

Synthesis and Thermal Characterization of Random Poly(butylene terephthalate-co-2-methyl-ethylene terephthalate) Copolyesters

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ABSTRACT: Poly(butylene terephthalate-co-2-methyl-ethylene terephthalate) (PBT/MET) was synthesized by incorporating 1,2-propandiol(1,2-PDO) into PBT chains. The molar composition and chemical structure of PBT/MET copolyesters were confirmed by means of FT-IR and ¹H-NMR. To investigate the effect of 1,2-PDO on the thermal properties of PBT/MET copolyesters, the copolymerizations were carried out by varying various contents of MET units, and the prepared materials were evaluated by differential scanning calorimetry and thermogravimetric analysis. Results suggested that with the increase of the content of 1,2-PDO, the amount of crystallinity and the melting tem-

perature decline, while the glass transition temperature increases and the copolyesters become more transparent and brittle with respect to PBT homopolymer. In addition, the T_g -composition and T_m -composition data are well subjected to the Wood equation and Flory's equation, respectively. All these copolyesters are found to consist of the general trend displayed by copolymers reported elsewhere. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 750–755, 2010

Key words: poly(butylene terephthalate); glass transition temperature; melting temperature; random copolyesters; copolymerization; melt; NMR

INTRODUCTION

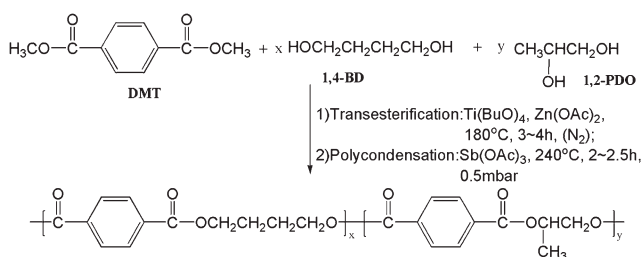
The development of industrial applications has already given a great impulse to explore more and more new materials to modify some properties of existing polymers. Recently, one of the most common ways of varying the properties of polymeric materials is represented by copolymerization. The properties of the polymeric materials obtained by copolymerization can be easily adjusted by changing copolymer composition. Thus, the correlation between the physical properties and the chemical structure of these materials should be studied in detail. In particular, the investigation on the thermal properties is fundamental for the improvement of manufacturing processes and of properties of the polymeric materials. Statistical copolyesters based on terephthalic acid, alkylene, and alkylene ether glycols (mainly ethylene, diethylene, and triethylene glycols and 1,3- or 1,4-butanediol) have been pro-

posed as compostable materials with good mechanical properties and processability.^{1,2}

Poly(butylene terephthalate) (PBT) as a widely used semi-crystalline polymer has attracted much attention for its good thermal properties and mechanical properties, and high chemical resistance. Accordingly, numerous studies on thermal properties, crystallization kinetics, rheological, and mechanical properties have been reported in the literature.^{3–11} Nevertheless, its low glass-transition temperature (T_g) and lower dimension precision compared with amorphous and scarcely crystallizable plastics make it unsuitable for many applications. As means for moderating the foregoing defects, copolymerization of unsymmetrical diols has been proved to be an effective method. A polyester copolymer containing these diols as one component is irregular in structure and low in crystallinity. It is expected that this will lead to improvement of T_g and dimensional stability. Until now, there are no publications in the literature on incorporating 1,2-propandiol (1,2-PDO) into PBT chains. 1,2-PDO, 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

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Scheme 1 Synthesis routes of PBT/MET random copolyesters.

terephthalic and 1,2-PDO.^{12–15} However, these copolyesters are amorphous and described as being not formable for manufacturing useful fibers due to their “inherently” poor physical properties.¹² To extend the utilization of 1,2-PDO and modify the properties of PBT, we report on the synthesis and characterization of the copolyesters resulting from the polycondensation of 1,4-butanediol (1,4-BD), 1,2-PDO, and 1,4-dimethyl terephthalate (DMT), to be called PBT/MET. A study on chemical structure and crystallization behavior of PBT/MET copolyesters is reported in this contribution and the effect of incorporation of 1,2-PDO by copolymerization on the thermal properties of PBT has been also investigated. The other evaluation of the crystallization kinetics, mechanical properties, and rheological behaviors of these copolyesters will be reported in an upcoming article.

EXPERIMENTAL

Materials

1,4-Dimethyl terephthalate (DMT) (99+%), 1,4-Butanediol (1,4-BD) (99+%), and 1,2-Propanediol (1,2-PDO) purchased from Sinopharm Chemical Reagent (Shanghai, China) were of reagent grade and used as received. Tetrabutyl titanate (TBT), phosphorus (Sinopharm Chemical Reagent, Shanghai, China), and Antimony acetate (Sb_2O_3) (Sigma-Aldrich, Shanghai, China) were used as transesterification catalyst, stabilizer, and polycondensation catalyst, respectively. Solvents used for purification and characterization were all of high purity grade, and were used without further purification.

Synthesis of PBT and PBT/MET

PBT, poly(2-methyl-ethylene terephthalate) (PMET), and poly(butylene terephthalate-co-2-methyl-ethylene terephthalate) (PBT/MET) random copolyesters were synthesized by the traditional two-step polymerization, starting from different molar ratio of 1,4-BD, DMT, and from 1,2-PDO, taking TBT (200 ppm in relation to DMT) as a transesterification catalyst. Additionally, in order to obtain high molecular weight polymers, a small amount of phosphorus

was added to the reaction system to prevent the 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 3–4 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, Sb_2O_3 (200 ppm in relation to DMT) was used. The pressure was slowly reduced to 0.5 mbar under 30 min, 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 N_2 to prevent any possible oxidative degradation. Prior to characterization, the PBT/METs samples were dissolved in *m*-cresol and precipitated with methanol, collected by filtration and washed with methanol several times, and then dried in a vacuum oven for 12 h at 80°C. The synthesis routes are shown in Scheme 1.

Characterization

Fourier transform infrared (FT-IR) spectra were performed on a Nicolet AVATAR 360 FT-IR spectrometer in the range of 4000–500 cm^{-1} .

$^1\text{H-NMR}$ 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 on a Perkin-Elmer Diamond DSC instrument (Shelton, CT) 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 50°C/min, held there for 5 min, and then rapidly quenched to –10°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 pre-transition and post-transition enthalpy data.¹⁶ The melting temperature (T_m), and the crystallization

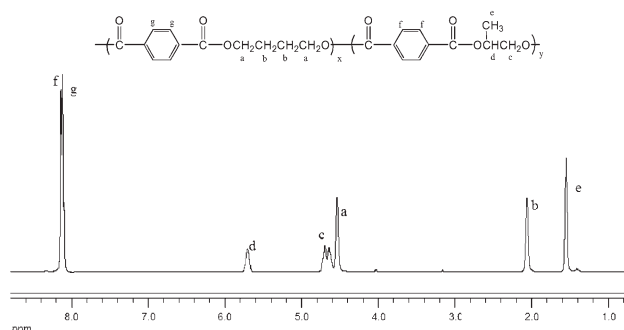


Figure 1 $^1\text{H-NMR}$ of PBT/MET-4 copolyester.

TABLE I
Molecular and Thermal Characterization Data of PBT/MET Random Copolymers

Sample nos.	Mol ratio ^a	η_{inh} (dl/g)	T_g (°C)	Δc_p (J/g °C)	T_m (°C)	T_c (°C)	ΔH_m (J/g)
PBT	100/0	1.07	–	–	224	191	44.2
PBT/MET-1	84/16	0.75	50	0.235	203	163	19.9
PBT/MET-2	67.8/32.2	0.70	57	0.443	174	–	14.0
PBT/MET-3	56.4/43.6	0.63	65	0.327	–	–	–
PBT/MET-4	36.4/63.6	0.56	77	0.303	–	–	–
PBT/MET-5	19.4/80.6	0.50	87	0.331	–	–	–
PMET	0/100	0.48	102	0.527	–	–	–

^a Mole ratio was confirmed by ¹H-NMR in TFA at room temperature.
–, Undetected.

temperature (T_c) were taken as the endothermic and exothermic 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.

Thermal stability was investigated by thermogravimetric analysis (TGA) with a SDT Q600 (USA TA Instrument Corporation, New Castle, DE) from 50°C to 600°C at a heating rate of 15°C/min in a nitrogen atmosphere.

Intrinsic viscosities of copolyesters dissolved in 0.5 g/dL concentrated mixture solvent of phenol/1,1,2,2-tetrachloroethane ($w:w=60:40$) were measured with an Ubbelohde viscometer thermostated at $25 \pm 0.5^\circ\text{C}$ in a water bath.

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 ($\beta=1.540 \text{ \AA}$) radiation. WAXD profiles were recorded at room temperature with diffraction angles (2θ) which were from 5° to 60° . The data were collected for 6 s at angular intervals of $2\theta=0.1^\circ$.

RESULTS AND DISCUSSION

Characterization of PBT/MET

Both FT-IR and ¹H-NMR were used to confirm the molar composition and chemical structure of polymers. The FT-IR spectra show a strong absorption at 1728 cm^{-1} and $1204\text{--}1160 \text{ cm}^{-1}$, characteristics of C=O and C–O stretching vibration of the ester group, respectively. Meanwhile, the characteristic methyl group absorption bands are at 2962 cm^{-1} and 2854 cm^{-1} . The characteristic absorption bands of PBT also appear in the IR spectra of PBT/MET random copolyesters.

Representative ¹H-NMR spectrum of PBT/MET-4 is depicted in Figure 1. As shown in Figure 1, the molar ratio of 1,2-PDO and 1,4-BD is calculated according to the following equation:

$$N_{1,2\text{-PDO}} : N_{1,4\text{-BD}} = 4A_e : 3A_b$$

where A_e and A_b are the area for the protons from 1,2-PDO and 1,4-BD units, respectively. The compositions of the copolyesters determined from the data afforded by ¹H-NMR spectra are given in Table I.

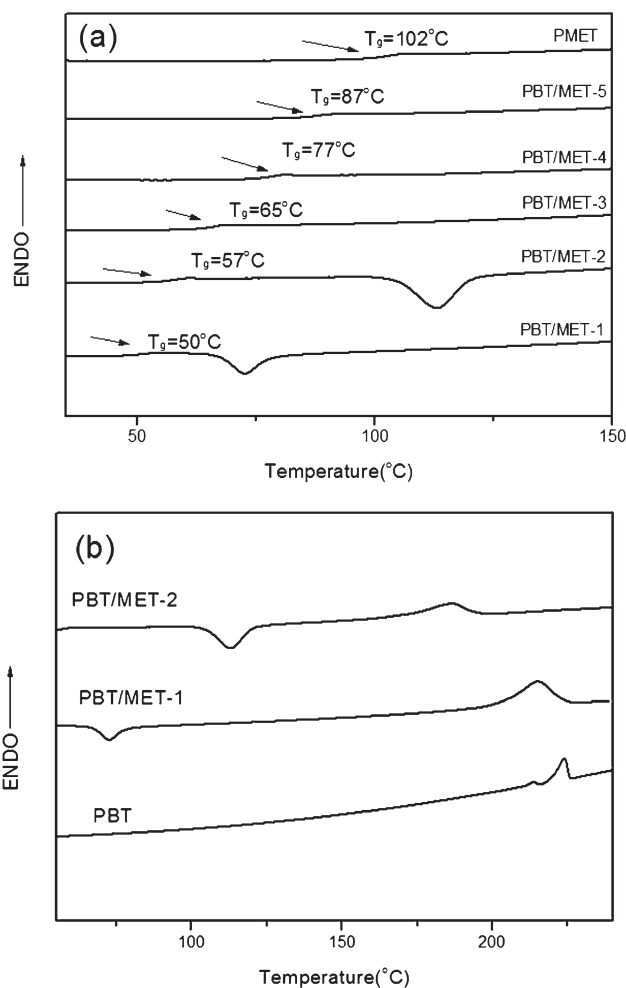


Figure 2 (a) Calorimetric curves of PBT/MET random copolyesters and PMET (heating rate = 20°C/min) in the glass transition range. (b) Calorimetric curves of PBT, PBT/MET-1, and PBT/MET-2.

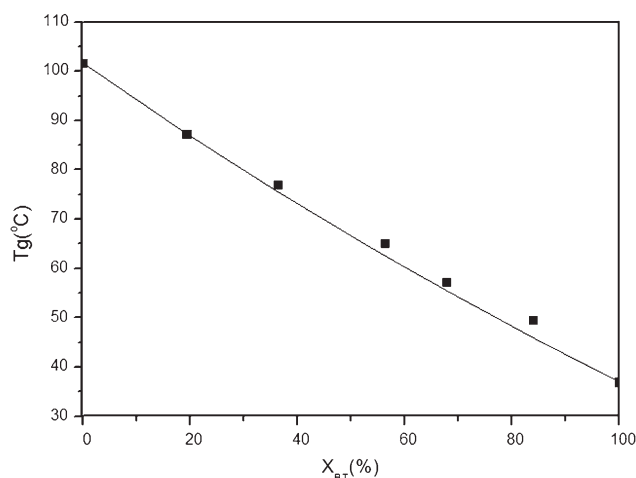


Figure 3 Composition dependence of T_g for PBT/MET random copolyesters. Solid line: theoretical curve of T_g vs. composition calculated on the basis of Wood equation.

The η_{inh} values of all copolyesters are listed in Table I. The viscosities are decreasing as the amount of MET units is increased, which may be attributed to the steric hindrance of lateral methyl group and instability of the secondary hydroxyl group of the 1,2-PDO. However, the intrinsic viscosity of the copolyesters is at least 0.48 dL/g.

Thermal and crystallization behavior of PBT/MET

It is well known that the previous thermal history plays an important role in the melting behavior of a polymer. Therefore, prior to thermal analysis, all the samples were annealed at 100°C for 24 h in an oven under vacuum to eliminate their previous thermal history. Typical calorimetric curves of such samples are collected in Figure 2(a,b), and the results are also collected in Table I. As a matter of fact, PBT cannot be easily frozen in an amorphous glassy state due to its high rate of crystallization.¹⁷ Thus, the glass transition phenomenon of pure PBT can never be experimentally observed with our cooling procedures.

As regards the calorimetric curves of pure PMET and PBT/MET-3, PBT/MET-4, PBT/MET-5 copolyesters, only an endothermal baseline deviation associated with the glass transition is observed. Therefore, the phase behavior of all copolyesters depends on composition, that is, when the amount of MET units is higher than 43.6 mol %, the polymers are completely amorphous, whereas the others are partially crystalline. The values of T_g as a function of BT unit content are plotted in Figure 3. As far as the trend of the T_g with the composition is concerned, it can be observed that the values of T_g increase as the amount of MET units is increased, which is responsible for the unsymmetrical lateral

methyl group deriving from MET units in the polymeric chains.

Among the various equations proposed to describe the composition dependence of the T_g of random copolyesters, the Wood one is widely used¹⁸:

$$T_g = (w_I T_{gI} + k w_{II} T_{gII}) / (w_I + k w_{II})$$

where k is a constant parameter and w_I and w_{II} are the respective weight fraction of butylene terephthalate units and 2-methyl-ethylene terephthalate units.

The equation fits well with the experimental data (with the adjustable parameter k equal to 0.999), using the T_g of PMET experimentally measured by us, and fixing for PBT the value of 37°C reported in literature.¹⁷ As shown in Figure 3, when the amount of MET units is less than 43.6 mol %, the experimental T_g data of PBT/MET polymers are in general higher than the predicted values, even though they follow the same trend, i.e. T_g values increase with an increasing amount of MET units. This may be attributed to the crystallites hindering the motion of the amorphous chains. Furthermore, the crystallites acting as physical crosslinking raise the T_g through their restrictive effect on the segmental motions of the amorphous polymer chains. The similar trend of T_g of PBT copolyesters was also observed by Lotti.^{19,20}

The T_m depression in a random copolymeric system can be expressed as a function of the composition as predicted by Flory,²¹ Baur,²² Sanchez and Eby,²³ Helfand and Lauritzen,²⁴ and others.^{25,26} In particular, when only one co-unit can crystallize, the second one being completely excluded from the crystals, the melting point reduction is commonly

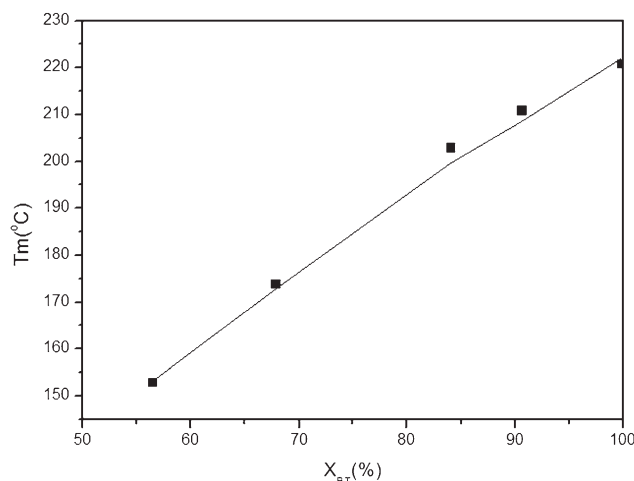


Figure 4 T_m as a function of composition for PBT/MET random copolyesters. Solid line: theoretical curve of T_m vs. composition calculated on the basis of Flory equation.

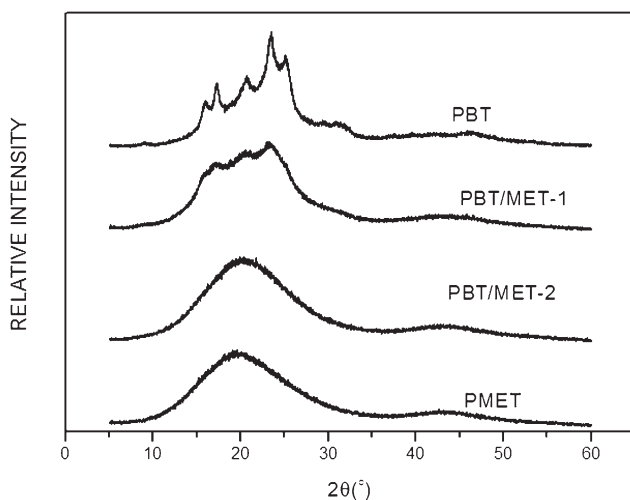


Figure 5 Wide-angle X-ray spectra of PBT, PMET, and some of PBT/MET random copolyesters.

examined using Flory's equation. Flory's treatment,²¹ commonly used in the past and derived assuming that the fusion concerns the disappearance of long sequences of crystallizable units, underestimates the melting point depression of random copolyesters. Flory's equation is as follows:

$$1/T_m - 1/T_m^0 = -(R/\Delta H_m^0) \ln \chi_c$$

where T_m is the melting temperature of a random copolymer with mole fraction X_c of the crystallizable comonomer C, T_m^0 and ΔH_m^0 are the equilibrium T_m and the heat of fusion of the completely crystalline homopolymer C (in this case PBT), and R is the universal gas constant, wherein, the T_m^0 and ΔH_m^0 values estimated on the basis of Flory's equation are found to be 227°C and 146J/g, respectively, which is in good agreement with Munari's previous works.^{19,27,28}

The experimental and the theoretical T_m of copolyesters were plotted as a function of BT unit content in Figure 4. As can be seen in Figure 4 and from the data collected in Table I, the T_m is markedly influenced by the amount of MET units in the chain. An increase in the amount of comonomer leads to a reduction of the T_m in samples subjected to the same thermal history. This behavior is typical of random copolyesters in which only on co-unit takes part in the crystallization process. Meanwhile, X-ray measurements carried out on PBT, PMET and some of the copolyesters can reasonably elucidate this phenomenon.

The X-ray diffraction patterns of PBT, PMET, and some of PBT/MET copolyesters are reported in Figure 5. PBT shows well-defined sets of crystalline diffraction peaks. On the contrary, when the amount of

MET units is higher than 32.2 mol %, PBT/MET copolyesters appear to be completely amorphous, similar to PMET homopolymer. The incorporation of MET unit which contains unsymmetrical lateral methyl group into the polymer backbone leads to an irregular chain structure and thereby inhibits regular chain packing for crystallization. These WAXD results have proved that the crystal phase which develops in the copolyesters is related to the lattice characteristic of the butylene terephthalate units.

Thermal stability of PBT/MET

Some typical weight-loss curves as a function of temperature carried out in nitrogen atmosphere are shown in Figure 6, and the data obtained for the whole set of copolyesters are compared in Table II. As can be seen from Figure 6 and Table II, the weight loss takes place practically in one step. The thermal stabilities of all copolyesters are quite comparable and they are practically stable up to 300°C. Furthermore, the thermal stability and the char residue of all samples depend on composition, being regularly lower as the amount of MET units is increased. This effect must be associated with the lateral methyl group which is unstable at a relatively high temperature. As a matter of fact, a detailed analysis of TGA curves in the 300–400°C range (see the window in Fig. 6) permits detection of a slight weight loss at low temperature.

CONCLUSION

PBT/MET random copolyesters containing different 1,2-PDO contents, in the complete range from PBT to PMET, were synthesized by traditional two-step polycondensation and studied in terms of molecular structure and thermal properties. DSC results

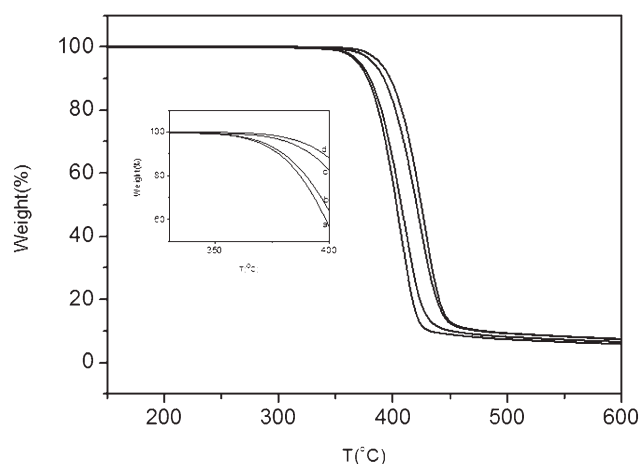


Figure 6 TGA curves in N_2 at 20°C/min: (a) PMET; (b) PBT/MET-5; (c) PBT/MET-3; (d) PBT.

TABLE II
TGA Data of PBT/MET Random Copolymers

Sample no.	T_d^a (°C)	Char at 600°C	T_{max} (°C)
PBT	393	7.42	431
PBT/MET-1	389	7.37	427
PBT/MET-2	382	7.03	422
PBT/MET-3	383	7.52	424
PBT/MET-4	376	6.57	413
PBT/MET-5	372	6.52	410
PMET	370	5.88	407

^a 5% Weight loss in N₂.

showed that T_g increased with increasing the content of MET units. On the contrary, T_m was found decreasing. The values of T_g and T_m are well subjected to the Wood's and Flory's equation, respectively. Moreover, the application of these equations is a further evidence of the random nature of the copolyesters under investigation, besides ¹H-NMR. As far as the thermal stability is concerned, it was found to be good and similar to that of PBT for all the copolyesters, but decreasing with increasing the content of MET units. The instability of lateral methyl group at relatively high temperature is the main reason.

At room temperature the appearances of these copolyesters change from semi-crystalline to transparent and become more brittle with increasing the content of MET units. When the samples contain from 16 to 32.2 mol % of MET units, T_m can be observed on DSC curves. However, when the samples containing up to 43.6 mol % of MET units appear as completely amorphous materials, which is consistent with the results obtained by X-ray measurements. Adjusting the composition of copolyesters is a potential approach toward the design of new PBT materials with a higher T_g and a better dimension stability.

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