On the crystal structure of poly(1,4-*trans*-cyclohexanediyl-dimethylene terephthalate)

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(*Received* 8 *March* 1982; *revised* 10 *May* 1982)

Poly(1,4-*trans*-cyclohexanediyl-dimethylene terephthalate) has a triclinic unit cell and belongs to the space group P1. The calculated crystalline density of 1.266 g cm^{-3} indicates that there is only one chain stem per unit cell. The determination of the structure has been made by first building a chain using the bond distances and angles obtained from the single crystal structure determination of 1,4-*trans*-cyclohexanediyldimethylene dibenzoate a model compound for the above mentioned polyester. Packing analysis followed by an X-ray intensity calculation confirmed the structure. The agreement index $R = \Sigma|\Delta F| / \Sigma F0$ has the value of 0.127 at the end of the refinement. The chain conformation and the packing of the chains in the unit cell are discussed and compared with those of other polyesters in the same series, *x*GT (*x*=2, 4 and 6). The 'flexible' segment, *trans*-dimethylene-1,4 cyclohexane, $-O-CH_2-(C_6H_{10})-CH_2-O-$, has the conformation $t_t^g(tgt)_g^t$ (*g*, *gauche* and *t*, *trans*).

Keywords Polyester; poly(1,4-*trans*-cyclohexanediyl-dimethylene terephthalate); model compound; crystal structure; conformational analysis

INTRODUCTION

The first structural investigation of poly(oligomethylene terephthalates) $[-C_6H_4-CO-O-(CH_2)_x-O-CO-]_n$ or *x*GT, where *x* is the number of methylene groups, was reported in 1954 by Daubeny, Brown and Bunn for poly(ethylene terephthalate), 2GT[1]. The structures of 3GT[2,3], 4GT[4-6] and 5GT[7] have since been established while the structure of 6GT is still under investigation[8-10]. The above polyesters are constituted of a flexible methylenic sequence sandwiched between rigid terephthaloyl groups.

Poly(1,4-*trans*-cyclohexanediyldimethylene terephthalate), $[-C_6H_4-CO-O-CH_2-C_6H_{10}-CH_2-O-CO-]_n$ or poly(*t*-CDT), is a related member of the above-mentioned series of polyesters, especially 6GT. However, because of the existence of the cylohexyl group it does not have the flexibility of the latter. Boye[11] studied this polyester and concluded from the value of its fibre repeat that it had a fully extended conformation. Although this proved to be correct, no comparison of the observed and calculated X-ray intensities was reported.

EXPERIMENTAL

Sample preparation

Poly(*t*-CDT) chips were obtained from the Aldrich Chemical Company, Inc. The fibres of poly(*t*-CDT) were prepared in the following manner: After heating to 180°C, the softened polymer was quickly drawn and quenched to room temperature. The fibre was further elongated by keeping it under tension at 150°C. The fibre was finally annealed at 180°C for 24 h. In another attempt, a film of the polymer was obtained after it had been dissolved in toluene at 110°C. When the solution was poured on a cold TEFLON plate, the solvent evaporation yielded a thin film that was further treated as described above. The precipitation of the polymer dissolved in nitrobenzene was achieved by adding n-dodecane to the solution. The polycrystalline material so obtained was used for powder X-ray diffraction. The X-ray fibre diagrams were recorded in a cylindrical camera using the multiple film technique. The diffracted intensities were visually estimated from the fibre diagram using a calibrated intensity scale. The structure factors were then derived after correction for the Lorentz and polarization factors.

Conformational analysis

Although the cyclohexanedimethylene moiety of poly(*t*-CDT) is related to the hexamethylene sequence in 6GT, a new conformational analysis had to be performed similar to that described by Poulin-Dandurand[12] for poly(oligomethylene terephthalates).

Intrinsic torsional potential with a three fold barrier of 2.8 kcal mol^{-1} was assigned to rotations about the bonds while the torsional barrier for the C–O bond was taken to be zero. The rotation between this carboxy group and the benzene group of atoms was not allowed. The van der Waals interactions between nonbonded atoms were evaluated using 6–12 potential functions, with the parameters proposed by Scott and Scheraga[13,14]. Electrostatic interactions were evaluated by assigning partial charges to the atoms using a Coulomb's law potential function[15]. The following values for the bond moments[16] were used C–C = 0.0, C–O = 0.82, C$\overset{\cdots}{-}$O = 0.74, C = O = 2.34 and C–H = 0.38 in Debyes. Isoenergy contours were plotted at 1 kcal mol^{-1} intervals with respect to the minimum energy which was arbitrarily set to zero.

Model compound

As indicated earlier one of the model compounds related to poly(*t-CDT*) *is 1,4-trans*-cyclohexanediyldimethylene dibenzoate. This compound has been synthesized and its crystal structure established[17] from

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Table 1 Crystal data for poly(*t*-CDT)

$[C_{16}H_{18}O_4]_n$	$MW = 274.32$	
Triclinic unit-cell, space group $P\bar{1}$		
$a = 6.46(1)$	$b = 6.65(1)$	$c = 14.2(2)$ Å (fibre axis)
$\alpha = 89.4(5)$	$\beta = 47.0(3)$	$\gamma = 114.9\ (5)^\circ$
$V = 358$ Å^3	$d_0 = 1.23$	$d_c = 1.266$ (g cm^{-3})
$Z = 1$	$\lambda CuK\alpha = 1.54178$ Å	

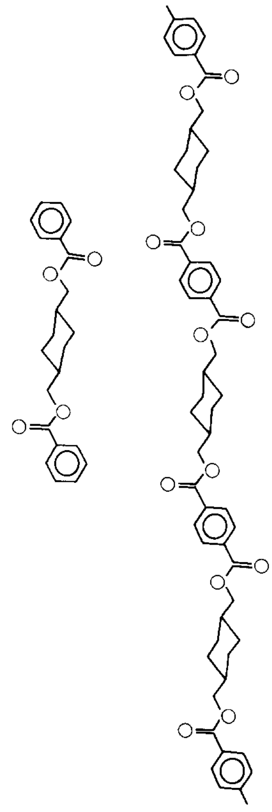

Figure 1 Poly(1,4-*trans*-cyclohexanediyldimethylene terephthalate) in relation to its model compound 1,4-*trans*-cyclohexanediyldimethylene dibenzoate

three-dimensional X-ray diffraction data for the sole purpose of this investigation.

STRUCTURE DETERMINATION

Unit cell dimensions and space group

The unit cell dimensions of poly(*t*-CDT), first reported by Boye[11], have been confirmed using data from both fibre and powder diagrams and are presented in *Table 1* together with other crystal data of interest. As proposed by Boye, we chose the $P\bar{1}$ space group. This choice was arrived at by indirect supporting evidence: Add xGT's whose structures were established belong to the $P\bar{1}$ space group and the density calculated from the unit cell dimensions indicated that only one monomer is present in one unit cell. The chain is oriented along c, the fibre axis, and the centres of both the terephthaloyl group and the 1,4-*trans*-bis(hydroxymethyl)cyclohexane moiety are on some crystallographic centres of symmetry of the $P\bar{1}$ space group.

Determination of the chain conformation

Figure 1 presents side by side the polymer and its model compound while in *Figure 2* are given the bond distances and angles derived from the structure of the model compound[17]. Since the 1,4-*trans*-bis(hydroxymethyl)cyclohexane is situated on a centre of symmetry, the following relationships exist between the torsion angles of interest (see *Figure 3*).

$\varphi_1 = C(4)–O(2)–C(5)–C(6) = -\varphi_1'$, $\varphi_2 = (2)–C(5)–C(6)–C(8) = -\varphi_2'$, $\varphi_3 = C(5)–C(6)–C(7)–C(8') = -\varphi_3'$, $\varphi_4 = C(5)–C(6)–C(8)–C(7') = -\varphi_4'$, $\varphi_5 = C(6)–C(7)–C(8')–C(6') = -\varphi_5'$.

The torsion angles φ_3, φ_4, φ_5 and their centrosymmetrically related counterparts do not need to be varied since they define the conformation of the cyclohexanediyldimethylene moiety. Therefore only a (φ_1,φ_2) energy map needs to be computed with the following fixed values: $\varphi_3 = -177.1$, $\varphi_4 = 179.5$ and $\varphi_5 = 56.4$. This map is shown in *Figure 3*. It is only for a conformation ($\varphi_1 = 179$, $\varphi_2 = 176$) close to that of the model compound that the fibre repeat coincides with an energy minimum (the second lowest).

The (φ_1,φ_2) pairs for the calculated minima with the above constraints are compared in *Table 2* with the actual conformation of the model compound.

Packing analysis

Since the centres of the terephthaloyl and the cyclohexyl groups are on crystallographic centres of symmetry

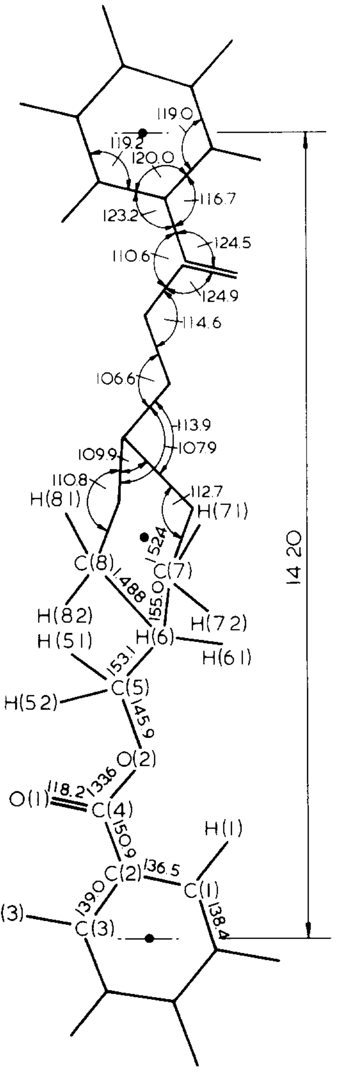

Figure 2 Bond distances (pm) and angles (degrees) used for poly(*t*-CDT)

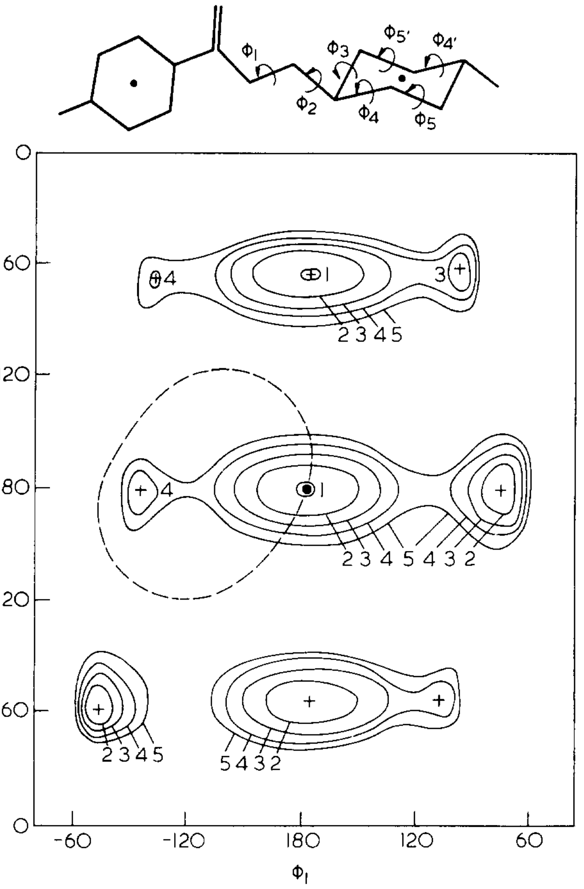

Figure 3 Identification of the torsion angles and energy map of poly(*t*-CDT). The energy minima are shown by (+). The model compound conformation is shown by (•). Combinations of ϕ_1 and ϕ_2 which yield the observed fibre repeat of 14.2 Å are shown by the dotted line

Table 2 Conformational analysis of poly(*t*-CDT). Conformational angles corresponding to the computed minima and their relative energies

Conformation angles (degrees) ϕ_1	ϕ_2	Energy (kcal mol^{-1})
177	64	0.00
179	176	0.09
77	176	0.15
174	−61	0.39
−74	−55	0.51
97	59	1.59
94	176	2.20
−107	−61	2.58
−103	69	3.05
Conformation of the model compound		
−173.5	−175.6	
Actual conformation in the polymer		
−168.0	−175.6	

along *c*, the chain of poly(*t*-CDT) has only one degree of freedom, the rotation around the *c*-axis. The interchain interactions are minimized following William's procedure[18]. The packing index, $R_p = \Sigma w(d_0 - d_{ij})^2$, measures the degree of interactions between chains. In this expression, d_0 is a reference distance, d_{ij} in the actual distance between atoms *i* and *j* is adjacent chains while *w* is a weighting parameter. The values of d_0 and *w* used here are taken from Williams[18]. Starting from an arbitrary orientation, the chain is rotated until R_p reaches the reasonably low value of 10.2 kcal mol^{-1}. Up to this point the benzene and carboxylic groups are coplanar. However, it has been shown[19] that very often the carboxylic plane and the benzene ring plane are not coplanar. They are found to be tilted with respect to one another by as much as 9°. For this reason, the torsion angle C(1)–C(2)–C(4)–O(2) is varied by small increments and the packing procedure is resumed until R_p is lowered to 8.5 kcal mol^{-1}. At this minimum value, C(1)–C(2)–C(4)–O(2) is now 173.1°. This is equivalent to a 7° tilt of the benzene ring plane to that of the carboxylic group of atoms.

X-ray diffraction

The set of coordinates corresponding to the chain orientation having the least interactions with its neighbours is used to compare observed and calculated structure factors after refinement of the scale factor and an overall isotropic temperature factor *B*. At first the *R*-factor $= \Sigma|\Delta F|/\Sigma Fo$ reached 0.14, while $B = 16$ Å^2. The chain is then slightly rotated at 1° intervals from the minimum R_p value and the *R*-factor is computed for each new position. *Figure 4* shows the variation of *R* as a function of the rotation of the chain. The minimum *R*-value of 0.127 is reached for a position 1° away from that obtained by packing for the 14 measured reflections. When all reflections down to $d = 3.200$ Å are included, $R = 0.23$. The final atomic coordinates are given in *Table 3* while the list of observed and calculated structure factors is shown in *Table 4*. The X-ray scattering factors are taken from Cromer and Waber[20] for C and O atoms and from Stewart, Davidson and Simpson[21] for H atoms.

DISCUSSION

Although poly(*t*-CDT) and 6GT are related, the presence of the cyclohexane at the centre of the methylenic

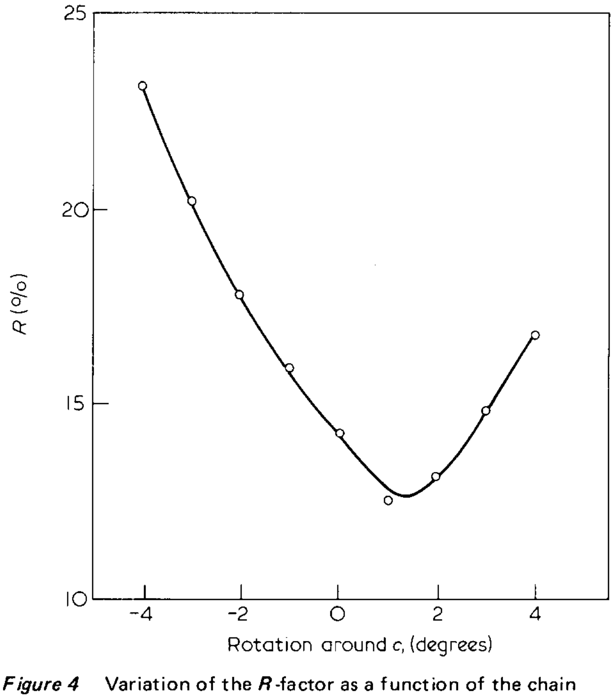

Figure 4 Variation of the *R*-factor as a function of the chain orientation within its unit cell

Table 3 Fractional atomic coordinates ($\times 10^4$ for O and C, $\times 10^3$ for H atoms) of poly(*t*-CDT)

ATOM	*X*	*Y*	*Z*
O(1)	−1210	−4488	2046
O(2)	1004	−954	2127
C(1)	637	1298	663
C(2)	99	−951	782
C(3)	−536	−2104	113
C(4)	−29	−2363	1679
C(5)	572	−2245	3143
C(6)	1124	−508	3766
C(7)	−1471	118	4566
C(8)	970	−1743	4762
H(1)	110	216	114
H(3)	−93	−375	20
H(51)	252	−246	260
H(52)	−191	−370	392
H(61)	347	110	302
H(71)	−135	94	392
H(72)	−390	−142	532
H(81)	281	−207	421
H(82)	−132	−339	553

Table 4 Observed and calculated structure amplitudes (×10) for poly(*t*-CDT)

h	*k*	*l*	F_o	$\lvert F_c \rvert$
0	1	0	270	282
1	−1	0	187	164
1	0	0	463	473
1	−2	0	113	114
0	0	1	50	33
0	1	1	141	169
1	−1	1	191	230
1	0	1	–	37
0	−1	1	202	219
−1	1	1	219	297
1	−2	1	–	10
1	0	2	83	77
1	−1	2	–	81
0	1	2	160	143
0	0	2	–	41
1	1	2	–	29
1	0	3	71	67
1	−1	3	85	113
1	1	3	–	9
0	1	3	–	22
0	0	3	74	61
1	0	4	–	9

sequence brings about a certain rigidity which prevents chain motions that may take place in 6GT. Because of this, poly(*t*-CDT) resembles 2GT rather than 6GT especially when one compares their melting points. For 2GT[1] and poly(*t*-CDT)[22] these are 264 C and 294 295 C respectively, while that of 6GT[23] is only 148 C.

The chain of poly(*t*-CDT) in its unit cell is shown in various projections on *Figure 5*. Since poly(*t*-CDT), 2GT, 4GT and 6GT all have triclinic monomolecular unit cells and all belong to the $P\bar{1}$ space group, it is not too surprising that they all have very similar packing arrangements. This point may be more clearly appreciated using the two angles φ and ψ defined by Hall and Pass[6]. φ is the angle between the crystallographic axis c and the C(2) C(4) bond while ψ is the angle between the same c axis and the normal to the benzene ring. The φ and ψ angles in poly(*t*-CDT), 2GT, 4GT and 6GT presented in *Table 5* are indeed very similar. As noted earlier the six methylene groups in 6GT are replaced by the less flexible 1,4-*trans*-bis(hydroxymethyl)cyclohexane group. Because of this only the φ_1 and φ_2 angles have no torsion restriction. The observed conformation for poly(*t*-CDT) is $t_t^g(tgt)_g^t t$ depending which side of the cyclohexane ring is followed. This is why, the fibre repeat of poly(*t*-CDT) is only 14.2 A while it is 15.738 A in 6GT which has the *tttttt* conformation.

Table 5 Comparison of the φ and ψ angles in poly(*t*-CDT), 2GT, 4GT and 6GT

	poly(*t*-CDT)	2GT	4GT	6GT
φ	36	24	26	28
ψ	73	86	82	64
Reference	this work	1	4	10

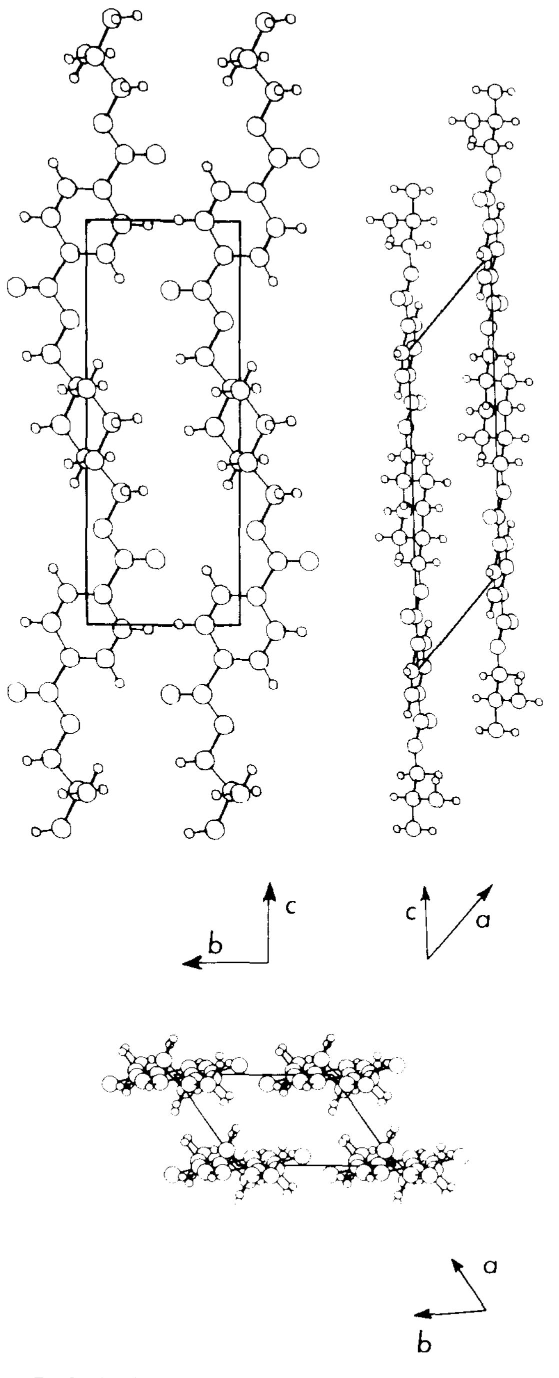

Figure 5 Projections showing the organization of the polymer chains in the unit cell

ACKNOWLEDGEMENTS

The authors wish to thank the Natural Sciences and Engineering Research Council of Canada for its grant in aid of research.

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