Fourier Transform Analysis of Models for the Disordered Phases (IV and I) of Poly(tetrafluoroethylene)

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ABSTRACT: Fourier transform calculations for bundles of parallel helices of poly(tetrafluoroethylene) are compared to the diffraction profiles of fibers at 21 and 50 °C. In both cases, long-range order of the chain axes is present; for phase IV, long-range order of the atoms seems to be maintained along the chain axis and, to a lesser amount, in the other directions. Some kind of order involving the translations of the chains parallel to their long axes seems to be present both in phase IV as well as in phase I, at least at the lower temperatures of stability. The diffraction data on the layer line which corresponds to the unit height h would correspond to the local positioning of the fluorine atoms in neighboring helices nearly at the same height. Rows of like-handed helices would be present in phase IV but absent in phase I, where helical reversals would occur along each molecular stem.

Introduction

The disordered crystal phases of poly(tetrafluoroethylene) (PTFE), which are stable between 19 and 30 °C (phase IV) and above 30 °C (phase I), were investigated by X-ray diffraction many years ago.[1]

The nature of the intermolecular disorders was investigated by Clark and Muus[2] on the basis of the diffraction theory for helical structures[3] extended to include the effects of specific types of intermolecular disorder, which preserve the parallelism of the chain axes and their periodic placement.[4] On the basis of that theoretical work, which only refers to the Bragg reflections without considering the diffuse halos, it was suggested that the X-ray diffraction patterns of PTFE can be accounted for by small angular displacements of the molecules about their long axes above the 19 °C transition with the angular displacements becoming much larger above the 30 °C transition.[2]

The effect of a specific type of intramolecular disorder (the disordered succession of helical stretches having spirals of opposite sense) on the Fourier transform of isolated PTFE chains was also described.[5] It was shown that some aspects of the Fourier transforms, calculated for this kind of intramolecular disorder, are in qualitative agreement with the X-ray diffraction patterns for the high-temperature phase of PTFE (phase I).

In this paper Fourier transform calculations for bundles of parallel chains will be presented, in order to elucidate the kinds of order which are retained in the high-temperature phases of PTFE. The diffraction profiles from fibers of the phases IV and I, not reported previously in the literature, are shown and compared with the calculated Fourier transforms.

Experimental Part and Calculation Method

The PTFE fibers were supplied by Montefluos S.p.A. The X-ray diffraction patterns for stretched fibers were obtained by using a Nonius automatic X-ray diffractometer with Ni-filtered Cu Kα radiation. The Lorentz–polarization (LP) correction was applied (LP = $(1 + \cos^2 2\theta)/\sin 2\theta$) for all the layer lines according to the diffraction geometry.

The transformation of the corrected intensities $I(\theta)$ into $I(\xi)$ was performed graphically in such a way that

$$\int_{\xi_1(\theta_1)}^{\xi_2(\theta_2)} I(\xi)\, d\xi = K \int_{\theta_1}^{\theta_2} I(\theta)\, d\theta$$

for sufficiently small intervals $(\theta_2 - \theta_1)$.

For the calculation of the Fourier transforms, the method described in ref 6 was used. The calculated intensities were multiplied by a thermal factor of the kind

$$\exp(-\tfrac{1}{2}B_\xi \xi^2) \exp(-\tfrac{1}{2}B_\zeta \zeta^2)$$

On the assumption that the disorder along the chain axis is less pronounced than in the lateral directions, anisotropic parameters with $B_\xi > B_\zeta$ have been assumed. In particular, the parameters were chosen on the basis of the experimental intensity ratios at 21 °C between the equatorial reflections and the meridional reflection on the 15th layer line (B_ξ = 10 Å^2 and B_ζ = 5 Å^2). In fact these intensity ratios are nearly independent of the orientation and of the handedness of the helices in the models.

The calculations of the Fourier transforms were performed on pseudohexagonal bundles of parallel chains of PTFE, with a constant distance between the axes of adjacent chains (5.66 Å). In all the models the chains have a 15/7 helical symmetry, with an axis length of nearly 50 Å (40 carbon atoms). In order to have reasonable computation times the calculations were performed on bundles with a small number of chains (generally 20 and in some particular cases 60), whereas much larger bundles should have been considered in order to account for the sharpness of the reflections. As a consequence the reflections in the calculated pattern are generally broader than the reflections in the experimental patterns.

For the models with intramolecular helix reversals, the junctions between stretches of different handedness were realized as described in ref 5. These junctions leave the molecules confined in cylindrical envelopes, having the same radius as that of a helix without reversals, and are energetically feasible.[5]

Diffraction Profiles

The fiber patterns of low-temperature (T < 19 °C) phase II present sharp spots on all the layer lines, corresponding to an ordered arrangement of molecules with a nearly 13/6 helical symmetry in a triclinic lattice.[1,2,7,8]

During the 19 °C transition, the molecules untwist slightly assuming a 15/7 helical symmetry and the molecular packing changes from an ordered structure with a triclinic cell, corresponding to a nearly hexagonal positioning of the chain axes ($a = b$ = 5.59 Å; γ = 119.3°), to a partially disordered structure with a hexagonal positioning of the chain axes ($a = b$ = 5.66 Å; γ = 120°). These features characterize both phase IV and phase I.

The main features of the fiber pattern of phase IV are the sharp intense reflections on the equator and on the 7th, 8th, and 15th layer lines and the presence of a diffuse halo on the second layer line. The diffraction profiles at 21 °C for the corresponding ζ values (0, 0.103, 0.359, 0.410, 0.769 Å^{-1}), as a function of 2θ, and of the reciprocal coordinate ξ are reported in Figure 1.

The main features of the fiber pattern of phase I are sharp reflections on the equator and on the 15th layer line, as well as the presence of an intense diffuse halo in which the seventh and eighth layer lines merge. The diffraction profiles at 50 °C, for the corresponding ζ values, as well as for a ζ value intermediate between the seventh and eighth layer lines, are reported in Figure 2.

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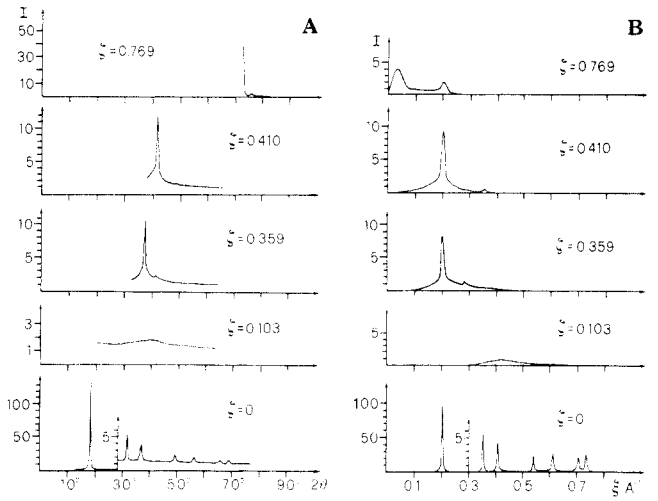

Figure 1. Experimental X-ray diffraction patterns of a fiber of PTFE at 21 °C, at the indicated reciprocal lattice coordinate ζ (Å^{-1}): (A) measured intensities as a function of 2θ; (B) corrected intensities as a function of the reciprocal lattice coordinate ξ (Å^{-1}).

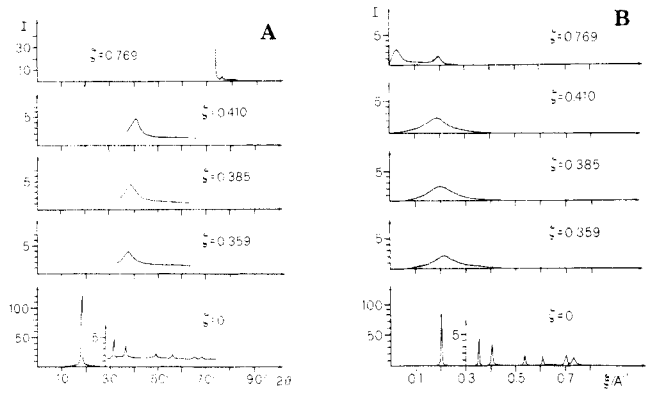

Figure 2. Experimental X-ray diffraction patterns of a fiber of PTFE at 50 °C, at the indicated ζ (Å^{-1}): (A) measured intensities as a function of 2θ; (B) corrected intensities as a function of ξ.

On the basis of measurements of the line broadening of the equatorial reflections, for both phase IV and I, a long-range order of the chain axes (nearly 250 Å) is pointed out.

Results of the Calculations and Discussion

Relative Heights of the CF_2 Groups in Neighboring Chains. The already cited theoretical analysis of the diffraction patterns of the high-temperature phases of PTFE pointed out the presence of some translational order along c.[2] In this section we try to clarify the kind of translational order involved as well as the range to which this order is extended.

The calculated intensities on the 15th layer line are nearly independent of the presence of rotational disorder as well as of the handedness of the helices and hence can give easily information on the relative heights of the CF_2 groups of neighboring helices, along the chain axes.

As an example, the Fourier transforms for the 15th layer line for pseudohexagonal bundles of 20 parallel chains arranged in alternating rows of right-handed and left-handed helices, in complete rotational disorder, are reported in Figure 3A–E. One model presented the CF_2 groups of all the helices at the same heights (Figure 3A), while in other models 50% of the helices, randomly distributed in the bundle, were shifted along the chain axis by $^1/_8h$ (Figure 3B), $^1/_4h$ (Figure 3C), $^1/_3h$ (Figure 3D), $^1/_2h$ (Figure 3E) (the unit height h being equal to 1.3 Å). It is apparent that a qualitative agreement with the diffracted intensities of phases IV and I (Figures 1B and 2B, respectively) is reached only for nearly equal relative heights of the chains.

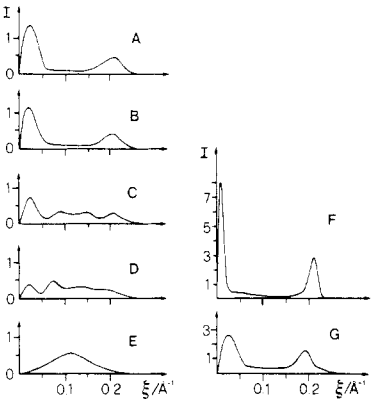

Figure 3. (A–E) Fourier transforms, for the 15th layer line (ζ = 0.769 Å^{-1}), for models in which the helices are 50/50 divided in two sets, each set characterized by a same height for the CF_2 units; the chains of the two sets are randomly distributed in the pseudohexagonal structure. The two sets are shifted by (A) Δz = 0, (B) $\Delta z = {}^1/_8h$, (C) $\Delta z = {}^1/_4h$, (D) $\Delta z = {}^1/_3h$, and (E) $\Delta z = {}^1/_2h$. (F, G) Fourier transforms for the 15th layer line for a model of 60 chains in which (F) all the helices have the same height and (G) two ordered "domains" are at a given height and the two other ordered domains are shifted by $^1/_2h$.

The same conclusion was also reached by considering ordered pseudohexagonal models which can be described by one-chain triclinic cells.

This result is in agreement with the energy calculations for pairs of molecules with either the same or opposite hand and for various relative orientations: the lowest energies were usually obtained when the CF_2 units on the two molecules were at the same level.[10]

The size of the domains, in which this correlation in the relative heights of the helices is maintained, is certainly smaller than the size of the bundles, in which the strict parallelism of the chain axes is present. In fact, already for a bundle of 60 chains (diameter of nearly 50 Å), the transform on the 15th layer presents a too narrow main peak, shifted toward too low ξ values (Figure 3F) in comparison with the experimental patterns (Figures 1B and 2B).

The relative shifts along the chain axes of the "ordered" domains (ordered with respect to the relative heights of the CF_2 groups) inside the crystalline bundles do not affect substantially the transform on the 15th layer. The transform on the 15th layer for a bundle of 60 helices comprising two "ordered" domains at a given height and two "ordered" domains shifted by $^1/_2h$ is, for instance, reported in Figure 3G. Also for this limiting model the transform is quite similar to the transform of the isolated domain (Figure 3A).

In summary, for both phase IV and phase I, a local order (<50 Å), consisting in the positioning of the fluorine atoms of neighbouring helices nearly at the same height, is suggested.

Phase IV

For phase IV, the theoretical approach of Clark and Muus, besides the presence of some translational order along c, pointed out the absence of random rotations of the helices, while the occurrence of small angular displacements, around the fixed values typical of an unspecified ordered structure, was suggested.[2]

In agreement with that analysis, any model characterized by random rotations of the helices along c, as well as by disordered distributions of helices of different handedness, does not give rise to sharp reflections on the seventh and

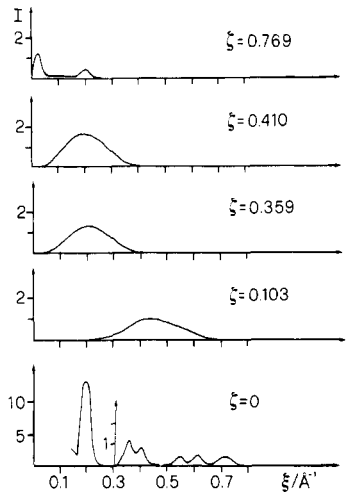

Figure 4. Results of the calculations of Fourier transforms, at the indicated ζ (Å^{-1}), on a model having the CF_2 units of different chains at the same height, after the introduction of random angular displacement of the helices.

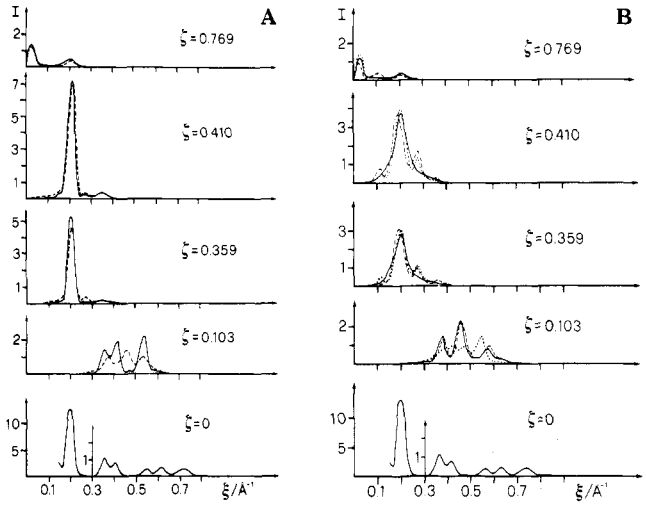

Figure 5. Results of the calculations of Fourier transforms on ordered models at the indicated ζ (Å^{-1}): (A) models with all isomorphic chains, (—) a model having all the helices with the same height and setting angle, (- - -) the model of Figure 7 of ref 9; (B) models with two enantiomorphic chains in the unit cell, (—) the model of Figure 5 in ref 9, (- - -) the model of Figure 6 in ref 9, (···) a model having all the helices with the same height and setting angle.

eighth layer lines (see, e.g., Figure 4), which are instead present in the experimental patterns of phase IV (Figure 1).

For this reason our analysis of possible models for phase IV started with the selection of ordered models in which, in a successive step, to introduce some partial rotational disorder along c.

Fourier transform calculations for the most relevant ζ values, for some ordered structures presenting all the chains nearly at the same height, are reported in Figure 5. In particular, the triclinic perfect structures resulting from the energy analysis of Farmer and Eby,[9] as well as some other simple regular models are considered.

The Fourier transforms of Figure 5A refer to models with all isomorphic chains: the model of Figure 7 of ref 9 and the model with all the helices at the same height and orientation. The Fourier transforms of Figure 5B refer to models with two enantiomorphic chains in the unit cell: the triclinic structures of Figures 5 and 6 of ref 9 and a model with all the chains with a same height and orientation.

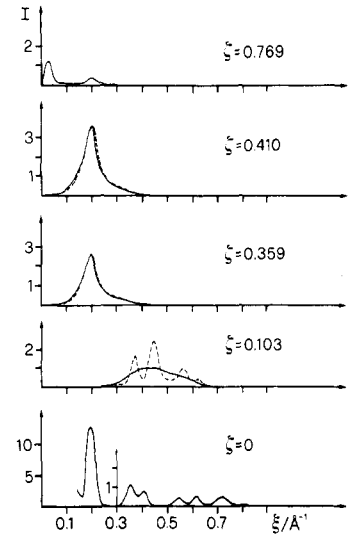

Figure 6. Results of the calculations of Fourier transforms, at the indicated ζ (Å^{-1}), on one of the models of Figure 5B: (- - -) ordered model (full lines of Figure 5B); (—) after the introduction of small angular displacement of the helices in the range −30°, +30° around the values of the ordered model.

As will be shown in the following, the introduction of small angular displacements in the ordered structures does not change significantly the intensities on the seventh and eighth layer lines. As a consequence the models with all like-handed helices are unsuitable, since the calculated intensities on the seventh and eighth layer lines are too strong compared with the intensities on the other layer lines. A better fit occurs for the calculated intensities of the models presenting rows of like-handed helices (Figure 5B); however, it is not possible on the basis of our calculations to discriminate between the individual models.

The presence of rows of like-handed helices in phase IV was also suggested on the basis of energy calculations[9,11] and characterizes also the structures proposed for the low-temperature phase of PTFE (phase II).[8,10,13]

The similarity of the Fourier transforms of the ordered models, with rows of like-handed helices and with all the helices nearly at the same height, implies that, in this framework, the choice of the starting model, on which to introduce the different kinds of disorder, is not critical. Just as an example, the results relative to the introduction of small angular displacements in the triclinic model of Figure 5 of ref 9 will be presented.

The Fourier transforms of the model with small angular displacements about the long axis, in particular for random displacements included in the range −30°, +30° around the values of the chosen ordered structure, are reported in Figure 6. In agreement with the theoretical result,[2] this kind of disorder leaves nearly unchanged the peaks on the 15th layer line while the peaks on the second layer line are much more depressed than those on the seventh and eighth layer lines. The calculated patterns of Figure 6 fit well the experimental pattern for phase IV (Figure 1B) as far as the positions and intensity of the peaks and the shape of the halos are concerned; the broadness of the calculated peaks is instead an artifact due to the small size of the bundles considered.

Bundles of helices presenting randomly oriented domains, characterized by ordered angular arrangements of the helices, were also investigated. These models are, however, unsuitable, since, in order to destroy the sharp reflections on the second layer line, it is necessary to reach very small domain sizes (~10 helices), resulting in too broad reflections also on the seventh and eighth layer lines.

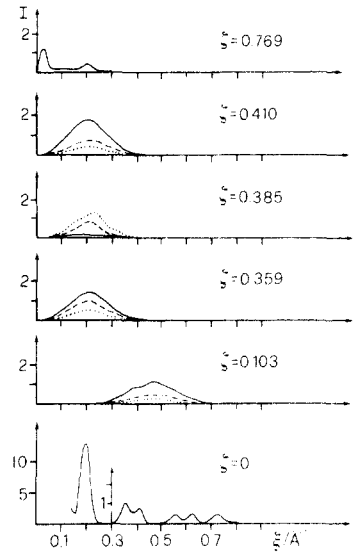

Figure 7. Results of the calculations of Fourier transforms, at the indicated ζ (Å^{-1}), on the models having the CF_2 units of different chains at the same height, after the introduction of random rotational disorder and reversals of the helical hand: (—) *no reversal of the helical hand*; (- - -) *one reversal of the helical hand on average every 20 carbon atoms*; (···) one reversal of the helical hand on average every 10 carbon atoms.

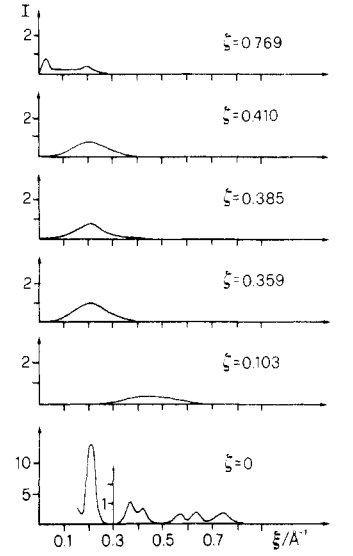

Figure 8. Calculated intensities, at the indicated ζ (Å^{-1}), on a model having the CF_2 units of different helices nearly at the same heights (small displacements in the range −0.25 to +0.25 Å are allowed) with a random rotational disorder and one reversal of the helical hand on average every 20 carbon atoms.

In summary the comparison between the diffraction profiles of phase IV and the calculated Fourier transform of the models indicates the presence of small angular displacement about the long axis, in an unspecified ordered structure, containing rows of like-handed helices.

Phase I

Up to now we considered only intermolecular disorders, which do not change the conformation of the molecules; consequently the transform remains prevailingly confined to the layer lines.

For phase I, due to the presence of a continuous diffraction intensity in the region between the seventh and eighth layer lines, some intramolecular disorder has to be invoked.[5]

The transforms of a model, with random rotational disorder, presenting no reversal or one reversal of the helical hand on average every 20 and 10 carbon atoms, are reported in Figure 7. The transform is also reported for $\zeta = 0.385$ Å^{-1}, a section intermediate between the seventh and eighth layer lines. As already shown in ref 5 for an isolated chain, the presence of helical reversals produces a collapse between the seventh and eighth layer lines. The maintenance of the Bragg reflections on the 15th layer line is related to the translational order along *c* while the absence of them in other layer lines is related to the rotational disorder about the long axis.

The slight reduction of the intensities of the reflections on the 15th layer line (compare Figure 1 and Figure 2) can be accounted for by small translational displacements around the average values (Figure 8).

At higher temperatures, also this residual translational order would be lost, as pointed out by the gradual disappearance of the sharp peaks on the 15th layer line.[12]

The presence of the relevant diffracted intensity at $\zeta = 0.385$ Å^{-1} even for a small amount of helix reversals (e.g., one reversal every 20 carbon atoms, as shown in Figure 7) suggests that this disorder is not present in phase IV.

Conclusions

On the basis of the literature analysis and of the present Fourier transform calculations, some general conclusions on the kinds of disorder which are present in the disordered phases of PTFE are drawn.

A long-range order in the periodic placement of the chain axes (~250 Å) is present both in phase IV and in phase I.

A short-range order (<50 Å) consisting of the positioning of the fluorine atoms of neighboring helices nearly at the same height is present both for phase IV and phase I. However, for phase I, small translational displacements along *c*, around the average values, would be allowed at low temperatures. Any residual translational order would be lost at higher temperatures.

Small angular displacements along *c* of the helices with respect to an ordered structure would be present in phase IV while a completely random angular arrangement is present in phase I.

Helix reversals, or analogous intramolecular defects, are substantially absent in phase IV but would be present in phase I. As a consequence, while rows of like-handed helices would be present in phase IV, such rows are absent in phase I.

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