Poly(1,4-*trans*-cyclohexanediyldimethylene adipate): Polymorphism and the structure of form I, using X-ray diffraction

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(*Received 5 July 1984*)

Poly(1,4-*trans*-cyclohexanediyldimethylene adipate) or poly(*t*-CDA) crystallizes in two forms. Form **I** of poly(*t*-CDA) is analogous to the one reported for poly(*t*-CDS). Poly(*t*-CDA) has a monoclinic unit-cell of dimensions $a=6.938$, $b=9.761$, $c=15.97$ Å and $\beta=41.4°$ and belongs to the $P2_1/n$ space group. The calculated crystalline density of 1.181 g cm^{-3} indicates that there is one chemical unit per fibre-repeat and two chains per unit-cell. The crystal structure of poly(*t*-CDA), form **I** was established using published structural data on related molecules for model building combined with a packing minimization procedure. The structure was confirmed by a comparison of calculated and observed structure amplitudes derived from an X-ray fibre diagram. The agreement index *wR* has the value of 0.153 for 31 observed diffraction data. The $-O-CH_2(C_6H_{10})CH_2-O-$ moiety of the polyester has the conformation $t_g^2(tg\pm t)_t^{g^-}g$ (*g*, *gauche* and *t*, *trans*), while the adipate group is in the *trans* conformation. Form **II** of poly(*t*-CDA) was identified through its distinct X-ray diffraction pattern, but its structure has not yet been established.

(Keywords: poly(1,4-*trans*-cyclohexanediyldimethylene adipate; polymorphism; X-ray diffraction)

INTRODUCTION

Structural studies of aliphatic polyesters have been undertaken for almost fifty years[1,2]. The first crystalline structures were established in the ethylene glycol polyesters series, $\{O(CH_2)_2O-CO(CH_2)_xCO\}_n$, where $x=0$, 2, 4 and 6[3,4]. When the ethylene glycol part is replaced by 1,4-*trans*-cyclohexanedimethanol, some physical properties such as the melting point and the glass transition temperature are very similar for corresponding members in the two series of polyesters ($x=0$ or 2). However, when $x=4$, poly(ethylene adipate) and poly(*t*-CDA) have melting points of 47°C and 109°C–112°C respectively. Recently we reported the crystalline structure of the first member of this polyester family, poly(1,4-*trans*-cyclohexanediyldimethylene succinate) or poly(*t*-CDS), $\{O-CH_2(C_6H_{10})CH_2-O-CO(CH_2)_xCO\}_n$ ($x=2$), using electron and X-ray diffraction[5]. In the present paper, we describe the crystal structure determination of form **I** of poly(1,4-*trans*-cyclohexanediyldimethylene adipate) or poly(*t*-CDA) ($x=4$). Like poly(ethylene adipate)[6], this aliphatic polyester crystallizes in two forms.

EXPERIMENTAL

Sample preparation

Poly(*t*-CDA) powder was obtained from the Aldrich Chemical Company, Inc. The molecular weight of the polyester, calculated from tonometric measurement[7] is equal to 4000 g. At this low molecular weight, the highly crystalline polyester could not be drawn. The polymer has therefore been treated with tolylene-2,4-diisocyanate to produce a higher molecular weight compound according to the method described by Iwakura, Taneda and Ushida[8]. Following this treatment, the molecular weight was increased to 9600 g. A similar approach was also successfully used in the case of poly(*t*-CDS)[5]. This treatment does not affect the structural determination since it is believed that only the pure ester sections of the chains crystallize, while the amide portions remain in the amorphous region of the polymer[4]. Fibres of poly(*t*-CDA) could then be obtained by cold drawing. Poly(*t*-CDA) crystallizes in two forms depending upon the annealing conditions. When the poly(*t*-CDA) fibres are annealed under tension for 6 h at 95°C, form **I** is obtained. If, however, a tension is applied for 30 min at 102°C, this results in form **II**. The polyester also crystallizes in form **II** when the fibres are annealed at 95°C for several days. Micro-single crystals of poly(*t*-CDA) could be grown by slow evaporation of a solution of 0.1% of commercial poly(*t*-CDA) in benzene.

X-ray diffraction

X-ray fibre diagrams of the two forms were recorded in Warhus, precession or Weissenberg cameras using the multiple film technique and nickel filtered CuKα radiation, (λ CuK$\bar{\alpha}=1.54178$ Å). For form **I**, some diffracted intensities were visually estimated while others were measured with a Joyce–Loebl microdensitometer. The structure factors were then derived after correction for the relevant Lorentz and polarization factors. The X-ray scattering factors were obtained from Cromer and Waber[9] for C and O atoms and from Stewart, Davidson and Simpson[10] for H atoms.

Model building

No new model compound was synthesized for the

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structural determination of poly(*t*-CDA). We used the bond distances and angles drawn from the model compounds of poly(1,4-*trans*-cyclohexanediyldimethylene terephthalate) or poly(*t*-CDT) and of poly(*t*-CDS)[11]. When cyclohexane is 1,4-*trans*-disubstituted, it was observed that the conformation does not vary significantly from the calculated values for cyclohexane itself[12]. The cyclohexylene part was constructed with the data from poly(*t*-CDS) model compound. For the adipate section, the construction data were obtained by averaging of corresponding values taken from crystal structures containing the adipate fragment[13–20]. The torsion angles were adjusted so that the distance between the centres of two consecutive cyclohexylene groups would be equal to the *c*-dimension of the unit cell.

Structure determination of poly(t-*CDA*), *form* I

Unit-cell dimensions and space group. The X-ray fibre diagram of poly(*t*-CDS) form I is shown in *Figure 1a.* This pattern, very reminiscent of that of poly(*t*-CDS), differs significantly from that shown in *Figure 1b* which is referred to as form **II**. The 2θ values of 31 reflections, up to the seventh layer-line, have been measured. The indexing of the fibre diagram is schematically represented in *Figure 1c.* An acceptable unit-cell fitting these reflections was obtained starting with the published parameters of poly(*t*-CDS) whose *c*-dimension was increased by 2.54 Å. This is the distance between three consecutive methylenic groups[21]. The monoclinic unit-cell dimensions thus derived are reported in *Table 1*. In the list shown in *Table 2* the observed and calculated $\sin^2\theta$ values are compared. By analogy with poly(*t*-CDS), the space group was chosen as $P2_1/n$. This choice was confirmed since the systematic absences are respected in the present indexing. The comparison of the calculated density with the experimental value, measured by flotation in a $ZnCl_2$ solution, indicates that there are two polymeric chains per unit-cell. Since in $P2_1/n$ the general position is of order 4, the two chains must occupy special positions in the unit-cell. The chains are parallel to *c*. One passes through the origin while the second one passes through the centre of the $\overline{ab}$ plane in such a way that the centres of the cyclohexylene groups and the midpoints of the CH_2–CH_2 central bonds in the adipate section must coincide with the centres of symmetry of the unit-cell.

Packing analysis. Atomic numbering, bond distances and valence angles derived from model compounds and published results chosen to build the poly(*t*-CDA) chain are given in *Figure 2.* The torsion angles values are reported in *Table 3*. The relative orientation of the chains in the unit-cell remains to be found. As the chains are held by the symmetry centres of the unit-cell, the rotation around the *c*-axis is the only packing parameter. The

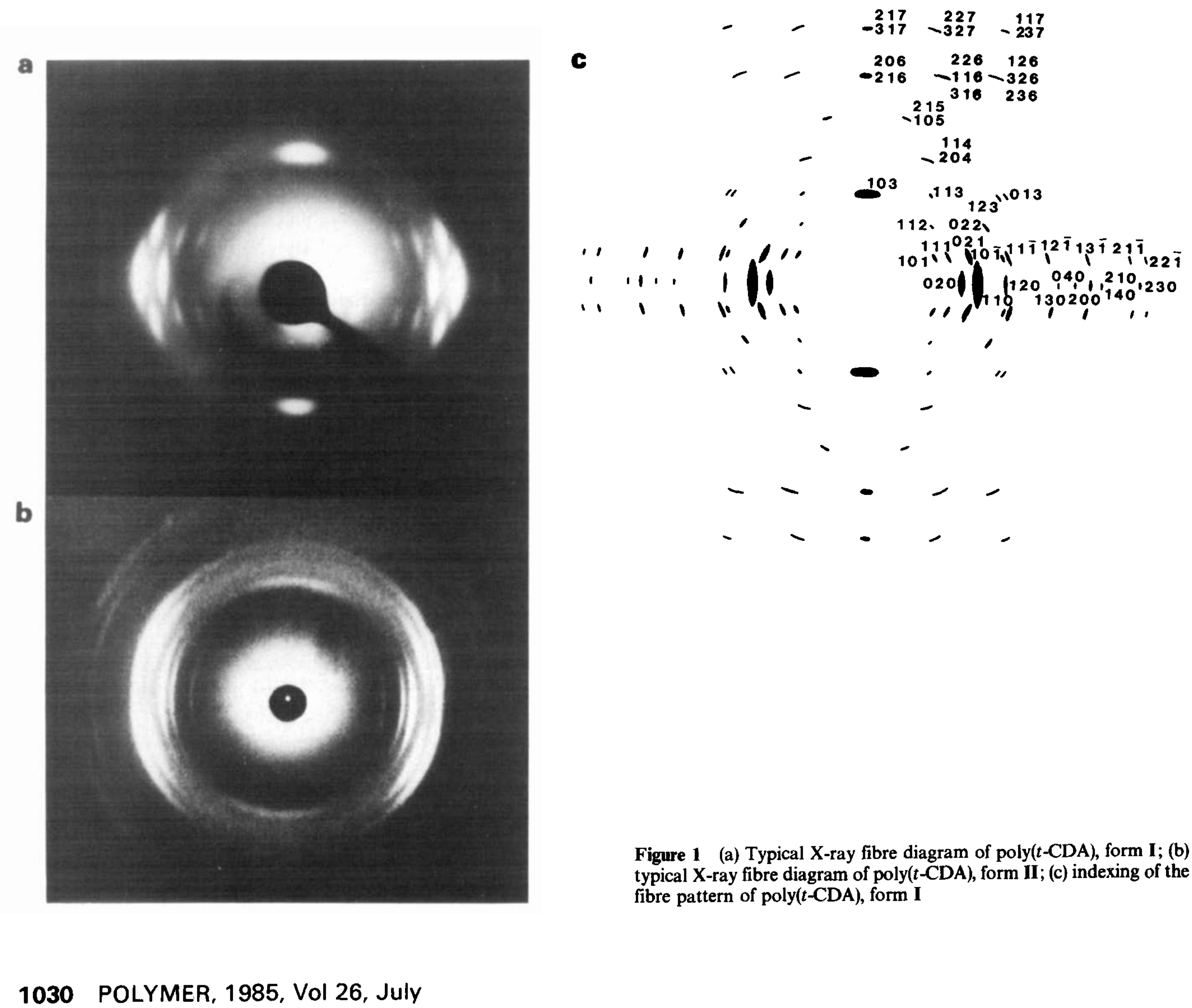

Figure 1 (a) Typical X-ray fibre diagram of poly(*t*-CDA), form **I**; (b) typical X-ray fibre diagram of poly(*t*-CDA), form **II**; (c) indexing of the fibre pattern of poly(*t*-CDA), form **I**

Table 1 Crystal data for poly(*t*-CDA), form **I**

$(C_{14}H_{22}O_4)_n$ $MW = 254.33$
Monoclinic unit-cell, space group $P2_1/n$
$a = 6.938(0)$, $b = 9.761(10)$, $c = 15.97(5)$ Å (fibre axis)
$\beta = 41.4(5)°$, $V = 715$ Å^3, $Z = 2$, $d_0 = 1.15$, $d_c = 1.181$ g cm^{-3}

Table 2 Comparison of observed and calculated values of $\sin^2\theta$ (× 10^4) for poly(*t*-CDA), form **I**

hkl	$\sin^2\theta_0$	$\sin^2\theta_c$
020	251	249
110	344	345
120	535	533
130	845	845
040	1000	996
200	1117	1127
210	1224	1191
230	1683	1693
101	148	151
111	213	215
021	306	306
$10\bar{1}$	522	518
$11\bar{1}$	583	581
$12\bar{1}$	774	769
$13\bar{1}$	1084	1081
$21\bar{1}$	1617	1611
$22\bar{1}$	1794	1799
112	201	191
022	465	462
103	220	209
113	270	273
123	474	462
013	548	541
114 204	483	462 509
215 105	681	685 693
216	932	903
226	1057	1093
126	1321	1347
217	1247	1227
227	1413	1417
237	1753	1732

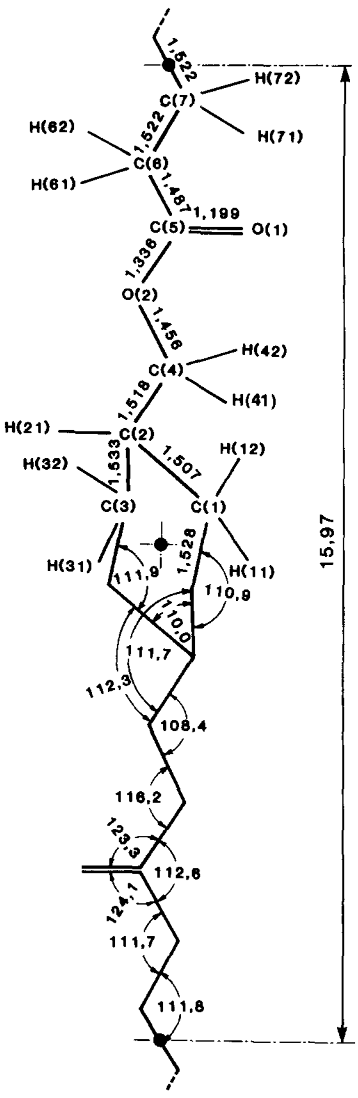

Figure 2 Bond distances and angles chosen to build the polymer's repeat unit

Table 3 Torsion angles values in poly(*t*-CDA), form **I**

Torsion angles	Values (degrees)
C(2′)–C(3′)–C(1)–C(2)	– 56.6
C(3′)–C(1)–C(2)–C(3)	56.2
C(1)–C(2)–C(3)–C(1′)	– 55.7
C(1)–C(2)–C(4)–O(2)	64.7
C(3)–C(2)–C(4)–O(2)	– 171.2
C(2)–C(4)–O(2)–C(5)	– 173.5
C(4)–O(2)–C(5)–O(1)	0.0
C(4)–O(2)–C(5)–O(6)	– 177.9
O(2)–C(5)–C(6)–C(7)	– 177.7
C(5)–C(6)–C(7)–C(7′)	– 175.0
C(6)–C(7)–C(7′)–C(6′)	180

interchain interactions are minimized following William's procedure[22]. The packing index $R_p = \Sigma w(d_0 - d_{ij})^2$, measures the degree of interactions between adjacent chains, where d_0 is a reference distance, d_{ij}, the distance between atoms i and j of two adjacent chains and w, a weighting parameter. The values of d_0 and w used here are taken from William[22]. The packing index gives an indication of how weak these interactions are. The plot of R_p as a function of the chain orientation is reported in *Figure 3*. A minimum R_p value of 13 kcal mol^{-1} is reached at 168° of the initial starting position. With this orientation, the shortest contact, at 3.39 Å, is observed between O(1) and C(3′).

Confirmation of the structure

Since it has been found that the actual chain orientation usually deviates slightly from that obtained by packing analysis, small chain adjustments are needed. The chain passing through the origin and the second chain, passing through the centre of the $\underline{ab}$-plane, were concomitantly rotated by ± 15° from the best packing orientation, by 5° intervals. At each orientation, the observed and calculated structure factors were compared after refinement of the scale factor and an overall isotropic temperature factor, B. The values taken by the quantities $R = \Sigma|\Delta F|/\Sigma F_0$ and $wR = [\Sigma w\Delta F^2/\Sigma w F_0{}^2]^{1/2}$, which measure the agreement between observed and calculated structure factors, are plotted as a function of the chain orientation on *Figure 3*. The minimum values of R and wR reached are 0.195 and 0.153 respectively for 31 diffraction spots with $B = 11$ Å^2 and a chain orientation of 172° only 4° away from the above orientation. Thus the crystal structure of poly(*t*-CDA) form **I** is satisfactorily confirmed. When all observed and unobserved X-ray reflections are considered, the R-factor minimum value is 0.232 at the same orientation. The atomic coordinates corresponding to this orientation are reported in *Table 4* and the list of observed and calculated structure factors corresponding to the above minimum are given in *Table 5*.

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

Atom	x	y	z
O(1)	4	−2081	3211
O(2)	−773	−312	2608
C(1)	1706	455	161
C(2)	−973	−411	1165
C(3)	−1496	−1319	566
C(4)	−812	−1249	1912
C(5)	−339	−876	3218
C(6)	−439	147	3940
C(7)	181	−508	4585
H(11)	348	−14	−44
H(12)	203	106	55
H(21)	−275	18	175
H(31)	−332	−186	124
H(32)	11	−200	−1
H(41)	−254	−187	251
H(42)	99	−182	132
H(61)	99	90	336
H(62)	−238	61	458
H(71)	−113	−131	510
H(72)	220	−90	393

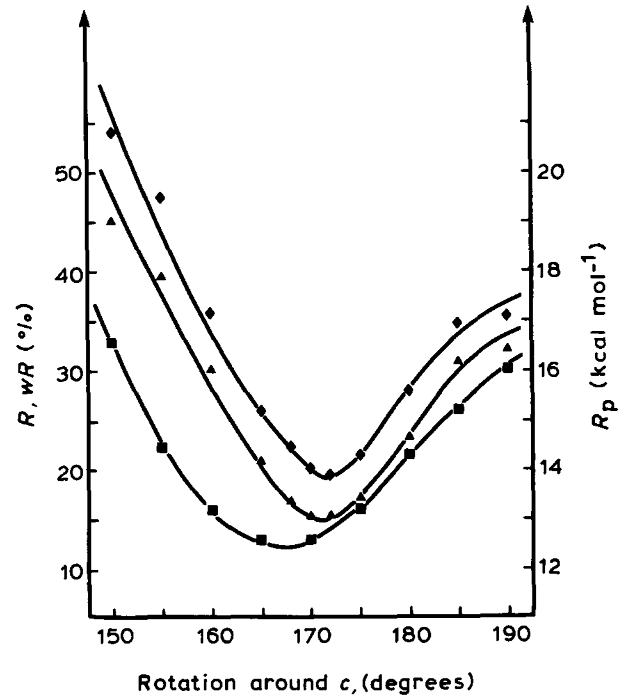

Figure 3 Variation of R_p and the conventional R- and wR-factors as the chains are rotated away from the minimum energy orientation: (◆) R; (▲) wR; (■) R_p

Table 5 List of observed and calculated structure factors ($\times 10$) for poly(*t*-CDA), form **I**

hkl	*w*	F_0	$\|F_c\|$
020	1.00	153	162
110	1.00	259	246
120	0.10	104	76
130	0.30	26	19
040	0.20	27	25
200	0.65	77	82
210	0.50	39	39
140			
220		(13)	14
230	0.60	51	42
011		(19)	14
101	0.70	50	54
111	0.90	52	67
021	1.00	130	139
121		(19)	15
$10\bar{1}$	0.75	90	98
$11\bar{1}$	0.90	90	114
031		(19)	22
131		(19)	4
$12\bar{1}$	0.65	48	41
211		(19)	8
221		(19)	8
041		(19)	10
$13\bar{1}$	0.75	69	62
141		(19)	19
231		(19)	3
$14\bar{1}$		(19)	22
$21\bar{1}$	0.65	56	65
051		(19)	10
151		(19)	10
$22\bar{1}$	0.40	37	33
112	0.25	15	15
002		(8)	10
012		(8)	7
122		(8)	8
022	0.50	30	34
103	1.00	95	74
113	0.40	21	23
123	0.50	29	34
013	0.50	31	37
114 204	0.50	43	20
215 105	0.60	51	36
206 216	0.65	71	52
226 116 316	0.75	78	84
126 326 236	0.75	69	42
217 317	0.65	57	50
227 327	0.75	70	71
107		(29)	19
117 237	0.65	57	54

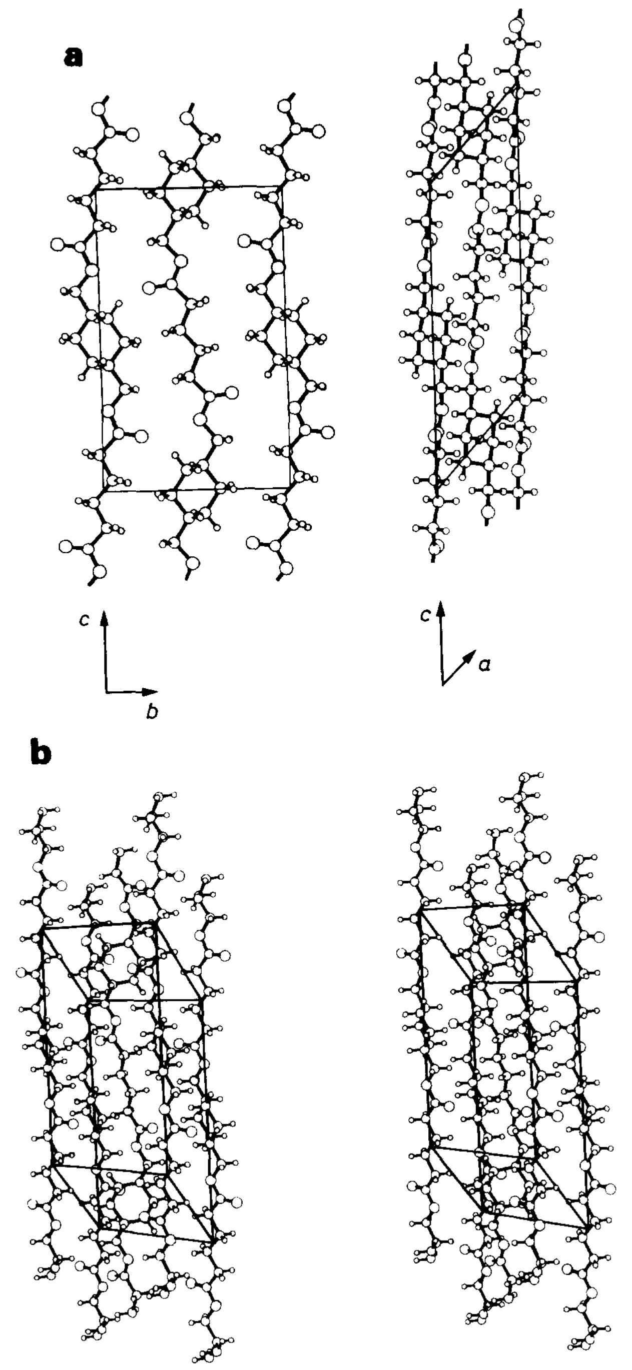

Figure 4 (a) Projections of the chains along the $\underline{a}$ and $\underline{b}$-axis. (b) Stereopair showing the packing of the chains of poly(*t*-CDA), form **I** in their unit-cell

DISCUSSION

The chains of poly(*t*-CDA) in their unit-cell are shown in projections on the *ac* and *bc* planes and by a stereoscopic pair in *Figures 4a* and *4b* respectively. The observed $t_g^t(tg^{\pm}t)_t^{g^-}t$ (*g*, *gauche* and *t*, *trans*) depending which side of the cyclohexane ring is followed. The adipate group is in *trans* conformation. Not surprisingly there is a great similitude between the molecular packing of poly(*t*-CDA), form **I** and poly(*t*-CDS).

Poly(*t*-CDA) crystallizes in two forms like poly(ethylene adipate)[6]. We have obtained the fibre diagrams of the second form (*Figure 1b*), but in spite of our repeated efforts the diffraction spots could not be well resolved. The layer-lines are not clearly defined so that the fibre repeat could not be established with any degree of certainty. Micro-single crystals of poly(*t*-CDA) have been grown successfully from a dilute benzene solution. Although, poly(*t*-CDS) and poly(*t*-CDA), form **I** are in a sense 'isomorphous', the morphologies of the micro-single crystals are very different. Poly(*t*-CDS) micro-single crystals have a diamond-shape, while those of poly(*t*-CDA) are rectangular. Hence these micro-single crystals might represent form **II** of poly(*t*-CDA). Electron diffraction must be used to complement the investigation of the polymorphism of poly(*t*-CDA).

ACKNOWLEDGEMENTS

We are very grateful to the Natural Science and Engineering Research Council of Canada for its financial support (grant A-5968).

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