. In the present work, the effect of inclusion of PEG segments in the chain replacing the 1,3 PDO unit is presented. When the PEG content in the copolyesters is higher than 5 wt%, the minimum $t_{1/2}$ increases with increasing PEG and the crystallization temperature of minimum $t_{1/2}$ (T_c^{min}) shifts to lower temperature in accord with the trend of decreasing rate of crystallization with increasing PEG unit. Also there is a tendency for the curve to become narrower and for the bottom of the curve to sharpen with increasing PEG content. The minimum $t_{1/2}$ covers a progressively narrower range of temperatures implying that greater temperature control is required for the moulding of crystalline materials with high PEG unit content. However, for PTEG2000-97.39/2.61, its smaller $t_{1/2}$ s than neat PTT at all the crystallization temperature implying that a small quantity of PEG2000 molecules (about 2.6 wt%) incorporated into

PTT could promote its crystallization rate to some extent. Detailed studies of crystallization and melting behavior of PTEG copolyesters with an emphasis on crystallization kinetics and morphology are in progress and will be published shortly

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