Synthesis of a Stereoregular Poly(ester amide) Derived from L-Arabinose

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ABSTRACT: L-Arabinose was transformed into 2,3,4-tri-*O*-methylarabinonamide which, by reduction, gave the corresponding 1-aminoarabinitol derivative. Via blocking group manipulations, a selective succinylation at C-5, and activation, the precursor **7** could be obtained, which was used to synthesize a new type of stereoregular poly(ester amide) that displays optical activity. The polymerization reaction was carried out in different polar solvents, and the polymers were characterized by elemental analysis, IR, and ^{1}H and ^{13}C NMR. Both viscosimetry and GPC were used to estimate the molecular weights. Thermal studies revealed that the different samples of this poly(ester amide) melt above 135 °C, being stable up to 250 °C under nitrogen.

Introduction

Synthetic polymers containing carbohydrates in the main chain are considered, with steadily increased interest, as a new type of polymeric material[1−3] due to their potential as biodegradable and biocompatible material useful for medical applications. In spite of their multifunctionality, which introduces severe limitations to their straightforward use, carbohydrates stand out as highly convenient raw materials for the synthesis of stereoregular polymers containing several stereocenters in the main chain, due to their easy availability and great stereochemical diversity. On the other hand, the presence of stereocenters in the repeating unit makes it possible to adjust the physical properties by controlling the tacticity as well as studying the effect of chirality on biological activity.[4] Several contributions on the synthesis of polymers derived from carbohydrate monomers have been recently achieved.[1−3,5−9]

Whereas several poly(ester amides) have been described,[10−14] to our knowledge no stereoregular poly(ester amides) derived from sugars have been reported so far. Our interest in this field of study is 2-fold: (a) development of suitable monomers for polymerization that let us obtain optically active polymers with ordered spatial configurations and (b) preparation and characterization of the resulting polymers. The present paper describes the synthesis of a poly(ester amide) derived from L-arabinose and succinic anhydride, by applying the active ester polycondensation method.

Experimental Section

Materials. Chemicals were all used as purchased from Aldrich Chemical Co. Solvents were dried and purified when necessary, by appropriate standard procedures. Methyl β-L-arabinopyranoside, methyl 1,2,3,4-tetra-*O*-methyl-β-L-arabinopyranoside, 2,3,4-tri-*O*-methyl-L-arabinopyranose, and 2,3,4-tri-*O*-methyl-L-arabino-1,5-lactone were prepared as described.[15]

General Methods. Optical rotations were measured at 20 ± 5 °C with a Bellingham & Standley Inc., P20 polarimeter (5-cm cell). TLC was performed on silica gel 60 F_{254} (Merck) with detection by UV light or charring with sulfuric acid. Compounds containing an NH group were visualized by reaction with ninhydrin. Flash column chromatography: Merck silica gel 60 (230−400 mesh). FT IR spectra (films or KBr disks) were recorded with a Michelson 100 spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker 200 AC-P spectrometer. Chemical shifts are reported as parts per million downfield from tetramethylsilane. The following abbreviations are used to present the ^{1}H NMR spectra results: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad. Intrinsic viscosity measurements were determined in dichloroacetic acid (DCA) with a Cannon-Ubbelohde 100/L30 semimicroviscometer placed in a water bath with the temperature maintained at 25.0 ± 0.1 °C. Elemental analyses were determined in the Microanalysis Laboratories at the Universidad de Sevilla and the Universidad Complutense de Madrid. Gel permeation chromatography (GPC) analyses were carried out in a Waters apparatus fitted with a waters Model 410 RI detector, and a Millenium 2010 computerized data station. Two GPC columns were placed in series, and the analysis was performed in DMF at a flow rate of 1 mL/min. Molecular weight studies were determined relative to polystyrene; calibration was done using 12 polystyrene samples of narrow molecular weight distribution. Melting points were determined with a Gallenkamp apparatus and are uncorrected. Differential scanning calorimetry (DSC) was carried out under a nitrogen atmosphere on a Perkin-Elmer DSC-4 instrument. Samples with sizes of 8−11 mg were heated at a rate of 15 °C/min and cooled to room temperature at high rates. The peak temperatures were taken as melting points. Thermogravimetric analysis (TG) was performed with a Perkin-Elmer 7 instrument at a heating rate of 15 °C/min under nitrogen. For X-ray diffraction the samples were placed in a vacuum, and the diffraction patterns were recorded in a Statton camera using a pinhole collimated, Ni-filtered Cu Kα X-ray source.

2,3,4-Tri-*O*-methyl-L-arabinonamide (3). Ammonia was bubbled into a cooled solution of 2,3,4-tri-*O*-methyl-L-arabino-1,5-lactone (5.0 g, 0.026 mol) in dry methanol (100 mL) for 2.5 h. After evaporation of the solvent under reduced pressure, the syrupy residue was chromatographed on a silica gel column (eluent 20:1 to 10:1 CH_2Cl_2/MeOH) to give **3** as a solid (5 g, 92%), mp 99−101 °C (recrystallization from ethanol); $[\alpha]_D$ +27.1° (*c* 1.2, chloroform). IR: ν_{max} 3600−3040 (NH, OH), 1675 (CO) cm^{-1}. NMR data (DMSO-d_6): ^{1}H δ 3.11 (ddd, 1H, $J_{3,4}$ 8.5 Hz, $J_{4,5}$ 2.3 Hz, $J_{4,5'}$ 4.0 Hz, H-4), 3.23 (s, 3H, OCH_3), 3.29 (s, 6H, 2 OCH_3), 3.37 (m, 1H, H-5′), 3.53 (dd, 1H, $J_{2,3}$ 2.4 Hz, H-3), 3.58 (d, 1H, H-2), 3.72 (ddd, 1H, $J_{5,5'}$ 11.9 Hz, H-5), 4.52 (dd, 1H, $J_{5,OH}$ 4.8 Hz, $J_{5'OH}$ 6.1 Hz, OH), 7.33 and 7.35 (2 bs, 2H, $CONH_2$); ^{13}C δ 58.66 (C-5), 57.05, 58.91, 59.54 (3 OCH_3), 79.76 (C-3), 80.16 (C-4), 81.14 (C-2), 173.49 (CO). Anal. Calcd for $C_8H_{17}NO_5$: C, 46.37; H, 8.27; N, 6.76. Found: C, 46.40; H, 8.22; N, 6.36.

1-(*tert*-Butoxycarbonylamino)-1-deoxy-2,3,4-tri-*O*-methyl-L-arabinitol (4). A solution of **3** (5.0 g, 24.0 mmol) in dry

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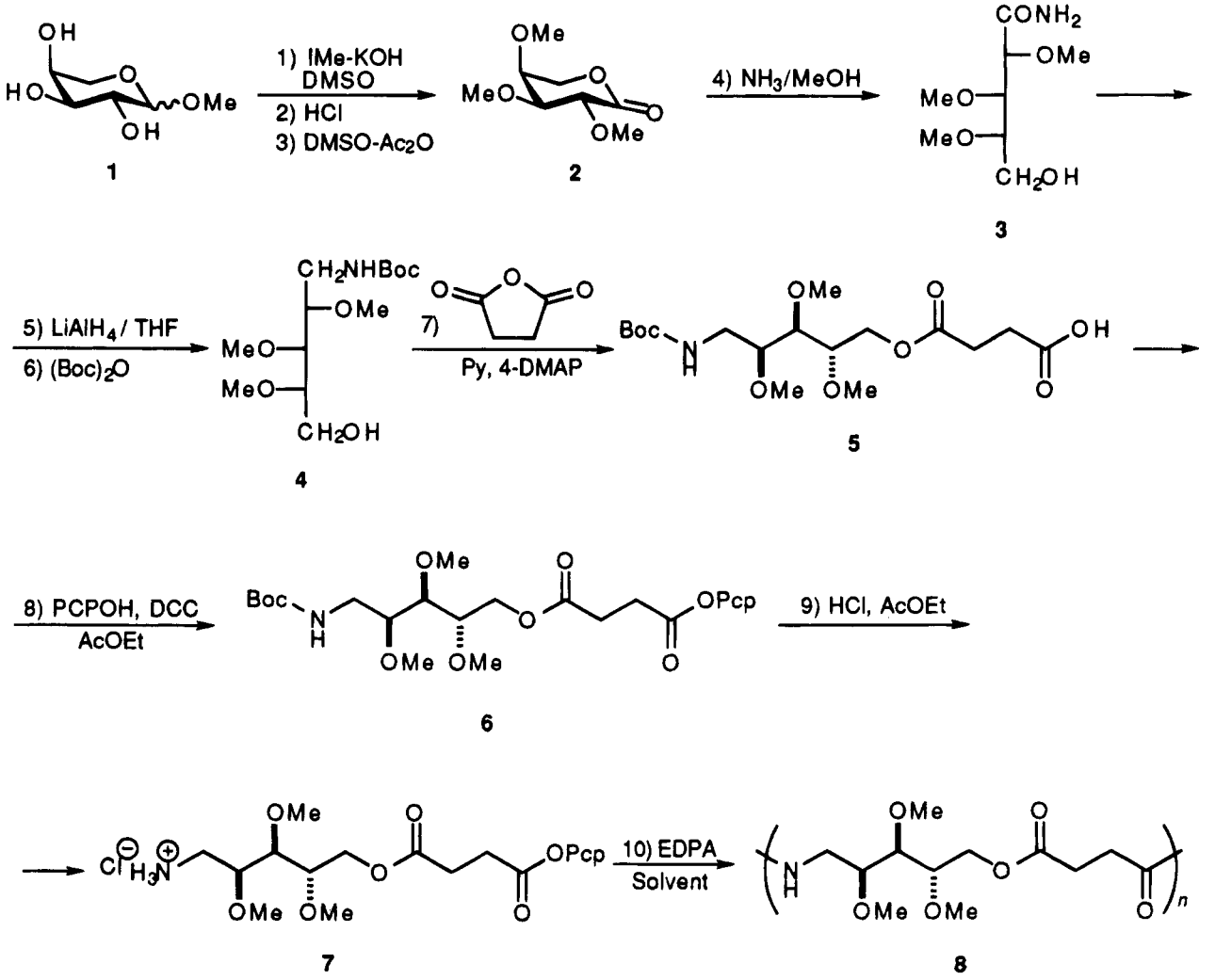
Scheme 1



THF (50.0 mL) was slowly added under nitrogen to a stirred solution of lithium aluminium hydride in dry THF (1 M, 82.0 mL). Once the addition was complete, the suspension was refluxed for 5 h and then allowed to cool to room temperature. After 2 h, water (128.0 mL) and 15% sodium hydroxide (3.0 mL) were added, the mixture was filtered, and the solid was washed with THF. The filtrate and washings were combined, and to this stirred solution was added di-*tert*-butyl dicarbonate (6.0 g, 0.027 mmol). After stirring at room temperature for 24 h, the solution was concentrated under diminished pressure and the residue was chromatographed on a silica gel column (eluent 2:1 to 1:1 hexane/ethyl acetate) to give **4** as an oil (5.85 g, 83%); $[\alpha]_D$ −2.7° (*c* 1.46, chloroform). IR: ν_{max} 3600−3150 (NH, OH), 1702 cm^{-1} (CO). NMR data (DMSO-d_6): ^1H δ 1.37 (s, 9H, 3 CH_3), 2.92−3.16 (m, 2H, CH_2N), 3.28, 3.29, 3.32 (3 s, 9H, 3 OCH_3), 3.12−3.40 (m, 3H, H-2,3,4), 3.36 (ddd, 1H, $J_{4,5}$ 2.0 Hz, $J_{5,5'}$ 11.9 Hz, H-5), 3.70 (ddd, 1H, $J_{4,5'}$ 3.9 Hz, H-5'), 4.48 (bt, 1H, $J_{OH,5(5')}$ 5.0 Hz, OH), 6.84 (bt, 1H, $J_{NH,1(1')}$ 5.7 Hz, NH); ^{13}C δ 28.14 (CCH_3), 40.30 (CH_2N), 57.13, 58.46, 60.49 (3 OCH_3), 59.16 (CH_2O), 79.02 (CCH_3), 78.71, 80.39, 80,39 (C-2,3,4), 155.9 (CO). Anal. Calcd for $C_{13}H_{27}NO_6$: C, 53.23; H, 9.28; N, 4.77. Found: C, 52.94; H, 9.19; N, 4.71.

1-(*tert*-Butoxycarbonylamino)-1-deoxy-2,3,4-tri-*O*-methyl-5-*O*-succino-L-arabinitol (5). A mixture of **4** (8.0 g, 27.27 mmol), succinic anhydride (5.48 g, 54.76 mmol), and 4-(dimethylamino)pyridine (0.70 g, 5.73 mmol) in dry pyridine (120.0 mL) was heated at 40 °C for 24 h. The solvent was evaporated under diminished pressure to give a residue that was treated with dichloromethane (25.0 mL), and the solid formed filtered out and was washed with more dichloromethane. The filtrate and washings were combined, concentrated, and chromatographed (eluent 0 to 10:1 dichloromethane/methanol) to give the title compound as a slightly yellow oil (10.0 g, 93%); $[\alpha]_D$ −4.5° (*c* 0.67, chloroform). IR ν_{max} 3565−2500 (NH, OH acid), 1743, 1717 cm^{-1} (CO). NMR data ($CDCl_3$): ^1H δ 1.38 (s, 9H, 3 CH_3), 2.61 (s, 4H, 2 CH_2), 3.33, 3.39 (2 s, 9H, 3 OCH_3), 3.10−3.50 (m, 5H, H-2,3,4 and CH_2N), 4.05 (dd, 1H, $J_{4,5'}$ 3.5 Hz, $J_{5,5'}$ 12.2 Hz, H-5'), 4.53 (dd, 1H, $J_{4,5}$ 2.6 Hz, H-5), 4.99 (bs, 1H, NH), 9.50 (bs, 1H, COOH); ^{13}C δ 28.25 (CCH_3), 28.77, 28.90 ($2CH_2$), 40.50 (CH_2N), 57.52, 58.64, 60.63 (3 OCH_3), 61.93 (CH_2O), 79.42 (CCH_3), 78.29, 78.59, 80.67 (C−2/4), 156.14 (CONH), 171.91 (CO ester), 176.28 (COOH). Anal. Calcd for $C_{17}H_{31}NO_9 \cdot {}^1/_4 H_2O$: C, 51.31; H, 7.98; N, 3.52. Found: C, 51.40; H, 7.88; N, 3.45.

Table 1. Polycondensation of 1-Amino-1-deoxy-2,3,4-tri-*O*-methyl-5-*O*-[(pentachlorophenoxy)succinyl]-L-arabinitol Hydrochloride in Various Solvents[a]

solvent[b]	base	yield (%)	$[\alpha]_D$[c]
HMPA	EDPA	69%	−25.0
CH_2Cl_2	EDPA	58%	−45.3
NMP	EDPA	66%	−28.8
Py		47%	*d*

[a] Monomer concentration: 1.08 mmol/mL. Reaction time: 10 days at 25 °C. [b] NMP: *N*-methylpyrrolidone. HMPA: hexamethylphosphotriamide. Py: pyridine. [c] Measured in dimethyl sulfoxide. [d] Mixture of oligomers.

1-(*tert*-Butoxycarbonylamino)-1-deoxy-2,3,4-tri-*O*-methyl-5-*O*-[(pentachlorophenoxy)succinyl]-L-arabinitol (6). To a solution of **5** (9.17 g, 23.31 mmol) in dry ethyl acetate (125.0 mL) were added pentachlorophenol (6.19 g, 23.24 mmol) and dicyclohexylcarbodiimide (4.8 g, 23.26 mmol). After 72 h, the solid formed was separated out and washed with ethyl acetate. The filtrate and washings were combined, concentrated, and chromatographed (eluent 5:1 to 2:1 hexane/ethyl acetate) to give **6** as a foam (9.8 g, 66.0%); $[\alpha]_D$ −2.0° (*c* 2.0,

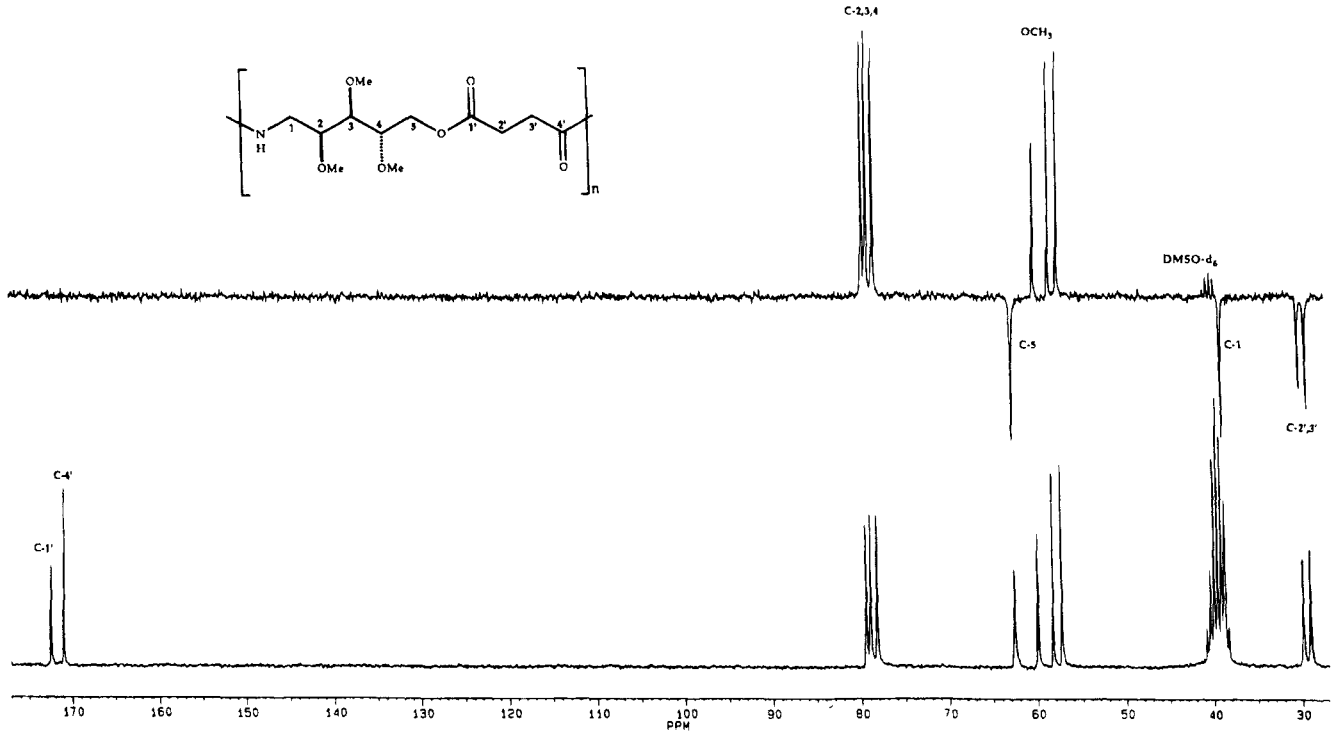


Figure 1. 50.3-MHz ^{13}C NMR spectrum (lower line) and DEPT-135 experiment (upper line) recorded at room temperature in DMSO-d_6 of poly(ester amide) **8**, obtained in HMPA.

chloroform). IR: ν_{max} 3440–3350 (NH), 1786, 1739, 1712 cm^{-1} (CO). NMR data ($CDCl_3$): ^1H δ 1.40 (s, 9H, 3 CH_3), 2.79 (m, 2H, CH_2), 3.01 (m, 2H, CH_2), 3.36, 3.42 (2 s, 9H, 3 OCH_3), 3.14–3.56 (m, 5H, H-2,3,4 and CH_2N), 4.11 (dd, 1H, $J_{4,5'}$ 4.35 Hz, $J_{5,5'}$ 12.1 Hz, H-5'), 4.59 (dd, 1H, $J_{4,5}$ 2.6 Hz, H-5), 4.87 (bs, 1H, NH); ^{13}C δ 28.33 (CCH_3), 28.55, 28.65 ($2CH_2$), 40.51 (CH_2N), 57.77, 58.76, 60.76 (3 OCH_3), 62.51 (CH_2O), 79.30 (CCH_3), 78.44, 78.67, 80.84 (C-2/4), 127.59, 131.58, 131.93, 142.88 (phenyl), 156.00 (CONH), 168.19 (COPCP), 171.31 (CO ester). Anal. Calcd for $C_{23}H_{30}NO_9Cl_5$: C, 43.05; H, 4.71; N, 2.18. Found: C, 43.09; H, 4.67; N, 2.16.

1-Amino-1-deoxy-2,3,4-tri-*O*-methyl-5-*O*-[(pentachlorophenoxy)succinyl]-L-arabinitol Hydrochloride (7). A solution of **6** (9.0 g, 14.45 mmol) in dry ethyl acetate (36.0 mL) was added to a cooled 14% HCl solution in ethyl acetate (54.0 mL). After stirring for 4 h, a stream of nitrogen was bubbled into the solution giving a gel, which was filtered out and washed thoroughly with dry ethyl ether to give **7** as a solid (7.55 g, 93%), mp 149–151 °C; $[\alpha]_D$ −18° (*c* 1.4, chloroform). IR: ν_{max} 3400–2500 (broad, NH_3^+), 1772, 1750 cm^{-1} (CO). NMR data (DMSO-d_6): ^1H δ 2.70–2.86 (m, 2H, CH_2), 2.80–3.08 (m, 2H, $J_{1,2}$ 4.3 Hz, $J_{1',2}$ 8.3 Hz, $J_{1,1'}$ 13.3 Hz, CH_2N), 2.98–3.14 (m, 2H, CH_2), 3.31, 3.35, 3.38 (3 s, 9H, 3 OCH_3), 3.42–3.55 (m, 2H, H-3,4), 3.67 (ddd, 1H, $J_{2,3}$ 2.6 Hz, H-2), 4.03 (dd, 1H, $J_{4,5}$ 4.7 Hz, $J_{5,5'}$ 12.1 Hz, H-5), 4.41 (dd, 1H, $J_{4,5'}$ 1.9 Hz, H-5'), 8.19 (bs, 3H, NH); ^{13}C δ 28.33 ($2CH_2$), 39.44 (CH_2N), 57.34, 58.88, 59.60 (3 OCH_3), 62.55 (CH_2O), 77.50, 78.07, 79.24 (C-2,3,4), 127.17, 130.75, 131.25, 143.75 (phenyl), 168.69 (COPCP), 171.31 (CO ester). Anal. Calcd for $C_{18}H_{23}NO_7Cl_6$: C, 37.40; H, 4.01; N, 2.42. Found: C, 36.96; H, 4.02; N, 2.41.

Polymerization. To a stirred suspension of **7** (2.5 g, 4.47 mmol) in 2.4 mL of the chosen solvent (cf. Table 1) was added ethyldiisopropylamine (EDPA, 1.6 mL). After 10 days at 25 °C, the polymer was precipitated out by pouring the viscous solution into ethyl ether (1500 mL). The product was recovered by filtration on a glass filter, washed thoroughly with acetone and ethanol, and finally, dried under vacuum at 40 °C. Yields obtained ranged between 58 and 70%. IR: ν_{max} 3360 (NH), 3070 (amide, B), 1734 (CO), 1659 (amide I), 1539 cm^{-1} (amide II). NMR data (DMSO-d_6): ^1H δ 2.29–2.45 (m, 2H, CH_2), 2.45–2.61 (m, 2H, CH_2), 3.11–3.49 (m, 5H, H-2,3,4, and CH_2N), 3.28 (s, 3H, OCH_3), 3.31 (s, 6H, 2 OCH_3), 3.94 (dd, 1H, $J_{4,5}$ 5.3 Hz, $J_{5,5'}$ 12.0 Hz, H-5), 4.36 (dd, 1H, $J_{4,5'}$ 2.1 Hz, H-5'), 7.97 (bt, 1H, J_{NH} 5.4 Hz, NH); ^{13}C δ 28.95, 29.77 ($2CH_2$), 38.77 (CH_2N), 57.23, 58.21, 59.90 (3 OCH_3), 62.52 (CH_2O), 78.14, 78.89, 79.40 (C-2/4), 170.89, 172.35 (CO).

Results and Discussion

The synthesis of the monomer was carried out in seven steps. Although there is a difference in reactivity between primary and secondary hydroxyl groups in sugars, it is not high enough to attain perfect reaction selectivity.[10] To rule out the possibility of branching and to obtain linear polymers, the secondary hydroxyl groups had to be protected. Thus, commercial L-arabinose was easily transformed by described methods[15] into the crystalline 2,3,4-tri-*O*-methyl-L-arabino-1,4-lactone (**2**), in which the secondary hydroxyl functions were blocked as methyl ethers. Opening of the lactone ring by ammonia gave the amide **3** which was reduced with lithium aluminum hydride in dry tetrahydrofuran. Subsequent reaction of the corresponding amino alcohol with di-*tert*-butyl dicarbonate afforded the *N*-*tert*-butoxycarbonyl derivative **4** which was isolated by column chromatography as an oil (83%, in the two steps). Compound **4** was condensed with succinic anhydride in dry pyridine to yield **5** as a syrup which was treated with dicyclohexylcarbodiimide and pentachlorophenol to give the active ester **6**. Removing the N-protecting group with HCl in dry ethyl acetate led to the hydrochloride **7**, which should be a suitable monomer for the formation of poly(ester amides).

In order to examine the solvent effect on the polycondensation of **7**, the polymerization was carried out in different media. The solvent systems tested were *N*-methyl-2-pyrrolidone (NMP), hexamethylphosphotriamide (HMPA), dichloromethane, and pyridine (py). Ethyldiisopropylamine (EDPA) was added as an acid acceptor except when pyridine was present in the polymerization medium. The results of these polymerizations are displayed in Tables 1 and 2. The yields do not appear to be significantly affected by the nature of the solvent except in the case of pyridine, in which the lowest yield was obtained. In addition, the isolated poly(ester amide) was contaminated with a series of

Table 2. Physical Properties of the Poly(ester amides) Obtained in Various Solvents

solvent	$[\eta]^a$ (dL/g)	$M_v{}^b$	$M_n{}^c$	$M_w{}^c$	M_w/M_n	$T_m{}^d$ (°C)	$T_{de}{}^e$ (°C)	elemental anal.^{f} (%) found C	H	N
HMPA	0.85	21 000	114 000	171 000	1.50	135	313	50.69	7.17	4.97
CH_2Cl_2	0.96	26 000	113 000	166 000	1.47	137	310	50.73	7.44	4.97
NMP	1.58	65 000	251 000	367 000	1.46	139	310	50.85	7.21	4.88

[a] Intrinsic viscosities measured in dichloroacetic acid at 25 °C. [b] Calculated by applying the viscosimetric equation reported for nylon 6,6.[16] [c] Determined by GPC analysis with polystyrene standards. [d] Determined by DSC. [e] The onset decomposition temperature determined by TGA. [f] Calculated for $C_{12}H_{21}NO_7$: C, 49.48; H, 7.27; N, 4.81.

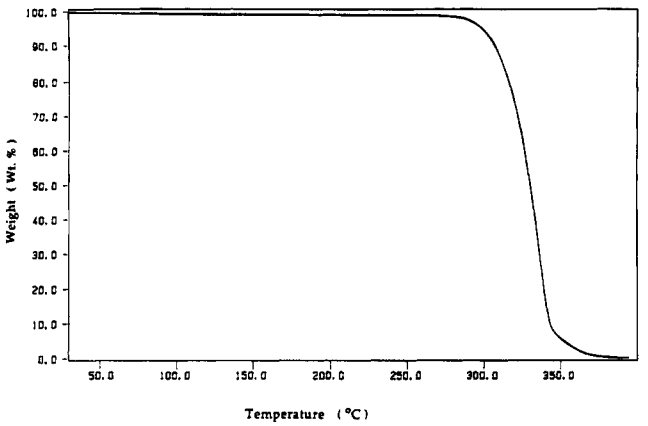


Figure 2. TG plot of the poly(ester amide) **8**, obtained in NMP.

oligomers from which it could not be separated in accetable yield. Polar aprotic solvents like NMP or HMPA are adequate for the polymerization of monomer **7**. Although the highest yield of the poly(ester amide) was obtained in HMPA, it was found that the highest intrinsic viscosity was achieved when the polymerization was carried out in NMP. In this solvent, the polydispersity ratio (M_w/M_n) value was also narrower than in the others, which may reflect a narrower molecular distribution of higher molecular weight.

The poly(ester amides) were obtained as pale yellow powdery materials and were soluble at room temperature in polar solvents such as NMP, HMPA, dimethyl sulfoxide, and dichloroacetic acid and also soluble in chloroform but insoluble in ethyl ether, acetone, or ethanol. This poly(ester amide) is not soluble in water, although, as we can anticipate, it could display hydrophilicity due to the presence of hydrophilic methoxy groups in the chain.

Characteristic absorption bands of the amide and ester were found at 1659, 1539, and 1734 cm^{-1}, respectively. The broad band around 3360 cm^{-1} was attributed to the stretching band of the NH function. The ^{13}C-NMR spectral data revealed that no epimerization occurs during the polymerization reaction, being that the chemical shifts and intensities are consistent with the structure expected for the poly(ester amide). The corresponding spectrum was essentially identical to that of monomer **7**, except for those signals arising from the pentachlorophenyl group, as expected. Figure 1 shows representative proton-decoupled ^{13}C-NMR and DEPT-135 spectra of the poly(ester amide) obtained in HMPA. The signals at higher field are due to the two methylene carbons of the succinyl moiety that, as expected, appear with inverse phase in the DEPT-135 spectrum; the two methylenes of the sugar moiety appear, also with inverse phase in the DEPT spectrum, at 38.77 and 62.52 ppm, the higher field corresponding to that bonding to the nitrogen; the three methoxyl carbons give signals at 57.23, 58.21, and 59.90 ppm, and the methine carbons

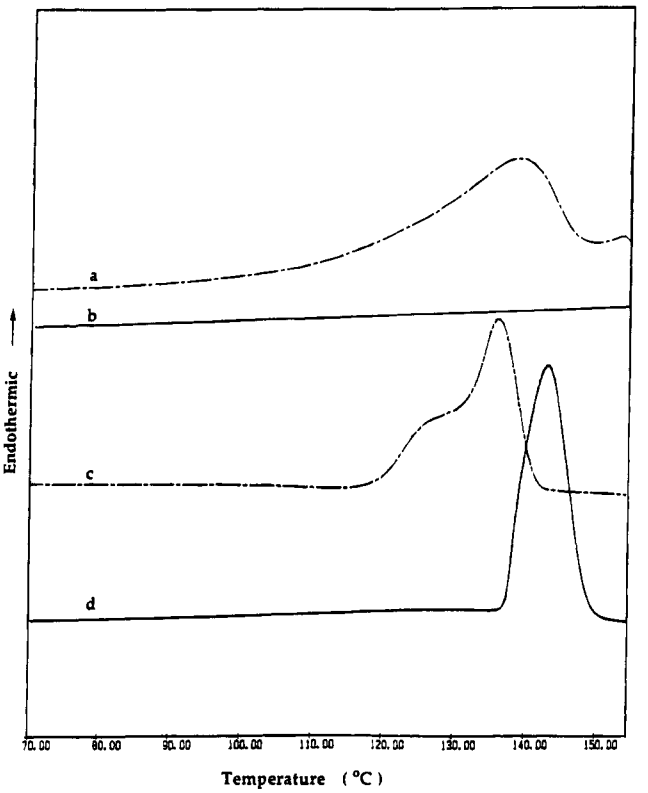


Figure 3. DSC thermograms of poly(ester amide) **8**, obtained in NMP: (a) first heating trace; (b) second heating trace after rapid cooling to room temperature; (c) heating a sample annealed at 120 °C for 64 h; (d) heating a sample annealed at 120 °C for 120 h.

C-2,3,4 appear at 78.18, 78.89, and 79.40. The lower field signals are due to the two carbonyl groups that disappear in the DEPT-135 spectrum. No signals from solvents or impurities are present. The molecular weight distributions of these poly(ester amides) were studied by gel permeation chromatography using μ-Styragel columns and dimethylformamide as the mobile phase. The M_n and M_w values obtained from GPC data are listed in Table 2. The molecular weights estimated by GPC are unusually high for polymers prepared by the active ester method; occurrence of aggregations may account for observed discrepancies in addition to the fact that we used polystyrene samples of narrow molecular weight distribution as calibration standards. However, a reasonable correspondence between GPC data, intrinsic viscosities, and melting points can be observed. More reasonable values of molecular weights were obtained from viscosimetry by using the Mark–Houwink parameters reported for nylon 6,6,[16] despite that the application of this viscosimetric equation in estimating the size of this poly(ester amide) may be rather inadequate. Additional evidence in support of the stereoregularity of this poly(ester amide) is provided by the remarkably high optical activity that is displayed in solution (Table 1) regarding the low specific rotation

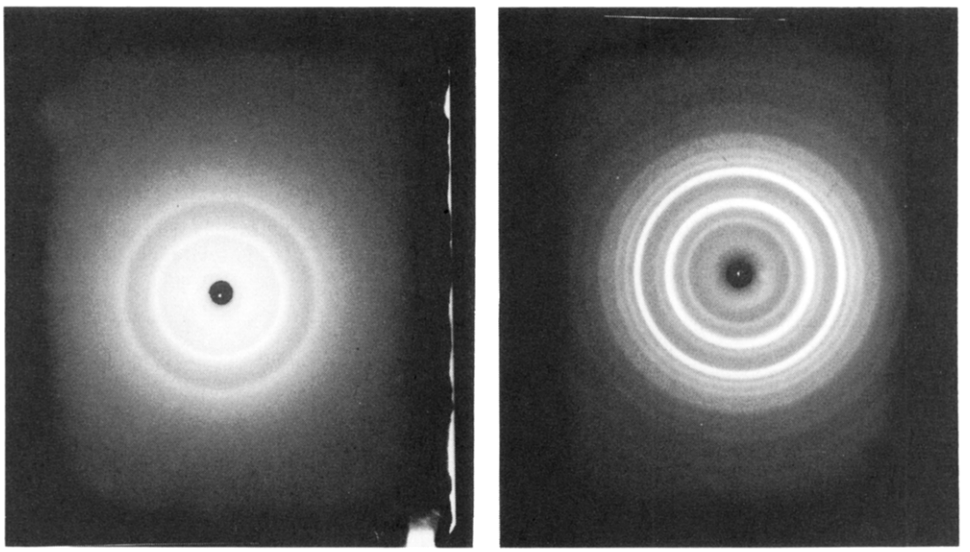


Figure 4. Powder X-ray diffraction pattern of poly(ester amide) **8** obtained in NMP, (a, left) precipitated; (b, right) after annealing a sample at 120 °C for 120 h.

power observed for its monomer. The thermal behavior of the different samples of this poly(ester amide) have been studied by TGA and DSC. A typical TGA plot is shown in Figure 2. The onset of decomposition temperatures are listed in Table 2 (T_{de}). The TGA thermogram indicated that this poly(ester amide) is stable up to 250 °C under nitrogen. Figure 3 shows a representative DSC of the poly(ester amide) obtained in NMP, and the melting temperatures are given in Table 2. In all cases, broad endotherms corresponding to melting transitions appeared during the first heating cycle. After rapid cooling to room temperature, second heating thermograms were recorded for each sample. We observed that no thermal transitions occurred during this second heating cycle, presumably because the crystallization did not occur. However, we were able to recrystallize the poly(ester amide) by annealing the sample at 120 °C under a nitrogen atmosphere. It could be observed that the transition width is considerably narrower, suggesting reduction in the degree of microstructural heterogeneity. The increase in the melting temperature may be attributed to perfection of chain packing in crystallites by thermally-enhanced backbone motions. Longer annealing allows more motional opportunities for chains to improve packing efficiency. The percentage of crystallinity in semicrystalline polymers can increase with annealing owing to improved chain packing or incorporation of more chain segments in crystallites. Thus, in a preliminary study, powder X-ray diffraction of this poly(ester amide) revealed that the precipitated product was slightly crystalline with a few fairly defined rings (Figure 4a). About seven reflections may be seen in the original picture appearing at 12.1, 7.7, 6.2, 5.3, 4.1, 3.5, and 3.0 Å. However, a well-defined diagram was obtained when the poly(ester amide) was annealing at 120 °C for 120 h (Figure 4b), which reveals that the sample has increased its crystallinity after annealing. The Bragg spacings displayed in the corresponding diagrams of the polymer are 12.1, 7.7, 5.7, 5.0, 4.1, 3.8, 3.5, 3.1, 2.9, 2.7, 2.4, and 2.3 Å. Unfortunately, when fibers were pulled from a concentrated solution of this polymer in chloroform, only slightly oriented fibers could be obtained so far. Further studies are obviously required in order to gain insight into the crystal structure.

It could be concluded that stereoregular, high intrinsic viscosity poly(ester amides) containing carbohydrate residues in the main chain can be synthesized by a direct polycondensation reaction.

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