

Synthesis of Hexafluoroisopropylidene Isophthalic Polyesters and Copolyesters and the Relationship Between Their Structure and Gas Transport Properties

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ABSTRACT: Two aromatic polyesters and three copolyesters were synthesized by interfacial polycondensation using 4,4'-(hexafluoroisopropylidene)diphenol (HFD) and two phthalic dichlorides, isophthaloyl dichloride (ISO) and 5-tertbutyl-isophthaloyl dichloride (TERT). The polymers obtained were soluble in common chlorinated solvents. The properties of these aromatic polyesters and copolyesters were characterized by FTIR, density, inherent viscosity, TGA, and DSC. Thermal properties such as glass transition temperature, onset of decomposition, and thermal stability of the homopolymer, poly(hexafluoroisopropylidene)5-tertbutylisophthalate (HFD/TERT), were higher than those of homopolymer poly(hexafluoroisopropylidene)isophthalate (HFD/ISO). Thermal properties of the copolyesters HFD/TERT-co-HFD/ISO depend upon the amounts of the tertbutyl group HFD/TERT, present in the copolymer. Gas permeability coefficients of all polyarylates were measured at

35°C. The effect of different concentrations of the bulky tertbutyl group at the 5-position in the isophthaloyl moiety on He, O₂, N₂, and CO₂ permeability, diffusion, and solubility coefficients were determined. Gas permeability and diffusivity increase as the concentration of TERT moiety increases in the copolymers. The results indicate that polymers containing the largest amounts of the bulky lateral tertbutyl group show the highest gas permeability. The increment in gas permeability and diffusivity produces a decrease in selectivity, which is attributed to the effect of the large pendant tertbutyl groups in the aromatic polyesters and copolyesters, which decrease the chain packing efficiency and induce a larger fractional free volume. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2207–2216, 2007

Key words: gas permeation; polyesters; copolymerization; diffusion; fluoropolymers

INTRODUCTION

The use of membranes for gas separation is one of the most significant separation processes that has emerged in the chemical industry in the last 35 years.¹ The economical separation of gases by this procedure is competitive with traditional gas separation technologies such as cryogenic distillation, adsorption, and pressure swing adsorption.² Different polymeric materials have been used as gas separation membranes in several applications such as the recovery of hydrogen from the product stream of ammonia syntheses, the removal of helium from natural gas, the production of high purity nitrogen or oxygen enrichment from air.^{2–4}

Membrane materials and membrane structure govern the separation performance of a polymeric membrane used in a given gas separation process, while the inherent separation properties of a polymeric material are determined by its chemical composition and chain structure.² The ideal polymeric materials for membranes

used for gas separation should possess high gas permeability and high selectivity for gas separation as well as high mechanical and thermal stability.^{2,5–7} Typically, there is a so-called “trade-off” between permeability and selectivity in polymeric materials. Materials exhibiting higher gas permeability usually show lower selectivity.^{2,7,8} Further progress in this technology requires the development of new polymer membranes that exhibit both properties: high gas permeability and selectivity. A large number of publications and patents on the synthesis, structure, and gas transport properties of polymeric materials have appeared over the past decades. Special attention has been focused on the development of polymers with high glass transition temperature, such as polyaramides,^{6,9–11} polyarylates,^{7,12,13} polysulfones,^{3,8} polyimides,^{2,14} and poly(aryl ethers),^{5,15} which should lead to a new generation of gas separation membrane materials.

Previous studies^{5,9–11,16} have demonstrated that both permeability and selectivity may be enhanced by incorporation of a tertiary butyl pendant group in glassy polymer membranes because this group simultaneously decreases chain packing efficiency, which in turn increases polymer fractional free volume (FFV) available for gas permeation, and hinders torsional

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mobility. As a result, the tertiary butyl group diminishes chain packing efficiency, which may improve permeability, while the reduction in torsional mobility may improve selectivity. This is the case for the polyarylates based on 4,4'-(hexafluoroisopropylidene) diphenol, (HFD) reported elsewhere.⁷

The preparation of copolyesters based on the above-mentioned polyarylates offers the possibility of obtaining membranes with gas permeabilities and gas separation selectivity that are not available with the homopolyesters. Therefore, one may be able to tailor their physical and gas separation properties by careful control of comonomer ratio in such a way that it could be suitable to be used in a given application.

Here we report the synthesis, characterization, and gas transport properties of the polyesters synthesized from HFD poly(hexafluoroisopropylidene)-5-tertbutylisophthalate, HFD/TERT, and poly(hexafluoroisopropylidene)isophthalate, HFD/ISO. The synthesis will be carried out by interfacial polymerization, which is a faster polymerization method than solution polymerization and it requires milder conditions. We also report the preparation and characterization for the same properties in copolyesters, HFD/TERT-co-HFD/ISO synthesized with different

concentrations of the HFD/TERT moiety which bears a bulky lateral tertbutyl group. It is expected that the copolymerization process will allow the control of physical and gas transport properties. The results of this study may provide the knowledge to design materials with controlled specific physical properties, gas permeability and permselectivity, by adjusting the monomer ratio in a random copolyester system such as the one described here.

EXPERIMENTAL

Materials

The monomers used for the synthesis of aromatic polyesters and copolyesters are shown in Table I. The 4,4'-(hexafluoroisopropylidene)diphenol (HFD) was purified by vacuum sublimation. Isophthaloyl dichloride (ISO) was purified by vacuum distillation. 5-Tertbutylisophthaloyl dichloride (TERT) was synthesized by reacting 5-tertbutylisophthalic acid with thionyl chloride under reflux as reported in the monomer synthesis section later. Benzyltriphenyl phosphonium chloride (BTPC, Aldrich) was used as an interfacial catalyst. The reactants thionyl chloride

TABLE I
Reactants Used in the Synthesis of Aromatic Polyesters and Copolyesters

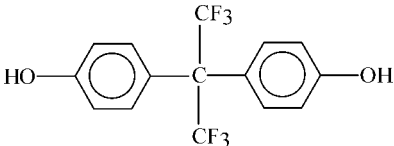
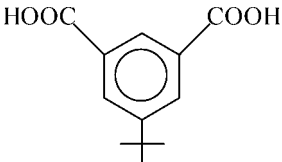
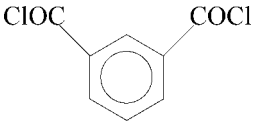
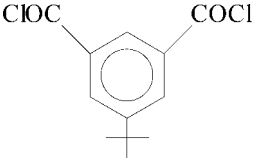
	Structure	Source	Purity
Diol 4,4'-(Hexafluoroisopropylidene)diphenol (HFD)		Aldrich Chemical Corp.	97%
Diacid 5-Tertbutylisophthalic		Aldrich Chemical Corp.	98%
Dichloride Isophthaloyl dichloride (ISO)		Aldrich Chemical Corp.	98%
5-Tertbutylisophthaloyl dichloride (TERT)		Prepared from thionyl chloride	99%

TABLE II
Polyester and Copolyester Formulations Used in the Interfacial Polycondensation Reactions

Polymer	Dichloride		
	Diol HFD (mmol)	TERT (mmol)	ISO (mmol)
HFD/TERT	10	10	0
HFD/TERT75	10	7.5	2.5
HFD/TERT50	10	5.0	5.0
HFD/TERT25	10	2.5	7.5
HFD/ISO	10	0	10

(Baker), pyridine (Aldrich), petroleum ether (Baker), methanol (Química Monterrey), 1,2-dichloroethane (DCE; Aldrich), chloroform (CHCl₃; Baker), and sodium hydroxide (Química Monterrey) were used as received.

Monomer synthesis

TERT was obtained from 5-tertbutylisophthalic acid by chlorination, using thionyl chloride and pyridine. The monomer was obtained following a procedure outlined elsewhere.^{7,17} A typical synthesis procedure used here is as follows. In a 250 mL round bottom flask equipped with a condenser, 0.05 mol of 5-tertbutylisophthalic acid and 0.25 mol of thionyl chloride were added. The solution was stirred at room temperature, and a few drops of pyridine (0.3 mL) were added. The reaction was refluxed at 76°C for about 4 h until the resultant solution turned completely clear. After, removal of the excess thionyl chloride by distillation, the crude product was recrystallized from petroleum ether and then purified by vacuum distillation.

Polyester and copolyester polymerization

The polyesters and copolyesters described in this study were synthesized via interfacial polycondensation as described by Morgan.¹⁸ Copolyester synthesis was performed with three different molar concentrations of the dichlorides ISO and TERT as described in Table II. The aromatic polyesters synthesized from ISO or TERT and HFD are designated poly(hexafluoroisopropylidene)isophthalate, HFD/ISO, and poly(hexafluoroisopropylidene)5-tertbutylisophthalate, HFD/TERT respectively. The copolyesters HFD/TERT75, HFD/TERT50, and HFD/TERT25 correspond to copolymers that were synthesized with 75, 50, and 25 mol % of TERT respectively.

The polymerization reactions were carried out in a 250-mL three-neck European-type flask equipped with a mechanical stirrer under nitrogen atmosphere. A schematic reaction for this synthesis is given in Figure 1.

In a typical copolymerization reaction, HFD/TERT50, HFD (0.01 mol) was dissolved in an aqueous sodium hydroxide solution (0.02 mol of NaOH)

prepared with 100 mL of deionized water. The solution was stirred until the diol dissolved completely. After that, BTPC (2 wt %), with respect to the expected final weight of polymer, was added in the reaction system until it dissolved completely. At this point, a mixture of TERT and ISO (0.005 mol each) in 30 mL of DCE was added to the resultant solution and the mixture was stirred vigorously. The copolymer was produced in the organic phase that quickly increased its viscosity to form a gel. After, a reaction period of 1 h at room temperature, the aqueous phase was separated from the organic phase, and the organic phase was dispersed in 50 mL of CHCl₃ to reduce its viscosity. Finally, the copolymer was precipitated in methanol by stirring vigorously using a Waring laboratory blender. The copolymer was collected by filtration and then washed several times with methanol. The copolyester as obtained was dried in a vacuum oven at 100°C for 24 h. All aromatic polyesters and copolyesters were prepared by the same procedure.

Aromatic polyester and copolyester films were prepared by solution casting from solutions containing 0.5 g of the polymer dissolved in 10 mL of CHCl₃. These solutions were poured into aluminum rings on the surface of a glass plate and maintained under CHCl₃ atmosphere. The films obtained were vacuum dried at 100°C for 24 h. A second drying step was performed at 160°C for 24 h, to make sure that all the solvent was eliminated from the films.

Characterization

Infrared spectra were obtained using a Fourier transform infrared spectrometer, FTIR Nicolet Protégé 460. Dilute CHCl₃ solutions of each polymer were placed onto a KBr disk and then dried at 100°C to obtain a thin film. The spectra were recorded in the range between 4000 and 400 cm⁻¹ with a 4 cm⁻¹ resolution and averaging 100 scans. The solubility of each polyester and copolyester was tested in differ-

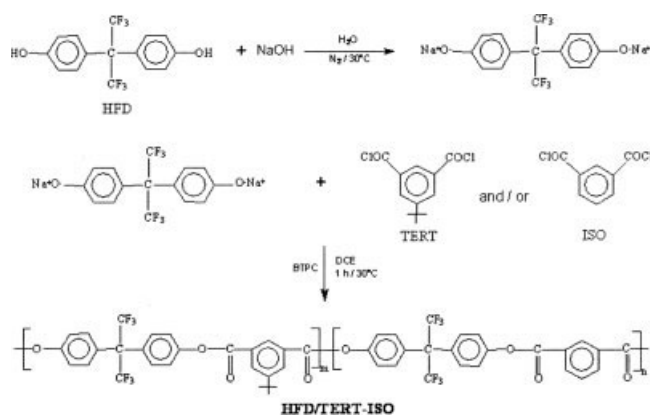


Figure 1 Schematic reaction for synthesis of aromatic polyesters and copolyesters by interfacial polycondensation.

ent solvents using 0.1 g of the polymer in 5 mL of solvent. CHCl₃, DCE, 1,1,2,2-tetrachloroethane (TCE), tetrahydrofuran (THF), dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidone (NMP) were used.

Wide-angle X-ray diffraction (WAXD) scattering measurements of the polyester and copolyester films were performed on a Siemens D5000 X-ray diffraction equipment using Cu K_α radiation ($\lambda = 1.54 \text{ \AA}$), at 40 kV and 15 mA. The measurements were made between 0° and 60° 2 θ at a scanning rate of 0.5°/min. The inherent viscosity (η_{inh}) of each aromatic polyester and copolyester was determined in CHCl₃ at a concentration of 1 g/dL with a Ubbelohde viscometer No. 50 at 25°C. The density of each polymer was measured in a density gradient column (Technique Corp.) based on aqueous calcium nitrate solutions, between 1.28 and 1.42 g/cm³ at 23°C. The glass transition temperature (T_g) of each polymer was measured using a PerkinElmer DSC-7 differential scanning calorimeter at a heating rate of 20°C/min between 50 and 350°C under nitrogen atmosphere. The polymer samples were heated twice and the T_g was evaluated as the midpoint of the transition on the second scan. Thermogravimetric analysis was carried out using a TGA-7 (PerkinElmer), at a heating rate of 10°C/min, between 50 and 600°C under nitrogen atmosphere.

Gas permeability and diffusion coefficients for four different gases—helium (He), oxygen (O₂), nitrogen (N₂), and carbon dioxide (CO₂)—were determined in a permeation cell of the constant volume type built in our laboratories.⁹ All gases had purities >99.99% and were obtained from Praxair Corp. Gas permeability coefficients were determined under steady-state conditions and different upstream pressures (2, 5, 7.5, and 10 atm). The measurements were made at 35°C for each pure gas. For safety reasons O₂ permeability coefficients were not determined at pressures higher than 5 atm.

The permeability coefficient, P , is known to be the product of the apparent diffusion and solubility coefficients:

$$P = D_a S \quad (1)$$

where D_a is the apparent diffusion coefficient and S is the solubility coefficient.

The apparent diffusion coefficients, D_a , for O₂, N₂, and CO₂ were estimated by the time-lag method (θ) using the relation

$$D_a = \frac{l^2}{6\theta} \quad (2)$$

where l is the film thickness and θ the time-lag. Apparent diffusion coefficients for He were not estimated because the permeation of this gas is too fast to be measured. Ideal gas separation factors ($\alpha_{A/B}$) were calculated from the ratio of pure gas permeability coefficients using the following equation:^{4,9,19,20}

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (3)$$

where P_A and P_B are the permeability coefficients of the pure gases A and B respectively.

RESULTS AND DISCUSSION

All polyesters and copolyesters synthesized in this work could be cast readily from CHCl₃ solutions to form transparent, tough, and flexible films that were used for their characterization. The transparency of the films was indicative of an amorphous polymer, and DSC measurements do not show a melting point in the range measured.

The inherent viscosities (η_{inh}) of HFD/TERT, HFD/ISO, and their copolymers are given in Table III. The η_{inh} value, as an indirect measurement of the molecular weight of the polyesters and copolyesters, was found to fall between 0.70 and 0.95 dL/g, except for HFD/TERT25, which had a value of 0.58 dL/g. It was also found that there is a tendency for η_{inh} to increase with increasing concentration of HFD/TERT in the copolyester. The exception may be associated with a lower molecular weight for HFD/TERT25 copolymer, and this result was reproducible when the reaction was carried out under the same conditions. Even with this difference, the latter copolyester produced acceptable, transparent, and flexible films that were used in the other characterizations.

TABLE III
Inherent Viscosity, Density, Fractional Free Volume (FFV) and Thermal Properties of HFD/TERT, HFD/ISO and Their Copolyesters

Polymer	Inherent viscosity, η_{inh}^a (dL/g)	Density (g/cm ³)	FFV ^b	T_g (°C)	T_d (°C)	Weight loss at 500°C (%)
HFD/TERT	0.951	1.292	0.200	215.5	476.3	16.5
HFD/TERT75	0.902	1.321	0.196	214.1	471.9	13.7
HFD/TERT50	0.709	1.353	0.190	205.4	468.9	18.2
HFD/TERT25	0.589	1.385	0.186	191.6	464.9	16.8
HFD/ISO	0.708	1.418	0.183	190.4	461.4	22.2

^a Measured in chloroform at 30°C.

^b Estimated by Bondi's group contribution method.

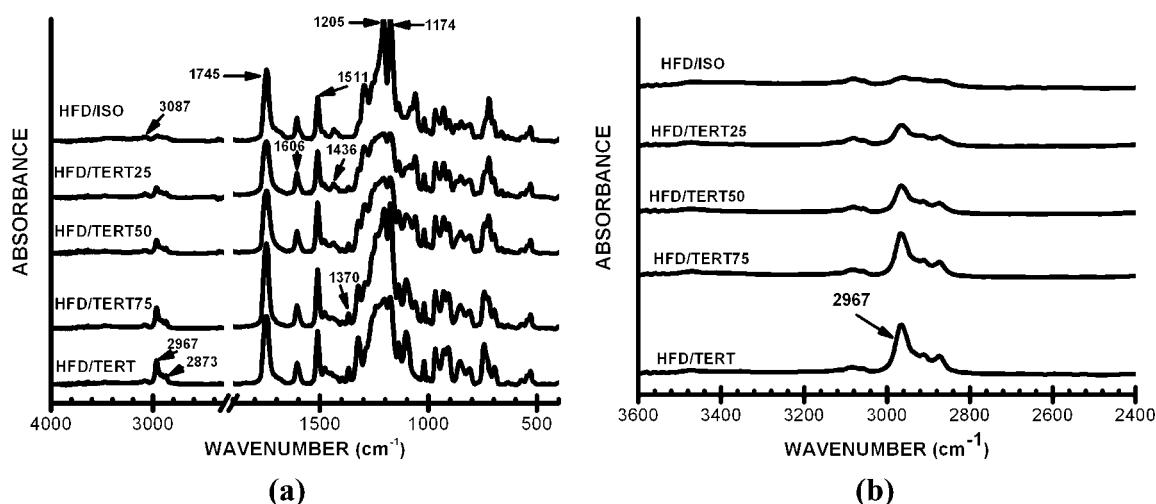


Figure 2 (a) FTIR spectra of HFD/TERT, HFD/ISO, and their copolyesters. (b) FTIR spectra between 3600 and 2400 cm^{-1} of HFD/TERT, HFD/ISO, and their copolyesters.

FTIR spectroscopic analysis was used to confirm the formation of the desired polyesters and copolyesters. FTIR spectra in the 4000–400 cm^{-1} range for HFD/TERT, HFD/ISO, and their copolyesters are shown in Figure 2(a). All spectra were normalized with the band at 1606 cm^{-1} (C=C stretching vibrations of aromatic structure) as a reference. They show a band at 3087 cm^{-1} due to stretching absorption resulting from aromatic C–H linkages. The formation of the ester linkage is detected by the presence of a band with a maximum at 1745 cm^{-1} . This band corresponds to the stretching absorption of the carbonyl group (C=O). Around 1205 and 1174 cm^{-1} , there are two bands that have been assigned to vibrations involving C–O–C stretching.

Moreover, there are three absorption bands around 1606, 1511, and 1436 cm^{-1} due to C=C stretching of phenyl groups. FTIR spectra of HFD/TERT and the copolyesters show two absorptions bands at 2967 and 2873 cm^{-1} characteristic of C–H linkages. The latter bands are assigned to asymmetric and symmetric stretching vibrations resulting from CH_3 bonds. This band presents confirmation by an absorption band at 1370 cm^{-1} (C–H bending).^{21–23} Figure 2(b) shows a

close up of the same FTIR spectra in the 3600–2400 cm^{-1} region for all polymers. HFD/TERT presents a larger absorption than do the other polymers in the asymmetric stretching C–H of the methyl group band (2967 cm^{-1}). This band is not present in the HFD/ISO spectra. In the copolymers spectra, there is an increase in the absorption of this band, due to an increment on the concentration of the tertbutyl group HFD/TERT in the copolyester formulation. The relative height of the methyl group band at 2967 cm^{-1} was used as a reference to determine, in a comparative manner, the amount of HFD/TERT present in the copolyesters. These results are shown in Table IV. As can be seen, the copolyester HFD/TERT75 presents a higher absorption than do the other copolymers in the stretching C–H of the methyl group band. The largest difference of the percentage relative height appears in this copolyester (HFD/TERT75), with 87% instead of the expected value of 75 mol %, whereas HFD/TERT25 shows only a small difference with respect to the expected value. The molar percentage of HFD/TERT50 was close to the expected value.

All polymers were soluble in solvents such as CHCl_3 , NMP, DMAc, THF, DCE, and TCE. In gen-

TABLE IV
Relative Height of FTIR Spectral Bands on HFD/TERT, HFD/ISO, and Their Copolyesters

Polymer	Relative height of FTIR bands (cm^{-1})		Relative height of methylene band at 2964 cm^{-1}	
	1606	2964	Calculated (%)	Expected (mol %)
HFD/TERT	1	1.1599	100	100
HFD/TERT75	1	1.0312	87.1	75
HFD/TERT50	1	0.6503	49.1	50
HFD/TERT25	1	0.4653	30.6	25
HFD/ISO	1	0.1581	0	0

eral, the introduction of bulky pendant groups, such as CF₃ and tertbutyl groups in this case, enhances their solubility.^{6,17}

The densities of the homopolymer and copolymer films are shown in Table III. The density of HFD/ISO was 1.418 g/cm³ whereas that of HFD/TERT was 1.292 g/cm³. In the copolyesters the density decreased as the concentration of comonomer with bulky pendant groups (TERT) increased in the copolymer, reporting values of density between 1.321 and 1.385 g/cm³. This behavior is attributed to the bulky structure of HFD/TERT that could inhibit chain packing efficiency and hinder torsional mobility. It is also seen that a lower density implies a lower packing efficiency and it is expected to increase the FFV.^{5,6,10} The measured density for each polymer was used to calculate the FFV from

$$\text{FFV} = \frac{(V - V_0)}{V} \quad (4)$$

where V is the specific volume of the polymer, which is obtained from experimental measurement of the polymer density. V_0 is the specific volume occupied by the polymer chains, calculated from the van der Waal's volume (V_w), estimated by Bondi's group contribution method,²⁴ according to the relation

$$V_0 = 1.3V_w \quad (5)$$

The occupied volume of the copolymer ($V_{0 \text{ cop}}$) was predicted using an inverse rule approach as reported elsewhere:¹¹

$$\frac{1}{V_{0 \text{ cop}}} = \frac{w_1}{V_{01}} + \frac{w_2}{V_{02}} \quad (6)$$

where V_{01} and V_{02} are the occupied volumes of each homopolymer, also w_1 and w_2 are the weight fractions of each comonomer in the copolymer.

The polymer FFVs calculated by using Bondi's method are listed in Table III. FFV values were found to be 0.183 for HFD/ISO and 0.200 for HFD/TERT. In the copolyesters the FFV increases as the concentration of the bulky group (TERT) increases in the copolymer. Previous studies have shown that polymers with a tertbutyl pendant group have higher free volumes than do the analog polymers without pendant groups.^{5,7,9-11} This result is consistent with the notion that the nonpolar tertbutyl groups effectively disrupt chain packing due to its bulkiness.¹⁰

T_g values of the polyesters and copolyesters prepared in this work are shown in Table III. All five polymers appear to be amorphous, due to film transparency and the absence of a crystalline melting point. The thermograms of the copolyesters show a single T_g between 190 and 215°C, which are the T_g

values of HFD/ISO and HFD/TERT respectively. As can be seen, the T_g of the copolymers tends to increase with increase in bulky comonomer (TERT) concentration. Figure 3 shows the behavior of the T_g as a function of composition for the homopolymers and copolymers as determined by DSC. The T_g obtained for HFD/TERT is around 20°C higher than that of HFD/ISO, suggesting that the bulky tertbutyl pendant group hinders the backbone motion important in the glass to rubber transition as reported elsewhere.¹⁰ In copolyesters the T_g increases as the concentration of the TERT group increases in the copolymer. Thus, for the copolyester formulations studied here, the highest T_g is that of HFD/TERT75, which has the greatest concentration of the bulky comonomer, TERT. This behavior agrees with that observed in other aromatic materials such as polyamides, polyimides, polycarbonates, and polysulfones.^{1,5,7,10,11,17} Moreover, the same figure not only shows the experimental T_g values of polyesters and copolyesters, but also compares them with the values predicted using Fox equation. This equation predicts that random copolymers will show a single glass transition at a temperature intermediate between those of the homopolymers as a function of concentration, according to the following equation:^{2,25,26}

$$\frac{1}{T_{g \text{ cop}}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (7)$$

where $T_{g \text{ cop}}$, T_{g1} , and T_{g2} are the glass transition temperatures of the copolymer and each homopolymer respectively, and w_1 and w_2 are the weight fractions of each comonomer in the copolymer. Experimental T_g values for the copolymers follow closely this mixing rule; Fox's equation predicts lower val-

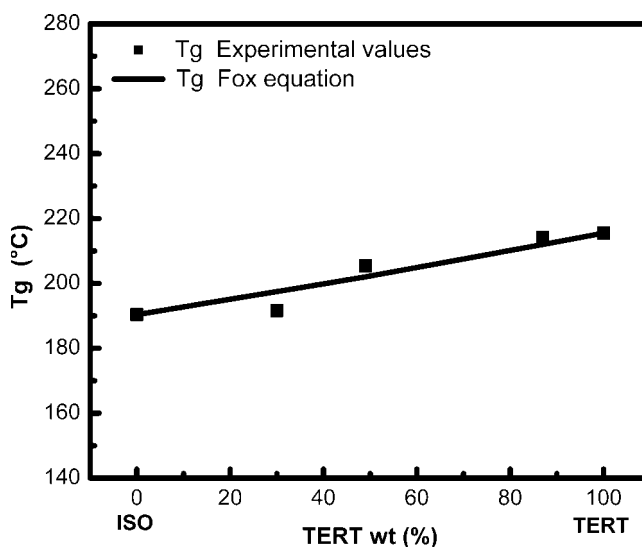


Figure 3 Glass transition temperatures as a function of TERT concentration in HFD/TERT-co-HFD/ISO copolyesters.

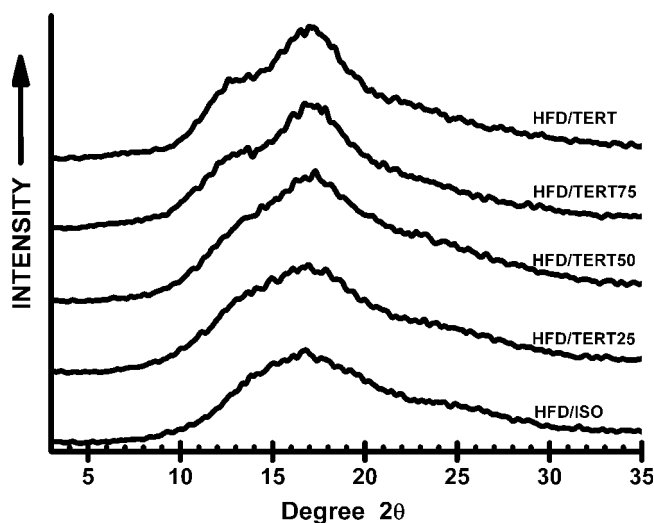


Figure 4 WAXD patterns of HFD/TERT, HFD/ISO, and their copolyesters.

ues than those found experimentally, with the exception of copolymer HFD/TERT25. The exception may be associated with a possible lower molecular weight for this polymer, as it was observed earlier that it presents the lowest η_{inh} for all homopolymers and copolyesters reported here.

The onset of decomposition temperature (T_d) and weight losses at 500°C of the polyesters and copolyesters are shown in Table III. The temperature for the onset of decomposition, T_d , for all polymers was reported between 461 and 476°C under nitrogen atmosphere. The T_d observed is consistent with the

T_g behavior of polyesters and copolyesters. As the concentration of TERT group increases in a regular fashion, the T_d increases in these copolyesters. In the same table, the weight loss at 500°C under nitrogen atmosphere for each polyester and copolyester is reported. The weight loss at 500°C was recorded to compare the thermal stability of the polymers after decomposition had started. The results indicate that the polymers and copolyesters show high thermal stability with weight loss below 22 wt % at 500°C. These results are consistent with earlier observations of an increase in polymer thermal stability upon incorporation of bulky tertbutylisophtalic (TERT) moiety in the polymer.^{11,27}

The WAXD patterns for the aromatic polyesters, HFD/ISO and HFD/TERT, and their copolyesters are shown in Figure 4. All polymers show a typical amorphous pattern. HFD-ISO shows only one broad diffraction peak whereas HFD-TERT shows also one broad diffraction peak with a small shoulder. This shoulder decreases with increase in ISO content in the copolyester formulation. The most prominent peak, located in the range of 16.7°–17.3° 2 θ , which corresponds to a d -spacing as calculated from Bragg's equation $n\lambda = 2d \sin \theta$ of 5.1–5.3 Å, has been attributed, by several authors,^{7,28} to the average chain spacing. The secondary peak, situated in the range of 12.7°–14.7° 2 θ , which corresponds to a d -spacing of 6.0–6.9 Å, has been attributed to the alignment of pendant groups on adjacent polymer chains, in this case, the tertbutyl group; furthermore, this behavior has been reported to occur for polymers with phenyl rings.^{28–30} Pixton and Paul⁷ reported

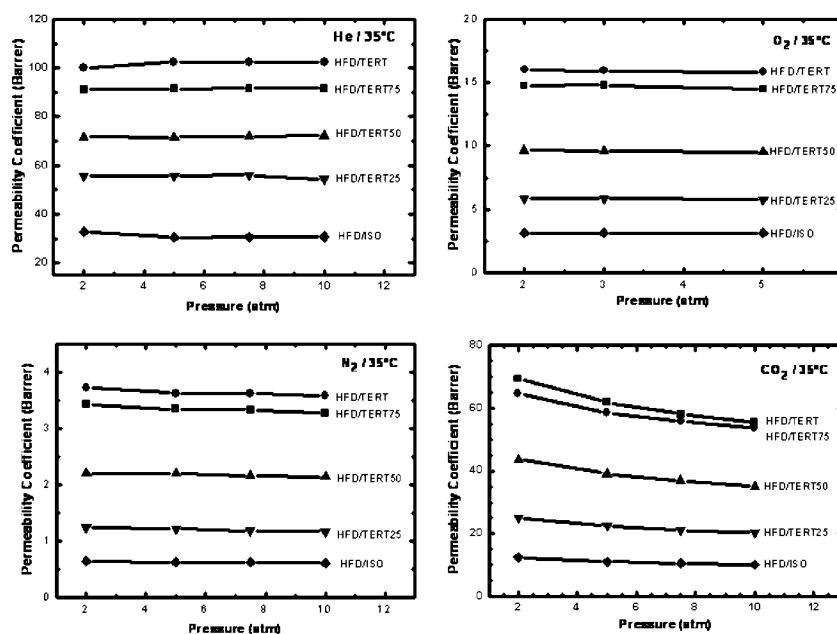


Figure 5 Effect of upstream pressure on gas permeability coefficients for HFD/TERT, HFD/ISO, and their copolyesters.

TABLE V
Pure Gas Permeability Coefficients of HFD/TERT, HFD/ISO, and Their Copolyesters at 2 atm and 35°C

Polymer	<i>P</i> (Barrer)			
	He	CO ₂	O ₂	N ₂
HFD/TERT	100	69.28	15.98	3.72
HFD/TER75	91.33	64.6	14.72	3.42
HFD/TERT50	71.65	42.72	9.53	2.21
HFD/TERT25	55.60	25.05	5.87	1.25
HFD/ISO	32.72	12.46	3.13	0.65

Measured at 35°C and 2 atm upstream pressure.

similar results for polyarylates based on phenolphthalein as well as fluorene bisphenol and they obtained the primary and secondary peaks near 5 and 6.9 Å, respectively.

In general, it was found that the characteristics of the homopolyesters HFD/ISO and HFD/TERT obtained by interfacial polymerization are only slightly different from those reported for the same polyesters synthesized by solution polymerization.⁷ This fact and the fast reaction times at room temperature for the interfacial polymerization indicate that, depending on the circumstances, it is possible to prepare these polyesters by interfacial polymerization with a minimal change in their characteristics when compared with the solution method.

Gas transport properties

In Figure 5, gas permeability coefficients for He, O₂, N₂, and CO₂ are shown as a function of pressure. Pure gas permeability coefficients in all polyesters and copolyesters are independent of pressure, with the exception of CO₂, where permeability coefficients decrease with increase in pressure. This behavior is typical for the permeation of gases in glassy polymers over the moderate pressure range considered in this study.^{6,10,16,31} It is also observed that gas permeability coefficients follow the order $P_{\text{He}} > P_{\text{CO}_2} > P_{\text{O}_2} > P_{\text{N}_2}$, indicating that they are larger for the gas that has the smallest kinetic diameter, He, and

TABLE VI
Pure Gas Apparent Diffusion and Solubility Coefficients of HFD/TERT, HFD/ISO, and Their Copolyesters at 2 atm and 35°C

Polymer	<i>D_a</i> (10 ⁷ cm ² /s)			<i>S</i> (10 ³ cm ³ (STP)/cmHg cm ³)		
	CO ₂	O ₂	N ₂	CO ₂	O ₂	N ₂
HFD/TERT	4.77	10.86	3.76	14.49	1.47	0.98
HFD/TER75	4.04	9.21	2.86	15.97	1.59	1.19
HFD/TERT50	3.04	6.52	2.82	14.01	1.46	0.78
HFD/TERT25	2.18	5.73	1.83	11.49	1.02	0.68
HFD/ISO	0.84	2.84	0.76	14.84	1.10	0.85

Measured at 35°C and 2 atm upstream pressure.

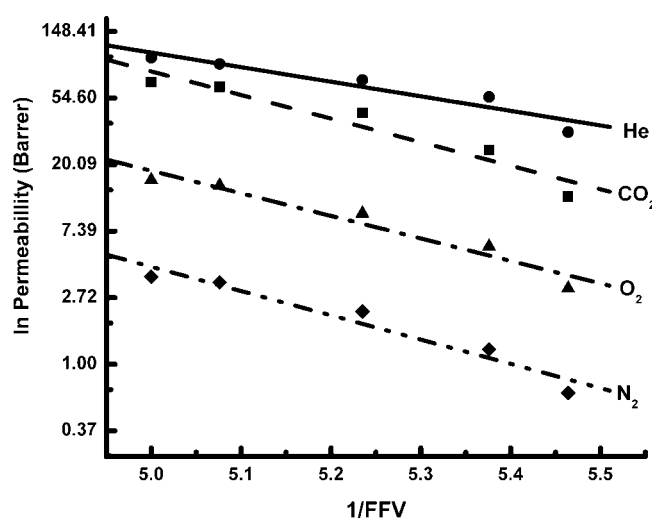


Figure 6 Gas permeability coefficients as a function of reciprocal fractional free volume for HFD polyesters and copolyesters at 2 atm and 35°C.

decrease as the kinetic diameter increases to the ones with the larger kinetic diameter O₂ and N₂.

Values of permeability, apparent diffusion, and solubility coefficients for He, O₂, N₂, and CO₂ through membranes of HFD/TERT, HFD/ISO, and their copolyesters at 35°C and 2 atm upstream pressure are presented in Tables V and VI respectively. HFD/TERT shows the highest permeability and apparent diffusion coefficients, while HFD/ISO shows the lowest permeability and diffusion coefficients for all gases. Values of the permeability and apparent diffusion coefficients in the copolyesters fall between those of the homopolymers. Comparison with the literature data indicates that the permeability and diffusion coefficients are in the range of those reported by other authors for HFD/TERT and HFD/ISO obtained by solution polycondensation.⁷ Figure 6 shows the permeability coefficients as a function of reciprocal FFV at 35°C and 2 atm. The dependence of permeability with FFV usually follows an Arrhenius type behavior:

$$P = P_0 \exp \left[-\frac{B}{\text{FFV}} \right] \quad (8)$$

where P_0 is a preexponential factor and B is a constant.^{7,8,11,14} Thus, for amorphous polymer systems, the logarithm of the permeability coefficient has been reported to increase linearly with the reciprocal of the FFV.^{5,6} As is evident from the plots in Figure 6 for the polyesters and copolyesters considered in this study, their permeability coefficients generally follow closely an Arrhenius behavior. Moreover, permeability coefficients for polyesters and copolyesters to several gases fall in the following order depending on the concentration of the bulky group (TERT): $P_{\text{HFD/TERT}} > P_{\text{HFD/TER75}} > P_{\text{HFD/TERT50}} > P_{\text{HFD/TER25}} >$

$P_{\text{HFD/ISO}}$. HFD/TERT is the most permeable polymer considered in this study and it has the highest FFV. These results are attributed to the effect of the large pendant tertbutyl groups in aromatic polyesters and copolyesters, which decrease the chain packing efficiency and induce a larger FFV. These results are similar to those reported by several authors for other amorphous glassy polymers, where permeability and diffusion coefficients increase as FFV in the polymer increases.^{5,7,9,14,16}

For all polymers studied here, the apparent diffusion coefficients, D_a , rank in the following order: $D_{\text{O}_2} > D_{\text{CO}_2} > D_{\text{N}_2}$. The relative magnitudes of D_a for CO_2 and O_2 do not follow the order of kinetic diameters, σ_K , because $D_{\text{O}_2} > D_{\text{CO}_2}$ whereas $\sigma_K(\text{O}_2) > \sigma_K(\text{CO}_2)$. Similar behavior has been observed for other glassy polymers.^{2,6,7,10,11} Under normal conditions the very high solubility of CO_2 in these polymers causes the CO_2 to present a permeability coefficient higher than that of O_2 because the permeability coefficient of a gas is the product of the apparent diffusion (D_a) and solubility (S) coefficients.

In Table VI gas solubility coefficients for polyesters and copolyesters at 35°C and 2 atm are presented. From the data in this table, gas solubility changes in the following order: $S_{\text{CO}_2} > S_{\text{O}_2} > S_{\text{N}_2}$. This trend is consistent with the decreasing condensability of the penetrants.^{4,19} Gas solubility generally increases with increase in critical temperature in the absence of specific polymer–penetrant interactions. In the polyesters and copolyesters tested here, there are no appreciable changes in solubility coefficients and the variations are minimal with structural changes in homopolymers and copolymers. Thus, the presence of the bulky tertbutyl group in the polyesters and copolyesters obtained in this work has a larger effect on the diffusivity of a gas molecule, because of an increase in FFV for the gas permeation process, while the solubility does not show a large dependence on it.

Ideal separation factors for the gas pairs O_2/N_2 and CO_2/N_2 at 35°C and 2 atm are shown in Table VII. Of these polyesters HFD/ISO is the most selective polymer, followed by the copolyesters where the ideal separation factor decreases as the concentration of the TERT moiety increases. Finally HFD/TERT exhibits the lowest selectivity. This result agrees with the trade off reported for glassy polymers where as permeability coefficients increase their selectivity decreases.^{5,7,9,10,16} In fact the polyesters and copolyesters in this work show high permeability coefficients for glassy polymers and low selectivity. Interestingly, the gas permeability between the most permeable HFD/TERT and the less permeable HFD/ISO is up to five times larger for gases such O_2 and N_2 . However, the loss in ideal separation factors is minimal: less than 0.5 when compared

TABLE VII
Ideal Separation Factors for the Gas Pairs O_2/N_2 and CO_2/N_2 for HFD/TERT, HFD/ISO, and Their Copolyesters at 2 atm and 35°C

Polymer	$\alpha_{\text{O}_2/\text{N}_2}$	$\alpha_{\text{CO}_2/\text{N}_2}$
HFD/TERT	4.29	18.62
HFD/TERT75	4.30	18.88
HFD/TERT50	4.36	19.74
HF/TERT25	4.69	19.90
HFD/ISO	4.82	19.19

Measured at 35°C and 2 atm upstream pressure.

with the large increase in permeability afforded by the inclusion of the bulky tertbutyl group in these polyesters.

CONCLUSIONS

Two aromatic polyesters HFD/TERT and HFD/ISO and three different copolyesters from these polyesters containing 75, 50, and 25 mol % of HFD/TERT were synthesized by interfacial polycondensation. The method yielded polymers and copolymers that produced flexible transparent films when they were cast from solution. The properties of the homopolymers HFD/ISO and HFD/TERT show minimal differences from those reported for the same homopolymers obtained by solution polycondensation elsewhere.⁷ The advantage of interfacial polymerization is that it requires shorter reaction time and it could be performed at room temperature. Values of physical, thermal, and gas transport properties in the copolyesters fell between those of the homopolymers and were dependent on the amounts of comonomers HFD/TERT and HFD/ISO present in the copolyester. The substitution of the bulky tertbutyl group at position 5 on the isophthalate ring increases polymer thermal stability. Thermal properties of these aromatic polyesters and copolyesters and wide angle X-ray diffraction measurements indicate that they are amorphous polymers with T_g 's between 190 and 215°C. The onset of T_d 's for these materials are also above 460°C, and they show high thermal stability, with weight losses below 23 wt % at 500°C. These results situate them as engineering polymers with high temperature resistance. Gas permeability and diffusion coefficients increase as the concentration of the bulky group, TERT, increases in the copolymers. The increases in gas permeability can be related mainly to an increase on diffusion coefficients for all gases, which in turn are attributed to higher free volume, due to a decrease in the chain packing efficiency. These increments in gas permeability and diffusivity produce a decrease in selectivity, a common trade off observed in other glassy polymers,

but the decrease in selectivity is small when compared with the increase in permeability obtained.

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