Carbohydrate-Based Polycarbonates. Synthesis, Structure, and Biodegradation Studies

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ABSTRACT: Linear homo- and co-polycarbonates have been prepared from the sugar-based diols 2,3,4-tri-*O*-methyl-L-arabinitol and 2,3,4-tri-*O*-methylxylitol. Statistical co-polycarbonates were obtained from molar feed ratios of sugar:bisphenol A of 1:1 and 2:1. The polycarbonates were stable up to ~280 °C with maximum decomposition rate above 345 °C. The arabinitol-based homopolymer was found to be semicrystalline whereas the xylitol-based one was amorphous. All the copolymers were amorphous with T_g ranging between 60 and 80 °C. Both homo- and co-polycarbonates showed high resistance to chemical hydrolysis; however, they were enzymatically degraded in different degree. The xylitol-based polycarbonates were the more easily degraded by lipase B from *Candida antarctica* in acetonitrile at 70 °C—this enzyme showing a high selectivity toward the configuration of the sugar-based moiety.

Introduction

Because of their excellent mechanical properties, polycarbonates are very promising polymers in the molecular design of biomaterials.[1] Thus, some aliphatic polycarbonates have been found to be good biodegradable/bioresorbable materials for biomedical applications because of their biocompatibility, low toxicity, and biodegradability.[2−10] Moreover, linear poly(bisphenol A carbonate) (PBPAC) and its modified block copolymers are of greatest interest because of the availability of bisphenol A (BPA) and the exceptional properties of these polymers. PBPAC is one of the most-useful engineering plastics because of its heat resistance, good mechanical properties, and high degree of transparency.[11−13] Cyclic PBPAC has also been studied.[14] As the carbonate linkage is more stable than the common ester linkage, aliphatic polycarbonates show greater resistance to hydrolysis than do polyesters. Nevertheless, polycarbonates are expected to be enzymatically degradable.

It is well-known that carbohydrate-based polymers have some desirable properties, such as hydrophilicity and degradability, and are good biocompatible materials.[15−17] Furthermore, carbohydrates are a natural, inexpensive renewing source that provide great stereochemical diversity. On the basis of our experience in the preparation and study of carbohydrate-based polymers,[18a−c] we decided to investigate carbohydrate-based polycarbonates. This kind of polymer has drawn great attention during the past decade; thus, Acemoglu et al.[19] described the first example of bioerodible water-soluble polycarbonates from acyclic sugar-based monomers. Cyclic monomers, such as 1,4:3,6-dianhydrohexitols (especially the one having D-*gluco* configuration), have been employed.[20−22] Gross et al.[23] used the 1,2-*O*-isopropylidene-D-xylofuranose-3,5-cyclic carbonate in the syntheses of homo- and co-polycarbonates. Recently, a first example of ring-opening polymerization of a five-membered cyclic carbonate, methyl 4,6-*O*-benzylidene-2,3-*O*-carbonyl-α-D-glucopyranoside, to give medium molecular weight polycarbonates, in good yields, has been reported.[24] In this paper we describe the preparation of new arregic homo- and co-polycarbonates using acyclic O-protected sugar-based diols, specifically the 2,3,4-tri-*O*-methylpentitols having L-*arabino* and *xylo* configurations.[18b]

Experimental Section

General Methods. Solvents were dried and purified, when necessary, using appropriate standard procedures. Optical rotations were measured at 20 ± 5 °C (1 cm cell). Elemental analyses were determined in the Microanalysis Laboratories of the CSIC, Isla de la Cartuja, Seville, Spain. FT-IR spectra were obtained from films or KBr disks. NMR spectra were recorded with Bruker 200 AC-P and AVANCE 500 MHz spectrometers. Ten and 40 mg of sample dissolved in 1 mL of $CDCl_3$ were used for ^1H and ^{13}C, respectively. Chemical shifts are reported as parts per million downfield from Me_4Si. Experimental conditions for co-polycarbonates (500 MHz) were as follows: temperature 303 K, pulse length of 45°, 32K data points, 10 s of relaxation delay, and 16 transients. ^{13}C spectra were recorded for co-polycarbonates at 125 MHz with the following parameters: temperature 303 K, pulse length of 30°, 64K data points, 2 s of relaxation delay, and 12 288 transients. Gel permeation chromatography (GPC) analyses were carried with two Styragel HR columns (7.8 × 300 mm) placed in series, using chloroform as the mobile phase at a flow rate of 1 mL/min. Molecular weights were estimated against polystyrene standards. Intrinsic viscosity measurements were carried out in dichloroacetic acid with Cannon-Ubbelohde 100/L30 or 150/L12 semi-microviscometers at 25.0 ± 0.1 °C. The thermal behavior of the polycarbonates was examined by DSC using a Perkin-Elmer Pyris 1 instrument calibrated with indium. DSC data were obtained from samples of about 4−5 mg, at heating/cooling rates of 10 °C/min, and under a nitrogen flow. Thermogravimetric measurements were performed under an inert atmosphere with a Perkin-Elmer TGA6 thermobalance at a heating rate of 20 °C/min. 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.

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Table 1. Monomer Feed Ratio, Average Molecular Weight, Polydispersity, Molar Composition, and Repeating Unit Lengths of the Polycarbonates

polycarbonate[a]	f_{sugar}/f_{BPA}[b]	M_w[c] (g/mol)	M_w/M_n[c]	F_{sugar}/F_{BPA}[d]	L_{sugar}/L_{BPA}[e]
PArC	1:0	35 000	1.3	1:0	
PXyC	1:0	78 700	1.5	1:0	
P(0.6Ar-*co*-BPAC)	1:1	135 000	1.5	0.6:1	1.4:2.1
P(0.9Xy-*co*-BPAC)	1:1	212 200	1.2	0.9:1	1.8:1.8
P(1.1Ar-*co*-BPAC)	2:1	135 200	1.5	1.1:1	1.9:1.5
P(1.8Xy-*co*-BPAC)	2:1	214 000	1.3	1.8:1	2.3:1.5

[a] Co-polycarbonates are named taking into account the molar composition resulting from the ^{1}H NMR analysis. [b] Molar feed ratio. [c] By GPC against polystyrene standards, using chloroform as a mobile phase. [d] Molar composition estimated by ^{1}H NMR. [e] Average sugar and BPA repeating unit lengths determined by ^{13}C NMR.

Polymerization and Copolymerization Procedure. Argon was bubbled through a cooled solution (0 °C) of the corresponding sugar diol (0.776 g, 4 mmol) in dry pyridine (6 mL) for 15 min; then a solution of phosgene in toluene (20%) (8 mmol, 4 mL) was added dropwise. The resulting suspension was allowed to reach room temperature and stirred overnight. Finally, the mixture was bubbled with argon, diluted with dichloromethane (50 mL), and washed with sodium chloride solution (25 mL × 2) and water (25 mL × 2). The combined organic extracts were dried with anhydrous magnesium sulfate, filtered, and concentrated. The residue was treated with diethyl ether to give an amorphous solid that was filtered off and dried under vacuum.

For copolymerizations, the reaction conditions and workup were similar to those mentioned above. The sugar diol was copolymerized with bisphenol A in the feed ratio 1:1 and 2:1 (mol/mol) and the corresponding amount of phosgene.

The molar composition, average molecular weights, polydispersities, yields, and physical constants of the polycarbonates are collected in Tables 1 and 2. The spectroscopic data are given below:

PArC. IR: ν_{max} 1750 (CO) cm^{-1}. NMR data (200 MHz, $CDCl_3$): ^{1}H, δ 4.60 and 4.30 (2 m, 4 H, 2 CH_2), 3.65 (m, 2 H, 2 CH), 3.55−3.30 (m, 1 H, CH), 3.46, 3.43, 3.40 (3 s, 9 H, 3 OMe). ^{13}C (50 MHz): δ 155.3, 155.1, 154.9 (CO), 79.1, 78.0, 77.9 (C-2/C-3/C-4), 66.9, 65.6 (C-1/C-5), 60.8, 59.3, 58.0 (OMe). Anal. Calcd for $C_9H_{16}O_6 \cdot H_2O$: C, 45.37; H, 7.62. Found: C, 44.95; H, 7.18.

PXyC. IR: ν_{max} 1748 (CO) cm^{-1}. NMR data (200 MHz, $CDCl_3$): ^{1}H, δ 4.30 (m, 4 H, 2 CH_2), 3.64 (m, 2 H, 2 CH), 3.48 (s, 3 H, OMe), 3.45 (m, 1 H, CH), 3.43 (s, 6 H, 2 OMe). ^{13}C (50 MHz): δ 154.9 (CO), 79.4, 77.8 (C-2/C-3/C-4), 67.2 (C-1/C-5), 60.1, 58.8 (OMe). Anal. Calcd for $C_9H_{16}O_6$: C, 49.09; H, 7.27. Found: C, 49.17; H, 7.37.

P(0.6 Ar-*co*-BPAC). IR: ν_{max} 1769 (CO) cm^{-1}. NMR data (500 MHz, $CDCl_3$): ^{1}H, δ 7.07−7.28 (m, aromatic), 4.80−4.20 (m, CH_2), 3.69−3.81 (m, CH), 3,60 (m, CH), 3.55−3.35 (m, OMe), 1.67 and 1,70 (2s, CMe_2). ^{13}C (125 MHz): δ 155.3, 155.2, 154.9, 153.8, 153.6, 152.1 (CO), 148.8, 148.2, 148.1, 148.0, 127.8, 120.2 (aromatic), 78.9, 77.9, 77.6 (C-2/C-3/C-4), 66.8, 66.5 (C-1/C-5), 60.8, 59.4, 57.9 (OMe), 42.4 ($\mathit{C}Me_2$), 30.8 ($C\mathit{Me}_2$).

P(1.1 Ar-*co*-BPAC). IR: ν_{max} 1760 (CO) cm^{-1}. NMR data (500 MHz, $CDCl_3$): ^{1}H, δ 7.07−7.28 (m, aromatic), 4.80−4.20 (m, CH_2), 3.69−3.81 (m, CH), 3,60 (m, CH), 3.55−3.35 (m, OMe), 1.67 and 1,70 (2s, CMe_2). ^{13}C (125 MHz): δ 155.3, 155.2, 155.0, 153.8, 153.7, 153.6, 152.1 (CO), 149.1, 149.0, 148.3, 148.2, 148.1, 148.0, 128.1, 127.9, 127.8, 127.7, 120.4, 120.3, 120.1, 119.7, 119.6 (aromatic), 81.0, 80.9, 80.7, 79.4, 79.3, 79.2, 78.5, 78.2, 78.1, 78.0, 77.9 (C-2/C-3/C-4), 65.8, 65.7, 65.1 (C-1/C-5), 60.8, 60.7, 60.5, 60.2, 59.8, 59.4, 59.3, 58.5, 58.1, 58.0, 57.5, 57.3 (OMe), 42.6, 42.5 ($\mathit{C}Me_2$), 30.9 ($C\mathit{Me}_2$).

P(0.9 Xy-*co*-BPAC). IR: ν_{max} 1763 (CO) cm^{-1}. NMR data (500 MHz, $CDCl_3$): ^{1}H, δ 7.00−7.22 (m, aromatic), 4.25−4.52 (m, CH_2), 3.40−3.55 (m, CH and OMe), 1.66 (s, CMe_2). ^{13}C (125 MHz): δ 155.0, 153.6, 152.1 (CO), 149.0, 148.9, 148.2, 148.0, 127.9, 127.8, 120.4, 120.3 (aromatic), 79.6, 78.0, 77.9 (C-2/C-3/C-4), 67.7, 67.6, 67.3, 67.1 (C-1/C-5), 60.2, 60.1, 58.8, 58.7 (OMe), 42.5 ($\mathit{C}Me_2$), 30.9 ($C\mathit{Me}_2$).

P(1.8 Xy-*co*-BPAC). IR: ν_{max} 1740 (CO) cm^{-1}. NMR data (500 MHz, $CDCl_3$): ^{1}H, δ 7.00−7.22 (m, aromatic), 4.25−4.52 (m, CH_2), 3.40−3.55 (m, CH and OMe), 1.66 (s, CMe_2). ^{13}C (125 MHz): δ 155.0, 153.6, 152.1 (CO), 149.0, 148.9, 148.2, 148.1, 127.9, 127.8, 120.4, 120.3 (aromatic), 79.6, 78.0, 77.9 (C-2/C-3/C-4), 67.8, 67.3, 67.1 (C-1/C-5), 60.2, 60.1, 58.8, 58.7 (OMe), 42.5 ($\mathit{C}Me_2$), 30.9 ($C\mathit{Me}_2$).

General Enzymatic Degradation Procedure. A disk (100−200 μm in thickness, 20 mg) of the corresponding polycarbonate and B lipase from *Candida antarctica* (160 mg) in acetonitrile (2 mL) were stirred under an argon atmosphere, in a thermostated oil bath at 70 °C. After different periods of time, the reaction mixture was diluted with dichloromethane, and the insoluble enzyme was filtered off through diatomaceous earth. The solution was concentrated to dryness, and the residue was analyzed by GPC.

Results and Discussion

Synthesis and Characterization. We now present results on the preparation and characterization of polycarbonates derived from pentitols such as 2,3,4-tri-*O*-methyl-L-arabinitol (**Ar**) and 2,3,4-tri-*O*-methylxylitol (**Xy**). We have previously described the preparation of these sugar-derived monomers[18b] starting from L-arabinose and D-xylose (Scheme 1) as well as some polyamides based on L-arabinaric and xylaric acids.[18b,c] The preparation of analogous carbohydrate-based polyesters is in course.[25]

Sugar monomers **Ar** and **Xy** have been transformed into fully sugar-based homo-polycarbonates (**PSuC**) by reaction with phosgene and also copolymerized with BPA [**P(Su-*co*-BPAC)**] (Scheme 2). The new polycarbonates here described should combine both the properties due to carbohydrates and those of aliphatic and aromatic polycarbonates. In the preparation of **P(Su-*co*-BPAC)**, the sugar monomers were made to react with BPA in a molar feed ratio of 1:1 and 2:1, respectively.

PSuC were obtained with average molecular weights (M_w) (GPC, see Table 1) ranging from 35 000 to 78 000 g/mol and polydispersities (M_w/M_n) of 1.3−1.5. Other approaches, using trichloromethyl chloroformate (TCF), as a source of phosgene, in chloroform in the presence of triethylamine or pyridine, gave polycarbonates with lower molecular weights. For instance, a M_w of less than 5800 g/mol was obtained for **PArC**.

Copolymerizations with BPA gave co-polycarbonates with very high M_w (up to 214 000 g/mol) and polydispersities of 1.2−1.5. The M_w and polydispersity data, together with other constitutive characteristics of these polymers, are summarized in Table 1.

The co-polycarbonate molar compositions were estimated by ^{1}H NMR from the integration of the aliphatic signals corresponding to the sugar unit (16 H) in relation with the methyl groups of BPA (6 H). When a molar feed ratio of 1:1 was used, molar compositions of 0.6:1 and 0.9:1 were estimated for **P(Ar-*co*-BPAC)** and **P(Xy-*co*-BPAC)**, respectively. For a molar feed ratio of 2:1, compositions of 1.1:1 and 1.8:1 were estimated for **P(Ar-*co*-BPAC)** and **P(Xy-*co*-BPAC)**, respectively. Henceforth, the copolymers will be named taking into account the composition calculated from ^{1}H NMR. Figures 1 and 2 show the ^{1}H and ^{13}C NMR spectra of **P(1.1 Ar-*co*-BPAC)** and **P(1.8 Xy-*co*-BPAC)**, respectively.

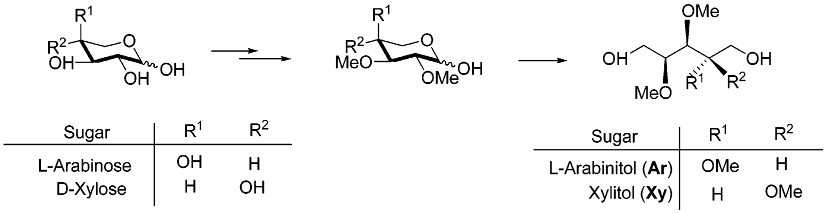
The ^{13}C NMR spectra of **PXyC** showed only one signal for all the carbonyl carbons at δ 154.9 ppm due to the

Table 2. Yield and Some Physical Constants of Polycarbonates

polycarbonate	yield (%)	$[\alpha]_D$[a] (deg)	$[\eta]$[b] (dL/g)	ν_{max}[c] (cm^{-1})	T_d°[d] (°C)	T_d[e] (°C)	T_g[f] (°C)	T_m[f] (°C)
PArC	90	15.6	0.34	1750	310	365	30	105
PXyC	83		0.56	1748	295	350	10	
P(0.6 Ar-*co*-BPAC)	98	−4.8	1.05	1769	310	365, 435	79	
PP(1.1 Ar-*co*-BPAC)	93	−3.8	0.94	1760	290	360, 430	50	
P(0.9 Xy-*co*-BPAC)	90		1.30	1763	285	345, 410	65	
P(1.8 Xy-*co*-BPAC)	81		1.25	1740	280	345, 410	80	
PBAC[g]					>400	>450	149	225

[a] *c* 0.5, chloroform, at 25 °C. [b] In dichloroacetic acid at 25 ± 0.1 °C. [c] IR absorption due to the carbonyl of the carbonate function. [d] Onset decomposition temperature corresponding to 5% of weight loss. [e] Maximum rate decomposition peaks. [f] Glass and melting temperatures measured by DSC. [g] Data taken from ref 26.

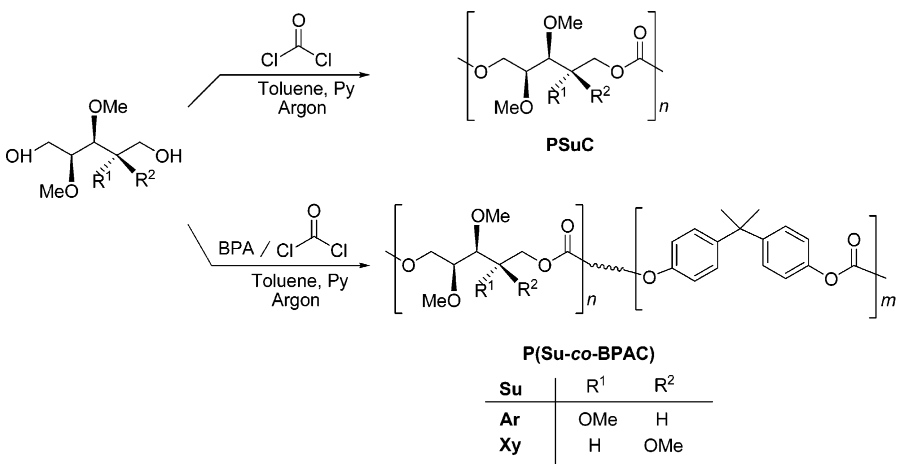
Scheme 1. Synthesis of the Sugar Monomers L-Arabinitol and Xylitol



Sugar	R^1	R^2
L-Arabinose	OH	H
D-Xylose	H	OH

Sugar	R^1	R^2
L-Arabinitol (**Ar**)	OMe	H
Xylitol (**Xy**)	H	OMe

Scheme 2. Preparation of PSuC and P(Su-*co*-BPAC)



PSuC

P(Su-*co*-BPAC)

Su	R^1	R^2
Ar	OMe	H
Xy	H	OMe

symmetry of the sugar monomer, whereas **PArC** showed a few signals between *δ* 156.0 and 154.9 ppm for these carbons.

For **P(Su-*co*-BPAC)**, the intensity of the ^{13}C NMR signals of the sugar moiety increased or decreased, corresponding to an increase or decrease in the sugar content of the co-polycarbonate. **P(Ar-*co*-BPAC)** showed a more complex carbonyl carbon region than the corresponding homopolymer (see Figure 1 and Experimental Section). The CO signals at *δ* 155.3 and 154.9 ppm were at the same positions as those for the homo-polycarbonates, suggesting the presence of sugar repeating unit segments in the polymer chain. The different carbonyl signals were assigned as follows: the above-mentioned downfield signals were due to the Ar−Ar repeating unit (comparing with the homopolymer **PArC**) and the signal at *δ* 152.1 ppm to BPA-BPA units (homo-**PBPAC** showed only one signal for the CO at *δ* 152.1 ppm); the intermediate signals should be due to CO between Ar and BPA units. An approximation of the repeating unit lengths of the co-polycarbonates was made based on the integration of the ^{13}C NMR signals due to the carbonyl carbons,[23c] according to eqs 1 and 2:

$$L_{\text{sugar}} = I_{\text{sugar-sugar}} + I_{\text{sugar-BPA}}/I_{\text{sugar-BPA}} \qquad (1)$$

$$L_{\text{BPA}} = I_{\text{BPA-BPA}} + I_{\text{sugar-BPA}}/I_{\text{sugar-BPA}} \qquad (2)$$

The calculated repeating unit lengths were short and quite similar, as indicated in Table 1, suggesting a structure with a random character rather than a block alternating constitution. The co-polycarbonate having the highest content of sugar was **P(1.8 Xy-*co*-BPAC)**, for which the highest repeating unit length was found.

The polycarbonates were obtained in the yields indicated in Table 2; those of co-polycarbonates were estimated as indicated therein. All of them were soluble in chloroform and were found to be hygroscopic, especially so the fully carbohydrate-based ones, **PArC** and **PXyC**. Other carbohydrate-based polymers, in particular polyamides,[18c] having methoxyl groups in the carbohydrate repeating unit, are also highly hygroscopic. As expected, only the L-arabinitol-based polycarbonates were optically active. The intrinsic viscosities measured in dichloroacetic acid were in accordance with the M_w found by GPC. In the IR spectra, all of them presented a strong absorption band in the region 1740−1770 cm^{-1}, due to the carbonate function. Table 2 also summarizes the optical rotation, intrinsic viscosity, main absorption in the IR, and thermal properties of these polycarbonates.

The thermal stability under an inert atmosphere was estimated by TGA. All the polymers started to decompose significantly above 280 °C, with maximum decom-

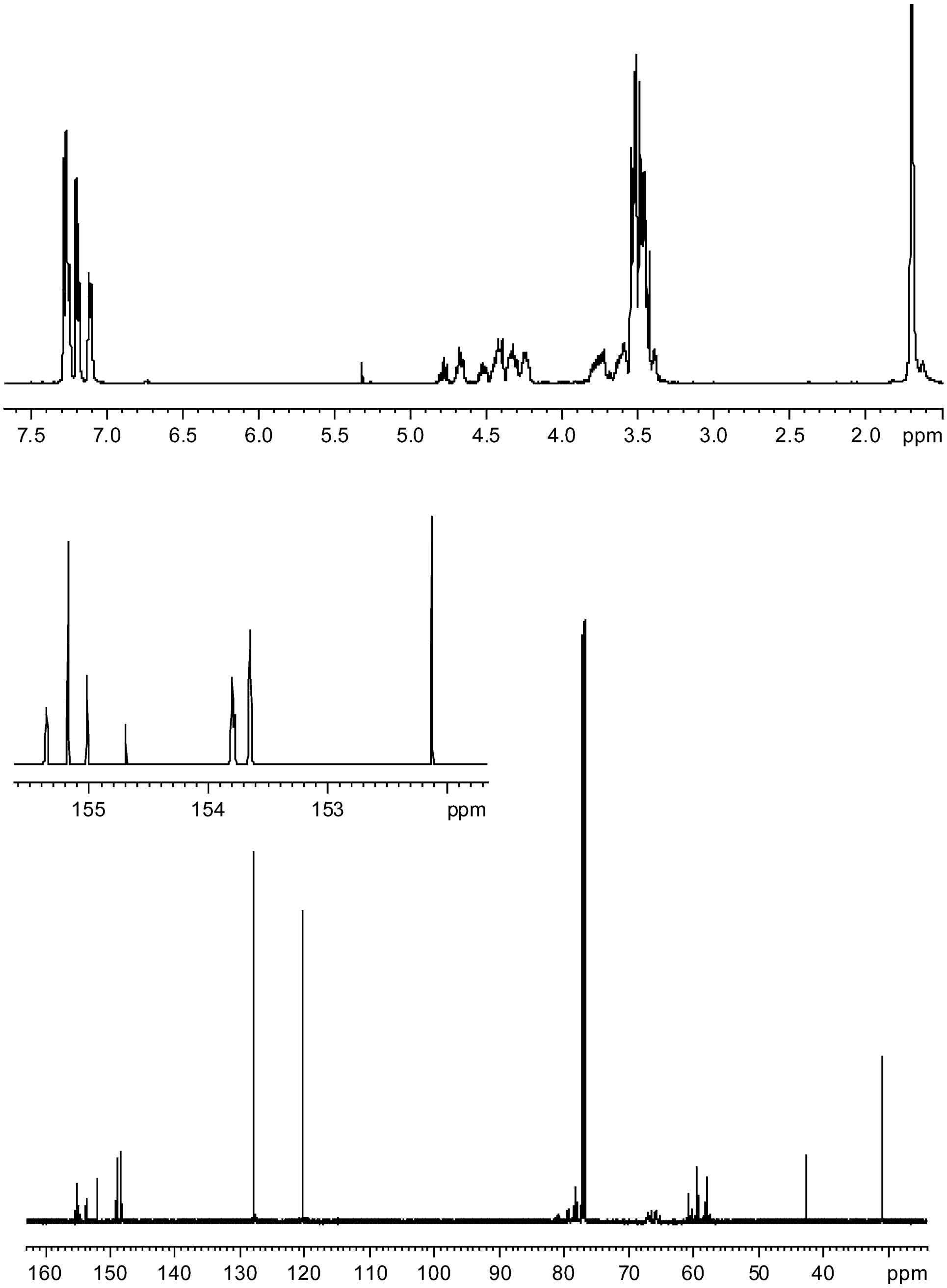


Figure 1. ^{1}H and ^{13}C NMR spectra (500 and 125 MHz, respectively, $CDCl_3$) of **P(1.1 Ar-*co*-BPAC)**.

position rates occurring above 345 °C (Figure 3). Decomposition of copolymers was observed to take place in two stages at temperatures roughly corresponding to those of the respective parent homopolymers. A comparison of TGA data shows that xylitol-based polycarbonates are slightly less stable than their corresponding arabinitol analogues.

DSC analyses of polycarbonates revealed that they are amorphous, except for the case of **PArC**; this observation was corroborated by powder X-ray diffraction. In Figure 4, the DSC traces of the homopolymer **PArC** and the copolymer **PA(0.6Ar-*co*-PBA)** are compared. The broad endotherm appearing on the initial heating trace of **PArC** became much sharper after annealing at 80 °C for 12 h. This heating exchange is attributed to a melting process starting at ~100 °C, with an enthalpy of about 40 J/g. The powder diffraction pattern recorded at room temperature from annealed **PArC** afforded further evidence of the semicrystalline nature of this polycarbonate. Up to 10 definite rings characteristic of crystalline material could be detected in the photograph (inset of Figure 3). In contrast, **PXyC** showed no sign of crystallinity. This striking result is in full agreement with our previous observations made on sugar-based polyamides[18c,27a] and poly(esteramides),[27b] which always showed a higher crystallinity for those polymers with sugar units having an L-*arabino* configuration than for those having *xylo* configuration. Such a difference in capacity for generating crystallinity may be explained in terms of the conformational preferences displayed by these two configurations. Whereas there are no constraints for the sugar segments having *arabino* configuration to adopt the extended *zigzag* planar conformation (**P**), those having *xylo* configuration largely adopt sickle conformations ($_3\mathbf{G}^+$ or $_2\mathbf{G}^-$) in order to avoid the unsta-

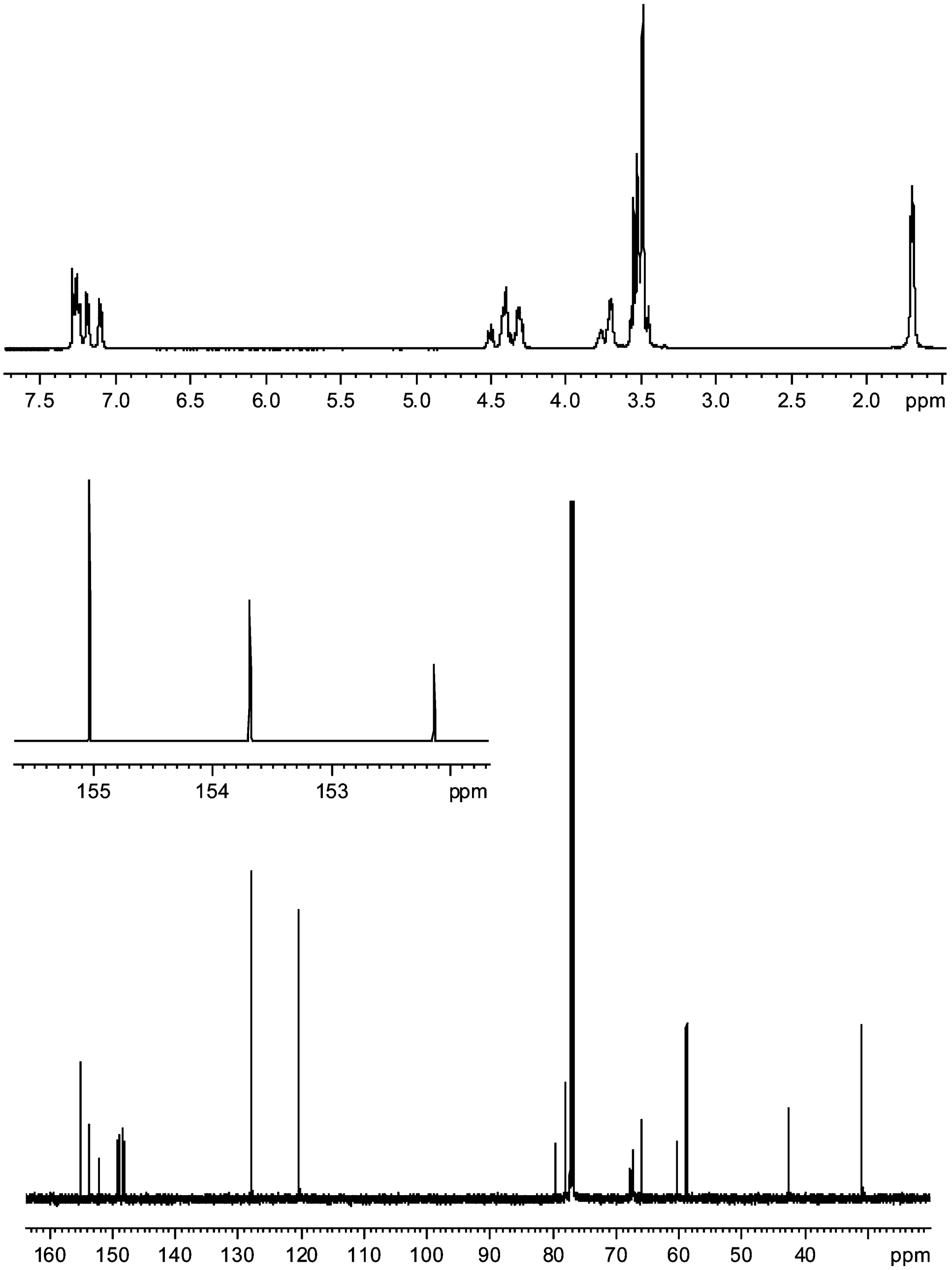


Figure 2. ^{1}H and ^{13}C NMR spectra (500 and 125 MHz, respectively, $CDCl_3$) of **P(1.8 Xy-*co*-BPAC)**.

bilizing *syn*-parallel 1,3-interaction between the methoxyl groups on C-2 and C-4[28,29] (Scheme 3). This would produce rotations around the main chain bonds, giving sickle conformations that might contribute to the decreasing of cohesive forces between the polymeric chains.

Incorporation of BPA units in the **PArC** removed crystallinity, as should be expected for a statistical copolymer made of two so different constitutional units. In fact, all the copolymers were amorphous, with T_gs ranging between 50 and 80 °C, intermediate between those of their respective parent homopolymers. Thermal parameters, including TGA and DSC data, are listed for the whole series in Table 2, in which data for the homopolycarbonate made entirely from BPA have also been included for comparison.

Enzymatic Degradation. Water-soluble poly(hydroxyalkylene carbonates) undergo rapid hydrolytic degradation even at neutral pH.[19] Furthermore, it has been noted that for some poly(ether carbonates) the hydrolytic cleavage of the polymer is limited by the low water content within the polymeric matrix. When modifications were made to increase the availability of water, the degradation rate increased.[9] Despite the high hygroscopicity of our polycarbonates, the attempts at hydrolytic degradation, under different conditions, for instance, pH 7.4 (phosphate buffer) at 37 °C or pH 4.0 (phosphate buffer) at 50 °C, gave no significant results.

It is well-known that aliphatic and aromatic polycarbonates can be obtained by enzymatic synthesis in an organic solvent or in bulk and that aliphatic polycarbonates can be degraded in an organic solvent.[1] We have assayed the enzymatic degradation of all the polycarbonates included in Tables 1 and 2. The best results were obtained when the transparent films, obtained by evaporation of their dichloromethane solutions, were treated in an organic solvent, such as acetonitrile at 70

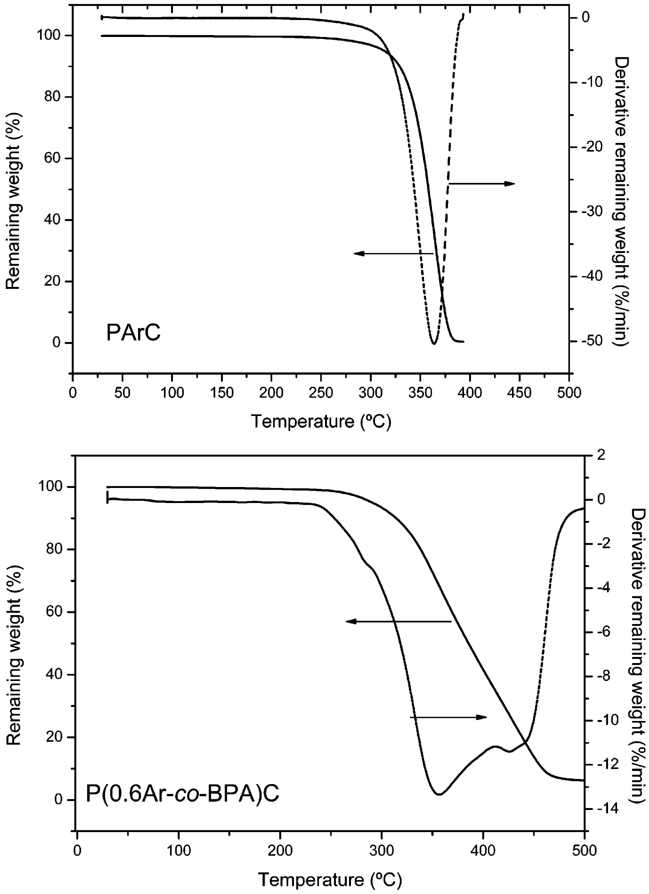


Figure 3. TGA traces (solid line) and their derivative curves (dashed line) for the indicated polycarbonates.

°C, with the immobilized lipase B from *Candida antarctica* (thermostable lipase absorbed on a macroporous resin), following the procedure described by Matsumura et al.[30]

We found very significant differences depending on the configuration of the carbohydrate moiety of the polymer. **PXyC** was the most labile under the cited degradation conditions, and the polymer was completely degraded after 7 days. By contrast, **PArC** did not degrade under the conditions described, and only at a higher temperature (80 °C) was a slight, slow loss of M_w noted.

Figure 5 shows the M_w decrease of **P(Su-*co*-BPAC)** during 5 weeks under the degradation conditions. GPC data show that **P(0.9 Xy-*co*-BPAC)** and **P(1.8 Xy-*co*-BPAC)** suffered a M_w loss of 65 000 g/mol in 1 week. After 5 weeks, M_w was 26 000 and 48 300 g/mol, respectively. **P(0.6 Ar-*co*-BPAC)** showed a decrease in M_w of 34 000 g/mol after 1 week and 52 000 g/mol in the next week. **P(1.1 Ar-*co*-BPAC)** lost 28 000 g/mol in a week, and then very slow degradation was observed. Homo-PBPAC did not degrade under the same conditions.

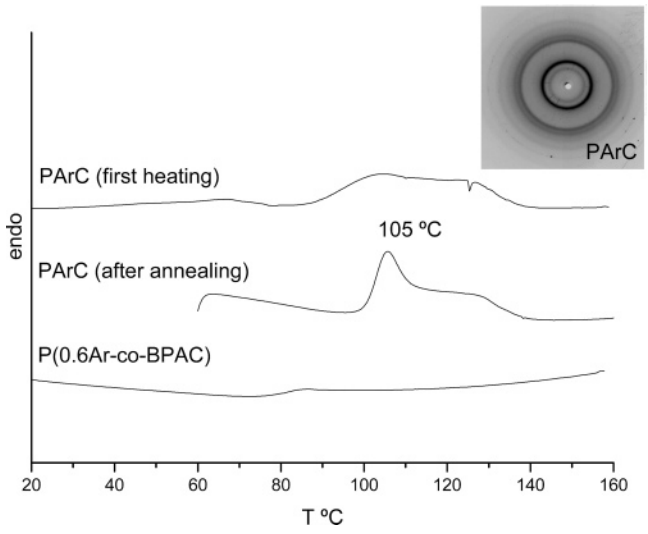


Figure 4. DSC heating traces of the indicated polycarbonates. Inset: powder X-ray diffraction pattern of annealed PArC.

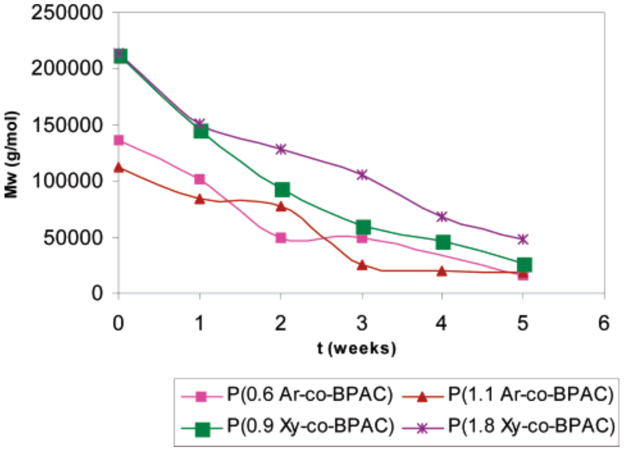
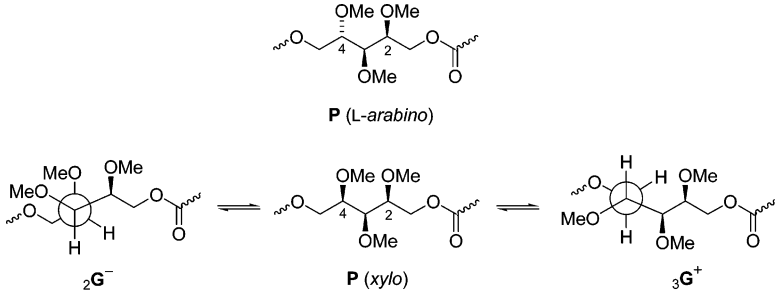


Figure 5. Enzymatic degradation of co-polycarbonates with B lipase from *Candida antarctica* in acetonitrile at 70 °C.

Figure 6 shows the percentage decrease of M_w (g/mol) for the polycarbonates after 3 weeks under the degradation conditions. The xylitol-based polycarbonates (bars 2, 4, 6) were degraded much faster than the L-arabinitol-based ones (bars 1, 3, 5), implying a relationship between the enzyme specificity and the configuration of the sugar moiety of the polycarbonate.

Scheme 3. Preferential Conformations of L-*Arabino* and *Xylo* Configurations



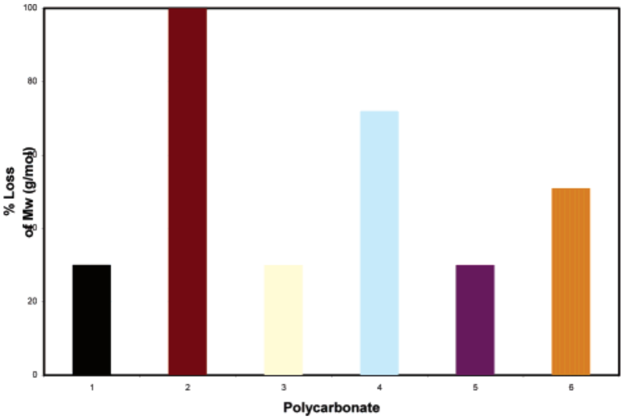


Figure 6. Percent loss of M_w of the polycarbonates after 3 weeks under the degradation conditions. For PArC, 80 °C was required. (1) **PArC**; (2) **PXyC**; (3) **P(0.6-Ar-*co*-BPAC)**; (4) **P(0.9-Xy-*co*-BPAC)**; (5) **P(1.1-Ar-*co*-BPAC)**; (6) **P(1.8-Xy-*co*-BPAC)**.

Conclusions

Homo- and co-polycarbonates based on sugar-derived diols and BPA were synthesized by polycondensation reactions. Co-polycarbonates were obtained from different molar feed ratio (1:1 and 2:1, respectively) with a sugar composition in the range 0.6−1.8:1 and a statistical microstructure. All of them are amorphous polymers except the homopolymer made from L-arabinitol, which showed a noticeable crystallinity and melting around 105 °C. The fastest degradation promoted by lipase B from *Candida antarctica* was observed for fully xylitol-based polycarbonate, followed by co-polycarbonates also based on xylitol, which revealed a marked stereospecifity of the enzyme toward this sugar. Neither the xylitol-based polycarbonates nor the arabinitol-based ones were significantly degraded in water in the absence of the enzyme.

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