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Optically Active Polyamides Derived from L-Tartaric Acid

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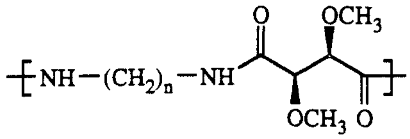
ABSTRACT: A series of polyamides *n*,4 (*n* from 2 to 12) containing one methoxy group stereoregularly attached to each α carbon atom of the diacid repeating unit has been prepared by using L-tartaric acid as the starting material. Polycondensation in a solution of bis(pentachlorophenyl) 2,3-*O*-dimethyl-L-tartrate with the corresponding 1,*n*-alkanediamines afforded stereoregular polymers with molecular weights between 7×10^3 and 5×10^4 depending upon the value of *n*, in high yields. These polyamides were fully characterized by elemental analysis and IR and $^1H/^{13}C$ NMR spectroscopy. They are hydrophilic, melt above 185 °C, and display large optical activity. All these properties were investigated and found to correlate well with the molecular structure of the polymer.

A number of optically active nonpolypeptidic polyamides were prepared during the 1960s and 1970s with the main purpose of investigating the influence of constitution on conformation.[1] Since then, incessant efforts have been devoted to the synthesis of new stereoregular polyamides differing either in architecture or in the type of precursors chosen for the preparation of the monomers. As a result, novel polyamides displaying unusual properties among this family of polymers have become available.[2,3] In the last few years, a renewed interest in the development of these polymers has arisen due to their potential as materials for biomedical applications.[4] Polyamides containing electron-withdrawing groups in the α-position of the carbonyl group are known to undergo hydrolysis faster and are particularly attractive as biocompatible polymers with enhanced biodegradability.[5] On the other hand, the presence of asymmetric carbons in the repeating unit makes it possible to adjust the physical properties by controlling the tacticity as well as to study the effect of chirality on biological activity.[6]

Carbohydrate derivatives have been traditionally envisaged as appropriate building blocks for the preparation of stereoregular polyamides provided that their multifunctionality has been reduced by making use of adequate protecting groups and that the convenient stereoisomeric form has been selected. By this means, optically active polyamides containing up to four chiral backbone carbon atoms have been successfully constructed.[7,8] In this context, L-tartaric acid ((2*R*,3*R*)-(+)-2,3-dihydroxybutanedioic acid) stands out as an easily accessible natural product which has been widely explored as a profitable source for obtaining poly(tartaramides).[9,10] Unfortunately, polycondensation of monomers derived from tartaric acid is by no means straightforward. If high-temperature conditions are applied, atactic or even cross-linked polyamides are usually obtained. On the other side, polycondensation in solution carried out under mild conditions fails in giving high molecular weight polymers. Very recently, we have reported that stereoregular poly(tartaramides) with molecular weights up to 5×10^4 may be obtained in high yield if both comonomers, the acid as a diactive diester and the diamine as a bis(trimethylsilyl) derivative, are properly activated.[11] The present paper is concerned with an extension of this approach to the preparation of a series of poly(alkylene-2,3-*O*-dimethyl-L-tartaramides) (referred to as P*n*DMLT), with the number of methylene units in the polymethylene sequence ranging from 2 to 12. The structures of these polyamides have been confirmed by elemental microanalysis, IR and $^1H/^{13}C$ NMR spectroscopy, and their thermal and optical properties as well as their hydrophilicity investigated in relation to the constitution of the polymer chain.



As discussed in a recent paper,[11] only the two optically active forms of tartaric acid, which are those containing a 2-fold axis normal to the C_2–C_3 bond, are suitable to generate stereoregular chains by condensation with 1,*n*-alkanediamines. The meso form instead would give rise to a statistical distribution of configurations depending upon the manner in which the diacid unit enters the growing polymer chain.

Results and Discussion

Synthesis of P*n*DMLT. The reaction strategy that we have followed to produce P*n*DMLT is outlined in Scheme I where the following abbreviations have been used: Pcp = pentachlorophenyl; TMS = trimethylsilyl; py = pyridine.

Compounds **I–III** were prepared according to procedures previously reported[12,13] with the modifications detailed in the Experimental Section. Methylation of compound **I** by dimethyl sulfate turns out to be the critical step of this sequence of synthesis due to the strong basis conditions required. Nevertheless, no competing reactions, implying either elimination or racemization, were observed to take place to a significant extent. On the other hand, both hydrolysis of the diethyl diester (**II**) and formation of the diactive diester bis(pentachlorophenyl) 2,3-di-*O*-methyl-L-tartrate (**IV**) proceeded without difficulties, the latter being isolated and purified by crystallization as large-needle crystals. The bis(trimethylsilyl)-diamines (**V*n***) are volatile compounds which are readily obtained and purified by distillation under vacuum; by this means, any remaining unreacted diamine, as well as those monotrimethylsilylated products which eventually formed, could be effectively removed. The extreme sensitivity to humidity of compounds **V*n*** made it difficult

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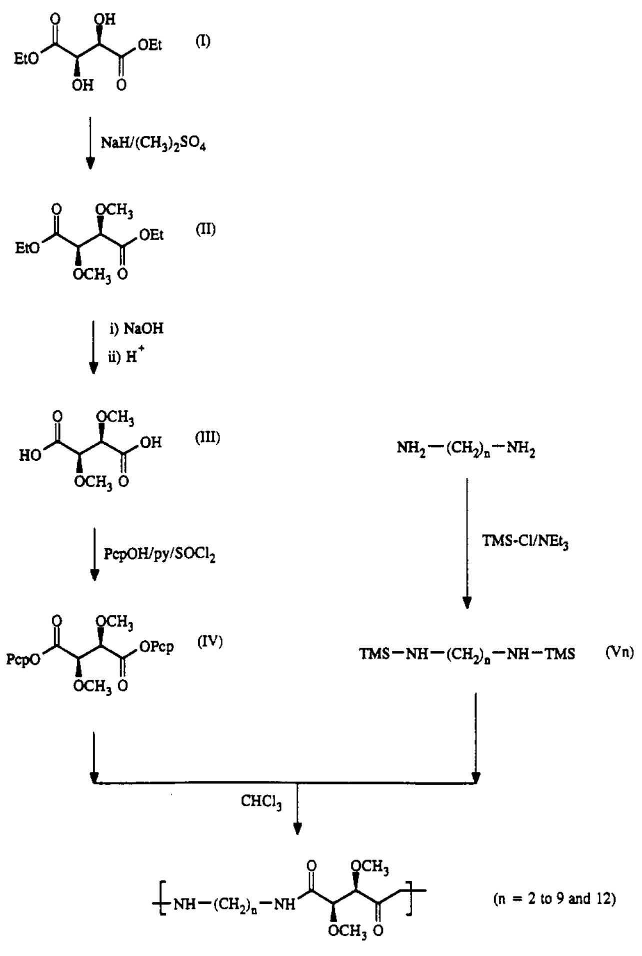
Scheme I



PnDMLT

to characterize them extensively; for such a reason their purity was only assessed by infrared spectroscopy.

Polycondensations from compounds **IV** and **V*n*** were conducted in a chloroform solution at room temperature. Under such conditions, polymerizations were found to proceed entirely in a homogeneous phase when diamines **V5**–**V12** were used. Conversely, P*n*DMLT generated from diamines **V2**–**V4** separated off at very early stages of the polycondensation and the reaction system gelatinized. As a consequence, recovery and purification of polymers from P2DMLT to P4DMLT required a much more laborious workup. In any case, the reaction rate was observed to decay at moderate conversions due to the high viscosity achieved by the system which made the polymerization become diffusion-controlled. In order to increase the molecular weight of the polymers, the reaction mixture was slightly diluted with an additional amount of solvent and the temperature elevated to 60 °C. By these means polyamides with limit viscosity numbers between 0.6 and 2.3 were obtained in yields exceeding 90% in most cases (Table I).

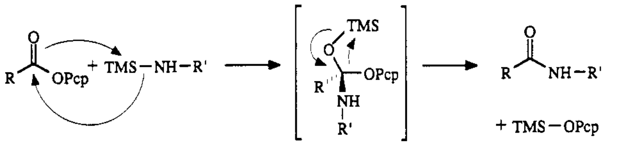
The effectiveness attained by this method of polycondensation in the preparation of poly(tartaramides) is understandable in light of the reaction mechanism and what can be expected from activation of the monomers. According to Oishi,[14] the amidation reaction involving *N*-trimethylsilylated amines should take place through the intermediate formation of the tetrahedral compound depicted in Scheme II. Elimination of the (pentachlorophenyl)oxy group leading to amide formation is favored by the trimethylsilyl group with the result of the byproduct TMSO–Pcp. On the other hand, the electron-withdrawing methoxy group attached to the α carbon atom of the diacid moiety will certainly enhance the carbonyl susceptibility toward the nucleophilic attack by the activated amine.

Table I. Compared Molecular Weights of PnDMLT Determined by Viscosimetry and GPC

polyamide	$[\eta]^a$ (dL/g)	$M_v{}^b$	$M_n{}^c$	$M_w{}^c$	M_w/M_n	DPn
P2DMLT	0.63	12 100	7 700	10 800	1.41	38
P3DMLT	0.69	14 300	14 900	22 100	1.48	69
P4DMLT	0.75	16 600	15 200	25 100	1.65	66
P5DMLT	0.75	16 600	18 300	26 500	1.45	75
P6DMLT	1.55	62 500	15 700	35 300	2.24	61
P7DMLT	0.65	12 800	12 400	23 900	1.92	46
P8DMLT	2.30	128 100	44 600	69 300	1.55	156
P9DMLT	1.08	32 300	14 500	26 600	1.82	48
P12DMLT	1.65	70 000	38 000	62 000	1.62	111

[a] Intrinsic viscosities measured in dichloroacetic acid at 25 °C. [b] Calculated by applying the viscosimetric equation reported for nylon 6,6.[16] [c] Determined by GPC of the trifluoroacetylated samples.

Scheme II



Characterization of PnDMLT. Determinations of molecular weight distributions were conducted by GPC. P*n*DMLT soluble in chloroform were first run in this solvent, but complex elution traces were observed likely due to the occurrence of aggregations. In order to prevent molecular interactions, polyamides were trifluoroacetylated by following the method of Schulz et al.[15] By these means, readily interpretable chromatograms could be obtained for the whole series. Number-average molecular weights measured by this technique were between 8×10^3 and 5×10^4, with polydispersities ranging from 1.4 to 2.2. It has been reported that partial cleavage of amide bonds to oligomers may take place in the trifluoroacetylation of certain polyamides, in particular of those containing peptide bonds and those derived from anhydroalditols.[8] In the present case, however, a fair agreement between GPC data and those obtained from viscosimetry by using the Mark–Houwink parameters reported for nylon 6,6[16] has been found (Table I). Hence, we may reasonably infer that chain degradation of P*n*DMLT by trifluoroacetylation, if any, should be negligible.

Elemental microanalysis assessed the constitution expected for P*n*DMLT. As anticipated, the presence of two methoxy groups in the repeating unit makes these polyamides markedly hygroscopic, an effect that logically increases with the concentration of such groups in the polymer chain. In fact, a complete removal of the moisture was not achievable even under severe conditions of drying, as was suggested by the slight deviations found in the combustion analyses. This affinity for water is particularly noticeable for P5DMLT down to P2DMLT where its presence becomes evident in both infrared and ^{1}H NMR spectra.

The chain structure of every P*n*DMLT was confirmed by infrared and ^{1}H and ^{13}C NMR, as summarized in the Experimental Section where a detailed enumeration of the most significant absorptions is given for each product. Infrared spectra showed the characteristic amide bands about 3280 (amide A), 3060 (amide B), 1650 (amide I), and 1530 cm^{-1} (amide II). Features of these spectra worth mentioning are the medium to weak shoulder peaks appearing around 3420 and 1720 cm^{-1}, respectively (Figure 1). A comparison of the spectra obtained from samples of the same polymer but differing in molecular weight revealed no correlation between the chain size and the

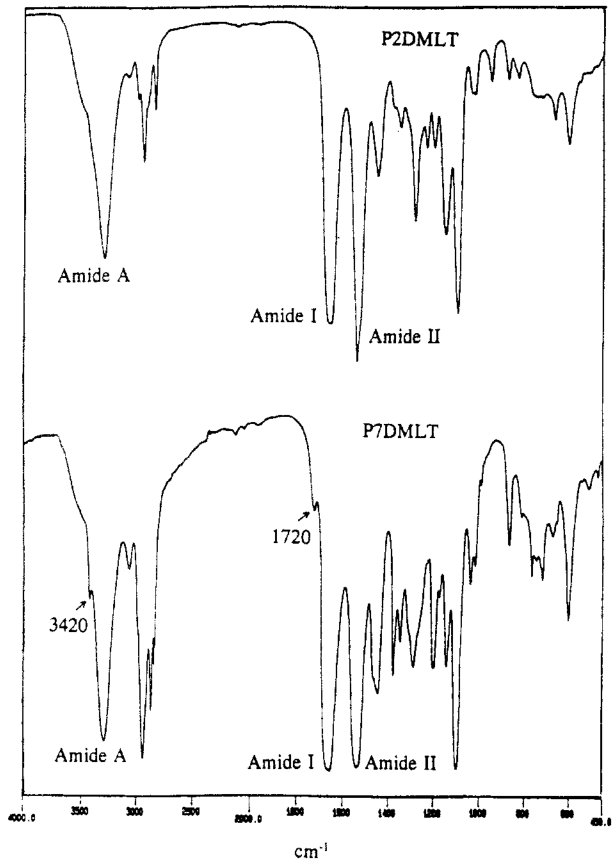


Figure 1. Infrared spectra of P2DMLT (a) and P7DMLT (b).

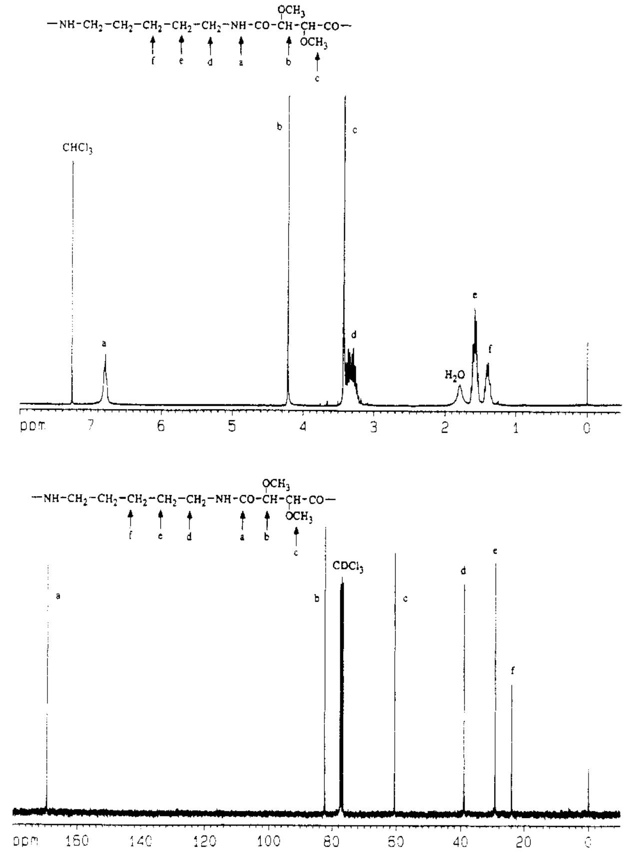


Figure 2. ^{1}H and ^{13}C NMR spectra (200 MHz) of P5DMLT.

Table II. Compared Qualitative Solubilities of P*n*DMLT[a]

	polyamide (P*n*DMLT)								
solvent	2	3	4	5	6	7	8	9	12
water	–	++	–	+	–	–	–	–	–
diethyl ether	–	–	–	–	–	–	–	–	–
ethanol	–	+	–	–	–	–	–	–	–
chloroform	–	±	±	++	++	++	++	++	++
DMSO	±	++	±	±	±	+	±	±	±
DMF	–	+	–	–	–	–	–	–	–
NMP	–	±	–	±	–	–	–	±	±
formic acid	++	++	++	++	++	++	++	++	++
TFE	++	++	++	++	++	++	++	++	++

[a] (–) Insoluble, (±) slightly swollen, (+) soluble on warming at 100 °C or at the boiling point, (++) soluble at room temperature. DMSO: dimethyl sulfoxide. DMF: *N,N*-dimethylformamide. NMP: 1-methyl-2-pyrrolidinone. THF: 2,2,2-trifluoroethanol.

intensity of the 1720-cm^{-1} peak, which neglects the possibility that such absorption corresponds to end chain groups. It is well-known that, in general, NH and carbonyl absorptions arising from non-H-bonded amide groups appear at higher frequencies than those arising from the associated state.[17] Therefore, the observed shoulder peaks may be made to correspond to a significant fraction of nonassociated amide groups present in these poly(tartaramides).

Both ^{1}H and ^{13}C NMR spectra displayed sharp signals whose chemical shifts and intensities were consistent with the microstructure expected for these polyamides (Figure 2). In particular, well-resolved singlets are observed in both the ^{1}H NMR spectra for the two protons attached to the respective asymmetric backbone carbon atoms and the ^{13}C NMR spectra for the two carbonyl groups contained in the repeating unit. It may be concluded, therefore, that the occurrence of tartaric moieties in the meso configuration, which could be thought to arise by undesirable racemization, should be considered negligible in these polymers.

Solubility. Qualitative solubilities of P*n*DMLT in a variety of solvents differing either in polarity or in their strength in breaking hydrogen bonds are listed in Table II. The solubility in chloroform is observed to increase steadily with the length of the polymethylene segment of the repeating unit of the polyamide to the point that members containing more than five methylene units are readily soluble in this solvent at room temperature. On the other hand, these polyamides are, in general, not soluble in water, although they display elevated hydrophilicity. In Figure 3, the moisture sorption determined at room temperature and under a relative humidity of 100% is shown for every P*n*DMLT. As anticipated, the water uptake increases with the density of hydrophilic methoxy groups in the polymer chain. The exceptional solubility in water observed for P3DMLT and P5DMLT is presumed to be due to the low crystallinity of the samples, as evidenced by DSC and discussed below. Hydrogen-bond-breaking solvents such as formic acid and trifluoroethanol are good solvents for all P*n*DMLT irrespective of their constitution. As expected, no solubility at all in nonaggressive oxygenated solvents such as acetone, ethyl acetate, or ethyl ether was observed. In summary, it can be concluded that the solubility of poly(tartaramides) is notably enhanced when compared with similar polyamides lacking pendant methoxy groups. The solubility in chloroform is also worth mentioning since chiral polyamides adopting regular conformations by intramolecular hydrogen bonding are known to be readily soluble in this solvent.[3]

Thermal Analysis. The occurrence of thermal transitions in P*n*DMLT was investigated by DSC on samples prepared by precipitation of the polymer from chloroform with ethanol or ether. In all cases, well-defined endotherms corresponding to melting transitions appeared during the first heating cycle. Two or three melting peaks were observed in certain cases. This is known to be a common

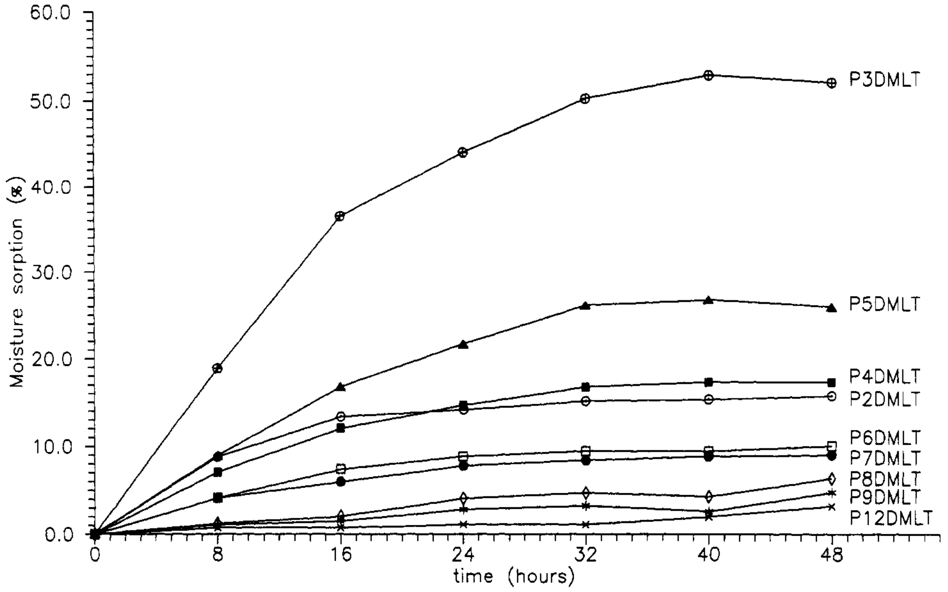


Figure 3. Moisture sorption of P*n*DMLT as a function of time at room temperature and under 100% relative humidity.

Table III. Thermal and Optical Properties of P*n*DMLT

				formic acid	
polyamide	T_g (°C)	T_m (°C)	T_g/T_m	$[\alpha]_D^{23}$	$[\Phi]_D^{23}$
P2DMLT		311.5		175.2	354.3
P3DMLT	123	254.2	0.75	147.2	318.3
P4DMLT	100	266.1	0.69	121.0	278.6
P5DMLT	113	217.0	0.79	111.6	272.6
P6DMLT	106	230.2	0.75	104.4	269.7
P7DMLT	87	209.0	0.75	92.6	252.2
P8DMLT	89	208.1	0.78	92.4	264.6
P9DMLT	84	204.7	0.75	87.0	261.3
P12DMLT	84	185.5	0.78	76.2	261.0

phenomenon amongst polyamides currently interpreted as due to the fusion of populations of crystallites differing in size.[18] Melting points given in Table III were those measured for peaks appearing at the highest temperature. It is seen that they increased along the whole series with the concentration of the amide groups in the polymer chain; this is apparently due to the increasing of cohesive forces exerted by hydrogen bonds. A zigzag curve was generated when the observed melting points were plotted against the number of methylenes contained in the diamine moiety, the local maxima corresponding to P*n*DMLT with an even value of *n* (Figure 4). Such a correlation is identical to that observed for the series of aliphatic polyamides prepared from diamines and dibasic acids[19] and other series of polycondensation polymers consisting of flexible polymethylene segments of different lengths.[20]

Both P3DMLT and P5DMLT are exceptional in showing exotherms due to cold crystallization. This indicates that, in contrast with all other members of the series, these polyamides were not well-crystallized upon precipitation. This may account for the exceptional hydrophilicity and solubility in water displayed by these polymers which was described above.

After rapid cooling to room temperature, second heating thermograms were recorded for each polymer. They display well-defined slope changes arising from second-order transitions in the temperature range 80–120 °C. The values calculated for the T_g/T_m ratio in degrees Kelvin lie between 0.69 and 0.79, not very far from the 2/3 value defined by the Boyer–Beaman rule.[21] All these data are compiled in Table III. These second heating traces, when registered from P*n*DMLT with $n \geq 4$, displayed crystallization exotherms followed by melting peaks comparable to those detected during the first heatings. On the contrary, no thermal flow was observed in thermograms obtained from either P2DMLT or P3DMLT at any cooling rate. These two polyamides seem to partially decompose on melting. For illustration, both first and second heating traces registered from P5DMLT and P8DMLT are reproduced in Figure 5.

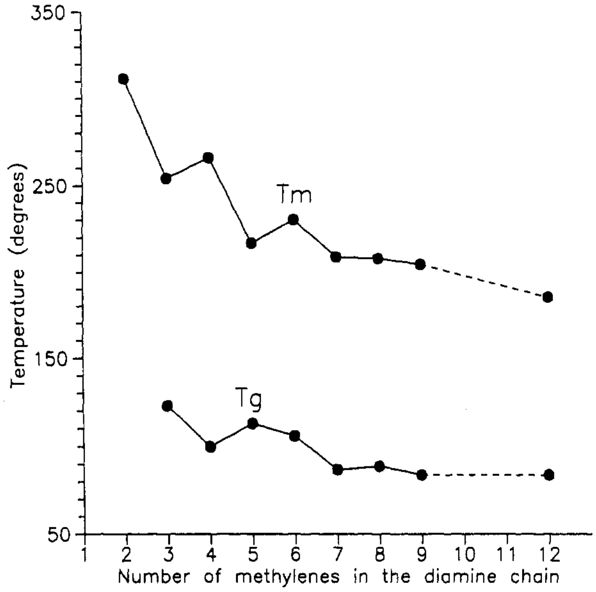


Figure 4. Observed glass transitions (T_g) and melting temperatures (T_m) of P*n*DMLT.

Optical Activity. One of the main purposes of designing our route of synthesis for the preparation of P*n*DMLT was to retain the original configuration of L-tartaric acid throughout the whole process. As discussed above, NMR data as well as the high crystallinity exhibited by these polyamides are in favor of their stereoregularity. Additional evidence in support of their stereoregular structure is provided by the large optical activity that they display in solution. In Figure 6, specific optical rotations measured in formic acid are plotted against the number of methylenes contained in the diamine unit and their values are given in Table III. As expected, optical activities are found to decrease with the density of chiral centers in the chain and their values fit well with those reported for *N*,*N*′-dialkyl-*O*-dimethyl-L-tartaramides,[13] in particular when compounds with the same number ratio of aliphatic carbon atoms to chiral centers are compared. A similar

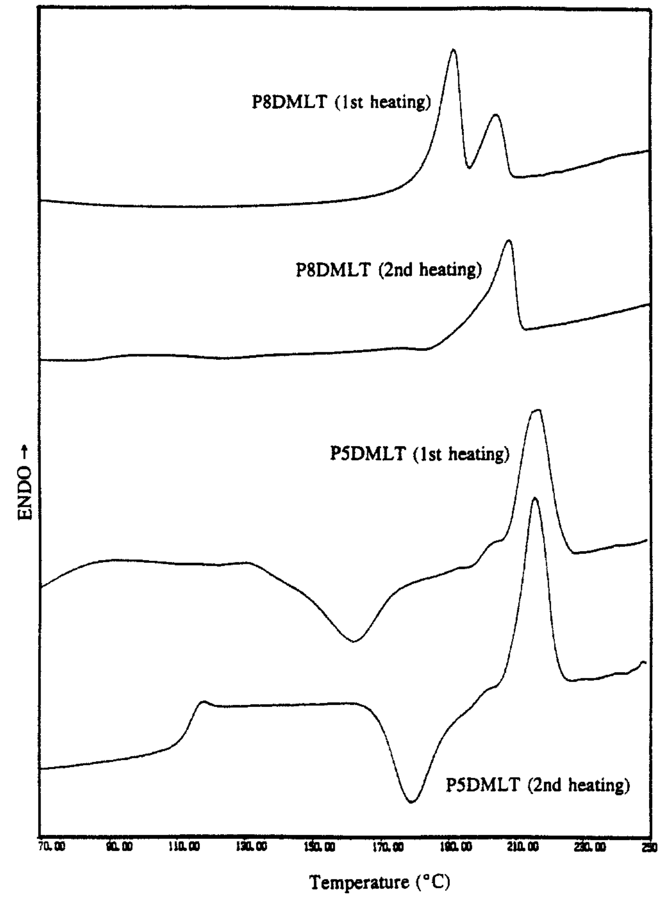


Figure 5. First and second heating traces recorded from polyamides P5DMLT and P8DMLT, as indicated.

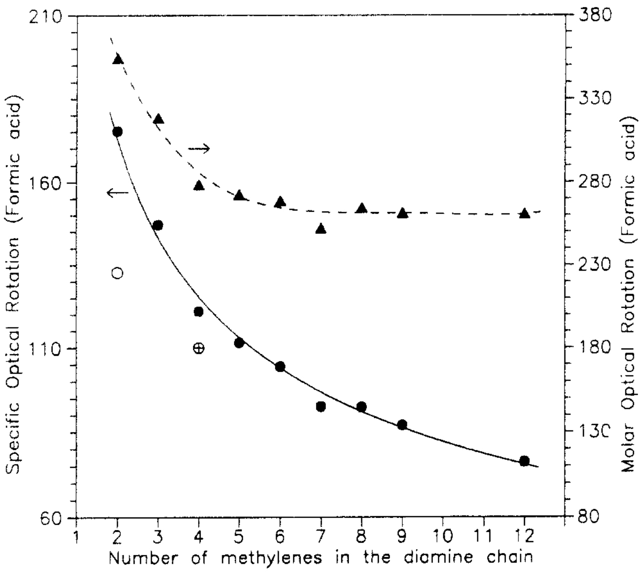


Figure 6. Specific and molar optical rotations of P*n*DMLT plotted against the number of methylenes in the repeating unit of the polymer. Measurements were made in formic acid at 23 °C. (○) *N,N'*-Dimethyldi-*O*-methyl-L-tartaramide. (●) *N,N'*-Diethyldi-*O*-methyl-L-tartaramide.

trend is observed for molar optical rotations ($[\Phi]^{23}_{\mathrm{D}} = [\alpha]^{23}_{\mathrm{D}} \times M_0/100$), which indicates that the distance between chromophores along the chain should be a second effect contributing to the optical activity.

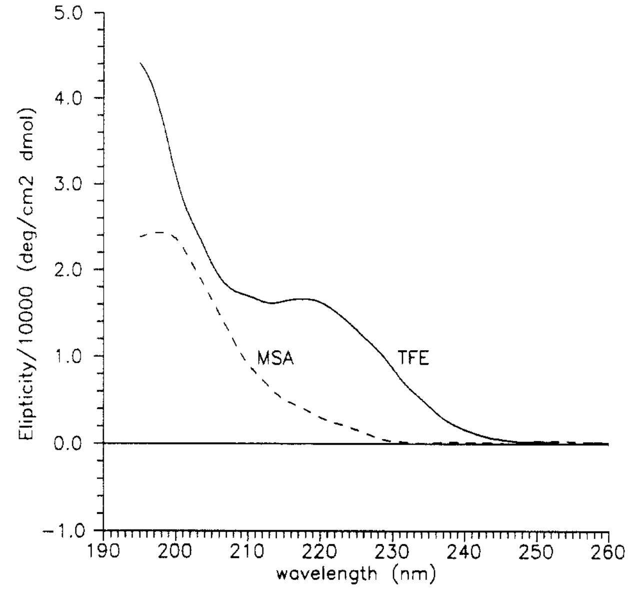


Figure 7. CD spectra of P2DMLT in trifluoroethanol (TFE) and methanesulfonic acid (MSA).

The flexibility of a P*n*DMLT chain will vary with the length of the polymethylene segment, the tartaric unit being rather rigid due to both the restricted rotation of the amide bonds and the repulsive interactions between the two side methoxy groups. In order to get insight into the conformation assumed by these polyamides in solution, we have examined them by circular dichroism in trifluoroethanol. A spectrum with a plateau centered around 220 nm, likely consisting of two overlapping maxima, was found to be common to all of these polyamides (Figure 7). This suggests that no qualitative conformational differences must exist amongst them. Nevertheless, drastic changes were observed when CD spectra were recorded in methanesulfonic acid. Although protonation of the amide unit will certainly cause a displacement of the maxima, such an effect is expected to be not as large as that observed in the present case. In a similar study carried out on asymmetric rigid polyamides derived from cyclic dicarboxylic acids and cyclic diamines, comparable displacements were observed which were explained in terms of the stabilization of the *trans* conformation over the *gauche* conformation due to protonation of amide groups.[22] Therefore, we may interpret in our case that a conformational changes takes place when trifluoroethanol is replaced by methanesulfonic acid, very probably involving the expansion of the polyamide chain due to both protonation and breaking of hydrogen bonds.

Concluding Remarks

Our results prove that high molecular weight stereoregular polyamides may be prepared from L-tartaric acid and alkanediamines once these compounds are conveniently modified into highly reactive monomers. The method may be considered of general application and valuable for the attainment of chiral polyamides of the AABB type, in particular when mild conditions are required in order to preserve configuration and to avoid side reactions leading to cross-linked polymers. The resulting poly(tartaramides) are markedly hydrophilic and optically active, and those containing polymethylene segments of four or more units can be reversibly melted. The study of the biodegradable properties of these new polyamides is currently under investigation.

Experimental Section

Materials. All reagents were PA grade or higher and used without further purification. Solvents to be used under anhydrous conditions were severely dried by standard methods. Viscosities were measured in dichloroacetic acid at 25.0 ± 0.1 °C, by using an Ubbelohde microviscosimeter. Infrared spectra were recorded on a Perkin-Elmer 783 spectrometer from films as either pure liquids or solids. ^{1}H and ^{13}C NMR spectra were registered in deuterated chloroform with a Varian XL GEM-200 (200 MHz) spectrometer. Molecular weight distributions were determined by GPC in a Waters Associates instrument fitted with a 10^4- and 10^3-Å PL gel column set. Calibration was made against polystyrene standards. Solubility tests were performed following the methodology described by Braun,[23] and water sorptions were measured at 100% relative humidity by the method described by Mori.[24] Thermal studies were carried out under a nitrogen atmosphere on a Perkin-Elmer DSC-4 instrument calibrated with indium. Samples with sizes of about 5 mg were heated at a rate of 20 °C/min and cooled down to room temperature at high rates. Optical rotations were measured in a Perkin-Elmer 141 polarimeter at 23 °C. Circular dichroism measurements were performed in solution (trifluoroethanol or methanesulfonic acid, $c = 10^{-3}$ mol/L) at 23 °C on a Jasco J-700 apparatus fitted with a cell of an optical path length of 1 mm.

Synthesis of Monomers. Diethyl Di-*O*-methyl-L-tartrate (II). A solution of diethyl L-tartrate (**I**; 103 g, 0.5 mol) in dimethyl sulfate (130 g, 1.0 mol) was added dropwise into a vigorous stirred suspension of sodium hydride (1 mol, 40 g of a 60% NaH dispersion in mineral oil) in dried diethyl ether under a nitrogen atmosphere, for a period of 3 h. The evolution of the reaction was followed by a change in color from gray to white. The generated salty solids were removed by filtration and the clear filtrate concentrated to a slightly yellow oil. This product was subjected to distillation under vacuum [87–89 °C (0.1 mm)] to give **II**. Yield: 100 g (85%). $[\alpha]^{23}_{\mathrm{D}}$: +78.5° (*c* 0.547, in ethanol) [lit.[12] $[\alpha]^{23}_{\mathrm{D}}$ +84°]. ^{13}C NMR (CDCl$_3$): δ 13.83, 59.30, 60.88, 80.71, 168.73. Anal. Calcd for $C_{10}H_{18}O_6$: C, 51.27; H, 7.75. Found: C, 51.00; H, 7.79.

Di-*O*-methyl-L-tartaric Acid (III). 1 M NaOH (400 mL) was added dropwise to a stirred solution of **II** (46.8 g, 0.2 mol) in ethanol (200 mL) cooled to 0 °C, for a period of 3 h. After stirring for another 1 h at room temperature, 12 M HCl (33.5 mL) was added dropwise to reach a pH between 2.0 and 3.0. The mixture was then evaporated, the residue dispersed in ethyl acetate–ethanol (9:1), and the dispersion concentrated to dryness. This operation was repeated twice. The final residue was suspended in boiling ethyl acetate, and any sodium chloride remaining undissolved was separated by hot filtering. Upon concentration of the filtrate, crystallization of **III** started and prosecuted overnight in the freezer. Additional amounts were recovered from the mother liquids upon further concentration. Yield: 26.1 g (73%). Mp: 152 °C (lit.[12] mp 155–157 °C). $[\alpha]^{23}_{\mathrm{D}}$: +84° (*c* 1.935, in ethanol) [lit.[12] $[\alpha]^{23}_{\mathrm{D}}$ +84 °C]. ^{13}C NMR (CDCl$_3$): δ 59.8, 80.3, 171.6. Anal. Calcd for $C_6H_{10}O_6$: C, 40.45; H, 5.66. Found: C, 40.37; H, 5.68.

Bis(pentachlorophenyl) Di-*O*-methyl-L-tartrate (IV). A total of 17.8 g (0.1 mol) of the diacid **III**, 53.3 g (0.2 mol) of pentachlorophenol, and 31.6 g (0.4 mol) of anhydrous pyridine were dissolved in 400 mL of chlorobenzene, and the mixture was cooled to 0 °C. To this solution was added dropwise under stirring 23.8 g (0.2 mol) of freshly distilled SOCl$_2$ in 100 mL of chlorobenzene. The reaction mixture was then heated to 60 °C, stirred at this temperature for 5 h, and left overnight at room temperature. The formed solids were filtered off, and the clear filtrate was evaporated to dryness. The solid residue was washed twice with diethyl ether and crystallized from carbon tetrachloride. Yield: 48.7 g (72%). Mp: 179.5 °C. $[\alpha]^{23}_{\mathrm{D}}$: −38.25° (*c* 2.08, in chloroform). IR (cm^{-1}, KBr): 1800 and 1771 (C=O). ^{1}H NMR (CDCl$_3$): δ 3.70 (s, CH$_3$, 6H), 4.80 (s, CH, 2H). ^{13}C NMR (CDCl$_3$): δ 59.9, 80.4, 127.4, 132.2, 132.4, 143.5, 164.8. Anal. Calcd for $C_{18}H_8Cl_{10}O_6$: C, 32.04; H, 1.19; Cl, 52.54. Found: C, 32.00; H, 1.18; Cl, 52.93.

***N,N'*-Bis(trimethylsilyl)alkanediamines (V*n*)** were prepared by following the general methodology described by Pierce[25] for the obtention of trimethylsilylated amines. The common procedure was as follows: To a solution of the diamine (0.1 mol) in the appropriate solvent (200 mL) was added under conditions of rigorous exclusion of moisture trimethylsilyl chloride (22.0 g, 0.202 mol). After stirring for 1 h, 0.202 mol (20.1 g) of triethylamine was added under vigorous stirring, which was maintained for a further 3 h. The mixture was then refluxed for 1 h, left to cool down to room temperature, and filtered under a nitrogen atmosphere. Upon concentration, the filtrate yielded an oily residue which was distilled to give the corresponding trimethylsilylated alkanediamine V*n*. Specific reaction conditions used in each case as well as some characterization data of these products are given in Table IV.

Table IV. Properties of *N,N'*-Bis(trimethylsilyl)alkanediamines (TMS–NH–(CH$_2$)$_n$–NH–TMS)

n	reaction solvent	yield (%)	bp (°C), pressure (mmHg)	characteristic IR bands (cm^{-1}) NH	characteristic IR bands (cm^{-1}) Si(CH$_3$)$_3$
2	diethyl ether	53.2	53–57, 1.0	3394	1449, 1389, 1245
3	benzene	54.0	74–80, 1.0	3398	1459, 1388, 1245
4	THF	52.2	114–117, 1.0	3402	1434, 1394, 1246
5	benzene	58.6	68–71, 0.1	3399	1433, 1393, 1244
6	toluene	69.0	77–80, 0.1	3402	1432, 1393, 1245
7	toluene	40.7	85–90, 0.1	3397	1458, 1392, 1244
8	toluene	58.6	102–105, 0.1	3401	1433, 1391, 1242
9	toluene	65.0	105–110, 0.1	3401	1460, 1393, 1245
12	toluene	65.0	120–130, 0.1	3399	1460, 1393, 1244

Synthesis of Polymers. General Procedure of Polycondensation. To a stirred solution of the corresponding *N,N'*-bis(trimethylsilyl)alkanediamine (**V*n***) in dried chloroform at 0 °C was added in small portions under a nitrogen atmosphere compound **IV**. The mixture was allowed to reach room temperature and left to proceed for 3 days. Then the reaction mixture was diluted with a half volume of chloroform and the solution heated at 60 °C for 2 h. The polyamide was precipitated by pouring the gelly reaction mixture onto either boiling ethanol or diethyl ether and recovered by centrifugation as a white powdered solid. After repeated washings with ethanol or ether, the polymer was dried under vacuum.

Poly(ethylenedi-*O*-methyl-L-tartaramide) (P2DMLT). A total of 6.62 g (9.8 × 10^{-3} mol) of **IV** was reacted with 2.00 g (9.8 × 10^{-3} mol) of **V2** in 20 mL of chloroform. The polymer was precipitated with ethanol and washed with ether. Yield: 1.92 g (96.7%). Anal. Calcd for $(C_8H_{14}O_4N_2\cdot{}^1/_2H_2O)_n$ [$(211.22)_n$]: C, 45.49; H, 7.16; N, 13.26. Found: C, 45.00; H, 7.00; N, 12.63. IR (cm^{-1}, film from TFE): 3292 (amide A), 3059 (amide B), 1654 (amide I), 1524 (amide II). ^{1}H NMR (TFA-*d*): δ 11.60 (s, H^a, 2H), 4.52 (s, H^b, 2H), 3.75 and 3.59 (2s, H^d and H^c, 10H). ^{13}C NMR (TFA-*d*): δ 174.42 (C^a), 82.45 (C^b), 61.90 (C^c), 40.77 (C^d).

Poly(trimethylenedi-*O*-methyl-L-tartaramide) (P3DMLT). A total of 9.72 g (14.4 × 10^{-3} mol) of **IV** was treated with 3.14 g (14.4 × 10^{-3} mol) of **V3** in 30 mL of chloroform. Addition of ethanol led to an emulsion from which the polymer was recovered by adding diethyl ether. Yield: 2.10 g (67.6%). Anal. Calcd for $(C_9H_{16}O_4N_2\cdot H_2O)_n$ [$(234.26)_n$]: C, 46.14; H, 7.74; N, 11.96. Found: C, 47.10; H, 7.47; N, 11.80. IR (cm^{-1}, film from TFE): 3286 (amide A), 3057 (amide B), 1649 (amide I), 1524 (amide II). ^{1}H NMR (TFA-*d*): δ 11.65 (s, H^a, 2H), 4.54 (s, H^b, 2H), 3.65 (s, H^c and H^d, 10H), 2.03 (m, H^e, 2H). ^{13}C NMR (TFA-*d*): δ 174.15 (C^a), 82.33 (C^b), 61.91 (C^c), 38.67 (C^d), 29.10 (C^e).

Poly(tetramethylenedi-*O*-methyl-L-tartaramide) (P4-DMLT). A total of 6.79 g (10.1 × 10^{-3} mol) of **IV** was treated with 2.34 g (10.1 × 10^{-3} mol) of **V4** in 20 mL of chloroform. Precipitation and washing of the polymer with diethyl ether were performed. Yield: 2.09 g (91.3%). Anal. Calcd for $(C_{10}H_{18}O_4N_2\cdot H_2O)_n$ [$(248.28)_n$]: C, 48.37; H, 8.12; N, 11.28. Found: C, 49.38; H, 7.70; N, 11.12. IR (cm^{-1}, film from TFE): 3273 (amide A), 3061 (amide B), 1654 (amide I), 1525 (amide II), 763 (amide V). ^{1}H NMR (TFA-*d*): δ 11.42 (s, H^a, 2H), 4.44 (s, H^b, 2H), 3.60 (2s, H^c and H^d, 10H), 1.76 (m, H^e, 4H). ^{13}C NMR (TFA-*d*): δ 174.15 (C^a), 82.33 (C^b), 61.91 (C^c), 38.67 (C^d), 29.10 (C^e).

Poly(pentamethylenedi-*O*-methyl-L-tartaramide) (P5-DMLT). A total of 3.64 g (5.4 × 10^{-3} mol) of **IV** was treated with 1.33 g (5.4 × 10^{-3} mol) of **V5** in 10 mL of chloroform. Precipitation and washing of the polymer with ethanol were performed. Yield: 1.20 g (91.3%). Anal. Calcd for $(C_{11}H_{20}O_4N_2\cdot{}^1/_2H_2O)_n$ [$(253.30)_n$]: C, 52.15; H, 8.36; N, 11.06. Found: C, 52.27; H, 7.95; N, 10.89. IR (cm^{-1}, film from TFE): 3287 (amide A), 3060 (amide B), 1655 (amide I), 1543 (amide II), 752 (amide V). ^{1}H NMR (CDCl$_3$): δ 6.80 (t, H^a, 2H), 4.21 (s, H^b, 2H), 3.42 (s, H^c, 6H), 3.32 (m, H^d, 4H), 1.59 (m, H^e, 4H), 1.42 (m, H^f, 2H). ^{13}C NMR

(CDCl$_3$): δ 169.39 (C^a), 82.28 (C^b), 60.57 (C^e), 38.94 (C^d), 29.22 (C^e), 23.96 (C^f).

Poly(hexamethylenedi-*O*-methyl-L-tartaramide) (P6-DMLT). A total of 6.75 g (10.0 × 10^{-3} mol) of **IV** was treated with 2.60 g (10.0 × 10^{-3} mol) of **V6** in 20 mL of chloroform. Precipitation and washing of the polymer with ethanol were performed. Yield: 2.40 g (92.9%). Anal. Calcd for $(C_{12}H_{22}O_4N_2)_n$ $[(258.32)_n]$: C, 55.80; H, 8.58; N, 10.84. Found: C, 55.23; H, 8.62; N, 10.64. IR (cm^{-1}, film from CHCl$_3$): 3276 (amide A), 3047 (amide B), 1651 (amide I), 1526 (amide II), 753 (amide V). ^{1}H NMR (CDCl$_3$): δ 6.72 (t, H^a, 2H), 4.21 (s, H^b, 2H), 3.42 (s, H^c, 6H), 3.31 (t, H^d, 4H), 1.54 (m, H^e, 4H), 1.37 (m, H^f, 2H). ^{13}C NMR (CDCl$_3$): δ 169.29 (C^a), 82.21 (C^b), 60.55 (C^c), 38.98 (C^d), 29.46 (C^e), 26.36 (C^f).

Poly(heptamethylenedi-*O*-methyl-L-tartaramide) (P7-DMLT). A total of 3.52 g (5.20 × 10^{-3} mol) of **IV** was treated with 1.42 g (5.20 × 10^{-3} mol) of **V7** in 10 mL of chloroform. Precipitation and washing of the polymer with ethanol were performed. Yield: 1.40 g (98.7%). Anal. Calcd for $(C_{13}H_{24}O_4N_2)_n$ $[(272.34)_n]$: C, 57.33; H, 8.88; N, 10.29. Found: C, 57.05; H, 8.81; N, 10.19. IR (cm^{-1}, film from CHCl$_3$): 3284 (amide A), 3058 (amide B), 1654 (amide I), 1525 (amide II), 755 (amide V). ^{1}H NMR (CDCl$_3$): δ 6.74 (t, H^a, 2H), 4.22 (s, H^b, 2H), 3.42 (s, H^c, 6H), 3.31 (t, H^d, 4H), 1.53 (m, H^e, 4H), 1.37 (m, H^f and H^g, 6H). ^{13}C NMR (CDCl$_3$): δ 169.28 (C^a), 82.25 (C^b), 60.57 (C^c), 39.09 (C^d), 29.51 (C^e), 26.70 (C^f), 28.82 (C^g).

Poly(octamethylenedi-*O*-methyl-L-tartaramide) (P8-DMLT). A total of 6.68 g (9.90 × 10^{-3} mol) of IV was treated with 2.85 g (9.90 × 10^{-3} mol) of **V8** in 20 mL of chloroform. Precipitation and washing of the polymer with ethanol were performed. Yield: 2.83 g (99.8%). Anal. Calcd for $(C_{14}H_{26}O_4N_2)_n$ $[(286.37)_n]$: C, 58.78; H, 9.15; N, 9.78. Found: C, 57.68; H, 9.03; N, 9.42. IR (cm^{-1}, film from CHCl$_3$): 3273 (amide A), 3057 (amide B), 1656 (amide I), 1524 (amide II), 753 (amide V). ^{1}H NMR (CDCl$_3$): δ 6.73 (t, H^a, 2H), 4.22 (s, H^b, 2H), 3.43 (s, H^c, 6H), 3.31 (m, H^d, 4H), 1.53 (m, H^e, 4H), 1.37 (m, H^f and H^g, 8H). ^{13}C NMR (CDCl$_3$): δ 169.29 (C^a), 82.29 (C^b), 60.60 (C^c), 39.15 (C^d), 29.54 (C^e), 26.74 (C^f), 29.13 (C^g).

Poly(nonamethylenedi-*O*-methyl-L-tartaramide) (P9-DMLT). A total of 6.75 g (10.0 × 10^{-3} mol) of **IV** was treated with 3.02 g (10.0 × 10^{-3} mol) of **V9** in 20 mL of chloroform. Precipitation and washing of the polymer with ethanol were performed. Yield: 2.88 g (96.0%). Anal. Calcd for $(C_{15}H_{28}O_4N_2)_n$ $[(300.40)_n]$: C, 59.98; H, 9.40; N, 9.33. Found: C, 59.36; H, 9.38; N, 9.18. IR (cm^{-1}, film from CHCl$_3$): 3276 (amide A), 3053 (amide B), 1651 (amide I), 1526 (amide II), 753 (amide V). ^{1}H NMR (CDCl$_3$): δ 6.74 (t, H^a, 2H), 4.22 (s, H^b, 2H), 3.43 (s, H^c, 6H), 3.31 (m, H^d, 4H), 1.53 (m, H^e, 4H), 1.29 (m, H^f, H^g, and H^h, 10H). ^{13}C NMR (CDCl$_3$): δ 169.24 (C^a), 82.21 (C^b), 60.55 (C^c), 39.10 (C^d), 29.48 (C^e) 26.68 (C^f), 29.03 (C^g), 29.32 (C^h).

Poly(dodecamethylenedi-*O*-methyl-L-tartaramide) (P12-DMLT). A total of 6.75 g (10.0 × 10^{-3} mol) of **IV** was treated with 3.44 g (10.0 × 10^{-3} mol) of **V9** in 20 mL of chloroform. Precipitation and washing of the polymer with ethanol were performed. Yield: 3.29 g (96.0%). Anal. Calcd for $(C_{18}H_{34}O_4N_2)_n$ $[(300.40)_n]$: C, 59.98; H, 9.40; N, 9.33. Found: C, 59.36; H, 10.08; N, 8.01. IR (cm^{-1}, film from CHCl$_3$): 3276 (amide A), 3055 (amide B), 1651 (amide I), 1527 (amide II), 754 (amide V). ^{1}H NMR (CDCl$_3$): δ 6.73 (s, H^a, 2H), 4.23 (s, H^b, 2H), 3.43 (s, H^c, 6H), 3.32 (m, H^d, 4H), 1.53 (m, H^e, 4H), 1.29 (m, H^f, H^g, H^h, and H^i, 16H). ^{13}C NMR (CDCl$_3$): δ 169.30 (C^a), 82.21 (C^b), 60.51 (C^c), 39.11 (C^d), 29.45 (C^e), 26.78 (C^f), 29.16 (C^g), 29.45 (C^h and C^i).

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References and Notes

(1) Selegny, E.; Merle-Aubry, L. In *Optically Active Polymers*; Selegny, E., Ed.; Reidel: Dordrecht, The Netherlands, 1979; pp 15–110.
(2) Hashimoto, K.; Sumimoto, H. *Macromolecules* **1980**, *13*, 786.
(3) Muñoz-Guerra, S. *Makromol. Chem., Macromol. Symp.* **1991**, *48/49*, 71.
(4) Lenz, R. V.; Guerin, P. *Polym. Sci. Technol.* **1983**, *23*, 219.
(5) Kumar, G. S. *Biodegradable Polymers: Prospects and Progress*; Marcel Dekker: New York, 1987; pp 50–55.
(6) Vert, M. *Angew. Makromol. Chem.* **1989**, *166/167*, 155.
(7) Bird, T. P.; Black, W. A. P.; Deward, E. T.; Hare, J. B. *J. Chem. Soc.* **1963**, 1208.
(8) Thiem, J.; Bachmann, F. *Makromol. Chem.* **1991**, *192*, 2175.
(9) Minoura, Y.; Urayama, S.; Noda, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1967**, *5*, 2441.
(10) Ogata, N.; Hosoda, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1793.
(11) Rodríguez-Galán, A.; Bou, J. J.; Muñoz-Guerra, S. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 713.
(12) Felner, I.; Schenker, K. *Helv. Chim. Acta* **1970**, *53*, 754.
(13) Seebach, D.; Kalinowski, H.; Bastani, B.; Crass, G.; Daum, H.; Dörr, H.; DuPreez, N. P.; Ehrig, V.; Langer, W.; Nüssler, C.; Oei, H.; Schmidt, M. *Helv. Chim. Acta* **1977**, *60*, 301.
(14) Oishi, Y.; Kakimoto, Y.; Imai, Y. *Macromolecules* **1988**, *21*, 547.
(15) Jacobi, E.; Schuttennberg, H.; Schulz, R. C. *Makromol. Chem., Rapid. Commun.* **1980**, *1*, 397.
(16) Bandrup, J.; Immergut, H. *Polymer Handbook*; Wiley: New York, 1989; Vol. VII, p 25.
(17) Cannon, C. G. *Spectrochim. Acta* **1960**, *16*, 302.
(18) Bell, J. P.; Slade, D. E.; Dumblenton, J. H. *J. Polym. Sci., Polym. Phys. Ed.* **1968**, *6*, 1773.
(19) Kinoshita, Y. *Makromol. Chem.* **1959**, *33*, 1.
(20) Doak, K.; Campbell, H. N. *J. Polym. Sci.* **1955**, *XVIII*, 213.
(21) Van Krevelen, D. W. *Properties of Polymers*; Elsevier: Amsterdam, The Netherlands, 1990; p 166.
(22) Montaudo, G.; Finocchiaro, P. In *Optically Active Polymers*; Selegny, E., Ed.; Reidel: Dordrecht, The Netherlands, 1979; pp 199–218.
(23) Braun, D.; Chedron, H.; Kern, W. *Praktikum der Makromolekularen Organischen Chemie*; Alfred Huthig Verlag: Heidelberg, Germany, 1966.
(24) Mori, T.; Tanaka, R.; Tanaka, T. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1633.
(25) Pierce, A. E. *Silylation of Organic Compounds*; Pierce Chemical Co.: Rockford, IL, 1968.