# Liquid crystalline main chain polymers with a poly(*p*-phenylene terephthalate) backbone: 4. X-ray diffraction of the polyester with dodecyloxy side chains

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*(Received 14 September 1992)*

A detailed X-ray investigation on oriented fibres and films of poly(*p*-phenylene 2,5-didodecyloxyterephthalate) revealed that this polymer can exist in two stable crystal modifications, A and B, at room temperature. Modification B is a highly crystalline classical structure. In modification A the side chains do not follow the restrictions imposed by their regular attachment to the main chains; they form clusters between the main chain layers. Upon heating to above the side chain disordering temperature $T_s$ ($T_s$(A)$\approx$40°C, $T_s$(B)$\approx$100°C) these modifications transfer to the less ordered structure A', in which the side chains are disordered but the position of the main chains, relative to each other, remains strongly correlated. Above the main chain melting temperature $T_m$ ($\approx$170°C) part of the positional ordering of the main chains is lost and a mesophase with biaxial ordering exists. This biaxial ordering is lost at $T_i$ ($\approx$240°C) and an isotropic melt is formed.

**(Keywords: X-ray diffraction; crystal structure; rigid rod polymer; thermotropic; phase behaviour)**

## INTRODUCTION

Thermotropic polymers with a rigid main chain have received much attention in the recent past. This is due largely to their phase behaviour; their thermotropic behaviour can give rise to a very low melt viscosity and orientation of the extended chains can be obtained fairly easily.

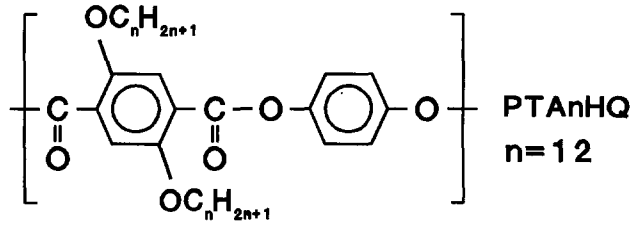
Melt processability of a rigid rod main chain polymer can be obtained by several methods[1], one of which is the attachment of flexible side chains to the rigid rod main chain. In previous publications[2–6] it was shown that the phase behaviour is significantly affected by the position and length of the side chains. The polymer described in this publication consists of a rigid poly(*p*-phenylene terephthalate) main chain with flexible dodecyloxy side chains on the terephthalate moiety (poly(*p*-phenylene 2,5-didodecyloxyterephthalate) (PTA12HQ)), the structure of which is shown in *Scheme 1*.

For this polymer a phase behaviour as shown in *Figure 1* was proposed in another paper[7]. At room temperature two stable modifications, A and B, as well as a 'frozen-in layered mesophase' $L_f$ could be obtained. Upon heating, these phases subsequently transform to the intermediate phase A', the layered mesophase $L_m$ and the isotropic phase I. The phase transition at $T_s$ was associated with a side chain disordering[3].

In other publications this group reported on the rheology and mechanical properties of this polymer[5,7,8]. It was shown that the layered mesophase $L_m$ behaves like a solid rather than a liquid[5]. For the three room temperature structures very different mechanical properties were found[7,8].

It is the aim of this paper to elucidate the amount of ordering present in the various phases (*Figure 1*) and the disordering processes taking place at the phase transitions. The understanding gained will be compared with the rheological and mechanical behaviour reported earlier[5,7,8]. An overview of the existing literature is therefore necessary.

Based on other studies[4,6,9,10] three-dimensional representations of the two stable room temperature structures A and B can be made. These structures are shown schematically in *Figure 2*. From modelling studies and wide-angle X-ray diffraction measurements it has been proposed by Cervinka and Ballauf[9] that, in the case of a polymer with hexadecyloxy side chains (PTA16HQ), structure A is a non-classical structure. In this structure the main chains form a superstructure with characteristic distances of 25.6 Å along $x$ (layer distance $d$) and 3.6 Å




**Scheme 1**

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along $y$ for PTA16HQ. The length of the side chains in PTA16HQ allows for a decoupling between the position of the main chains and the packing of the side chains. In this way the side chains can form regions with a locally denser ordering (clustering) between the main chain layers.

The conformation of the side chains in modifications A, B and A′ of PTA16HQ was investigated in more detail by Baldwin-Frech *et al.*[11]. Using $^{13}$C-nuclear magnetic resonance (n.m.r.) measurements they showed that in structures A and B the side chains are in rather extended *trans* conformations. To be more specific, the side chains in modification A are less crystalline and in a less extended form at the end of the side chain than in modification B. For modification A it was proposed that microcrystals of the side chains are located between the main chain layers somewhat remote from the polymer backbone[11]. At the solid–solid phase transition where structure A transforms into A′, conformational order decreases and only a small portion of the side chains ($\approx$20%) remains in an extended *trans* conformation. The above-mentioned studies regarding main and side chain packing will be used as a starting point in our investigations.

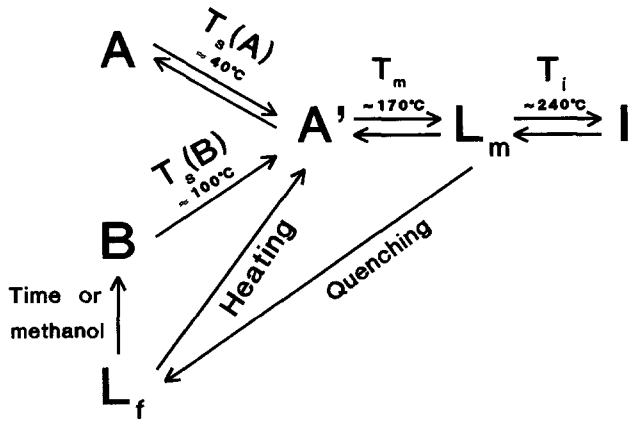


**Figure 1** Schematic representation of the phase behaviour in PTA12HQ fibres[7]. The two room temperature structures A and B can transfer to the intermediate phase A′ at the respective side chain disordering temperatures $T_s$(A) and $T_s$(B). At the main chain melting temperature $T_m$ the layered mesophase $L_m$ is formed and the isotropic melt I is reached at the clearing temperature $T_i$. By quenching from the layered mesophase $L_m$ the 'frozen-in layered mesophase' $L_f$ is obtained, which slowly transforms to modification B

## EXPERIMENTAL

### *Characterization methods*

PTA12HQ was prepared by solution polycondensation[5] and oriented fibres and films were prepared as described elsewhere[7,8].

Fibre and film diffractograms were recorded in transmission mode using Ni-filtered Cu K$\alpha$ radiation (flat film, sample-to-film distance 6 or 9 cm). The orientation angle $\varphi$ of the fibres was determined by measuring the half-width at half-height of the major equatorial reflections (azimuthal scan).

High-temperature X-ray diffractograms of the fibres were made using a Statton camera equipped with a heating unit (sample-to-film distance 3 cm).

A Guinier-Lenné camera equipped with a heating unit was used to determine the temperature dependence of the equatorial reflections. A heating rate of 1°C min$^{-1}$ was used.

Infra-red measurements of oriented films were performed on a Perkin–Elmer spectrometer in transmission mode.

Densities were determined by a density gradient column (NaBr/$H_2O$) with an accuracy of 0.004 g cm$^{-3}$.

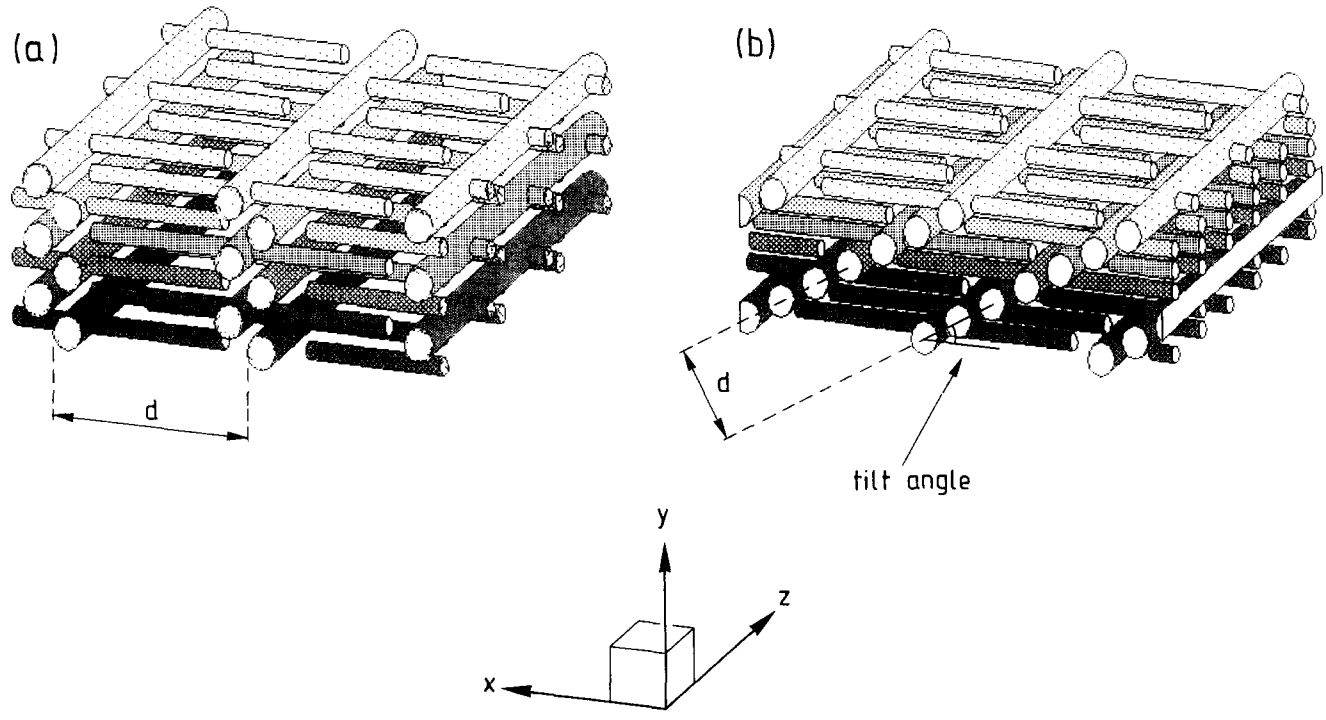


**Figure 2** Schematic representations of the layered modifications A (a) and B (b) in PTA$n$HQ. The layer spacing $d$ is characteristic for each modification. For ease of drawing the tilt angle in modification B is taken in the $xy$ plane. It should be noted that the same layer distance can also be obtained by tilting the side chains with respect to the main chains in the $xz$ plane

## RESULTS AND DISCUSSION

As explained in the second paper in this series[7], oriented PTA12HQ fibres with a fairly high degree of orientation (orientation angle $\varphi \approx 6°$) can be obtained by drawing in the layered mesophase. For these fibres a schematic representation of the phase behaviour is given in *Figure 1*. In the previous paper in this series the drawing and mechanical properties of PTA12HQ films ($\varphi \approx \sim 3$–$10°$) were described[8].

*X-ray diffraction on oriented films and fibres at different temperatures*

For oriented films of PTA12HQ it is known[8,12] that the layer distance $d$ is found preferentially in the thickness direction of the film. X-ray diffraction with the primary beam perpendicular or parallel to the film surface thus yields valuable information concerning the origin of reflections.

*Modification A*. The X-ray diffraction patterns of an oriented film in modification A are shown in *Figure 3*. The equatorial scans of these X-ray diagrams can be compared in *Figure 4*. They show that the reflections arising from the layer distance $d$ (at respectively 21, 10.5 and 7 Å) are more prominent in *Figure 3b*. As the fibre repeat distance (derived from the layer lines) is $12.6 \pm 0.05$ Å and the measured density is $1.055\ g\ cm^{-3}$ a characteristic distance along the $y$ direction (*Figure 2*) of $3.6 \pm 0.1$ Å can be calculated. This distance would be expected to give rise to a very prominent reflection in the diffractogram with the beam perpendicular to the film surface, which is indeed the case (see *Figure 4a*). A distance along the $y$ direction of 3.6 Å was also reported for PTA16HQ by Cervinka and Ballauf[9] and Adam and Spiess[10]. It was explained by the structure shown in *Figure 2a*.

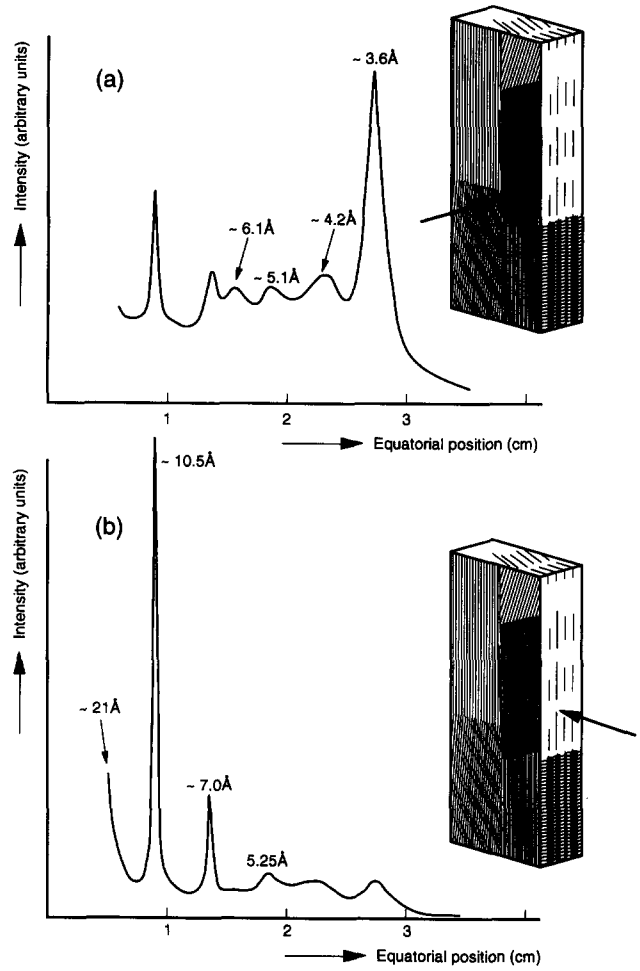


**Figure 4** Equatorial scans of the intensity distribution of the films shown in *Figure 3*

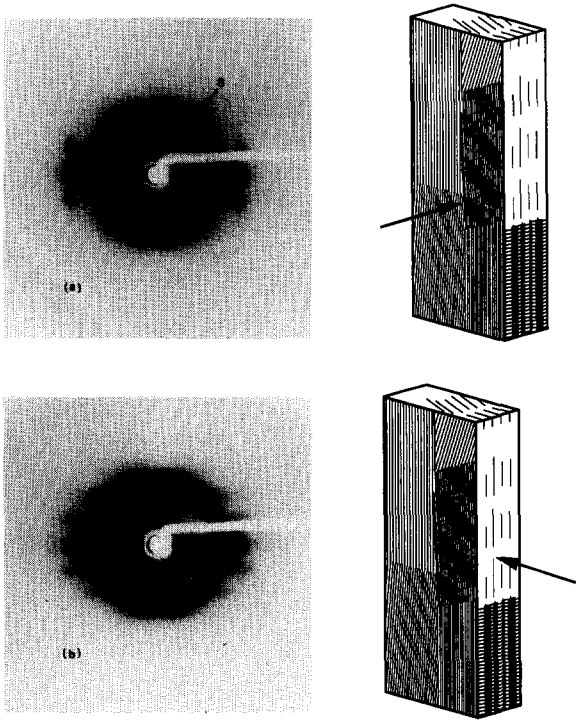


**Figure 3** Flat-plate X-ray diffractogram of an oriented PTA12HQ film in modification A with the primary beam (a) perpendicular to or (b) parallel with the film surface. Orientation direction is vertical, sample-to-film distance 6 cm

Regarding the zigzag arrangement of the main chains[10] in this structure, it is useful to have an idea of the closest possible distance between two adjacent main chains. Coulter *et al.*[13] proposed a monoclinic unit cell with $a = 7.98$ Å, $b = 5.33$ Å, $c = 12.6$ Å and $\beta = 98.98°$ for the unsubstituted poly(*p*-phenylene terephthalate) (pPT) main chain. From their model we calculate a closest possible distance between two adjacent pPT chains of 4.7 Å, thus confirming the necessity for zigzag arrangement of the main chains in our system. Thus we can conclude that within the $xy$ plane a packing as indicated in *Figure 2a* must exist, which results in a very strong reflection at 3.6 Å.

On the first layer line (near the meridian) a very strong reflection at $\approx 12$ Å and a weaker one at $\approx 9.4$ Å are found. They indicate that the positions of two adjacent main chains in the $xz$ plane are correlated with each other. If the 12 Å reflection is indexed as the (0 0 1) reflection in a monoclinic unit cell a tentative unit cell with $a = 22.05$ Å, $b = 7.2$ Å, $c = 12.6$ Å and $\beta = 107.8°$ can be proposed (note that a similar unit cell with $a = 15.6$ Å and $\beta = 115.2°$ has been proposed[7] for PTA6HQ in modification A). In this monoclinic unit cell the reflection of medium intensity on the first layer line at 3.34 Å can be indexed as the (1 2 1) reflection. As there is, however, only a very limited number of other off-axis reflections

it is inferred that the three-dimensional ordering in modification A is far from perfect.

In the above, most of the reflections were explained in terms of a monoclinic unit cell and in accordance with the repeat distance of 12.6 Å of the PTA12HQ main chain. There is, however, a very prominent reflection at 4.5 Å (labelled S in *Figure 3a*), which is located on a layer line of ≈5.5 Å. As this layer line does not harmonize with the repeat distance of the main chain it must be caused by a structure (of the side chains) which is incommensurate with the main chain repeat distance. This is in accordance with a recent paper by Cervinka and Ballauf[9] who proposed that the positions of the main and side chains of PTA16HQ are decoupled and that the aliphatic side chains of PTA16HQ form clusters between the main chain layers. The exact crystal structure within these clusters cannot be resolved completely from the present results, but is most likely to be similar to the hexagonal or triclinic arrangements as in polyethylene and paraffins[14]. The differential scanning calorimetry (d.s.c.) endotherm around 40°C[7] can then be explained by a 'melting' of these side chain clusters[9].

In summary, the following image of modification A can be drawn. The main chains are arranged in layers which are kept at a distance $d$ by the interdigitating side chains (*Figure 2a*). Within these layers the positions of the main chains are correlated with each other. The position of the main chains over the layer distance $d$ (within the $xz$ plane) also shows correlation; most probably the interdigitating side chains do not only keep the main chain layers at the layer distance $d$, but also fix the position of these layers relative to each other. The resulting main chain superstructure (which is tentatively indexed on a monoclinic unit cell) does not, however, give rise to a diffraction pattern, which might be expected for a classical three-dimensional crystal structure. From this it can be concluded that, although there is ordering of the main chains in the $yz$ plane as well as in the $xz$ plane, no fully crystalline three-dimensional main chain structure is present in modification A.

The side chains form clusters between the main chain layers, thus enabling the formation of microcrystals resembling the triclinic or hexagonal unit cell of paraffins. The reflections arising from these clusters show incommensurate ordering with respect to the main chain repeat distance. Thus it can be concluded that the position of the side chains is not fully imposed by their regular attachment to the main chains.

It is noteworthy that upon increasing the side chain length one would expect an even lower degree of three-dimensional ordering of the main chains, which is in agreement with the X-ray diffraction patterns on oriented films of PTA16HQ in modification A described by Schrauwen *et al.*[12]. A shorter side chain length would be expected to give a higher amount of 3D ordering of the main chains, while the side chain positions cannot be decoupled easily from the main chains. This is in agreement with results[7] on PTA6HQ in modification A, showing a highly crystalline 3D structure (very probably including the side chains).

*Modification B.* This highly crystalline structure is probably the most favourable structure thermodynamically at room temperature[7]. The X-ray diffractograms of such a film are shown in *Figure 5*. The equatorial scans of these X-ray diagrams can be compared in *Figure 6*.

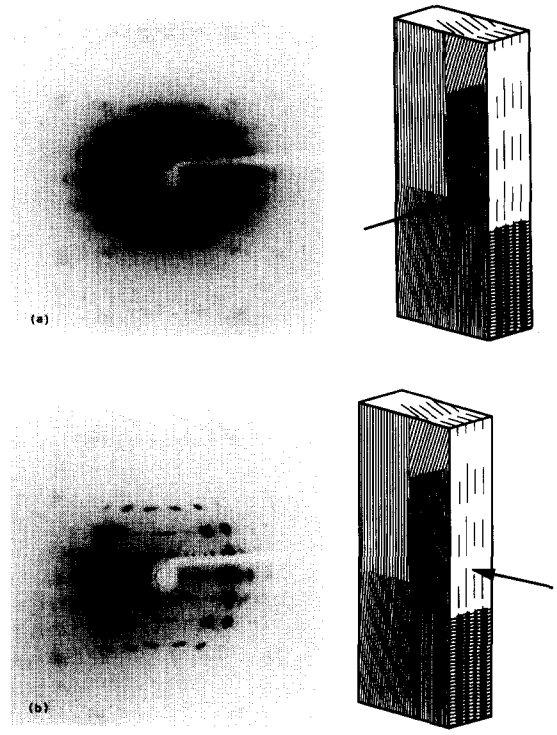


**Figure 5** Flat-plate X-ray diffractogram of an oriented PTA12HQ film in modification B with the primary beam (a) perpendicular to or (b) parallel with the film surface. Orientation direction is vertical, sample-to-film distance 6 cm

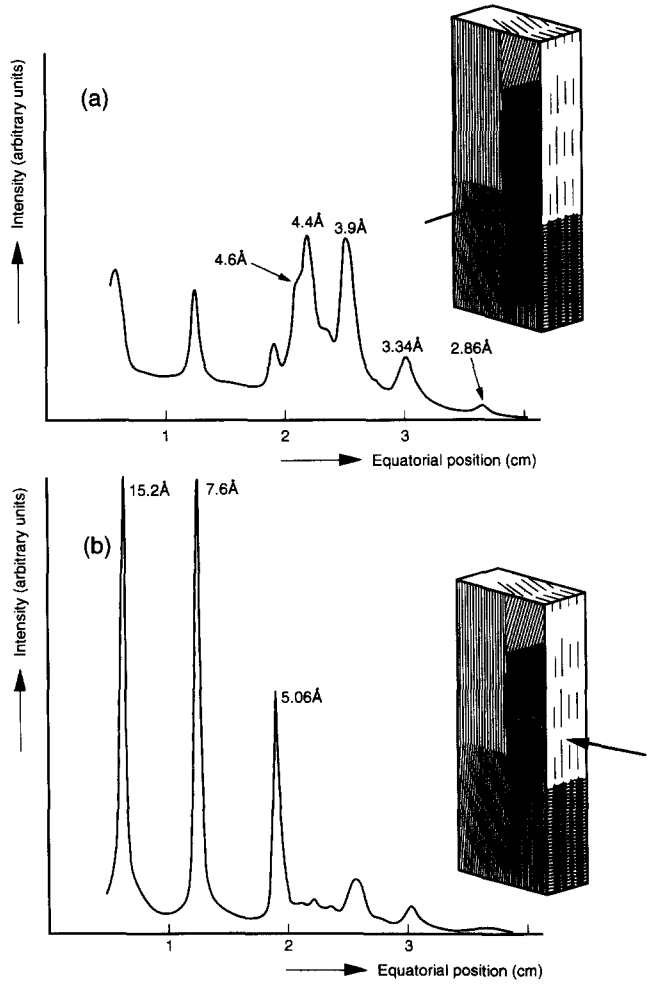


**Figure 6** Equatorial scans of the intensity distribution of the films shown in *Figure 5*

**Table 1** Observed X-ray reflections of modification B

| | Spacing (Å) | | | | | |
|---|---|---|---|---|---|---|
| Position | Equator | 1st layer | 2nd layer | 3rd layer | 4th layer | 5th layer |
| Meridian | | | | | | 2.46 (vw) |
| 1 | 15.2 (vs) | 12.2 (vs) | 6.27 (m) | 4.08 (s) | 2.21 (vw) | 2.35 (vw) |
| 2 | 7.59 (vs) | 11.0 (vs) | 6.13 (m) | 3.67 (s) | 2.03 (vw) | 2.19 (w) |
| 3 | 5.06 (vs) | 8.59 (m) | 5.50 (w) | 3.22 (w) | | 2.11 (vw) |
| 4 | 4.60 (m) | 7.35 (m) | 5.24 (w) | 3.01 (vw) | | 2.06 (w) |
| 5 | 4.41 (m) | 5.83 (m) | 4.50 (vs) | 2.81 (vw) | | |
| 6 | 4.17 (m) | 5.15 (m) | 3.67 (vs) | 2.69 (vw) | | |
| 7 | 3.90 (s) | 4.39 (w) | | | | |
| 8 | 3.86 (w) | 3.99 (s) | | | | |
| 9 | 3.34 (s) | 3.55 (w) | | | | |
| 10 | 2.86 (vw) | 3.37 (w) | | | | |
| 11 | | 3.06 (vw) | | | | |
| 12 | | 2.88 (vw) | | | | |
| 13 | | 2.67 (vw) | | | | |

vs, Very strong; s, strong; m, medium; w, weak; vw, very weak

They show that the reflections arising from the layer distance $d$ (at 15.2, 7.6 and 5.06 Å) are more prominent in *Figure 5b*. The layer distance of 15.2 Å corresponds with the value reported earlier by Ballauff and Schmidt[3] for modification B. As the fibre repeat distance is 12.6 Å and the measured density is 1.084 g cm$^{-3}$ a characteristic distance between the main chains (in the main chain layers) of 4.9 Å can be calculated. This means that a zigzag arrangement of the main chains, as in modification A, is no longer needed. The splitting of the off-axis reflections (for instance, the strong reflections near the meridian on the first layer line), which indicates that the crystal structure is not orthorhombic, is worthy of note. Indexing of all reflections (see *Table 1*) on a monoclinic unit cell also proved to be impossible and the existence is inferred of a triclinic unit cell in which the side chains are tilted with respect to the main chain layers, as well as with respect to the long axis of the main chains. The present results are, however, not sufficient to allow for a complete indexing in terms of a triclinic unit cell. With regard to the packing of the side chains in this unit cell, it might very well be that they pack in an orthorhombic subcell, as infra-red measurements show more vibrations arising from the alkyl groups than in modification A (similar arguments were used by Chapman[15] in describing the structure of long chain alkyl compounds).

In summary, it seems likely that a triclinic unit cell is needed to describe the packing in modification B. In this unit cell the side chains are probably packed in an orthorhombic subcell. It is interesting to note that a similar problem has been discussed extensively for poly(n-alkylethylene)s by Turner-Jones[16]. By comparing the X-ray diffraction patterns of polymers with different side chain length he was able to distinguish the reflections arising from the orthorhombic subcell from the other reflections. Thus a comparison between the X-ray diffraction pattern of PTA12HQ with PTA*n*HQ of longer side chain length (oriented, modification B) might elucidate further the crystal structure of PTA12HQ in modification B.

*Heating of modifications A and B.* In *Figure 7a* the value of the layer distance $d$ is plotted as a function of temperature when going from modification A or B to phase A′ and phase $L_m$ subsequently. From this figure it may be concluded that at the phase transition A→A′

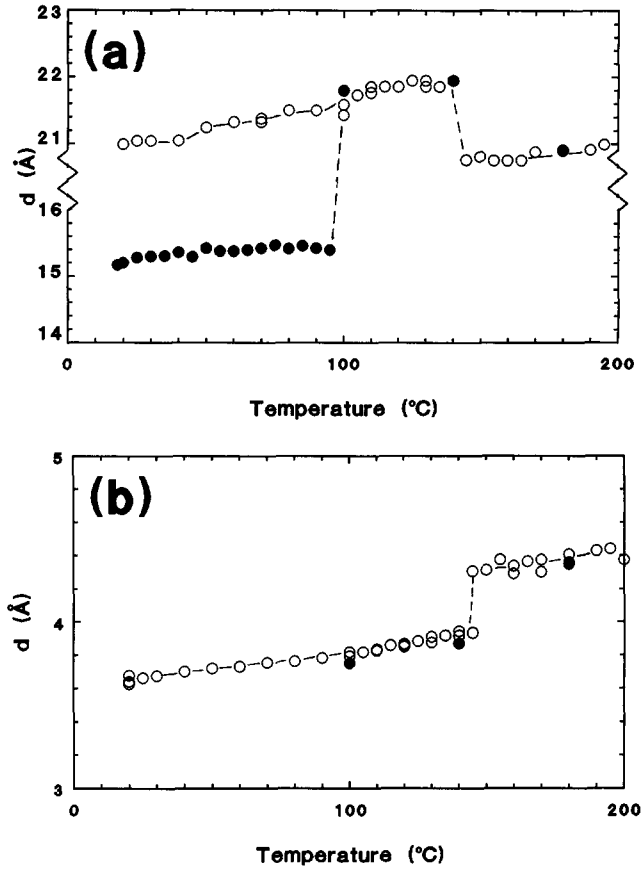


**Figure 7** Temperature dependence of (a) the layer distance $d$ and (b) the distance between the main chain layers along the $y$ direction, for (○) modification A and (●) modification B

(≈40°C) a slight increase in layer distance occurs. At about 110°C another discontinuity in the diagram is observed. A stepwise decrease of the layer distance occurs at about 150°C, corresponding to the start of the phase transition A′→$L_m$ as observed by d.s.c.[7] The characteristic distance in the $y$ direction at ≈3.6 Å is plotted as a function of temperature in *Figure 7b*. The phase transition A→A′ is not discernible in this figure. As in *Figure 7a*, at about 100°C a change in slope is observed and at the phase transition A′→$L_m$ a stepwise increase is observed. While the first change might be associated with a glass transition, the second change points to a first-order phase

transition. The simultaneous decrease of the layer distance $d$ and increase of the 3.6 Å reflection indicate a significant amount of reordering taking place at the main chain melting temperature $T_m$. This reordering could very well be a simultaneous loss of the zigzag arrangement of the main chains and a small increase of side chain tilting. By plotting the layer distance $d$ (*Figure 7a*) and, above $T_s$(B), the prominent reflection at about 3.6 Å (*Figure 7b*) of modification B as a function of temperature the assumption made earlier[7] that modification B and modification A both transfer to the same phase A′ above $T_s$ is given more support. Above $T_s$ they both show the same characteristic spacings.

*Phase A′*. From the preceding it is concluded that modifications A and B transform to the same intermediate phase A′ above $T_s$. The X-ray fibre diffractogram of this phase is shown in *Figure 8*. When comparing the X-ray diffractograms of structures A′ and A it is evident that the main difference between these two structures is the ordering of the side chains. The disappearance of the reflections labelled S in *Figure 4* and the appearance of an amorphous halo at ≈4.6 Å confirm the assumption from the d.s.c. measurement[4–6] that the side chains are not crystallized in phase A′. This agrees well with n.m.r. observations by Baldwin-Frech *et al.*[11] who showed that the conformation of the side chains changes from predominantly *trans* to *gauche* at $T_s$. Further evidence is found from observations on comb-like polymers such as poly(α-olefin)s. In such polymers a halo at a similar distance of 4.6–4.7 Å is found which is attributed to the interaction between the olefinic side chains[14].

The low-angle equatorial reflections indicate the existence of a layered structure with a layer spacing $d$ of 22 Å. The strong equatorial reflection at ≈3.9 Å, labelled M, is caused by the characteristic distance in the $y$ direction. The reflections near the meridian on the first layer line indicate that the main chains are ordered in a similar way in the $xz$ plane as in modification A. The other reflection on the first layer line (labelled $M_z$) indicates that ordering of the main chains in the $yz$ plane is present. This leads to the conclusion that three-dimensional order of the main chains is present in phase A′.

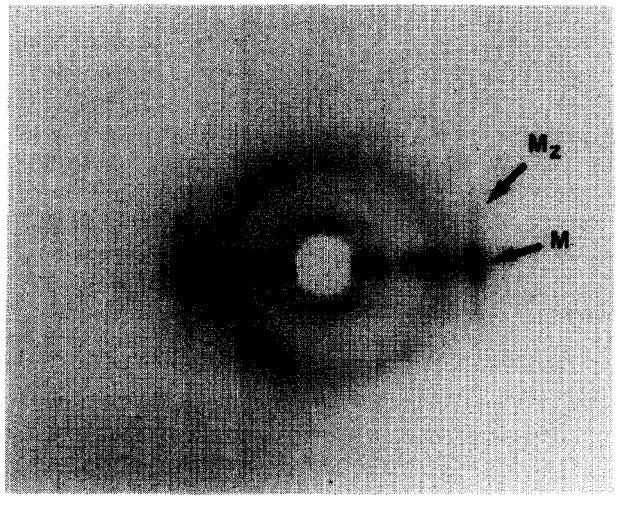


**Figure 8** Flat-plate X-ray diffractogram of a PTA12HQ fibre at 140°C (phase A′). Fibre axis vertical, sample-to-film distance 3 cm

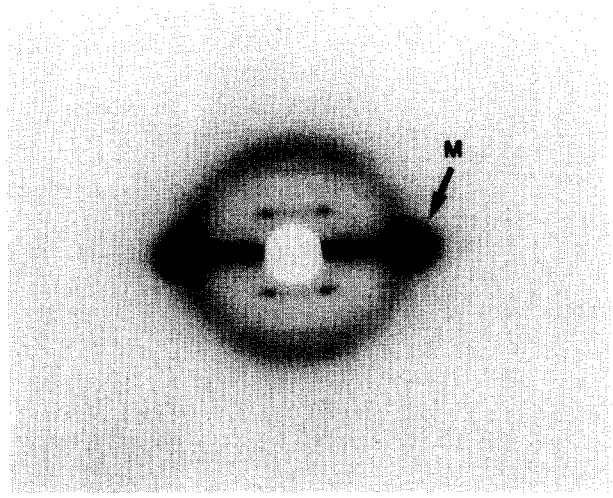


**Figure 9** Flat-plate X-ray diffractogram of a PTA12HQ fibre at 200°C (phase $L_m$). Fibre axis vertical, sample-to-film distance 3 cm

*Phase $L_m$*. By further heating to above the main chain melting temperature $T_m$ the layered mesophase $L_m$ is reached. The X-ray diffraction pattern of an oriented fibre in this phase is shown in *Figure 9*. The loss of three-dimensional ordering of the main chains is most evident from the disappearance of the off-equatorial reflection labelled $M_z$ in *Figure 8*. The broad equatorial reflection at 4.4 Å is indicative of a badly defined distance between the main chains within the main chain layers ($yz$ plane, *Figure 2*). The off-equatorial reflection near the meridian on the first layer line shows that ordering is present within the $xz$ plane. The halo at ≈4.8 Å is caused by some amorphous scattering of the polymer as well as the side chains which behave in a liquid-like manner.

Thus above the main chain melting temperature the main chains are arranged in layers (due to their incompatibility with the aliphatic side chains). Because of this incompatibility and their rigidity the main chains are also aligned parallel to each other, though not in a regular, crystal-like packing. Apparently the side chains, which are 'molten', fill the space between the main chain layers in such a way that they influence the arrangement of the main chains in the $xz$ plane. In this way a biaxial phase is formed.

*Phase $L_f$*. When an oriented film is quenched from 200°C to room temperature a 'frozen-in layered mesophase' structure, $L_f$, is obtained. In *Figure 10* the X-ray diffractograms of such a film are displayed. These diffractograms closely resemble the diffractogram at 200°C. From the equatorial scans of these X-ray diagrams, shown in *Figure 11*, the assignment of the broad equatorial reflection at 3.85 Å (labelled M) to a distance between the main chain layers is affirmed. The very weak off-axis reflections and the small intensification of the amorphous halo on the layer lines indicate the development of a small amount of three-dimensional ordering.

*Relation between structure and properties*

In *Figure 12* the X-ray fibre patterns of the different phases are shown schematically. Up to the isotropic melt I the main chains are arranged in layers, separated by

the interdigitating side chains (see *Figure 2*). All transitions can be understood in terms of the amount of ordering of the main chains within these layers (*yz* plane) and/or in the *xz* plane. Below the side chain disordering temperature $T_s$ the side chains can be incorporated in a three-dimensional lattice (modification B) or they can form clusters between the main chain layers (incommensurate ordering, modification A). Modification A and modification B both transform to the intermediate phase A′ above the side chain disordering temperature $T_s$ (for modification B the main chains are also likely to rearrange at this transition). This intermediate phase shows some three-dimensional ordering of the main chains, while the side chains are disordered. At the main chain melting temperature $T_m$ a significant amount of reordering takes place; the main chain layer distance *d* decreases, while the distance in the *y* direction increases.

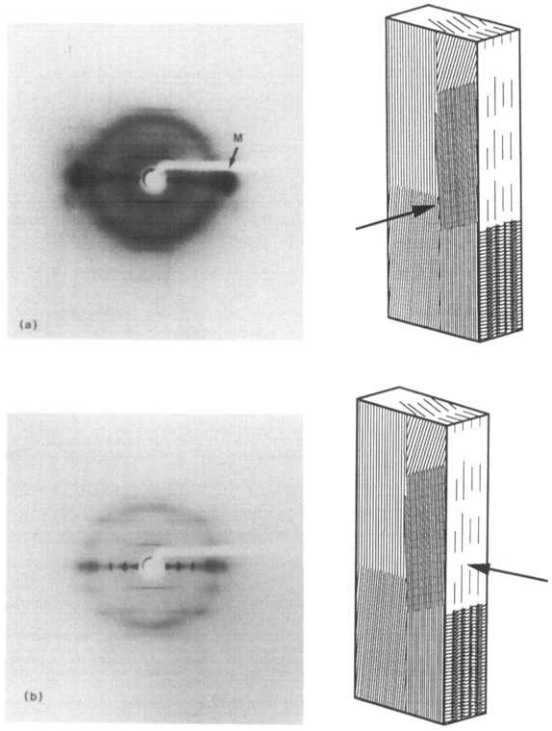


**Figure 10** Flat-plate X-ray diffractogram of an oriented PTA12HQ film in phase $L_f$ with the primary beam (a) perpendicular to and (b) parallel with the film surface. Orientation direction is vertical, sample-to-film distance 6 cm

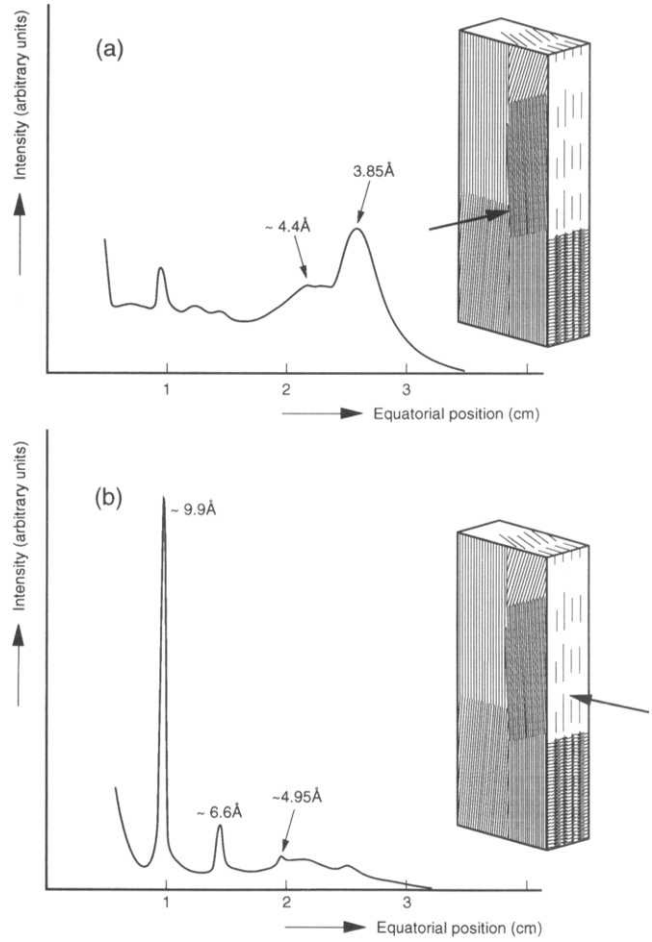


**Figure 11** Equatorial scans of the intensity distribution of the films shown in *Figure 10*

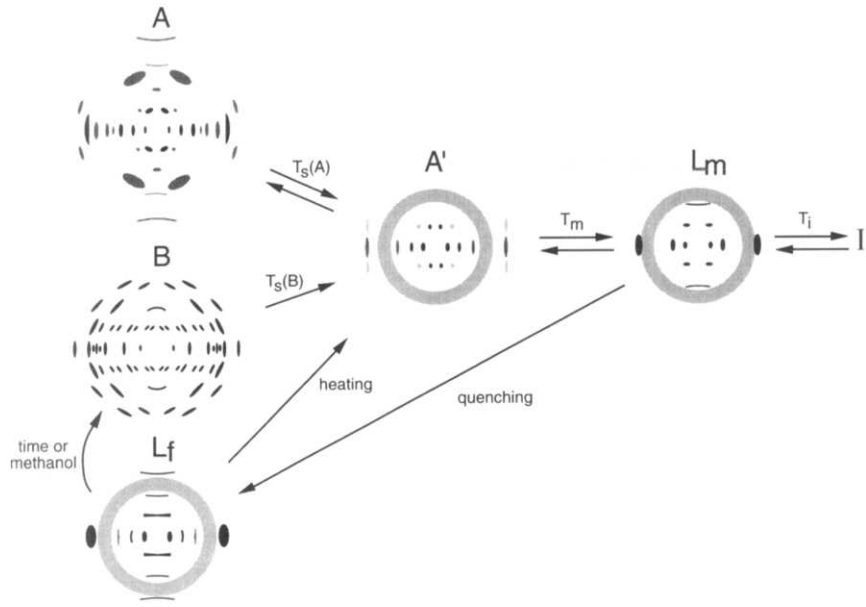


**Figure 12** Schematic representation of the X-ray fibre diagrams of the various phases

Some ordering within the $xy$ plane is preserved, while the ordering within the main chain layers is lost. Quenching of this phase to room temperature yields the 'frozen-in layered mesophase' $L_f$.

By rheological measurements it was shown earlier[5] that the viscosity shows a small stepwise decrease at the main chain melting temperature $T_m$. From these and other measurements it was concluded that the layered mesophase $L_m$ behaves more like a solid than a liquid. This is affirmed by the present results, showing that phase $L_m$ is a biaxial phase.

Dynamic mechanical measurements on oriented films[8] showed that the tensile modulus in modification B at room temperature is significantly higher than in modification A. Above $T_s$(B) the moduli of both modifications become equal, which is in agreement with the present results showing that both modifications transform to phase A′ above $T_s$. At the main chain melting temperature $T_m$ another significant drop of the modulus (from $\approx 10$ to $\approx 1$ GPa) was observed. This is in agreement with the loss of ordering within the main chain layers observed by X-ray diffraction.

## CONCLUSIONS

From X-ray diffraction measurements at room temperature on oriented fibres and films of PTA12HQ in modification A it is concluded that the side chains do not follow the restrictions imposed by their regular attachment to the main chains; they do not pack in the same crystal lattice as the main chains, but form clusters between the main chain layers. In the highly crystalline modification B both main and side chains form a classical three-dimensional crystal structure, which is thought to be triclinic.

It is concluded from high-temperature X-ray diffraction on oriented fibres of PTA12HQ that at each transition temperature part of the ordering is lost. Above $T_s$(A) or $T_s$(B) the side chains have lost most of their ordering, while the main chains remain in a lattice. At the main chain melting temperature $T_m$ the main chains lose their three-dimensional ordering and a layered mesophase is formed. This mesophase shows biaxial ordering. The parallel ordering of the main chains is lost at the transition temperature to the isotropic melt, $T_i$.

By quenching the layered mesophase $L_m$, a 'frozen-in layered mesophase', $L_f$, can be obtained.

Good agreement with rheological and mechanical measurements performed earlier was found.

## ACKNOWLEDGEMENTS

The authors are indebted to Professor Dr M. Ballauff, Dr Ir. J. A. H. M. Buijs and Ir. F. P. M. Mercx for stimulating discussions and careful reading of the manuscript. Performance of the X-ray diffraction measurements by E. J. Sonneveld is greatly appreciated. Financial support from NWO (grant for S.B.D.), the Dutch Ministry of Economic Affairs (IOP-PCBP 302) and DSM is gratefully acknowledged.

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