Molecular packing and conformation of liquid crystalline polyesters with bulky side groups*

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The conformational analysis of some liquid crystalline polyesters with bulky side groups has been carried out by means of computer modelling. The possible packings of the macromolecular fragments with overlapped tilted side groups are proposed on the basis of analysis of the conformational states and the corresponding X-ray data. Some trends in the formation of ordered structures in the liquid crystalline state of the studied polyesters are discussed.

(**Keywords: liquid crystalline polyesters; structure of polymers; molecular packing; conformational state; biaxial nematics**)

INTRODUCTION

To obtain liquid crystalline (LC) properties for 'classical' linear polymers with rigid backbones (such as polyesters) it is necessary to carry out some chemical modifications of the macromolecular chains. One of the ways involves the attachment of bulky side groups to the rigid backbones[1]. The variation of the chemical structure of such side groups and the points of their attachment leads to a dramatic change in the structural ordering of polymeric materials. So, for a number of polymers of this type, a new type of mesophase was proposed with 'plane' packing of fragments (named sanidic liquid crystals)[2]. The formation of the new type of ordering is due mainly to the strong anizodiametric shape of the rigid fragments. Steric interactions and the mutual positions of the backbones and the side groups determine the features of the resulting ordering.

In order to elucidate the changes in the backbone conformation and the type of possible molecular packing in crystalline and LC phases for a set of polyesters with bulky side groups, conformational calculations and the appropriate analysis of the acceptable X-ray data have been carried out.

EXPERIMENTAL

For the present analysis a set of LC polyesters with various side groups, such as phenyl rings, methyl groups and bromine atoms, were chosen. The chemical structures of the monomeric units are given in *Table 1*. The X-ray data of these systems in crystalline and LC states are published in references 3 and 4.

To study the possible packing of the macromolecules corresponding computer molecular models have been built and the most favourable conformations of the monomeric units have been calculated. Firstly, for all systems studied, a conventional conformational analysis with atom–atom, torsional and electrostatic interactions was performed. To search for a global energetic minimum molecular dynamics was used as an intermediate step. The exact positions of the energetic minima were checked by separate rotation of some of the torsion angles (such as angle T for the central ester group, see *Table 1*).

Secondly, after conventional conformational analysis (number of iterations = 300–600) the molecules were studied using quantomechanical calculations. From the results obtained, in the manner described above, the molecular models for the data were deduced (values of the torsion angle T, dipole moments, etc.).

To build an initial molecular model the program INSIGHT II (Biosym) was used[5]. Conformational analysis and molecular dynamics were performed in the framework of the program DISCOVER (Biosym)[6]. Quantomechanical calculations were performed by means of the program MOPAC 5.0 in the package INSIGHT II[5,7]. For all calculations a Silicon Graphics computer system was used.

To elucidate the possible parameters of the crystalline cell from d-spacings from published X-ray data the program INDEX has also been used[8].

RESULTS AND DISCUSSION

From X-ray scattering data analysis the parameters of a cell in the crystalline state and the formation of a nematic phase in the LC state have been proposed earlier for some of the polyesters considered[3,4]. Models of structural ordering in a crystalline state with overlapped side groups have been proposed. However, the type of possible molecular packing was discussed without consideration of possible conformational states of macromolecular fragments.

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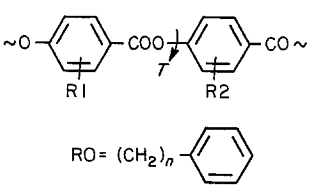
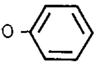
Table 1 Characteristics of the polyesters studied



	a	b	c	d	e	f	g
R1	H	R0, $n = 0$	R0, $n = 0$	R0, $n = 1$	R0, $n = 2$	RO  , $n = 0$	R0, $n = 3$
R2	H	CH_3	Br	Br	Br	CH_3	Br
l_1 (nm)[a]	1.24	1.28	1.24	1.27	1.25	1.25	1.25
d_1 (nm)[b]		–	1.25	1.25	1.25	–	1.25
l_t (nm)[a]	–	0.58	0.62	0.69	0.83	0.9	0.98
d_t (nm)[b]	–	–	1.2	1.36	1.56	–	1.67
T (deg)	69	79	74	78	82	85	84
Dp (D)[c]	–	1.9	2.6	2.4	2.5	2.1	2.2

[a] $l_{1,t}$ are the longitudinal and transverse lengths of the monomeric unit
[b] $d_{1,t}$ are the corresponding d-spacings from X-ray data[3,4]
[c] Calculated dipole moment

In this paper the possible packing of macromolecular fragments in the most favourable conformation is discussed in detail. The conformational changes of the backbone as a result of the attachment of various bulky side groups for isolated molecules is discussed as a first step. Then the possible models of molecular packing in a crystalline state taking into account the calculated conformations and the corresponding structural parameters published in references 3 and 4 are considered. Finally, structural properties of the polyesters in the LC state are discussed.

Conformations of isolated fragments

As is known from the analysis of the conformation and structural investigations of similar polymers (phenylbenzoates)[9], the backbones of polyesters without bulky side substitutents adopt a non-planar conformation with the torsion angle T for the central group in the range of 67–69° (*Table 1*). Our preliminary calculations for such a model system lead to a value for T in the range of 68–69° which corresponds quite well to the literature data and is a test of the validity of the approach used.

The computer calculations described above were performed for a set of substituted polyesters with various side substituents (*Table 1*, *Figures 1–4*). As can be concluded from the calculated data the presence of bromine atoms, methyl groups and additional phenyl rings as side groups to the polyester backbone leads to considerable deviation in conformation from that proposed for common phenylbenzoate chains (*Figures 1* and *2*). These deviations are determined by the nature of the side groups and may be summarized as follows.

1. The change of the point of attachment of side groups to the backbone (two possible positions for every phenyl ring) leads to a minor deviation in the conformation of the backbone for a given side group (variation of the torsion angle T of 2–3°) and in geometric length of the monomeric unit along and

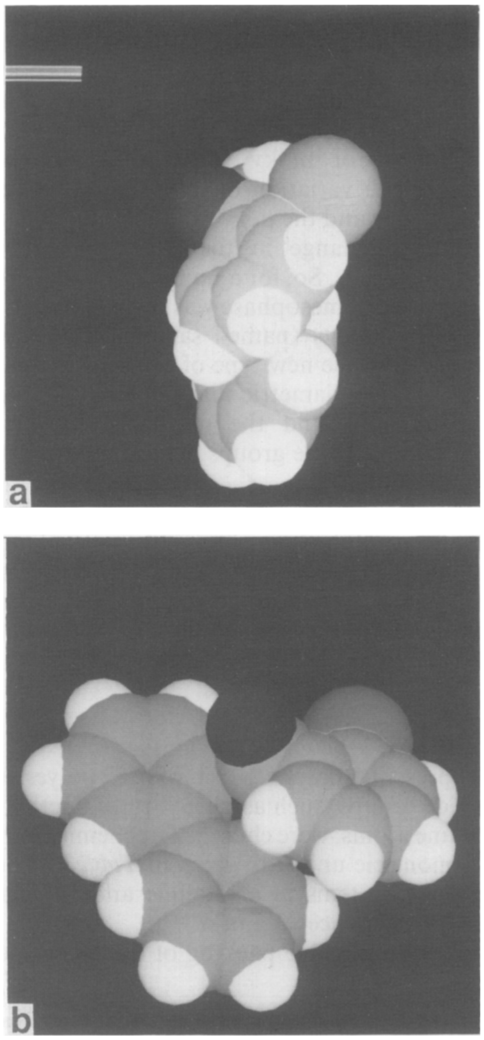


Figure 1 Conformation of the monomeric unit of the polyester with a short side group (c, *Table 1*). Projection (a) along and (b) orthogonally to the backbone

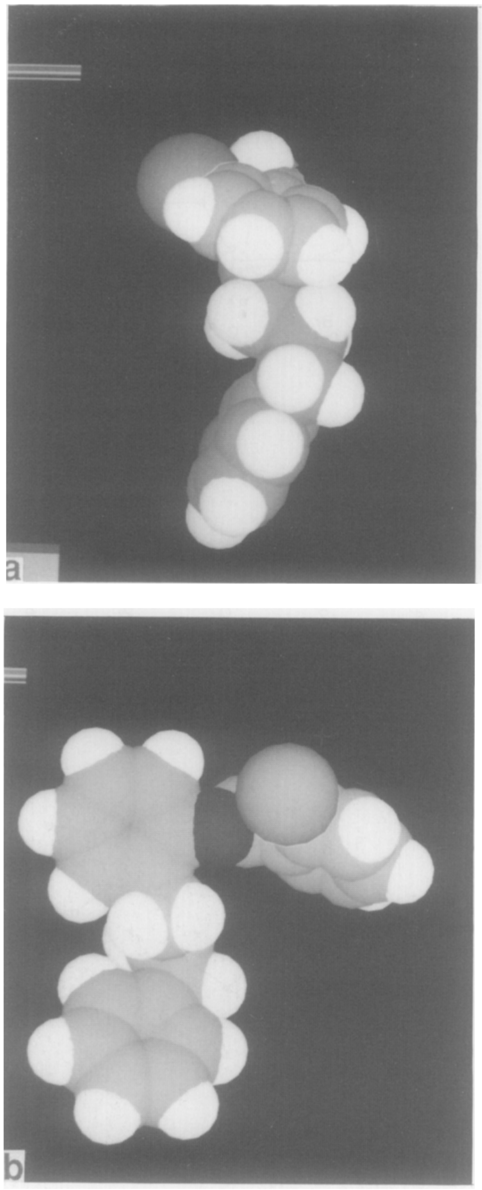


Figure 2 Conformation of the monomeric unit of the polyester with a long side group (g, *Table 1*) (labels as in *Figure 1*)

transverse to the backbone. The largest changes are observed for the closest arrangement of side groups. (In further calculations such configurations have been used.)

2. The changes in the chemical structure of a bulky side group lead to significant changes in the conformation of the molecular fragments:
   - (i) the presence of phenyl rings and bromine atoms directly attached to the backbone leads, as a result of steric interactions, to the change in the torsion angle *T* of the central group in the backbone (and correspondingly to the angle between the planes of neighbouring phenyl rings) from 69 to 74° (*Table 1*). A slight rotation of the plane of a side phenyl ring with respect to the phenyl ring in the backbone (up to 3–4°) as compared to a standard 'plane' conformation of the biphenyl fragments is also detected;
   - (ii) the substitution of bromine atoms for the bulky side methyl groups leads to an increase in the torsional angle *T* up to 79°;
   - (iii) the introduction of some methylene links between the backbone and the side phenyl ring leads to an increase in the torsional angle *T* up to 84°. As a result, in these systems the planes of the two phenyl rings in the backbone are arranged virtually orthogonally;
   - (iv) the general direction of a side group is not orthogonal to the direction of the backbone but the corresponding angle is varied in the range of 65–80°;
   - (v) the attachment of additional phenyl rings to a side group leads to a virtually T-shaped monomeric unit;
   - (vi) the character of the orientation of the dipole moment of a monomeric unit as a whole according to the direction of the backbones depends on the nature of the side groups: for polyesters with methyl groups (b, *Table 1*) and with the longest side substituents (f and g, *Table 1*) a dipole moment is oriented normally to the direction of the backbone while for all other systems it orients along the backbone (*Figures 3* and *4*).

Models of molecular packing

Using the most favourable conformations obtained for every analysed system the appropriate models for dense packing of monomeric units has been sought taking the following points into consideration: the minimal possible distances for contacts between the various groups of atoms, known from the published X-ray data *d*-spacings for longitudinal and transversal (with respect to the backbone) directions (*Table 1*); the minimal variation of the torsion angles from the calculated values for isolated fragments; and monitoring of the calculated density of packing (1.2–1.4 g cm^{-3}) according to literature data[3,4].

Analysis of possible dense packing of the monomeric units in the systems studied taking into consideration the above-mentioned principles leads to a model of antiparallel packing in the backbones with overlapped, tilted side groups (*Figures 5* and *6*). Tilting of the side groups in the proposed model differs from the earlier proposed model in which the side groups are arranged orthogonally to the backbone[4].

From the published *d*-spacings obtained from X-ray data for one of the considered polyesters (g, *Table 1*)[4] the parameters of the crystalline cell have been calculated in a conventional manner[8].

The calculated parameters of the corresponding cell are: $a = 0.5$ nm, $b = 1.78$ nm, $c = 1.28$ nm, $\alpha = \beta = 90°$, $\gamma = 75°$. Two of the most intense peaks in the X-ray curves in the low-angle region could be indexed as (010) and (001) reflections and a sharp peak in the wide-angle region could be assigned to the (100) order[4].

The cell parameters are very close to the values proposed earlier[4] but the arrangement of the monomeric unit in the cell differs greatly. In the proposed models the value of $\gamma = 90°$ is due to the coherent shift of the neighbouring backbones along the *c*-axis due to the tilted arrangement of the overlapped side groups (*Figures 5* and *6*). In the previous model[4] the value of the angle $\gamma = 90°$ and the value of the angle $\alpha = 60–70°$ is determined by the shift in the lateral packing in the *a*–*b* plane of the neighbouring backbones.

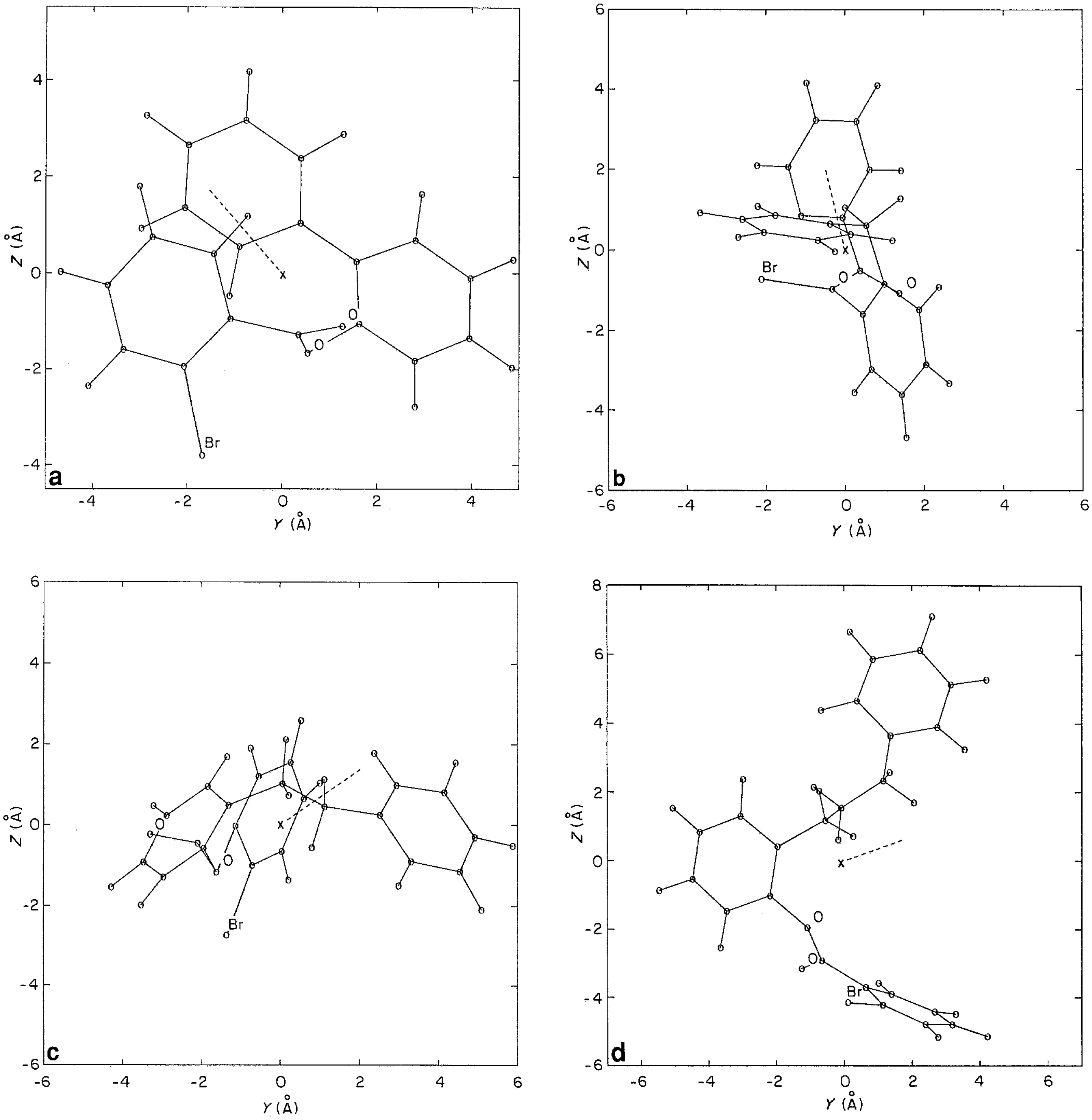


Figure 3 Orientation of the monomeric unit of the bromine containing polyesters in the $Z-Y$ plane along the main axis of polarizability (Z): (a) system c; (b) system d; (c) system e; (d) system g (see *Table 1*). The broken line marks the value and orientation of a dipole moment

Structural ordering in the LC state

For the systems studied as a result of the melting of the partially crystalline polymer at higher temperatures a nematic LC phase is detected[3,4]. From the calculated conformations of a molecular fragment and the proposed model of molecular packing in a crystalline state some additional suggestions about the features of the structural ordering in the LC state could be made. The ground for such an approach is the fact that structural ordering and the corresponding features of molecular packing in a crystalline state very frequently determine the type of ordering in a corresponding LC phase[10,11]. Therefore the following can be proposed.

First, the presence of tilted, bulky side groups could lead to the realization in the LC phase of corresponding tilted structures (which will be probably quite similar to C-type smectics or skewed nematics[10,11]).

Second, the strong interaction of the neighbouring backbones due to the overlapped side groups could lead to the formation in a mesomorphic state of ordered structures from 'double' packed backbones. Evidently (*Figures 5* and *6*), such a structural 'block' from rigid molecular fragments has an essentially anizodiametric 'board-like' type shape. This could promote the realization of biaxial LC phases which were frequently detected for sanidic systems with 'board-like' shaped molecular fragments[2].

Third, the analysis of changes in conformation and polarizability (the value and direction of a dipole moment) in the polyesters with various side groups leads

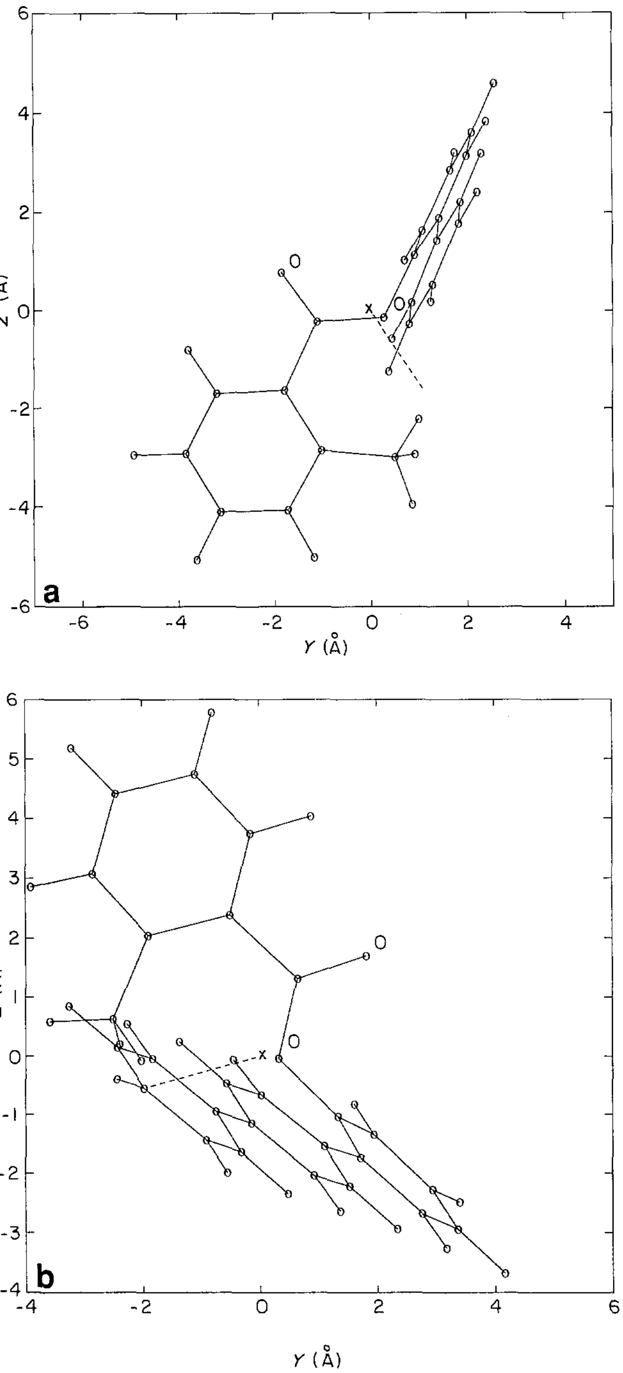


Figure 4 Orientation of the monomeric unit of the polyesters in the Z–Y plane along the main axis of polarizability (Z): (a) system b; (b) system f (see *Table 1*). The broken line marks the value and orientation of a dipole moment

to two main suggestions:

1. The strong deviations in the conformation of the backbones from the planar conformation for polyesters with the longest side groups and the strong restrictions of the longitudinal mobility of the macromolecular chains due to the overlapped side groups could lead to distortion of the local lateral packing of the backbones with the preservation of the longitudinal (along the backbone) correlations after the melting of a crystalline state and the transition to a LC phase. As a result, there is a high probability for the formation in the LC melt of a smectic phase with a one-dimensional long-range translational order along the backbone similar to that observed in conventional main-chain LC polymers[11].
2. The calculated absolute value of the dipole moment for the systems studied (*Table 1*, *Figures 3* and *4*) is higher for bromine containing polyesters compared to conventional polyesters. This could lead to the formation of more ordered structures in the LC phase due to stronger dipole–dipole interactions. Such systems could form highly oriented materials in an external electric field[10,11]. Moreover, the dipole moments in the various systems are different in the various directions (*Figures 3*, *4* and *7*). The dipole moments of the polyester with the longest side groups lie virtually normally to the backbone and to the calculated values for bromine containing polyesters. Thus, it can be concluded that the character of the orientation and corresponding macroscopic anisotropic properties of these systems oriented in the external fields should also be very different.

CONCLUSIONS

From the analysis of the conformational state of a set of LC polyesters with various bulky side groups it is possible

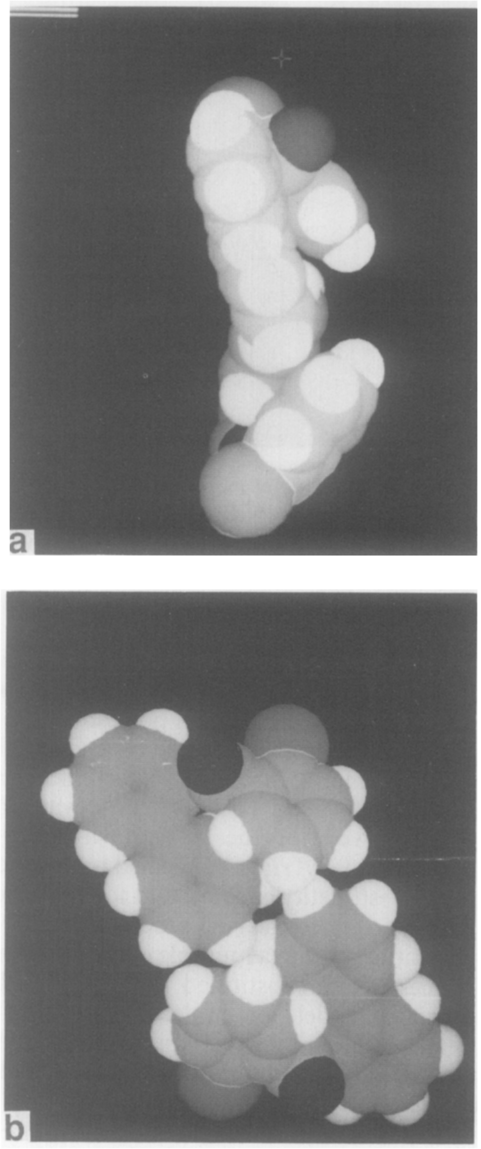
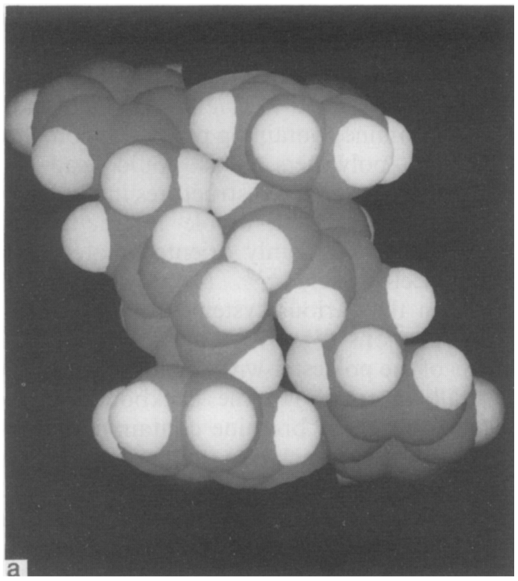


Figure 5 Models of packing of the monomeric units of polyester c (see *Table 1*) (two projections, see *Figure 1*)



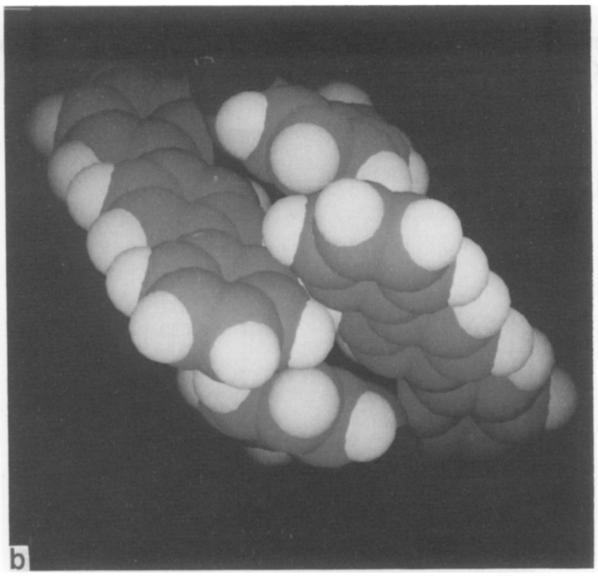


Figure 6 Models of packing of monomeric units of polyesters: (a) system b; (b) system f (see *Table 1* and captions to *Figures 1* and *5*)

to draw the following conclusions about features of ordering in these materials:

1. The introduction of bulky side groups leads to a large deviation in the conformation of the backbone from the conventional one for 'pure' polyesters: the torsion angle for the central groups between neighbouring phenyl rings changes from 68–69° (typical value for polyesters) to 74–85°. The strongest deviation (up to 85°) is observed for the system with side methyl groups, with phenyl rings connected to the backbones by the longest methylene link and for polyesters with two phenyl rings in the side groups.
2. Consideration of the favourable conformations of the backbones in the substituted polyesters leads to an appropriate model for molecular packing of the macromolecular chains with an antiparallel arrangement of the rigid backbones and overlapped tilted side groups.

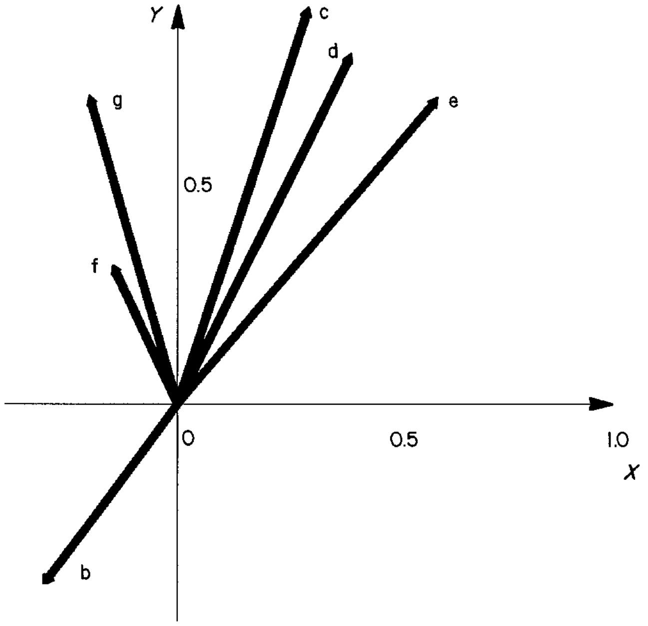


Figure 7 Directions of orientation of the dipole moments of monomeric units in the Y–X plane (for b–g see *Table 1*)

3. From the proposed models, some additional suggestions about the features of LC ordering in a substituted polyester can be made: the possibility of the formation of biaxial nematic and smectic phases of tilted type and the different orientation behaviour of the polyesters with different side groups in the external fields (the type of arrangement of the backbones according to the direction of the external field). The proposed features could be elucidated by the direct structural study of the LC phase and the oriented behaviour of these systems.

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REFERENCES

1 Balauff, M. *Angew. Chem.* 1989, **26**, 253
2 Ebert, M., Herrmann-Schonher, O., Wendorff, J., Ringsdorf, H. and Tschirner, P. *Liq. Cryst.* 1990, **7**, 63
3 Heitz, W. and Schmidt, H. *Makromol. Chem., Macromol. Symp.* 1990, **38**, 149
4 Kampschulte, U. *PhD Dissertation* University of Marburg, 1989
5 INSIGHT II, Biosym Technology, San Diego, 1991
6 DISCOVER, ver. 2.7.0. Biosym Technology, San Diego, 1991
7 Stewart, J. *J. Comp. Mol. Dis.* 1990, **1**, 1
8 Paszkowicz, W. *J. Appl. Cryst.* 1987, **20**, 161
9 Coulter, P. and Windle, A. *Macromolecules* 1989, **19**, 1129
10 Tsukruk, V. and Shilov, V. 'Structure of Polymeric Liquid Crytals', Naukova Dumka (Science), Kiev, 1990
11 Weis, R. and Ober, C. (Eds) 'Liqiuid-Crystalline Polymers', VCH, New York, 1990