

Synthesis and Properties of Poly(trimethylene terephthalate-co-2-methyl-ethylene terephthalate) Random Copolyesters

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ABSTRACT: Poly(trimethylene terephthalate-co-2-methyl-ethylene terephthalate) random copolymers of various compositions were synthesized via traditional two-step polycondensation by incorporating of 1,2-propanediol. The molar composition of trimethylene terephthalate and 2-methyl-ethylene terephthalate units and chemical structure were confirmed by means of ¹H-NMR and Fourier transform infrared. The thermal properties of the copolyesters were evaluated by DSC and TGA. As far as the thermal properties is concerned, the main effect of incorporation of 1,2-propanediol was a lowering in the melting temperature, and an increment of glass transition temperature compared to homopolymer PTT. Due to the effect of the lateral

methyl groups in the polymeric chain, the thermal stability is slightly decreased as the amount of the MET units is increased. Furthermore, the crystals of PTT/MET copolyesters were observed by hot-stage optical polarizing microscopy at the indicated crystallization temperatures. As expected, the incorporation of MET units in the polymer chain of PTT was found to decrease the dimension of the crystals. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3419–3426, 2010

Key words: 1,2-propanediol; poly(trimethylene terephthalate); poly(2-methyl-ethylene terephthalate); copolymerization; copolyesters

INTRODUCTION

Aromatic polyester poly(trimethylene terephthalate) (PTT), also called poly(propylene terephthalate) (PPT), as a semicrystalline polymer has aroused more and more attention on account of its excellent characteristics, such as elastic recovery, chemical resistance and resilience, compared with poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT).^{1,2} It was first patented by Whinfield and Dickson in 1946,³ but not commercially available up to 1990s, due to the high production cost of the starting raw material for 1,3-propanediol (1,3-PDO). The breakthrough in the production of 1,3-PDO made PTT available in industrial quantities, thus offering new opportunities in carpet, textile, film, packing, and engineering thermoplastics markets.⁴ However, some applications are limited arising from relatively low glass transition temperature of PTT. Moreover, PTT crystallization rate is too fast, which causes difficulties in the manufacturing processes.

As well known, copolymerization affords an amenable means of modifying the crystallinity, morphol-

ogy, melting point (T_m), glass transition temperature (T_g), solubility, etc. For these reasons, there is a great motivation for incorporating a third component into PTT polymeric chains to overcome the undesirable properties. Ponnusmy and Balakrishnan⁵ reported the preparation and characterization of P(ET/TT) copolymers in varying compositions. Joon et al.⁶ synthesized P(TT/BT) random copolymers to study the molecular structure and the thermal properties. Smith et al.⁷ investigated the physical properties of P(ET/TT) and P(ET/BT) copolymers. Soccio et al.⁸ introduced neopentyl glycol to PTT polymeric chains and studied the relations between structure and properties.

Generally, incorporation of diols with methyl groups would lead to significant variations in the thermal properties. In particular, an increment of the glass transition temperature and an undoing of the ability to crystallize would be induced. 1,2-PDO, a diol containing lateral methyl group, is a less expensive raw material in comparison with other glycols. Numerous patents and articles have been published disclosing polyesters derived from terephthalic and 1,2-PDO.^{9–12} However, these copolyesters are amorphous and described as being not formable for manufacturing useful fibers due to their “inherently” poor physical properties.⁹ Recently, we have reported on PBT copolymers based upon copolymer-

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ized with 1,2-propanediol.¹³ In these copolymers (PBT/MET), the presence of the asymmetrical methyl group introduced significant changes in the crystallizability and thermal properties of PBT. In this article, we focused on the copolymerization of dimethyl terephthalate with mixtures of 1,2-propanediol and 1,3-propanediol, to be called PTT/MET. And the relationship between the composition of TT/MET and thermal properties and crystallization behaviors of copolyesters was studied in detail. The other evaluation of the crystallization kinetics, mechanical properties, and rheological behaviors of these copolymers will be explored in an upcoming article.

EXPERIMENTAL

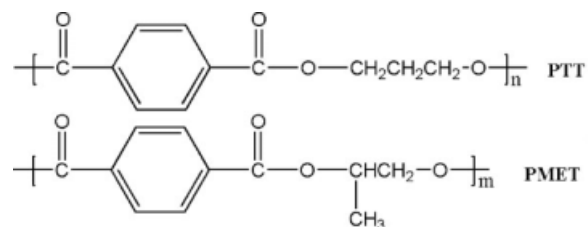
Materials

1,4-dimethyl terephthalate (DMT) (99+%), 1,3-propanediol (1,3-PDO) (99+%), and 1,2-propanediol (1,2-PDO) (99+%) purchased from Sinopharm Chemical Reagent (Shanghai, China) were reagent grade and used as received. Zinc acetate dehydrate (Sinopharm Chemical Reagent), phosphorous (Sinopharm Chemical Reagent), and antimony trioxide (Sigma-Aldrich Co.) were used as catalyst for transesterification, stabilizer, and polycondensation, respectively. Solvents used for purification and characterization were all of high purity grade, and were used without further purification.

Synthesis

Poly(trimethylene terephthalate) (PTT), Poly(2-methyl-ethylene terephthalate)(PMET), and Poly(trimethylene terephthalate-co-2-methyl-ethylene terephthalate) (PTT/MET) random copolyesters were synthesized by the traditional two-step polymerization, starting from different molar ratio of 1,3-PDO, 1,2-PDO, and from DMT, taking zinc acetate dehydrate (200 ppm in relation to DMT) as a transesterification catalyst. Additionally, in order to obtain high molecular weight polymers, a small amount of phosphorous were added to the reaction system to prevent the possible oxidation of the secondary hydroxyl group of the 1,2-PDO. In first stage, the temperature was raised to 180°C and maintained at this temperature for 2.5–3 h according to the initial composition of the reaction system. In the second stage, after more than 90% of the theoretical amount of methanol was distilled off, phosphorous (100 ppm in relation to DMT) and antimony trioxide (200 ppm in the relation of DMT) were placed into the flask as the stabilizer and polycondensation catalyst. Then, the pressure was slowly reduced to 0.5 mbar and maintained during the polycondensation time. The temperature was increased to 240°C for a predetermined period time to acquire satisfied molecular weight.

Finally, the resulting polymer melt was forced out of the flask under N₂ to prevent any possible oxidative degradation. The chemical structures of the two parent homopolymers were:



Before characterization, all the samples were purified by dissolution in *m*-cresol and precipitated in methanol several times, filtered off and then dried in a vacuum oven for 12 h at 80°C.

Characterization

Fourier transform infrared (FTIR) spectra were performed on a Nicolet AVATAR 360 FTIR spectrometer in the range of 4000–500 cm⁻¹. ¹H-NMR was recorded in deuterated trifluoroacetic acid with a Bruker ARX400 NMR spectrometer, and spectra were internally referenced to tetramethylsilane (TMS).

Differential scanning calorimetry (DSC) measurements were carried out using a Perkin-Elmer DSC-7, equipped with a liquid subambient accessory and calibrated using In standards. The samples (ca. 10 mg) were heated to 250°C at a rate of 20°C/min, hold there for 5 min, and then rapidly quenched to -30°C. Finally, they were reheated to 250°C at a heating rate of 20°C/min. The glass transition temperature (*T_g*) was taken as the fictive temperature, that is the temperature defined by the intersection of the extrapolated pretransition and post-transition enthalpy data.¹⁴ The melting temperature (*T_m*) and the crystallization temperature (*T_c*) were taken as the endothermal and exothermal phenomenon in the DSC curve, respectively. The heat of fusion and the heat of crystallization of the crystal phase were calculated from the area of the DSC endotherm and exotherm, respectively. Repeated measurements on each sample showed excellent reproducibility. The crystallinity of the samples was obtained from DSC data. From the measured heat of fusion ΔH_m an apparent degree of crystallinity was calculated as follows:

$$X_c = \Delta H_m / \Delta H_m^0 \quad (1)$$

where ΔH_m^0 is the melting heat of 100% crystalline PTT polymer. A value of 145 J/g has been adopted for ΔH_m^0 .¹⁵

Thermal stability was investigated by thermogravimetric analysis (TGA) with a SDT Q600 (USA TA Instrument Corporation) from 50 to 600°C at a heating rate of 10°C/min in a nitrogen atmosphere.

The intrinsic viscosity $[\eta]$ of the samples dissolved in 0.5 g/dl concentrated mixture solvent of phenol/1,1,2,2-tetrachloroethane ($w : w = 60 : 40$) was determined using an Ubbelohde viscometer thermostated at $30 \pm 0.5^\circ\text{C}$ in a water bath. The measurements were carried out at only one specific concentration according to the single-point method.¹⁶

Wide-angle X-ray diffraction (WAXD) were performed on an X-ray diffraction analyzer (XRD, Rigaku D/Max-III, Japan) equipped with a rotating Cu anode generator system using Cu/K- α ($\lambda = 1.540 \text{ \AA}$) radiation. WAXD profiles were recorded at room temperature with diffraction angles (2θ) which were from 5° to 60° . The data were collected for 6s at angular intervals of $2\theta = 0.1^\circ$.

Samples for polarized optical microscopy (POM) measurements were performed on small fragment of polymer, inserted between two thin microscope cover glasses, and subjected to the following thermal progress: PTT, PTT/MET4, PTT/MET13, PTT/MET23 were heated to 260, 256, 243, and 227°C , respectively, kept at this temperature for 3 min under nitrogen and immediately transferred to an adjacent chamber preheated to the selected crystallization temperature T_c , where isothermal crystallization was carried out for 60 min. POM observations were performed with an Olympus BX51-P at room temperature.

RESULTS AND DISCUSSION

Molecular characterization

Both FTIR and $^1\text{H-NMR}$ spectroscopy were used to confirm the chemical structure and the molar composition of polymers. As shown in Figure 1, the representative FTIR spectrum of PTT/MET34 shows a strong absorption at 1728 cm^{-1} and $1204\text{--}1160 \text{ cm}^{-1}$, characteristics of the C=O and C–O stretching

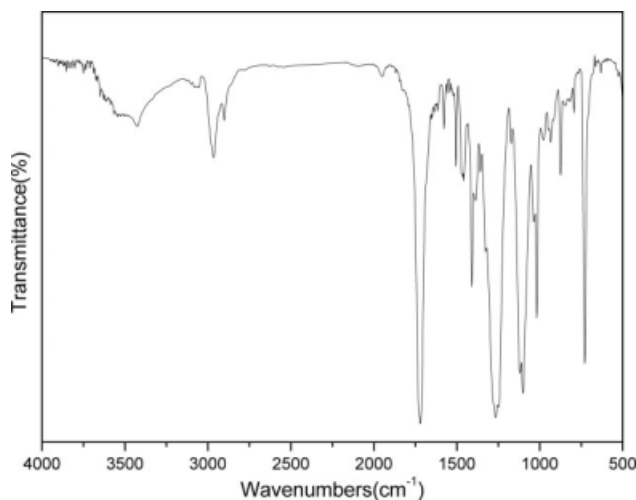


Figure 1 FTIR spectrum of PTT/MET44 copolyester.

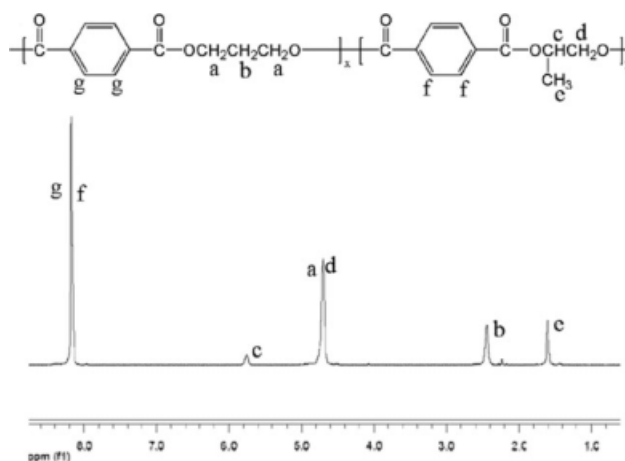


Figure 2 $^1\text{H-NMR}$ of PTT/MET34 copolyester.

vibration of the ester group, respectively. Meanwhile, the characteristic methyl group absorption bands are at 2962 and 2854 cm^{-1} . Additionally, the characteristic absorption bands of PTT also appear in the FTIR spectra of PTT/MET random copolyesters.

Representative $^1\text{H-NMR}$ spectrum of PTT/MET34 is depicted in Figure 2. As shown in Figure 1, the molar ratio of 1,2-PDO and 1,3-PDO is calculated according to the following equation:

$$N_{1,2\text{-PDO}} : N_{1,3\text{-PDO}} = 2A_e : 3A_b \quad (2)$$

where A_e and A_b are the area for the protons from 1,2-PDO and 1,3-PDO units, respectively. The compositions of the copolyesters determined from the data afforded by $^1\text{H-NMR}$ spectra are summarized in Table I.

The $[\eta]$ values of all samples calculate according to the following equation,¹⁷ are also listed in Table I.

$$[\eta] = \frac{\sqrt{2(\eta_{\text{sp}} - \ln \eta_{\text{rel}})}}{c} \quad (3)$$

TABLE I
Composition and Molecular Weight of PTT/MET Copolymers

Sample No.	Molar ratio ^a	$[\eta]/(\text{dL/g})$	M_v^b
PTT	0/100	0.892	46,500
PTT/MET4	96/4	0.818	41,100
PTT/MET13	87/13	0.885	46,000
PTT/MET23	77/23	1.119	64,700
PTT/MET34	66/34	0.975	53,000
PTT/MET44	54/44	0.549	23,000
PMET	100/0	0.485	-

^a Molar ratio was confirmed by $^1\text{H-NMR}$ in TFA at room temperature.

^b Estimated from the measured intrinsic viscosity.

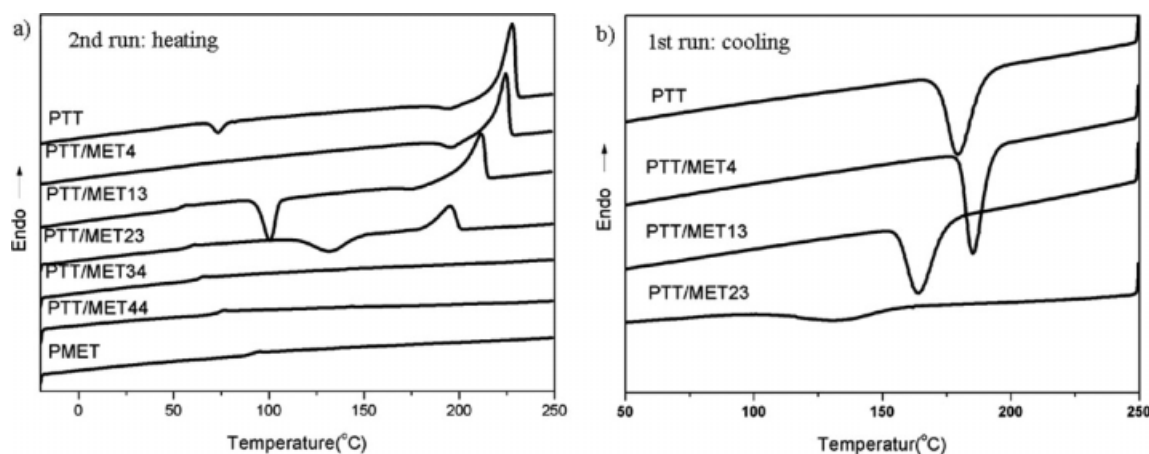


Figure 3 a) Calorimetric curves of PTT/MET random copolyesters and homopolymers (2nd scan after quenching). b) Cooling curves of PTT, PTT/MET4, PTT/MET13, and PTT/MET23.

Meanwhile, the M_v values were obtained from the following Mark-Houwink equation:¹⁶

$$[\eta] = 5.36 \times 10^{-4} M_v^{0.69} \quad (4)$$

where M_v is the viscosity average molecular weight. The Mark-Houwink constants employed in this study have been found for PTT rather than PTT/MET copolyesters, so that their M_v 's might be under- or over-estimated and the values of M_v are used for comparison. From the data collected in Table I, it can be seen that if the amount of MET units is higher than 44 mol %, the viscosities are decreasing dramatically. This phenomenon can be explained by the following reasons. Firstly, the steric hindrance of lateral methyl group leads to the oxygen atom in 1,2-PDO to be less electronegative than those in other symmetrical aliphatic diols. Secondly, the secondary hydroxyl group of the 1,2-propanediol is instable at the high temperature (240°C) in the polycondensation conditions.¹¹ However, when the amount of MET units is less than 34 mol %, the polymers are characterized by high molecular weights, which could be considered as a proof that appropriate polymerization conditions and a good synthesis control were obtained. If the amount of 1,2-PDO is relatively higher than 34 mol %, the as-synthesized copolyesters are amorphous, and increase in transparency because of lowered crystallinity, but have deteriorated thermal and mechanical properties. As a result, the applications of the copolymers are confined. Therefore, to evaluate the effect of incorporation of 1,2-PDO on the PTT at some extent, copolymerizations were carried out based on a mole percent of 1,2-PDO ranging from 4 to 44 mol %.

Thermal properties

It is well known that a partially crystalline material is expected to exhibit different glass transition behavior

than completely amorphous one. Although some conflicting results are reported in the literature,¹⁸ crystallinity usually acts like crosslinking and raises T_g through its restrictive effect on segmental motion of amorphous polymer chains. To study the influence of chemical structure on the glass transition of random copolymers, the phenomenon should be examined in the total absence of crystallinity. Rapid cooling (quenching) from the melt is the method commonly used to prevent crystallization and obtain polymers in a completely amorphous condition.

As a matter of fact, PTT cannot be easily frozen in an amorphous glassy state because of its high rate of crystallization.¹⁹ In the cases of PTT and PTT/MET4 copolymers, there is unobvious endothermal baseline deviation associated with the glass transition temperature which could hardly be observed. As can be seen in Figure 3(a) and from the data collected in Table II, the values of T_g are influenced by the amount of MET units in the PTT chain, which increase as the amount of MET units is increased. The result is not surprising, taking into account that PMET is characterized by a higher glass transition temperature than that of PTT. For high molecular weight polymers, the flexibility of the chain is undoubtedly the most important factor influencing T_g .⁸ Nevertheless, the presence of MET units in the copolyesters must contribute significantly to enhance the T_g due to the steric effect of the lateral methyl group which hinders the rotation, imposing restrictions. Furthermore, all the copolymers exhibit a single T_g rather than two T_g 's corresponded to possible blocks of trimethylene terephthalate and 2-methyl-ethylene terephthalate. This indicates that the as-synthesized copolymers are random copolymers, which are consistent with previously reported literatures. Furthermore, it is well known that melt copolymerization usually generates random copolyesters independent on the reactivity of the monomers, because

TABLE II
Thermal Properties of PTT/MET Copolymers

Samples No.	T_g (°C)	ΔC_p (J/g°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔT (°C)	ΔH_c (J/g)	X_c^a (%)	T_{id}/T_{max} (°C)
PTT	45.8	0.10	228	63.4	179	49	55.7	43.7	382/411
PTT/MET4	52.4	0.31	224	55.5	185	39	56.5	38.3	377/411
PTT/MET13	53.5	0.38	211	49.7	164	47	47.5	34.2	375/405
PTT/MET23	56.4	0.39	195	30.7	133	62	21.7	21.2	370/405
PTT/MET34	62.7	0.27	–	–	–	–	–	–	368/403
PTT/MET44	72.4	0.34	–	–	–	–	–	–	366/398
PMET	89.5	0.36	–	–	–	–	–	–	328/382

^a Calculated according to eq. (1).

of the occurrence of transesterification reactions in the molten state.^{20–22}

Additionally, in all cases, both the values of T_m and X_c of copolyesters are depressed as the amount of MET units is increased, which is as usually found in random copolymers.^{6,23,24} Furthermore, the increase in the amount of the comonomer incorporated into PTT chains results in a reduction of the heat of fusion, indicating a reduced level of crystallinity in the copolymers with respect to the homopolymer PTT. This trend indicates a decrement of the overall crystallization rate of PTT, due to the presence of noncrystallizable MET counits, which act as obstacles in the regular packing of PTT polymer chains. In addition to the endothermic melting peak, PTT, PTT/MET13, and PTT/MET23 show an exothermic peak over the temperature region between the glass and melting transition. The peak comes from the recrystallization occurred on the heating run in the DSC measurement. When the copolyesters contain above 23 mol % MET units, the copolyesters are completely amorphous.

The crystallization temperature of PTT/MET4 is increased 6°C compared to homopolymer PTT ($T_c = 179^\circ\text{C}$) when 4 mol % MET units were incorporated (Table II, Figure 3b), which might be attributed to the low molecular weight of PTT/MET4. This phenom-

enon has not been observed in other PTT copolyesters.^{8,20} Soccio et al.⁸ found that incorporation of 5.1 mol % nepoenthyt terephthalate counits led to a lowering crystallization temperature about 20 to 170°C [PTT ($T_c = 190^\circ\text{C}$)] for the approximate molecular weight between PTT and PTT/PNT5. However, when the amount of MET units is higher than 4 mol %, the trend of T_c is as the same as PTT copolymers reported elsewhere. At the same time, the degree of supercooling ($\Delta T = T_m - T_c$) of the copolyester is also listed in Table II. In addition, the values of ΔT are plotted in Figure 4 as a function of MET unit content. As can be seen, the general trend of the ΔT is increased as the MET unit content is increased. This phenomenon is common for other copolyesters when incorporated noncrystallizable counits.^{8,25} Moreover, the crystallization exothermal of the copolyester shows gradual widening in the range with increasing MET units, which suggests a gradual long crystallization time.

Thermal stability

The investigation on the thermal stability was carried out in N_2 , and the weight-loss curves of PTT, PMET, and some PTT/MET copolyesters as a function of temperature are shown in Figure 5. The

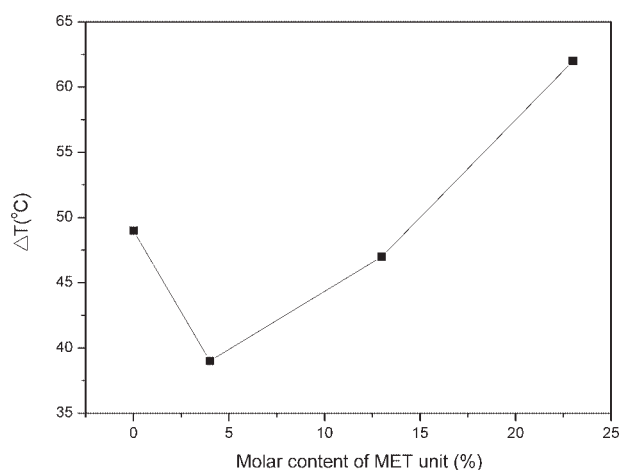


Figure 4 T_m and T_c as a function of composition for PTT/MET copolymers.

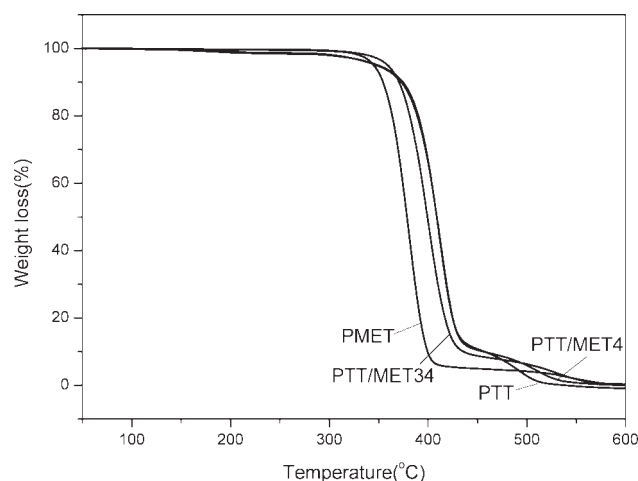
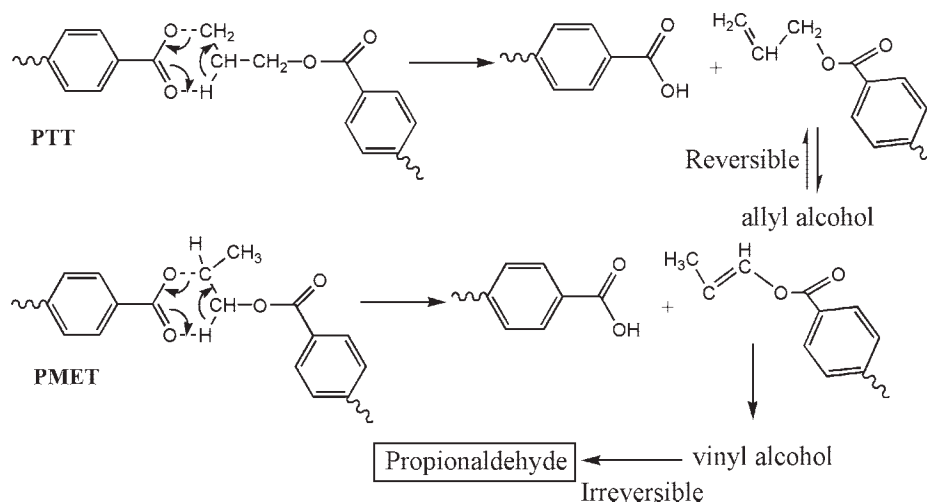


Figure 5 TGA curves of PTT, PMET, and some of PTT/MET copolyesters.



Scheme 1 β -scission mechanism for PTT and PMET.

initial decomposition temperature (T_{id}) and the maximum temperature (T_{max}) of copolyesters are summarized in Table II. As can be seen from Figure 5, the weight loss takes place practically in one step and is practically 100%. The thermal stabilities of all copolyesters are quite comparable and they are practically stable up to 300°C. It is well known that the main thermal degradation pathway of polyesters is highly dependent on the nature of the diol subunit. The most important mechanism in the decomposition of the diol subunit is the β -scission,^{26,27} shown for PTT in the Scheme 1. The thermal stability is found to be dependent on the copolymer composition, being lower as the amount of MET unit increases. This phenomenon is inconsistent with that found for PTT/PNT copolyesters, which derive from neopentyl glycol.⁸ In the case, PNT has two symmetrical lateral methyl groups, which prevents the β -scission, making PNT polyester significantly more thermal stable than PTT. Moreover, both the lateral methyl group unstable at a relative high temperature and the low molecular weight of copolymers result in the poor thermal stability of copolymers.

XRD analysis

XRD patterns of PTT/MET copolymers and the parent polymers were obtained to evaluate the crystal structure, as shown in Figure 6. The WAXD pattern of PTT shows seven characteristic peaks at the scattering angles 2θ of $\sim 15.3^\circ$, 16.8° , 19.4° , 21.8° , 23.6° , 24.6° , and 27.3° , corresponding to the reflection planes of (010), (0 $\bar{1}$ 2), (012), (102), (102), (1 $\bar{1}$ 3), and (10 $\bar{4}$), respectively.²⁸ PMET has a single broad peak in the whole range for its amorphous structure. As can be seen, PTT/MET23 has the same crystalline diffraction peaks as PTT homopolymer. These results prove that the crystal structure that develops

in PTT/MET4, PTT/MET13, and PTT/MET23 copolymers corresponds to the characteristic lattice of the homopolymer PTT. Meanwhile, when the amount of MET units is above 34 mol %, PTT/MET copolyesters appear to be completely amorphous, similarly to PMET homopolymer. However, as to the PBT/MET copolyesters,¹³ when the amount of MET units is above 43.6 mol %, the copolyesters become amorphous. This may be ascribed to the different crystalline capability of trimethylene terephthalate units and the butylene terephthalate units; the former is harder to crystallize. The incorporation of MET unit, which containing unsymmetrical lateral methyl group into the polymer backbone leads to an irregular chain structure and thereby inhibits regular chain packing for crystallization.

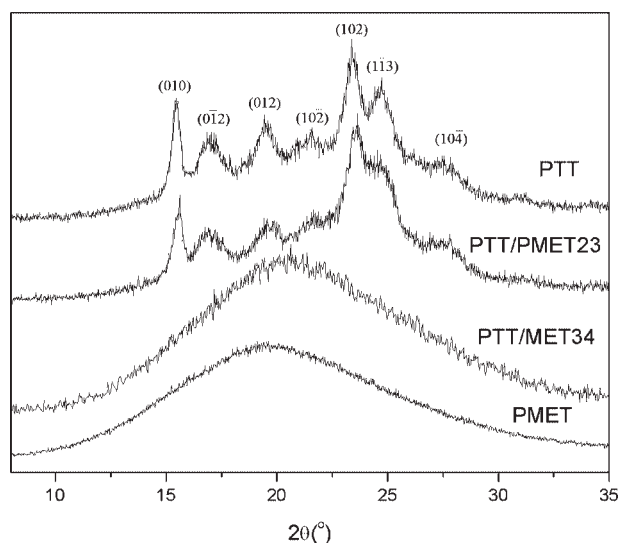


Figure 6 Wide-angle X-ray spectra of PTT, PMET and some of PTT/MET copolyesters.

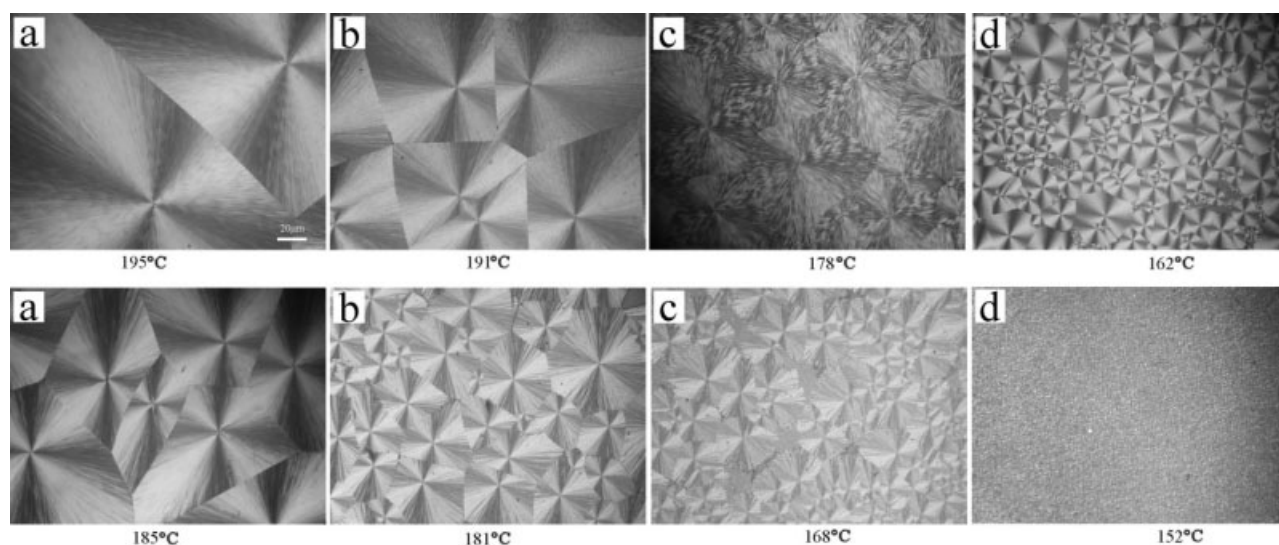


Figure 7 Optical micrographs of PTT (a), PTT/MET4 (b), PTT/MET13 (c), and PTT/MET23 (d), isothermally crystallized at the indicated T_c 's.

Spherulitic morphology

Generally speaking, POM is one of the predominant and most informative tools used for investigating spherulitic morphologies. Figure 7 shows the micrographs of PTT, PTT/MET4, PTT/MET13, and PTT/MET23 spherulites formed in the hot stage of a polarizing optical microscope at two different isothermal crystallization temperatures (T_c 's). The Maltese cross extinction patterns can be clearly seen in the images, except for PTT/MET23. Probably, in this case the regular packing of PTT polymer chains becomes difficult, because of the rejection from the crystalline phase of relevant amounts of 2-methyl-ethylene terephthalate units, so that only highly disordered lamellae with many defects form. These phenomena have been found by Soccio et al.²⁹ The spherulite dimension for each sample increases with increasing T_c , owing to a decrease of the nucleation rate producing fewer spherulites that can grow larger before impinging. Moreover, it is clear to see that the spherulite dimensions of the copolyesters decrease with the increment of the amount of MET units. As a matter of fact, the noncrystallizable comonomeric units hinder the crystallization process, leading to small crystallites under the same undercooling temperature. When the copolymers contain above 34 mol % MET units, their crystalline morphologies can not be observed using a polarized optical microscope at the same conditions. These phenomena are in good agreement with the results investigated by wide X-ray measurement.

CONCLUSION

A series of PTT/MET copolyesters were synthesized and studied in terms of molecular structure using FTIR and $^1\text{H-NMR}$. At room temperature the

appearances of these copolyesters change from semi-crystalline to transparent and become more brittle with increasing the amount of MET units. XRD results indicated that the copolyesters containing MET units ranging from 4 to 23 mol % are crystallizable, while the amount of MET units above 34 mol %, they appear as completely amorphous materials. Moreover, morphology studied on POM further elucidated the crystallizability of the PTT/MET copolyesters, which is in agreement with the results of obtained by means of XRD measurements. The crystallizability of copolymers was decreased with the increment of MET units, due to the rejection from the crystalline phase of the noncrystallizable MET units, which makes more difficult the regular packing of PTT polymer chains.

DSC was used to investigate the effect of the compositions on the thermal properties of copolymers. The value of T_g shows an increment as the amount of the MET units is increased whereas T_m decreases. The thermal stability of the PTT/MET copolymers was good and comparable to that of PTT, which slightly decreased with increasing the amount of MET units, as a result of the instability of lateral methyl group at relative high temperature. In conclusion, by incorporating of asymmetric 1,2-propanediol to PTT is a potential approach toward the design of new materials with a higher T_g , and at the same time lowering the cost.

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