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On the linearization problem of the bent chain in amorphous polycarbonate

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The linearization problem of the bent (banana-like) polycarbonate chain is solved and two linear chains are found that differ in alternation of *trans* and *cis* conformations. Calculation of neutron scattering curves from ordered (crystalline-like) regions with linear and bent chains in different arrangements and comparison with experimental scattering curves exclude the existence of linear chains and of crystalline-like ordering in amorphous polycarbonate.

(Keywords: intermolecular order; polycarbonate; neutron scattering; crystalline structure)

INTRODUCTION

The banana shape of the polycarbonate (PC) of 2,2-bis(4-hydroxyphenyl)propane chain is a consequence of the fact that the bonding angle in the tetrahedral isopropyl group is 109° whereas the bonding scheme of the carbonate group brings the axis of two neighbouring phenyl groups into an angle of 134° (see *Figures 1* and *3*).

Figure 1 shows a PC segment consisting of all *trans* (*T–T*) conformations. The phenyl rings are tilted out of the *xy* plane by $\pm 45°$, i.e. with dihedral angles of 0° and 90°, in a sequence of alternating sign[1]. A recent paper[2] documents that the most stable conformation is a structure with the dihedral angles (ϕ, ψ) having values $(51°, 51°)$. A geometrical structure having orthogonal phenyl ring planes with the dihedral angles $(0°, 90°)$ or $(90°, 0°)$ is higher in energy than the $(51°, 51°)$ structure by $1.9\,\mathrm{kcal\,mol^{-1}}$. Previous studies[3] have shown that the various mutual orientations of phenyl rings had no effect on the neutron scattering pattern in the low wide-angle scattering region. Bond lengths and bond angles were taken from refs. 1, 4 and 5. One problem in the linearization of the PC chain is that the distribution of conformations in amorphous PC is not accurately known even though there is little doubt that the (*T–T*) conformation is the most probable one. Furthermore, there are indications[4,6] that the banana-like (*T–T*) conformation shown in *Figure 1* or a distorted version of it should be a basis for the PC chain in the crystalline state and that it should be overwhelmingly dominant. Amorphous PC has a tendency to crystallize slowly. This has been attributed[7] to either a preliminary ordering of chains or a change of polymer conformation. The solution of the linearization problem is important in order to discuss these effects.

LINEAR CHAINS IN CRYSTALLINE POLYCARBONATE

The necessity to find out the intermolecular structure of the linear PC chain increases also in view of a possible refinement of structures of partially crystalline polycarbonate phases.

The most detailed study of crystalline polycarbonate is given by Bonart[4]. In *Figure 2* we show the lattice cell and its projections according to ref. 4. The original description of the axes by Bonart is given with small letters. Because the γ angle in the monoclinic cell is by definition obtuse, we have included the more consistent description described by capital letters ($\gamma = 96°$).

Polycarbonate crystallizes monoclinically in the space group C_s^2 with four chains each in the lattice cell; the fibre identity period comprises two monomeric units, so that eight monomeric units are located in the lattice cell. The chain structure is rotated by 180° and shifted $B/4$ and $C/4$ from the original position. The remaining two chains are shifted approximately by $C/8$.

The intermolecular structure is mentioned in Bonart's paper at two occasions:

(i) It is pointed out that in the fully stretched chain one monomer unit is about 1.3 nm long; however, two monomer units are characterized by an identity period that is not 2.6 but only 2.08 nm long. This can be

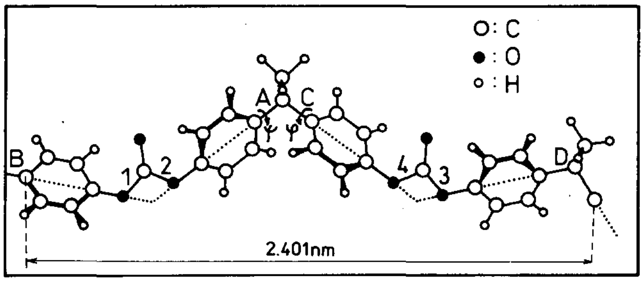

Figure 1 PC segment in a *trans–trans* conformation. Numbers and letters designate the bonds used as 180° rotation axes in the linearization procedure. Dihedral torsion angles ϕ, ψ are marked. In this and following *Figures 5* to *9* only one CH_3 group is shown because in this (*YZ*) projection the pictures of both CH_3 groups are identical

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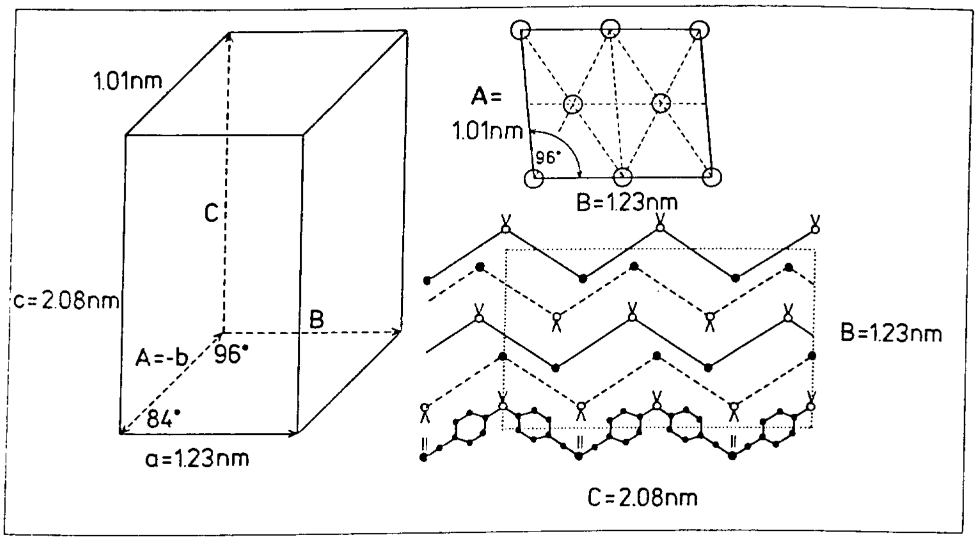

Figure 2 The lattice cell and its projection for polycarbonate according to Bonart[4]. In the *XY* projection molecular axes are shown by circles. In the *YZ* projection the upper chains are drawn with full lines, the lower ones with broken lines. For one of these upper chains we reproduced the intermolecular ordering as visualized schematically in ref. 4. See also text for details

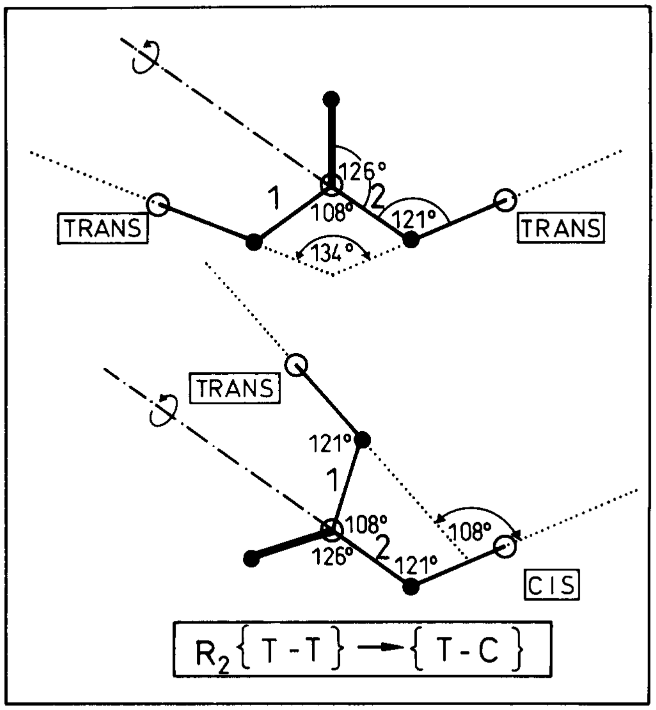

Figure 3 Transformation of a *trans–trans* into a *trans–cis* conformation by a R_2 rotation

explained by a special configuration of carbonyl groups or also by a 'zig-zag'-like chain configuration. Helix-like configurations are improbable, because it is not possible with them to reach a sufficient packing of chains in the direction perpendicular to the chain axis. For these reasons only plane chain configurations were studied.

(ii) The second occasion is a schematic picture of chain ordering in the proposed elementary cell, which presents the intermolecular structure in the form as shown in *Figure 2* (see the *YZ* projection).

Because these representations of the intermolecular structure are not sufficient for a detailed calculation of X-ray scattering, this was a further reason why we have undertaken the following study of chain conformations.

TOPOLOGICAL BASIS FOR LINEARIZATION

The operations involved in the linearization procedure are shown schematically in *Figure 3*. The topological basis for the linearization of the bent PC chain lies in the observation that a 180° rotation of part of the PC chain around the O–C bond 2 in the carbonate group changes the angle formed by the axes of two neighbouring phenyl rings from its original value of 134° to 108°. This value is close to the angle of 109° formed by the tetrahedral bonds of the isopropyl group. The 180° rotation that is designated R_2 rotation transforms the original *trans–trans* (*T–T*) conformation of the carbonate group into a *trans–cis* (*T–C*) conformation. In symbolic notation this operation can be written:

$$R_2\{T\text{–}T\} \rightarrow \{T\text{–}C\} \qquad (1)$$

ROTATION SCHEME FOR LINEARIZATION

In the subsequent part of this paper we discuss the linearization procedure in more detail using *Figures 1* and *3*. In a chain segment consisting of two monomers there are two carbonate units and therefore four C–O axes labelled 1 to 4 for possible 180° rotations. The rotation matrix shown in *Figure 4* may be used to describe the rotations around the four axes. Simultaneous rotations of the type (R_1+R_2) and (R_3+R_4) must be excluded from this matrix since they lead to a non-linear conformation. We further exclude rotations of the type (R_1+R_1) and (R_2+R_2), etc., which result in identical conformations. Since the final conformation is independent of the sequence of rotations, i.e. $(R_1+R_3)=(R_3+R_1)$, the number of conformations is reduced to only four, namely (R_1+R_3), (R_1+R_4), (R_2+R_3) and (R_2+R_4).

LINEARIZATION PROCEDURE

We now study linearization procedures evoked by the four principle rotation sequences mentioned in the preceding section.

Rotations (R_1+R_4)

We start with a 180° rotation around axis 1 (rotation R_1), which involves that part of the PC chain found on the right side from bond 1 (see *Figure 5a*). Then, in order to bring a section of the rotated PC chain into the supposed straight direction, it is necessary to make an additional 180° rotation around the A axis of the isopropyl group (see *Figure 5b*). The result of the two operations is summarized by the notation $R_1(A)$. Similarly, after a 180° rotation around the axis 4 (R_4) shown in *Figure 5c*, we obtain the linear conformation in *Figure 6* by an additional rotation around the D axis, notation $R_4(D)$. Extending the notation used in equation (1) the operations in this procedure can be written:

$$R_1(A)\{T\text{–}T\}+R_4(D)\{T\text{–}T\}\rightarrow\{C\text{–}T\}+\{C\text{–}T\} \quad (2)$$

The result is a linear chain (see *Figure 6*), characterized by a regular alternation of *cis* and *trans* conformations.

	R_1	R_2	R_3	R_4
R_1	R_1+R_1	R_1+R_2	R_1+R_3	R_1+R_4
R_2	R_2+R_1	R_2+R_2	R_2+R_3	R_2+R_4
R_3	R_3+R_1	R_3+R_2	R_3+R_3	R_3+R_4
R_4	R_4+R_1	R_4+R_2	R_4+R_3	R_4+R_4

	T - T
R_1	C - T
R_2	T - C
R_3	T - C
R_4	C - T

Figure 4 Rotation scheme for the linearization of the PC molecule. From all possibilities it is sufficient to investigate only operations in the thick frame (see text for details). The smaller table (below) shows the conformation that results from a *trans–trans* conformation when the rotation R is performed. See *Figures 1* and *2* for the labelling of the rotation axis

Rotations (R_2+R_3)

The linearization procedure is described by:

$$R_2(B)\{T\text{–}T\}+R_3(C)\{T\text{–}T\}\rightarrow\{T\text{–}C\}+\{T\text{–}C\} \quad (3)$$

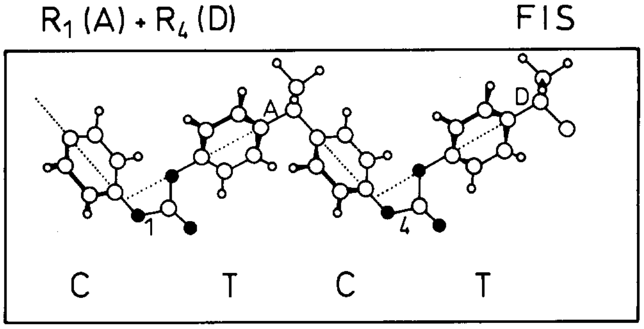

Figure 6 Linear chain of the FIS type (length of two monomer units is 2.104 nm) as a result of the operation $R_1(A)+R_4(D)$. See text for details

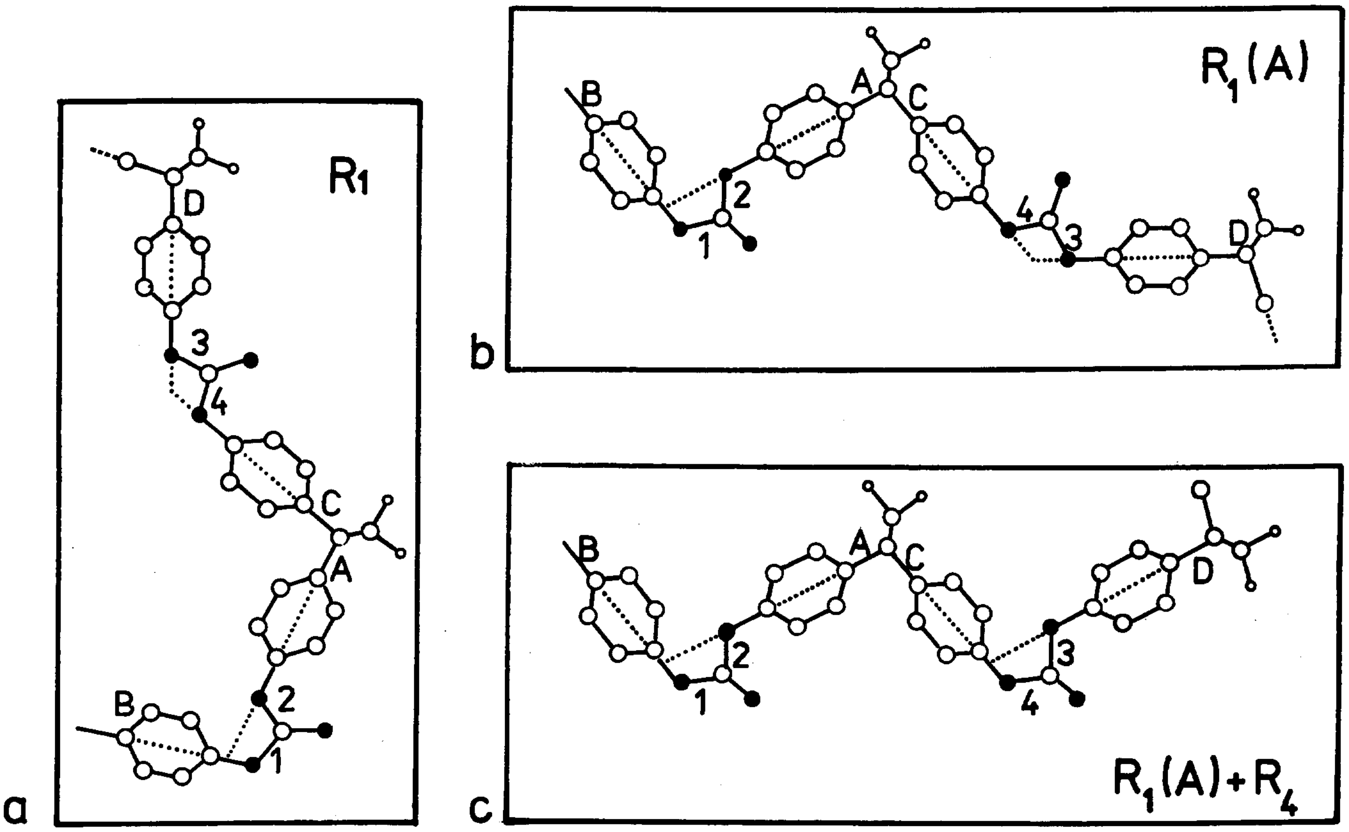

Figure 5 A sequence of operations demonstrating the transformation of a *trans–trans* conformation shown in *Figure 1* into a linear chain of the FIS type in *Figure 6*: (a) the R_1 operation; (b) the $R_1(A)$ operation; (c) the result of $R_1(A)+R_4$ operations

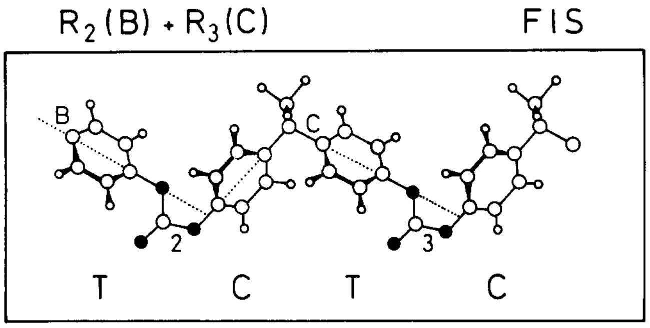

Figure 7 Linear chain of the FIS type (length of two monomer units is 2.104 nm) as a result of the operation $R_2(B)+R_3(C)$. See text for details

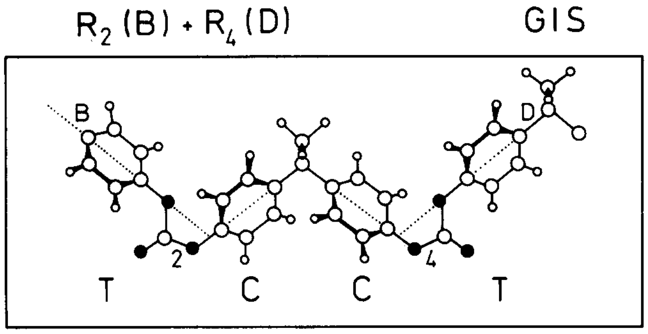

Figure 8 Linear chain of the GIS type (length of two monomer units is 2.066 nm) as a result of the operations $R_2(B)+R_4(D)$ or $R_1(A)+R_3(D)$

The resulting chain is as a mirror picture of the previous one. The mirror plane is perpendicular to the chain axis and passes through the centre of either the isopropyl or carbonyl groups (*Figure 7*).

We call the linear conformations of chains in the two above sections FIS conformations.

Rotations (R_2+R_4)

The linearization process can be written:

$$R_2(B)\{T\text{-}T\}+R_4(D)\{T\text{-}T\}\rightarrow\{T\text{-}T\}+\{C\text{-}C\} \tag{4}$$

This linear chain, which consists of an alternating sequence of *trans–trans* and *cis–cis* conformations, is shown in *Figure 8*. This chain conformation is called GIS conformation.

Rotations (R_1+R_3)

The linearization operation is given by:

$$R_1(A)\{T\text{-}T\}+R_3(C)\{T\text{-}T\}\rightarrow\{C\text{-}T\}+\{T\text{-}C\} \tag{5}$$

The chain conformation is identical to that in the above section.

LENGTH OF LINEAR CHAINS

Figure 9 illustrates the differences between linear chains of the FIS and GIS type, which consist of four monomer units. In the FIS chain both the isopropyl and carbonyl groups lie on a straight line with an equal distance of 1.052 nm to the next groups. In the GIS chain only carbonyl groups lie on a straight line with distance alternating from 0.892 to 1.174 nm. On the other hand, the isopropyl groups form a zig-zag arrangement with a mutual distance of 1.051 nm.

Two monomer units of the FIS and GIS chains are 2.104 and 2.066 nm long, respectively. The average value of 2.085 nm corresponds precisely to the length of the repeat unit in crystalline PC as measured by Bonart[4]. He found that crystalline PC is monoclinic with unit cell dimension $A=1.01$, $B=1.23$ and $C=2.08$ nm. It is worth mentioning that the corresponding distance in the bent banana-like chain is 2.401 nm (*Figure 1*).

CONSEQUENCES OF THE LINEARIZATION PROCEDURE

The fact that there exist two types of linear chains raises several questions: (1) Which type of linear chain is energetically more stable? (2) Do linear chains exist in amorphous PC? (3) Which type of linear chain occurs in the crystalline phase?

We shall try to find the answer to the second question in the subsequent section. The answer to the third question is more complex and is treated elsewhere[8,9].

The elucidation of the first problem is not simple. In the amorphous state, the PC chain predominantly consists of units in *trans–trans* conformation with respect to the carbonate group and only occasionally in *cis–trans* or *trans–cis* conformation. Jones estimated[10] that the barrier heights exceed by 1–2 times the C–O bond rotational energy, which is only about 10 kJ mol^{-1} (refs. 11–13). Furthermore, Laskowski *et al.*[14] calculated the energy difference between the *cis* and *trans* conformations of the carbonate group to be 11.5 kJ mol^{-1} and the energy barrier for the *trans*-to-*cis* transition to be 32.7 kJ mol^{-1}. The results of these calculations demonstrate that the conformational barriers to rotation are low for PC. The geometry of the carbonate unit allows for a process in which most of the repeat unit is not appreciably reoriented while the small carbonate unit is reoriented. Partial or complete linearization of a PC chain as proposed above and leading to FIS or GIS type chains is therefore possible. Moreover, conformational calculations[2] show that the accessible area of the (ϕ, ψ) surface for the diphenylpropane segment is large, even though the rotations in diphenylpropane torsion angles ϕ and ψ should be synchronized ($\phi+\psi=90°$ or $270°$). The variety of conformations that are accessible to the repeat unit in solution and in the amorphous state allow the linearization of chains as discussed above. However, long annealing times may be required for the linearization and crystallization of chains.

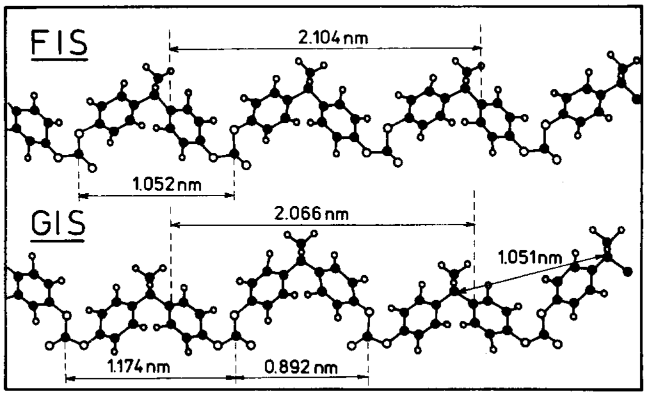

Figure 9 Comparison of linear FIS and GIS chains consisting of four monomer units (carbon, full circles; oxygen, large open circles; hydrogen, small open circles)

ORDERED REGIONS WITH LINEAR CHAINS

Parallel ordering with linear chains

In this section we discuss the question as to whether linear chains exist in amorphous PC. The same method as described previously[3] has been used to calculate the neutron scattering of highly ordered units consisting of PC segments arranged parallel to each other. In our previous paper we studied bent chain segments. In this paper we consider chain segments in FIS or GIS conformations. The calculated scattering curves are compared to experimental data. The basis for the calculation is the Debye equation:

$$I(q)=\sum_i \sum_j b_i b_j \frac{\sin(qr_{ij})}{qr_{ij}} \qquad (6)$$

where b_i and b_j are the scattering lengths of the atoms i and j, respectively, r_{ij} denotes the distance between these atoms and $q=(4\pi/\lambda)\sin(\theta/2)$ is the magnitude of the scattering vector. Equation (6) has been used to calculate the scattering from highly ordered units consisting of four parallel PC segments. Each segment comprised two monomer units in configurations labelled h3 and h4 (*Figure 10*).

It turns out that the most sensitive comparison of calculated and experimental scattering curves with respect to intermolecular chain distances and longitudinal chain arrangements is achieved for the perdeuterated PC-D sample. *Figure 11* shows differences in scattering curves calculated for the h3 and h4 configurations of different types of linear chains and for the same configurations of bent chains. The characteristic splitting of the main maximum with peaks located at 0.115 and 0.140 nm^{-1} is reproduced only by the scattering curve calculated for the bent chains. Linear chains of both the FIS and GIS type exhibit a larger splitting by about 0.043 nm^{-1}.

This result has to be expected since the splitting of the main maximum reflects the internal structure of the deuterated chain. As we pointed out above, the linear chain is shorter than the bent chain and the characteristic motives of the linear chain (i.e. phenyl rings, carbonyl and isopropyl groups) are situated closer than those of the banana-like chain. The splitting of the main maximum in reciprocal space must therefore be larger for the linear chains.

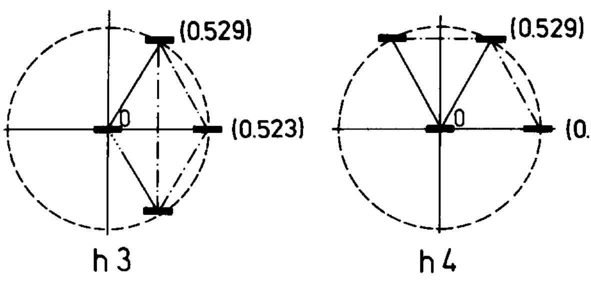

Figure 10 Schematic representation of a highly ordered unit consisting of four parallel PC segments in intermolecular configurations labelled h3 and h4. The thick bar represents a projection of the plane of a chain characterized by zig-zag axis of phenyl rings. This plane is perpendicular to the plane of the picture. Numbers in parentheses give the distances from the chain to the centre

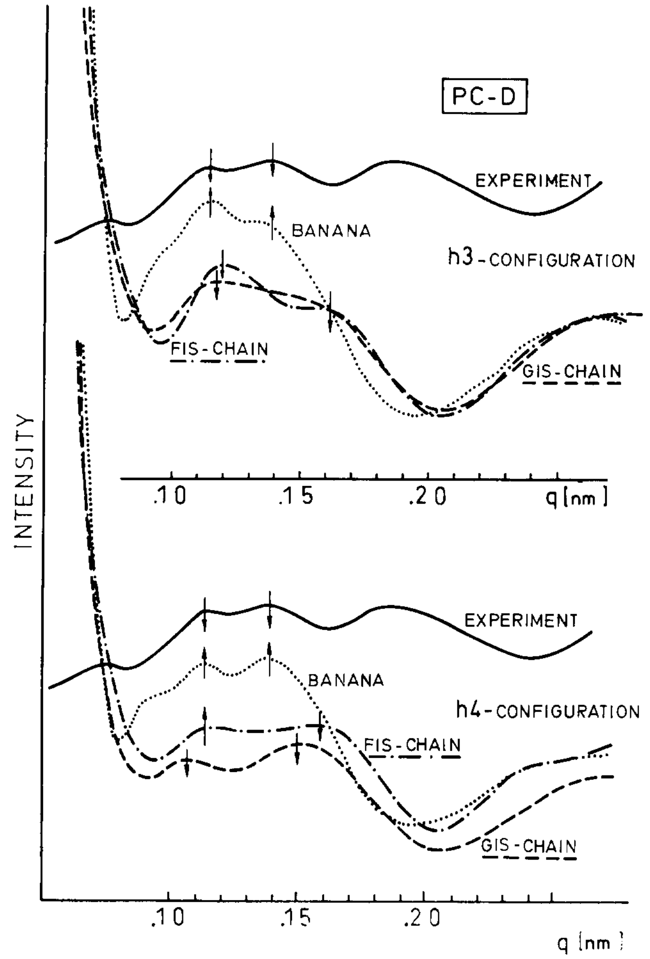

Figure 11 Neutron scattering curves calculated for ordered regions built from four-segment banana-like and linear chains of PC-D (perdeuterated PC) in h3 and h4 configurations: (······) bent chain, (– – – –) GIS chain, (—·—·—) FIS chain

Crystalline-like ordering

In this section we focus on the question of whether crystalline regions exist in amorphous PC. In order to simplify calculations, we have arranged four linear PC chains in an orthorhombic brick $X=2.08$ nm, $Y=1.23$ and $Z=1.01$ nm (see *Figure 12*), which with the exception of the γ angle is identical with Bonart's cell (*Figure 2*). To answer the questions raised above, we studied PC chains in the FIS conformation, model C_1. In fact, as shown in *Figure 13*, the FIS conformation is similar to the conformation of PC chains postulated by Bonart. *Figure 14* shows the neutron scattering curves calculated for such a four-segment region. For both the PC-H and PC-D, the calculated scattering curves do not reproduce the characteristic maxima of the experimental data.

In our previous study[3] we found that the medium intersegmental distance in amorphous PC is 0.527 nm. We therefore decreased the interchain distances in the crystalline-like C_1 model so that they might correspond to this value. These new interchain distances are shown in *Figure 12b* in parentheses. The scattering curves calculated for these new values are also presented in *Figure 14*. As expected, the maximum of the scattering curve calculated for PC-H is situated at the correct value of 0.125 nm^{-1}. However, the scattering curve calculated for PC-D does not reproduce the experimental data.

On the other hand, we have previously demonstrated that the scattering curves calculated for ordered regions consisting of bent chains in partially and fully deuterated PC are in good agreement with the experimental results

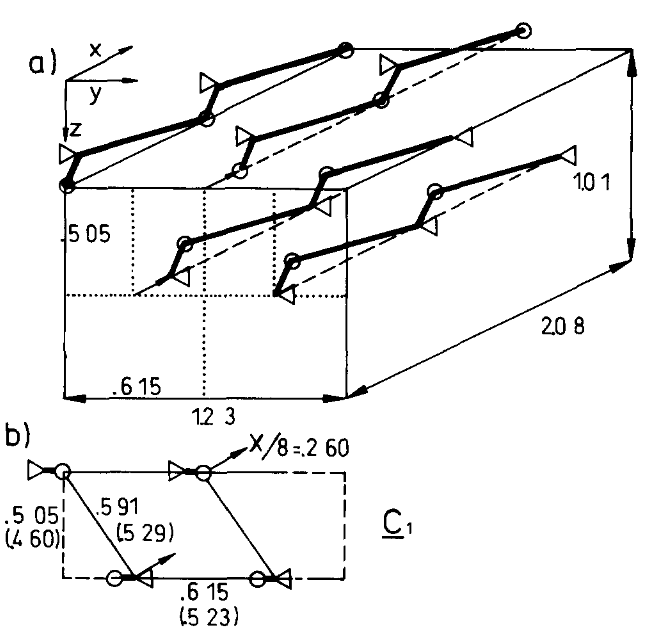

Figure 12 (a) Schematic picture of an orthorhombic approximation of crystalline PC labelled C_1. Linear FIS type chains are arranged according to Bonart[4]. Triangles and circles show the positions of isopropyl and carbonyl groups respectively. (b) A (*YZ*) projection of the C_1 arrangement; compare also with *Figure 15*. Intermolecular distances in parentheses are distances that were optimized for a three-segment arrangement of bent chains in ref. 3

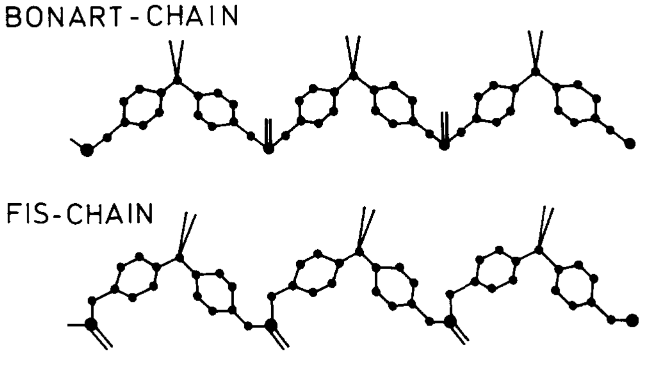

Figure 13 Comparison of a linear chain according to Bonart[4] with a FIS chain

provided the correct set of configurational coordinates is used for these calculations. It must therefore be concluded that crystalline-like ordered regions with linear chains do not exist in glassy PC.

We studied several other models, which also have their origin in the crystalline-like arrangement shown in *Figure 12*. These models are schematically drawn in *Figure 15*. They differ in the mutual chain orientation (see e.g. the mutual position of the isopropyl groups marked with triangles in neighbouring chains). Furthermore, the $x/8$ parameter (see *Figure 12a*) has been put equal to zero, to study the effect of the mutual shift of chains in the direction of the chain axis on the scattering behaviour. The calculated scattering curves are for the PC-H sample not sensitive to structural changes described by models C_1, C_2, C_3 and C_4. They all have the same position of the main peak at $0.115\,\mathrm{nm}^{-1}$ and differ only a little in the heights of the peak maximum. Therefore, we show in *Figure 16* the scattering curves calculated for the models C_1, C_2, C_3 and C_4 only for the structure-sensitive

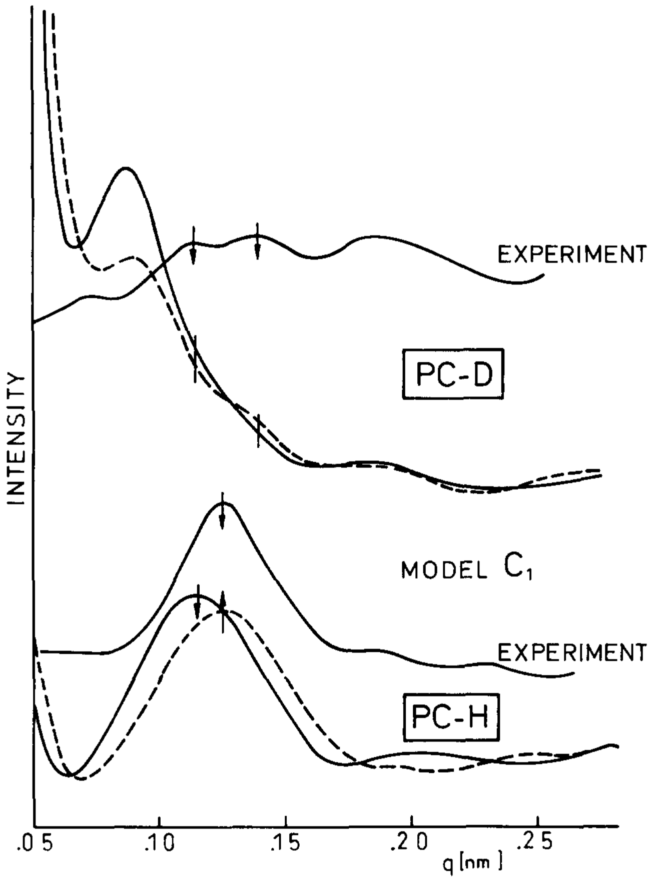

Figure 14 Scattering curves calculated for the crystalline arrangement of FIS chains: (——) model C_1 in *Figure 12*; (– – –) intermolecular distances as in ref. 3

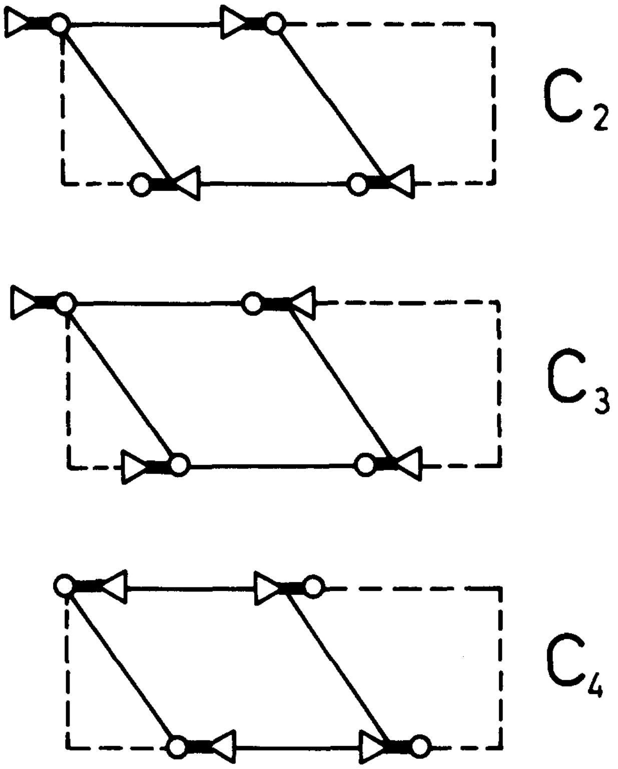

Figure 15 Structural models C_2, C_3 and C_4, which were examined in order to study different mutual orientations of linear FIS type chains in a crystalline-like arrangement

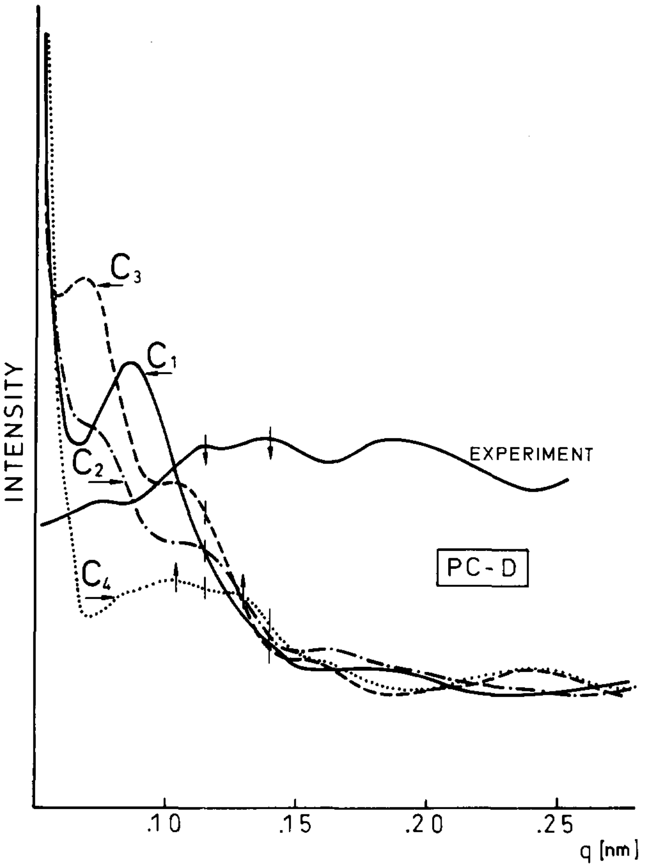

Figure 16 Scattering curves for PC-D corresponding to models C_2, C_3 and C_4 described in *Figure 15*. Curve C_1 (model C_1, see also *Figure 14*) is drawn for comparison to show the effect of mutual shift of chains in the direction of the chain axis. For PC-H the main peak is not sensitive to structural differences between models C_1, C_2, C_3 and C_4

PC-D case. The great differences between the calculated and experimental scattering curves confirm our preceding conclusion that crystalline-like regions with linear chains do not exist in amorphous PC.

CONCLUSIONS

It has been demonstrated that the bent (banana-like) PC chain can be linearized. This operation can be described by a transformation matrix consisting of combined 180° rotations around C–O bonds of the carbonate group and around C–C bonds of the isopropyl group. The general solution of the linearization problem shows that there are two types of linear chains. In the FIS conformation the alternation sequence with respect to the carbonate groups is ... *-trans-cis-trans-cis*...; in the GIS configuration the alternation sequence is ...*-trans-trans-cis-cis-*.... These results may be used to find out whether linear chains exist in amorphous PC. Different models with a parallel ordering and crystalline-like arrangement of linear chains were constructed. The size of the ordered regions was not greater than $0.5 \times 0.9 \times 2.1\ \mathrm{nm}^3$, i.e. sufficiently small not to produce crystalline peaks in the scattering diagram. We were able to show that the scattering curves calculated for PC-D did not reproduce the main features of the experimental data. We must therefore assume that amorphous PC does not consist of regions of parallel linear chains.

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