Macromolecules **2002,** *35,* 2977−2984

Carbohydrate-Based Copolymers. Synthesis and Characterization of Copoly(ester amide)s Containing L-Arabinose Units

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Received July 23, 2001; Revised Manuscript Received December 10, 2001

ABSTRACT: Copoly(ester amide)s, abbreviated as PVGA*n*, have been prepared by random copolymerization of 1-amino-1-deoxy-2,3,4-tri-*O*-methyl-5-*O*-[(pentachlorophenoxy)succinyl]-L-arabinitol hydrochloride and 5-amino-1-*O*-[(pentachlorophenoxy)glutaryl]pentanol hydrochloride by the active ester polycondensation method. The molar ratios of the two comonomers in the feed varied from 1/99 to 50/50. The two monomeric units are randomly distributed within the copolymers, as assessed by NMR analysis, and the degree of randomness and average sequence lengths of the different copoly(ester amide)s have been experimentally determined. Thermal properties depend on the copoly(ester amide) composition, since it was found that the melting and the decomposition temperatures decreased as the molar fraction of carbohydrate-based monomer unit increased, whereas the glass-transition temperature increased in parallel.

Introduction

The preparation of synthetic polymers containing units of carbohydrate derivatives in their structures is one of our main topics. The synthesis of this type of polymer is in most cases time-consuming due to the multifunctionality of the sugar monomer, which forces us to use a block−unblock chemistry. A particular case is the preparation of stereoregular polymers of AABB type. Monomers with a 2-fold axis of symmetry must be used. Otherwise, regioisomerism will likely occur, affording aregic polymers.[1,2] Regioregular polymers of AABB type from nonsymmetric monomers have been prepared, but the procedure implies the differentiation between the two extremes of the diacid.[3] Despite these drawbacks, the preparation of novel carbohydrate-based polymers and copolymers is interesting, not only for the availability of carbohydrates with different chemical and stereochemical structures but also because they come from natural regrowing resources and are expected to improve properties such as biodegradability and biocompatibility.

We have previously reported—as a part of our studies concerned with the synthesis and characterization of new polymers based on carbohydrate monomers—stereoregular AB-type polyamides[4] and copolyamides.[5] Aliphatic poly(ester amide)s have been suggested as a potential family of polymers endowed with optimum mechanical and thermal properties, processability, and susceptibility to degradation.[6]

In our laboratory, we have prepared poly(ester amide)s[7] containing conveniently modified natural sugar residues such as L-arabinose or D-xylose joined to four- or five-carbon diacid units. These poly(ester amide)s displayed very different behavior when subjected to hydrolysis[8,9] under physiological conditions (i.e., 37 °C, pH 7.4). It was found that both aregic and isoregic poly(ester amide)s containing four-carbon diacid units were easily hydrolyzed in water, whereas those not fitting such a constitution pattern displayed hydrolytic stability. With the purpose of modulating the rate of hydrolysis of poly(ester amide)s showing a low degradation rate, we undertook the present investigation.

This paper deals with the synthesis and characterization of several copoly(ester amide)s with structures having increasing amounts of succinic units along the polymer chain. These copolymers have been synthesized by polymerization of 1-amino-1-deoxy-2,3,4-tri-*O*-methyl-5-*O*-[(pentachlorophenoxy)succinyl]-L-arabinitol hydrochloride (**1**)[7a] and 5-amino-1-*O*-[(pentachlorophenoxy)glutaryl]pentanol hydrochloride (**2**)[7b] via the active ester polycondensation method (Scheme 1). They are abbreviated as PVGA*n*, where *n* indicates the percentage of carbohydrate monomer incorporated in the copoly(ester amide) chain, VG indicates the 5-aminopentyl glutarate unit, and A indicates the 5-aminoarabinitol succinate unit. The structures of these copoly(ester amide)s have been determined by elemental microanalysis and IR and NMR spectroscopies. Their thermal properties have been studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Their in vitro hydrolysis has been evaluated and studied in a different paper.[10]

Experimental Section

Measurements. IR spectra (films or KBr disks) were recorded with a Jasco FT/IR-410 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AMX-500 spectrometer at 60 °C operating at 500.13 and 125.76 MHz, respectively. Two-dimensional ^{1}H−^{1}H homonuclear and ^{13}C−^{1}H heteronuclear (short-range and long-range coupling) shift correlation spectra were recorded with the *cosy*, *hetcor*, and *hmbc* pulse sequences. Quantitative ^{13}C NMR spectra were recorded with a pulse width of 4 μs (50°) and relaxation delays of 20 s with an inverse gated decoupling pulse sequence. Chemical shifts are reported as parts per million downfield from tetramethylsilane. Elemental analyses were determined in the Microanalysis Laboratories at the Universidad Complutense (Madrid). Intrinsic viscosity measurements were determined in dichloroacetic acid (DCA) with a Cannon-Ubbelohde semi-microviscometer placed in a water bath with the temperature maintained at 25.0 ± 0.1 °C. The thermal properties of the precipitated copoly(ester amide)s were determined by DSC and TGA. DSC was carried out under a nitrogen atmosphere on a Perkin-Elmer DSC-7 instrument calibrated with indium. Samples of about 2−3 mg were heated at a rate of 10 °C/min and rapidly cooled to room temperature.

10.1021/ma011301b CCC: $22.00

Scheme 1

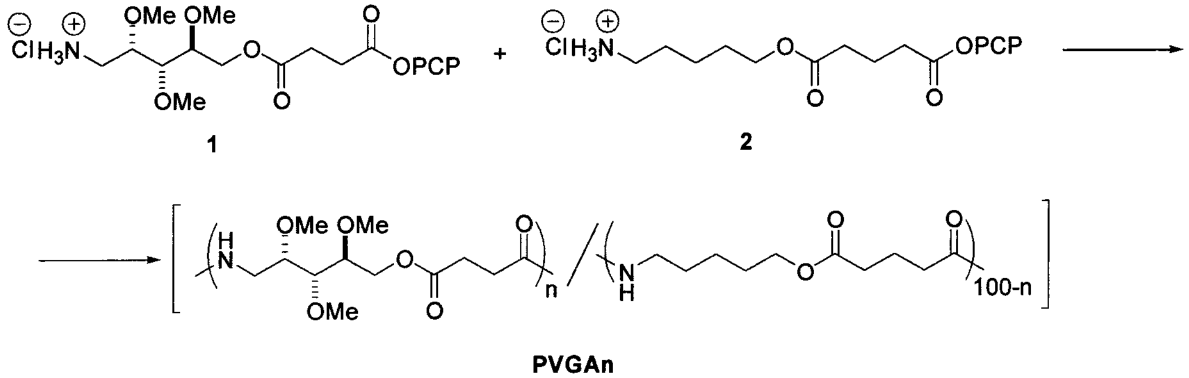

Table 1. Feed Composition and Some Characterization Data of PVGA*n*

copolymer	AS/VG[a]	yield (%)	$[\eta]^b$ (dL/g)	M_v^c
PVG[d]	0/100	86	0.63	12 100
PVGA1	1/99	89	0.99	27 600
PVGA5	5/95	79	0.86	21 300
PVGA8	10/90	68	0.70	14 700
PVGA21	25/75	41	0.59	10 700
PVGA46	50/50	55	0.34	3 900
PAS[d]	100/0	66	1.58	65 000

[a] Monomer ratio in the feed. [b] Intrinsic viscosities measured in dichloroacetic acid at 25 °C. [c] Calculated by applying the viscosimetric equation reported for nylon-6,6.[11] [d] Homopolymers previously reported.[7]

The peak temperatures were taken as melting points. TGA was performed with a Setaram TG-12 instrument. Samples of about 10–15 mg were heated at a rate of 10 °C/min under nitrogen.

General Procedure for the Synthesis of PVGA*n* Copoly(ester amide)s. To a stirred suspension of the comonomers mixture (3.0 g) in *N*-methyl-2-pyrrolidinone (NMP, 3.5 mL), ethyldiisopropylamine (EDPA, 2.5 mL) was added. After 15 days at 25 °C, the copolymer was precipitated by pouring the viscous solution into ethyl ether. The copolymer was recovered by filtration on a glass filter and washed thoroughly with ether, acetone, and 2-propanol. In the case of copoly(ester amide) PVGA46, the copolymer was washed thoroughly only with ethyl ether. The recovered copolymer was finally dried under vacuum at room temperature.

Results and Discussion

The copoly(ester amide)s (PVGA*n***)** described in this work were prepared by polycondensation of monomers **1**[7a] and **2**[7b] (Scheme 1). Polymerizations were conducted in NMP in the presence of ethyldiisopropylamine (EDPA) as an acid acceptor. Feed compositions, yields, and some characterization data of these polymerizations are displayed in Table 1. AS/VG molar ratios in the feed were varied from 1/99 to 50/50 in order to cover a wide range of compositions. Both homopolymers PAS[7a] and PVG[7b] were used for comparison. All the copoly(ester amide)s were obtained as powdery solids, except PVGA46, which was obtained as a yellow-brown foam. The yields ranged from 89 to 41%, decreasing as the amount of incorporated carbohydrate increased. The higher yield obtained in the case of PVGA46 could be ascribed to the higher solubility of this copoly(ester amide), which forced us to use a different purification procedure. The intrinsic viscosities of the copoly(ester amide)s prepared in this work ranged from 0.34 to 0.99 dL g^{-1} (Table 1), their values decreasing as the amount of incorporated sugar monomer increased. M_v values between 3900 and 27 600 were estimated roughly from such viscosity numbers, using for calculation[11] the Mark–Houwink parameters reported for nylon-6,6, despite the fact that this viscosimetric equation may be somewhat inappropriate for estimating the size of these copoly(ester amide)s.

Results from the elemental analyses of the resulting polymers were consistent with the expected chemical constitutions, since these contain a small amount of absorbed water (Table 2). As anticipated, the presence of the sugar monomer in the polymer chain makes these copoly(ester amide)s hygroscopic.

The chemical constitution of the resulting copolymers was confirmed by FTIR and ^{1}H and ^{13}C NMR. Poly(ester amide)s with different compositions exhibit similar IR spectra, showing the characteristic absorption bands anticipated: 3300 (amide A), 3080 (amide B), 1740 (CO, ester), 1640 (amide I), and 1540 cm^{-1} (amide II). The composition of the copoly(ester amide)s was determined using NMR spectroscopy. In Figure 1, the ^{1}H and ^{13}C NMR spectra of copoly(ester amide) PVGA46, recorded in DMSO-d_6 at 60 °C, are shown for illustration. Assignment of the peaks appearing in both types of spectrum was possible on the basis of NMR data previously reported for poly(ester amide)s,[7] comparison of the spectra obtained for the different copoly(ester amide)s, and data correlation provided by two-dimensional NMR *cosy*, *hetcor*, and *hmbc* spectra.

Table 2. Composition of Copoly(ester amide)s PVGA*n*

		AS/VG		elemental analysis (C, H, N, %)					
				calcd[d]			found		
copolymer	AS/VG[a]	^{1}H[b]	^{13}C[c]						
PVGA1	1/99	1/99		60.19	8.59	7.00	59.72	8.56	6.92
PVGA5	5/95	5/95		58.70	8.58	6.78	58.96	8.46	6.78
PVGA8	10/90	8/92	7/93	58.42	8.55	6.71	58.23	8.51	6.67
PVGA21	25/75	21/79	20/80	57.23	8.34	6.41	56.96	8.29	6.38
PVGA46	50/50	46/54	45/55	54.59	8.12	5.83	54.36	8.10	5.79

[a] Monomer ratio in the feed. [b] Copolymer composition determined from the oxymethylene protons by ^{1}H NMR. [c] Copolymer composition determined from the methylene carbon resonances of the glutaric/succinic units by ^{13}C NMR. [d] Elemental analysis calculated for the copolymer compositions determined by ^{1}H NMR: PVGA1, PVGA5.1/5H_2O, PVGA8.1/5H_2O, PVGA21.1/5H_2O, and PVGA46.1/3H_2O.

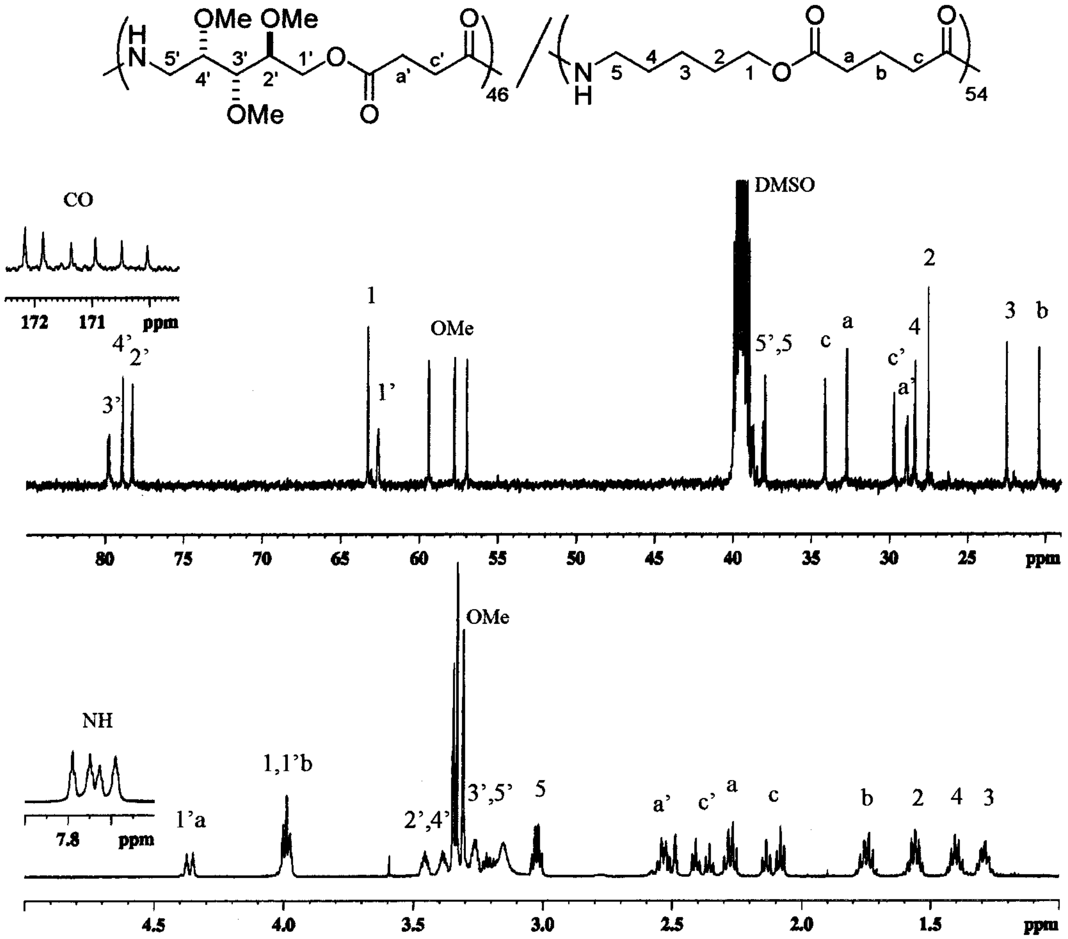

Figure 1. ^{1}H NMR (500.13 MHz, bottom) and ^{13}C NMR (125 MHz, top) spectra of PVGA46 recorded in DMSO-d_6 at 60 °C.

As reported in the scientific literature, the carbonyl resonances observed by ^{13}C NMR spectroscopy of the aliphatic polyesters are sensitive to the sequence effect.[12,13] To illustrate the assignment of the carbonyl signals of the copolymers studied in this paper, the different types of triad and the expanded carbonyl and aminomethylene regions of the ^{13}C NMR spectrum of the copoly(ester amide) PVGA46 are shown in Figure 2. The homopolymers are included in this figure for comparison. The presence of long monomers such as **1** and **2** prevents the copolymer from showing triad sensitivity. However, dyad sensitivity was observed both in ^{1}H and in ^{13}C NMR spectra. Thus, in ^{13}C NMR spectra, apart from the carbonyl resonances, dyad sequences were observed for the aminomethylene carbon atoms (CH_2NH) of VG and AS units (Figure 2). By comparison with the chemical shift of the aminomethylene carbon atom of PVG that appeared at 38.02 ppm, the resonance at 37.98 ppm has been assigned to the VG−VG dyad (resonance g). Analogously, the resonance at 38.11 ppm (resonance h) was assigned to the AS−VG dyad, taking into account the chemical shift of the aminomethylene carbon atom in PVS that appeared at 38.12 ppm. The signal observed at 38.80 ppm was assigned to the AS−AS dyad (resonance i) by comparison with the resonance of the aminomethylene group in PAS observed at 38.80 ppm. Finally, the resonance appearing at 38.70 ppm was assigned to the VG−AS dyad (resonance j) by comparison with the chemical shift of the aminomethylene carbon atom of poly(ester amide) PAG, which resonates at 38.71 ppm. Similarly, the dyad sequences observed in the ^{1}H NMR spectra for the amide protons and the amidomethylene (CH_2CONH) protons (Figure 3A,B) were assigned accordingly. Signal assignment was supported by correlation data provided by 2D NMR hetero multiple bond correlation (hmbc) spectra (Figure 3C).

On the basis of these data, the average lengths of the AS sequences (L_{AS}) and VG sequences (L_{VG}) and the degree of randomness (R) have been calculated with the following equations:

$$L_{AS} = \frac{N_{ASAS} + \frac{N_{VGAS}}{2}}{\frac{N_{VGAS}}{2}} \qquad \text{(I)}$$

$$L_{VG} = \frac{N_{VGVG} + \frac{N_{VGAS}}{2}}{\frac{N_{VGAS}}{2}} \qquad \text{(II)}$$

$$R = \frac{1}{L_{AS}} + \frac{1}{L_{VG}} \qquad \text{(III)}$$

where N_i represents the molar fraction of the sequence concerned. Its values are directly proportional to the integrated area under the peaks. The results obtained are shown in Table 3. The calculated results for a Bernoullian dyad distribution with the copoly(ester amide) composition determined by ^{1}H NMR are also shown for comparison. The number-average sequence

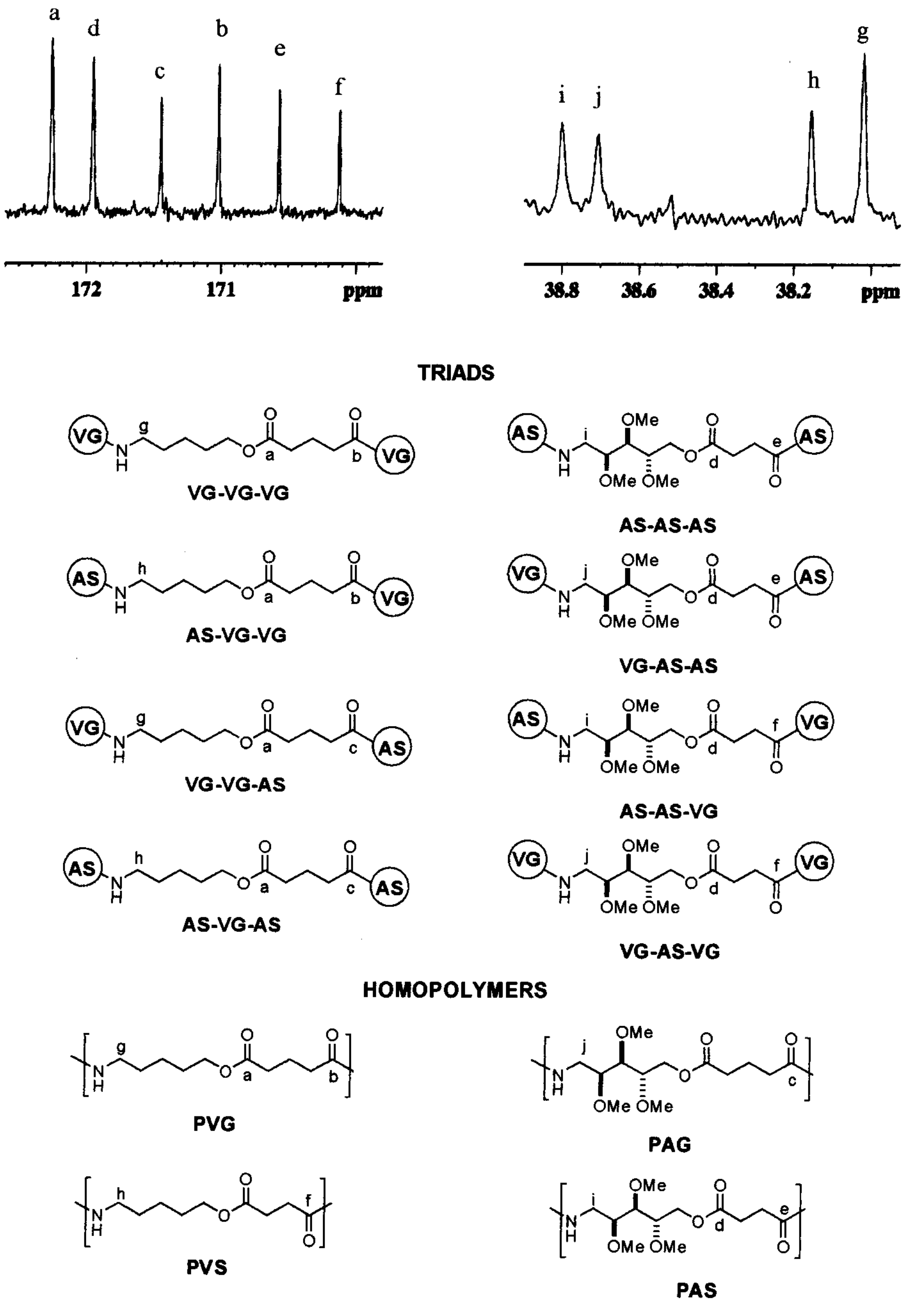

Figure 2. Expanded ^{13}C NMR spectra of the copoly(ester amide) PVGA46 in the carbonyl and aminomethylene regions.

Table 3. Composition,[a] Average Sequence Lengths, and Randomness[b] of Copoly(ester amide)s PVGA*n*

	composition		dyads (mol %)			av sequence lengths		
copolymer	^{X}VG	^{X}AS	VGVG	VGAS	ASAS	^{L}VG	^{L}AS	randomness *R*
PVGA1	99	1						
PVGA5	95	5						
			90	*9*	*1*	*20*	*1*	*1*
			(90.2)	(9.5)	(0.2)	(20.0)	(1.0)	(1.00)
PVGA8	92	8	**85**	**15**	**0**	**12**		
			84	*15*	*1*	*12*	*1*	*1*
			(85.0)	(14.4)	(0.6)	(12.8)	(1.1)	(1.00)
PVGA21	79	21	**63**	**30**	**6.9**	**5**	**1**	**1**
			63	*30*	*7*	*5*	*1*	*1*
			(63.0)	(32.7)	(4.2)	(4.8)	(1.2)	(1.00)
PVGA46	54	46	**30**	**44**	**26**	**2**	**2**	**1**
			30	*45*	*25*	*2*	*2*	*1*
			(29.3)	(49.6)	(21.1)	(2.2)	(1.8)	(1.00)

[a] Determined from the oxymethylene proton resonances by ^{1}H NMR. [b] Experimental values calculated by applying the equation mentioned in text: from ^{13}C NMR data in bold; from ^{1}H NMR in italics. Theorical values (in parentheses) were calculated on the basis of Bernoullian dyad distribution.

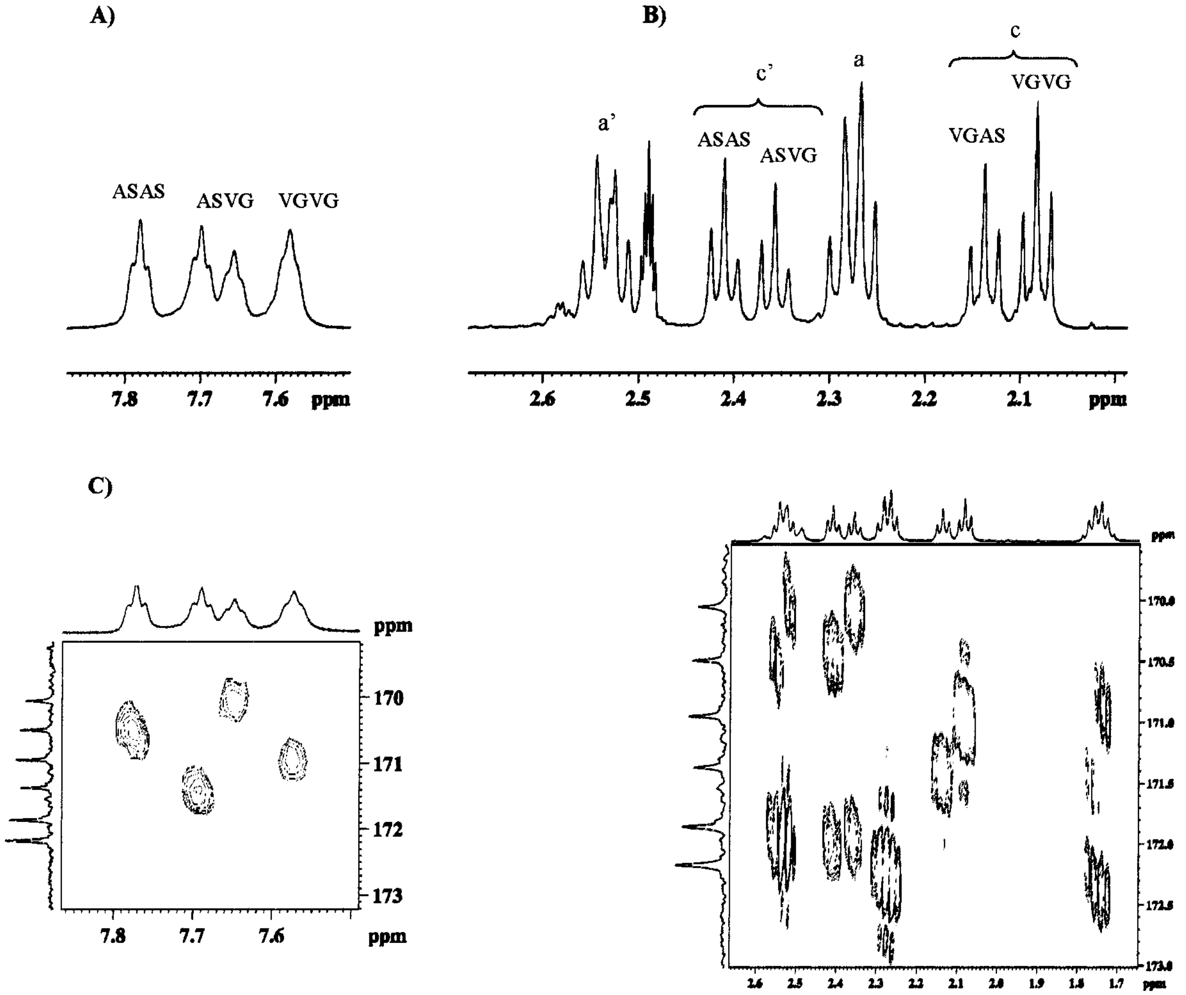

Figure 3. Expanded ^{1}H NMR spectra of PVGA46: NH (a) and CH_2CONH (b) regions; (c) $^1H-^{13}C$ hetero multiple bond correlation (hmbc) spectra.

lengths calculated with the composition provided by ^{1}H NMR and, in those cases where available, by ^{13}C NMR were in good agreement. It could also be observed that the average sequence lengths determined experimentally were close to the values predicted on the basis of ideal copolymerization statistics, although some departure from Bernoullian behavior was observed.

Infrared spectroscopy is not sensitive to the copolymer composition because the ester/amide ratio is not affected by variations in the feed composition. Quantitative evaluation of the copoly(ester amide) compositions could be accomplished for all the copolymers by ^{1}H NMR. Thus, the multiplet at 4.36 ppm assigned to H-1′a of the oxymethylene group of the arabinose−succinyl unit and the signal appearing at 3.99 ppm arising from the oxymethylene group of the aminopentanol residue (H-1) plus the proton H-1′b of the AS unit were used for this purpose. The percentage of AS units relative to VG units in a copoly(ester amide) PVGA*n* is given by

$$\%\,\mathrm{AS} = \frac{A_{\mathrm{CH(AS)}}}{\dfrac{A - A_{\mathrm{CH(AS)}}}{2} + A_{\mathrm{CH(AS)}}} \times 100 \qquad \text{(IV)}$$

In this expression, $A_{\mathrm{CH(AS)}}$ is the area of the multiplet at 4.36 ppm and A is the total area of the signal appearing at 3.99 ppm. The compositions thus calculated are given in Table 2. As observed in this table, the amount of carbohydrate residue (AS units) introduced in the final composition of copoly(ester amide)s PVGA*n* is close to that selected for the respective feeds. This suggests that the two monomers may have similar reactivities. Copolymer composition was also determined by ^{13}C NMR spectroscopy. For this purpose, the methylene carbon resonance (CH_2COO) of the succinyl/glutaryl units, which appeared clearly resolved in the spectra, was used. The results were in excellent agreement with those obtained by ^{1}H NMR, and they have been included in Table 2 for comparison.

Table 4. Compared Qualitative Solubilities of PVGA*n*[a]

solvent	PVGA1	PVGA5	PVGA8	PVGA21	PVGA46
water	−	−	−	−	++
ether	−	−	−	−	−
ethanol	+	+	+	+	+
chloroform	−	−	+	++	++
DMSO	+	+	+	++	++
DMF	+	+	+	+	++
acetone	−	−	−	−	−
ethyl acetate	−	−	−	−	−
formic acid	++	++	++	++	++

[a] Estimated according to the method of Braun.[14] (−) Insoluble, (±) slightly swollen, (+) soluble on warming at 100 °C, (++) soluble at room temperature.

Qualitative solubilities[14] of copoly(ester amide)s are compared in Table 4. Independent of their composition, all the copolymers were easily soluble in hydrogen-bond-breaking solvents such as formic acid, and they were

Table 5. Results of Thermal Analysis

copolymer	T_{de}^{a} (°C)	T_g^{b} (°C)	T_m^{c} (°C)	ΔH^{c} (J/g)
PVGA1	371	−6.0	115.4	47.5
PVGA5	369	−4.4	113.0	33.9
PVGA8	362	−3.6	106.0	44.1
PVGA21	343	6.3	93.0	21.7
PVGA46	320	21.2		

[a] The onset-of-decomposition temperature determined by TGA. [b] Measured by DSC, second heating after rapid cooling to room temperature. [c] Measured by DSC, annealed samples.

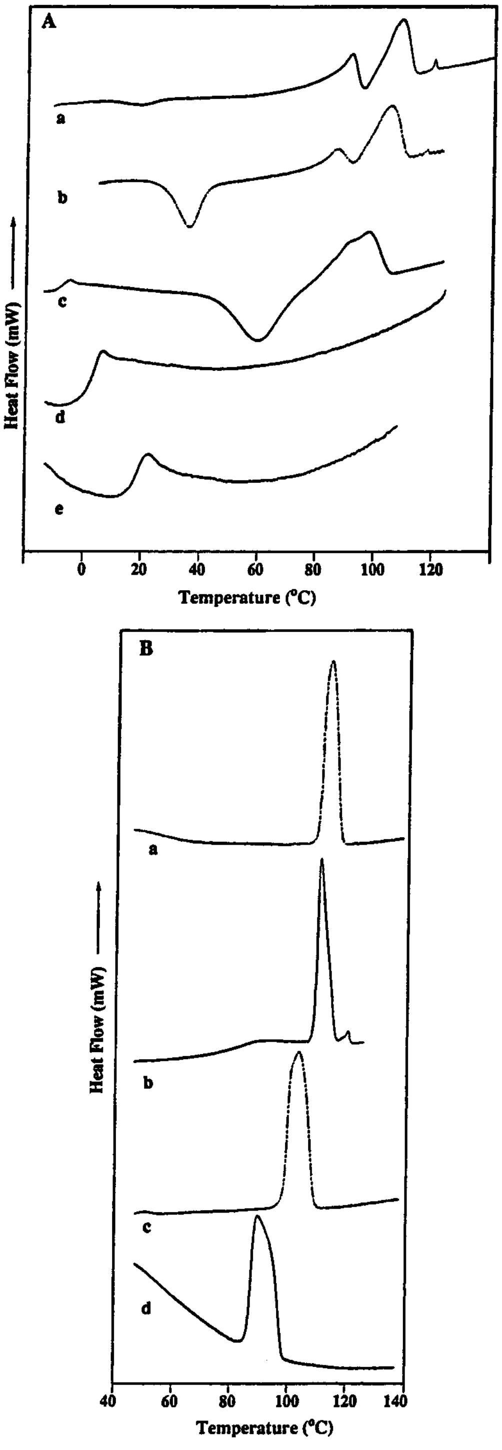

Figure 4. DSC thermograms of the copoly(ester amide)s conducted at a heating rate of 10 °C/min. (A) Second heating traces: PVGA1 (a), PVGA5 (b), PVGA8 (c), PVGA21 (d), and PVGA46 (e). (B) Annealing traces: PVGA1 (a), PVGA5 (b), PVGA8 (c), and PVGA21 (d).

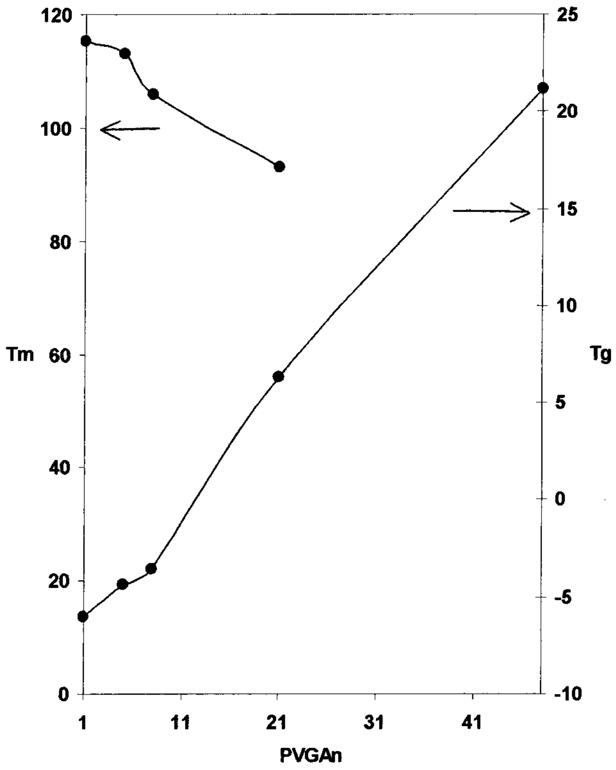

Figure 5. Evolution of the melting temperature (T_m) and the glass-transition temperature (T_g) vs the copoly(ester amide) compositions.

not soluble in nonaggressive oxygenated solvents such as ether, acetone, or ethyl acetate. All the copolymers were soluble in polar aprotic solvents such as DMSO or DMF. However, they showed a different solubility pattern in the case of chloroform. Only copoly(ester amide)s containing up to 8% of the sugar monomer were soluble in this solvent. Although these copoly(ester amide)s are hydrophilic, as expected from their structures and confirmed by their elemental analysis, only one of them, PVGA46, was soluble in water.

The thermal transitions in PVGA*n* have been analyzed using DSC. The characteristic parameters resulting from these measurements are given in Table 5. In all cases except PVGA46, well-defined endotherms corresponding to melting transitions appeared during the first heating cycle. Figure 4 shows the second heating and the annealing traces of copoly(ester amide)s. In certain cases (PVGA1 and PVGA5), three melting peaks were observed (Figure 4A), a common phenomenon currently interpreted as due to the fusion of populations of different-sized crystallites.[15] After annealing these samples at 10−20 °C below their respective melting points, both produced traces consisting of a single endotherm (Figure 4B). Copoly(ester amide) PVGA8 showed a single broad endotherm preceded by an exotherm peak due to cold crystallization. The postmelting slow-cooling trace did not show any crystallization transition. However, it was possible to recrystallize the copoly(ester amide) by annealing the sample at 93 °C under a nitrogen atmosphere. The thermograms of the copoly(ester amide)s containing the highest amounts of carbohydrate-based monomer did not show any thermal transition associated with melting during the second heating cycle. Only well-defined slope changes due to second-order thermal transitions were observed. In contrast to PVGA46, copoly(ester amide) PVGA21

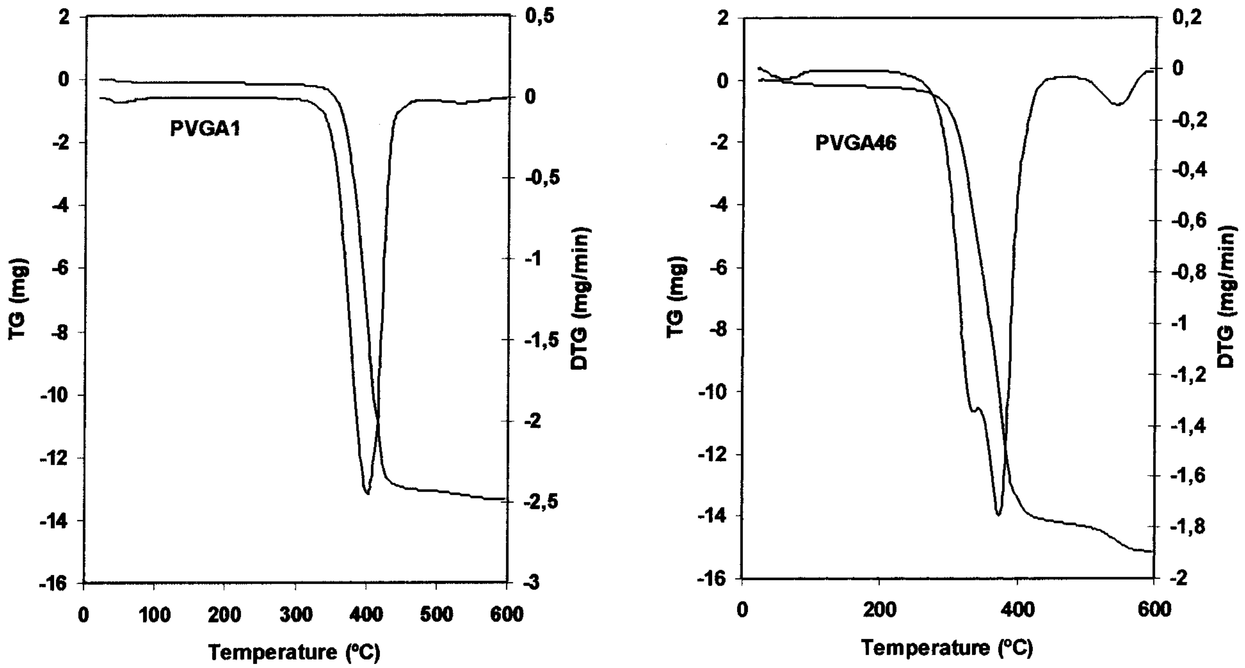

Figure 6. TGA traces and derivative curves of PVGA1 and PVGA46.

was able to crystallize after the sample was annealed at 62 °C under a nitrogen atmosphere.

Second-order thermal transitions were observed for all the copoly(ester amide)s during the second heating traces after rapid cooling to room temperature. The melting temperature (T_m) and the glass-transition temperature (T_g) of PVGA*n* are graphically compared in Figure 5. As shown in this figure, copolymerization of VG with increasing amounts of carbohydrate-based monomer (AS) modified the T_g and T_m values. The only T_g observed was found to increase with increasing amounts of arabinose–succinyl (AS) units. As expected, chain mobility in the amorphous phase appears to be more restricted as the amount of AS units in the copoly(ester amide) composition increased. The melting temperature of PVGA*n* decreased with increasing amounts of AS units. The reduction in T_m and the increasing difficulty in crystallization of the copoly(ester amide)s are considered the result of the disturbances provoked by AS units in the crystalline structure. Thus, for PVGA46, containing about 50% of AS units, the copoly(ester amide) was completely amorphous.

Thermal stability of these copoly(ester amide)s was studied by TGA. TGA measurements were carried out under a nitrogen atmosphere from room temperature to 600 °C. The data obtained from these measurements are collected in Table 5. As an illustration, Figure 6 shows the TGA traces of copoly(ester amide) PVGA1 and PVGA46, together with their respective derivative curves. All the copolymers were stable up to 200 °C, with only a small weight loss at the beginning of the TGA analysis due to the loss of absorbed water.

In contrast with the case of copoly(ester amide)s PVGA1, PVGA5, and PVGA8, which seem to be degraded in one step, the thermal degradation of copoly(ester amide)s PVGA21 and (especially) PVGA46 happened mainly in two steps, where the samples lost about 92% of their weight. In PVGA21, the first step is hardly observed as a shoulder of the main degradation step at 383 °C. However, in copoly(ester amide) PVGA46, the two steps are clearly observed around 365 and 375 °C. In both cases, a third step was noted in the TGA traces at 534 and 545 °C, respectively. All these values were measured on the derivative curves.

Conclusions

We have shown that copolymerization of 1-amino-1-deoxy-2,3,4-tri-*O*-methyl-5-*O*-[(pentachlorophenoxy)succinyl]-L-arabinitol hydrochloride and 5-amino-1-*O*-[(pentachlorophenoxy)glutaryl]pentanol hydrochloride leads to random copolymers. The copolymer composition was determined by ^{1}H and ^{13}C NMR and was close to that of the feed. The NMR analysis showed that the carbonyl and aminomethylene carbon resonances, and the NH and the amidomethylene proton resonances, were sensitive to dyad distribution, allowing the determination of the degree of randomness and average sequence lengths of the copoly(ester amide)s. Melting temperatures of the copolymers were found to decrease as the amount of the carbohydrate-based monomer increased, whereas the glass-transition temperature increased in parallel. The thermal stability of the copolymers under nitrogen decreased with increasing amounts of the sugar monomer.

Acknowledgment. We thank the C.I.C.Y.T. (Comisión Interministerial de Ciencia y Tecnología) of Spain for financial support (Grant MAT99-0578-C02-01).

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MA011301B