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Stereocopolyamides Derived from 2,3-Di-*O*-methyl-D- and -L-tartaric Acids and Hexamethylenediamine. 1. Synthesis, Characterization, and Compared Properties

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ABSTRACT: Poly(hexamethylene-2,3-di-*O*-methyl-D,L-tartaramide)s [P6DM(D,L)T], with enantiomeric D/L ratios ranging from 1:9 to 1:1 and weight average molecular weights up to ~80 000, were obtained by the active ester polycondensation method. The microstructure of these stereocopolyamides was investigated by ^{1}H and ^{13}C NMR using as model compound a copolytartaramide the racemic composition of which was ensured by chemical synthesis. No evidence was observed from these studies which led to the interpretation that the microstructure of P6DM(D,L)T was other than that consisting of a statistical distribution of D and L configurations. All the copolyamides were found to be highly crystalline with melting points close to that of the optically pure polymer, which is about 230 °C, and T_g's decreasing from 106 to 68 °C as the D/L ratio increased from 0 to 1. Powder X-ray diffraction indicated that a crystal structure very similar to that described for the pure enantiomorph, poly(hexamethylene-2,3-di-*O*-methyl-L-tartaramide) (P6DMLT), seems to be adopted by all these copolyamides. It was concluded that the replacement of L units by D units is feasible over the whole range of enantiomeric compositions without much distortion of the crystal lattice and properties.

Introduction

Stereoregular polyamides derived from 2,3-di-*O*-methyl-L-tartaric acid and aliphatic diamines, referred in earlier works as polytartaramides (P*n*DMLT,[1,2] where *n* denotes the number of methylenes contained in the diamine), are highly crystalline polymers displaying notable optical activity. Moreover, they exhibit an enhanced hydrophilicity and hydrolytic degradability when compared to conventional nylons whereas their thermal and mechanical properties do not appear to be seriously deteriorated.[3,4] Such a desirable combination of properties makes these polytartaramides highly interesting not only for academic studies but also from a technical point of view. Potential applications in the biomedical field have been pointed out for these polyamides.[4]

Among P*n*DMLT, poly(hexamethylene-2,3-di-*O*-methyl-L-tartaramide) (P6DMLT) has been object of preferential attention because of its outstanding properties and reliable preparation. This polytartaramide, which can be envisaged as a modified nylon 6,4, is obtained by condensation of 1,6-hexanediamine activated as an *N*,*N*′-trimethylsilyl derivative with bis(pentachlorophenyl)-2,3-di-*O*-methyl-L-tartrate in a chloroform solution.[1] The polymer is soluble in chloroform and shows strain−stress mechanical moduli comparable to nylon 6.[4] It melts reversibly at 226 °C and its T_g is around 106 °C. P6DMLT films absorb about 10% of water under 100% relative humidity and degrade slowly but significantly by water at pH 7.4 and 37 °C.[3] Nevertheless, hydrophilicity and degradability displayed by this polymer are lower than expected for a nylon 6,4 bearing two methoxy groups in the repeating unit. Crystallinity is thought to be the major factor limiting water uptake and degradation. P6DMLT shows a strong tendency to form highly crystalline powders, films, and fibers. It crystallizes in a folded conformation, implying a shortening of about 2Å per chemical repeating unit with respect to that would be a fully extended conformation. The crystal lattice is triclinic with all hydrogen bonds intermolecularly set and aligned along a unique direction within the crystal.[5]

The stereoregularity of a polyamide chain of AABB-type as is the case with P6DMLT, relies upon the existence of C_2 symmetry in the monomers from which it is generated; otherwise regioisomerism will likely occur, giving rise to atactic polyamides with the chiral building blocks randomly oriented along the polymer chain (Figure 1). Accordingly, only the optically active forms of tartaric acid will be able to produce stereoregular polytartaramides, which will have *threodiisotactic* configuration. Conversely, the pure *meso* form as well as mixtures of L/D-enantiomers will lead to atactic polymers consisting of irregular sequences of *erythro* or *threo* configurations, respectively.

Copolymerization of mixtures of enantiomers is a method frequently applied to generate stereochemical microheterogeneities in a polymer chain. By these means the crystallinity degree is depressed and related properties may be conveniently modified.[6,7] Whereas the configurational composition of the copolymer is controlled by the enantiomeric ratio of the feed, the chain microtacticity becomes determined by the stereochemistry imposed by the polymerization mechanism. In the absence of stereoselective catalysts and chiral solvents, atactic polymers following Bernouillian statistics are usually obtained;[8] copolymers consisting of stereoregular blocks would be generated under such conditions only if the growing polymer chain assumes a helical conformation able to discriminate between the two antipodes.[9]

In this paper we report on a series of poly(hexamethylene-2,3-di-*O*-methyl-D,L-tartaramide)s, abbreviated

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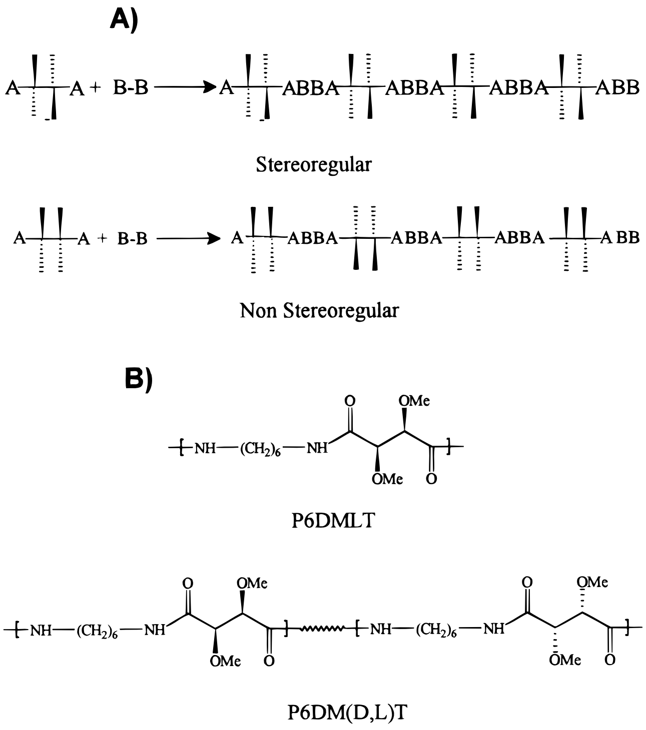


Figure 1. (A) Stereoregularity of polycondensates of AABB-type made from monomers containing two asymmetric centers. (B) Chemical repeating unit for the stereoregular polytartaramide P6DMLT and for the racemic copolyamide P6DM(D,L)T.

P6DM(D,L)T, with D/L ratios varying from 1:9 to 1:1 obtained from mixtures of D- and L-tartaric acids and hexamethylenediamine. The polymers are prepared by polycondensation in solution according to the method developed by Katsarava,[10] which takes advantage of activating the two monomers, the diamine, and the diacid, intervening in the reaction. The microstructure of the resulting copolytartaramides is investigated by NMR with the help of model compounds, and their crystal structure and some of their relevant properties are compared with those exhibited by the optically pure polymer. The main purpose of the study is to evaluate the influence of the stereochemical composition on the pattern of behavior of polytartaramides, particularly on those properties closely related to degradability.

Experimental Section

Materials and Methods. All chemicals were obtained commercially from either Aldrich or Merck. They were of 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 either dichloroacetic or formic acid at 25.0 ± 0.1 °C using an Ubbelhode microviscometer. Gel permeation chromatography (GPC) was conducted on a Waters Associates instrument fitted with a refractive index detector and a set of two Styragel columns of 10^4 and 10^3 Å. Monodisperse polystyrene standards purchased from Waters Millipore were used to create a calibration curve. The polyamides were trifluoroacetylated by treating the samples (5 mg) with a solution of trifluoroacetic anhydride (0.5 mL) in dry chloroform (1 mL) for 12 h. After evaporation to dryness, the trifluoroacetylated samples were dissolved in chloroform to obtain 0.25% (w/v) solutions which were immediately used for injection.

Infrared spectra were recorded from films as either pure liquids or solids on a FT-IR Perkin-Elmer 2000 instrument. ^{1}H and ^{13}C NMR spectra were obtained at room temperature on Bruker AMX-300 and AMX-500 spectrometers. Spectra of monomers and intermediate compounds were registered in pure $CDCl_3$ and D_2O and those of polymers in $CDCl_3$ containing 10% of trifluoroacetic acid at sample concentrations of 1 and 5% (w/v) for ^{1}H and ^{13}C, respectively. Tetramethylsilane (TMS) and 3-(trimethylsilyl)propanesulfonic acid (TSPSA) were used as internal references for $CDCl_3$ and D_2O, respectively. Spectral widths of 3.6 and 6.8 kHz were used for 300.13 and 500.14 MHz ^{1}H NMR spectra with 16K of data points. ^{13}C NMR measurements were made under proton decoupling conditions at 74.48 and 125.77 MHz with spectral widths of 17.86 and 27.8 kHz, respectively, and 32K of data points. For typical ^{1}H NMR and ^{13}C NMR spectra, the number of accumulated scans were 64 and 300 to 1500, respectively.

Optical rotations of polymers were measured on a Perkin-Elmer 141 polarimeter at 23 °C in chloroform solution at polymer concentrations of 0.5−1.0 g dL^{-1}. Thermograms were recorded using either a Perkin-Elmer DSC-4 or a Mettler instrument calibrated with indium. Samples of 3−8 mg were placed under a nitrogen atmosphere and heated at a rate of 10 °C min^{-1} and cooled at different rates over a temperature range from 30 to 260 °C. X-ray diffraction diagrams were obtained with a modified Statton camera using nickel-filtered Cu Kα radiation of wavelength of 1.542 Å and they were calibrated with molybdenum sulfide (d_{002} = 6.147 Å).

For hydrolytic degradation assays, disk samples with a thickness of 0.2 mm and a diameter of 14 mm were die-cut from films which had been prepared by casting from a 4% solution of polymer in chloroform. A 0.1 M Na_2HPO_4/KH_2PO_4 buffer solution of pH 7.4 containing 0.03% of sodium azide was used as incubation medium. Three temperatures, 37, 55, and 70 °C, were tested and the degradation evolution was followed by measuring the changes taking place in both sample weight and viscosity. Only one sample was used for each measurement.

Synthesis of Intermediate Compounds and Monomers. Bis(pentachlorophenyl)-2,3-Di-*O*-methyl-D- and -L-tartrates (I and II) were prepared from D- and L-tartaric acids, respectively, by following the synthetic route which was described in full detail in an earlier work.[1] The procedure involves four reaction steps corresponding to esterification, hydroxyl masking, hydrolysis, and activation. These crystalline compounds are obtained in highly pure form with an overall yield of about 30−40% and have melting points between 180 and 182 °C.

***N,N′*-Bis(trimethylsilyl)-1,6-hexanediamine (III)** was prepared by reaction of 1,6-hexanediamine with trimethylsilyl chloride in a molar ratio 1:2 according to the method developed by Pierce.[11] Specific conditions used in the synthesis of this compound as well as its main characteristics were give elsewhere.[1] *N,N′*-(Bistrimethylsilyl)-1,6-hexanediamine is a volatile compound that can be readily isolated by distillation under vacuum (bp: 80 °C, 0.1 mmHg) but that has to be handled with care because of its extreme sensitivity to water.

Di-*O*-methyl-D- and -L-tartaric anhydrides (IV and V) were obtained in approximately 80% yield by treatment of respective di-*O*-methyl-D- and -L-tartaric acids with acetic anhydride at 80 °C.[12] Mp: 77 °C.

(2*R*,3*R*)-11-Amino-5-aza-2,3-dimethoxy-4-oxoundecanoic Acid (VI). An equimolar mixture of di-*O*-methyl-L-tartaric anhydride (**V**) and 1,6-hexanediamine was dissolved in dry tetrahydrofuran containing a few drops of pyridine under an inert atmosphere. After stirring the clear solution for a few minutes at room temperature, the title compound precipitated as a white hygroscopic solid which was recovered by filtration, washed with tetrahydrofuran and diethyl ether, and crystallized from boiling ethanol. Yield: 80%. Mp: 55 °C. ^{1}H NMR (D_2O): δ 4.31 (d, OCOC*H*, 1H), 4.21 (d, NHCOC*H*, 1H), 3.42 (s, CH_3OCHCOO, 3H), 3.40 (s, CH_3OCHCONH, 3H), 3.28 (m, CONHCH_2, 2H), 2.99 (t, CH_2-NH_2, 2H), 1.66 (m, $CH_2CH_2NH_2$, 2H), 1.55 (m, CONHCH_2CH_2, 2H), 1.40 (m, CONH$CH_2CH_2CH_2CH_2$, 4H). ^{13}C NMR (D_2O): δ 175.94 (*C*ONH), 173.45 (*C*OO), 84.73 (NHCO*C*H), 82.62 (OCO*C*H), 62.45 (CH_3OCHCOO), 61.94 (CH_3OCHCONH), 42.03, 41.54, 30.76, 29.21, 27.95, 27.80 (6CH_2).

(2*R*,3*R*,14*S*,15*S*)-5,12-Diaza-2,3,14,15-tetramethoxy-4,13-dioxohexadecanedioic Acid (VII). To a solution of compound **VI** (2g, 7.2 mmol) in pyridine (3 mL) placed in a flask

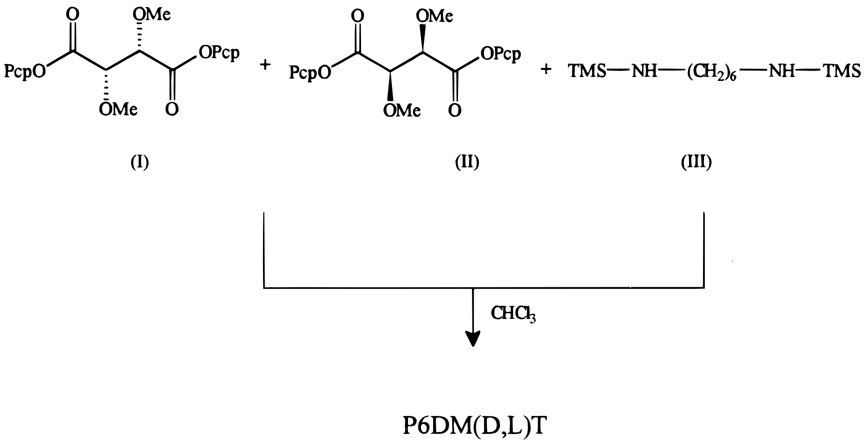


Figure 2. General scheme of polycondensation leading to copolyamides P6DM(D,L)T.

Table 1. Polymerization Data and Elemental Compositions of Polyamides and Copolyamides

polyamide	repeating unit formula	yield (%)	H_2O (%)	elemental analysis (C, H, N) calculated			found		
P6DMDT	$C_{12}H_{22}O_4N_2{\cdot}{}^1/_4H_2O$	92	1.7	54.82	8.63	10.66	54.62	8.38	10.35
P6DMLT	$C_{12}H_{22}O_4N_2{\cdot}{}^1/_4H_2O$	92	1.7	55.82	8.63	10.66	55.23	8.62	10.64
P6DM(D,L)T (1:9)	$C_{12}H_{22}O_4N_2{\cdot}{}^1/_2\ H_2O$	85	3.5	53.90	8.68	10.48	53.84	8.39	10.30
P6DM(D,L)T (2:8)	$C_{12}H_{22}O_4N_2{\cdot}{}^1/_2\ H_2O$	87	3.5	53.90	8.68	10.48	53.73	8.52	10.30
P6DM(D,L)T (3:7)	$C_{12}H_{22}O_4N_2{\cdot}{}^1/_2H_2O$	82	3.5	53.90	8.68	10.48	53.21	8.32	10.20
P6DM(D,L)T (1:1)	$C_{12}H_{22}O_4N_2{\cdot}{}^1/_2\ H_2O$	85	3.5	53.90	8.68	10.48	53.91	8.65	10.40
P6DM(D-L)T	$C_{12}H_{22}O_4N_2{\cdot}H_2O$	60	7.0	52.16	8.75	10.14	51.72	8.41	9.90

Table 2. Compared Viscosimetry Data and Molecular Weights of Polyamides and Copolyamides

	DCA[a]		HCOOH[b]		GPC[c]		
polyamide	[η] (dL g^{-1})	M_v[d]	[η] (dL g^{-1})	M_v[d]	M_n	M_w	PD
P6DMDT	0.87	21 800	0.48	11 100	11 400	22 300	1.9
P6DMLT	0.85	20 800	0.47	10 800	8 100	17 100	2.1
P6DM(D,L)T (1:9)	3.20	233 000	1.49	42 300	32 500	83 600	2.6
P6DM(D,L)T (8:2)	0.87	21 800	0.69	17 100	12 500	26 500	2.1
P6DM(D,L)T (7:3)	0.36	4 300	0.34	7 300	5 600	9 000	1.5
P6DM(D,L)T (1:1)	2.09	107 000	1.19	32 500	22 500	50 200	2.2
P6DM(D−L)T	0.30	3 400					

[a] Intrinsic viscosities measured in dichloroacetic acid at 25 °C. [b] Intrinsic viscosities measured in 90% formic acid at 25 °C. [c] Gel permeation chromatography of trifluoroacetylated samples calibrated against polystyrene standards. [d] Viscosity average molecular weights calculated by using the equations reported for nylon 6,6 in dichloroacetic and 90 % formic acid.[14]

under a nitrogen atmosphere was added compound **V** (1.4 g, 8.7 mmol). The mixture was left stirring for 3 h at room temperature and then refluxed for another 3 h. After cooling down to room temperature, the solvent was rotoevaporated and the residue dispersed in ethyl acetate at 0 °C to render compound **VII** in 76% yield as a very hygroscopic white solid which melts at 145−147 °C. The crude product was used without further purification for preparing the active diester described below.

(2*R*,3*R*,14*S*,15*S*)-Bis(pentachlorophenyl) 5,12-Diaza-2,3,14,15-tetramethoxy-4,13-dioxohexadecanedioate (VIII). To a stirred solution of compound **VII** (2.0 g, 4.6 mmol) and pentachlorophenol (2.86 g, 10.8 mmol) in chloroform (25 mL) was added dropwise at 0 °C a solution of *N*,*N*′-dicyclohexyl carbodiimide (2.22 g, 10.8 mmol). The mixture was left stirring for a few hours, the dicyclohexyl urea precipitate was filtered off, and the clear solution successively washed with 1 M HCl, 5% $NaHCO_3$, and saturated sodium chloride solution. The residue resulting from evaporation to dryness was extracted firstly with boiling ethyl acetate, then with chilled chloroform, and finally with ether. After crystallization from tetrahydrofuran, chromatographically pure compound **VIII** was obtained. Yield: 1.70 g (45%). Mp: 192−4 °C. ^1H NMR ($CDCl_3$): δ 6.6 (t, NH, 2H), 4.63 (d, OCOC*H*, 2H), 4.32 (d, NHCOC*H*, 2H), 3.57 (s, CH_3OCHCOO, 6H), 3.53 (s, CH_3OCHCONH, 6H), 3.35 (m, CONHCH_2, 4H), 1.55 (m, CONHCH$_2$CH_2, 4H), 1.40 (m, CONHCH$_2$CH$_2$CH_2, 4H). ^{13}C NMR ($CDCl_3$): δ 168.05 (*C*ONH), 166.32 (*C*OO), 82.59 (NHCO*C*H), 80.56 (*C*HCOO), 60.27 (CH_3), 39.14 and 39.11 (CONH*C*H$_2$), 29.51 (CONHCH$_2$*C*H$_2$), 26.35 and 26.33 (CONHCH$_2$CH$_2$*C*H$_2$). Anal. Calcd for $C_{30}H_{30}N_2O_{10}Cl_{10}$: C, 38.58; H, 3.21; N, 3.00; Cl, 38.05. Found: C, 38.42; H, 3.20; N, 2.91; Cl, 37.87.

Synthesis of Polymers. General Procedure of Polycondensation. The procedure used for the preparation of copolymers exactly followed the methodology of polycondensation applied previously by us to the preparation of optically pure polytartaramides.[1,13] In brief, to a stirred solution of a mixture of monomers **I** and **II** at the calculated ratio in chloroform precooled to 0 °C was added an equimolecular amount of *N*,*N*′-(bistrimethylsilyl)-1,6-hexanediamine (**III**) in small portions under a nitrogen atmosphere. The solution was allowed to reach room temperature and left to proceed for 3 days under such conditions. The gel-like mass was diluted with a half volume of chloroform and heated at 60 °C for 2 h. The polymer was precipitated by pouring the reaction mixture into boiling ethanol or 2-propanol and recovered by centrifugation. The product was repeatedly washed with diethyl ether and finally dried under vacuum.

Results and Discussion

Synthesis of Copolyamides P6DM(D,L)T. The polycondensation reaction used for the preparation of copolymers P6DM(D,L)T is schematically represented in Figure 2, where the following abbreviations have been used: Pcp, pentachlorophenyl; TMS, trimethylsilyl. Polymerizations were conducted in chloroform at room temperature. Under such conditions, no substantial

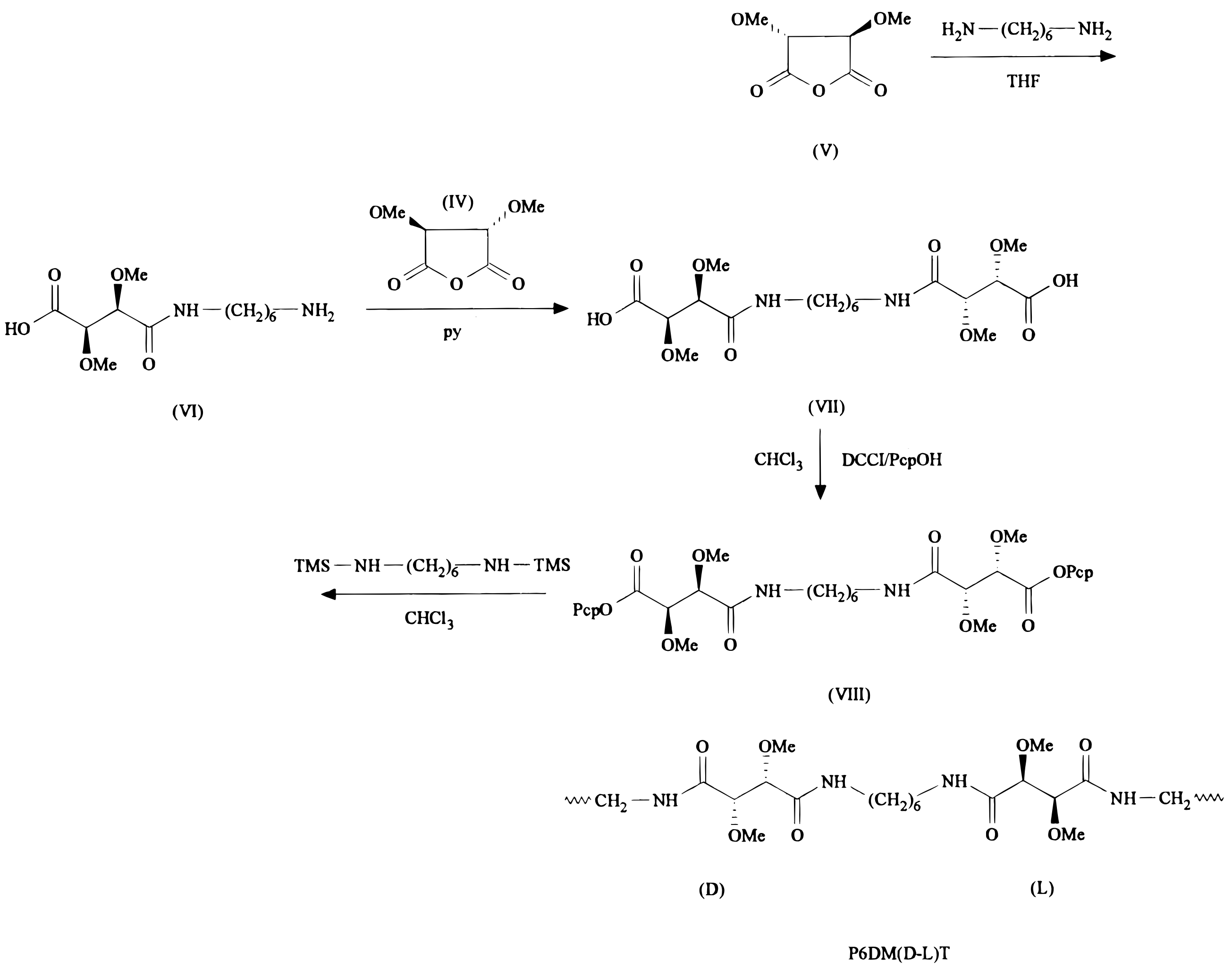


Figure 3. Synthetic route leading to polytartaramide P6DM(D-L)T.

epimerization of asymmetric centers is known to take place. Mixtures of **I** and **II** at 1:9, 2:8, 3:7, and 1:1 ratios were polymerized with **III** to render stereocopolymers D,L with enantiomeric compositions close to the corresponding feeding ratios, as was ascertained by optical rotation measurements. Both infrared and NMR spectroscopic data were in agreement with the chemical structure expected for these copolyamides. In Table 1, some relevant polymerization and characterization data are given for the four prepared P6DM(D,L)T copolytartaramides, as well as for optically pure homopolymers P6DMDT and P6DMLT obtained under identical conditions. Polymerization yields were within the range 80–90%, and elemental analyses found for the resulting polymers were consistent with their expected chemical compositions provided that they contain about 5–10% (w/w) of absorbed water. This is a reasonable assumption since these polyamides are known to be markedly hydrophilic. In fact, similar water contents were estimated to be bound to the series of optically pure polytartaramides P*n*DMLT[1] as well as to its isomeric polyamides obtained from 2,3-dimethoxy-1,4-butanediamine and aliphatic diacids.[13] In both cases, the amount of water present in each polymer was found to increase as the value of *n* diminished within the series.

Our preceding works on polytartaramides[1,13] demonstrated that activation of the two comonomers used in the polycondensation turns to be crucial to obtain reasonably high molecular weights. This was perfectly applied to copolyamides P6DM(D,L)T, for which intrinsic viscosities ranging from 0.36 up to 3.2 dL g^{-1} have been measured in dichloroacetic acid (Table 2). Average molecular weights between 4500 and 233 000 are calculated from such viscosities by using the Mark–Houwink parameters reported for nylon 6,6.[14] Molecular weights estimated from viscosities measured in dichloroacetic acid appear to be overestimated with regard to those obtained by GPC, where M_w ranging from 9000 to 83 000 with polydispersities varying from 1.5 to 2.6 were determined. Much more consistent results could be obtained when dichloroacetic acid was replaced by 90% formic acid for viscosity measurements. In such a case, limiting viscosities ranging from 0.34 to 1.49 and corresponding to M_v between 7300 and 42 000 resulted instead, which appear to be much more reasonable values for polymers obtained by polycondensation. According to earlier observations reported on conventional nylons,[15] some sort of nonspecific aggregation is likely to take place in dichloroacetic acid, a trend that appears to be more pronounced when large molecular weight polymers are concerned.

Synthesis of Copolyamide P6DM(D–L)T. This copolytartaramide was prepared to be used as reference compound in the study of the microtacticity of copolyamides P6DM(D,L)T. In order to ensure the racemic composition of the copolyamide chain, a strategy of synthesis based on the use of a D–L-sesquiomer was followed for the synthesis of this polymer. Thus, *N*,*N*′-bis(trimethylsilyl)-1,6-hexanediamine (**III**) was polycondensated with diester **VIII** to produce P6DM(D–L)T

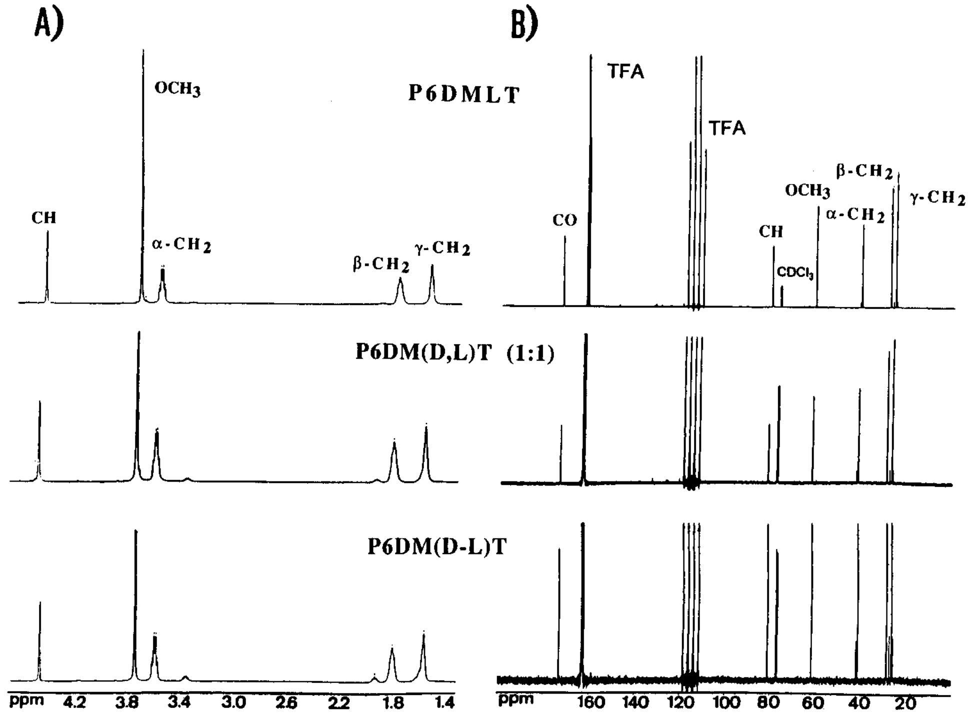
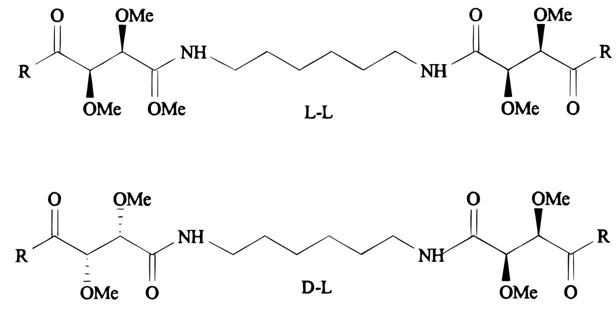


Figure 4. Comparison of ^1H (500 MHz) (A) and ^{13}C (125.7 MHz) (B) NMR spectra of optically pure polytartaramide P6DMLT and racemic copolyamides P6DM(D,L)T and P6DM(D-L)T.

with an intrinsic viscosity of 0.30 in 60% yield. Compound **VIII** was obtained from di-*O*-methyl-D- and -L-tartaric anhydrides and 1,6-hexanediamine by a synthetic route consisting of three steps (Figure 3). When compared to copolyamide PDM(D,L)T (1:1), copolyamide P6DM(D−L)T retains larger amounts of water after drying and is less soluble in chloroform (Table 1). Although both types of copolyamides have a D/L ratio equal to unity, their stereochemical microstructure should be different since no more than two successive tartaric units with the same configuration may occur in the latter. Such constraint ensures the nonexistence of *threodiisotactic* blocks in the copolymer. The relatively poor yield and low molecular weight obtained for P6DM(D−L)T are features which must not be related with the particular constitution of the polymer but rather to the spontaneous gelatinization taking place in the earlier stages of polycondensation.

NMR Characterization. As indicated above, ^1H and ^{13}C NMR spectra of P6DM(D,L)T were consistent with the chemical constitution anticipated for these copolyamides. At the stereochemical level, a certain complexity in the fine structure of the signals reflecting the occurrence of different configurational D/L sequences might be expected. However, both ^1H and ^{13}C NMR spectra registered in a 500 MHz spectrometer consist of single peaks practically indistinguishable from those appearing in the spectra of optically pure P6DMLT or P6DMDT polymers. At first, such similarities seem to indicate either a microstructure in blocks composed of long stereoregular D and L sequences or a physical mixture of the two enantiomorphic polymers. However similar simplified spectra were found to arise from P6DM(D−L)T, a copolyamide synthesized in such a way that the occurrence of configurational microheterogeneity in the chain is ensured. The NMR spectra of the three aforementioned polytartaramides are compared in Figure 4 in order to illustrate the similarities existing among them.



Compound	R	Diastereoisomer
a	OPcp	L-L
b	OPcp	D-L
c	$NHCH_2CH_2CH_3$	L-L
d	$NHCH_2CH_2CH_3$	D-L

Figure 5. Model compounds used in the NMR analysis of polytartaramides.

The low sensitivity of NMR to configurational perturbations in a poly(hexamethylene tartaramide) chain could be anticipated from the results obtained in the analysis of monomers and model compounds shown in Figure 5. In the case of the pentachlorophenyl diesters, the signal arising from methoxy, methine, and methylenes in α and γ positions appeared split in the ^{13}C NMR spectrum of the D−L compound whereas single peaks were observed in the case of the L−L diastereoisomer. Conversely, an identical spectrum was obtained for both diastereoisomers in the case of the *N*,*N'*-di-*n*-propyl ditartaramides which revealed how the spectroscopic differences rapidly vanished as the two acetyl groups linked to the tartaric unit becomes closer in nature. In Table 3, the chemical shifts and corresponding assignments of those peaks concerned in this analysis are collected and compared with those observed for polytartaramides and copolytartaramides.

Table 3. ^{13}C NMR Chemical Shifts of Polytartaramides[a] and Model Compounds[b]

	chemical shifts (ppm)						
compound	CH	OCH_3	α-CH_2	β-CH_2	γ-CH_2	CONH	COO
a[c]	82.59, 80.57	60.29, 60.28	39.12	29.52	26.34	168.08	166.33
b[c]	82.59, 80.56	60.29, 60.27	39.14, 39.11	29.51	26.35, 26.33	168.08	166.33
c[c]	82.36	60.65, 60.61	39.05	29.56	26.45	169.37, 169.33	
d[c]	82.35	60.66, 60.62	39.04	29.56	26.45	169.37, 169.33	
P6DMLT	80.85	61.61	41.54	28.79	26.54	173.13	
P6DM(D,L)T (1:1)	80.97	61.69	41.63	28.89	26.63	173.23	
P6DM(D−L)T	81.10	61.14	41.60	28.93	26.63	173.13	

[a] In $CDCl_3$−TFA (10:1). [b] In $CDCl_3$. [c] Compounds given in Figure 5.

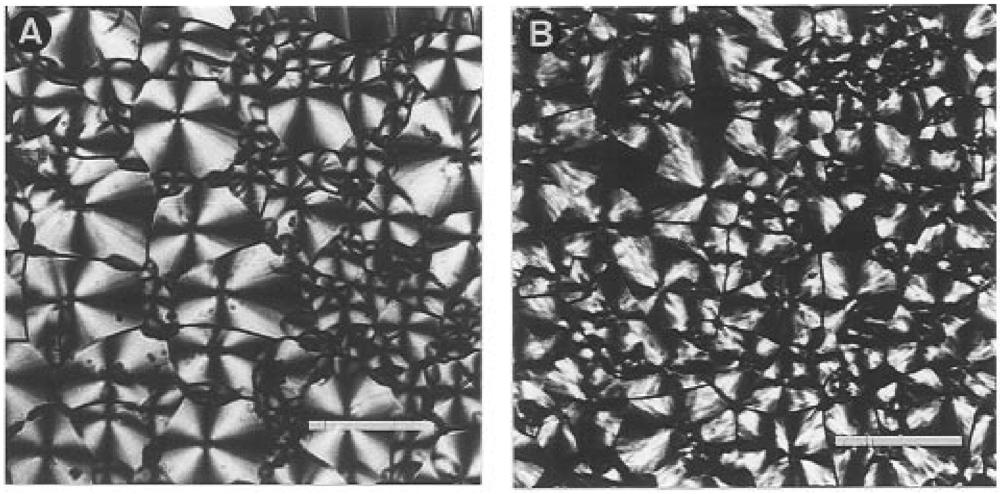


Figure 6. Optical micrograph (crossed polarizers) of spherulites of P6DMLT (A) and P6DM(D,L)T (1:1) (B) grown by slow evaporation of a formic solution of the polymer at room temperature. The bar denotes 0.1 mm in both cases.

Table 4. Optical Rotations and Calorimetric Data of Polyamides and Copolyamides

		melting data[b]			
polyamide	$[\alpha]^{25}_{D}$[a]	T_m (°C)	ΔH_m (cal g^{-1})	T_g (°C)	T_g/T_m (K/K)
P6DMLT	90.4[c]	230/232	14.8/13.5	106	0.76
P6DM(D,L)T (1:9)	73.4[c]	226/226	9.9/10.5	95	0.73
P6DM(D,L)T (2:8)	41.5	225/225	11.2/6.9	74	0.69
P6DM(D,L)T (3:7)	29.8	224/225	11.7/5.8	71	0.68
P6DM(D,L)T (1:1)	2.0	223/226	12.8/12.0	68	0.68

[a] Specific optical rotations measured in chloroform at a concentration of 1.0 g dL^{-1} (unless indicated otherwise). [b] Melting points (T_m) and fusion enthalpies (ΔH_m) measured by DSC on samples coming directly from synthesis and after annealing at 200−210 °C for 2 h. [c] $c = 0.5$ g dL^{-1}.

Thermal Characterization. The crystalline nature of these copolyamides was firstly evidenced by the formation of spherulitic morphologies in samples which were crystallized either from the melt or from solution. The textures of films of P6DMLT and P6DM(D,L)T (1:1) obtained by slow evaporation of a formic acid solution on a glass slide are compared in Figure 6. In both cases, spherulites of similar size displaying similar features were developed. The DSC analysis corroborated the optical microscope observations and showed that all of them exhibit a melting−crystallization behavior very similar to the optically pure polymer. The traces of P6DM(D,L)T (1:1) obtained at different heating and cooling rates are shown in Figure 7A, illustrating the pronounced trend exhibited by the polymer toward crystallization in spite of its lack of stereoregularity. The variation in the thermal properties of P6DM(D,L)T with the enantiomeric composition was followed by DSC, and the results are collected in Table 4. It should be said that water adsorption values and corresponding effects on thermal behavior of the polymers were not determined in this work. Copolyamide samples coming directly from synthesis exhibit an endotherm located within the range of 222−226 °C with an associated enthalpy ranging from 9.9 to 12.8 cal g^{-1} as illustrated in Figure 7B. The melting temperatures decrease slightly with the optical compensation, but differences are too small to be considered indicative of any significant structural change. The same may be said about the trend detected in the heats of fusion which run parallel to the optical purity with the exception of P6DM(D,L)T (1:1), which has an enthalpy similar to that of P6DMLT. After subjecting the samples to annealing for a couple of hours at temperatures between 200 and 210 °C, the melting point slightly increased and differences among them are even smaller. On the contrary, differences in enthalpies become more remarkable, indicating a relative reluctance of polymers with intermediate compositions to be reorganized in the solid state. The glass transition was found to be particularly sensitive to the configurational composition with T_g steadily decreasing from 106 to 68 °C as the enantiomeric D/L ratio increases from 0 to 1.

X-ray Analysis. Powder X-ray diffractograms displaying discrete scattering indicative of high crystallinity were recorded from all P6DM(D,L)T samples. These diagrams are shown in Figure 8 together with that produced by the homopolytartaramide P6DMLT, and the spacings associated with the characteristic rings are compared in Table 5. At first glance, all these patterns seem to be similar to each other in both spacing and intensity. However, significant differences were noticed among them when examined in detail. Firstly, the sharpness of the pattern increases with the level of optical compensation attained in the polymer, so the degree of crystallinity observed for the racemic copolyamide approaches closely that displayed by the ho-

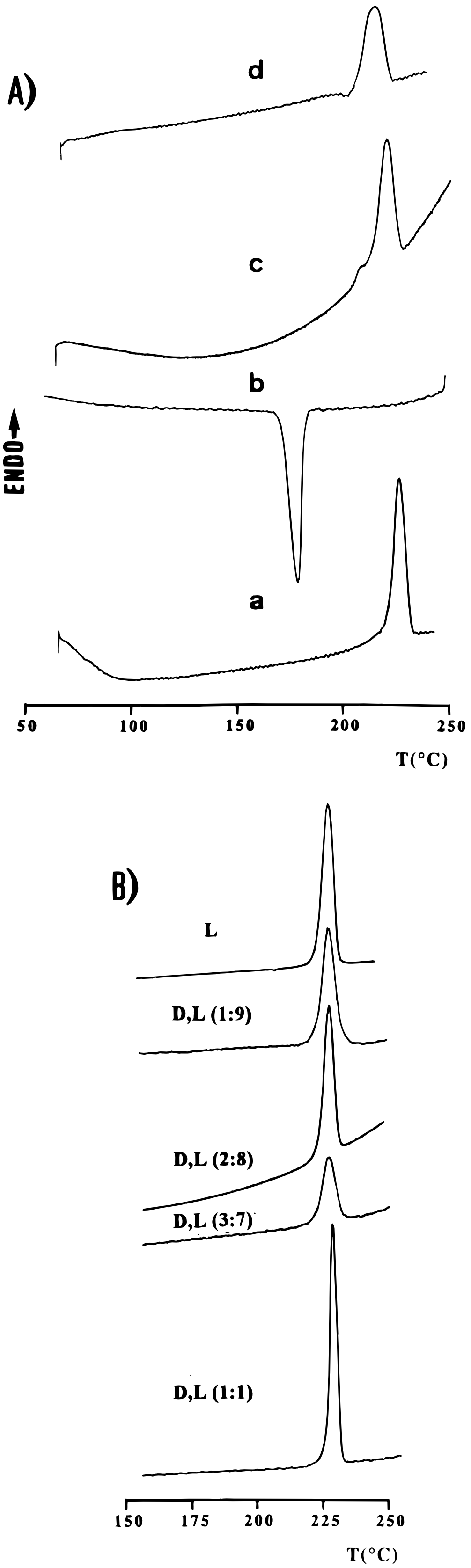


Figure 7. (A) DSC traces of polyamide P6DM(D,L)T (1:1) (a) first heating, (b) cooling trace obtained form the melt, (c) second heating, (d) heating trace obtained from a sample quenched from the melt. (B) Comparison of melting endotherms for polytartaramides differing in the enantiomeric composition.

mopolymer. This is in agreement with the calorimetric observations described above. Although the Bragg spacings fluctuate slightly with composition without showing any apparent regular trend, the observed variations fall out of the acceptable margin of experimental error. Therefore they should be related to the occurrence of small changes in the lattice parameters caused by the incorporation of antipode units in the crystal phase. What is particularly remarkable is the appearance of a weak ring with a spacing of about 4.9 Å in the pattern of P6DM(D,L)T (1:1). The same feature is observed in the diagram of the polytartaramide P6DM(D−L)T and, even more clearly, in the diagram produced by a racemic mixture of polymers P6DMLT and P6DMDT. In contrast, such reflection is absent in diagrams of optically pure polytartaramides as well as in stereocopolytartaramides containing low D/L ratios. The presence of this reflection is associated therefore with the coexistence of similar amounts of D- and L-tartaric units in the crystal lattice and strongly suggests the occurrence of a peculiar crystal structure with specific features. A detailed analysis of the crystal structure of both racemic P6DM(D,L)T and the racemic mixture of P6DMDT and P6DMLT will be the subject matter of the following accompanying paper.

Hydrolytic Degradation. The susceptibility of copolyamides P6DM(D,L)T to hydrolysis at pH 7.4 was assayed at three different temperatures. Variations in both weight and viscosity of the initial samples were used to follow the evolution of degradation for an incubation period extending up to near 2 months. As expected, both parameters were found to decay with time at a rate that increased with temperature. Such variations are plotted in Figure 9 for the case of polyamide P6DM(D,L)T (1:9). A weight loss of 10% over about 10 days (invariant of the temperature used) was observed after which the loss is much less with extended incubation time. Such behavior indicates the presence in the original sample of relatively low molecular weight leachable components which are lost during the initial time of incubation. The maximum loss of mass observed was 15% for a sample incubated at 70 °C for about 2 months with the limiting viscosity decreasing from 3.2 to 0.5 g mL^{-1} along this period of time. At 37 °C the hydrolysis is much slower, involving a weight loss of only 10% and a final intrinsic viscosity of 2.9. These results are by no means very different from those obtained in the degradation of the homopolymer P6DMLT which has been studied in detail in a preceding work.[3]

In contrast to other degradable polymers, like polylactic acid (PLA), where the stereochemical configuration plays a crucial role in the hydrolytic degradation,[16] the copolymerization of D- and L-tartaric units does not alter substantially the hydrolytic behavior of polytartaramides. The fact that the two enantiomeric forms of tartaric acid can be accommodated in the same crystal without seriously disturbing the lattice allows sterocopolytartaramides to display a considerable degree of crystallinity. As a consequence, water diffusion is not clearly improved and the hydrolysis rate remains essentially unaffected with variations in the configurational composition. This behavior is distinctly different from poly(D,L-lactic acid) stereocopolymers which are reported to be amorphous for contents in D units as low as 10%.[17] As a result, water permeation is greatly facilitated and the amount of adsorbed water in P(D,L)LA (1:1) is 1 order of magnitude higher than in optically pure PLLA. As a consequence, the racemic polymer degrades in both buffer and enzyme far more

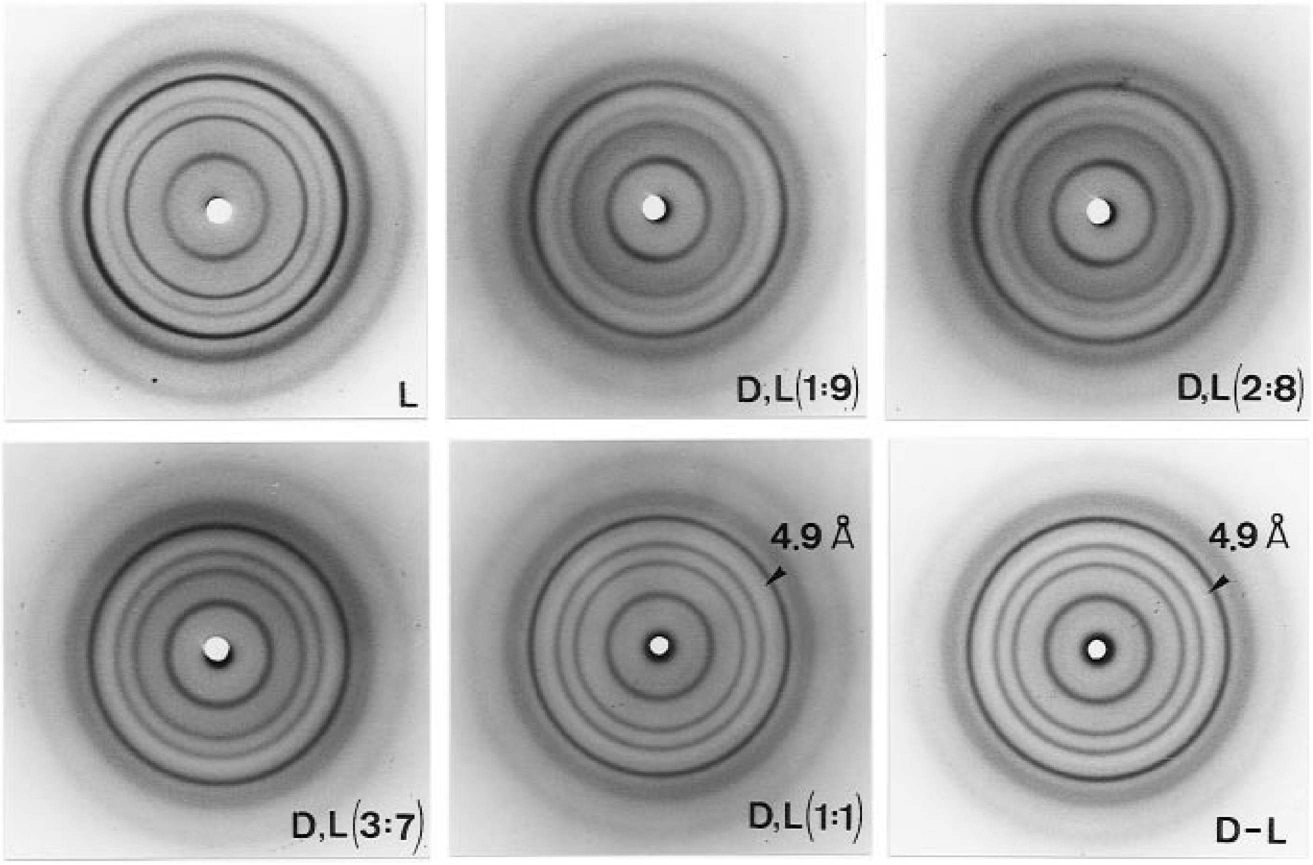


Figure 8. Powder X-ray diffraction diagrams of polyamide P6DMLT and copolyamides P6DM(D,L)T with different enantiomeric compositions. Note that the reflection at 4.9 Å is only observed for a D/L ratio equal to unity.

Table 5. Observed Spacings (Å) in Powder X-ray Diagrams of Polyamides and Copolyamides

					P6DM(D,L)T				P6DM-
h	k	l^a	I^b	P6DMLT	1:9	2:8	3:7	1:1	(D−L)T
0	0	1	m	11.50	11.1	10.8	10.8	10.7	10.9
0	1	1	m	6.35	6.50	6.65	6.70	6.74	6.74
0	1	0	m	5.40	5.52	5.54	5.60	5.63	5.64
			w					~4.9	~4.9
1	0	0	s	4.60	4.52	4.50	4.48	4.52	4.51
0	−1	1	m	4.17	4.12	4.15	4.08	4.11	4.12
1	0	2	m	3.95	3.86	3.86	3.84	3.86	3.87
−2	1	0	w	2.50	2.50	2.50	2.50	2.50	2.50

[a] Indexed on the basis of the triclinic lattice established for P6DMLT (a = 5.00 Å, b = 6.84 Å, c = 13.20 Å, α = 61.5°, β = 90°, γ = 111.6°). [b] Intensities visually estimated and denoted as s = strong, m = medium, and w = weak.

rapidly than the optically pure polymer.[16]

Concluding Remarks

The polycondensation of *N*,*N*′-bis(trimethylsilyl)-1,6-hexanediamine with mixtures of bis(pentachlorophenyl)-2,3-di-*O*-methyl-D- and -L-tartrates in chloroform solution at room temperature afforded a series of poly(hexamethylene-2,3-di-*O*-methyl-D,L-tartaramide)s (P6DM(D,L)T) with enantiomeric D/L ratios ranging from 1:9 to 1:1. The microstructure of these stereocopolyamides is interpreted in light of NMR analysis to consist of a statistical distribution of D and L configurations, which is the constitution that should be expected from the conditions used in the polymerization reaction. All these stereocopolymers are crystalline and produce the same type of powder X-ray diffraction pattern, with the racemic copolymer P6DM(D,L)T (1:1) being unique in showing a new reflection at 4.9 Å. The changes in enantiomeric composition become only partially reflected in their thermal properties; whereas melting points remain approximately constant at 225–

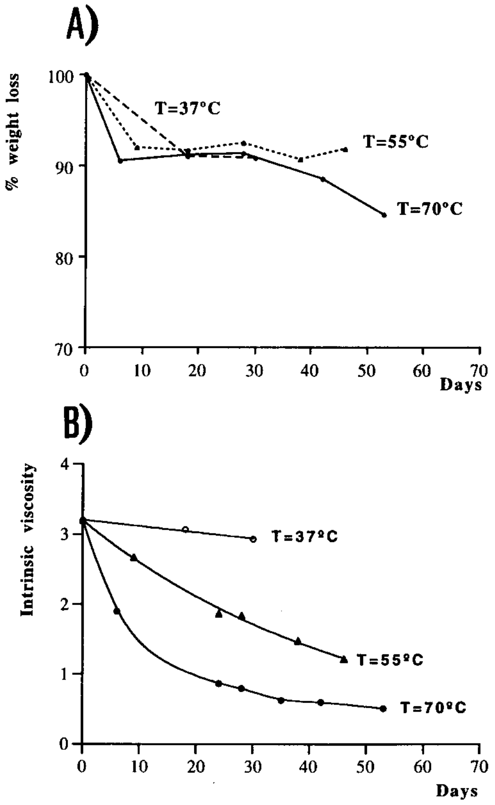


Figure 9. Degradation plots of weight loss (A) and viscosity decay (B) of P6DM(D,L)T (1:9) against incubation time.

226 °C, the glass temperature steadily decreases, with the optical compensation falling from 106 °C for the optically pure P6DMLT down to 68 °C for the racemic copolymer. On the other hand, the susceptibility toward the hydrolytic degradation is not significantly enhanced with respect to that displayed by the optically pure polymer. This is consistent with the moderate decay in crystallinity that is achieved by stereocopolymerization. Our results show that the incorporation of the antipode units in the same lattice is feasible over the whole range of enantiomeric compositions of polytartaramides and strongly suggest the occurrence of a specific crystal structure when the system is fully optically compensated. This aspect merits special attention and constitutes the subject of the second part of this work, where it will be examined in full detail.[18]

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