Poly(ester amide)s Derived from L-Tartaric Acid and Amino Alcohols. 1. Regic Polymers

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Received June 29, 1999; Revised Manuscript Received September 23, 1999

ABSTRACT: Stereoregular poly(ester amide)s (PEAT*n*) containing equal amounts of ester and amide groups have been obtained by polycondensation in solution from di-*O*-methyl-L-tartaric acid and aliphatic amino alcohols $H_2N(CH_2)_{n-1}CH_2OH$. Suitable synthetic routes were designed to prepare either *syndioregic* (*s*-PEAT*n*, $n = 5,6$) or *isoregic* (*i*-PEAT*n*, $n = 5, 6, 11$) polymers. All the newly synthesized poly(tartarester amide)s were characterized by elemental analysis, size exclusion chromatography, and IR and NMR spectroscopies. They all display optical activity in solution and, except for *s*-PEAT5, are highly crystalline with T_m's within the range 100−150 °C and T_g's oscillating between 10 and 30 °C. Thermal decomposition of PEAT*n* onsets above 200 °C with T_d values depending upon both the regicity of the chain and the length of the polymethylene segment. For comparative purposes, two poly(esteramide)s, one *syndioregic* (*s*-PEAS6) and another *isoregic* (*i*-PEAS6), were prepared from succinic acid and 6-amino-1-hexanol, and their properties were evaluated in parallel. Major differences between PEAS6's and PEAT6's concerned solubility and hygroscopicity whereas crystallinity and thermal transitions were found to be scarcely affected by the presence of the methoxy side groups.

Introduction

Polyamides and polyesters based on carbohydrates are polymers of increasing interest for both their natural origin and their potential as biodegradable/biocompatible materials useful in biomedicine. Thus, a good number of papers dealing with the preparation and properties of polyamides made from adequately functionalized sugar derivatives as aldaric acids, diamino alditols, or amino aldonic acids appeared in the recent literature.[1] Particular efforts in this area are being addressed to obtain stereoregular polymers able to combine good mechanical and thermal properties with a pattern of behavior of biological interest.[2−4] In addition, the ability of these polymers to be processed by standard techniques is highly desired. This would imply T_m well below T_d, a good thermal stability, and, if possible, high rates of crystallization from the melt.

Poly(tartaramide)s are polyamides made from tartaric acid (2,3-dihydroxysuccinic acid) and 1,*n*-alkanediamines whose synthesis was first reported in the early 1970s.[5] In these past years a variety of stereoregular poly(alkylene-di-*O*-methyltartaramide)s have been prepared in our laboratory and their properties thoroughly investigated.[6] These polyamides are nylon *n*,4 derivatives bearing two methoxy side groups attached to the two respective aliphatic carbons of the diacidic unit. It was found that these compounds are highly crystalline, retain most of the good mechanical and thermal properties characteristic of conventional nylons, and display a remarkable hydrophilicity. However, poly(tartaramide)s degrade slowly in water under physiological conditions with weight losses less than 10% of the initial sample after 1 year of incubation.[7] It is apparent that the inherent high resistance of the amide linkage to hydrolysis is not very much affected by the −OR side groups attached to the polymer main chain.

Incorporation of relatively unstable ester groups in a polyamide chain is an approach widely used to render this type of polymers more degradable.[8] In a recent paper we described a series of nonstereoregular poly(ester amide)s prepared from L-tartaric acid, succinic acid, 1,6-hexanediol, and 1,6-hexanediamine containing up to 20% of ester groups.[9] As expected, the hydrolytic degradability of these compounds increased significantly with the content in ester groups, but their physical properties decayed in parallel as a consequence of the random heterogeneity introduced in the microstructure of the polymer. To our knowledge, only two stereoregular poly(ester amide)s derived from carbohydrates have been described up to date.[10] They were obtained from conveniently protected 1-amino-1-desoxyalditols derived from L-arabinose or D-xylose and glutaric or succinic acids. These sugar-based poly(ester amide)s contain three methoxy side groups in the repeating unit, have melting points around 100 °C, and start to decompose at temperatures far above their melting points. They display high hygroscopicity and degrade very fast in water. However, no data on the mechanical properties of these interesting poly(ester amide)s were reported.

In this work we wish to describe the synthesis and properties of stereoregular poly(ester amide)s derived from the natural occurring L-tartaric acid and aliphatic *n*-amino-1-alkanols. Two series of polymers differing in the regicity of the chain are examined. In both cases the hydroxyl side groups of L-tartaric acid were converted into methoxy groups to avoid undesired side reactions. The *syndioregic* poly(ester amide)s (*s*-PEAT*n*) are prepared by reaction of the *p*-toluenesulfonate salt of the bis(*n*-aminoalkyl) diesters with bis(pentachlorophenyl) L-tartrate whereas i*soregic* poly(ester amide)s (*i*-PEAT*n*) are obtained by polycondensation in solution using the activated ester−amino acid as the unique monomer. Optical, thermal, and mechanical properties are measured and evaluated in relation to the constitution of the polymers. To appraise the effect exerted by

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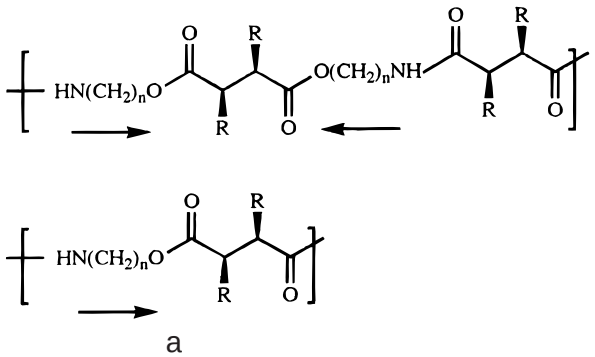
10.1021/ma991050v CCC: $18.00
Published on Web 11/03/1999

Scheme 1



a

	PEAT*n*		PEAS*n*	
	R	n	R	n
syndioregic	-OCH_3	5,6	H	6
isoregic	-OCH_3	5,6,11	H	6

b

the methoxy side groups on properties, the two isomeric poly(ester amide)s, *s*-PEAS6 and *i*-PEAS6, have been synthesized from succinic acid and 6-amino-1-hexanol, and their properties have been examined in parallel. The chemical structures of the poly(ester amide)s investigated in this work are represented in Scheme 1. As a second part of our project, a similar investigation is being carried out on similar poly(tartaraester amide)s having *aregic* microstructure which is intended to be published soon.[11] The compared study of the hydrolytic degradability of all these novel poly(tartarester amide)s constitutes the third and last part of this research, which will be reported in a forthcoming paper.[12]

Experimental Section

A. Materials and Methods. All chemicals were obtained commercially from either Aldrich or Merck. They were analytical grade or higher and used without further purification. Solvents to be used under anhydrous conditions were dried by standard methods. Viscosities were measured in dichloroacetic acid at 25.0 ± 0.1 °C using an Ubbelohde microviscometer. Gel permeation chromatography was performed on a Waters Associates instrument fitted with a refractive index detector and a set of two Styragel columns of exclusion limits at 10^3 and 10^2 nm. The mobile phase was a mixture of chloroform:*o*-chlorophenol (9:1), and monodisperse polystyrene standards purchased from Waters Millipore were used to create a calibration curve.

Infrared spectra were recorded from films on a FT-IR Perkin-Elmer 2000 instrument. ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker AMX-300 spectrometer. Spectra of intermediate compounds, monomers, and polymers were taken in $CDCl_3$ either pure or containing about 10% of trifluoroacetic acid (TFA) or formic acid. Sample concentrations about 1 and 5% (w/v) were used for ^{1}H and ^{13}C analyses, respectively. Tetramethylsilane (TMS) was used as internal reference. ^{13}C NMR measurements were made under proton decoupling conditions at 74.48 MHz. For typical ^{1}H NMR and ^{13}C NMR spectra, the number of accumulated scans was 64 and 300−1500, respectively.

Hygroscopicities were measured according to Mori et al.[13] in a 100% relative humidity atmosphere at 20 °C using either film or powdered samples. The method described by Braun was used for the estimation of polymer solubilities.[14] Optical rotations of polymers were measured on a Perkin-Elmer 141 polarimeter at 23 °C in chloroform or trifluoroethanol (TFE) solutions at polymer concentrations within the 0.5−1.0 g dL^{-1} range. Differential scanning calorimetry (DSC) was carried out using either a Perkin-Elmer DSC-4 instrument calibrated with indium. The 2−5 mg samples placed under a nitrogen atmosphere were heated at a rate of 20 °C min^{-1} and cooled at varying rates in the 30−200 °C temperature range. Thermogravimetric measurements (TGA) were performed with Mettler TA4000 equipment at a heating rate of 10 °C min^{-1}. Tensile properties were measured under room conditions on a stress−strain machine Miniature Materials Tester of Polymer Laboratories operating at deformation rates of 1 mm min^{-1}. Specimens were rectangular strips of approximate dimensions 30.0 × 3.0 × 0.20 mm which were cut from films prepared by casting from chloroform. X-ray diffraction patterns were obtained from powdered samples in a modified Statton camera using nickel-filtered Cu Kα radiation of wavelength 0.1542 nm. They were recorded on flat photographic films and were calibrated with molybdenum sulfide (d_{002} = 0.6147 nm).

B. Synthesis of Intermediate Compounds and Monomers. Amino alcohols with five and six carbon atoms were purchased from Aldrich. 11-Amino-1-undecanol is not commercially available and had to be synthesized from 11-aminoundecanoic acid by esterification with methanol and subsequent reduction with $LiAlH_4$. Bis(pentachlorophenyl) 2,3-di-*O*-methyl-L-tartrate was obtained from commercial diethyl-L-tartrate by a sequence of reactions including methylation with dimethyl sulfate, hydrolysis to the diacid, and esterification with pentachlorophenol as previously described in full detail.[6] 2,3-Di-*O*-methyl-L-tartaric acid anhydride was prepared by treating 2,3-di-*O*-methyl-L-tartaric acid with acetic anhydride as reported elsewhere.[15]

Bis(*n*-aminoalkyl) Di-*O*-methyl-L-tartrate *p*-Toluenesulfonate Salts (II). General Procedure. The general procedure used for the preparation of these compounds was as follows: A mixture of the corresponding amino alcohol (**I**) (1 mol) and *p*-toluenesulfonic acid (1 mol) in toluene was heated under reflux for 2 h in a flask provided with a Dean-Stark. Di-*O*-methyl-L-tartaric acid (0.5 mol) was then added and the reflux maintained for 36 h with continuous removal of the distilling water−toluene azeotrope. The solid residue left after distillation was dispersed in ether, filtered, and crystallized in 2-propanol.

The bis(6-aminohexyl) di-*O*-methyl succinate di(*p*-toluenesulfonate) salt to be used for the synthesis of *s*-PEAS6 was prepared in a similar way. A detailed description of the synthesis and characterization of this compound has been described by us elsewhere.[15]

Bis(5-aminopentyl) Di-*O*-methyl-L-tartrate *p*-Toluenesulfonate. Yield: 85%. Mp: 128−130 °C. $[\alpha]^{23}_D$: +31.49° (*c* 0.94, in MeOH). ^{1}H NMR ($CDCl_3$:TFA): δ 1.50 (m, 4H, $2CH_2C\mathbf{H}_2CH_2$), 1.77 (m, 8H, $2C\mathbf{H}_2CH_2O$ and $2C\mathbf{H}_2CH_2N$), 2.42 (s, 6H, $2CH_3$), 3.20 (br, 4H, $2CH_2N$), 3.46 (s, 6H, $2OCH_3$), 4.29 (t, 4H, $2CH_2O$), 4.33 (s, 2H, 2CH), 6.80 (br, 6H, $2NH_3$), 7.28 (d, 4H, H_{ar}), 7.68 (d, 4H, H_{ar}). ^{13}C NMR ($CDCl_3$:TFA): δ 21.44 (CH_3), 22.45 ($\mathbf{C}H_2CH_2CH_2O$), 26.69 ($\mathbf{C}H_2CH_2O$), 27.63 ($\mathbf{C}H_2CH_2N$), 41.22 ($\mathbf{C}H_2N$), 60.06 (OCH_3), 66.72 (CH_2O), 81.16 (CH), 125.87 129.95, 137.15, 143.97 (C_{ar}), 171.11 (COO). Anal. Calcd for $C_{30}H_{48}N_2O_{12}S_2$: C, 52.01; H, 6.98; N, 4.04; S, 9.25. Found: C, 51.66; H, 6.98; N, 4.02; S, 9.10.

Bis(6-aminohexyl) Di-*O*-methyl-L-tartrate *p*-Toluenesulfonate. Yield: 77%. Mp: 136−138 °C. $[\alpha]^{23}_D$: +32.20° (*c* 0.97, in MeOH). ^{1}H NMR ($CDCl_3$:TFA): δ 1.45 (m, 8H, $2C\mathbf{H}_2C\mathbf{H}_2CH_2CH_2O$), 1.74 (m, 8H, $2C\mathbf{H}_2CH_2O$ and $2C\mathbf{H}_2CH_2N$), 2.41 (s, 6H, $2CH_3$,), 3.20 (br, 4H, $2CH_2N$), 3.47 (s, 6H, $2OCH_3$), 4.31 (t, 4H, $2CH_2O$), 4.38 (s, 2H, 2CH), 6.72 (br, 6H, $2NH_3$), 7.31 (d, 4H, H_{ar}), 7.69 (d, 4H, H_{ar}). ^{13}C NMR ($CDCl_3$: TFA): δ 21.46 (CH_3), 25.22, 25.61 ($\mathbf{C}H_2\mathbf{C}H_2CH_2CH_2O$), 27.17 ($\mathbf{C}H_2CH_2O$), 28.05 ($\mathbf{C}H_2CH_2N$), 41.62 ($\mathbf{C}H_2N$), 60.18 ($OCH_3$), 67.40 ($CH_2O$), 81.32 (CH), 125.97, 130.08, 137.50, 144.26 (C_{ar}), 171.45 (COO). Anal. Calcd for $C_{32}H_{52}N_2O_{12}S_2$: C, 53.32; H, 7.27; N, 3.89; S, 8.89. Found: C, 53.28; H, 7.26; N, 3.81; S, 8.74.

***n*-Aminoalkylpentachlorophenyl Di-*O*-methyl-L-tartrate Hydrobromides (VII). General Procedure.** To a solution of the corresponding amino alcohol (**I**) in CH_2Cl_2 or $CHCl_3$ (0.1 mol in 60 mL) was slowly added di-*tert*-butyl dicarbonate (0.108 mol). The mixture was left for 12 h at room temperature under stirring, and it was then diluted with ether (120 mL) and successively washed with water and $NaHCO_3$ and NaCl saturated solutions. The organic phase was then dried on Na_2SO_4 and concentrated to a syrup. Distillation under vacuum of the residue rendered the *N*-*tert*-butoxycarbonyl alcohols (**IV**) as pure oils in yields above 65%.

Compounds **IV** (1 mmol) were mixed with di-*O*-methyl-L-tartaric anhydride (1 mmol) in $CHCl_3$ (1.3 mL), and the mixture was left to react for 4−5 days under stirring at room temperature under an inert atmosphere. The solvent was then evaporated and the oily residue dissolved in ethyl acetate, washed with water, and dried on Na_2SO_4. Evaporation of the organic solution to dryness led to crude compounds **V** in approximately quantitative yields. These compounds were then subjected to ester activation without further purification. The esterification reaction was carried out by adding dropwise a solution of dicyclohexylcarbodiimide to a solution of an equimolar mixture of the *N*-blocked amino acid **V** and pentachlorophenol in ethyl acetate at room temperature. The dicyclohexylurea generated in the reaction was filtered off, and crude *N*-blocked pentachlorophenyl amino esters (**VI**) were obtained by evaporating the clean solution to dryness.

Removal of the *tert*-butoxycarbonyl group from compounds **VI** was performed as follows: 27 mmol of **VI** was dissolved in HBr−AcH (16.5%, 94 mL) and the solution left under stirring at room temperature for 1.5 h. The residue resulting from evaporation of the excess of acids was washed first with ether and then with ethyl acetate. Crystallization in chlorobenzene led to activated amino ester bromides (**VII**) in the pure form. These compounds were fully characterized prior to polycondensation to the corresponding poly(ester amide)s.

A similar procedure with minor modifications was followed for the preparation of 6-aminohexylpentachlorophenyl di-*O*-methyl-L-succinate hydrobromide by using commercial succinic acid anhydride instead of L-tartaric acid anhydride. This monomer will be used for the preparation of the *isoregic* poly(ester amide) *i*-PEAS-6.

5-Aminopentylpentachlorophenyl Di-*O*-methyl-L-tartrate Hydrobromide. Mp: 58−62 °C. $[\alpha]^{23}_D$: +23.96 (*c* 0.91, in CH_3OH). ^{1}H NMR ($CDCl_3$): δ 1.61 (m, 2H, C**H**$_2$CH$_2$CH$_2$N), 1.78 (m, 2H, C**H**$_2$CH$_2$N), 1.92 (m, 2H, C**H**$_2$CH$_2$O), 3.12 (m, 2H, CH$_2$N), 3.60 (s, 3H, C**H**$_3$OCHCOOCH$_2$), 3.61 (s, 3H, C**H**$_3$OCHCOOPcp), 4.32 (t, 2H, CH$_2$O), 4.48 (d, 1H, C**H**COOCH$_2$), 4.64 (m, 1H, C**H**COOPcp), 7.96 (br, 3H, NH$_3$). ^{13}C NMR ($CDCl_3$:TFA): δ 23.10 (**C**H$_2$CH$_2$CH$_2$N), 26.68 (**C**H$_2$CH$_2$O), 28.07 (**C**H$_2$CH$_2$N), 39.96 (CH$_2$N), 60.02 (**C**H$_3$OCHCOOCH$_2$), 60.26 (**C**H$_3$OCHCOOPcp), 65.52 (CH$_2$O), 80.58 (**C**HCOOCH$_2$), 80.93 (**C**HCOOPcp), 127.29, 132.14, 132.27, 143.42 (C$_{ar}$), 165.17 (COOPcp), 168.75 (COOCH$_2$). Anal. Calcd for $BrC_{17}Cl_5H_{21}NO_6$: C, 34.46; H, 3.57; N, 2.36. Found: C, 35.04; H, 3.98; N, 2.76.

6-Aminohexylpentachlorophenyl Di-*O*-methyl-L-tartrate Hydrobromide. Mp: 151−154 °C. $[\alpha]^{23}_D$: +27.36 (*c* 0.87, in CH_3OH). ^{1}H NMR ($CDCl_3$): δ 1.48 (m, 4H, C**H**$_2$C**H**$_2$CH$_2$CH$_2$N), 1.76 (m, 2H, C**H**$_2$CH$_2$N), 1.86 (m, 2H, C**H**$_2$CH$_2$O), 3.10 (m, 2H, CH$_2$N), 3.57 (s, 3H, C**H**$_3$OCHCOOCH$_2$), 3.59 (s, 3H, C**H**$_3$OCHCOOPcp), 4.30, (dm, 2H, CH$_2$O), 4.46 (d, 1H, C**H**COOCH$_2$), 4.62 (m, 1H, C**H**COOPcp), 7.93 (br, 3H, NH$_3$). ^{13}C NMR ($CDCl_3$): δ 24.96, 25.77 (**C**H$_2$**C**H$_2$CH$_2$CH$_2$N), 26.96 (**C**H$_2$CH$_2$O), 28.11 (**C**H$_2$CH$_2$N), 40.06 (CH$_2$N), 59.91 (**C**H$_3$OCHCOOCH$_2$), 60.22 (**C**H$_3$OCHCOOPcp), 65.52 (CH$_2$O), 80.52 (**C**HCOOCH$_2$), 80.96 (**C**HCOOPcp), 127.33, 132.10, 132.25, 143.48 (C$_{ar}$), 165.15 (COOPcp), 168.73 (COOCH$_2$). Anal. Calcd for $BrC_{18}Cl_5H_{23}NO_6$: C, 35.64; H, 3.82; N, 2.31. Found: C, 35.63; H, 3.75; N, 2.36.

11-Aminoundecylpentachlorophenyl Di-*O*-methyl-L-tartrate Hydrobromide. Mp: 64.3 °C. $[\alpha]^{23}_D$: +19.89 (*c* 0.94, in CH_3OH). ^{1}H NMR ($CDCl_3$): δ 1.25 (br, 14H, (C**H**$_2$)$_7$CH$_2$CH$_2$N), 1.73 (m, 2H, C**H**$_2$CH$_2$N), 1.94 (m, 2H, C**H**$_2$CH$_2$O), 3.04 (m, 2H, CH$_2$N), 3.57 (s, 3H, C**H**$_3$OCHCOOCH$_2$), 3.58 (s, 3H, C**H**$_3$OCHCOOPcp), 4.30, (dm, 2H, CH$_2$O), 4.45 (d, 1H, C**H**COOCH$_2$), 4.62 (m, 1H, C**H**COOPcp), 7.96 (br, 3H, NH$_3$). ^{13}C NMR ($CDCl_3$): δ 26.51−29.47 (**C**H$_2$)$_9$CH$_2$N), 40.22 (CH$_2$N), 59.78 (**C**H$_3$OCHCOOCH$_2$), 60.09 (**C**H$_3$OCHCOOPcp), 65.82 (CH$_2$O), 80.51 (**C**HCOOCH$_2$), 81.01 (**C**HCOOPcp), 127.34, 131.97, 132.17, 143.53 (C$_{ar}$), 165.27 (COOPcp), 168.63 (COOCH$_2$). Anal. Calcd for $BrC_{18}Cl_5H_{23}NO_6$: C, 35.64; H, 3.82; N, 2.31. Found: C, 35.63; H, 3.75; N, 2.36.

6-Aminohexylpentachlorophenyl Succinate Hydrobromide. Mp: 140−142 °C. ^{1}H NMR ($CDCl_3$): δ 1.44 (br, 4H, C**H**$_2$C**H**$_2$CH$_2$CH$_2$N), 1.67 (m, 2H, C**H**$_2$CH$_2$N), 1.83 (m, 2H, C**H**$_2$CH$_2$O), 2.79 (t, 2H, C**H**$_2$COOCH$_2$), 3.04 (t, 2H, C**H**$_2$COOPcp), 3.05 (br, 2H, CH$_2$N), 4.13, (t, 2H, CH$_2$O), 7.97 (br, 3H, NH$_3$). ^{13}C NMR ($CDCl_3$): δ 25.12, 25.95 (**C**H$_2$**C**H$_2$CH$_2$CH$_2$N), 27.22 (**C**H$_2$CH$_2$O), 28.14 (**C**H$_2$CH$_2$N), 28.63 (**C**H$_2$COOCH$_2$) 28.78 (**C**H$_2$COOPcp), 39.98 (CH$_2$N), 64.71 (CH$_2$O), 127.59, 131.59, 131.98, 143.88 (C$_{ar}$), 168.33 (COOCH$_2$), 171.65 (COOPcp). Anal. Calcd for $BrC_{16}Cl_5H_{19}NO_4$: C, 35.16; H, 3.50; N, 2.56. Found: C, 35.13; H, 3.49; N, 2.58.

C. Synthesis of Polymers. Syndioregic Poly(tartarester amide)s. General Procedure. To a solution of a mixture of triethylamine (4 mmol) and the corresponding bis(*n*-aminoalkyl) diester *p*-toluenesulfonate salt (**II**) (1.5 mmol) was added bis(pentachlorophenyl) di-*O*-methyl-L-tartrate (**III**) (1.5 mmol) in small portions for 1 h. The mixture was left to react for 3 days at room temperature and then refluxed for 3 h. After cooling to room temperature, the polymer was precipitated by addition of the appropriate solvent as indicated below.

***s*-PEAT5.** Precipitating solvent: hexane. Yield: 65%. $[\alpha]^{23}_D$: +87.93° (c 0.87, in $CHCl_3$). IR (film from $CHCl_3$): 3290 (amide A), 3068 (amide B), 2936, 2865, 2833, 1757, 1732 (COO), 1649 (amide I), 1532 (amide II), 1453, 1346, 1272, 1191, 1149, 1095, 1026, 755 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.45 (m, 4H, 2C**H**$_2$CH$_2$CH$_2$N), 1.57 (m, 4H, 2C**H**$_2$CH$_2$N), 1.71 (m, 4H, 2C**H**$_2$CH$_2$O), 3.28 (m, 2H, 2**H**CHN), 3.36 (m, 2H, 2HC**H**N), 3.43 (s, 6H, 2C**H**$_3$OCHCON), 3.45 (s, 6H, 2C**H**$_3$OCHCOO), 4.21 (m, 4H, 2CH$_2$O), 4.22 (s, 4H, 4CH), 6.76 (t, 2H, 2NH). ^{13}C NMR ($CDCl_3$): δ 23.09 (**C**H$_2$CH$_2$CH$_2$N), 28.28 (**C**H$_2$CH$_2$O), 29.24 (**C**H$_2$CH$_2$N), 38.97 (**C**H$_2$N), 59.66 (**C**H$_3$OCHCOO), 60.64 (**C**H$_3$OCHCON), 65.02 (CH$_2$O), 81.16 (**C**HCOO), 82.33 (**C**HCON), 169.22 (COO), 169.42 (CONH). Anal. Calcd for $C_{22}H_{38}N_2O_{10}\cdot H_2O$: C, 51.96; H, 7.93; N, 5.51. Found: C, 51.64; H, 7.68; N, 5.37.

***s*-PEAT6.** Precipitating solvent: 2-propanol. Yield: 90%. $[\alpha]^{23}_D$: +86.96° (*c* 0.92, in $CHCl_3$). IR (film from $CHCl_3$): 3420, 3289 (amide A), 3073 (amide B), 2936, 2860, 2835, 1757, 1732 (COO), 1657 (amide I), 1532 (amide II), 1461, 1449, 1262, 1191, 1108, 1093, 1028, 799 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.4 (m, 8H, 2C**H**$_2$C**H**$_2$CH$_2$CH$_2$N), 1.55 (m, 4H, 2C**H**$_2$CH$_2$N), 1.67 (m, 4H, 2C**H**$_2$CH$_2$O), 3.25−3.38 (m, 4H, 2CH$_2$N), 3.43 (s, 6H, 2C**H**$_3$OCHCON), 3.45 (s, 6H, 2C**H**$_3$OCHCOO), 4.16 (m, 4H, 2CH$_2$O), 4.22 (s, 4H, 4CH), 6.73 (t, 2H, 2NH). ^{13}C NMR ($CDCl_3$): δ 25.53, 26.46 (**C**H$_2$**C**H$_2$CH$_2$CH$_2$N), 28.58 (**C**H$_2$CH$_2$O), 29.56 (**C**H$_2$CH$_2$N), 39.08 (**C**H$_2$N), 59.67 (CH$_3$OCHCOO), 60.67 (**C**H$_3$OCHCON), 65.20 (CH$_2$O), 81.20 (**C**HCOO), 82.35 (**C**HCON), 169.28 (COO), 169.36 (COON). Anal. Calcd for $C_{24}H_{42}N_2O_{10}\cdot H_2O$: C, 53.72; H, 8.26; N, 5.22. Found: C, 53.99; H, 8.06; N, 5.24.

Syndioregic Poly(succinester amide) (*s*-PEAS6). To a solution of bis(6-aminohexyl) di-*O*-methyl succinate di(*p*-toluenesulfonate) and bis(pentachlorophenyl) succinate (0.38 mmol of each) in *N*-methylpyrrolidone (NMP) (0.35 mL) at 37 °C was added triethylamine (0.9 mmol) dropwise. The mixture was left under stirring for 7 days and cooled to room temperature, and the polymer precipitated from there upon addition of 2-propanol. The polymer was filtered, washed with ether, and dried under vacuum. Yield: 74%. IR (pure film): 3311 (amide A), 3109 (amide B), 2940, 2864, 1720 (COO), 1686, 1638 (amide I), 1552 (amide II), 1439, 1362, 1209, 1181, 1138, 802, 724 cm^{-1}. ^{1}H NMR ($CDCl_3$:TFA): δ 1.39 (m, 8H, 2C**H**$_2$C**H**$_2$CH$_2$CH$_2$N), 1.69 (m, 4H 2C**H**$_2$CH$_2$N), 1.71 (m, 4H, 2C**H**$_2$CH$_2$O), 2.78 (s, 4H, 2CH$_2$CON), 2.88 (s, 4H, 2CH$_2$COO), 3.41 (m, 4H, 2CH$_2$N), 4.19 (t, 4H, 2CH$_2$O), 8.04(br, 2H, 2NH). ^{13}C NMR ($CDCl_3$:TFA): δ 25.34, 26.32 (**C**H$_2$**C**H$_2$CH$_2$CH$_2$O), 28.10 (**C**H$_2$-

CH_2O, **C**H_2CH_2N), 29.43 (CH_2CO), 42.24 (CH_2N), 67.15 (CH_2O), 176.55 (COO), 176.72 (CON).

Isoregic Poly(tartarester amide)s. General Procedure. To a stirred solution of the corresponding compound **VII** (1 mmol) in *N*-methylpyrrolidone was added triethylamine (1.5 mmol) dropwise. The mixture was left under stirring for a period of 3 days and then heated at 70 °C for 3 h. After cooling to room temperature, the reaction mixture was diluted with $CHCl_3$, and the polymer precipitated upon addition of 2-propanol. The polymer was filtered, washed with ether, and dried under vacuum.

***i*-PEAT5.** Yield: 68%. $[\alpha]^{23}_D$: +68.56° (*c* 0.92, in $CHCl_3$). IR (film from $CHCl_3$): 3326 (amide A), 3067 (amide B), 2934, 2864, 2834, 1752 (COO), 1668 (amide I), 1539 (amide II), 1457, 1350, 1261, 1192, 1144, 1101, 1022, 871 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.45 (m, 2H, C**H**$_2$CH$_2$CH$_2$N), 1.55 (m, 2H, C**H**$_2$-CH$_2$N), 1.74 (m, 2H, C**H**$_2$CH$_2$O), 3.24 (m, 2H, CH$_2$N), 3.41 (s, 3H, C**H**$_3$OCHCON), 3.44 (s, 3H, C**H**$_3$OCHCOO), 4.10 (d, 1H, C**H**CON), 4.21 (m, 2H, CH$_2$O), 4.23 (d, 1H, C**H**COO), 6.66 (br, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 23.26 (**C**H$_2$CH$_2$CH$_2$N), 28.20 (**C**H$_2$CH$_2$O), 29.00 (**C**H$_2$CH$_2$N), 38.79 (CH$_2$N), 59.80 (CH$_3$-OCHCOO), 60.13 (**C**H$_3$OCHCON), 65.10 (CH$_2$O), 80.41 (**C**H-COO), 83.08 (**C**HCON), 168.65 (COO), 169.10 (CON). Anal. Calcd for $C_{11}H_{19}NO_5 \cdot {}^1/_2H_2O$: C, 51.96; H, 7.93. N, 5.51. Found: C, 52.01; H, 7.73; N, 5.58.

***i*-PEAT6**. Yield: 75%. $[\alpha]^{23}_D$: +78.29° (*c* 0.76, in $CHCl_3$). IR (film from $CHCl_3$): 3305 (amide A), 3065 (amide B), 2988, 2933, 2859, 2833, 1753 (COO), 1659 (amide I), 1535 (amide II), 1459, 1262, 1195, 1146, 1102 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.39 (m, 4H, C**H**$_2$C**H**$_2$CH$_2$CH$_2$N), 1.53 (m, 2H, C**H**$_2$CH$_2$N), 1.69 (m, 2H, C**H**$_2$CH$_2$O), 3.20 (m, 2H, **H**CHN), 3.38 (m, 2H, HC**H**N), 3.41 (s, 3H, C**H**$_3$OCHCON), 3.44 (s, 3H, C**H**$_3$CHCOO), 4.10 (d, 1H, C**H**CON), 4.21, (m, 2H, CH$_2$O), 4.24 (d, 1H, C**H**COO), 6.65 (m, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 25.54, 26.28 (**C**H$_2$**C**H$_2$-CH$_2$CH$_2$N), 28.52 (**C**H$_2$CH$_2$O), 29.40 (**C**H$_2$CH$_2$N), 38.92 (CH$_2$N), 59.81 (CH$_3$OCHCOO), 60.11 (**C**H$_3$CHCON), 65.27 (CH$_2$O), 80.38 (**C**HCOO), 83.08 (**C**HCON), 168.63 (COO), 169.89 (CON). Anal. Calcd for $C_{12}H_{21}NO_5 \cdot {}^1/_2H_2O$: C, 54.63; H, 8.21; N, 5.31. Found: C, 54.61; H, 8.15; N, 5.34.

***i*-PEAT11.** Yield: 63%. $[\alpha]^{23}_D$: +51.41 (*c* 0.88, in $CHCl_3$). IR (film from $CHCl_3$): 3324 (amide A), 3061 (amide B), 2925, 2854, 1756 (COO), 1731, 1668 (amide I), 1532 (amide II), 1465, 1260, 1192, 1144, 1102, 1022, 753 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.27 (s, 14H, (C**H**$_2$)$_7$CH$_2$CH$_2$N), 1.51 (m, 2H, C**H**$_2$CH$_2$N), 1.68 (m, 2H, C**H**$_2$CH$_2$O), 3.23 (m, 2H, CH$_2$N), 3.41 (s, 3H, C**H**$_3$-OCHCON), 3.45 (s, 3H, C**H**$_3$CHCOO), 4.10 (s, 1H, C**H**CON), 4.20, (br, 2H, CH$_2$O), 4.23 (s, 1H, C**H**COO), 6.63 (br, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 25.85−29.47 (**C**H$_2$)$_9$CH$_2$N), 39.10 (CH$_2$N), 59.78 (CH$_3$OCHCOO), 60.03 (**C**H$_3$CHCON), 65.46 (CH$_2$O), 83.12 (**C**HCON), 80.38 (**C**HCOO), 168.60 (COO), 169.96 (CON). Anal. Calcd for $C_{17}H_{31}NO_5$: C, 61.98; H, 9.48; N, 4.25. Found: C, 60.76; H, 9.36; N, 4.24

Isoregic Poly(succinester amide) (*i*-PEAS6). To a solution of the corresponding compound **VII** (n = 6, R = H) (0.5 mmol) in *N*-methylpyrrolidone (0.5 mL) at room temperature and under a nitrogen atmosphere was added triethylamine (1.1 mmol) dropwise. The mixture was left under stirring at 38−40 °C for 7 days and cooled to room temperature, and the polymer precipitated upon addition of 2-propanol. The polymer was filtrated, washed with ether, and dried under vacuum. Yield: 83%. IR (film from $CHCl_3$−HCOOH): 3314 (amide A), 3086 (amide B), 2935, 2862, 1753 (COO), 1643 (amide I), 1609, 1551 (amide II), 1427, 1348, 1272, 1177, 1067, 963, cm^{-1}. ^1H NMR ($CDCl_3$:HCOOH): δ 1.33 (s, 4H, C**H**$_2$C**H**$_2$CH$_2$CH$_2$N), 1.50 (m, 2H, C**H**$_2$CH$_2$N), 1.62 (m, 2H, C**H**$_2$CH$_2$O), 2.58 (t, 2H, C**H**$_2$-CON), 2.68 (t, 2H, C**H**$_2$COO), 3.22 (m, 2H, C**H**$_2$NH), 4.09 (t, 2H, CH$_2$O). ^{13}C NMR ($CDCl_3$:HCOOH): δ 25.08, 25.99 (**C**H$_2$**C**H$_2$-CH$_2$CH$_2$N), 27.95 (**C**H$_2$COO), 28.45 (**C**H$_2$CH$_2$O), 29.53 (**C**H$_2$-CH$_2$N), 30.50 (**C**H$_2$CON) 39.93 (CH$_2$N), 65.42 (CH$_2$O), 174.06 (COO), 174.27 (CON). Anal. Calcd for $C_{10}H_{17}NO_3 \cdot {}^1/_2H_2O$: C, 57.67; H, 8.71; N, 6.72. Found: C, 57.49; H, 8.32; N, 6.68.

Results and Discussion

Synthesis. The routes of synthesis followed for the preparation of *syndioregic* and *isoregic* poly(ester amide)s

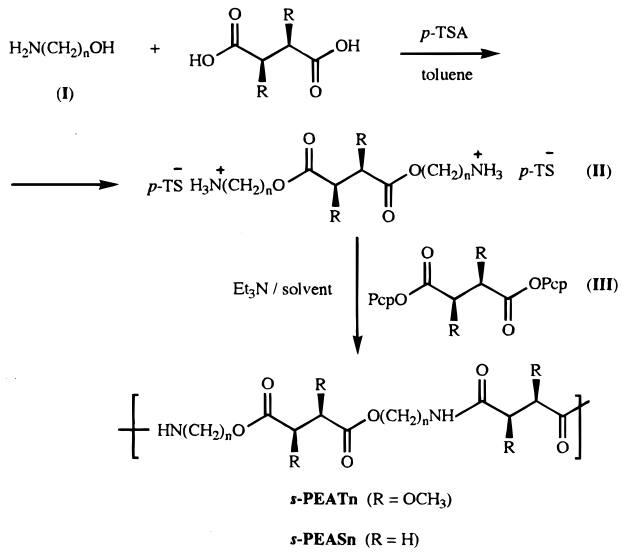


Figure 1. Scheme of synthesis leading to *syndioregic* poly(ester amide)s.

are depicted in Figures 1 and 2, respectively, where the following abbreviations have been used: *p*-TSA = *p*-toluenesulfonic acid; Pcp = pentachlorophenyl; BOC = *tert*-butoxycarbonyl; DCCI = dicyclohexylcarbodiimide; r.t. = room temperature. The synthesis of these poly(tartarester amide)s relies on the same basic principles guiding the preparation of poly(tartaramide)s investigated previously by us: hydroxyl side groups were protected to avoid secondary reactions causing polymer branching or cross-linking, and the carboxylic group was activated toward polycondensation as pentachlorophenyl ester to make unnecessary the application of severe reaction conditions. Relevant polymerization data for all the poly(tartarester amide)s prepared in this work are shown in Table 1.

The reaction pathway leading to poly(tartarester amide)s *s*-PEAT*n* is relatively simple and rendered polymers with higher molecular weights in slightly higher yields than in the case of *isoregic* isomers. Intermediate compounds and monomers were obtained without special difficulties. Polymerization took place in a homogeneous phase with the resulting polymer remaining dissolved in the reaction mixture. Since the amino alcohol unit is alternating in orientation along the chain, the structural repeating unit comprises two chemical repeating formulas. On the other hand, since the two comonomers (compounds **II** and **III**) are disymmetric, a unique spatial arrangement is adopted by the tartaric unit in the polymer whichever is the orientation with which the monomers enter in the growing chain. As a result, the polymers yielded by this method are *syndioregic* and *diisotactic;* the two pairs of stereocenters contained in the repeating unit are in the same spatial configuration.

The synthesis of *isoregic* poly(tartarester amide)s *i*-PEAT*n* and *i*-PEAS*n* was feasible by polycondensation of amino acid monomers bearing the ester group as part of the main chain. The preparation of these compounds (**VII**) is carried out by a four-step procedure that relies on formation of the amino ester tartaric acid (**V**) by selective condensation of 1 mol of di-*O*-methyl-L-tartaric anhydride with 1 mol of the N-blocked amino alcohol (**IV**). Prior to polycondensation, the amino ester acid is activated as pentachlorophenyl ester (**VI**) in the usual manner. It should be said that although a number of

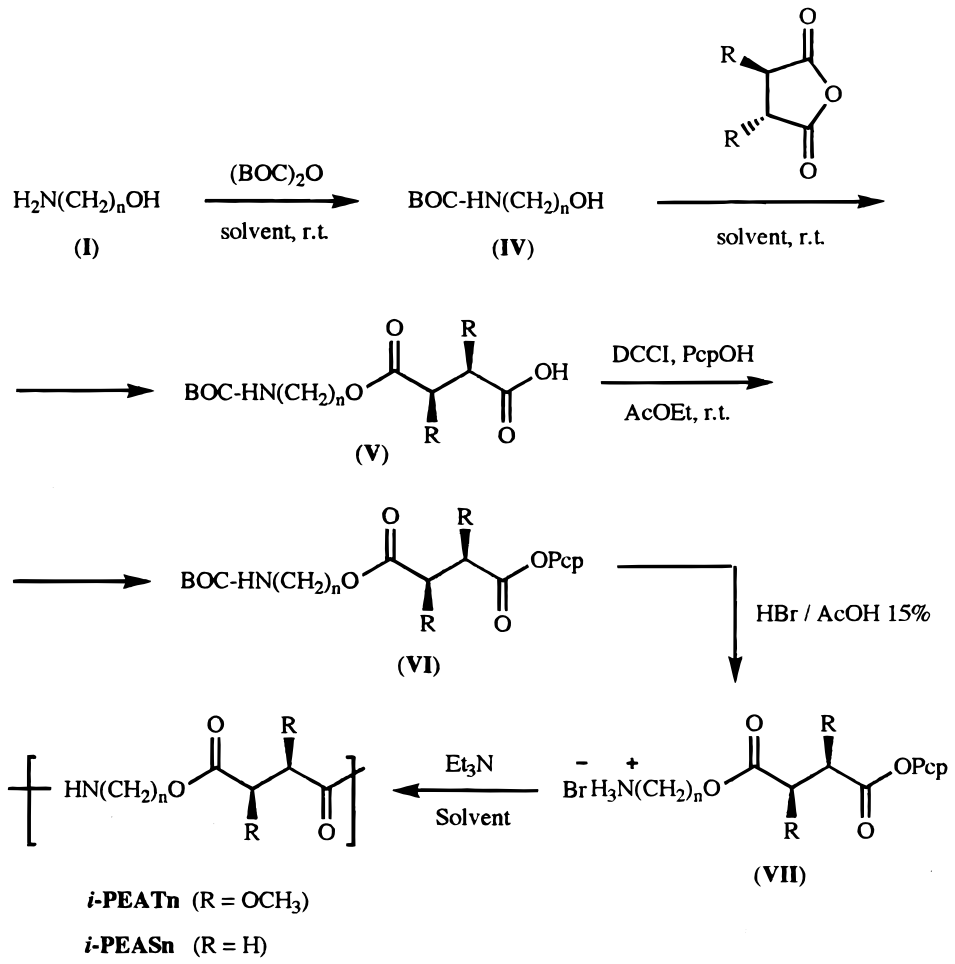


Figure 2. Scheme of synthesis leading to *isoregic* poly(ester amide)s.

Table 1. Synthesis Results

polymer[a]	solvent	[M][b]	Et_3N/M	yield (%)	$[\eta]$[c] (dL/g)	M_n[d]	M_w[d]
s-PEAT5	$CHCl_3$	0.25	2.7	65	0.94	53 000	98 000
s-PEAT6	$CHCl_3$	0.25	2.7	78	0.88	19 500	64 000
i-PEAT5	$CHCl_3$	4.22	1.5	60	0.35	7 600	9 500
i-PEAT6	NMP	1.10	1.5	60	0.74	22 900	44 500
i-PEAT11	NMP	1.23	2.4	63	0.60	16 200	32 000
s-PEAS6	NMP	1.08	2.4	75	0.45		3 200
i-PEAS6	NMP	1.08	2.4	75	1.12		32 000

[a]For explanation of acronyms see Scheme 1. [b]Monomer concentration in mol L^{-1}. [c]Intrinsic viscosity measured in dichloroacetic acid at 25 °C. [d]Molecular weights determined by SEC using chloroform:*o*-chlorophenol (95:5) as mobile phase.

reactions are involved in this synthesis, the method turns out to be fairly reliable since protecting and deprotecting steps proceed without difficulty giving usually high yields. Polymerization of compounds **VII** was performed in solution at room temperature to afford polymers *i*-PEAT*n* with molecular weights between 10 000 and 45 000 and polydispersities between 1.25 and 2. The polymers are alternating poly(ester amide)s with a structural repeating unit coinciding with the repeating chemical formula. Since all the amino alcohol units are pointing to the same direction and the tartaric unit has the *threo* configuration, the polymers resulting from this synthesis are *isoregic* and *isotactic*.

All the poly(ester amide)s were duly characterized. Elemental analyses were in agreement with the expected chemical compositions provided that an amount of water between 5 and 10% (w/w) is assumed to be bound to the polymers. This is consistent with all observations that have been reported so far on tartaric acid-based polyamides and poly(ester amide)s.[6,9] The fact that the content in water increases with the density of amide or ester groups in the chain does make sense since the hygroscopicity of the polymer increases in the same direction. Both IR and ^1H and ^{13}C NMR spectra displayed all the characteristic bands and signals anticipated for the constitution of the poly(ester amide)s with clear identification of amide and ester groups. No sign of racemization, which would be reflected in the appearance of additional signals arising from *meso* units, was detected in either ^1H or ^{13}C NMR spectra. Furthermore, significant differences in the CH_2N and CH_2O signals of *isotactic* and *syndiotactic* polymers consistent with their respective sequences were observed in the ^1H NMR spectra. A detailed account of the spectral data of all new compounds synthesized in this work is given in the Experimental Section.

Hygroscopicity and Solubility. The poly(ester amide)s PEAT's were obtained as white or slightly yellowish powders displaying a tendency to uptake moisture spontaneously from the environment that varies with their constitution. Hygroscopicities of the polymers were comparatively quantified by measuring the sorption of water as a function of the exposure time in a 100% relative humidity atmosphere at 20 °C. The obtained results are presented in the curves plotted in Figure 3. A steady increase in water sorption with time is observed for all cases within the first 24 h of exposure to reach a more or less stationary maximum after 2−3

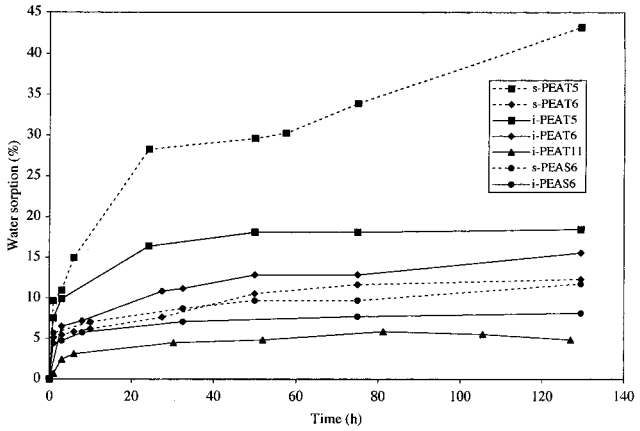


Figure 3. Water sorption in poly(ester amide)s as a function of exposure time.

days. The plot shows that hygroscopicity increases with the content of the polymer in amide groups and with the presence of tartaric units in the poly(ester amide). The exceptionally high response found for *s*-PEAT5 is doubtless due to the amorphous nature of this polymer as will be discussed below. Conversely, comparison of data for *isoregic* and *syndioregic* polymers for either pair PEAS6 or PEAT6 does not permit to draw any definite conclusion about the effect exerted by chain regicity on this property.

Poly(tartarester amide)s are more sensitive to solvents than conventional polyamides whereas poly(succinester amide)s display an intermediate behavior. An overview of the solubility pattern of the poly(ester amide)s investigated in this work is given in Table 2. Despite their high hydrophilicity, they are not dissolved by water except for the case of *s*-PEAT5 which appears to be attacked in warm. As expected, they all are soluble in hydrogen-bond-breaking solvents such as formic acid or trifluoroacetic acids and insoluble in nonpolar organic solvents such as ethyl acetate or ethers. The behavior of poly(tartarester amide)s in chloroform deserves some additional comment. At difference with poly(succinester amide)s and other linear poly(ester amide)s described in the literature,[8] stereoregular poly(tartarester amide) are known to be readily soluble in this solvent. This is a remarkable property that seems to arise from the presence of the tartaric acid in the poly(ester amide) chain and that has been associated with the ability of these polymers to adopt ordered conformations in solution.

Optical, Thermal, and Mechanical Properties. Data relative to these properties for the whole set of poly(ester amide)s here investigated are comparatively shown in Table 3. As could be ascertained from NMR spectra, the initial L-configuration of tartaric acid was retained throughout the whole synthesis process. This is further supported by the high optical activity exhibited by the polymers in chloroform solution where specific rotations ranging from about 50° to 90° were measured. Higher [α] values were found for the *syndioregic* polymers than for their *isoregic* isomers, and in both series they were observed to decrease with the increase of *n*. It should be noticed however that specific optical activities displayed by poly(tartarester amide)s are significantly lower than those measured for poly(tartaramide)s with similar densities of chiral centers in the repeating unit, which suggests differences in conformation between the two classes of polymers.

Thermal analysis by DSC of cast films revealed the occurrence of melting−crystallization transitions for all the polymers except *s*-PEAT5. Representative thermograms at both heating and cooling are shown in Figure 4 for the case of *i*-PEAT6 and *s*-PEAT6 compared to *i*-PEAS6. At the first heating poly(tartarester amide)s produced broad melting endotherms with associated low enthalpies sometimes preceded by an exotherm characteristic of cold crystallization. After annealing at temperatures near the melting point, well-defined fusion peaks were observed with higher intensity. Crystallization from the melt was found to proceed with difficulty as could be revealed by the bimodal broad endotherm present in the second heating traces. Conversely, samples of poly(succinester amide)s coming directly from synthesis exhibited rather stronger melting peaks that are reproduced with higher intensity after crystallization from the melt. These results illustrate how chain mobility becomes hindered by the presence of lateral methoxy groups, an effect that appears to be more pronounced in the molten state. T_m and T_g data for all the poly(ester amide)s investigated in this work are compared in Table 3. It is there seen that melting temperatures of *syndioregic* poly(ester amide)s are invariably lower than those of their *isoregic* isomers and that, according to predictions, they decrease as the length of the polymethylene chain increases. It is also observed that insertion of methoxy groups entails a decay about 20 °C in the melting points, a decrement not so large as one could initially expect. Glass transitions temperatures were found to display a similar trend; they could be observed with clarity on the first heating traces of poly(tartarester amide)s and on the rapid cooling traces of poly(succinester amide)s. Differences in the T_g values between the two classes of polymers are small.

A preliminary evaluation of the mechanical behavior of poly(tartarester amide)s was obtained by measuring the tensile properties of *i*-PEAT6 and *s*-PEAT6 as representative members. The measured mechanical parameters are given in Table 3. The profile displayed by these samples fit into the characteristic pattern expected for a flexible semicrystalline polymer with an elastic moduli E of 600−700 MPa and elongation at breaks ϵ between 10 and 20%. Large variations in the stress−strain behavior were detected, however, not only between samples of the two polymers prepared by the same technique but also between two specimens of the same polymer crystallized under different conditions. Such differences are attributable to differences in either texture or crystallinity. It has been shown that poly(tartaramide)s in the dried state may attain elastic moduli and stress at yields of about 1700 and 60 MPa, respectively, which are not far from those exhibited by conventional nylons.[16] It has been reported that such values fall down to 1300 and 50 MPa, respectively, when 3% of amide groups were replaced by ester groups. The magnitude of the fall in the elastic moduli observed for poly(tartarester amide)s PEAT's is therefore in the range that should be expected for a poly(tartaramide) with 50% of its amide groups replaced by ester groups. As a consequence, the apparent mechanical behavior changes from being rigid and strong to flexible and weak. Further work addressed to examine the effect of thermal treatments on the mechanical strength is required for a conclusive evaluation of the tensile properties of these poly(tartarester amide)s.

Table 2. Compared Qualitative Solubilities of Poly(ester amide)s[a]

solvent	*s*-PEAT5	*s*-PEAT6	*i*-PEAT5	*i*-PEAT6	*i*-PEAT11	*s*-PEAS6	*i*-PEAS6
water	+	−	−	−	−	−	−
diethyl ether	−	−	−	−	−	−	−
ethyl acetate	−	−	−	−	+	−	−
ethanol	+	±	+	+	+	+	+
$CHCl_3$	++	++	++	++	++	+	−
NMP	+	+	++	+	+	+	+
formic acid	++	++	++	++	++	++	++
TFE	++	++	++	++	++	++	++

[a] (−) Insoluble, (±) slightly swollen, (+) soluble on warning, (++) soluble at room temperature.

Table 3. Properties and X-ray Data of Poly(ester amide)s

		thermal data[b]		mechanical parameters[c]					
polymer	$[\alpha]_D$[a]	T_g (°C)	T_m (°C)	E (MPa)	σ_{max} (MPa)	d_{hkl} (nm)[d]			
s-PEAT5	+87.9	23							
s-PEAT6	+87.0	24	134	700	23	1.0 (s)	0.61 (s)	0.45 (m)	0.37 (w)
i-PEAT5 5	+68.6	30	99			1.0 (s)	0.59 (m)	0.44 (m)	0.37 (w)
i-PEAT6	+78.3	26	151	600	15	1.0 (s)	0.70 (m)	0.47 (m)	0.37 (w)
i-PEAT11	+51.4	12	109			1.4 (s)	0.59 (m)	0.44 (m)	0.37 (w)
s-PEAS6		48	157			1.3 (s)		0.40 (m)	0.37 (w)
i-PEAS6		32	166			1.3 (s)		0.40 (m)	0.37 (w)

[a]Measured in chloroform at 25 °C. [b]Measured by DSC. [c]Measured in stress−strain tests. E = elastic modulus; σ_{max} = stress at yield. [d]Intensities visually estimated and denoted as s = strong, m = medium, and w = weak.

Crystalline Structure. Evaporation of solutions of poly(ester amide)s in a variety of solvents as formic acid, chloroform, or trifluoroethanol produced spherulitic films as those shown in Figure 5. Morphological features, sizes, and signs of spherulites were found to be highly dependent on both evaporation conditions and polymer constitution. In any case they prove the crystalline nature of all the poly(ester amide)s investigated in the present work with the only exception of *s*-PEAT5.

X-ray diffraction results were consistent with DSC and optical microscopy observations described above. Well-defined Debye−Scherrer diffraction patterns of the type shown in Figure 6 were usually recorded. *s*-PEAT-5 was unique in producing a diffuse pattern consisting of an halo characteristic of the amorphous state. Bragg spacings measured for crystalline compounds with indication of their visually estimated intensities are listed in Table 3. It should be noticed that similar diffraction patterns are produced by poly(succinester amide)s *s*-PEAS6 and *i*-PEAS6. They contain the two spacings at ∼0.40 and ∼0.37 nm related to the side-by-side packing of the chains and the long spacing at 1.3 nm associated with the axial repeat of the structure. It can be concluded therefore that the crystalline structure is the same for both poly(ester amide)s despite their differences in regicity and that such structure is likely not far from the well-known layered model of nylons with the chain in a slightly contracted conformation due to the presence of the ester groups.

The poly(tartarester amide)s adopt crystal packings with chains spaced out by the side methoxy groups and with a contraction in the axial repeat considerably higher than in the case of PEAS6's. The structure should be similar to that of poly(tartaramide)s which is described as a stacking of hydrogen-bonded sheets made of chains with the tartaric unit in the gauche arrangement.[17] The higher chain contraction observed in the present case is thought to be caused by the torsion of the ester group. It should be stressed that similar structures are adopted by *i*-PEAT*n* with odd values of *n*, i.e., *i*-PEAT5 and *i*-PEAT11. The only difference observed in the X-ray diffraction patterns of these two polymers concerns the long spacing that appears at 1.0

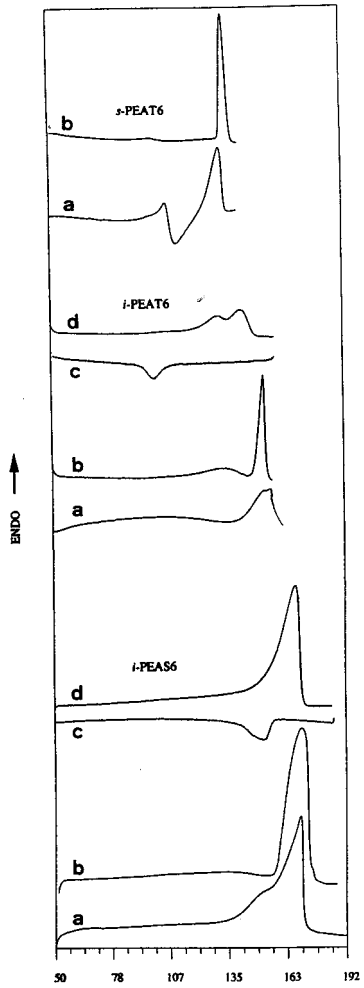


Figure 4. DSC of poly(ester amide)s. Top: heating traces of *s*-PEAT6 before (a) and after (b) annealing at 127 °C for 30 min. Middle: heating traces of *i*-PEAT6 before (a) and after (b) annealing at 143 °C for 2 h (b), cooling trace after melting (c), and second heating trace (d). Botton: traces of *i*-PEAS6 recorded like for *i*-PEAT6 (annealing temperature was 150 °C in this case).

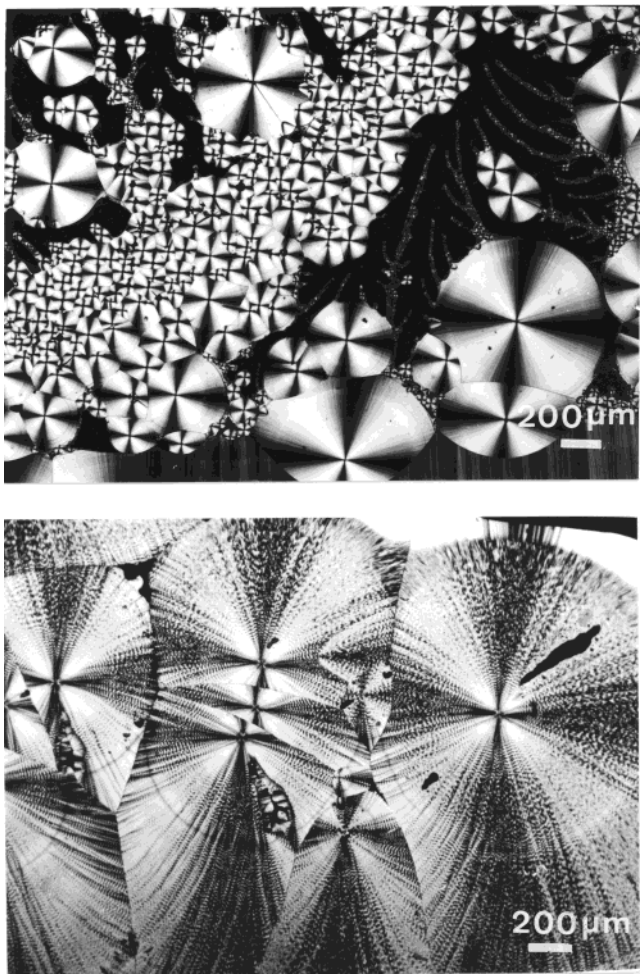


Figure 5. Spherulitic films of poly(tartarester amide)s: (a) *s*-PEAT6; (b) *i*-PEAT11. The scale bar represents 0.2 mm for both cases.

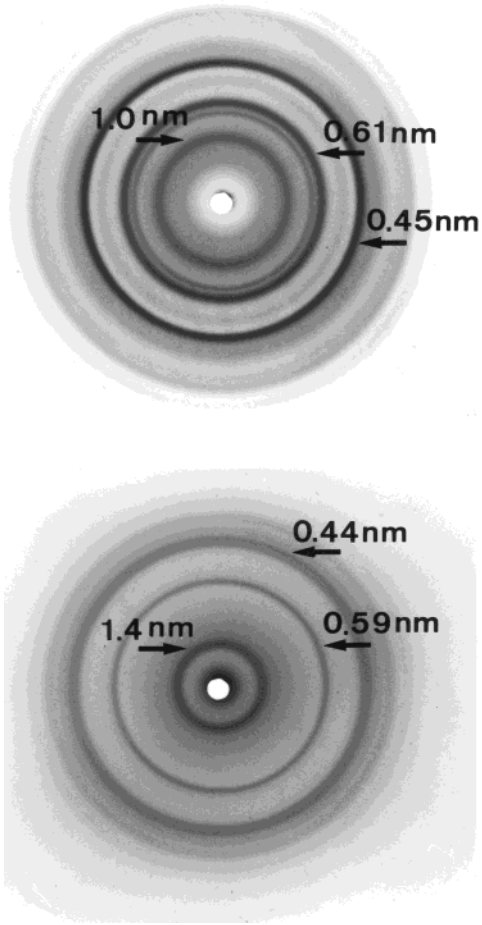


Figure 6. X-ray diffraction patterns of poly(tartarester amide)s: (a) *s*-PEAT6; (b) *i*-PEAT11.

and 1.4 nm, respectively. Since the ratio of d_{hkl} spacing to the length of the fully extended chemical residue is similar for the two polymers, they are expected to assume the same conformation. On the contrary, significant deviations were observed for *i*-PEAT6, suggesting the occurrence of a different crystal structure for even-numbered *isoregic* poly(tartarester amide)s. Structural differences of this type were also found between odd and even members in the poly(tartaramide) series.[17]

Thermal Degradation. The sensitivity of poly(ester amide)s to heating was examined by TGA using two types of essays. First, weight losses as a function of time were measured for samples held at a constant temperature 40−50 °C above their respective melting points. Second, weight losses were measured as a function of temperature for samples heated at a rate of 10 °C min^{-1} up to temperatures near to 500 °C. TGA data for the whole set of compounds are compared in Table 4. Results obtained from isothermal experiments indicated a good thermal stability of poly(ester amide)s in general with small weight losses (<6%) taking place after 10 min of heating. Loss weight−temperature TGA curves revealed that decomposition happens in two stages. In the first stage a sudden fall takes place within the temperature range 250−350 °C with weight losses between 40 and 95% of the initial sample. The second decomposition stage entails much lower weight losses except in the case of *i*-PEAT11 where decomposition occurs in the two stages to a similar extent. In all cases

Table 4. Thermal Decomposition Parameters

	I[a]		II[a]		isothermal[b]	
polymer	T_d^I (°C)	ΔW (%)	T_d^{II} (°C)	ΔW (%)	T	ΔW (%)
s-PEAT5	338	77	445	10	190	1
s-PEAT6	350	72	445	17	180	1
i-PEAT5	270	75	445	14	150	0.4
i-PEAT6	273	74	445	17	180	6
i-PEAT11	252	41	473	47	160	2
s-PEAS6	317	50	359	43	190	2
i-PEAS6	301	95			180	0.5

[a] Decomposition temperatures T_d and weight losses ΔW (% of the initial weight) for steps I and II of thermal degradation. [b] Weight losses for isothermal degradation after 10 min of treatment at the given temperatures T.

the sample weight remaining at the end of the treatment is only about 10% of the initial value.

An estimation of the relative stability of compounds can be inferred by direct comparison of weight losses taking place on samples heated at the same temperature. Thus, *i*-PEAT6 appeared to be much less stable than *s*-PEAT6 since a weight loss 6 times higher took place for the former when both polymers were heated at 180 °C for 10 min. Furthermore, T_d^0 and T_d^1 were found to be considerably lower for the *isoregic* isomer. This applies also to the other two pairs (PEAT5 and PEAS6) that can be compared. With the purpose of disclosing whether polymer regicity could be the reason for such differences in thermal stability, the material remaining after the first decomposition step of *s*-PEAT6 and *i*-PEAT6 was analyzed by infrared and NMR

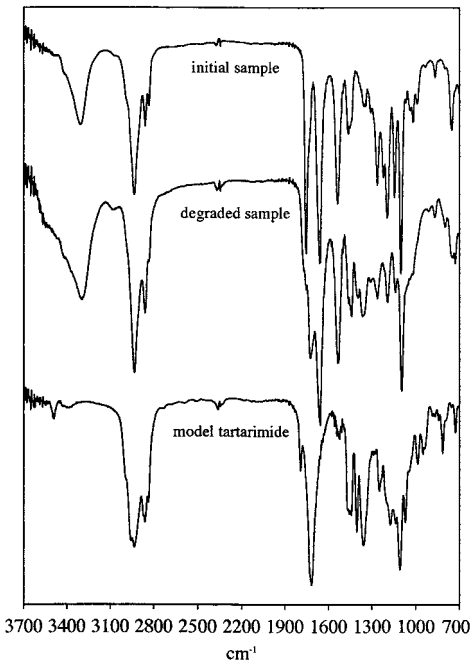


Figure 7. Infrared spectra of *i*-PEAS6 before (top) and after (middle) thermal degradation. Botton: spectrum of the model compound 2,3-di-*O*-methyl-L-tartarimide.

spectroscopies. The infrared spectra of *i*-PEAT6 recorded before and after heating at 273 °C are shown in Figure 7 where the spectrum of the model compound di-*O*-methyl-L-tartarimide has been included for reference. The presence of the bands at 1800 and 1725 cm^{-1} and the diminished peak of ester at 1750 cm^{-1} observed in the spectrum of the degraded sample reveal that decomposition of the poly(ester amide) evolved through formation of tartarimide units. This interpretation is further supported by the appearance in the ^1H NMR spectra of a signal at 3.7 ppm arising from the methoxy groups attached to the tartarimide ring. Similar results were obtained from the analysis of the residue left by *s*-PEAT6 after heating at 350 °C. A mechanism based on imide formation due to the intramolecular nucleophilic attack of the amidic nitrogen to the neighboring ester CO was reported some years ago to account for the pyrolysis of a series of nylon 3 derivatives bearing a carboxylate side group.[18] It should be noted that an imidation process of such a type will be favored in the *isoregic* polyamide since it can happen via formation of a stable five-membered tartarimide ring. Since this mechanism appears to be incompatible with a *syndioregic* microstructure, the lower thermal stability displayed by *i*-PEAT*n* when compared to *s*-PEAT*n* may be convincingly explained in terms of differences in regicity. Similar arguments are applicable of course to account for the differences observed between *i*-PEAS6 and *s*-PEAS6 with succinimide being the ring generated in this case.

Concluding Remarks

Modification of L-tartaric acid by well-known peptide synthesis techniques combined with the active ester polycondensation method has made possible the preparation of *syndioregic* and *isoregic* stereoregular poly(tartarester amide)s containing equal amounts of ester and amide groups. The same methodology has been applied to the preparation of poly(ester amide)s from succinic acid. The tartaric acid based poly(ester amide)s display an enhancement in both hydrophilicity and solubility when compared with homologous poly(ester amide)s bearing no attached side groups. They show optical activity and are in general highly crystalline. Although both regicity and the presence of methoxy side groups were found to exert a significant influence on crystal structure, thermal transitions are not largely affected by such features. Thermal degradation of poly(ester amide)s has proven to happen through imide cyclization, a mechanism that is favored by the *isoregic* nature of the poly(ester amide) chain.

Acknowledgment. Financial support for this work given by CICYT (Grant MAT-96-1181-CO3-03) is gratefully acknowledged. I. Villuendas thanks the Ministry of Education and Culture of Spain for the award of a FPI scholarship that allowed her to receive her Ph.D.

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MA991050V