Synthesis and Characterization of Aromatic Polyesters and Copolyesters from 4,4'-(1-Hydroxyphenylidene)diphenol and 4,4'-(9-Fluorenylidene)diphenol

María I. Loría-Bastarrachea,[1] Humberto Vázquez-Torres,[2] Manuel de J. Aguilar-Vega[1]

[1]*Centro de Investigación Científica de Yucatán A.C., Unidad de Materiales, Calle 43 No. 130, Col. Chuburná de Hidalgo, CP 97200, Mérida, Yucatán, Mexico*
[2]*Universidad Autónoma Metropolitana Unidad Iztapalapa, Departamento de Física, Apartado Postal 55-534, 09340, México, Distrito Federal, Mexico*

ABSTRACT: Two isophthalic polyesters from 4,4'-(1-hydroxyphenylidene)diphenol (BAP/ISO) and 4,4'-(9-fluorenylidene)diphenol (BF/ISO), and three different copolyesters containing 75, 50, and 25 mol % of BAP/ISO were synthesized by interfacial polycondensation. This preparation method yielded polymers and copolymers that produced flexible and transparent films when they were cast from solution. Proton NMR spectrometry studies showed that the isophthalic copolyesters were obtained as random copolymers with differences in comonomer composition no larger than 2.5 mol % with respect to the expected compositions. Wide-angle X-ray diffraction measurements indicated that all the polyesters and copolyesters were amorphous. The copolyesters showed amorphous patterns with maxima that fell between those of the polyesters. It was also found that thermal properties such as glass-transition temperature, onset of decomposition temperature, thermal stability, dynamic mechanical storage modulus, and maximum on the α-transition of the damping factor tan δ of BF/ISO were higher than those of BAP/ISO. The values of these thermal properties in the copolyesters fell between those of the polyesters and were dependent on the amounts of BF/ISO and BAP/ISO present in the copolyester in a linear fashion. Therefore, the thermal properties of a given copolyester can be predicted directly from the comonomers' composition. Overall, it shows that the interfacial polycondensation method is suitable to obtain these copolyesters in a controlled manner and that their properties can be tailored to be between those of the homopolyesters. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2515–2522, 2002

Key words: aromatic polyesters; copolyesters; thermal properties; polycondensation; WAXD

INTRODUCTION

It is well known that physical and chemical properties of polymers depend strongly on composition, the kind of functional groups present, and the arrangement of the structural units in the polymeric chain. The possibility of a controlled modification of the structure would allow the tailoring of the properties of polymers for specific applications. A large number of aromatic polyesters have been synthesized from different kinds of bisphenols.[1–3] The properties of these bisphenol polyesters depend on the kind of substitutions that the central carbon between the two phenyl groups presents. In this kind of polyesters, those that bear phenyl groups or large cross planar substituents show higher thermal properties; they are soluble in common organic solvents such as chloroform; and, in some cases, they do not show a tendency to crystallize.[2] There are reports in the literature on the synthesis of aromatic copolyesters from bisphenol-A and different concentrations of isophthalic and terephthalic diacid chlorides[4] that form random copolyesters, with properties that depend on the relative amounts of isophthaloyl and terephthaloyl units present in the copolyester. There are also studies on different copolyesters, mainly those that form liquid crystalline polymers (LCPs), in which the composition of the copolyester is varied in the diol structure rather than in the diacid chloride structure,[5,6] to control the final properties of the polymer. On the other hand, there has been little interest in copolyesters from different bisphenols copolymerized using the same diacid chloride that present high thermal stability but do not form LCPs. These copolyesters represent an option in which a proper choice of the bisphenols would allow the control of different properties for use in different applications.[7–9]

In this work we study the properties of isophthalic polyesters based on the reaction between 4,4'-(1-hydroxyphenylidene)diphenol (BAP) or 4,4'-(9-fluorenylidene)diphenol (BF), with isophthaloyl dichloride by interfacial polycondensation. Using the same reaction, the synthesis of isophthalic copolyesters with

TABLE I
**Polyester and Copolyester Formulations Used
in the Polycondensation Reactions**

Polymer	BAP (mmol)	BF (mmol)	ISO (mmol)
BAP/ISO	10.0	0.0	10
BAP75/ISO	7.5	2.5	10
BAP50/ISO	5.0	5.0	10
BAP25/ISO	2.5	7.5	10
BF/ISO	0.0	10.0	10

different concentrations of BAP and BF in their structure was carried out. The resulting polyesters and copolyesters were characterized to understand the influence that the changes in composition and degree of aromaticity have on the thermal, physical, and chemical properties afforded by copolymerization.

EXPERIMENTAL

Materials

The polyesters and copolyesters were prepared from 4,4′-(1-hydroxyphenylidene)diphenol (BAP, 99%; Ken Seika Corp., Japan) and 4,4′-(9-fluorenylidene)diphenol (BF, 99%; Aldrich Chemical Co., Milwaukee, WI). They were used as received. Isophthaloyl dichloride (ISO, 98%; Aldrich) was purified by distillation under reduced pressure. Benzyltriphenyl fosfonium chloride (BTPC, 99%; Aldrich) was used as the interfacial catalyst. The reactants chloroform (Mallinckrodt Baker, Paris, KY), 1,2-dichloroethane (Aldrich), and sodium

hydroxide (97% in the form of pellets; Química Monterrey, Mexico) were used as received.

Polymerization

The isophthalic polyesters and copolyesters described in this study were synthesized by interfacial polycondensation as described by Morgan.[2,3,10] For copolyester synthesis three different molar concentrations of the diols BAP and BF were used as described in Table I. The isophthalic polyesters synthesized from 4,4′-(1-hydroxyphenylidene)diphenol and 4,4′-(9-fluorenylidene)diphenol are designated BAP/ISO and BF/ISO, respectively. The isophthalic copolyesters BAP75/ISO, BAP50/ISO, and BAP25/ISO correspond to 75, 50, and 25 mol % of BAP diol, respectively, in the initial reaction to synthesize the copolyester.

The polymerization reactions were carried out in a 250-mL three-neck flask equipped with a mechanical stirrer under nitrogen atmosphere. A schematic representation of the reaction is given in Figure 1. In a typical copolymerization reaction, BAP50/ISO, a mixture of BAP and BF (0.005 mol each) was dissolved in a sodium hydroxide, aqueous solution (0.02 mol of NaOH) prepared with 100 mL of distilled water. The mixture was stirred until the diols had 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 solution of 0.01 mol of isophthaloyl dichloride in 25 mL of 1,2-dichloroethane (DCE) was added to
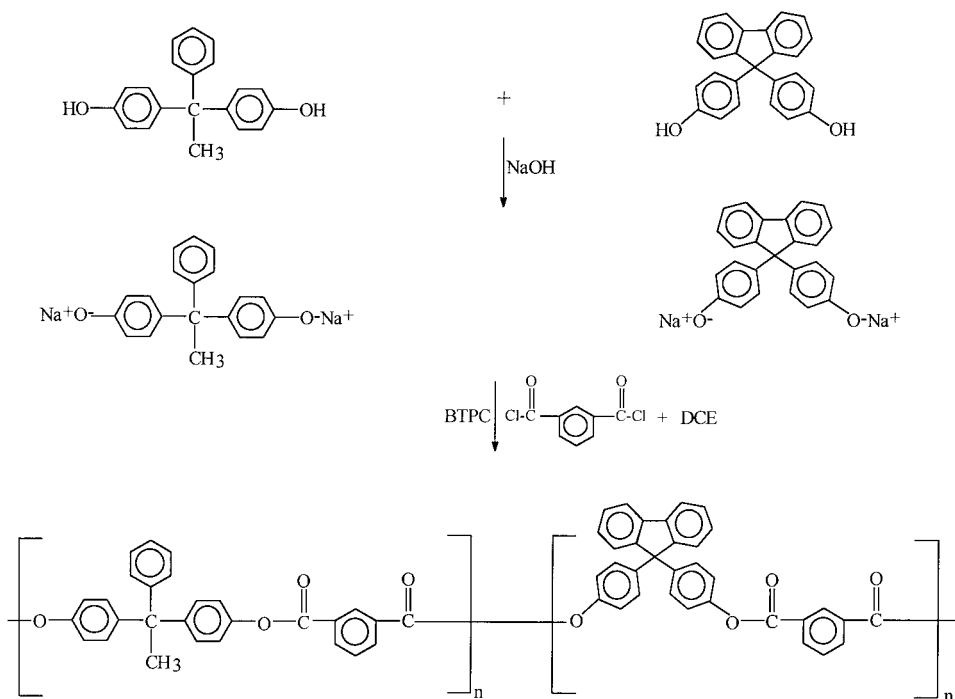

Figure 1 Schematic reaction for synthesis of isophthalic copolyesters by interfacial polycondensation.

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 heavy gel. After a reaction period of 45 min at room temperature, the aqueous phase was separated from the organic phase, and it was dispersed in 50 mL of chloroform to reduce the viscosity. Finally, the copolyester was precipitated in 300 mL of methanol by stirring vigorously using a Waring laboratory blender (Waring Products, New Hartford, CT). The white precipitate was collected by filtration and then washed several times with methanol. The copolymer as obtained was dried in a vacuum oven at 100°C for 24 h. All the polyesters and copolyesters were prepared under the same procedure. For BF/ISO, it was necessary to heat the initial solution slightly to obtain a complete dissolution of the diol.

Isophthalic polyester and copolyester films were prepared by solution casting from solutions containing 1.0 g of the polymer dissolved in 10 mL of chloroform. These solutions were poured into stainless steel rings on the surface of a glass plate and maintained under chloroform 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

Polymer and copolymer films were characterized by thermal analysis using differential scanning calorimetry (DSC), thermogravimetrical analysis (TGA), and dynamical mechanical measurements as a function of temperature. Glass-transition temperatures of the polyesters and copolyesters were determined by DSC on a DSC-7 (Perkin Elmer Cetus Instruments, Norwalk, CT), at a scanning rate of 20°C/min, between 50 and 350°C under nitrogen atmosphere. Thermal decomposition changes as a function of temperature for isophthalic polyesters and copolyesters were recorded using a TGA-7 (Perkin Elmer Cetus Instruments). These measurements were performed with samples heated between 50 and 600°C under nitrogen atmosphere at a rate of 10°C/min. Dynamic mechanical properties of polyesters and copolyesters as a function of temperature were determined in films strips 15 × 2.2 mm (length × width), between 0.15 and 0.19 mm thick. The determination was carried out in a DMA-7 (Perkin Elmer Cetus Instruments), using the extension mode between −120 and 350°C, at frequency of 1 Hz and a heating rate of 4°C/min under nitrogen atmosphere. The inherent viscosity (η_{inh}) of each polyester and copolyester was determined in chloroform at a concentration of 1.0 g/dL with a Ubbelohde viscometer No. 50 at 30°C. Wide-angle X-ray diffraction measurements of the polymer films were performed in a Philips 1140 X-ray diffractometer (Philips, The Netherlands) between 5 and 60° 2θ. For these measurements Cu–K$_\alpha$ radiation (λ = 1.54 Å) and a scanning rate of 0.5° in 2θ were used. Density measurements for the polymer films were obtained by a density gradient column (Techne Corp., Princeton, NJ), filled with Ca(NO$_3$)$_2$ (Aldrich) aqueous solutions, between 1.20 and 1.30 g/cm^3 at 25°C. ^{1}H-NMR spectra were obtained using a Bruker DMX500 (Bruker Instruments, Billerica, MA). The polymers were dissolved in CDCl$_3$ and tetramethylsilane was used as an internal standard.

RESULTS AND DISCUSSION

The polyesters and copolyesters described in this study were synthesized readily using the interfacial polycondensation method. This method as described and reported by Morgan yields polyesters of different types easily and in a very short time.[2,3] It has been used successfully to obtain aromatic copolymers from bisphenol-A and a mixture of terephthalic and isophthalic acid chlorides.[4] Although these copolymers are noteworthy because the amounts of isophthalic and therephthalic units present in the copolyester allow for control of crystallinity, the difference in glass-transition temperature and thermal decomposition behavior between the isomers is not significant. In the polyesters synthesized here, the difference in glass transition is around 80°C, whereas the thermal stability should be greater for the polyester containing the fluorene group in their structure. Thus the copolymerization using both bisphenols should result in thermal properties between those exhibited by the homopolyesters, which would depend on the relative amounts of the bisphenol comonomers present in the copolyester. Other properties of the copolyesters should follow the same trend. The interfacial method worked well for the formation of the copolyesters without any significant changes. All polyesters and copolyesters could be cast readily from chloroform 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.

To determine the isophthalic copolyester compositions, ^{1}H-NMR spectra were obtained for BAP/ISO, BF/ISO, and their copolyesters. The results show some differences in the isophthalic polyesters BAP/ISO and BF/ISO, as can be seen in Figure 2. They show different characteristic peaks at resonances between 6 and 9 ppm that are attributed primarily to the phenyl protons. At these low fields BAP/ISO has a singlet at δ = 9.1 ppm, whereas BF/ISO shows one at δ = 8.93 ppm. This particular singlet increases and decreases as the concentration of BAP or BF changes in the copolyesters with overlapping and developing of multiple peaks. There is also a doublet between 7.73 and 7.8
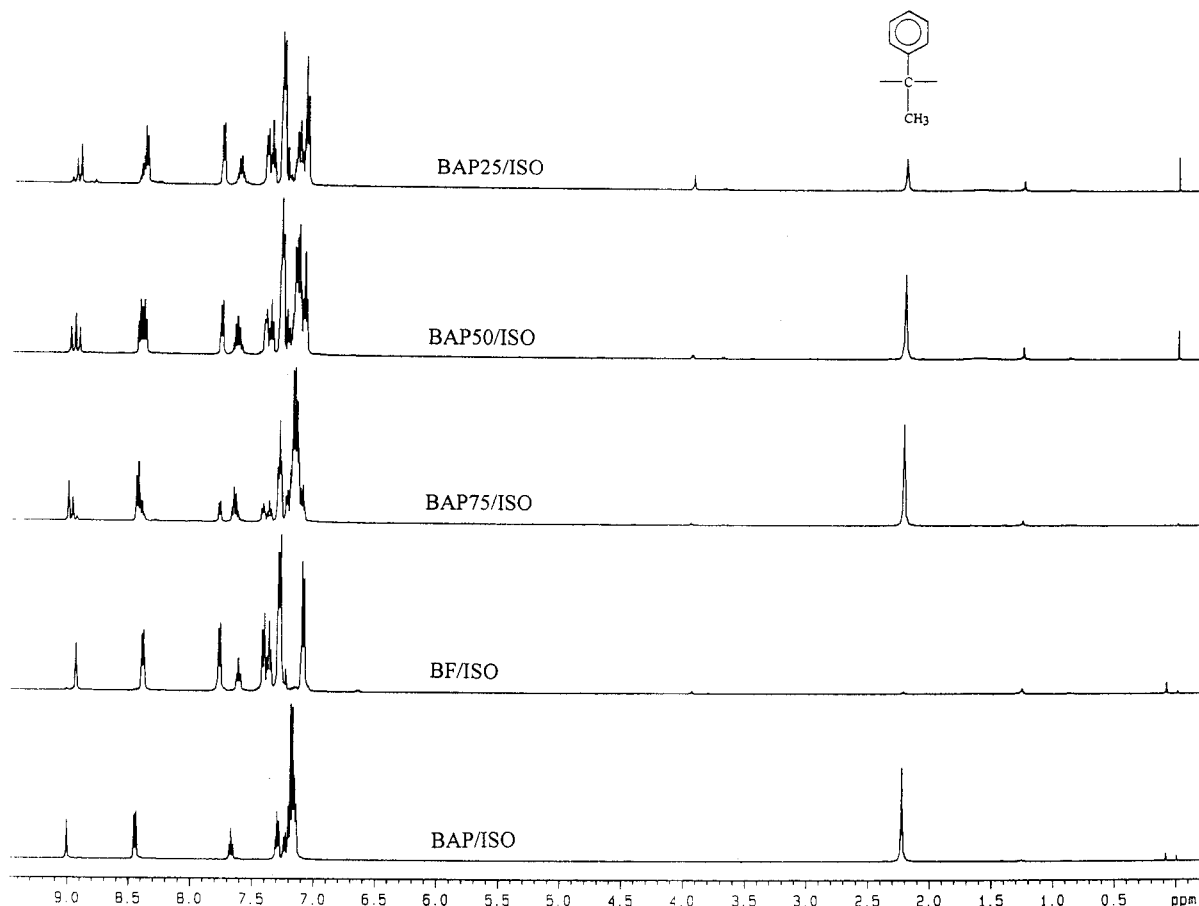
Figure 2 ^{1}H-NMR spectra of BAP/ISO, BF/ISO, and their copolyesters.

ppm that appears in BF/ISO and does not appear in BAP/ISO. On the other hand, the polyester BAP/ISO shows a peak at $\delta = 2.23$ ppm that does not appear in BF/ISO. This resonance was assigned to the protons of a methyl group bonded to a quaternary carbon bearing a terminal phenyl group. In these copolyesters such a group is present only in the BAP/ISO comonomer attributed to the (1-phenylethylidene) moiety.[11] In the different copolyesters this resonance peak increases or decreases as the concentration of BAP/ISO comonomer changes in the copolyester. The resonance peak at $\delta = 2.23$ ppm was used as an internal reference to determine, in a comparative manner, the amount of BAP/ISO present in the copolyesters. The results are shown in Table II. As can be seen, the molar percentage of BAP/ISO in the copolyesters is very close to the expected value. The largest difference appears in BAP75/ISO with 72.4 mol % instead of the expected value of 75 mol %, whereas BAP50/ISO and BAP25/ISO show only small differences with respect to the expected values. Overall, the ^{1}H-NMR results show that interfacial polycondensation is a suitable method for the preparation of these aromatic copolyesters, given that the deviation from the expected composition is not large. This result also indicates that in this

particular case the comonomers used do not show great differences in reactivity, although the NMR results point toward a slightly greater amount of the comonomer BF/ISO in the copolyesters.

The inherent viscosities of BAP/ISO, BF/ISO, and their copolymers is given in Table III. The η_{inh} value, as an indirect measurement of the molecular weight of the isophthalic polyesters and copolyesters, was found to be between 0.51 and 0.62 dL/g, except for BAP25/ISO, which had a value of 0.45 dL/g. It was also found

TABLE II
Proton NMR Integration of the Resonance Peak at δ = 2.23 ppm of BAP/ISO Polyester and Copolyesters: Calculated and Expected Concentrations of BAP/ISO in the Copolymers

Polymer	Integral $\delta = 2.23$ ppm	BAP/ISO calculated (mol %)	BAP/ISO expected (mol %)
BAP/ISO	3.729	100	100
BAP75/ISO	2.702	72.45	75
BAP50/ISO	1.850	49.74	50
BAP25/ISO	0.924	24.78	25
BF/ISO	—	—	—

TABLE III
Inherent Viscosity and Density of BAP/ISO, BF/ISO, and Their Copolyesters

Polyester	Inherent viscosity $(\eta_{inh})^a$ (dL/g)	Density (ρ) (g/cm³)
BAP/ISO	0.51	1.2289
BAP75/ISO	0.57	1.2288
BAP50/ISO	0.59	1.2229
BAP25/ISO	0.45	1.2225
BF/ISO	0.62	1.2110

[a] Measured in chloroform at 30°C.

TABLE IV
Thermal Transitions and Thermal Stability of BAP/ISO, BF/ISO, and Their Copolyesters

Polymer	T_g (°C)	T_d (°C)	Weight loss at 500°C (%)	T_α (°C)
BAP/ISO	202	475.9	25.8	205.7
BAP75/ISO	227	477.3	25.6	213.8
BAP50/ISO	245	478.8	22.8	232.1
BAP25/ISO	253	481.9	18.3	253.2
BF/ISO	274	483.5	10.5	275.9

that there is a tendency of increasing η_{inh} with increasing concentration of BF/ISO in the copolyester. The exception may be associated with a lower molecular weight or different molecular hydrodynamic dimensions of the BAP25/ISO copolymer, and the 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 other characterizations.

The densities of the polyester and copolyester films are shown in Table III. The density of BAP/ISO film was 1.2289 g/cm³, whereas that of BF/ISO film was 1.2110 g/cm³. In the copolyesters the density decreased as the concentration of BF/ISO increased in the copolymer. This behavior indicates that, as the degree of rigidity and aromaticity is greater in the copolymer, there is an inhibition on packing of the polymer chains. This is attributed to the bulky structure of BF/ISO that could produce both effects.

Wide-angle X-ray diffraction patterns for isophthalic polyesters and copolyesters are shown in Figure 3. These diffraction patterns indicate that all the poly-
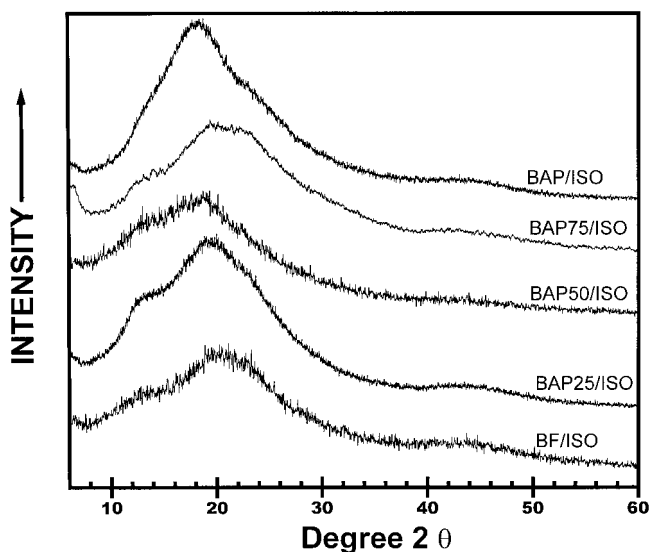

Figure 3 WAXD patterns of BAP/ISO, BF/ISO, and their copolyesters.

mers and copolymers synthesized are amorphous. The diffraction pattern of BAP/ISO shows an amorphous halo with a maximum at 18° 2θ, whereas the pattern of BF/ISO also shows an amorphous halo with a maximum at 20° 2θ and a small shoulder at around 12° 2θ. These results are the same as those reported by Charati et al.[12] and Pixton and Paul.[13] The copolyesters with different concentrations of comonomers show amorphous diffraction patterns with maxima between those of the polyesters. The shoulder at 12° 2θ observed in BF/ISO is more evident in BAP25/ISO, which is the copolyester with the greatest concentration of this comonomer.

Experimentally determined T_g values for BAP/ISO, BF/ISO, and their copolyesters are listed in Table IV. The thermograms of the copolyesters show a single T_g between 202 and 274°C, which are the T_g values of BAP/ISO and BF/ISO, respectively. No melting endothermic peak was observed from DSC thermograms. These results are consistent with those of X-ray diffraction measurements and with the transparency observed in the as-cast films, which indicate the amorphous nature of the polyesters and copolyesters. Figure 4 shows the behavior of the glass-transition temperature T_g as a function of composition for the homopolymers and copolymers as determined by DSC. It can be seen that the T_g value obtained for BF/ISO is greater than that of BAP/ISO, and this behavior is attributed to a larger degree of aromaticity and steric hindrance in the BF/ISO structure, which is in agreement with that observed in other aromatic materials such as polycarbonates, poliamides, and polysulfones.[14–16] In the copolyesters the T_g increases as the concentration of BF/ISO increases in the copolymer. Thus, for the copolyester formulations studied here, the highest T_g is that of BAP25/ISO, which has the greatest concentration of the most aromatic comonomer, BF/ISO, in its composition. Figure 4 shows not only the experimental T_g values of polyesters and copolyesters but also compares them with the values predicted using a simple mixing rule, the Fox equation. This equation predicts that random copolymers will show a single glass transition at temperatures intermediate between those of the homopoly-
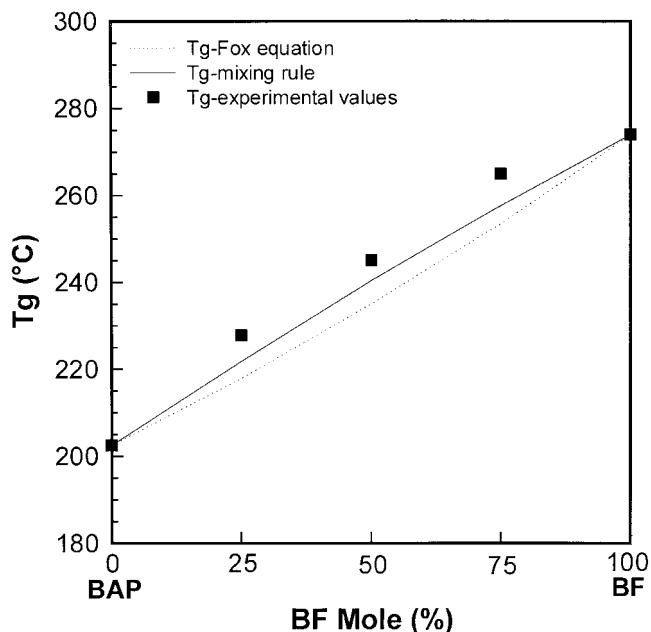
Figure 4 Glass transition temperatures as a function of concentration in BAP/ISO–BF/ISO copolyesters.

mers as a function of concentration, according to the following equation[17,18]:

$$\frac{1}{T_{gc}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (1)$$

where T_{gc}, 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. In this case Fox's equation predicts lower values than those found experimentally. There are several approaches to predict the expected T_g in a random copolymer or miscible blend as a function of composition. To find whether other simple rules of mixing, as described by Aubin and Prud'homme,[19] would improve the prediction, results from several approaches were taken. From these results, it was seen that a direct mixing rule using a linear approach such as

$$T_{gc} = w_1 T_{g1} + w_2 T_{g2} \qquad (2)$$

will better predict the experimental T_g values for the isophthalic copolyesters synthesized here. The initial decomposition temperatures (T_d) and weight losses at 500°C of the isophthalic polyesters and copolyesters are shown in Table IV. The onset of T_d for all polymers was found between 475 and 483°C under nitrogen atmosphere. The T_d observed is consistent with the T_g behavior of polyesters and copolyester. As the concentration of BF/ISO increases in the copolyester, the T_d also increases in a regular fashion. In the same table the weight loss at 500°C under nitrogen atmosphere

for each polyester and copolyester is reported. It is also observed that there is a regular decline in the amount of weight loss at this temperature as the concentration of BF/ISO increases in the copolyester. Overall, it can be seen that as the amount of the most aromatic and rigid comonomer BF/ISO increases in the copolyesters, the T_d and T_g show an increase that is linear with the concentration. A similar behavior was reported by Kane et al.[7] for a series of aromatic copolyesters.

The dynamic mechanical behavior of BAP/ISO, BF/ISO, and their copolyesters as a function of temperature is given in Figure 5, for the storage modulus E', and Figure 6, for the damping factor tan δ. As shown in Figure 5, the storage modulus E' of polyesters and copolyesters at low temperatures is of the order of 10^9 Pa. It can also be seen that the temperature at which the onset of the glass-to-rubber transition occurs increases gradually as the concentration of BF/ISO in the copolyesters increases. This behavior is attributed to an increase in the stiffness of the materials resulting from the presence of greater amounts of aromatic groups in the structure.

Figure 6 shows values of tan δ for BAP/ISO, BF/ISO, and their copolymers. Each curve has been shifted by the factor preceding it, to exhibit the data more clearly. All polymers show a well-defined maximum for the α-transition (T_α) that in BAP/ISO appears at 205°C, whereas that of BF/ISO appears at 275°C. The maximum in tan δ for the different copolyesters increases as the concentration of BF/ISO increases in the copolymer. The experimental maximum values of T_α for BAP/ISO, BF/ISO, and their copolyesters are listed in Table IV. As was observed in the glass-transition behavior, there is a single transition whose maximum increases as the concentration of BF/ISO, the more rigid aromatic comonomer, increases in the copolyester in a regular fashion. These results are also indicative that completely random copolymers were obtained during the synthesis process.

CONCLUSIONS

Two aromatic polyesters BAP/ISO and BF/ISO and three different copolyesters from these polyesters containing 75, 50, and 25 mol % of BAP/ISO were synthesized by interfacial polycondensation. The method yielded polymers and copolymers that produced flexible transparent films when they were cast from solution. ^{1}H-NMR studies showed that the isophthalic copolyesters were obtained as random copolymers, with differences in comonomer concentration no greater than 2.5 mol % with respect to the expected values. Wide-angle X-ray diffraction measurements indicated that all the polyesters and copolyesters were amorphous. The copolyesters showed amorphous pat-
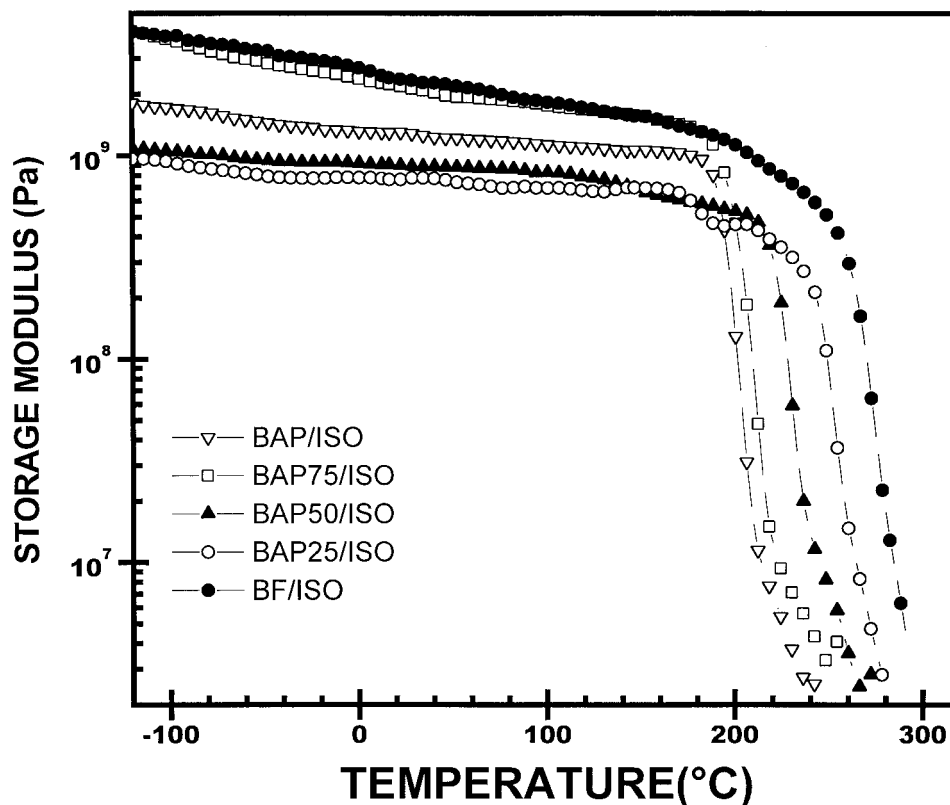
Figure 5 Storage modulus (E') as a function of temperature for BAP/ISO, BF/ISO, and their copolyesters.

terns with maximum values between those of the homopolyesters.

It was also found that thermal properties such as glass-transition temperature, onset of decomposition temperature, thermal stability, dynamic mechanical storage modulus, and maximum on the α-transition in tan δ of BF/ISO are higher than those of BAP/ISO.
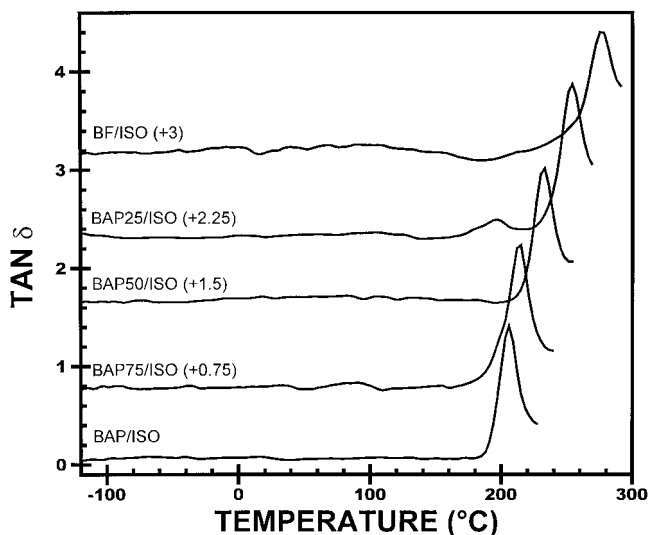
Values of these thermal properties in the copolyesters fell between those of the homopolyesters and were linearly dependent on the amounts of comonomers, BF/ISO and BAP/ISO, present in the copolyester. Therefore, the thermal properties of a given copolyester can be predicted directly from the comonomers' composition therein. The overall results showed that the interfacial polycondensation method is suitable for the preparation of aromatic copolyesters. It has been found, in this particular pair of comonomers, that copolyester properties depend on the concentration of comonomers in a linear fashion, which would allow synthesis of materials in which the properties could be tailored to be between those of the homopolyesters.

References

1. Korshak, K.; Vinogradova, V. J Macromol Sci Rev Macromol Chem 1974, C11, 45.
2. Morgan, P. W. Macromolecules 1970, 3, 536.
3. Morgan, P. W. J Polym Sci Part A 1964, 2, 437.
4. Pessan, L. A.; Koros, W. J. J Polym Sci Polym Phys Ed 1993, 31, 1245.
5. Choe, E.; Borzo, M. J Appl Polym Sci 1994, 53, 621.
6. Makhija, S.; Jaffe, M. J Appl Polym Sci 1994, 53, 609.
7. Kane, K.; Wells, L.; Cassidy, E. High Perform Polym 1991, 3, 191.
8. Zhao, Z.; Wu, X.; Lin, Y.; Mclean, J. J Appl Polym Sci 1994, 52, 1529.
9. He, Z.; Mitchell, G. R. Polym Commun 1994, 25, 1322.

Figure 6 Damping factors (tan δ) as a function of temperature for BAP/ISO, BF/ISO, and their copolyesters.

10. Morgan, P. W. In: Macromolecular Syntheses; Biley, W. J., Ed.; Wiley–Interscience, New York, 1972; Vol. 4, pp 29–33.

11. Williams, D. A.; Fleming, I. Spectroscopic Methods in Organic Chemistry, Vol. 73; McGraw-Hill, London, 1989.

12. Charati, S. G.; Houde, A. Y.; Kulkarni, S. S.; Kulkarni, M. G. J Polym Sci Polym Phys Ed 1991, 29, 921.

13. Pixton, M. R.; Paul, D. R. J Polym Sci Polym Phys Ed 1995, 33, 1135.

14. Aguilar-Vega, M.; Paul, D. R. J Polym Sci Polym Phys Ed 1993, 31, 1599.

15. McHattie, J. S.; Koros, W. J.; Paul, D. R. J Polym Sci Polym Phys Ed 1991, 29, 731.

16. Likhatchev, D.; Gutierrez-Wing, C.; Kardash, I.; Vera-Graziano, R. J Appl Polym Sci 1996, 59, 725.

17. Armeniades, C. D.; Baer, E. In: Introduction to Polymer Science and Technology: An SPE Textbook; Kaufman, H. S.; Falcetta, J. J., Eds.; Wiley–Interscience, New York, 1977; Chapter 6.

18. Martuscelli, E.; Palumbo, R.; Kryszewski, M. Polymer Blends; Plenum Press, New York, 1980; p 114.

19. Aubin, M.; Prud'homme, E. Macromolecules 1988, 21, 2945.