Synthesis and Properties of Stereoregular Polyamides Derived from L-Tartaric Acid: Poly[(2*S*,3*S*)-2,3-Dimethoxybutylene alkanamide]s

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Received February 18, 1994; Revised Manuscript Received May 23, 1994®

ABSTRACT: The synthesis of (2*S*,3*S*)-(−)-2,3-dimethoxy-1,4-butanediamine to be employed in the preparation of stereoregular polyamides 4,*n* containing two chiral carbons in the diamine repeating unit has been carried out by using L-tartaric acid as a raw material. Polycondensation in a chloroform solution of this diamine activated as the *N*,*N*′-bis(trimethylsilyl) derivative with pentachlorophenyl esters of even aliphatic diacids ranging from 4 to 12 carbons afforded the title polyamides with DP_n in the range 20–100 depending upon the value of *n*. They were characterized by elemental analysis, IR and $^1H/^{13}C$ spectroscopies, and powder X-ray diffraction. These highly crystalline polyamides melted in the range 150–190 °C, had a pronounced affinity to water, and exhibited moderate optical activity. All these properties were investigated in relation to the molecular structure and compared with those observed for their isomeric poly[alkylene 2,3-di-*O*-methyl-L-tartaramide]s, on which we have recently reported in detail.

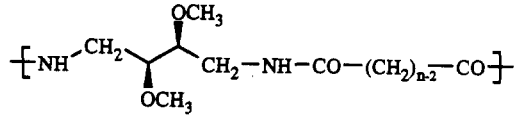
Introduction

The interest in the synthesis of acyclic carbohydrate-based polyamides is rapidly increasing.[1–4] The aim is not only to take benefit from these naturally occurring sources but also to develop advanced polymers with improved properties such as biodegradability and biocompatibility. On the other hand, the utilization of carbohydrate-based monomers gives access to a class of synthetic polymers containing several chiral centers in the backbone of the repeating unit. However, polycondensation of such highly functionalized compounds has several limitations, in particular when the preparation of stereoregular polymers is intended. One is the occurrence of side reactions on the hydroxyl lateral groups leading to either epimerization or branching. Another is the need to convert condensation monomers into activated derivatives prior to polycondensation. Although a variety of procedures are available for direct condensation of diacids with diamines,[5] the rather severe conditions usually required by these methods preclude their application to sensitive monomers. A last problem, which is related to the symmetrical properties of carbohydrate-based building blocks, is the possible regioisomerism (directional isomerism) that may occur in polyamides of the AABB type made from monomer lacking a 2-fold axis normal to the backbone of the molecule.

Polyaldaramide, i.e., polyamides derived from aldaric acids, have been the source of considerable interest for many years.[6–8] We have recently reported on optically active polytartaramides which were successfully obtained by polycondensation in solution of adequate protected bis(pentachlorophenyl) L-tartrates with *N*,*N*′-bis(trimethylsilyl) 1,*n*-alkanediamines.[9–11] They are in fact stereoregularly substituted polyamides *n*,4 containing two stereocenters in the diacid repeating unit. Since L-tartaric acid [(2*R*,3*R*)-(+)-2,3-dihydroxysuccinic acid] contains a 2-fold axis normal to the C_2–C_3 bond, the resulting polymers were regiochemically ordered. Because of their stereoregularity, an interesting combination of properties is observed for these substituted polyamides; they are highly crystalline, have mechanical properties comparable to those of nylons,[10] and may undergo hydrolytic degradation under physiological conditions.[12]

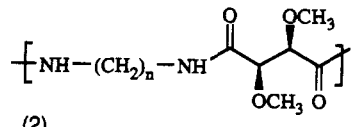
Whereas stereoregular polyaldaramides can be straightforwardly attained from natural L-tartaric acid and other accessible aldaric acids containing a 2-fold axis such as D-mannaric and D-idaric acids, the synthesis of optically active regioregular polyamides of the AABB type carrying the chiral carbons in the diamine moiety turns out to be much more laborious, since chiral diamines with C_2 symmetry are not easily available.

In this paper we describe the synthesis and properties of a series of stereoregular polyamides 4,*n* of general formula **1** by polycondensation of (2*S*,3*S*)-(−)-2,3-dimethoxy-1,4-butanediamine with aliphatic dicarboxylic acids. The optically active diamine has been prepared from L-tartaric acid by following a synthetic route through which the initial configuration of the hydroxy acid is preserved so that the regiochemical order of the resulting polymers may be ensured (Scheme 1). These poly(2,3-dimethoxybutylene alkanamide)s, abbreviated PDMBA*n*, are isomers of the corresponding poly(alkyene 2,3-di-*O*-methyl-L-tartaramide)s, abbreviated P*n*DMLT, of general formula **2**, which were described in full detail in a preceding paper.[11] These two polyamide series differ one from another only in the position occupied by the chiral unit with respect to the amide group. However, significant changes in conformation as well as in a number of related properties can be expected from such modification in the chemical structure. To appraise more precisely what are the consequences of such structural differences, continuous comparison between the two isomeric series will be made throughout this work.



PDMBA*n*

(1)



P*n*DMLT

(2)

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® Abstract published in *Advance ACS Abstracts*, August 1, 1994.

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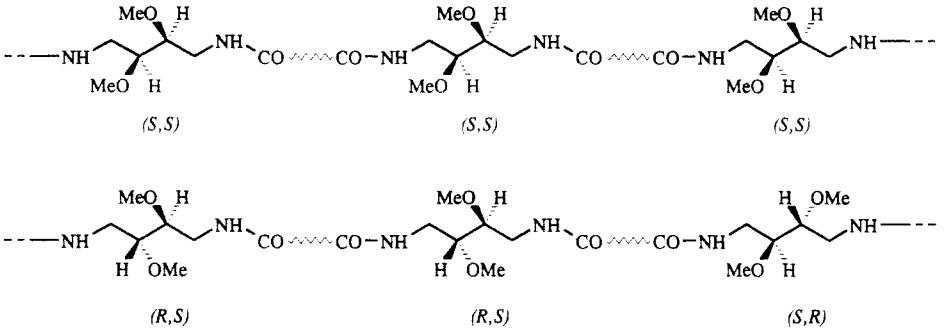
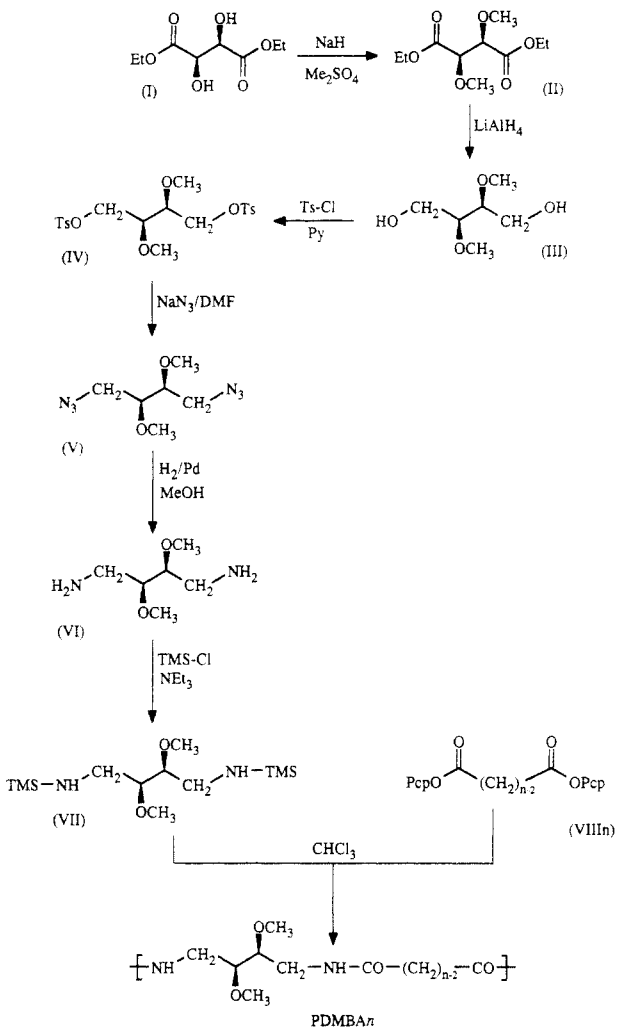
Scheme 1



Scheme 2



Results and Discussion

Synthesis. The route of synthesis designed for the preparation of PDMBA*n* is outlined in Scheme 2, where the following appreviations have been used: Ts = tosyl; DMF = *N*,*N*′-dimethylformamide; Pcp = pentachlorophenyl; TMS = trimethylsilyl. Polycondensations have been carried out in solution with the diamine activated as the trimethylsilyl derivative and the diacid as the pentachlorophenyl ester. This methodology had been successfully used by us in the preparation of both poly(alkylene 2,3-di-*O*-methylene-L-tartaramide)s[9] and poly(alkylene 2,3-di-*O*-methyl-L-tartaramide)s.[11] In the present case, hydroxyl side groups of L-tartaric acid have been converted into methyl ethers. In our experience, methylation has proven to be a very convenient protecting method because high stability is gained without increasing excessively the size of the repeating unit of the polyamide.

Commercial diethyl L-tartrate (**I**) is the starting material we have employed for obtaining the diamine **VI** by means of a sequence of synthesis consisting of five steps. Methylation of **I** to diethyl di-*O*-methyl-L-tartrate (**II**) was performed with dimethyl sulfate. Although this reaction requires strong basic conditions, both $^1H/^{13}C$ NMR and optical rotation data obtained from **II** indicated that no detectable epimerization took place in this step. **II** was transformed efficiently into the diazide **V** via the easily crystallizable ditosylate intermediate **IV**. Hydrogenation of **V** with palladium on charcol afforded the diamine **VI** in 84% yield. The ^1H and ^{13}C NMR spectra of **VI** assessed the high optical purity achieved in the preparation of this compound. It should be mentioned that the synthesis of **VI** has been earlier accomplished by reduction of di-*O*-methyl-L-tartaramide with lithium aluminum hydride in 9% yield.[13] We find that the method via diazide represents an efficient alternative route to attain **VI** in good yields and high purity. The *N*,*N*′-bis(trimethylsilyl) diamine **VII** was readily prepared by treating diamine **VI** with the trimethylsilyl chloride; although this compound may be conveniently isolated and purified by distillation, its extreme sensitivity to moisture makes difficult its extensive characterization by usual methods.

The synthesis of bis(pentachlorophenyl) esters (**VIII*n***) was performed by esterification of the corresponding aliphatic dicarboxylic acids by standard methods and proceeded without difficulties; all the active esters were purified by repeated crystallization. A compilation of the most relevant synthesis and characterization data of these compounds is given in the Experimental Section.

Polycondensations were carried out in a chloroform solution. We initially explored the conditions we had used for obtaining P*n*DMLT[11] and found that, in the present case, the reaction temperature needs to be increased to about 50 °C to solubilize the alkanedioic pentachlorophenyl esters in the polymerization solvent. Whereas polymerization reactions using compounds **VIII8**–**VIII12** entirely proceeded in a homogeneous phase, those leading to PDMBA4 and PDMBA6 were observed to take place with precipitation of the forming polymer from the reaction medium. As a result, considerably lower molecular weights were encountered for these products (Table 1). Attempts to carry out polycondensations in other solvents of known

Table 1. Polymerization Data of Polyamides PDMBA*n*

polyamide	yield (%)	$[\eta]$ (dL/g)[b]	M_v[c]	M_n[d]	M_w[d]	D	DP[e]
PDMBA4	54[a]	0.44	6260	4300	7100	1.65	19
PDMBA6	50[a]	0.45	6520	13900	16900	1.21	54
PDMBA8	91	0.80	18700	28600	62700	2.19	100
PDMBA10	65[a]	0.53	8800	19500	26900	1.38	62
PDMBA12	85	0.77	17400	29200	44800	1.53	85

[a] After precipitation from formic acid with acetone. [b] Measured in dichloroacetic acid at 25 °C. [c] Calculated by applying the viscosimetric equation reported for nylon 6,6,[16] $100[\eta] = 0.5 + 0.352M^{0.561}$. [d] Obtained by GPC of trifluoroacetylated samples calibrated against polystyrene standards. [e] Average polymerization degrees calculated from M_n.

effectiveness for these polyamides, as is the case for *N*-methylpyrrolidone, but in which the active esters remained unsolubilized invariably resulted in oligomeric products.

Previous procedures described in the literature to obtain L-tartaric acid-based polyamides from nonactivated monomers fail in yielding stereoregular polymers with acceptable molecular weights.[14,15] Our preceding work on polytartaramides[11] revealed that activation of both comonomers seems to be essential to attain satisfactory results. In the case of PDMBA*n*, limiting viscosity numbers between 0.44 and 0.80 have been achieved by this method. M_v between 6000 and 19000 are roughly estimated from such viscosity numbers if the viscosimetric parameters reported for nylon 6,6 are used for calculations.[16] The molecular weight distributions of these polyamides were analyzed by GPC of trifluoroacetylated samples according to the method of Schulz.[17] M_w within the range 7000–63000 and polydispersities varying from 1.2 to 2.2 were measured by this technique which indicate that the estimates obtained by viscosimetry should be only taken as approximate minimum references. Although the molecular weights of these polyamides may be considered as satisfactory when compared with those reported on polytartaramides prepared by direct methods, they are clearly inferior to those achieved for polyamides P*n*DMLT. These differences are understandable in light of the reaction mechanism and what can be expected from the influence exerted by the electron-withdrawing methoxy group on reactivity in each case. The presence of the methoxy in the diamine is expected to diminish the basicity of this compound and therefore to hinder the nucleophilc attack on the carboxyl carbon of the diacid. This effect is just opposed to that operating when such a group is attached to the diacid, as happens in the synthesis of P*n*DMLT; in such a case, the carbonyl susceptibility toward the nucleophilic attack will be enhanced and the amidation reaction therefore favored.

Characterization of PDMBA*n*. Elemental microanalysis data are consistent with the constitution expected for these polyamides. The chain structure of PDMBA*n* was confirmed by both infrared and ^1H and ^{13}C NMR spectroscopies, as detailed in the Experimental Section. Infrared spectra exhibited characteristic absorptions frequencies of polyamides appearing at about 3280 (amide A), 3070 (amide B), 1640 (amide I), and 1540 cm^{-1} (amide II) in addition to a strong band at nearly 1100 cm^{-1} corresponding to the stretching of the C–O–C ether group. No absorptions indicative of end chain groups are detected.

Both ^1H and ^{13}C NMR spectra in DMSO-d_6 are also in full agreement with the chemical structure of PDMBA*n* and neither of them contains signals corresponding to end chain groups. However, signals arising from different types of protons in the diamine moiety appear overlaid in the ^1H spectra. To verify the stereoregularity of the polymers, additional efforts were made to analyze the proton spectra in detail. When spectra were registered in deuterated trifluoroacetic acid solution, every signal was observed to move slighlty downfield due to ionization of NH groups. Furthermore, the complex signal arising from the CH_2CH system became resolved as an apparent pentuplet which was well separated from the singlet corresponding to the methyl protons. On the other hand, ^{13}C spectra exhibit well-resolved signals for every carbon contained in the repeating unit including those in the polymethylene chain; no resonance splitting is detected for those carbons which are expected to be particularly sensitive to stereochemical configuration, as they are $HNCH_2$, CH, and OCH_3. An accurate assignment of both ^1H and ^{13}C spectra could be achieved with the assitance of 2D analysis including homonuclear ^1H–^1H and heteronuclear ^1H–^{13}C correlation experiments. Both 1D- and 2D-NMR spectra of polyamide PDMBA10 obtained by polycondensation of diamine **VII** with the bis(pentachlorophenyl) ester of sebacic acid are shown in Figure 1 for illustration. The ^1H–^{13}C spectra revealed that ^{13}C peaks appearing below 40 ppm correlate with protons in the diacid unit whereas the peaks at 43.5 and 81.2 ppm correlate with the diastereotopic methylene and methine protons, respectively. The peak at 60.2 ppm obviously corresponds to the methyl side carbon. The ^1H–^1H spectra showed clearly that the five peaks appearing with chemical shifts between 3.70 and 4.20 ppm arise from a single ABX system integrated by the methine and methylene protons of the diamine unit. These results allow us to conclude that no significant epimerization giving rise to *R,S* or *R,R* configurations happened during the synthesis of PDMBA*n*.

Films of PDMBA*n* prepared by slow evaporation of formic acid solutions display a notable birefringence associated with a well-developed spherulitic texture (Figure 2a). Powder X-ray diagrams produced by these films consist of a number of well-defined ring reflections, indicating that the crystallinity of these polyamides is remarkable. The X-ray pattern registered from a sediment of spherulites of PDMBA12 obtained by crystallization in glycerine is reproduced in Figure 2b for illustration. Well-oriented fiber diagrams are also obtained from samples stretched both from solution and from the melt. Bragg spacings corresponding to the reflections which are characteristic for each polyamide are indicated in the sixth column of Table 3. Spacings within the range 1.04–1.28 nm steadily increase with the length of the repeating unit of the polyamide, indicating that they must be associated with *hkl* planes with $l \neq 0$. On the other hand, reflections at about 0.50 and 0.44 nm remain substantially unchanged along the series as logically expected for *hk*0 interplanar distances. A simple comparison of these patterns with those arising from unsubstituted nylons reveals significant deviations from the typical crystal structures of nylons. In Figure 3, the powder X-ray profiles of two selected PDMBA*n* are compared with that corresponding to nylon 4,6. The pattern of this nylon consists essentially of two reflections at 0.44 and 0.38 nm arising from the 100 and 010 planes, respectively,[18] which are the spacings characteristic of unsubstituted nylons in the α form.[19] The presence of reflections corresponding to spacings above ~0.7 nm in the X-ray diagrams of PDMBA*n* strongly suggest that not only the lateral packing of the chains is changed in these polyamides, as reasonably anticipated from the existence of lateral groups, but the conformation of the main chain should be also different. A detailed structural study including both the P*n*DMLT and PDMBA*n* polyamide series will be published in the near future.

Properties of PDMBA*n*. The two methoxy groups attached to the backbone chain make these polyamides markedly hydrophilic. Adsorbed water becomes so tightly bound to the polymer that it cannot be removed by the usual methods of drying. This effect would logically increase with the concentration of methoxy groups in the repeating unit of the polyamide. Such a prediction is confirmed by the increasing amount of water that is necessary to add to the repeating unit formula to fit the experimental combustion analysis data to the calculated values; by these means water contents ranging from 2 to 5% (w/w) were estimated to be present in PDMBA*n* depending on the value of *n*. The situation is quite similar to that observed for P*n*DMLT[11] although in the latter case the presence of moisture could be only detected for polyamides with $n \leq 5$.

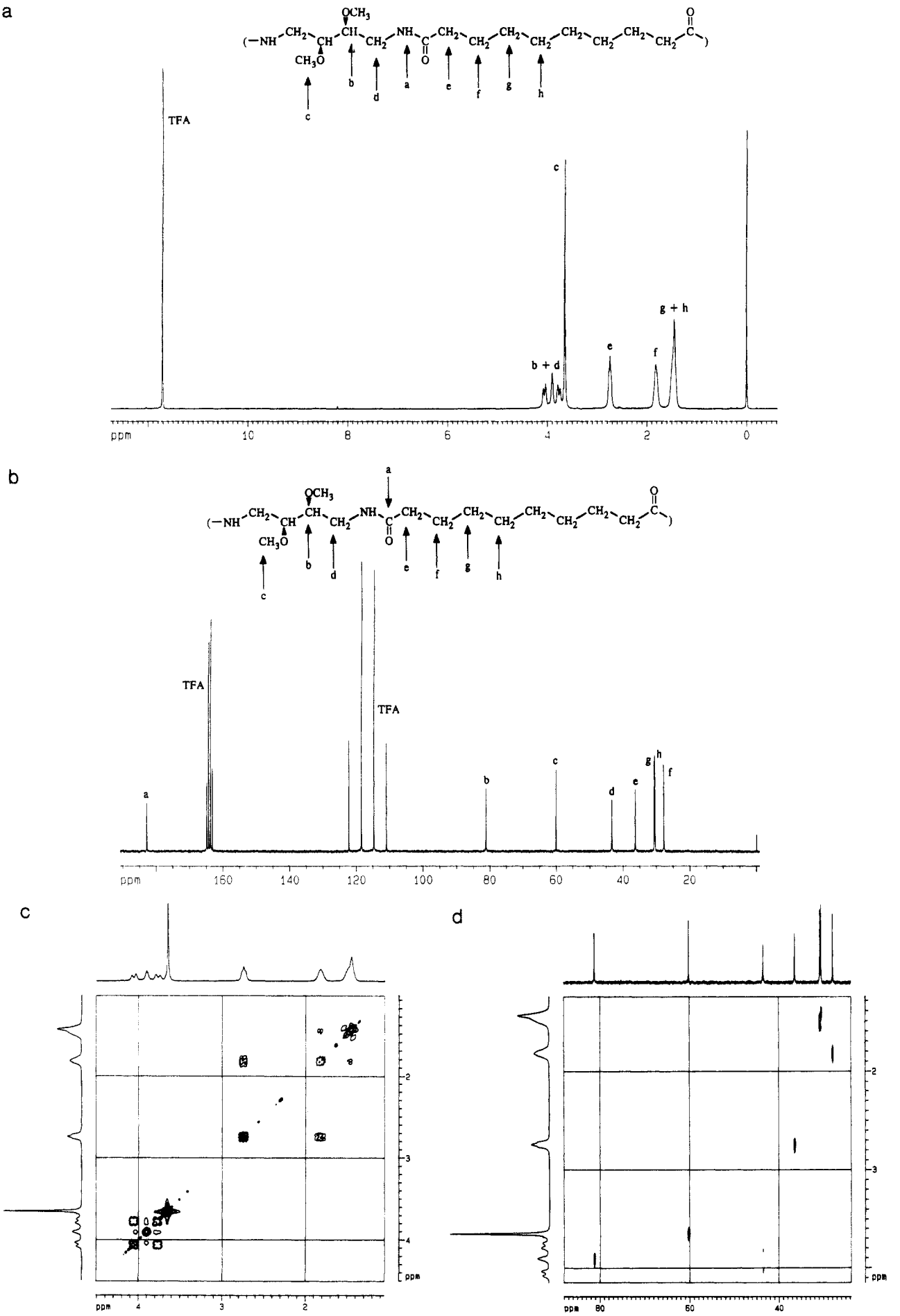


Figure 1. NMR spectra of PDMBA10 recorded in CF_3COOD at 25 °C: (a) and (b), 300.13 MHz ^1H NMR and 70.48 MHz ^{13}C NMR spectra, respectively: (c) ^1H–^1H (COSY) 2D-NMR spectrum; (d) ^1H–^{13}C (HXCO) 2D-NMR spectrum.

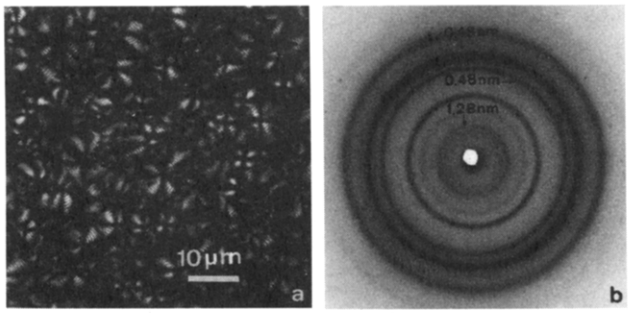


Figure 2. (a) Spherulitic film of PDMBA12 obtained by casting in formic acid. (b) Powder X-ray diagram from a spherulitic sediment of the same polyamide.

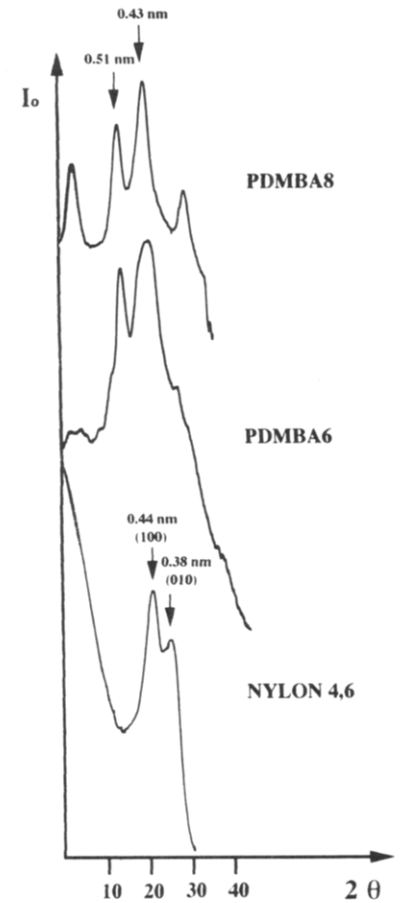


Figure 3. Comparative plot of the powder X-ray profiles of PDMBA6, PDMBA8, and nylon 4,6.

Table 2. Compared Qualitative Solubilities of PDMBA*n*[a]

solvent	PDMBA4	PDMBA6	PDMBA8	PDMBA10	PDMBA12
water	++	++	±	–	–
diethyl ether	–	–	–	–	–
ethanol	++	++	+	+	+
chloroform	±	–	●	+	+
DMSO	++	++	+	+	+
DMF	●	+	±	±	±
NMP	±	+	+	+	+
formic acid	++	++	++	++	++
TFE	++	++	++	++	++

[a] Estimated according to the method of Braun.[25] (–) 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; TFE = trifluoroethanol.

Qualitative solubilities of PDMBA*n* in a variety of solvents are compared in Table 2. Noticeable differences in solubility between these polyamides and P*n*DMLT were found. In sharp contrast to the latter, they are scarcely soluble in chloroform, a solvent which appears highly efficient for optically active polyamides adopting regular conformations in solution.[20] On the contrary, they swell or even become dissolved in ethanol, a very unusual solvent for conventional polyamides. The appreciable solubility in water displayed by the lower members of the series is not less striking, in particular that observed for PDMBA6, since its P6DMLT isomer was found to be water resistant. As reasonably anticipated, all PDMBA*n* are readily soluble in hydrogen bond-breaking solvents as formic acid and trifluoroethanol and they do not dissolve in nonaggresive oxygenated solvents as acetone or ethyl ether. In summary, it can be concluded that the solubility of these polyamides appears to be notably enhanced when compared not only with conventional nylons but also with their P*n*DMLT isomers.

Differences in hydrophilicity and solubility between PDMBA*n* and P*n*DMLT may be explained if dissimilarities in the distribution of polar and nonpolar groups along their respective chains are taken into account. Both types of polyamides may be envisaged as consisting of a succession of highly hydrophilic blocks regularly spaced out by hydrophobic polymethylene segments. Whereas in P*n*DMLT the spacer consists of n CH_2 units, only $n-2$ methylenes are inserted between two consecutive amide groups in the chain of isomeric PDMBA*n*, the other two being incorporated in the hydrophilic block.

The thermal behavior of PDMBA*n* was investigated by DSC on samples coming straight from synthesis. Typical traces are shown in Figure 4 for the case of PDMBA10. In general, well-defined endotherms corresponding to melting transitions were found during the first heating cycle at temperatures between 149 and 187 °C (Table 3). Two peaks were observed in some cases due to the fusion of two populations of crystallites of different size.[21] Melting points turn out to be notably lower than those

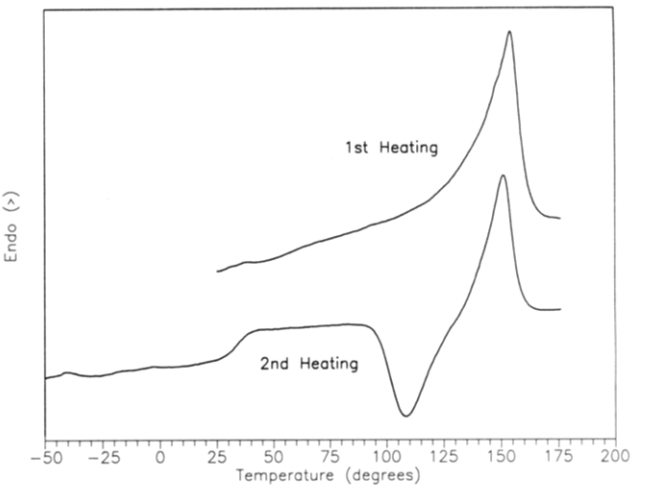


Figure 4. First and second heating traces from PDMBA10.

Table 3. Some Properties and Characterization Data of Polyamides PDMBA*n*

polyamide	$[\alpha]^{23}_D$[a]	T_g (°C)[b]	T_m (°C)[b]	T_g/T_m (K/K)	*d* (nm)[c]
PDMBA4	–14.1	80	187	0.77	0.53, 0.44, 0.35
PDMBA6	–12.3	63	149	0.80	1.04, 0.78, 0.53, 0.44, 0.35
PDMBA8	–11.5	52	172	0.73	1.06, 0.76, 0.51, 0.43, 0.35
PDMBA10	–10.4	35	154	0.72	1.10, 0.69, 0.48, 0.43, 0.35
PDMBA12	–9.13	33	153	0.72	1.28, 0.68, 0.48, 0.43, 0.36

[a] Measured in formic acid at the concentrations indicated at the Experimental Section. [b] Measured by DSC. [c] Values corresponding to the characteristic spacings appearing in the X-ray diagrams. The innermost reflections with spacings longer than 1 nm are weak in powder diagrams but clearly seen near the meridian in oriented patterns taken from fibers.

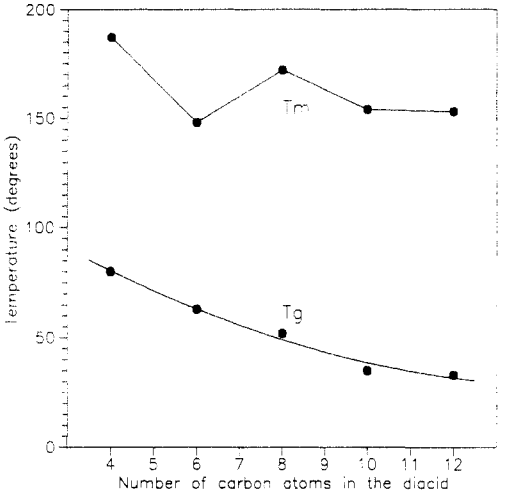


Figure 5. Glass transitions (T_g) and melting points (T_m) of polyamides PDMBA*n*.

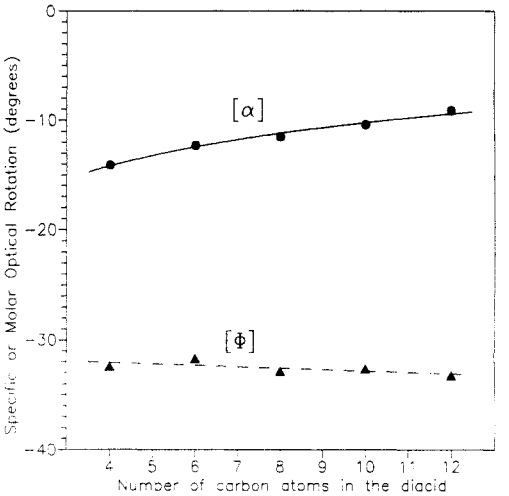


Figure 6. Specific ($[\alpha]_D$), and molar ($[\Phi]_D$) optical rotations of PDMBA*n* plotted against the number of carbons contained in the diacid repeating unit. Measurements were made in formic acid solution at 23 °C.

reported for isomeric P*n*DMLT and, in contrast with them, they do not show logical correlation with the chemical structure. In particular, an abnormally low melting temperature was observed for PDMBA6 that remains essentially unchanged after subjecting the polymer to annealing at 140 °C. As seen in Figure 5, numerical values of T_m may be approximately fitted in a descending zigzag contour when plotted against the number of carbon atoms contained in the diacid. It should be kept in mind however that differences in molecular weights of the PDMBA*n* samples can result in appreciable differences in the overall trend of T_m with n. Nevertheless, it is reasonable to surmise that the distance between the relatively bulky diamine moieties must be a decisive factor in determining the side-by-side chain packing efficiency in the crystal structure; this would be duly reflected in the corresponding melting temperature values.

After rapid cooling to room temperature, second heating traces displayed well-defined slope changes due to second-order thermal transitions in the range 30–80 °C. Glass transition temperatures of PDMBA*n* are found to decrease steadily with the increase of n. Calculated values for the T_g/T_m ratio in kelvins fall within the range 0.80–0.72, slightly higher than the 2/3 value given by the Boyer–Beaman rule of thumb,[22] as usually corresponds to hydrogen bond-forming polymers. Melting peaks preceded by crystallization exotherms were additionally observed in reheating traces of PDMBA*n* for n equal to or higher than 8. This behavior is shared by P*n*DMLT although in this case the borderline for observing cold crystallization was defined at $n = 4$.

Optical activity should be expected for polyamides PDMBA*n* according to their stereoregular structure. Specific optical rotations, $[\alpha]^{23}_D$, in the range −9 to −14° were measured for these polyamides in formic acid solution, with values steadily decreasing with the concentration of chiral carbons in the repeating unit (Figure 6). An approximately constant value was found instead for molar optical rotations, $[\Phi]^{23}_D = [\alpha]^{23}_D \times M_0/100$, which indicates that secondary effects arising from interfactions between neighboring chromophores may be considered as negligible. It should be noted that optical activities of PDMBA*n* turn out to be much weaker than those displayed by polyamides P*n*DMLT,[11] where specific optical rotations between +175 and +76° were measured, but comparable to values reported for poly(2,3-di-*O*-methylene-L-tartaramide)s.[9]

In contrast with P*n*DMLT, circular dichroism of PDMBA*n* in trifluoroethanol does not show any indication of secondary structure in solution. The typical spectrum

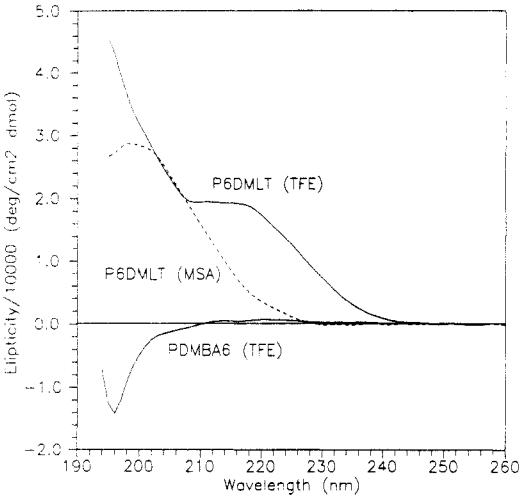


Figure 7. CD spectrum of PDMBA6 in trifluoroethanol (TFE). CD spectra of P6DMLT registered in TFE and methanesulfonic acid (MSA) are included for comparison.

of these polyamides resembles in shape that obtained for P*n*DMLT in methanesulfonic acid, where a complete denaturation of the polyamide is assumed to take place[11] (Figure 7). Such a difference may be explained in terms of chain conformational flexibility; the methylene group inserted in the diamine unit of polyamides PDMBA*n* undoubtedly contributes to relieve steric 1–3 and 1–4 interactions between the carbonyl and the neighboring pair of methoxy groups. Such interactions are known to operate in certain aldaramide[23] and aldonamide model compounds[24] where rotations around the main chain bonds are hindered and consequently sickle conformations favored both in solution and in the solid state.

Experimental Section

Materials. All reagents were of analytical 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 using an Ubbelohde microviscometer. Molecular weight distributions were determined by GPC in a Waters instrument fitted with a 10^3 and 10^2 nm column set and using chloroform as eluent. Calibration was made against polystyrene standards. The derivatization of the polyamides was accomplished by treating the samples (4 mg) with a solution of trifluoroacetic anhydride (0.5 mL) in dry chloroform (2 mL) for 12 h. After rotavaporation 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 either a Perkin-Elmer 783 or an FT-IR Perkin-Elmer 2000 instrument. ^1H and ^{13}C NMR spectra were obtained with either a Varian XL GEM-200 (200 MHz) or a Bruker AMX-300 (300 MHz) spectrometer. Spectra of intermediate compounds were registered in deuterated chloroform and those of polymers in deuterated dimethyl sulfoxide or trifluoroacetic acid. The ^1H–^1H homonuclear and ^1H–^{13}C heteronuclear shift correlation 2D-NMR spectra were recorded using the standard pulse sequences COSY and HXCO, respectively. X-ray diffraction diagrams were obtained in a modified Statton camera using a nickel-filtered Cu Kα radiation of wavelength of 0.1542 nm and were calibrated with molybdenum sulfide. Solubility tests were performed following the methodology described by Braun.[25] 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 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 trifluoroethanol solution ($c = 10^{-3}$ mol/L) at 23 °C on a Jasco J-700 instrument fitted with a cell of an optical path length of 1 mm.

Synthesis of Monomers. Diethyl (2*R*,3*R*)-(+)-2,3-Dimethoxybutanedioate (Diethyl 2,3-Di-*O*-methyl-L-tartrate) (II). Synthesis of this compound was performed from diethyl L-tartrate (I) by treatment with dimethyl sulfate as previously reported.[11]

(2*S*,3*S*)-(+)-2,3-Dimethoxy-1,4-butanediol (2,3-Di-*O*-methyl-L-threitol) (III). To a dispersion of $LiAlH_4$ (39.8 g, 1.05 mol) in dried diethyl ether (900 mL) a solution of diethyl 2,3-di-*O*-methyl-L-tartrate (**II**) (93.6 g, 0.4 mol) in diethyl ether (600 mL) was added dropwise under vigorous stirring at room temperature. The mixing was refluxed for 4 h and then left to stand overnight at room temperature. Water (42.1 mL), 15% NaOH solution (42.1 mL), and water (128.8 mL) were successively added dropwise. The slightly yellowish precipitate that appeared after stirring was filtered off and exhaustively washed with acetone. The filtrates were pooled, concentrated, and distilled under vacuum (105–110 °C (0.1 mm)) to give **III** as an oil which crystallized spontaneously. Yield: 39.1 g (65%). Mp: 39–41 °C. $[\alpha]^{23}_D$: +7.1° (*c* 1.16 in ethanol). ^{13}C NMR ($CDCl_3$): δ 58.76, 60.47, 81.62. Anal. Calcd for $C_6H_{14}O_4$: C, 47.98; H, 9.40. Found: C, 47.75; H, 9.41.

(2*S*,3*S*)-(+)-2,3-Dimethoxy-1,4-bis((*p*-tolylsulfonyl)oxy)butane [2,3-Di-*O*-methyl-1,4-bis(*p*-tolylsulfonyl)-L-threitol] (IV). To a solution of **III** (34.27 g, 0.228 mol) in anhydrous pyridine (170 mL) cooled to 0 °C was added 96.0 g (0.502 mol) of *p*-toluenesulfonyl chloride in small portions under stirring. The mixture was left overnight at room temperature and then poured into 450 mL of chilled water. After stirring for 15 min, the mixture was extracted with diethyl ether (4 × 400 mL), and the organic layer was successively washed with 0.1 M HCl, 0.1 M $NaHCO_3$, and water. Upon concentration of the ether solution, crystallization of **IV** suddenly started. Additional crops of crystals were obtained upon further concentration of the mother liquors. The raw product was recrystallized from ether. Yield: 63.7 g (61%). Mp: 61–64 °C. $[\alpha]^{23}_D$: +7.1° (*c* 1.68, in chloroform). ^{13}C NMR ($CDCl_3$): δ 21.64, 59.21, 67.55, 77.37, 127.69, 129.92, 132.51, 145.09. Anal. Calcd for $C_{20}H_{26}O_8S_2$: C, 52.39; H, 5.72; S, 13.97. Found: C, 52.46; H, 5.74; S, 13.96.

(2*S*,3*S*)-(+)-2,3-Dimethoxy-1,4-diazidobutane (2,3-Di-*O*-methyl-1,4-diazido-1,4-dideoxy-L-threitol) (V). To a solution of **IV** (60 g, 0.131 mol) in *N*,*N*-dimethylformamide was added 34.1 g of sodium azide (0.524 mol), and the mixture was heated at 100 °C for 1.5 h under stirring. The salty solids formed were filtered off, and the clear filtrate was evaporated under vacuum to a residue which was repeatedly extracted with diethyl ether. Evaporation followed by distillation of the ether solution gave **V** (71–73 °C (0.1 mm)). Yield: 21.3 g (81%). $[\alpha]^{23}_D$, +19.8° (*c* 1.38, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 3.40 (m, CH_2CH, 6H), 3.38 (s, CH_3, 6H). ^{13}C NMR ($CDCl_3$): δ 50.20, 58.98, 79.78. Anal. Calcd for $C_6H_{12}N_6O_2$: C, 35.99; H, 6.05; N, 41.98. Found: C, 35.96; H, 6.05; N, 41.74.

Table 4. Bis(pentachlorophenyl) Alkanedioates VIII*n*: Preparation and Characterization Data

n	starting compd	yield (%)	mp (°C)	crystallization solvent	anal. (C,H,Cl)[a]
4	diacid	65	250–252	chlorobenzene	31.26, 0.66, 57.67
					31.25, 0.64, 57.77
6	diacid	63	191–193	chloroform	33.63, 1.25, 55.15
					33.54, 1.25, 55.30
8	diacid	75	164–165	chloroform	35.80, 1.80, 52.85
					35.68, 1.78, 52.88
10	dichloride	75	132–134	carbon tetrachloride	37.81, 2.31, 50.73
					37.84, 2.26, 50.74
12	diacid	70	124–125	carbon tetrachloride	39.65, 2.77, 48.77
					39.55, 2.68, 48.91

[a] Calculated values are given in the first row, and found values are given in the second row.

(2*S*,3*S*)-(−)-2,3-Dimethoxy-1,4-diaminobutane (2,3-Di-*O*-methyl-1,4-diamino-1,4-dideoxy-L-threitol) (VI). Compound **V** (21.0 g, 0.105 mol) was dissolved in methanol (200 mL) and hydrogenated with 10% Pd/C (300 mg) at room temperature in a hydrogen atmosphere. Thin-layer chromatography revealed that conversion of **V** had been completed after 4.5 h. After the catalyst was filtered off, the solution was concentrated and the residue distilled to give **VI** (58–62 °C (0.1 mm)) as a colorless syrup which sometimes crystallized spontaneously. Yield: 12.2 g (84%). $[\alpha]^{23}_D$: −23.1° (*c* 1.04, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.32 (s, NH_2, 4H), 2.60 (m, CH_2, 4H), 3.12 (m, CH, 2H), 3.29 (s, CH_3, 6H). ^{13}C NMR ($CDCl_3$): δ 41.64, 59.11, 83.32. Anal. Calcd for $C_6H_{16}N_2O_2{\cdot}2H_2O$: C, 39.12; H, 10.94; N, 15.21. Found: C, 39.10; H, 10.53; N, 14.62.

(2*S*,3*S*)-(−)-*N*,*N*′-Bis(trimethylsilyl) 2,3-Dimethoxy-1,4-diaminobutane [*N*,*N*′-Bis(trimethylsilyl) 2,3-Di-*O*-methyl-1,4-diamino-1,4-dideoxy-L-threitol] (VII). Silylation was performed according to the general methodology described by Pierce.[26] To an ice-cold solution of diamine **VI** (12.2 g, 0.082 mol) in toluene (125 mL) trimethylsilyl chloride (18.04 g, 0.166 mol) and triethylamine (16.8 g, 0.166 mol) were added dropwise under stirring with rigorous exclusion of moisture. The mixture was then refluxed for 1 h and left to stand overnight at room temperature. The formed solids were filtered off and the solution was concentrated to a yellowish syrup which was distilled under vacuum to give **VII** (85–90 °C (1 mm)) as white crystals. Yield: 13.57 g (57%). $[\alpha]^{23}_D$: −8.2° (*c* 1.0, $CHCl_3$). IR (cm^{-1}, pure): 3375, 2944, 2815, 1451, 1395, 1246, 1184, 1110, 1093, 878, 846, 747. ^1H NMR ($CDCl_3$): δ 1.0 (broad, $SiCH_3$), 2.79 (m, CH_2), 3.22 (m, CH), 3.44 (s, OCH_3).

Preparation of Bis(pentachlorophenyl) Alkanedioates (VIII*n*). General Procedure. Starting from the corresponding aliphatic dicarboxylic acids, compounds **VIII*n*** for n = 4, 6, 8, and 12 were prepared according to the following procedure: To an ice-cold solution of the diacid (0.05 mol), pentachlorophenol (0.1 mol), and pyridine (0.2 mol) in chlorobenzene (200 mL) was added dropwise a solution of thionyl chloride (0.1 mol) under stirring. The mixture was heated at 40 °C for 4 h, left to stand at room temperature for a few hours, and filtered, and the collected solids were extracted with chloroform. Filtrates and extracts were pooled and evaporated to dryness. The residue consisting mainly of **VIII*n*** was crystallized from an appropriate solvent. For the preparation of **VIII10**, commercial sebacoyl dichloride was used as the starting material; 0.05 mol of this compound was treated with 0.1 mol of pentachlorophenol and 0.1 mol of pyridine in chlorobenzene, and the reaction mixture was worked up as described above. Specific preparation conditions used in each case as well as some characterization data of the title compounds are collected in Table 4.

Synthesis of Polymers. General Procedure of Polycondensation. To a stirred solution of diamine **VII** in dried chloroform at room temperature was added an equimolecular amount of the corresponding diacid **VIII*n***. The solution was then heated to 50 °C and left to stand at this temperature for 3 days under stirring. The formed polymer was recovered from the gelatinous reaction mixture as a white solid by precipitation with acetone and centrifugation. Purification was accomplished by repeated washing with acetone and drying under vacuum for a few days. PDMBA4, -6, and -10 were further purified by dissolving the polymer in formic acid and precipitating it with acetone.

Poly[(2*S*,3*S*)-2,3-Dimethoxybutylene succinamide] (PDMBA4). Yield: 54%. IR (cm^{-1}, film from TFE): 3283 (amide A), 3065 (amide B), 1639 (amide I), 1543 (amide II), 1090 (ether). ^1H NMR (DMSO-d_6): δ 2.32 (s, H^e, 4H), 3.04 (m, H^d, 4H), 3.32 (s, H^c, 6H), 3.27 (s, H^b, 2H), 7.88 (t, H^a, 2H). ^{13}C NMR (DMSO-d_6): δ 30.7 (C^e), 38.4 (C^d), 57.9 (C^c), 78.9 (C^b), 171.4 (C^a). Anal. Calcd for $(C_{10}H_{18}O_4N_2 \cdot {}^1/_2H_2O)_n$: C, 50.20; H, 8.00; N, 11.71. Found: C, 50.31; H, 7.73; N, 11.63.

Poly[(2*S*,3*S*)-2,3-Dimethoxybutylene adipamide] (PDMBA6). Yield: 50%. IR (cm^{-1}, film from TFE): 3284 (amide A), 3070 (amide B), 1637 (amide I), 1542 (amide II), 1086 (ether). ^1H NMR (DMSO-d_6): δ 1.44 (t, H^f, 4H), 2.06 (t, H^e, 4H), 3.05 (m, H^d, 4H), 3.31 (s, H^c, 6H), 3.25 (s, H^b, 2H), 7.80 (t, H^a, 2H). ^{13}C NMR (DMSO-d_6): δ 25.0 (C^f), 35.2 (C^e), 38.3 (C^d), 58.0 (C^c), 79.0 (C^b), 172.2 (C^a). Anal. Calcd for $(C_{12}H_{22}O_4N_2 \cdot {}^1/_2H_2O)_n$: C, 53.92; H, 8.67; N, 10.48. Found: C, 54.22; H, 8.46; N, 10.39.

Poly[(2*S*,3*S*)-2,3-Dimethoxybutylene octanamide] (PDMBA8). Yield: 91%. IR (cm^{-1}, film from TFE): 3287 (amide A), 3070 (amide B), 1637 (amide I), 1544 (amide II), 1091 (ether). ^1H NMR (DMSO-d_6): δ 1.22 (m, H^g, 4H), 1.47 (m, H^f, 4H), 2.06 (t, H^e, 4H), 3.07 (m, H^d, 4H), 3.33 (s, H^c, 6H), 3.26 (s, H^b, 2H), 7.84 (t, H^a, 2H). ^{13}C NMR (DMSO-d_6): δ 25.1 (C^f), 28.4 (C^g), 35.2 (C^e), 38.2 (C^d), 57.9 (C^c), 78.9 (C^b), 172.1 (C^a). Anal. Calcd for $(C_{14}H_{26}O_4N_2 \cdot {}^1/_4H_2O)_n$: C, 57.81; H, 9.18; N, 9.63. Found: C, 57.98; H, 9.05; N, 9.51.

Poly[(2*S*,3*S*)-2,3-Dimethoxybutylene decanamide] (PDMBA10). Yield: 65%. IR (cm^{-1}, film from TFE): 3272 (amide A), 3073 (amide B), 1637 (amide I), 1543 (amide II), 1092 (ether). ^1H NMR (DMSO-d_6): δ 1.12 (m, broad, H^g and H^h, 8H), 1.47 (m, broad, H^f, 4H), 2.06 (t, H^e, 4H), 3.05–3.25 (m, H^b and H^d, ABX, 6H), 3.32 (s, H^c, 6H), 7.82 (t, H^a, 2H). ^1H NMR (TFA-*d*): δ 1.45 (m, broad, H^g and H^h, 8H), 1.81 (m, broad, H^f, 4H), 2.75 (t, H^e, 4H), 3.65 (s, H^c, 6H), 3.70–4.20 (m, H^b and H^d, ABX, 6H). ^{13}C NMR (DMSO-d_6): δ 25.1 (C^f), 28.6 and 28.7 (C^g and C^h), 35.2 (C^e), 38.2 (C^d), 57.9 (C^c), 78.9 (C^b), 172.2 (C^a). ^{13}C (TFA-*d*): δ 27.0 (C^f), 30.6 and 31.0 (C^g and C_h), 36.5 (C^e), 43.5 (C^d), 60.0 (C^c), 81.0 (C^b), 183.0 (C^a). Anal. Calcd for $(C_{14}H_{26}O_4N_2 \cdot {}^1/_4H_2O)_n$: C, 60.26; H, 9.64; N, 8.78. Found: C, 59.75; H, 9.42; N, 8.72.

Poly[(2*S*,3*S*)-2,3-Dimethoxybutylene dodecanamide] (PDMBA12). Yield: 85%. IR (cm^{-1}, film from TFE): 3280 (amide A), 3074 (amide B), 1637 (amide I), 1543 (amide II), 1103 (ether). ^1H NMR (TFA-*d*): δ 1.45 (m, broad, H^g, H^h, and H^i, 12H), 1.46 (m, H^f, 4H), 2.05 (m, H^e, 4H), 3.06 (m, H^d, 4H), 3.33 (s, H^c, 6H), 3.25 (s, H^b, 2H), 7.81 (t, H^a, 2H). ^{13}C NMR (TFA-*d*): δ 27.9 (C^f), 30.7, 30.9, and 31.0 (C^g, C^h, and C^i), 36.4 (C^e), 43.5 (C^d), 60.2 (C^c), 81.3 (C^b), 183.0 (C^a). Anal. Calcd for $(C_{14}H_{26}O_4N_2 \cdot {}^1/_4H_2O)_n$: C, 62.31; H, 10.02; N, 8.07. Found: C, 61.70; H, 9.77; N, 7.85.

Acknowledgment. Support of this study by the CICYT (Comisión Interministerial de Ciencia y Tecnología, Grants MAT90-0779-CO2-02 and MAT93-0555-CO2-02) is gratefully acknowledged. The authors are also indebted to Mr. A. Martínez de Ilarduya for valuable assistance with NMR measurements.

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