Structural Study of Linear Polyesters. 1. Crystal Structure of Poly(trimethylene sebacate), Established from X-ray and Electron Diffraction Data

Nathalie Jourdan, Suzanne Deguire, and François Brisse*

Département de Chimie, Université de Montréal, C.P. 6128, Succursale Centre-ville, Montréal, Québec H3C 3J7, Canada

Received May 10, 1995; Revised Manuscript Received August 25, 1995[⊗]

ABSTRACT: The crystal structure of the poly(trimethylene sebacate) polyester, PE(3,8), was arrived at through a combined analysis of its electron, powder, and fiber diffraction patterns. PE(3,8) has an orthorhombic unit cell of dimensions $a = 5.032$, $b = 7.532$, and $c = 31.33$ Å (fiber axis) and belongs to the $P2_12_12_1$ space group. There are two chemical units per fiber repeat and the two chains within the unit cell are positioned on 2_1 screw axes, parallel to the c direction. The fiber repeat is 2.50 Å shorter than that for an all-trans conformation. The non-trans torsion angles are located in the glycolic moiety of the chemical repeat. A conformational analysis revealed several energy minima which, after minimization, yielded 18 potentially acceptable conformations. The most likely conformation for the $-O-(CH_2)_3-O-$ flexible segment of the polyester is $g^+tg^-g^+$, while the sebacate group is in the all-trans conformation. The final structure and its orientation and position within the unit cell were arrived at by a comparison of the theoretical and experimental intensities recorded on single crystal electron diffractograms and on X-ray diffraction powder patterns. The proposed structure is confirmed by the small values taken by the conventional R factor, $R = 0.108$ for 19 powder diffraction arcs and $R = 0.136$ ($R_w = 0.096$) for 12 independent spots on the electron diffraction recording.

Introduction

Aliphatic polyesters of the type $[-(CH_2)_X-O-OC-(CH_2)_Y-CO-O-]$, PE($X$,$Y$), have received much attention since they were first synthesized by Carothers in 1929.[1] From the structural point of view, the first diffraction studies were undertaken by Fuller and Erickson[2] for a series of ethylene glycol polyesters, PE(2,Y), $Y = 2, 4, 7, 8$. The authors reported on the linear variation of the fiber repeat as the number of methylene groups in the acid segment increases. The first crystal structures were established by Ueda, Chatani, and Tadokoro[3] for poly(ethylene oxalate), PE(2,0), and poly(ethylene succinate), PE(2,2). Turner-Jones and Bunn[4] determined the crystal structure of poly(ethylene adipate), PE(2,4), and that of poly(ethylene suberate), PE(2,6). In the early members of the series, PE(2,0) and PE(2,2), the glycol portion shows a considerable deviation from the trans conformation while the chains are in a fully extended conformation for all the other members of the family: PE(2,4), PE(2,6), PE(2,7), and PE(2,8). More recently, Ichikawa, Suzuki, Washiyama, and Moteki[5] studied the fiber diagrams of poly(tetramethylene succinate), PE(4,2), and showed that this polyester may take two distinct conformations. One of them is the usual all-trans conformation while the other adopts a non-trans arrangement with some deformations in the glycol segment. A similar observation was reported for poly(tetramethylene terephthalate).[6]

Good-quality single crystals of poly(oligomethylene decanedioates), PE(X,8), $X = 3, 4, 5, 6, 7, 8, 9, 10, 12$, were grown from solution. They were examined in the electron microscope and their electron diffractograms were recorded and analyzed by Deguire.[7] Following a comprehensive analysis of the X-ray fiber data and the electron diffractograms, it was established that the polyesters which have an odd number of methylene groups in the glycol or in the acid segment adopt an orthorhombic unit cell while the crystalline polyesters which have an even number of methylene groups in the glycol and in the acid part all crystallize with a monoclinic unit cell.

Fuller, Frosch, and Pape[8,9] studied the trimethylene glycol polyesters, the PE(3,Y) series where $Y = 2, 3, 4, 5, 6, 7, 8, 9, 10, 16$. The authors noted that the fiber repeat was systematically shorter, by 2.5Å, than that for an all-trans conformation. They proposed that, for this series of polyesters, the acid portion remains in the fully extended conformation while a considerable deviation from the trans conformation must take place in the glycol moiety.

In the present paper we propose a conformational description of the glycol segment on the basis of the quantitative analysis of the electron diffraction pattern and the X-ray fiber and powder diagrams of the poly(trimethylene sebacate) polyester.

Experimental Section

Polymer Synthesis. Poly(trimethylene sebacate) was prepared by following the method described by Sorenson and Campbell.[10] 1,8-Octane dichloride (0.1 mol) and 1,3-propanediol (0.1 mol) were reacted under a stream of N_2 in order to carry away the HCl formed during the reaction. Since the reaction is strongly exothermic, the reaction vessel was kept in a cold bath. After 1h the mixture, which had turned solid, was heated to 180 °C to boil off the residual HCl. The yield was 70%.

The molecular weight of the polyester was measured by the GPC technique: $M_w = 5546$ and $M_n = 1321$. Three different columns were used which have respective porosities of 10^3, 10^4, and 10^5Å. The solvent used was the tetrahydrofuran, and the column temperature was kept at 30 °C while the refractometer, Waters R401, had a temperature of 33 °C. A comparison of the experimental and calculated densities (Table 1) gives a crystallinity of 78%.

X-ray Powder Diffraction. The powder diagrams were recorded in a Debye-Sherrer camera, 114.6 mm in diameter, using the nickel-filtered Cu K α-radiation. The d values were accurately measured while the diffracted intensities, I_{obs}, were visually estimated. The structure factors were derived after

---

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1995.

Table 1. Crystal Data of Interest and Unit Cell Dimensions for PE(3,8)

params	
molecular formula	$[C_{26}H_{44}O_8]_n$
fw	484
mp, °C	54.3
cryst syst	orthorhombic
exp dens, g cm^{-3}	1.28
calc dens, g cm^{-3}	1.34
Z	2
space group	$P2_12_12_1$
a, Å	5.032 ± 0.025
b, Å	7.532 ± 0.095
c, Å	31.33 ± 0.15
V, Å^3	1188

a correction for the Lorentz and polarization factors was applied. The scattering factors used to calculate the X-ray structure amplitudes were taken from Cromer and Waber[11] for C and O atoms and from Stewart, Davidson, and Simpson[12] for H atoms.

Single Crystals and Electron Diffraction. A small amount of the polyester was dissolved in a mixture of toluene (0.5 mL) and 2-propanol (2.5 mL) (0.01–0.02 per volume), and the mixture was heated to 70 °C for 30 min. The solution was slowly cooled to 40 °C, when a slight precipitation was observed. The solution was kept for 1 h at this temperature and then slowly cooled to room temperature. The single crystals thus obtained were separated by centrifugation, then rinsed with the above solvent mixture, and preserved in toluene. For electron diffraction, drops of a suspension of the poly(trimethylene sebacate) single crystals in toluene were evaporated on carbon grids. For *d* spacing calibration of the electron diffractograms, gold was evaporated on some of the grids. The electron diffraction patterns were recorded on photographic film using a Philips EM400T electron microscope equipped with a specimen holder, allowing for the rotation of the grid as well as its inclination with respect to the microscope axis. The electron microscope was used at 80 kV for imaging and at 120 kV in the diffraction mode. The intensities of the electron diffraction photographs were evaluated with the EDFILMS program[13] using data recorded with an Optronics scanning densitometer which measured the optical density of the film. This computer program could recognize a diffraction spot from the background noise. The two most intense reflections were difficult to evaluate properly. To take this into account in the calculation of agreement index R_w, they were given a weight of 0.6 while all the other reflections were given a weight of 1.0. The scattering amplitudes for the calculation of the potential factors were taken from ref 14 for C, O, and H atoms.

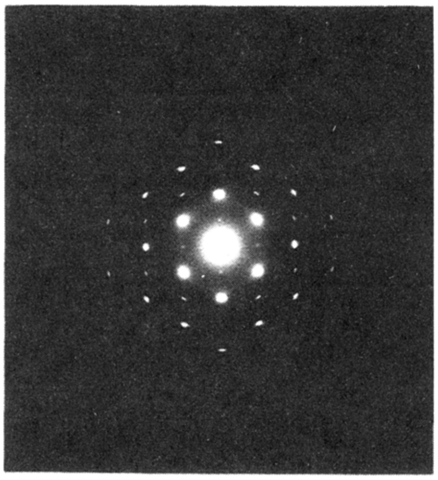


Figure 1. Electron diffractogram of poly(trimethylene sebacate), PE(3,8), *hk*0 section. a* is horizontal, b* is vertical.

Conformational Analysis and Packing Energy. The conformational analysis of a model for poly(trimethylene succinate) was carried out by energy calculations and minimization using the Hyperchem Release 2 package[15] running on an 80486-50 MHz IBM compatible personal computer. The conformations were minimized through a molecular mechanics force field[16] using the MM$^+$ force field.[17] The energy minimization relied on the Polak-Ribiere conjugate gradient technique. The storage and sorting of the energies were performed with the Excel software[18] with an interface between Hyperchem and Excel.

The packing energies were minimized using the Cerius2 release 1.5 package[19] running on a Silicon Graphics IRIS workstation with an Indigo2 processor. The Dreiding[20] force field and the Polak-Ribiere conjugate gradient technique were employed. During the packing minimization, the polyester chains were considered as rigid units to preserve the crystallographic restraints.

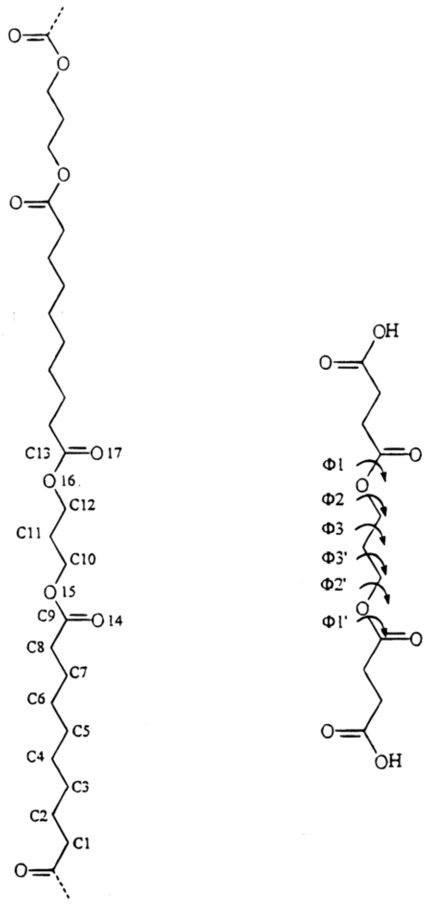
Results and Discussion

The variation of the fiber repeat of the poly(trimethylene dicarboxylates) polyesters,[9] *p*, as the number of methylene groups in the acid part increases, is linear.[8] Since the fiber repeat is significantly shorter than that for the fully extended conformation, the structure must have some non-trans torsion angles located in the trimethylene section. The density and the value of the

Table 2. Comparison of Observed and Calculated *d* Spacings[a] of PE(3,8)

electron diffraction			powder diffraction			fiber diffraction		
hkl	d_{obs}, Å	d_{cal}, Å	*hkl*	d_{obs}, Å	d_{cal}, Å	*hkl*	d_{obs}, Å	d_{cal}, Å
110	4.173	4.183	002	15.73	15.72	110	4.190	4.183
020	3.705	3.769	004	7.792	7.862	020	3.780	3.769
120	2.987	3.016	011	7.390	7.330	120	3.040	3.016
200	2.525	2.516	102	4.745	4.789	210	2.360	2.387
210	2.390	2.387	016	4.363	4.303	201	2.580	2.508
130	2.219	2.248	104	4.247	4.236	002	15.60	15.72
220	2.086	2.092	110	4.160	4.183	102	4.770	4.789
040	1.852	1.883	111	4.114	4.146	112	3.910	4.042
230	1.766	1.777	112	4.050	4.042	022	3.630	3.665
310	1.642	1.637	105	3.880	3.927	132	2.310	2.237
150	1.422	1.443	020	3.779	3.769	004	7.820	7.862
240	1.494	1.507	021	3.734	3.742	104	4.280	4.236
			114	3.678	3.693	024	3.380	3.414
			022	3.608	3.665	006	5.220	5.249
			115	3.477	3.483	008	3.860	3.936
			116	3.292	3.269	0,0,10	3.140	3.149
			120	3.052	3.016	0,0,12	2.560	2.624
			122	2.942	2.962	0,0,14	2.210	2.249
			130	2.254	2.248	0,0,16	2.100	1.968

[a] The *d* spacings were calculated for all three sets of data using the unit-cell dimensions given in Table 1. The experimental fiber diffraction *d* values are taken from refs 8 and 9.



a) b)

Figure 2. (a) Schematic representation of the polymer chain and atomic numbering. (b) Model used in the conformational analysis and definition of the torsion angles.

fiber repeat reveal the existence of two polyester chains per unit cell (parallel to the fiber axis) and two chemical units per fiber repeat.

Electron Diffractograms of Poly(trimethylene sebacate). The crystals of PE(3,8) are thin platelets (80–100 Å thick) with no recognizable or distinguishing feature. The electron diffractogram of PE(3,8) is shown in Figure 1. This diagram is almost identical to the electron diffraction patterns of all PE(X,8) where X equals 2 to 10[7]. Systematic absences are noted for $h00$, $h \neq 2n$ and $0k0$, $k \neq 2n$, indicating the existence of 2_1 helicoidal axes parallel to a and b, respectively.

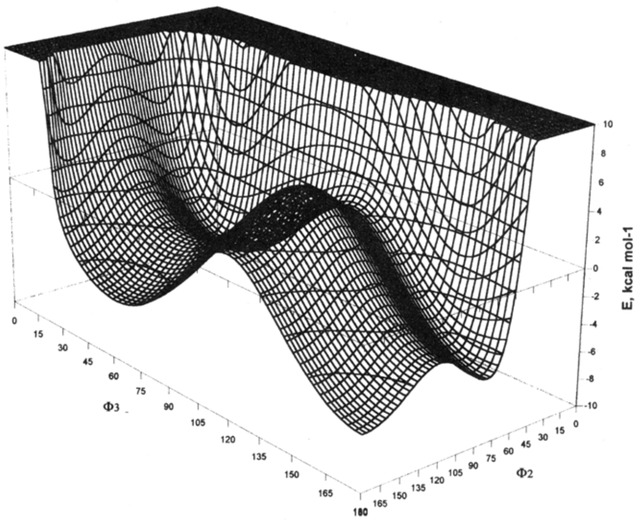


Figure 3. Three-dimensional energy plot for the trimethylene section of the model compound. $\Phi_1 = 180$, $\Phi_2 = \Phi_{2'}$, $\Phi_3 = \Phi_{3'}$.

X-ray Diffraction Data of Poly(trimethylene sebacate). PE(3,8) was also studied by means of its powder diffraction pattern which could be indexed with an orthorhombic unit cell. Upon refinement of the combined measurements from electron diffraction and X-ray diffraction data, the unit cell whose dimensions are given in Table 1 was arrived at. In order to complete this analysis we also used the experimental measurements reported by Fuller, Frosch and Pape.[8,9] This choice conforms with the published fiber diffraction data.[8,9] The published d values for poly(trimethylene sebacate)[9] could also be indexed with the above unit cell. The observed and calculated d spacings for the three diffraction patterns are compared in Table 2.

The unit cell is orthorhombic and there are two helicoidal axes 2_1 parallel to a and b. These indications are compatible with space groups $P2_12_12_1$, $P2_12_12$, $Pba2_1$, etc. However, since there are no further systematic absences from powder and fiber diffraction patterns and since there are two polymer chains per cell, the space group is $P2_12_12_1$.

Chain Conformation. Molecular mechanics calculations were used to perform a conformational analysis of the model compound, shown in Figure 2b, a fragment of poly(trimethylene succinate). In this molecule the glycol segment is straddled by two acid parts in order to preserve the appropriate environment for the conformational analysis of the glycol fragment. Six torsion

Table 3. Chain Conformations Φ_1, Φ_2, Φ_3, $\Phi_{3'}$, $\Phi_{2'}$, $\Phi_{1'}$, deg, and Calculated Energies, kcal mol^{-1}

$\Phi_{1'}$	$\Phi_{2'}$	$\Phi_{3'}$	Φ_3	Φ_2	Φ_1	E	identification
172	173	−57	−61	104	−178	−6.83	
179	−82	178	178	82	175	−7.20	
168	−83	−66	66	83	−175	−7.35	
−178	102	−65	180	82	−169	−7.38	a
180	80	56	57	80	−178	−7.41	b
171	174	−65	65	−174	−176	−7.49	
−176	−103	70	59	80	−177	−7.52	
177	80	177	178	79	179	−7.53	
175	172	62	59	79	178	−7.64	
−169	178	178	62	178	−178	−7.70	
175	82	177	−62	−176	169	−7.76	
172	77	58	177	−176	180	−7.92	
176	178	179	176	179	180	−7.95	
−175	83	62	172	83	−167	−8.02	
176	81	178	62	−176	179	−8.05	
−179	80	176	180	179	−170	−8.12	
173	177	62	62	177	175	−8.30	
−177	128	−57	−57	129	−179	−8.52	

Table 4. Two Potentially Acceptable Conformations for PE(3,8) and the Corresponding Chain Torsion Angles, deg, Packing Energies, kcal mol^{-1}, and Calculated Fiber Repeat, Å

conformation	Φ_1	Φ_2	Φ_3	$\Phi_{3'}$	$\Phi_{2'}$	$\Phi_{1'}$	E_{packing}	p
a	178	74	166	−72	85	−178	−104.0	31.47
b	−118	109	72	53	79	160	−88.5	31.50

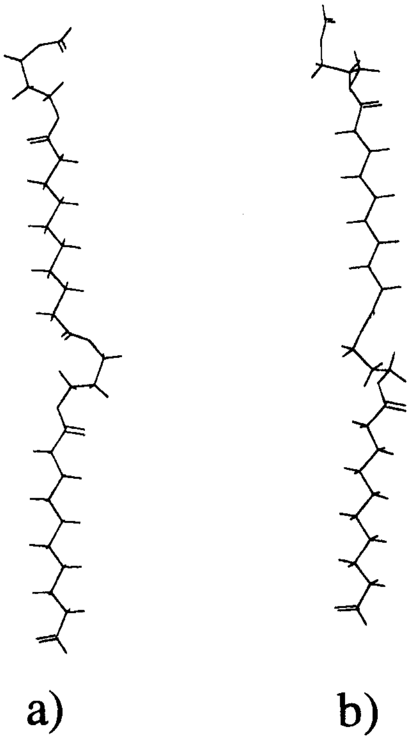


Figure 4. Two possible conformations (I) and (II) for the PE(3,8) polyester.

angles identified as Φ_1, Φ_2, Φ_3, $\Phi_{3'}$, $\Phi_{2'}$, and $\Phi_{1'}$ were considered as variables in the description of the glycol part (Figure 2b). In a first step, a symmetric molecule containing a C_2 axis, passing through the central C atom of the trimethylene sequence, was considered; thus $\Phi_1 = \Phi_{1'}$, $\Phi_2 = \Phi_{2'}$ and $\Phi_3 = \Phi_{3'}$, and the adjustable torsion angles were reduced to three. These torsion angles were varied from 0 to 180°, and for each generated conformation, the energy was calculated with the MM$^+$ force field. In this manner, 86 688 energy terms were computed and stored in output files. The energies were then sorted in order to extract the energy minima. Five such minima were found. Since the Φ_1 torsion angle was almost always trans, this angle was kept at 180° in further computations. At the same time the C_2 constraint was removed. Four torsion angles were now considered as variables, Φ_2, Φ_3, $\Phi_{3'}$, $\Phi_{2'}$. Energy calculations were run as above, and after further minimizations, 13 new energy minima were arrived at. All the probable conformations and their corresponding energies, which differ by less than 2 kcal mol^{-1}, are listed in Table 3. Since the chains are very flexible, the torsion angles were allowed to vary some more when the interchain interactions were considered. Figure 3, which represents the Φ_2−Φ_3 energy map when Φ_1 = 180°, shows very wide potential wells and for this reason the torsion angles Φ_2 and Φ_3 may differ significantly from their ideal values. In fact, the large potential wells confirm the flexibility of the polymer chains but, considering the values of the potential barriers (around 10 kcal mol^{-1}), it will not be easy to cross over from one minima to another. In conclusion, all the conformations in Table 3 are likely and the torsion angles describing the glycol parts have to be considered variable around their listed values.

Table 5. Comparison of the Calculated and Observed Structure Factors in the Powder Diffraction Pattern of PE(3,8)

hkl	$\lvert F_o\rvert$	$\lvert F_c\rvert^a$	*hkl*	$\lvert F_o\rvert$	$\lvert F_c\rvert^a$
002	2.580	2.674	020	10.010	9.742
004	1.110	0.786	021	2.380	3.299
011	0.530	0.766	114	1.080	1.079
102	3.670	3.386	022	0.770	0.529
016	1.590	1.814	115	1.280	1.372
104	2.090	1.996	116	1.940	2.139
110	4.730	4.016	120	2.680	2.133
111	4.270	4.018	122	1.930	2.151
112	3.460	3.702	130	2.540	2.787
105	2.020	1.750	020	10.010	9.742

[a] Calculated with isotropic temperature factor B = 9.0 Å^2.

Crystallographic Constraints. For each potentially acceptable conformation, a chemical unit was built and placed in the cell. The second chemical unit was generated by taking into account the 2_1 helicoidal axis parallel to c. Only those conformations that were still energetically favorable were kept. Then, a second condition had to be considered: the fiber period, p, which has a value of 31.33Å for the poly(trimethylene sebacate) polyester. With this taken into account only two conformations remained. These conformations are illustrated in Figure 4, and they were labeled conformations a and b, respectively.

Packing Analysis. The relative orientations and dispositions of the chains in the unit cell for the two remaining conformations had to be found. As the polymer chains must be on the 2_1 axes, the rotation around the c axis and the translation along the c axis are the only adjustable parameters. The interchain interactions were minimized using the Dreiding force field. The two chain conformations (a and b) and their corresponding packing energies and calculated fiber repeats are compared in Table 4. The packing energies are low and the two possibilities are reasonable.

Comparison of the Experimental and Theoretical Diffraction Diagrams. In order to find which is the most probable conformation for PE(3,8), the theoretical X-ray powder, fiber, and electron patterns were calculated with the Cerius software. The calculated structure factors were compared to their experimental counterparts. The scale factor and an isotropic temperature factor were refined.

The powder pattern calculated using the coordinates of the chain in conformation a (Table 4 and Figure 4) fits well with the experimental pattern. The agreement index, the R factor, takes the value of 0.108, while for the chain in conformation b, the R factor is 0.205. Thus, clearly, the best solution corresponds to conformation a whose torsion angles are Φ_1 = 178, Φ_2 = 74,Φ_3 = 166, Φ_3' = −72, Φ_2' = 85 and Φ_1' = −178 and the associated packing energy is −104 kcal mol^{-1}. A comparison of the observed and calculated structure factors is given in Table 5, while the theoretical and experimental powder diffraction patterns are compared in Figure 5.

The experimental intensities of the fiber diffraction pattern could not be quantitatively evaluated. However,

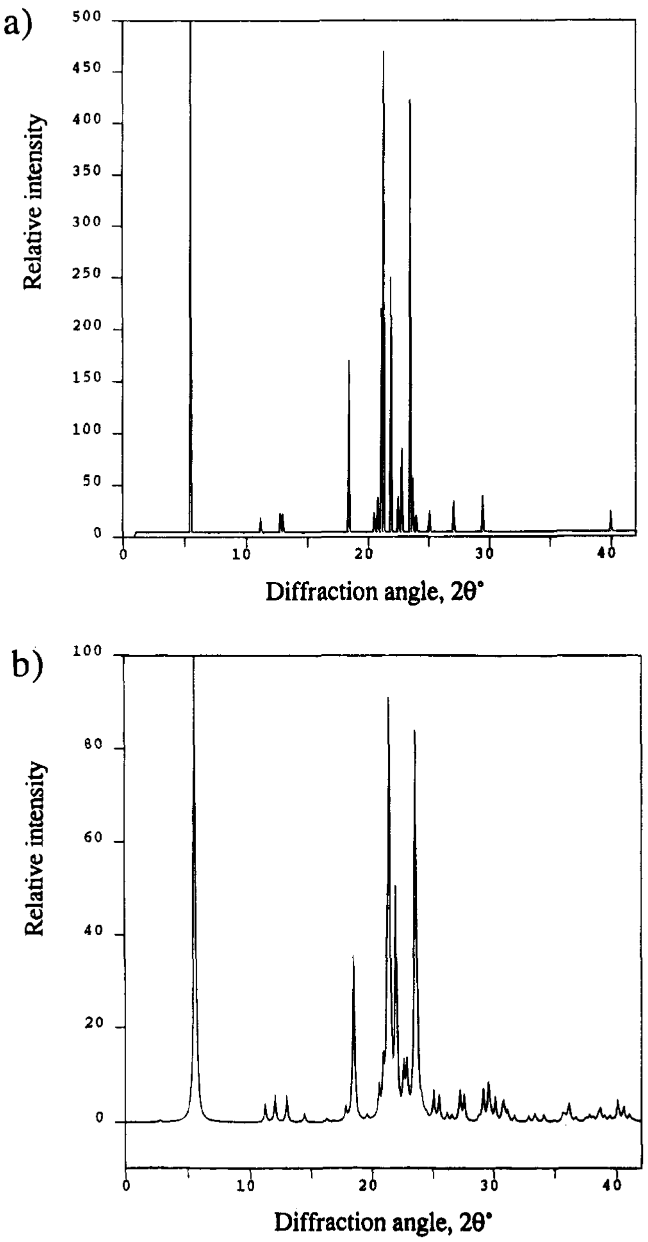


Figure 5. Experimental (a) and calculated (b) powder patterns for the PE(3,8) polyester in the unit cell.

there is a qualitative agreement between the published pattern and the calculated one.

The comparison of the experimental and theoretical electron diffraction patterns also confirms the above selection since the atomic coordinates for the chain in conformation a yield an R factor of 0.136 ($R_w = 0.096$) while the R factor is 0.29 ($R_w = 0.27$) in the case of conformation b. The observed and calculated structure factors for the most probable conformation are compared in Table 6 while the calculated electron diffraction pattern shown in Figure 6 compares very well with the experimental pattern illustrated in Figure 1. The atomic coordinates of conformation a are given in Table 7.

The reflections that appear on the electron diffractograms at the positions of 010, 100, and 030 (which should be absent since the space group is $P2_12_12_1$) are in fact 011, 101, and 031, respectively. This not uncommon occurrence in electron diffraction is due to the very short wavelength and the thinness of the microcrystals. Reflection 011 has an F value of 5.7, and reflections 101 and 031 have F values of 7.0 and 3.4, respectively. These three reflections are of the same order of magnitude as reflections 210 and 220. It is worth mentioning that the above potential calculations were done in the kinematic approximation with no provision for crystal bending correction.

Table 6. Comparison of the Calculated and Observed Structure Factors in the Electron Diffraction Pattern of PE(3,8)

hkl	$\vert F_o \vert$	$\vert F_c \vert^a$	*hkl*	$\vert F_o \vert$	$\vert F_c \vert^a$
110	35.0	31.17	220	8.0	4.31
020	65.0	66.11	040	11.2	9.82
120	7.5	14.00	230	4.8	5.27
200	13.1	12.92	310	4.9	0.71
210	5.9	6.01	150	4.7	5.07
130	13.8	14.88	240	1.7	1.65

[a] Calculated with an isotropic temperature factor $B = 8$ Å^2.

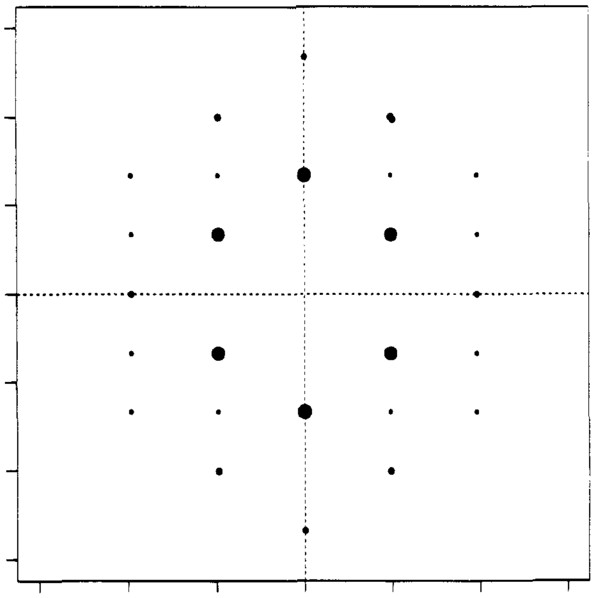


Figure 6. Calculated electron diffractogram of poly(trimethylene sebacate), *hk*0 section.

The experimental and theoretical electron diffraction patterns (Figures 1 and 6) are *hk*0 sections. Tilt experiments, around a^* and b^*, were conducted in the electron microscope but no new diffraction spots could be observed. The computed tilted patterns also confirm this, since very few additional diffraction spots were noted. Only 011, 031, 101, 012, 021, and 111 had any significant intensities. The first three spots were mentioned earlier. 012 is at the same position as 011 and it could not be visualized as an additional one on the experimental electron diffraction diagram, while the last spots are superposed on the very intense 020 and 110 spots. This behavior confirms the absence of further spots on the electron diffraction pattern after the crystal is tilted around the a^* and b^* directions.

Conclusion

The conformational study of PE(3,8) crystalline polyester was established through the interpretation of many diffraction data and a complete conformational analysis. Such flexible polymer chains are not easy to study because there are many possibilities for the torsion angles, but by combining several experimental approaches, it is possible to reduce the number of possibilities and to propose reasonable conformations. The packing of the polymeric chain of poly(trimethylene sebacate) is shown by the stereopair in Figure 7. The

Table 7. Fractional atomic coordinates for PE(3,8)

atom	x	y	z	atom	x	y	z
O14	0.332 66	0.414 35	0.550 17	H21	0.838 04	0.660 73	0.809 52
O15	0.667 1	0.495 45	0.505 8	H22	0.478 95	0.465 2	0.779 91
O16	0.344 76	0.601 09	0.393 64	H23	0.710 57	0.283 44	0.773 72
O17	0.551 53	0.333 11	0.382 05	H24	0.777 13	0.661 49	0.736 08
C1	0.824 97	0.433 19	0.850 99	H25	1.003 75	0.478 43	0.728 17
C2	0.863 22	0.512 92	0.808	H26	0.415 3	0.487 77	0.701 3
C3	0.691 66	0.431 31	0.774 5	H27	0.644 9	0.303 45	0.693 75
C4	0.790 12	0.513 6	0.733 67	H28	0.741 68	0.688 76	0.661 06
C5	0.629 91	0.451 39	0.697 36	H29	0.951 27	0.495 14	0.653 23
C6	0.741 15	0.540 85	0.658 58	H30	0.381 26	0.560 05	0.620 74
C7	0.571 14	0.483 69	0.622 15	H31	0.521 25	0.340 2	0.625 5
C8	0.726 03	0.500 4	0.581 34	H32	0.883 6	0.401 88	0.578 76
C9	0.557 44	0.470 23	0.545 32	H33	0.829 02	0.627 1	0.578 16
C10	0.520 12	0.424 8	0.472 59	H34	0.467 59	0.282 94	0.477 62
C11	0.277 45	0.542 61	0.466 35	H35	0.661 01	0.428 33	0.446 77
C12	0.164 2	0.524 07	0.422 59	H36	0.331 45	0.682 52	0.473 01
C13	0.530 18	0.491 07	0.374 52	H37	0.114 49	0.505 81	0.488 31
H18	0.638 19	0.484 99	0.864 86	H38	0.114 38	0.383 64	0.415 26
H19	0.816 02	0.286 29	0.849 28	H39	0.024 5	0.601 08	0.421 33
H20	1.074 85	0.491 45	0.798 52				

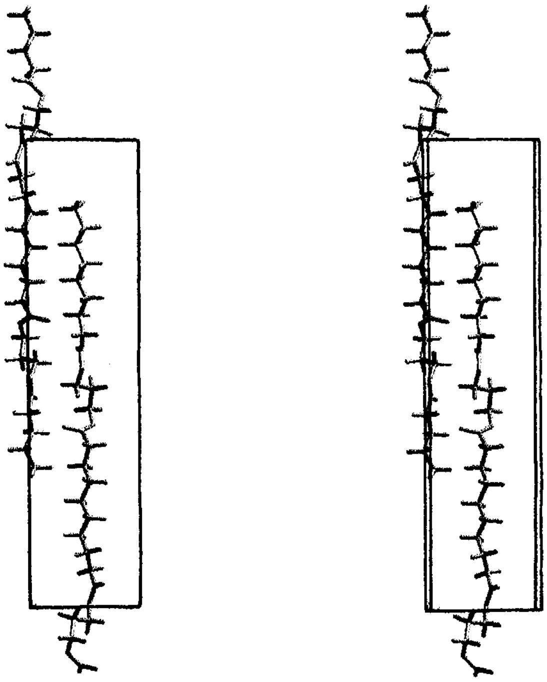


Figure 7. Stereopair showing the PE(3,8) chains in the unit-cell.

sebacate group is in a trans conformation, while the glycol part is $tg^+tg^-g^+$.

The crystal structure of PE(3,8) is the same whether the material is in the fiber form (X-ray data), as a single crystal (electron diffraction data), or as a crystalline powder (powder diffraction data).

This kind of chain conformation study, which combines structural information from diffraction data (X-ray and electron) and conformational information from molecular modeling, is very interesting for flexible polymer compounds. Indeed, it is often very difficult to obtain crystalline model compounds from such polymers because of their very low melting points. In addition, it is difficult to put forward a good chain conformation using only molecular modeling since in a crystal, the energy of the chain conformation is not necessarily the lowest energy of the isolated chain.

Acknowledgment. We thank the Echanges France Québec which allowed S.D. to travel to the laboratory of Dr. Chanzy (CERMAV, Grenoble, France). The help of Dr. Chanzy in recording the electron diffraction patterns is hereby acknowledged.

References and Notes

(1) Carothers, W. H. *J. Am. Chem. Soc.* **1929**, *51*, 2548.

(2) Fuller, C. S.; Erickson, C. L. *J. Am. Chem. Soc.* **1937**, *59*, 344.

(3) Ueda, A. S.; Chatani, Y.; Tadokoro, H. *Polym. J.* **1971**, *2*, 387.

(4) Turner-Jones, A.; Bunn, C. W. *Acta Crystallogr.* **1962**, *15*, 105.

(5) Ichikawa, Y.; Suzuki, J.; Washiyama, J.; Moteki, Y.; Noguchi, K.; Okuyama, K. *Polymer* **1994**, *35*, 3338.

(6) Palmer, A.; Poulin-Dandurand, S.; Brisse, F. *Can. J. Chem.* **1985**, *63*, 3079.

(7) Deguire, S. Ph.D. Thesis, Université de Montréal, 1994.

(8) Fuller, C. S.; Frosch, C. J. *J. Am. Chem. Soc.* **1939**, *61*, 2575.

(9) Fuller, C. S.; Frosch, C. J.; Pape, N. R. *J. Am. Chem. Soc.* **1942**, *64*, 154.

(10) Sorenson, W. R.; Campbell, T. W. *Preparative Methods of Polymer Chemistry*; Interscience Publishers: New York, 1968.

(11) Cromer, D. T.; Weber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(12) Stewart, R. I.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(13) Miller, D.; Chanzy, H.; Paradosi, G. *J. Phys., Colloq. C5* **1986**, Suppl. 8, *47*.

(14) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, p 155.

(15) HyperchemTM program: AutoDesk Inc., Scientific Modeling Division, 2320 Marinship Way, Sausalito, CA 94965-9910.

(16) Berkert, U.; Allinger, N. L. Molecular Mechanics; American Chemical Society Monograph 177; American Chemical Society: Washington, DC, 1982.

(17) The MM+ Force Field is an Extension of MM2. Hyperchem's Manual, Computational Chemistry, AutoDesk, Inc., Publication 100033-02, assy no. 100210, 1992.

(18) Excel Program, Microsoft Corp., version 5.0.

(19) Molecular Simulation Inc., 16 New England Executive Park, Burlington, Massachusetts, 01803-5297.

(20) Mayo, S. L.; Olafson, B. D.; Goddard, W. A. *J. Phys. Chem.* **1990**, *94*, 8897.

MA950631R