Structure of one crystal modification of poly(3,3-diethyl oxetane)

M. A. Gomez*, E. D. T. Atkins† and C. Upstill‡
H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK

and A. Bello and J. G. Fatou
Instituto de Plasticos y Caucho, Juan de la Cierva 3, 28006 Madrid, Spain
(*Received 8 June 1987; accepted 13 August 1987*)

The determination of the crystalline structure of one of the two forms of poly(3,3-diethyl oxetane) detected by calorimetric and X-ray analysis is described. The unit cell is monoclinic with parameters: $a=1.333(7)$ nm, $b=0.577(2)$ nm, c (fibre axis) $=0.474(2)$ nm and $\gamma=91.1(5)°$. After computerized refinement, the final model has a crystallographic R-value of 0.18. The molecular conformation is a planar zigzag, and two chain segments pass through the unit cell. The chain conformation and the packing of chains are discussed in detail and compared with other polyoxetanes.

(Keywords: polymer structure; X-ray diffraction; calorimetry)

INTRODUCTION

Poly(3,3-diethyl oxetane) is a member of the series of polymers with the general form $[\text{–O–CH}_2\text{–CR}_1\text{R}_2\text{–CH}_2\text{–}]_n$. The first and chemically the simplest of this series is polyoxacyclobutane or polyoxetane, with R_1 and R_2 both being hydrogen atoms. The substitution of R_1 and R_2 by CH_3 or C_2H_5 groups introduces important changes in the properties of this family of polymers. The effect of symmetrical pendant side groups on the conformation and their influence on chain–chain interactions and physical properties is of major interest in the study of this group of polymers.

The polyoxetanes are semicrystalline polymers and the crystalline structure of the first two members, polyoxetane (PTO) and poly(3,3-dimethyl oxetane) (PDMO), has been described by Tadokoro and coworkers[1–4]. However, no crystallographic information about poly(3,3-diethyl oxetane) (PDEO) has been reported.

In previous work[5], the thermal transitions and the influence of the crystallization temperature on the melting behaviour were studied for PDEO using differential scanning calorimetry (d.s.c.) and X-ray powder diffraction. The occurrence of two melting peaks in the d.s.c. curves, depending on the crystallization conditions, is because two different crystalline forms exist[5] and this has been confirmed by X-ray analyses. Modification I, with a melting point of 73°C, is obtained when the temperature of crystallization is greater than 40°C. The crystalline structure of modification I is reported in this paper. Modification II, with a melting point of 57°C, is obtained when the temperature of crystallization is less than 40°C. The determination of the crystalline structure of modification II will be the subject of further study.

The present work is concerned with the study of the more thermally stable crystalline modification of poly(3,3-diethyl oxetane) and with the comparison of the chain conformation of this polymer with the other two members of the series of polyoxetanes.

EXPERIMENTAL

Material and specimen preparation

PDEO was prepared in the Department of Physical Chemistry of Polymers (Instituto de Plasticos y Caucho, Madrid). The monomer was synthesized from the corresponding 1,3-diol as described by Schmoyer and Case[6] and the polymerization was carried out in methylene chloride at 0°C using triethyloxonium hexafluorantimoniate as initiator. The polymer was fractionated by precipitation in the system chlorobenzene–ethanol. The particular fraction used in this work had a number-average molecular weight $M_n = 10^5$.

Samples suitable for X-ray diffraction measurements were prepared by moulding the polymer into aluminium moulds at temperatures above the melting point, and these were then allowed to crystallize in a thermostatically controlled bath (50°C) for a period of time determined from previous dilatometric analysis[7]. Oriented specimens were obtained by stretching the films in an Instron dynamometer at room temperature. The draw ratio was 5:1. Density was measured at 25°C by the flotation method (water–ethanol mixtures): the value was 0.946 g cm^{-3} for the sample crystallized isothermally at 50°C, conditions in which only modification I is formed.

X-ray diffraction

X-ray diffraction photographs were taken using nickel-filtered Cu Kα radiation from an Elliot rotating-anode X-ray generator. Pinhole collimation and a flat-plate camera were used to record the X-ray patterns. The specimens were dusted with finely powdered calcite

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* Present address: AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, NJ 07974-2070, USA

† To whom correspondence should be addressed

‡ Plessey Research Roke Manor Ltd, Roke Manor, Romsey, Hampshire S051 0ZN, UK

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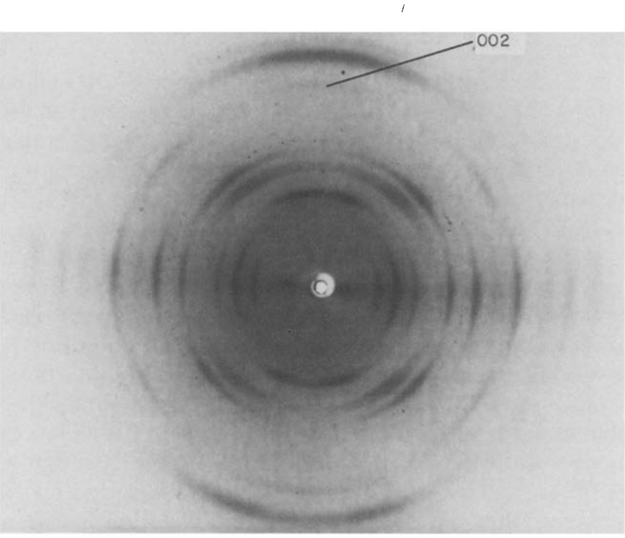

Figure 1 X-ray fibre diffraction photograph of poly(3,3-diethyl oxetane). The fibre axis is vertical but tilted slightly to enhance the 0 0 2 reflection (arrowed)

(characteristic spacing 0.3035 nm) to calibrate the diffraction patterns. *Figure 1* shows the X-ray fibre diffraction pattern obtained from the oriented sample. Specimens were tilted towards the incident beam at appropriate angles to register each $00l$ reflection at maximum intensity on the meridian (vertical bisector in *Figure 1*). From these X-ray patterns the fibre periodicity could be obtained accurately and also the systematic absences $l = 2n$ (where n is an integer), confirmed for $00l$ reflections.

Intensities were measured with a Joyce Loebl linear microdensitometer. Correction factors for Lorentz, polarization, multiplicity and oblique incidence on the film were applied. To compare the calculated intensities with more quantitative intensity data, diffraction patterns of the uniaxially oriented sample and the unoriented sample were taken with a powder goniometer.

COMPUTER MODELLING

Molecular models for PDEO were computer-generated and refined using a linked-atom least-squares system, the formal details of which may be found elsewhere[8]. The system can refine against stereochemical information, or jointly against stereochemistry and X-ray data, and geometrical constraints and restraints—such as helical symmetry, pitch, chain continuity and symmetry relationships dictated by the space group—may be imposed on the models using Lagrange multipliers.

The first step in the computer modelling was to construct an isolated molecule. For the structure of PDEO, values for bond lengths and angles were assumed to be the same as those in comparable low-molecular-weight compounds, and thus only the chain torsion angles and the orientation of the substituents remained to be determined. The atom labelling scheme used for PDEO is illustrated in *Figure 2*.

In a second refinement step, molecules were packed within the unit cell in accordance with the conditions imposed by the space group. The packing was refined by rotating and translating a fixed backbone and allowing rotation of the substituent groups.

The resulting model was then refined jointly against the observed X-ray data; stereochemical data were indicated in the conventional manner using the residual factor R.

RESULTS

Unit cell and space group

From the measured spacing of the Bragg reflections, the unit-cell dimensions were refined by a least-squares procedure, giving a monoclinic cell with dimensions $a = 1.333(7)$ nm, $b = 0.577(2)$ nm, c (fibre axis) $= 0.747(2)$ nm and $\gamma = 91.1(5)^\circ$. From density considerations, two chain segments must pass through this unit cell. The calculated density based on this supposition is $1.04\ \mathrm{g\,cm^{-3}}$, which is in good agreement with the measured density of the drawn fibre, $0.946\ \mathrm{g\,cm^{-3}}$. (Measured densities of polymer fibres are usually slightly lower than calculated because of the presence of some amorphous and less dense matter.) Meridional reflections ($00l$) were observed only when $l = 2n$. This selection rule, together with considerations about the symmetry of the molecule and density measurements favouring two chains in the unit cell, suggested that the most probable space group is $P2_1$.

Chain conformation

The molecular conformation of the isolated chain was

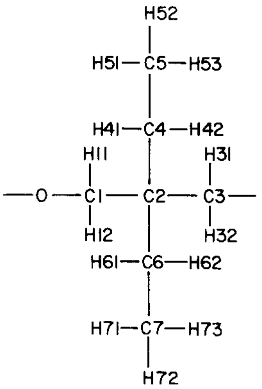

Figure 2 Atom labelling for PDEO

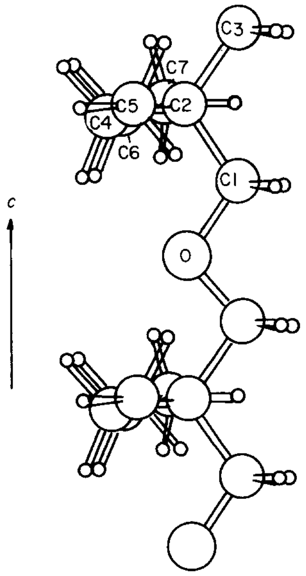

Figure 3 Projection of the chain conformation for PDEO

Table 1 Fractional atomic coordinates (nm)

Atom	x	y	z
O	0.2556	−0.3285	0.0000
C1	0.2502	−0.4757	0.2429
C2	0.2561	−0.3266	0.5120
C3	0.2498	−0.4849	0.7733
C4	0.1882	−0.1156	0.4792
C6	0.3434	−0.1487	0.4851
C5	0.0777	−0.1929	0.5160
C7	0.4439	−0.2722	0.5261
H11	0.1809	−0.5840	0.2331
H12	0.3123	−0.6004	0.2364
H41	0.2011	−0.0350	0.2703
H42	0.2058	0.0121	0.6470
H61	0.3407	−0.0654	0.2752
H62	0.3361	−0.0142	0.6498
H31	0.1822	−0.5985	0.7579
H32	0.3060	−0.6230	0.7550
H51	0.0559	−0.3115	0.3421
H53	0.0683	−0.2824	0.7209
H52	0.0293	−0.0390	0.5115
H71	0.4767	−0.2219	0.7320
H73	0.4310	−0.4622	0.5187
H72	0.4915	−0.2448	0.3375

considered to be a planar zigzag, giving good agreement between the observed fibre period of 0.474 nm and a calculated period of 0.485 nm, with bond lengths C–O = 0.143 nm, C–C = 0.154 nm, C–H = 0.109 nm and bond angles (tetrahedral angles) fixed. In order to match exactly the observed fibre repeat it was necessary to compress the C–O–C bond angle slightly. In trial computer models, the backbone was considered as a rigid body and only side-group orientations were treated as refinable. A minimum-energy calculation confirmed that the ethyl groups were in the *trans* conformation. In a second step, all the torsion angles of the chain were refined. A projection of the chain conformation is shown in *Figure 3*.

Chain packing

Two chain molecules were placed in the unit cell and packed in agreement with the space group. The space group symmetry, P2$_1$, related one chain to another as follows: $x_2 = 1 - x_1$, $y_2 = 1 - y_1$, $z_2 = z_1 + 0.5$, where x_2, y_2 and z_2 are the coordinates of an atom in chain 2 and x_1, y_1 and z_1 those of the equivalent atom in chain 1. Maintaining this relationship, the packed structure was refined by rotating the chains about their axes and translating them in *a* and *b* whilst allowing side-group orientations to vary.

The refined packed structure was used as the starting model for joint stereochemical and X-ray refinement. An overall isotropic temperature factor of 0.05 nm^2 was used (this was not refined). The resulting *R* value was 0.18. Even though refinable torsion angles and packing parameters were allowed to vary, the conformation and positions of the chains did not alter significantly during the X-ray refinement. The final coordinates of the structure are tabulated in *Table 1*. Calculated and observed structure factor amplitudes for the various reflections are presented in *Table 2*. The molecular arrangement in crystalline PDEO observed perpendicular to the *ab* and *ac* planes is shown in *Figure 4*.

DISCUSSION AND CONCLUSIONS

The X-ray results and structure analysis for PDEO allow comparison with results for the other two members of the series. The molecular conformation of the more stable crystalline modification of PDEO is a planar zigzag (i.e. all *trans* T_4). In *Table 3* the conformations of PTO[1–3], PDMO[4] and PDEO are listed for comparison.

PTO has four crystal modifications, one of which is a hydrate. The molecule assumes a planar zigzag conformation in the hydrate (modification I) and modification IV, $T_3GT_3\bar{G}$ in modification II and $(T_2G_2)_2$ in modification III. On the other hand, PDMO has three crystal modifications and the molecule assumes the planar zigzag conformation in modification I, $T_3GT_3\bar{G}$ in modification II, and $(T_2G_2)_2$ in modification III. Finally, PDEO has two crystal modifications: modification I with a planar zigzag conformation and modification II with a $(T_2G_2)_2$ conformation[9]. The structure of modification II will be reported in detail in a subsequent paper.

All the modifications for the three polymers have in common the four-bond repeat unit [–O–C–C–C–], the two O–C bonds are *trans* and the differences are in the conformation of the other two C–C bonds.

In the case of PTO, the more stable polymorph corresponds to modification III with molecular conformation $(T_2G_2)_2$ (ref. 5). In PDMO the stability of the crystal structure corresponds to a molecular conformation with one more bond *trans*, i.e. $T_3GT_3\bar{G}$ (ref. 5). The more stable modification in PDEO is the all-*trans* molecular conformation. This confirms that the stabilities of the main-chain conformations are affected by the size of the groups at the 3,3′-positions.

In polyoxacyclobutane and poly(3,3-dimethyl-oxacyclobutane) the planar zigzag modifications are less stable than the other modifications. In PDEO, the increment in the size of substituent increases the interaction of this with the main-chain groups, and, together with the intermolecular forces, stabilizes a crystal structure with the all-*trans*, planar zigzag conformation.

In summary, in these three polyoxetanes, the substitution of hydrogens in 3,3′-positions for methyl and

Table 2 Calculated and observed structure factor amplitudes

H	K	L	F_{calc}	F_{obs}
−2	0	0	44.7	41.6
1	1	0	61.1	55.0
2	1	0	31.1	33.4
4	0	0	29.8	27.1
4	1	0	35.2	32.4
2	2	0	21.3	24.6
3	2	0	34.6	31.2
4	2	0	18.4	13.8
−6	1	0	27.2	22.2
5	2	0	26.6	22.2
−1	0	1	20.6	41.2
2	0	1	0.6	1.5
0	1	1	26.6	24.1
−1	1	1	22.2	24.2
−2	1	1	24.5	33.8
4	0	1	6.6	1.5
0	2	1	20.0	20.3
−2	2	1	11.7	14.6
3	2	1	12.6	17.4
0	0	2	18.2	21.7
2	0	2	32.2	40.1

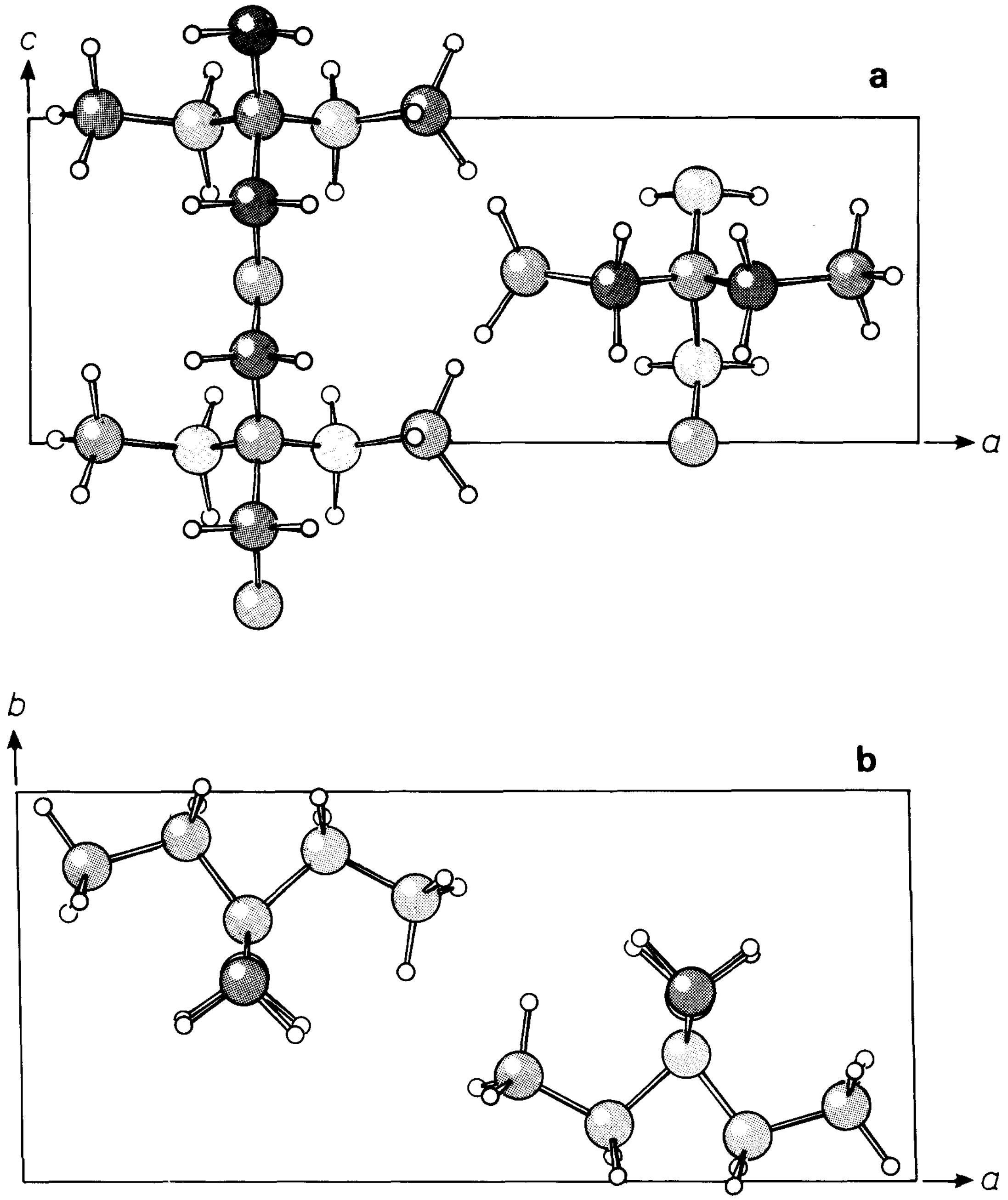

Figure 4 Crystal structure of PDEO: (a) the *ac* projection (perpendicular to the fibre axis) and (b) the *ab* projection, looking down the fibre axis

Table 3 Molecular structures of polyoxetane and its derivatives

Polymer	System	Conformation[a]
Polyoxacyclobutane (PTO)	Mod. I (hydrate), monoclinic	Planar zigzag
	Mod. II, trigonal	$T_3GT_3\bar{G}$
	Mod. III, orthorhombic	$(T_2G_2)_2$
	Mod. IV	Planar zigzag
Poly(3,3-dimethyl oxetane) (PDMO)	Mod. I	Planar zigzag
	Mod. II, monoclinic	$T_3GT_3\bar{G}$
	Mod. III, orthorhombic	$(T_2G_2)_2$
Poly(3,3-diethyl oxetane) (PDEO)	Mod. I, monoclinic	Planar zigzag
	Mod. II, orthorhombic	$(T_2G_2)_2$

[a] *T*, *G* and $\bar{G}$ denote *trans*, *gauche* and minus *gauche* conformations, respectively

for ethyl groups affects the stabilities of the crystal structure, favouring a crystal structure with higher number of *trans* bonds.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the help given by Professor Dr S. Garcia-Blanco and Professor Dr M. Martinez-Ripoll (Department of Crystallography, Institute Rocasolano, Madrid, Spain). One of us (MAG) gratefully acknowledges a short-term fellowship provided by EMBO. Financial support was provided in part by the Science and Engineering Research Council and the British Petroleum Venture Research Unit.

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