# Electron microscopy observations of a nematic polyester

G. MAZELET, M. KLÉMAN
*Laboratoire de Physique des Solides (associé au CNRS), Université de Paris-Sud, Bât 510 91450 Orsay, France*

We report electron microscope observations of thin films of a polyester prepared in the nematic phase and quenched or slowly cooled. At low voltage (75 keV) the sample suffers large irradiation damage and becomes amorphous in a few seconds. However one observes the remnants of a striped structure. At high voltage (2000 keV) and low beam intensity the nematic structure is conserved long enough, and we demonstrate, by using standard dark field techniques, that the stripes consist of alternating disordered and aligned polymeric chains perpendicular to the striped structure. The repeat distance is of the order of a polymer length. We have also observed a filamentary growth of a low temperature hexagonal phase which has not yet been reported.

## 1. Introduction

We have previously reported [1–8] optical observations of defects in a polyester nematic phase. These observations mainly involved the predominance of $S = \frac{1}{2}$ and $S = -\frac{1}{2}$ lines [1], and the core structure of those lines [2–8], as far as they can be gathered at optical scales. We proposed different core models for the $S = +\frac{1}{2}$ and the $S = -\frac{1}{2}$, which implied new types of molecular arrangements.

Optical microscope resolution is of the order of 1 μm. In order to obtain smaller scale observations, we decided to turn to electron microscopy. The very thin samples (~ 100 nm) prepared specifically for this purpose did not show up defects (we were, therefore, disappointed in our research for a better understanding of the core molecular arrangements), but we were able to make another fascinating observation, bearing on the local molecular arrangement in a thin sample and on the crystallization process at temperatures below the nematic phase.

A few electron microscopy observations of nematic polymers have already been made. They bear on various types of copolyesters, and show up alternating band structure in samples obtained either after shearing in order to obtain a thin film suitable for TEM (Donald *et al.* [2–8]) or after thermal quenching by dropping crumbs of the polymer onto hot phosphoric acid in order to freeze the structure in the liquid crystalline state [9]. The typical width of these bands, which are better observed in dark field microscopy by using the strong equatorial scattering, is of the order of 0.5 μm. The molecular chains are in the plane of the specimen in both cases. The geometry changes by annealing the samples: (a) it turns towards a three-dimensional banded texture with competition between homeotropic alignment and splay in the Donald *et al.* experiments; (b) the polyesters of Thomas *et al.* crystallize under anneal, and one observes the growth of

lamellae perpendicular to the overall molecular direction, which decorate the bands; this decoration is very visible in bright-field microscopy.

Our results differ quite markedly from those, and therefore enlarge the number of already described molecular arrangements at submacroscopic scale. In particular, we obtain an equilibrium stripe ("smectic") structure of the nematic phase, which is probably typical of very thin films (or of surface arrangements of bulk specimens?) with a repeat distance of the order of the polymer length and we also observe growth filaments of a crystalline (hexagonal) phase of the stripe structure of a type unknown up to now, as far as we know. The stripe structure resembles the lamellae of Thomas *et al.*, but is obtained in completely different circumstances. This paper does not intend to solve all the problems raised by these observations, but only to increase their interest and novelty to material scientists.

## 2. Experimental method
### 2.1. Sample preparation
The compound we have observed has the following chemical composition:

$$CH_3CO~[O-\langle\overline{O}\rangle COO-\langle\overline{O}\rangle OCO-(CH_2)_5-CO]_x-OH$$
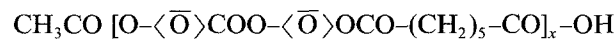
with $x \simeq 24$. Some preliminary observations of this compound were reported in [10].

The samples were prepared by spreading hot polymer in the nematic phase (180° C) on freshly cleaved KCl crystals. The sample and its substrate are then annealed for several hours at 180° C or not annealed at all. It is then more or less rapidly cooled. We shall call "unfrozen" samples those which are quenched at room temperature, and "frozen" those which are quenched in −30° C ethanol; finally other samples were cooled very slowly (0.2° C min⁻¹) to room temperature. The samples are then carbon coated, the
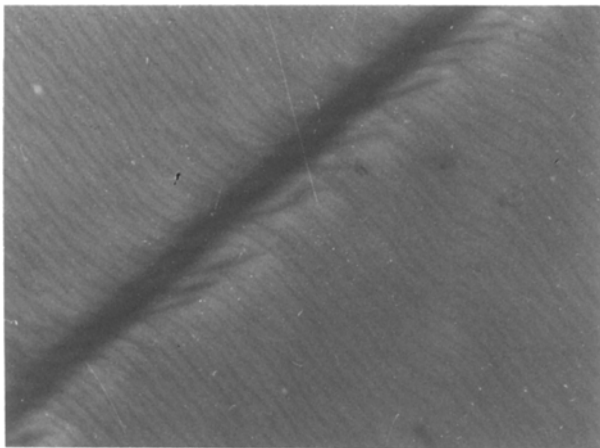
*Figure 1* 75 keV bright field picture. The sample has been annealed for 8 h at 180°C and we observe a fully irradiated ordered region.

substrate is dissolved in water, and the polymer picked up on a copper grid.

## 2.2. Electron microscopy
We used two types of microscopes. Our first observations were made with a HV 11 Hitachi microscope with a 75 kV accelerating voltage. The following observations were made with a 2000 kV accelerating voltage on a very high voltage microscope, in the "Laboratoire d'Optique Electronique" in Toulouse.

## 3. Observations
### 3.1. Preliminary observations
Some preliminary observations were made with the 75 kV Hitachi microscope, which belongs to an old generation and has very few automatisms; a good beam alignment is quite hard to achieve and the electron beam intensity is high. The samples were almost immediately fully irradiated: the lifetime of a sample is about two seconds; during this period of time, the diffraction pattern turns from nematic-like to amorphous-like.

The corresponding observed textures were visible only in bright field observations. They are made of very regular stripes, with period of about 40 nm (Fig. 1). These textures appear on the screen only after a few seconds, when the sample is fully irradiated. They are visible in annealed samples as well as in non-annealed ones; they show however a better con-
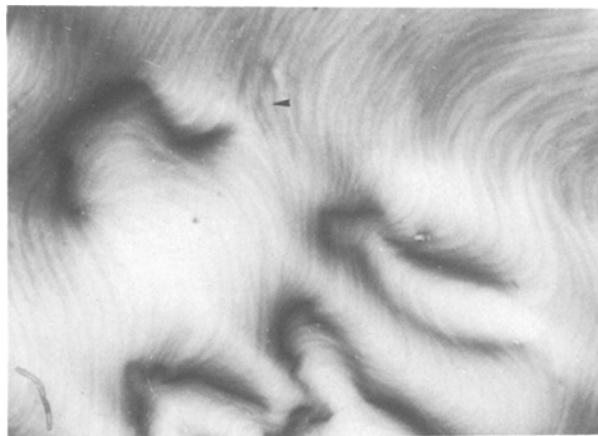


*Figure 2* Same samples as in Fig. 1. $\pm \frac{1}{2}$ disclinations are visible.

trast when the sample has been annealed. Unoriented regions are also visible in which the striped structure shows disclinations (Fig. 2).

### 3.2. High-voltage observations
The high voltage microscope is equipped with an image intensifier and very sensitive films. We were able to work with a very weak electron beam and the life time of the sample, before amorphization, was about ten minutes at room temperature. We observed different types of samples.

### 3.3. Annealed and unfrozen samples
We can observe two types of diffraction patterns. One of them shows two equatorial arcs at 0.425 nm and two others at 0.245 nm. Quite diffuse meridian arcs are visible at 0.205 nm as well as two very sharp spots at 0.66 nm (Fig. 3a); they are a third order of the mesogenic pattern (1.971 nm) shown by X-ray diffraction [10]. The equatorial arcs are more or less wide; they can be reduced to very intense spots. The 0.245 nm spots are then no longer visible, but we can see high orders of the 0.425 nm spots (Fig. 3b).

The equatorial dark fields made on the 0.425 nm spots show a striped contrast, perpendicular to the average molecular direction (Fig. 4). This contrast vanishes gradually as the sample is being irradiated. The periodicity of the stripe structure is between 30 nm and 70 nm in different regions of the sample. In some places, in addition to the striped contrast one can observe very bright spangles in the prolongation of the bright stripes, which are aligned one with another. Bright fields in non-irradiated samples show no striped contrast.

### 3.4 Annealed and frozen samples
Quenching the sample in −30°C ethanol allows to freeze the nematic structure, and avoids crystallization.

Indeed, the diffraction patterns show mainly two 0.425 nm equatorial arcs and higher order reflections are not visible, the 0.66 nm meridian spots are much weaker and the 0.205 nm meridian arcs are still visible (Fig. 5).

Equatorial dark field show the same stripe texture than in unfrozen samples, but no bright spangles are visible (Fig. 6).

We also made two dark field pictures on the two halves of the equatorial arc and we observed no contrast inversion.

### 3.5. Unannealed and unfrozen samples
The samples are quenched at room temperature immediately after having been spread. The diffraction patterns are very sharp, the 0.425 nm equatorial spots are very bright, and visible up to the third order. The 0.66 nm meridian spots are very bright, and 0.205 nm meridian arcs are much sharper than in other samples (Fig. 7).

Equatorial dark fields show a striped contrast but it is not as neat as in annealed samples, and the stripes are sometimes hardly visible. However, a lot of very well aligned bright spangles are visible. They are about 200 nm long and between 30 and 50 nm wide (Fig. 8).
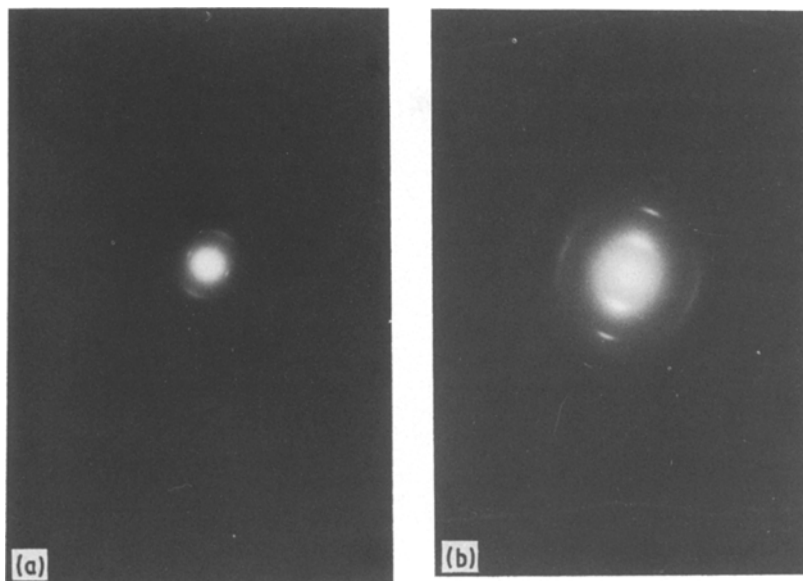
## 3.6. Unannealed and frozen samples

These samples show very poor diffraction patterns. Only the 0.425 nm equatorial arcs and the 0.205 nm meridian arcs are visible.

Equatorial dark fields show that the samples have been quite damaged and the contrast is very poor.

## 3.7. Slowly cooled samples

These samples have two types of regions, some of them are quite similar to unfrozen samples: stripes and spangles. Other regions show hexagonal diffraction patterns; the distance between reticular planes is 0.425 nm (Fig. 9). Dark field pictures show a weak striped contrast and bright filaments with no special orientation (Fig. 10).

## 4. Discussion
### 4.1. Diffraction patterns
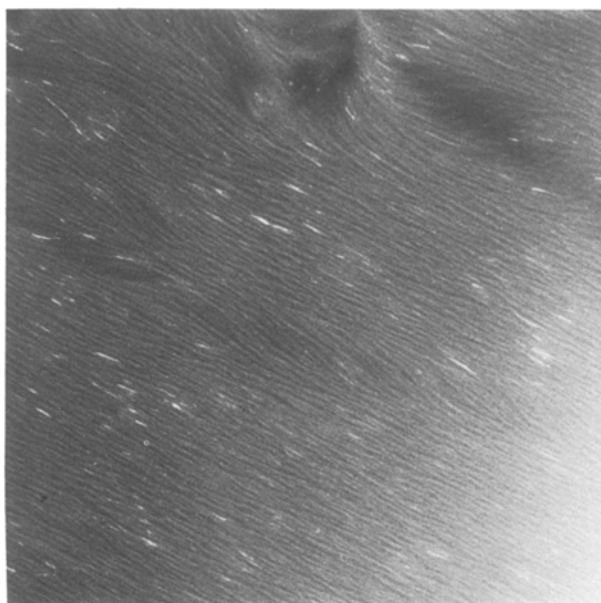
Diffraction patterns give information on the structure of the nematic phase. Equatorial reflections are related to the interchain correlations while meridian reflections are related to the intrachain correlations.

Diffraction patterns of unfrozen or slowly cooled samples give information on the crystalline state of the polymer at room temperature. With such long molecules, hexagonal patterns can only be linked to a homeotropic configuration (i.e. the average axis of the macromolecules is perpendicular to the preparation). Cooling seems to favour homeotropy but it needs to be slow enough so that the homeotropic configuration has time to emerge from the planar configuration forced when the material is spread on KCl.

The crystalline phases in slowly cooled and unfrozen samples are certainly the same; they show the same distances. Unfrozen samples show fibre diagrams of a planar configuration, the arrangement in a plane perpendicular to the fibre axis is then, hexagonal (Fig. 11). The pattern in Fig. 3 shows spots corresponding to $(\bar{1}\,1\,0\,0)$, $(0\,1\,\bar{1}\,0)$, $(\bar{1}\,0\,1\,0)$ planes at 0.425 nm and



*Figure 4* Unfrozen and annealed sample. 2000 KeV equatorial dark field. The striped contrast is perpendicular to the average molecular direction; some bright spangles are visible.
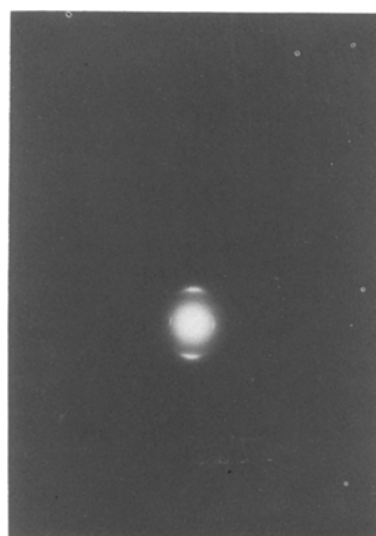


*Figure 5* Annealed and frozen sample. 2000 KeV diffraction pattern. Only 0.425 nm equatorial arcs are visible and the 0.66 nm spots are weak.
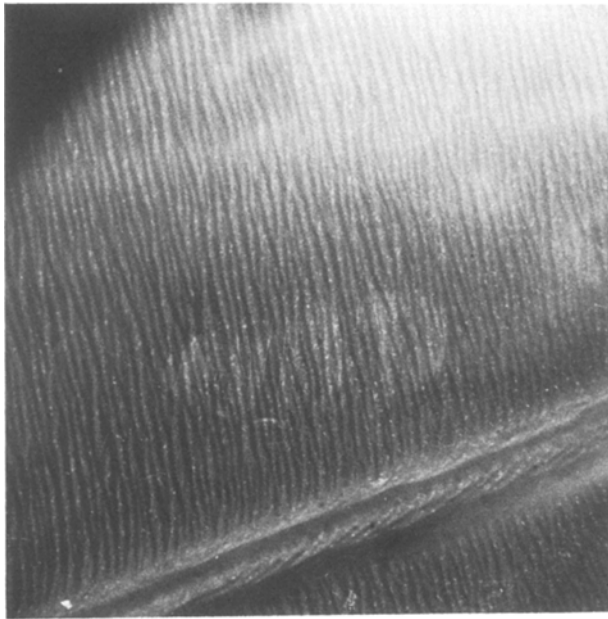
*Figure 6* Annealed and frozen sample. 2000 KeV equatorial dark field. Same striped texture as for unfrozen samples but no spangles are visible.
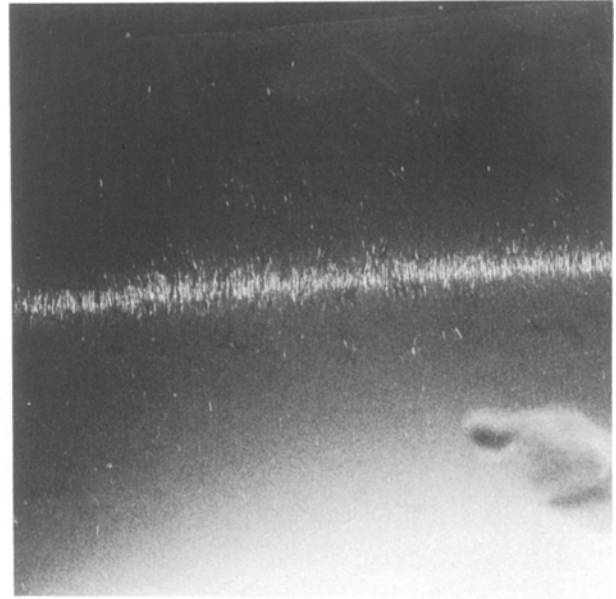


*Figure 8* Unannealed and unfrozen sample. 2000 KeV equatorial dark field; alignment of crystallites.

$(\bar{2}\,1\,1\,0)$, $(1\,\bar{2}\,1\,0)$, $(1\,1\,\bar{2}\,0)$ planes at 0.245 nm. If those two types of reflections are visible in planar samples with very small diffraction angles (10 mrad), these two types of planes have to be aligned with the electron beam. The beam passes through regions with those two different orientations.

Unlike Donald and Thomas, we observe no sign of biaxiality. The most convincing argument for uni-axiality of our polyester is the occurrence of an hexagonal crystalline phase. Liebert *et al.* [10] report on the existence of a quasi-hexagonal (hence biaxial phase) in bulk frozen samples. We do not confirm this observation in our thin samples.

## 4.2. Dark field observations: bright and dark stripes

The striped contrast is equatorial dark fields comes from alternating layers of diffracting (bright stripes) and non-diffracting (dark stripes). The very bright spangles correspond to crystallite of hexagonal phase.

It is clear that the bright, diffracting, stripes are made of organized molecules elongated in the plane of the sample, perpendicularly to the layers. However, the interpretation of the dark, non-diffracting, stripes, is more delicate. There are two possibilities: either they are not organized (amorphous), or they are organized and their diffraction spots have not been selected by the dark field aperture diaphragm. We exclude the last hypothesis for the following reasons.

Let us suppose that the dark stripes are organized; the molecules can stay in the plane of the sample, or they can be in the third dimension. If they were in the plane of the sample, we would see some widening or the diffraction spots in the form of arcs and this is indeed what we observe. This configuration should correspond to a serpentine trajectory of the macro-molecules and a fluctuation of the director. However, in such a case we should also observe a contrast
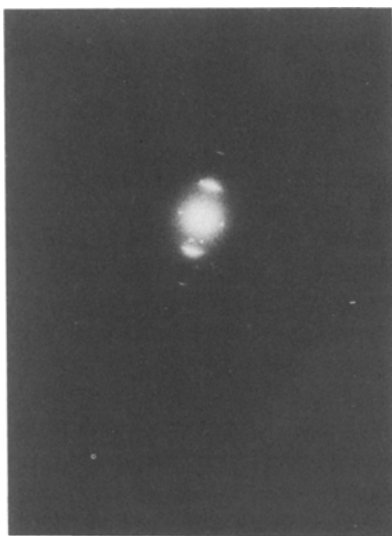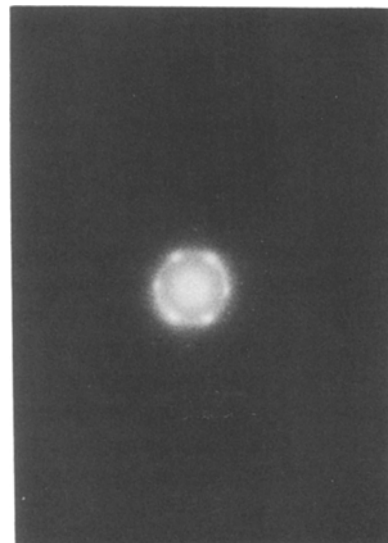


*Figure 7* Unannealed and unfrozen sample. 2000 KeV diffraction pattern. Very sharp 0.425 nm equatorial spots are visible up to the third order, 0.66 nm meridian spots are very bright and 0.205 nm meridian arcs are sharper than in other samples.



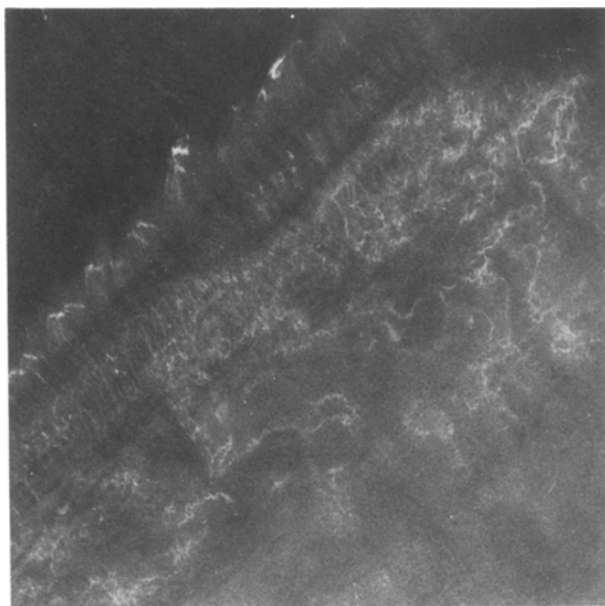*Figure 9* Slowly cooled sample. 2000 KeV hexagonal diffraction pattern. A second order is slightly visible.

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Figure 10 Slowly cooled sample. 2000 KeV dark field on an hexagonal diffraction spot. Filamentary regions.



Figure 11 Hexagonal arrangement of crystallized macromolecules, in a plane perpendicular to their long axis.

0.425 nm

0.245 nm

inversion in dark field pictures taken from two opposite halves of the equatorial arc; this is never observed. Consider now that the macromolecules stand out of the plane of the sample; from the diffraction point of view, this configuration would give similar results as for the planar configuration. The non-planar layers would also diffract in the same equatorial spot as the planar layers, and they would show bright stripes in equatorial dark fields, but this is not observed either. We therefore, conclude that the dark stripes are amorphous.

### 4.3. Alternating ordered and amorphous stripes

The configuration that we have just described does not occur immediately; it needs some annealing and is, therefore, most probably an equilibrium state of the molecules in thin films [7]. In the bright, organized, stripes, two types of chain configurations are possible: in one model, the chain can fold in hair pins and cross several times the same layer; in another model, the chains remain in extension (Fig. 12). These models were proposed by Thomas [9]. We prefer the second
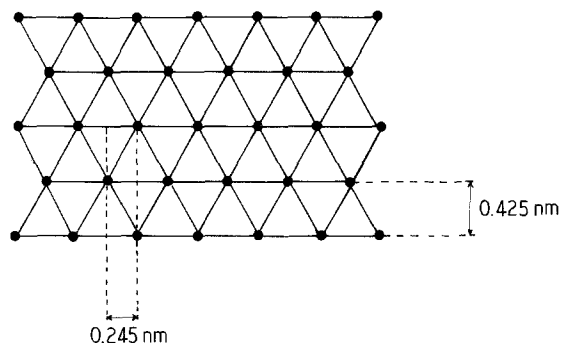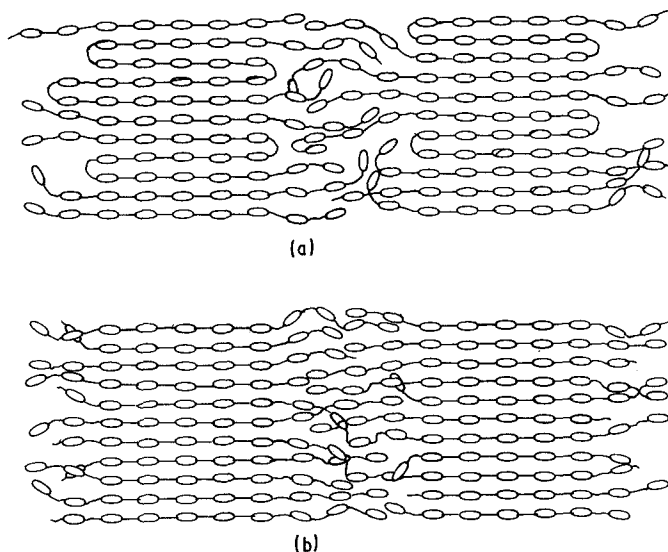
model; the first one would require the macromolecules to be very flexible which is not our case. Also (and this argument is convincing by itself alone) the length of a molecule is not larger than about 50 nm, even if its length be doubled by hydrogen bonds between two molecular ends. One chain can be present in two successive organized stripes. The type of organization in these stripes is of the nematic type.

### 4.4. Hexagonal phase

Now consider the hexagonal crystallites. Their presence raises quite new and interesting problems. They are always aligned in the molecular direction and seem to be confined to the higher temperature nematic organized stripes. However, the crystallinity is transmitted through the molecule from one layer to another by the mean of elastic strains. It seems moreover that it is not only the crystallinity, but also the hexagonal pattern and its orientation, which are transmitted through an amorphous layer. In homeotropic samples, the beam goes through a large number of layers and yet the hexagonal diffraction pattern is quite neat. There is very little disorientation of the hexagonal arrangement through the whole thickness of the sample. We can wonder whether elastic strains through an amorphous layer can lead to such a result or if some other phenomenon need to be involved, such as an imposed orientation transmitted from the KCl surface inside an organized layer.

The filamentary dark field pictures of an homeotropic sample suggest some kind of random lateral crystallization process, but we have no further information.



(a)



(b)

Figure 12 Two possible arrangements in ordered and amorphous stripes: (a) bent molecules (b) stretched molecules (after Thomas; [9]).
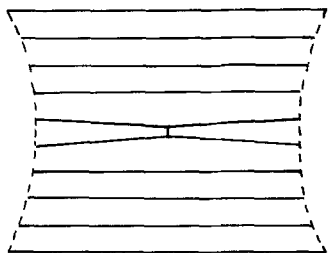
*Figure 13* Loss of thickness in a crystalline after a cross-link.

## 4.5. Bright field observations; irradiation

The contrast in bright field observation appears only after strong irradiation in the sample. This phenomenon has often been observed in polymers and is explained in [5]. The contrast is then an artifact resulting from radiation damage. In our polymer, radiation damage leads to the amorphization of the organized layers (as visible on diffraction patterns) and results from the creation of numerous cross links.

Electronic irradiation creates cross links between macromolecules, in ordered layers as well as in amorphous layers. This amorphization induces variations in the size of the ordered layer. A cross link in a perfect crystal diminishes its thickness (Fig. 13). This must be made up by dilation in another direction (for example, perpendicularly to the film). The observed contrast is then an absorption contrast resulting from a succession of thin layers (those that were amorphous) and thick layers (those that were ordered) (Fig. 14). This decoration method gives a permanent image of the configuration of the sample even in quite disordered regions.

## 5. Conclusion

Our observations did not allow us to reach our first aim: finer observation of core regions; however we obtained a lot of information on the microscopic arrangement of the macromolecules.

This succession of amorphous and ordered layers has already been observed by Thomas, but not by Donald; this behaviour is therefore not general for all nematic polymers. A possibility is that it depends on the flexible spacer: the polymer used by Thomas and us had flexible spacers while that used by Donald did not.

Our work raises several questions and a lot of investigations have to be done on this topic. The influence of parameters such as annealing temperature and annealing time has to be studied. As far as we know, it is the first time that high voltage microscopy is used to observe nematic polymers, and this method seems very promising and complementary with conventional electron microscopy.

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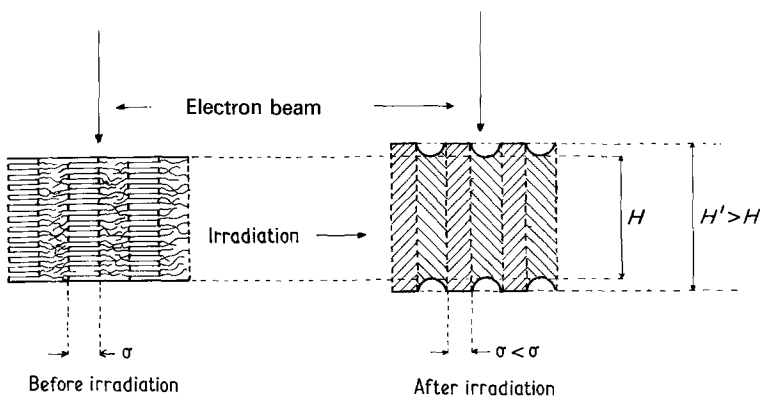11. D. T. GRUBBS, *J. Mater. Sci.* **9** (1974) 1715–1736.

*Figure 14* Absorption contrast after the amorphization of organized stripes during electron beam irradiation.