Poly(butylene terephthalate) Copolyesters Derived from L-Arabinitol and Xylitol

Abdelilah Alla,† Khalid Hakkou,‡ Francisca Zamora,‡ Antxon Martínez de Ilarduya,† Juan A. Galbis,*,‡ and Sebastián Muñoz-Guerra*,†

Departament d'Enginyeria Química, ETSEIB, Universitat Politècnica de Catalunya, 08028-Barcelona, Spain, and Departamento de Química Orgánica y Farmacéutica, Facultad de Farmacia, Universidad de Sevilla, 41071-Sevilla, Spain

Received November 10, 2005; Revised Manuscript Received December 20, 2005

ABSTRACT: The synthesis, characterization, and some properties of new copolyesters of poly(butylene terephthalate) based on L-arabinitol and xylitol are described. These copolyesters were obtained by polycondensation reaction in the melt of mixtures of 1,4-butanediol and 2,3,4-tri-O-methyl-L-arabinitol or 2,3,4-tri-O-methylxylitol with dimethyl terephthalate. Their weight-average molecular weights ranged between 20 000 and 40 000, with polydispersities oscillating from 1.5 to 2.2. All them had a statistical microstructure and were thermally stable well above 300 °C. Copolyesters containing up to 30% of alditol-derived units were found to be crystalline and to adopt the same crystal structure as the parent homopolyester poly(butylene terephthalate). The melting temperature and crystallinity were observed to decrease, and the glass transition temperature to increase, with increasing amounts of alditol incorporated in the copolyester. Crystallizability was depressed by copolymerization, whereas the hydrolytic degradability was significantly enhanced by the presence of alditol units. No relevant differences in either structure or properties were observed between the L-arabinitol and xylitol copolyester series.

Introduction

Poly(butylene terephthalate), PBT, is a semicrystalline thermoplastic, which is mainly produced by polycondensation of dimethyl terephthalate (DMT) with 1,4-butanediol (BD). PBT has a moderate melting temperature of around 225 °C and crystallizes very fast from the melt. This exceptional thermal behavior, together with its excellent mechanical properties, makes PBT the material of choice for durable goods that are manufactured by injection molding. PBT and poly(ethylene terephthalate) (PET) are the representatives of the aromatic polyester family.

PBT is a well-stable material, little affected by environmental conditions. Since PBT absorbs very little water (less than 0.1%), it is highly resistant to degradation in aqueous media. It is also very resistant to degradation by microorganisms. Currently, great efforts are being made to render aromatic polyesters more hydrophilic and susceptible to biodegradation, with the aim of making them usable in temporary applications.² It is known that all polyesters degrade eventually, hydrolysis being the dominant mechanism. However, degradation rates may range from weeks for certain aliphatic polyesters to decades for PET and PBT. Copolymers including aliphatic and aromatic counterparts are currently under investigation to develop biodegradable materials able to satisfy new demands.³

Recently, incorporation of highly polar or hydrophilic moieties in the PET chain has proven effective in increasing its hydrolytic sensitivity. This approach includes the use of comonomers such as substituted terephthalic acids⁴ or polyhydroxylated diols^{5,6} derived from carbohydrates. The insertion of carbohydrate moieties in polycondensates as polyamides and polycarbonates with the aim to obtain more hydrophilic and biodegradable polymers has been extensively explored in these

last years.^{7–9} In this paper we wish to report on the synthesis, characterization, thermal behavior, and hydrolytic degradation of a series of PBT copolymers obtained from dimethyl terephthalate and mixtures of 1,4-butanediol and 2,3,4-tri-O-methylpentitols with either L-arabino or xylo configurations. Special attention is paid to studying the influence of the copolymer composition on crystallizability because of the relevance that this property has for the technical use of PBT. Since both L-arabinitol and xylitol lack the C_2 symmetry axis, aregic structures should be expected to be formed in these polycondensations.

Experimental Section

Chemicals were all used as purchased from Aldrich Chemical Co. Solvents were dried and purified, when necessary, by appropriate standard procedures. The preparation of the sugar-based monomers 2,3,4-tri-O-methyl-L-arabinitol (Ar) and 2,3,4-tri-O-methylxylitol (Xy) from the naturally occurring L-arabinose and D-xylose has been previously described by us in full detail. ¹⁰

General Procedure of Preparation of Polyesters and Copolyesters. A magnetically stirred mixture of 2,3,4-tri-*O*-methyl-L-arabinitol or 2,3,4-tri-*O*-methyl-xylitol, 1,4-butanediol, and dimethyl terephthalate, in a molar ratio of the two diols to DMT of 2.2/1, was slowly heated to 180 °C under an argon atmosphere. After 1.5 h at this temperature, 0.6 mmol of titanium tetrabutoxide was added, and the mixture was heated first for 4 h at 195 °C and finally for 3 h at 200 °C under vacuum (0.5–1 mmHg). For the synthesis of PBT homopolyester, this second stage was carried out at 250 °C. After cooling to room temperature, the resulting slightly colored solid was dissolved in the minimum amount of chloroform or trifluoroacetic acid—chloroform mixture, and the solution was poured dropwise into diethyl ether. The precipitated white solid was purified by repeating the solution—precipitation procedure several times.

Measurements. Optical rotations were measured at 20 \pm 0.5 °C (1 cm cell). Intrinsic viscosity measurements were carried out in dichloroacetic acid with a Cannon-Ubbelohde 100/L30 semi-microviscometer at 25.0 \pm 0.1 °C. $^{1}\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra were recorded on a Bruker AMX-300 spectrometer at 25.0 °C operating

^{*} Corresponding authors. E-mail: (J.A.G.) jgalbis@us.es; (S.M.-G.) sebastian.munoz@upc.edu.

[†] Universitat Politècnica de Catalunya.

[‡] Universidad de Sevilla.

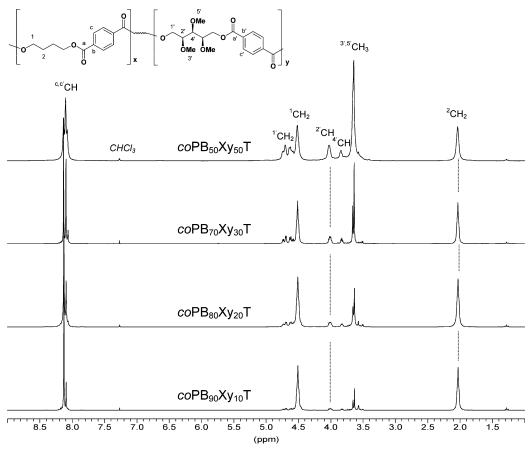


Figure 1. ¹H NMR spectra of copolyesters in CDCl₃/TFA 9/1. The areas of the assigned peaks were used to determine the compositions of copolyesters.

at 300.1 and 75.5 MHz, respectively. Polyesters and copolyesters were dissolved in a mixture of deuterated chloroform and trifluoroacetic acid (9:1), and spectra were internally referenced to tetramethylsilane (TMS). Here 10 and 50 mg of sample dissolved in 1 mL of deuterated solvent were used for ¹H and ¹³C NMR, respectively. Sixty-four scans were acquired for ¹H and 1000-10 000 for ¹³C with 32 and 64 K data points and relaxation delays of 1 and 2 s, respectively. Gel permeation chromatography (GPC) was carried out using chloroform as the mobile phase at 35 °C. GPC analysis was performed on a Waters GPC system equipped with a refractive index detector. Molecular weights were calculated against monodisperse polystyrene standards using the Maxima 820 software. The thermal behavior of the polyesters was examined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC Pyris 1 calibrated with indium. DSC data were obtained from samples of 4-6 mg at heating/cooling rates of 10 or 20 °C min⁻¹ under nitrogen circulation. Thermogravimetric analysis (TGA) was carried out with a Perkin-Elmer TGA-6 thermobalance at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere. Isothermal crystallization studies were made from samples heated to 250 °C, maintained at this temperature for 5 min, and then quickly cooled to the crystallization temperature T_c . The heat flow evolving during the isothermal crystallization was recorded as a function of time. Powder X-ray diffraction patterns were recorded on flat photographic films with a modified Statton camera using nickel-filtered Cu Kα radiation with wavelength 0.1542 nm, and they were calibrated with molybdenum sulfide. Optical microscope observations were made with an Olympus polarizing microscope equipped with a Linkam thermal stage. Hydrolysis experiments were carried out on disks prepared by casting at room temperature from a 10% (w/v) solution in chloroform. Disks were separately immersed in acidic (pH 2.0) and basic (pH 10.6) 0.1 M buffer solutions at 80 °C. After immersion for the fixed period of time, the remaining solid was recovered, rinsed with water, and dried to constant weight under vacuum. The evolution of degradation was followed by GPC.

Results and Discussion

Synthesis and Chemical Structure. The synthesis of the copolyesters was carried out by reaction of dimethyl terephthalate and mixtures of 1,4-butanediol and 2,3,4-tri-O-methyl-L-arabinitol or 2,3,4-tri-O-methylxylitol in the selected proportions. For comparison purposes, the parent homopolyesters (PBT, PArT and PXyT) were prepared by the same procedure from their respective pure diols. The polycondensation reaction proceeded in the melt through two stages following the procedure commonly used at the industrial scale to prepare PET and PBT (Scheme 1). In the first stage, transesterification of dimethyl terephthalate with the mixture of the two diols was CDV

Table 1. Composition, Microstructure, Molecular Size and Optical Activity of Polyesters and Copolyesters

composition a $(X_{\rm B}/X_{\rm P})$		dyads(mol %)			sequence lengths			molecular size			optical	
polyester	F	C	ВТВ	ВТР	PTP	ВТ	PT	R	$[\eta] (dL/g)^c$	$M_{ m w}{}^d$	PD^d	activity $[\alpha]_{D}^{e}$
PBT	100/0	100/0	100	0	0				1.07	45 700	2.3	
$coPB_{90}Ar_{10}T$	90/10	88/12	79.8 (78.0)	17.9 (20.7)	2.4 (1.4)	9.9 (8.6)	1.2 (1.1)	0.93 (1.00)	0.40	31 000	1.9	0
$coPB_{80}Ar_{20}T$	80/20	80/20	65.1 (64.0)	30.3 (32.0)	4.6 (4.0)	5.3 (5.0)	1.3 (1.2)	0.97 (1.00)	0.38	31 900	2.1	+1.6
$coPB_{70}Ar_{30}T$	70/30	67/33	45.4 (43.6)	46.8 (44.5)	10.8 (11.2)	2.9 (3.0)	1.5 (1.5)	1.03 (1.00)	0.44	42 100	2.0	+2.2
$coPB_{50}Ar_{50}T$	50/50	48/52	21.5 (23.0)	51.0 (49.9)	27.5 (27.0)	1.8 (1.9)	2.1 (2.1)	1.02 (1.00)	0.57	27 600	1.8	+5.9
PArT	0/100	0/100	0	0	100				0.29	21 000	1.5	+11.7
$coPB_{90}Xy_{10}T$	90/10	88/12	80.8 (77.3)	17.7 (21.3)	2.3 (1.5)	10.1 (8.3)	1.3 (1.1)	0.90 (1.00)	0.51	35 400	1.8	0
coPB ₈₀ Xy ₂₀ T	80/20	78/22	64.5 (61.5)	29.6 (33.9)	5.9 (4.7)	5.4 (4.6)	1.4(1.3)	0.90 (1.00)	0.46	40 970	2.2	0
coPB ₇₀ Xy ₃₀ T	70/30	69/31	49.4 (47.5)	41.5 (42.8)	9.1 (9.7)	3.4 (3.2)	1.4 (1.5)	0.99 (1.00)	0.41	33 600	2.1	0
coPB ₅₀ Xy ₅₀ T	50/50	47/53	25.1 (22.3)	49.8 (49.8)	25.1 (27.9)	2.0 (1.9)	2.0 (2.1)	1.00 (1.00)	0.32	28 300	1.9	0
PXyT	0/100	0/100	0	0	100				0.28	19 000	1.6	0

^a Composition of the feed (F) and the resulting copolyester (C) determined by ¹H NMR. ^b Copolymer microstructure determined by ¹³C NMR. In parentheses, values theoretically estimated applying the Bernoulli statistics are given. *R*: randomness. ^c Intrinsic viscosity measured in dichloroacetic acid at 25 °C. ^d Weight-average molecular weights and polydispersity determined by GPC using chloroform as the mobile phase, except for PBT, which was run in 1,1,1,3,3,3-hexafluoro-2-propanol. ^e Specific optical rotation measured at 25 °C.

accomplished with release of methanol. Polycondensation, leading to copolyesters containing arabinitol (coPBArT) or xylitol units (coPBXyT) or homopolyesters, took place in the second stage under vacuum at higher temperatures to facilitate the removal of the exceeding diol. Copolyesters were prepared from feed molar ratios of BD:alditol ranging from 90:10 to 50: 50. The chemical constitution and composition of the resulting polycondensates were ascertained by ¹H NMR (Figure 1), and their molecular weights were estimated by GPC and viscosimetry. Data provided by these analyses are given in Table 1, where it can be seen that the copolyesters had compositions essentially similar to those of their respective feeds. A close inspection of the composition values reveals, however, that the alditol unit content of the copolymers is in most cases slightly higher than in their corresponding feed. Such apparently preferential incorporation of the alditol may be attributed to slight losses of the more volatile BD taking place in the second stage of polycondensation.

The microstructure of copolyesters was determined by ¹³C NMR analysis. These spectra showed single signals for the carbon atoms of tetramethylene units, whereas complex signals were observed for the aromatic carbons of the terephthalic units, indicating that these units are sensitive to sequence effects. Thus, as shown in Figure 2, the resonance of the nonprotonated aromatic carbon appeared as four signals in the 133.3-134.3 ppm chemical shift interval corresponding to the three types of dyads (BTP or PTB, BTB, and PTP, P being either Ar or Xy) that are possible along the copolyester chain. The plot of the content in each type of dyad as a function of the copolyester composition reveals that the microstructure of the copolyester is clearly statistical, with randomness quite near unity in all cases. The weight-average molecular weights of copolyesters were found to be roughly within the 20 000-40 000 range, corresponding to intrinsic viscosities between 0.3 and 0.5 dL g^{-1} . Finally, it should be noted that, in agreement with the configuration of the pentitols used in each case, copolyesters made from optically active **Ar** displayed weak optical rotations, while no activity at all was observed for those incorporating the Xy monomer. Accordingly, the optical activities measured for the respective homopolymers PArT and PXyT were 11.7 and 0° .

Thermal Properties and Crystal Structure. The thermal behavior of copolyesters has been comparatively studied by DSC and TGA; the thermal parameters resulting from these analyses

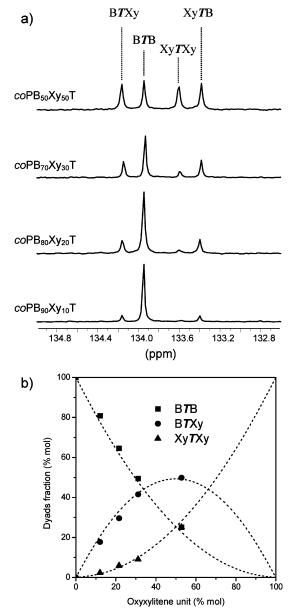


Figure 2. (a) Peak assignments for quantification of dyads in the *coPBXyT* copolyesters. (b) Plot of dyad contents in front of copolyester compositions. Dashed lines represent the theoretically calculated contents for random copolyesters.

Table 2. Thermal Properties and X-ray Spacings of Polyesters and Copolyesters

		DSC		TGA^a			X-ray spacings (Å) ^c							
	T _m (°C)	$\Delta H_{\rm m} ({\rm J/g})$	T_{g} (°C) b	$T_{\rm o}$ (°C)	T _d (°C)	ΔW (%)								
PBT	221	67.1	30	389	407	8	12.4 w	9.7 m	5.7 s	5.2 s	4.3 m	3.7 vs	3.6 m	3.1 vw
$coPB_{90}Ar_{10}T$	211	46.1	35	365	405	9	12.9 vw	10.0 w	5.7 m	5.2 s	4.3 m	3.7 s	3.6 s	3.1 vw
$coPB_{80}Ar_{20}T$	185	28.4	36	360	405	8	12.9 vw	10.0 w	5.7 m	5.3 m	4.4 w	3.8 m	3.6 w	
coPB70Ar30T	151	11.4	43	345	357/ 402	5			5.8 m	5.3 m	4.4 vw	3.9 m	3.6 w	
$coPB_{50}Ar_{50}T$			50	342	370/400	3								
PArT	91	27	60	340	374	0	13.5 w		7.5 s		4.2 w	3.9 w		
$coPB_{90}Xy_{10}T$	206	56.0	34	372	409	8	12.9 vw	9.7 w	5.6 m	5.2 s	4.3 w	3.8 s	3.5 s	3.1 w
$coPB_{80}Xy_{20}T$	185	38.0	33	364	407	4	12.9 vw	10.0 w	5.7 m	5.2 m	4.3 w	3.8 s	3.6 m	
coPB ₇₀ Xy ₃₀ T	157	16.3	35	350	351/ 407	4		10.4 vw	5.7 w	5.3 w	4.4 vw	3.8 w	3.6 vw	
coPB ₅₀ Xy ₅₀ T			44	341	365/ 399	3								
PXyT			50	338	364	0	13.5 w		6.3 s			3.9 s		

^a T_o: Temperature at which 10% of the initial mass is lost. T_d: maximum degradation rate. ΔW: remaining weight at the temperature of 600 °C. ^b T_o: Glass transition temperatures recorded at heating from quenched samples at a rate of 20 °C·min⁻¹. ^c Bragg spacings measured in powder diffraction patterns; Intensities visually estimated as follows: m, medium; s, strong; w, weak; vw, very weak.

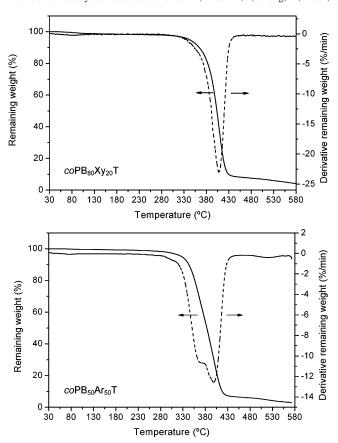


Figure 3. TGA traces of representative copolyesters derived from L-arabinitol and xylitol.

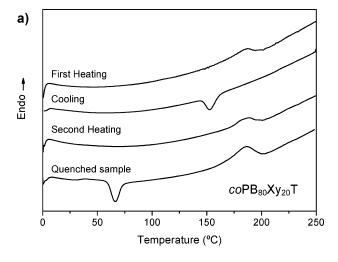
are given in Table 2. First, the effect of copolymerization on the thermal stability was evaluated. It can be said that the insertion of the methoxylated pentitols promotes a moderate decrease in the resistance to heat but all the copolymers remain unaltered up to 300 °C. As is illustrated in Figure 3, thermal decomposition of copolymers containing 20% and 50% of methoxylated comonomers happens in two clearly differentiated stages, with maximum decomposition rates differing by about 30-50 °C. Comparison of these temperatures with those observed for PBT and polyesters PArT and PXyT indicates that the higher and lower temperature stages should be made to correspond to the decomposition of the 1,4-butanediol- and pentitol-containing counterparts, respectively.

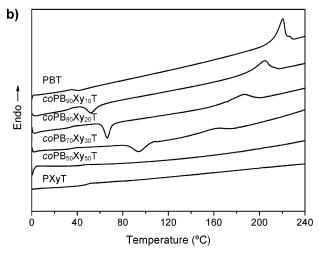
The DSC analysis revealed that the incorporation of the trimethoxylated pentitol in the chain of PBT induced significant changes in both melting and glass transition temperatures of the parent polymer PBT. As shown in Figure 4, well-defined

melting peaks, indicative of the presence of a crystalline phase, were observed for copolyesters containing up to 30% of pentitol units, with associated enthalpies that did not differ significantly between the two series of copolymers. In contrast, a striking difference was observed between the homopolymers PArT and PXyT concerning crystallinity, the former being crystalline with a melting temperature of 91 °C, whereas the latter appears to be amorphous. This result is in line with previously reported studies made on sugar-derived polyamides and polyesters, in which the thermal behavior clearly appeared to be depending on the configuration of the sugar residue used as monomer.^{3,11} It seems, therefore, that dilution of the sugar units in the copolyesters suppresses the configurational effects observed in the homopolymers. The glass temperature was found to increase steadily from 30 to 50 and 44 °C for the 50:50 copolymers of arabinitol and xylitol respectively, which is fully consistent with the values observed for the PArT and PXyT homopolymers, which are 60 and 50 °C, respectively.

The powder X-ray diffraction analysis corroborated DSC data, and revealed that the triclinic crystal structure of PBT¹² is retained in the copolymers. Representative patterns are compared in Figure 5, and Bragg spacings present in such patterns are listed in Table 2. The same basic pattern regarding both spacing and intensities is shared by all the copolymers. A question immediately arises concerning the location of the pentitol units in the biphasic semicrystalline state. Whereas it was earlier thought that a length of at least 16 BT repeating-units is the minimum required for crystallization, ¹³ recent observations have revealed that certain PBT copolymers are able to crystallize for chain segments consisting of only 2-5 repeating units.¹⁴ Conversely, the homopolymer PArT displayed a clearly dissimilar diffraction pattern, indicating that a different crystal structure must be adopted in this case. In agreement with DSC results discussed above, no discrete scattering characteristic of crystalline material was observed for the homopolyester PXyT.

Isothermal Crystallization Behavior. The influence of the presence of pentitol units on the crystallizability of the PBT copolyesters was evaluated by studying their isothermal crystallization from the melt. DSC traces (Figure 4a) show that crystallization of copolyesters with contents in sugar units equal to or less than 20% takes place sharply upon cooling from the melt, and that cold crystallization happens spontaneously when amorphous quenched samples are slowly heated from room temperature. Crystallization kinetics studies were carried out on copolyesters consisting of L-arabinitol and xylitol containing either 10 or 20% of pentitol units. These were heated to 250 °C and then left to crystallize isothermally at temperatures between 165 and 195 °C. For comparison, the isothermal CDV





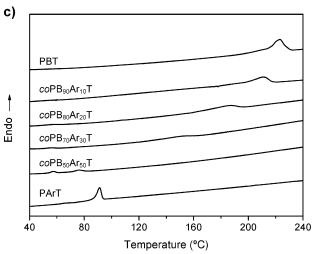


Figure 4. DSC traces of representative copolyesters derived from L-arabinitol and xylitol. Traces in part b were recorded at heating from quenched samples for T_g observation. Traces in part c were recorded from samples coming directly from synthesis.

crystallization of PBT was studied at 190 °C for a similarly heated sample. Avrami data plots $(\log[-\ln(1-X_t)])$ vs $\log(t-x_t)$ t_0)) and evolution of the relative crystallinity, X_t , vs crystallization time for some illustrative crystallization experiments are depicted in Figure 6. All the experiments carried out are gathered in Table 3, where the observed onset and half-crystallization times, as well as the corresponding calculated Avrami parameters, are given for each case. Avrami exponents were not far from 2.5, which is consistent with a nearly spherulitic crystal-

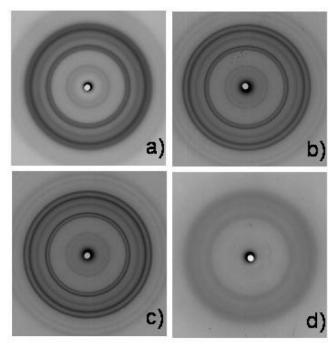


Figure 5. Powder X-ray patterns of (a) PBT, (b) coPB₉₀Ar₁₀T, (c) $coPB_{90}Xy_{10}T$, and (d) $coPB_{70}Ar_{30}T$.

Table 3. Isothermal Crystallization Data of Polyesters and Copolyesters

			Avrami parameters ^c				
	$T_{\rm c}{}^a({}^{\circ}{\rm C})$	$t_o{}^b$ (min)	n	log K	t _{1/2} (min)		
PBT	190	0.07	2.55	2.08	0.09		
$coPB_{90}Ar_{10}T$	185	0.27	2.32	0.29	0.63		
	190	0.40	2.44	-0.58	1.50		
	195	1.00	2.55	-1.97	5.25		
$coPB_{80}Ar_{20}T$	165	0.30	2.24	-0.49	1.41		
	170	1.09	2.46	-1.78	4.90		
	175	1.70	2.51	-2.32	7.63		
$coPB_{90}Xy_{10}T$	185	0.20	2.24	0.40	0.55		
•	190	0.50	2.58	-1.91	5.15		
	195	1.16	2.65	-2.51	7.85		
$coPB_{80}Xy_{20}T$	165	0.37	2.37	-0.34	1.20		
•• • •	170	0.53	2.36	-1.14	2.82		
	175	0.80	2.42	-1.64	4.30		

^a Crystallization temperature. ^b Onset crystallization time. ^c Avrami exponent n, constant of crystallization K (min⁻¹), and crystallization halftime $t_{1/2}$.

lization initiated by heterogeneous nucleation. In fact, parallel observation of the crystallization process under the polarizing optical microscope visually confirmed the instantaneous appearance of deficiently formed spherulites (Figure 7). The effect of temperature on crystallization rate was checked first. An increasing delay in the onset of crystallization, as well as in the crystallization rate, with temperature was observed for all the studied copolymers. The influence of composition on crystallizability had to be indirectly evaluated since the allowed crystallization temperature range varied with the copolymer composition. Nevertheless, comparison of crystallization data at 190 °C for 90:10 copolyesters with PBT evidenced that crystallization is greatly hindered by the incorporation of pentitol units. Furthermore, no clear differences were found between the arabinitol and xylitol series, revealing that configuration also has no significant effect on the crystallization process.

Hydrolytic Degradation Studies. Several previous studies on the hydrodegradability of polyamides containing sugar moieties have revealed that the presence of these units increases the hydrophilicity of the polymers and enhances the attack of CDV

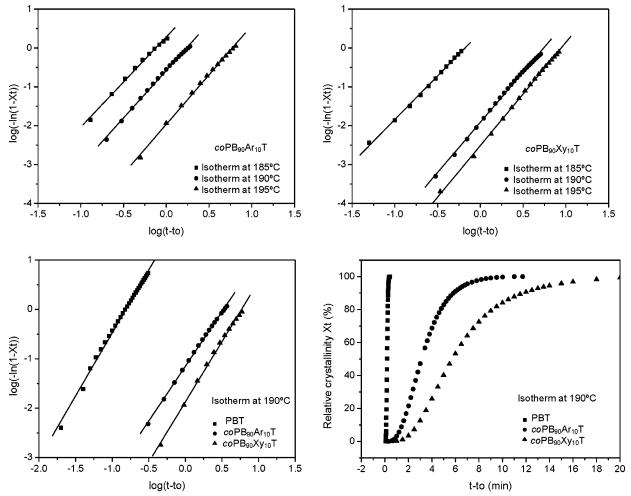


Figure 6. Compared isothermal crystallization data for PBT and the indicated copolyesters containing 10% L-arabinitol or xylitol.

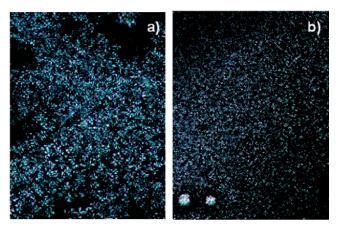


Figure 7. Polarizing optical micrographs of films of coPB₉₀Ar₁₀T (a) and coPB₈₀Ar₂₀T (b), crystallized at 195 and 175 °C, respectively.

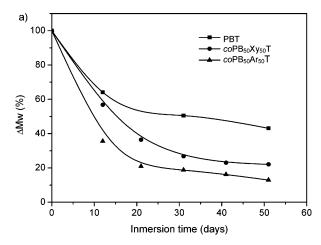
water on them.15 We have evaluated the effects that the incorporation of the trimethoxy pentitol units exerts on the hydrolysis of PBT. The changes taking place in the molecular weight of coPB50Ar50T and coPB50Xy50T at increasing incubation times in both acidic and basic aqueous buffer at 80 °C are depicted in Figure 8. Hydrolysis appears to be significantly enhanced by copolymerization, being more rapid under basic conditions. Results indicate that PBT degraded more slowly, and that this process seems to be not very sensitive to pH, so that similar degradation patterns were obtained under the two assayed conditions. On the other hand, the influence of the configuration of the pentitol unit on the hydrolysis rate is not

great, the slightly higher degradability observed for the arabinitol-containing copolymer at pH 2 not being significant enough for any meaningful conclusion to be drawn.

It is well-known that crystallinity hinders the hydrolysis of polyesters, so that the greater degradability observed here for the copolyesters cannot be excluded to be due in part to their amorphous nature. Unfortunately a separate evaluation of the contribution of the crystallinity effect was not feasible since fully amorphous samples of PBT were nor accessible due to the extremely high crystallizability displayed by this polyester.

Concluding Remarks

Preparation of PBT copolyesters containing up to 50% of trimethoxy pentitols derived from naturally occurring L-arabinose and D-xylose is feasible by polycondensation in the melt. The copolyesters have relatively high molecular weights and a random microstructure. They are semicrystalline up to contents of 30% pentitol, and they retain the crystal structure of PBT. The melting temperature of PBT is considerably depressed by the presence of the pentitol units, but its thermal stability is scarcely affected, being stable above 300 °C in all cases, a temperature much higher than required for melting. Crystallizability, measured as a combination of crystallization rate and crystallinity, is also diminished by copolymerization, although the copolymers with 10 and 20% of pentitol units continue to be readily crystallizable from the melt. The copolymers are much more sensitive to hydrolysis than is PBT, this effect being more pronounced under basic conditions. It can also be concluded that no significant differences in synthesis results, crystal CDV



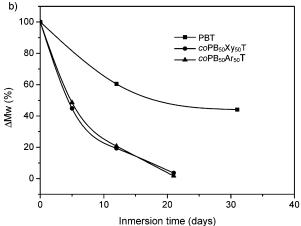


Figure 8. Changes in molecular weight upon hydrodegradation at 80 °C at pH 2.0 (a) and pH 10.6 (b).

structure, thermal behavior, or susceptibility to hydrolysis were observed between the L-arabinitol- and xylitol-derived copolyester series. In contrast to what was found in alditol-derived

homopolyesters, the influence of the configuration on structure and properties of copolyesters seems to be irrelevant.

Acknowledgment. We thank the CICYT (Comisión Interministerial de Ciencia y Tecnología) of Spain for financial support (Grant MAT2003-06955-C02).

References and Notes

- Gallucci, R. R.; Patel, B. R. In *Modern Polyesters*; Scheirs, J., Long, T. E., Eds.; John Wiley & Sons: New York, 2003; p 293.
- (2) Glenn Gallagher, F. In Modern Polyesters; Scheirs, J., Long, T. E., Eds.; John Wiley & Sons: New York, 2003; p 591.
- (3) Kint, D. P. R.; Muñoz-Guerra, S. Polym. Int. 1999, 48, 346–352.
- (4) (a) Kint, D. P. R.; Martínez de Ilarduya, A.; Muñoz-Guerra, S. J. Polym. Sci., Part A: Polym. Chem. 2001, 39, 1994. (b) Gaona, O.; Kint, D. P. R.; Martínez de Ilarduya, A.; Alla, A.; Bou, J.; Muñoz-Guerra, S. Polymer 2003, 44, 7281. (c) Kint, D. P. R.; Martínez de Ilarduya, A.; Muñoz-Guerra, S. Polym. Degrad. Stab. 2003, 79, 353.
- (5) Kint, D. P. R.; Wingstrom, E.; Martínez de Ilarduya, A.; Alla, A.; Muñoz-Guerra, S. J. Polym. Sci., Part A: Polym. Chem. 2001, 39, 3250.
- (6) Zamora, F.; Hakkou, K.; Alla, A.; Rivas, M.; Roffé, I.; Mancera, M.; Muñoz-Guerra, S.; Galbis, J. A. J. Polym. Sci., Part A: Polym. Chem. 2005, 43, 4570.
- (7) García-Martín, M. G.; Ruiz Pérez, R.; Benito Hernández, E.; Galbis, J. A. Carbohydr. Res. 2001, 333, 95.
- (8) Okada, M. Prog. Polym. Sci. 2001, 26, 67.
- (9) (a) Kiely, D. E.; Chen, L.; Lin, T.-H. J. Polym. Sci., Polym. Chem. 2000, 38, 594. (b) Tyron, S. D.; Kiely D. E.; Ponder, G. J. Carbohydr. Chem. 2003, 22, 142.
- (10) García-Martín, M. G.; Ruíz, R.; Benito, E.; Espartero, J. L.; Muñoz-Guerra, S.; Galbis, J. A. Macromolecules 2005, 38, 8664.
- (11) (a) García-Martín, M. G.; Benito, E.; Ruíz, R.; Alla, A.; Muñoz-Guerra, S.; Galbis, J. *Macromolecules* 2004, 37, 5550. (b) Mancera, M.; Zamora, F.; Roffé, I.; Bermúdez, M.; Alla, A.; Muñoz-Guerra, S.; Galbis, J. *Macromolecules* 2004, 37, 2779.
- (12) Boyle, C. A. Bull. Am. Phys. Soc. 1974, 19, 352.
- (13) Marchese, P.; Celli, A.; Fiorini, M. J. Polym. Sci., Polym. Phys. Ed. 2004, 42, 2821–2832.
- (14) Kuwabara, K.; Gan, Z. H.; Nakamura, T.; Abe, H.; Doi, Y. Biomacromolecules 2002, 3, 390.
- (15) (a) Ruíz-Donaire, P.; Bou, J. J.; Muñoz-Guerra, S.; Rodríguez-Galán, A. J. App. Polym. Sci. 1995, 58, 41. (b) Marqués, M. S.; Regaño, C.; Nyugen, J.; Aidampa, L.; Muñoz-Guerra, S. Polymer 2000, 41, 2765.

MA052398V