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LETTER

Thermal properties and crystallization behavior of Poly(trimethylene terephthalate) copolymers containing isophthalic units

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Poly(trimethylene terephthalate) (PTT) has received considerable attention recently as potential important fibers and engineering thermoplastics owing 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. Much studies have focused on this topic [4–7]. In a previous paper, we also carried out the kinetics analysis of PTT crystallization including the secondary crystallization process using a new mathematical model constructed by us [7]. Furthermore, 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. However, so far there's been little reported on the modification of the thermal properties of PTT by copolymerization. Recently the authors reported a investigation about the composition dependence of thermal properties of poly(trimethylene-co-ethylene terephthalate) [8]. In present work, copolyesters based on different molar ratios of polytrimethylene terephthalate to polytrimethylene isophthalate (PTI) have been synthesized and the thermal properties and crystallization behavior of them were explored. To our knowledge, it is the first time that the thermal properties of poly(trimethylene terephthalate-co-isophthalate) (PTTI) has been presented.

Different molar ratios of terephthalic acid (TPA) isophthalic acid (IPA) and equivalence of 1,3-propanediol were mechanically stirred and the mixture was kept in the temperature range of 458–533 K catalyzed by tetrabutyl titanate for 3 h, then the mixture was heated up to 543 K and kept for 3–3.5 h with reduced pressure so that polyesters with different molar ratios of PTT to PTI could be prepared. The ratio of TPA to IPA will be used to denote the copolyesters, e.g. PTTI100/0 and PTTI0/100 are used to refer to PTT and PTI 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 0.0645–0.0810 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 standard.

Differential scanning calorimeter (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 for 3 min, then cooled to 273 K. The second heating and cooling runs were recorded with a scanning rate of 10 K/min.

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. WAXD measurements were carried out with a Rigaku D/max-ra diffractometer using graphite monochromatized CuK_α radiation (λ=0.1542 nm; 40 kV; 80 mA; 2 kcps).

The depolarized light intensity (DLI) technique was used to follow the crystallization of samples. Isothermal crystallization in the present work was carried out with a

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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:

$$X_t = (I_t - I_0)/(I_\infty - I_0) \qquad (1)$$

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 PTTI copolyesters were determined by ^{13}C NMR spectroscopy. As shown in Fig. 1, the molar ratio of the TPA and IPA units on the polymer backbone was estimated from integrations of their specific chemical shifts. The results are summarized in Table 1. The determined compositions are in good agreement with the compositions of monomers fed in the first-step reaction (i.e. esterification reaction). This result indicates that TPA and IPA monomers have an almost same reactivity in the esterification reaction with 1,3 PDO.

Figure 2 shows the DSC thermograms of PTTI copolyesters with various compositions. As can be seen from Fig 2a, the copolyesters containing IPA unit of ≤30 mol% reveal three phase transitions when heating: first one appears over 312–316 K, which corresponds to the glass transition (T_g), the second over 342–387 K, which corresponds to the crystallization of these amorphous materials (T_{cc}) and the third over 444–503 K, which corresponds to the melting transition of crystals (T_m). It is found that the difference between T_m and T_{cc} ($\Delta T = T_m - T_{cc}$) of the copolyesters decreased with the content in IPA unit. Meanwhile, crystallization temperature of the copolyesters from melt (T_{ch}) also decreased with increasing the IPA unit (as shown in Fig 2b). These results indicate that PTTI copolyester becomes less crystallizable with involvement of PTI. This could be interpreted in terms of the poor crystallizability of IPA, which is due to its kinked meta-linkage.

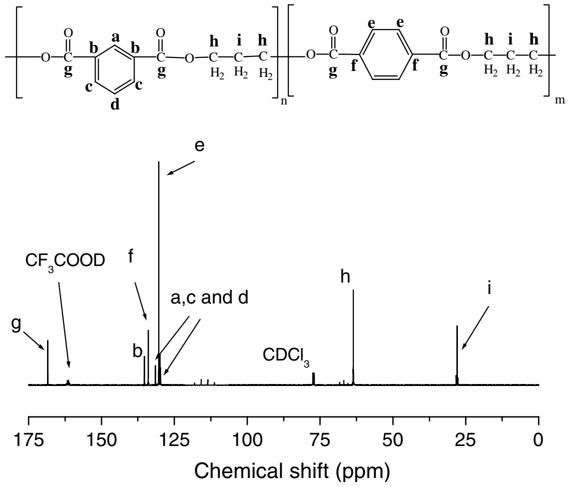

Fig. 1 ^{13}C NMR spectroscopy of PTTI60/40 dissolved in a mixture of $CDCl_3$ and CF_3COOD

ΔH_{ch} and ΔH_m are heat of crystallization during cooling runs and heat of fusion during heating runs, respectively. For PTTI copolyester, ΔH_{ch} and ΔH_m vary in the same way as T_{ch} and T_m i.e. decrease with increasing the composition of PTI. This suggests that the crystals both from cold- and hot-crystallization grow imperfectly, as the composition of PTI increases. As for PTTI 60/40, no exotherm or endotherm data could be gathered in a DSC analysis due to its too low rate of crystallization.

Figure 3 illustrates WAXD patterns of the copolyesters crystallized at 403 K for 1 h. It is easily seen that the PTTI copolyesters with PTI no more than 30% show crystalline peaks. The copolyester with 40% PTI becomes amorphous. The final apparent degrees of crystallinity measured by WAXD continuously decreases from 40.9% to 0% with increasing PTI. These results are consistent with the calorimetric study. Besides, it should be noted that 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. As well as PTTI60/40, pure PTI (PTTI0/100) cannot be crystallized at the abovementioned conditions.

It is of interest to compare such thermal properties and crystallization behavior of PTTI to those of poly(ethylene terephthalate-co-isophthalate) (PETI) in view of their similar potential application in non-fibrous area. PETI are currently used in the industry as thermally shrinkable package films as well as heat-sealable laminating films for steel cans and metal and ceramic sheets. Li et al. [9] have qualitatively explored the natures of a series of copolyesters based on different ratios of polyethylene terephthalate (PET) to polyethylene isophthalate (PEI), the results showed that only the copolyesters containing PEI below 15% are crystallizable, while the copolyester melt with 20% PEI is not easily crystallized at a cooling rate above 5 K/min. The present work indicated that PTTI copolyester containing IPA unit of 30% are able to crystallize from melt at a cooling rate of 10 K/min. Thus it can be concluded that the effect of IPA unit on hindering crystallization of polyesters is more important in PET than in PTT. This should be attributed to the added methylene group in PTT chain, which results in a more molecular mobility of PTTI copolyester than that of PETI copolyester

Table 1 Compositions, intrinsic viscosities and heat of thermal transition of PTTI copolyesters

Sample designation	Feed ratio[a] (TPA/IPA)	Copolyester composition[b] (TPA/IPA)	$[\eta]^c$ (m^3/kg)	ΔH_{ch} (kJ/kg)	ΔH_m (kJ/kg)
PTTI100/0	100/0	100/0	0.0804	−48.2	52.6
PTTI90/10	90/10	88.8/11.2	0.0784	−21.7	33.0
PTTI80/20	80/20	79.9/20.1	0.0810	−9.4	17.9
PTTI70/30	70/30	69.7/30.3	0.0796	–	6.4
PTTI60/40	60/40	60.4/39.6	0.0773	–	–
PTTI0/100	0/100	0/100	0.0645	–	–

[a] Molar ratio of TPA and IPA fed in the polymerization

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

[c] Estimated from the measured intrinsic viscosities

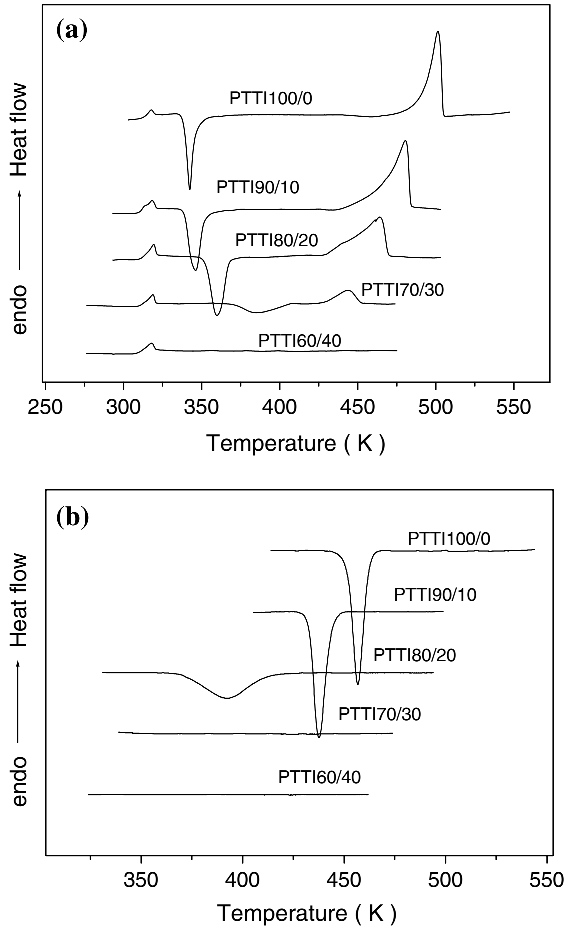

Fig. 2 DSC thermograms of PTTI copolyesters: (**a**) heating and (**b**) cooling rates are 10 K/min

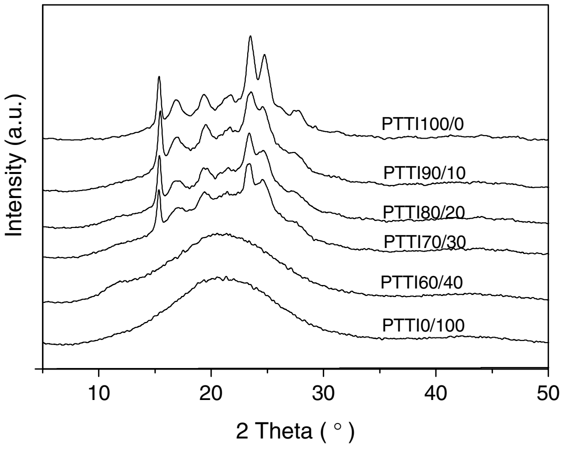

Fig. 3 WAXD patterns for PTTIopolyesters

with the same IPA unit content and hence PTTI copolyesters obtain more favorable growth of crystals.

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 4 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 PTTI100/0 does i.e. the rate of crystallization increases as the temperature decreases within the temperature range of 448–468 K. The detailed study of crystallization behavior of PTT homopolymer at both low and high degrees of undercooling will be reported in a separate

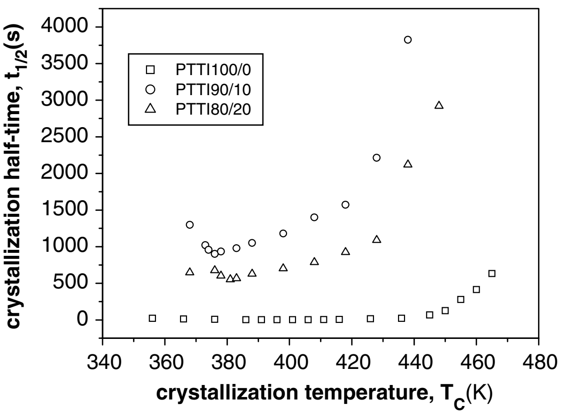

Fig. 4 Crystallization half-times of PTTI100/0, PTTI90/10 and PTTI80/20 as a function of T_c

paper. In the present work, the effect of inclusion of isophthalate unit in the chain replacing the terephthalate unit is presented. The minimum $t_{1/2}$ increases with increasing IPA unit 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 IPA unit. Also there is a tendency for the curve to become narrower and for the bottom of the curve to sharpen with increasing IPA unit. 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 of high IPA unit content. Detailed studies of crystallization and melting behavior of PTTI copolyesters with an emphasis on their crystallization kinetic analyses are in progress and will be published shortly.

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