

Poly(ethylene terephthalate) Copolymers That Contain 5-*tert*-Butylisophthalic Acid and 1-3/1-4-Cyclohexanedimethanol: Synthesis, Characterization, and Properties

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ABSTRACT: The effects of incorporating 5-*tert*-butylisophthalic acid (^tBI) and 1-3/1-4 cyclohexanedimethanol (CHDM) in the polymer chain of poly(ethylene terephthalate) (PET) on the crystallization behavior and thermal, optical and tensile properties of this polyester (PETGB) were evaluated. These random copolyesters that contained between 0 and 20 mol % of CHDM and between 0 and 10 mol % of ^tBI units were prepared by esterification followed by melt copolycondensation. The compositions and molecular weights of the copolyesters were determined by ¹H-NMR spectroscopy and viscometry, respectively. The composition of the polyester was consistent with the composition of the feed. The intrinsic viscosities of the copolymers ranged between 0.62 and 0.74 dL/g. The ther-

mal behaviors were investigated over the entire range of copolymer compositions, using DSC under the heating and cooling rate of 20°C/min and TGA. The copolyesters with ^tBI and CHDM of < 20 mol % were crystallizable, whereas the copolyesters with ^tBI and CHDM of ≥ 20 mol % were amorphous. They appeared to be stable up to 395°C. The optical transmissions of the amorphous polyesters were more than 88% in the visible region. The mechanical behavior was investigated by performing a tensile test. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 279–285, 2007

Key words: polyesters; copolymerization; amorphous; transparency; crystallization

INTRODUCTION

The favorable basic properties of poly(ethylene terephthalate) (PET) make this polymer attractive for an increasing variety of domestic and technical applications. Nevertheless, the tendency of PET to crystallize is a severe limitation on the expansion of uses of this polymer to new fields in which thicker transparent pieces are required. Particularly, thermal crystallization is generally undesirable because it reduces clarity and can occur during various stages of container manufacturing, such as perform cooling following injection molding, or perform heating prior to stretch blow molding.^{1–4}

Copolymerization using small amounts of a second glycol or diacid comonomer is frequently used to diminish the crystallinity and crystallization rate, and to modify the thermal properties of PET.^{5–8} The purpose is to introduce into the polymer a certain amount of

chain defects that can reduce molecular mobility and crystal packing without significantly altering the general behavior of the parent homopolymer. Due to its good commercial accessibility, the utilization of isophthalic acid as the second acidic comonomer has been extensively investigated to reduce the tendency of PET to crystallize.^{9–15} However, PET copolymers containing isophthalic acid have a glass-transition temperature (T_g) that is lower than that of PET, which constitutes a serious shortcoming of these copolyesters. The utilization of isophthalic acid with bulky side groups that enhance chain stiffness is considered to be a valuable alternative.^{16–19} Thus, enhancement of T_g of a wide variety of polycondensates, including polyamides and polyesters, by 5-*tert*-butylisophthalic units (^tBI) has been reported.^{8,9} Furthermore, a series of PET-related copolyesters prepared from ethylene glycol, terephthalic acid, and 5-*tert*-butylisophthalic acid has been claimed to exhibit a reduced tendency to crystallize and to have a higher T_g than PET.^{20,21} The effects of the ^tBI group on crystallization and thermal properties are concluded to be the same in all cases and these effects are determined to arise from changes in intermolecular and intramolecular interactions caused by the bulkiness of this group.

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1-3/1-4 cyclohexanedimethanol (CHDM) has been proven to be an extremely valuable diol in commercial polyesters.²² It has found large-volume use in PET container resins. The incorporation in low-level CHDM (<5 mol %) into PET is important in the development of PET for container applications. Replacing some of the ethylene glycol with secondary glycols slows the crystallization of the polyester. CHDM-modified PET copolyester (PETG) can be obtained by adding a sufficient amount of CHDM. This material is industrially used as an amorphous copolyester, which cannot crystallize. PETG offers a broader range of processing parameters than normal crystallizable polymers and is particularly useful for high-clarity amorphous molding.

The formulation of copolymers based on more than two comonomers is attracting interest as an approach for adjusting properties with high accuracy. Therefore, PET copolymers that contain isophthalic acid and cyclohexanedimethanol units are produced for new packaging applications.^{23,24} This study reports the preparation and properties of copolymers prepared from ethylene glycol, terephthalic acid, 1-3/1-4 cyclohexanedimethanol, and 5-*tert*-butylisophthalic acid, called PETGB. The thermal, optical, and mechanical properties of the new copolymers are examined.

EXPERIMENTAL

Materials

Terephthalic acid (TPA) (98%), ethylene glycol (EG) (99%+), cobalt acetate catalyst ($\text{Co}(\text{OAc})_2$), antimony acetate (99.99%) catalyst ($\text{Sb}(\text{OAc})_3$), and 5-*tert*-butylisophthalic acid (BI) (98%) were purchased from Aldrich (USA). 1-3/1-4 cyclohexanedimethanol (CHDM), which was an equilibrium mixture of 1,4-*trans*/1,4-*cis*/1,3-*trans*/1,3-*cis* 29.1/13.3/30.9/26.7, was purchased from Dow Chemical Company, USA. All chemicals were used as received without further purification. Solvents used for characterization, such as trifluoroacetic acid (TFA), phenol, and tetrachloroethane, were all either technical grade or high-purity grade, and were used as received.

Synthesis

All of the copolymers were prepared by two-stage melt polycondensation (esterification and polycondensation) in an autoclave reactor, and the details of the synthesis were described in the previous literature.^{15,18} In each preparation, the reaction mixture comprised excess EG, various amounts of diol and diacid (molar ratio of diol/diacid = 1.4), 350 ppm $\text{Sb}(\text{OAc})_3$, and 90 ppm $\text{Co}(\text{OAc})_2$ by weight. The reaction mixture was heated to the final temperature of 280°C in an atmosphere of nitrogen and stirred at a constant speed (500 rpm). This

first step (esterification) was considered to be completed after 4 h, when the theoretical amount of water (36.0 mL) was collected.

In the second step (polycondensation), a vacuum (5 Torr) was applied slowly over a period of about 30 min, to avoid excessive foaming and to minimize oligomer sublimation, which is a potential problem during the melt polycondensation. The temperature was increased simultaneously such that full vacuum was achieved at 30 min. The polycondensation was continued for about 2.5 h until the agitator speed decreased to 350 rpm. After the polycondensation reaction was completed, the product was obtained from the autoclave reactor. All white polyester samples were ground in a mill, sieved, washed with methanol, and dried at 60°C for 24 h at reduced pressure.

Characterization

The intrinsic viscosities of the polymers were measured using an Ubbelohde viscometer at 25°C in a mixture of phenol and tetrachloroethane (60 : 40, w/w).^{15,18} ¹H-NMR spectra were recorded on a Bruker DRX-400 spectrometer at 25°C and 400 MHz. Copolymers were dissolved in deuterated trifluoroacetic acid (TFA) and spectra were internally referenced to tetramethylsilane (TMS). Ten milligrams of sample was dissolved in 1 mL of deuterated solvent and used for ¹H. Sixty-four scans were acquired for ¹H with 32 K data points, with relaxation delays of 1 s.

Thermal characterization was performed in an atmosphere of dry nitrogen using a differential scanning calorimeter (DSC) (Seiko SSC-5200). Both temperature and heat flow were calibrated using indium and tin standards. In the DSC measurement, a polymer sample (3.0–5.0 mg) was preheated at 300°C for 10 min to remove its thermal history, and then cooled to 0°C at a rate of 20°C/min. Subsequently, the cooled sample was again heated to 300°C at a rate of 20°C/min. The melting temperature (T_m) and crystallization temperature (T_c) were chosen as the temperatures of the peak maximum transition measured in the heating run and the cooling run. T_g was chosen as the temperature at the middle point of the glass transition in the heating run. Thermogravimetric analysis (TGA) was carried out using a Seiko Exstar 6000 thermobalance at a heating rate of 20°C/min in an atmosphere of nitrogen.

The samples for X-ray analyses, UV ray transmittance tests, and tensile tests were prepared from the glassy, unoriented, amorphous powder or film, which were obtained by melt compression followed by immersion into ice-cold water.¹⁶ X-ray analyses were performed using a Siemens D-500 diffractometer with $\text{K}\alpha\text{-Cu}$ radiation at a wavelength of 1.5418 Å. The UV ray transmittance of the polyesters was measured on

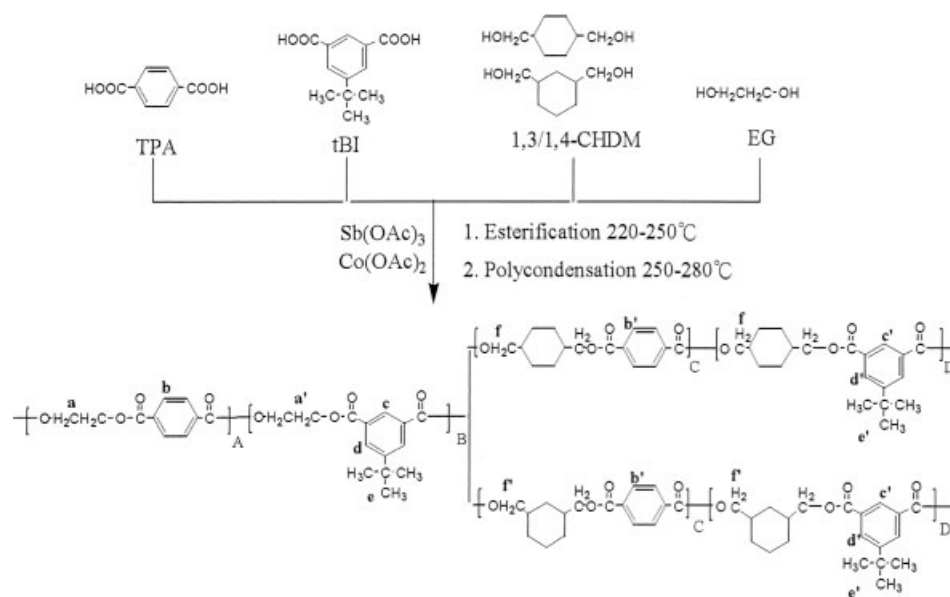


Figure 1 Outline of synthetic route followed for the preparation of PETGB copolyesters examined in this study. NMR assignments are indicated on the chemical formula of the copolymer.

a UV1000F ultraviolet spectrophotometer to characterize the UV radiation transmittance of the polyesters. Tensile testing was performed on rectangular specimens (55 × 5 mm) cut from amorphous, isotropic films with a thickness of about 200 μm. The tensile tests were conducted at room temperature on a Zwick BZ2.5/TN1S universal tensile testing apparatus operated at a constant crosshead speed of 10 mm/min with a 0.5 N preload and a grip-to-grip separation of

20 mm. All reported tensile data represented averages of at least six independent measurements.

RESULTS AND DISCUSSION

Synthesis

The PETGB copolyesters described in this work were prepared by a two-step melt-polycondensation, as indicated in Figure 1. TPA and ^tBI with EG and

TABLE I
Compositions, Viscosities, and Thermal Properties of Polyesters

Polyester	Composition ^a	Composition ^b	Viscosity ^c IV (dL/g)	Thermal properties				
	TPA/ ^t BI/EG/ CHDM (mole %)	TPA/ ^t BI/EG/ CHDM (mole %)		T_g^d (°C)	T_m^e (°C)	T_{ch}^e (°C)	T_{cc}^e (°C)	T_d^f (°C)
PET	100/0/100/0	100/0/100/0	0.74	78	254	142	183	414
PETB ₅	95/5/100/0	95.2/4.8/100/0	0.62	78	231	171	–	411
PETB ₁₀	90/10/100/0	90.2/9.8/100/0	0.70	80	221	–	–	411
PETG ₅	100/0/95/5	100/0/95.3/4.7	0.64	75	230	169	–	406
PETG ₅ B ₅	95/5/95/5	95.2/4.8/95.4/4.6	0.68	77	222	120	–	408
PETG ₅ B ₁₀	90/10/95/5	90.3/9.7/95.4/4.6	0.72	80	207	–	–	412
PETG ₁₀	100/0/90/10	100/0/90.4/9.6	0.67	76	221	–	–	404
PETG ₁₀ B ₅	95/5/90/10	95.1/4.9/90.5/9.5	0.68	78	212	–	–	409
PETG ₁₀ B ₁₀	90/10/90/10	90.2/9.8/90.4/9.6	0.65	79	–	–	–	411
PETG ₁₅	100/0/85/15	100/0/85.3/14.7	0.69	76	207	–	–	402
PETG ₁₅ B ₅	95/5/85/15	95.2/4.8/85.4/14.6	0.64	78	–	–	–	408
PETG ₁₅ B ₁₀	90/10/85/15	90.1/9.9/85.5/14.5	0.67	80	–	–	–	410
PETG ₂₀	100/0/80/20	100/0/80.6/19.4	0.65	76	196	–	–	399
PETG ₂₀ B ₅	95/5/80/20	95.2/4.8/80.7/19.3	0.66	79	–	–	–	404
PETG ₂₀ B ₁₀	90/10/80/20	90.2/9.8/80.6/19.4	0.64	80	–	–	–	408

^a Molar ratio in the initial feed.

^b Determined from ¹H NMR spectra.

^c Intrinsic viscosity (dL/g) measured at 25°C in a phenol/tetrachloroethane mixture 60/40 (w/w).

^d T_g was taken as the inflection point of the heating DSC traces of the melt-quenched samples recorded at 20 °C/min.

^e T_m and T_c of the pristine samples were measured by DSC at heating/cooling rates of 20°C/min.

^f Temperature at which a 10% weight loss was observed in the TGA traces recorded at 20 °C/min.

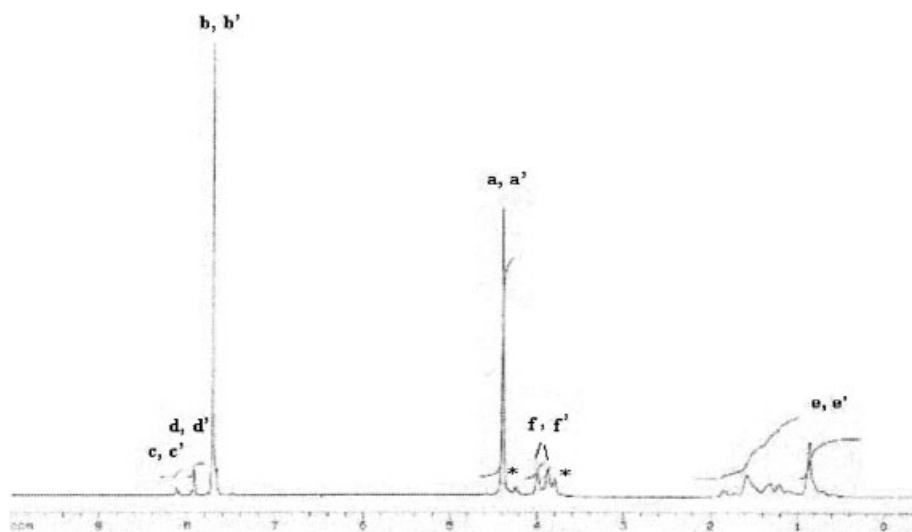


Figure 2 400 MHz $^1\text{H-NMR}$ spectra of $\text{PETG}_{20}\text{B}_{10}$ recorded in deuterated trifluoroacetic acid (TFA). Peaks that arise from diethylene glycol units, present in small amounts in the polyesters, are labeled (*).

CHDM were esterified to form low-molecular-weight hydroxy-capped esters in the first stage. This process occurred at 220–250°C with the generation of water, which was continuously removed from the system to drive the reaction in the desired direction. Copolycondensation of these compounds, leading to PETGB copolyesters, proceeded in the second step at 280°C and under vacuum conditions to eliminate the excess EG. Table I lists all of the polyesters examined in this work. The compositions, viscosities, thermal properties and feed comonomer contents in each case are presented. The TPA/ ^tBI /EG/CHDM molar ratios in the feed ranging from 100/0/100/0 to 90/10/80/20 covered a wide range of compositions. The determination of the intrinsic viscosity indicated that the compositions had relatively high molecular weights, given that their intrinsic viscosities were between 0.62 and 0.74 dL/g. The decrease of viscosities of other copolyesters in comparison of PET might cause from the lower reactivities of ^tBI and CHDM than TPA and EG. However, all samples had intrinsic viscosities higher than 0.6, which was consistent with the previous literature.¹⁸ The chemical structures of the polyesters were ascertained by $^1\text{H-NMR}$ spectroscopy. The spectra of those copolymers indicated clear differences in the chemical shifts of the signals from ^tBI and CHDM. These differences could be used to estimate the composition of the copolymer and to determine the microstructure of the chain, as shown in Figures 1 and 2. Figure 2 presents the $^1\text{H-NMR}$ spectra of the $\text{PETG}_{20}\text{B}_{10}$ copolymer with the assigned chemical shift indicated. Table I presents the compositions of the copolymers in the ^tBI and CHDM units determined from the $^1\text{H-NMR}$ spectra. The NMR analysis clearly indicated that the composition of the resulting copolymer was essentially the same as that of the feed from which it was generated.

Thermal properties

The thermal behavior of PETGB copolyesters was examined by TGA and DSC. Table I summarizes the characteristic parameters obtained from these measurements. Figure 3 presents DSC traces for polyesters PET, poly(ethylene terephthalate-co-5-*tert*-butylisophthalate (PETB), PETG, and PETGB during the heating and cooling process, both at a rate of 20°C/min. Introducing ^tBI and CHDM into the PET homopolymer significantly influenced both the melting temperature and the crystallinity of the copolyesters. Copolyesters that contained <20 mol % ^tBI and CHDM were crystallizable, whereas the copolyesters with ≥ 20 mol % ^tBI and CHDM were amorphous. Both melting temperature and crystallinity decreased steadily with copolymerization in two systems. This decrease was attributed to the increase in the population of defects in the crystals. The introduction of the noncrystallizing comonomer units into the crystal structure causes the formation of defects that increase the crystal surface energy and reduce the melting point of the crystals.²⁵ Although no T_m was observed in the samples ($\text{PETG}_{10}\text{B}_{10}$, $\text{PETG}_{15}\text{B}_5$, $\text{PETG}_{15}\text{B}_{10}$, $\text{PETG}_{20}\text{B}_5$, $\text{PETG}_{20}\text{B}_{10}$) in DSC experiments under the rate of 20°C/min, they might become crystalline at a lower heating or cooling rate. It is interesting for the further study including crystallization kinetics and properties for these polymers in the future.

The incorporation of the isophthalic units into PET causes a steady decrease in the T_g of PET.^{9–15} This trend is reversed, however, when the isophthalic units are replaced by ^tBI units.^{16–19} The variation of the T_g with the content of ^tBI unit along the five series (CHDM contents = 0, 5, 10, 15, and 20%) is compared in Table I, revealing that a nearly linear trend is followed in every case. DSC analysis revealed that the T_g increased

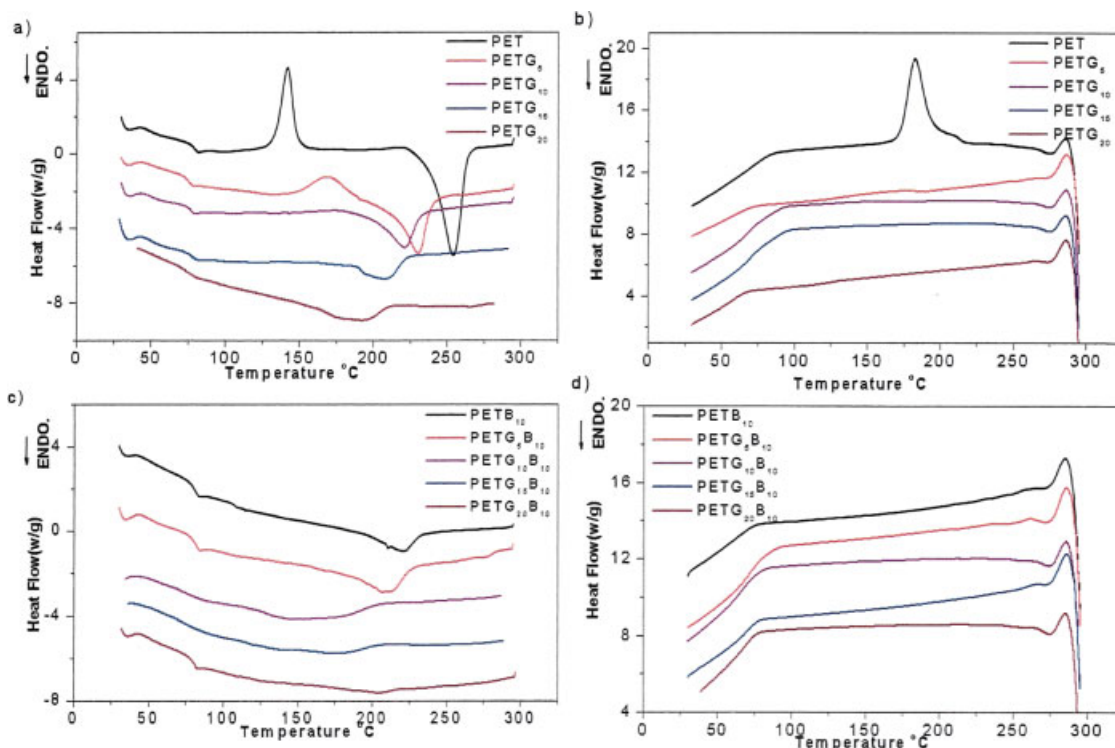


Figure 3 Top: Comparison of DSC traces for polyesters PET and copolyesters PETG: (a) second heating, (b) first cooling. Bottom: Comparison of DSC traces for polyesters PETB and copolyesters PETGB: (c) second heating, (d) first cooling. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

slightly and steadily along the series with the content of ^tBI units. Because the content of ^tBI in the copolymer was <20% in this work and the T_g of poly(ethylene 5-*tert*-butylisophthalate) was reported about 99°C only, the contribution of ^tBI units for increasing T_g of the final copolymer was limited.^{16–18} However, when the polyester contained 10 mol % ^tBI, the T_g of the polyester was 3–4°C higher than that of the polyester without added ^tBI. Such a change in the T_g with copolymerization is exactly the same as that observed for PET

copolymers that contain ^tBI units.^{16–19} These results are evidence of the exceptional ability of the ^tBI unit to restrict the chain mobility.

The incorporation of the CHDM in PET slightly lowered the T_g of the polyesters from 78 to 76°C, perhaps because the CHDM monomer contained 1,3-*cis* and 1,3-*trans* structures, which were similar to those of the IPA monomer in PETI (poly(ethylene terephthalate-*co*-

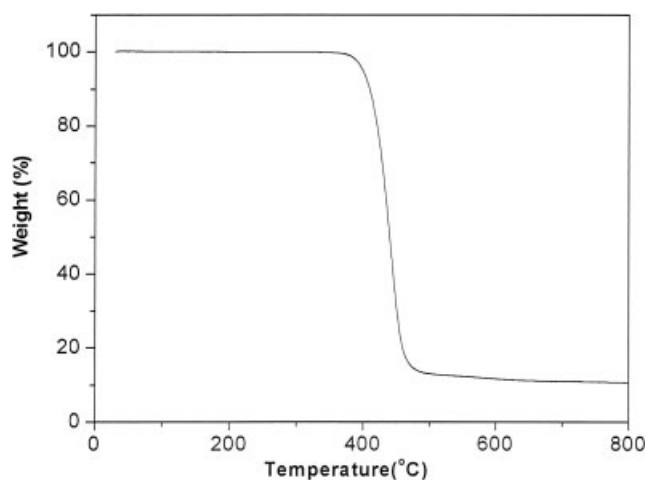


Figure 4 TGA trace of PETG₂₀B₁₀.

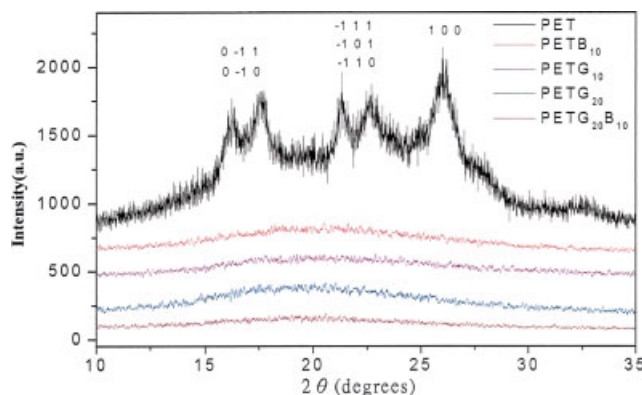


Figure 5 Powder X-ray diffraction profiles of crystalline polyesters and copolyesters, with the indicated compositions. Indexing based on the triclinic structure of PET: $a_0 = 4.56 \text{ \AA}$, $b_0 = 5.94 \text{ \AA}$, $c_0 = 10.75 \text{ \AA}$, $\alpha = 98.5^\circ$, $\beta = 118^\circ$, and $\gamma = 112^\circ$.²⁶ [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Optical Transmittance and Tensile Mechanical Properties of Polyesters

Polyester	Transmittance for $\lambda = 400$ nm (%)	Young's modulus (Mpa)	Yield stress (Mpa)	Tensile strength at break (Mpa)	Elongation at break (%)	Type ^a
PET	80.0	2297	65	50	173	HT
PETB ₁₀	86.3	2053	55	43	163	HT
PETG ₁₀	87.2	1821	57	42	162	HT
PETG ₂₀	88.4	2027	52	38	152	HT
PETG ₂₀ B ₁₀	88.7	1854	46	32	108	HT

^a HT, hard and tough.

isophthalate).^{9–15} Table I shows how T_g varies as the content of CHDM increases (PET, PETG₅, PETG₁₀, PETG₁₅, and PETG₂₀).

TGA measurements were made in an atmosphere of nitrogen in the 30–800°C temperature range, to evaluate the thermal stability of the polyesters. Data obtained from these measurements are collected in Table I and show that the incorporation of ^tBI units increases slightly the thermal stability of PET. This effect must be associated with the mere presence of *tert*-butyl structures in the polyester chain, because a similar increase in the decomposition temperature of PETB is also observed.^{16–18} However, the thermal stability of the polyesters was slightly reduced as CHDM content increased. Nevertheless, all polymers remained unaltered as the temperature was increased to 380°C. The maximum degradation rate was between 430 and 450°C. Figure 4 presents the TGA trace of PETG₂₀B₁₀. Table I compares the decomposition temperatures measured at 10% weight loss for the whole set of polyesters.

X-ray diffraction

Figure 5 compares the intensity profiles of the X rays scattered in reflection mode by powder pristine samples of the copolyesters examined in this work. All samples were prepared as amorphous materials by melt compression followed by immersion into ice-cold water. Although the PET sample was prepared as an amorphous material, it still showed high-intensity reflections in X-ray analysis. Three high-intensity reflections that were characteristic of the triclinic structure of PET appeared with 2θ values of around 17.0°, 22.8°, and 26.2°.²⁶ These results indicated that the PET sample had a higher crystallization rate than others. The polyesters of PETB₁₀, PETG₁₀, PETG₂₀ had no clear peaks in the X-ray analysis, but they had T_m without observation of T_{cc} (crystallization temperature on cooling) or T_{ch} (crystallization temperature on heating) in the DSC analysis. Perhaps those copolyesters had a low crystallization rate, so crystalline regions were not formed during sample preparations. Furthermore, the polyester of PETG₂₀B₁₀ had no peak in the X-ray spectrum and had no observation of T_m , T_{cc} , or T_{ch} in DSC analysis. It is a fully amorphous polyester.

Tensile and optical properties

The method usually used to evaluate the optical property of polyesters is to measure the transmittance of UV-visible rays through the polyesters. A higher UV-ray transmittance corresponds to a better optical property of that sample. Table II presents the specular light transmission values for $\lambda = 400$ nm. Figure 6 presents spectrograms of the samples. The transmittance of PET for $\lambda = 400$ nm was 80%. The optical transmittance increased with ^tBI and CHDM. The optical transmissions of the amorphous polyesters (PETG₂₀B₁₀) exceeded 88% in the visible region.

Tensile data, such as Young's modulus, yield stress, tensile strength at break, and elongation at break, were determined for amorphous, nonoriented PET and selective PETGB copolyester samples. Figure 7 plots the stress–strain traces of PETGB copolymers, and Table II presents the numerical results. Samples PET, PETB₁₀, PETG₁₀, PETG₂₀ showed cold crystallization during deformation, since they were crystallizable polymers and prepared as amorphous materials before the tensile test. However, the sample PETG₂₀B₁₀ did not have cold crystallization phenomenon, which indicated that this polymer was amorphous and consistent with DSC and X-ray results. The elongation at break and the maximum tensile stress decreased significantly as the content of any of the ^tBI and CHDM comonomers increased, perhaps because the crystallizable polymer

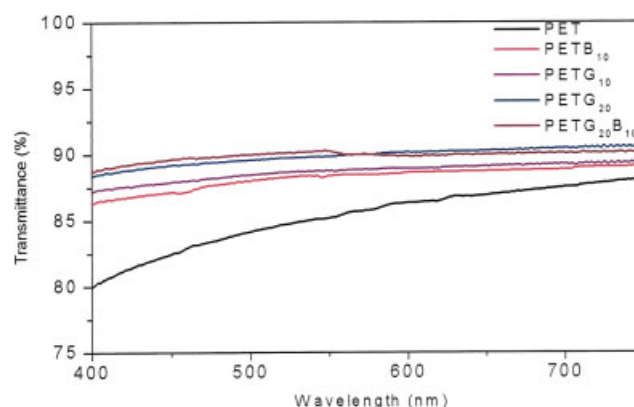


Figure 6 Optical transmittance of polyesters PET, PETB, PETG, and PETGB. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

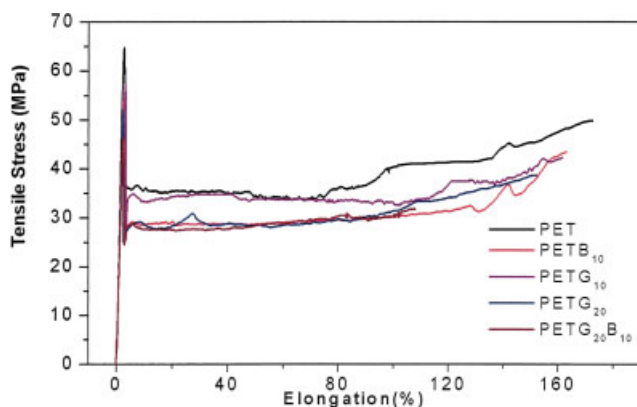


Figure 7 Typical stress–strain plots of polyester copolymers with the indicated compositions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

had a highly regular crystal array that contributes to high tensile stress. Among these samples, PET had a more deformability and higher tensile properties than the other copolyesters. In addition to the induced crystalline structure of PET, the higher molecular weight of PET than other samples might contribute this observation.

CONCLUSIONS

Novel PET copolyesters that contain various amounts of ^tBI and CHDM units are described in this manuscript. These copolyesters were successfully synthesized by esterification followed by melt copolycondensation. The composition of the copolymer was determined by ¹HNMR and was found very close to that of the feed. The melting temperatures of the copolymers decreased as the amounts of ^tBI and CHDM units increased. The copolyesters that contained <20 mol % ^tBI and CHDM were crystallizable, whereas those that contained ≥20 mol % with ^tBI and CHDM were amorphous. DSC analysis revealed that T_g increases steadily along the series with the ^tBI unit content. The possibility of tuning the crystallizability of these copolymers by adjusting the composition may be amenable to exploitation in the design of new

PET materials with a better balance among thermal, mechanical and optical properties.

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