Crystallographic and Structural Roots of Variation in Polymer Morphology [and Discussion]

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Crystallographic and structural roots of variation in polymer morphology†

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Present molecular understanding of the morphology of lamellar polymer crystals is briefly reviewed. The impact of crystal and fold structure (as opposed to molecular characteristics) is stressed. Investigation and decoration techniques giving access to local crystal and fold features are considered.

1. Introduction

Elucidation of the many facets of polymer morphology is both complicated and aided by the availability of a variety of crystallizable polymers with different chain conformation, helical structure, often crystal modifications, etc. Investigation of linear polymers, structurally and chemically 'featureless' such as polyethylene (PE) and polytetrafluoroethylene (PTFE) helps determine the major morphological and structural features linked with the long chain character of polymers. In this respect, it is fitting that chain folding was convincingly demonstrated with polyethylene single crystals, and that more elaborate forms of chain folding were demonstrated with short polyethylene oxide (Buckley & Kovacs 1984) and paraffin models: integral folding and, more recently, impact of non-integral folding and structural reorganization of lamellar crystals (Barham & Keller 1989; Rastogi *et al.* 1991). Conversely, observation of complicated or unusual morphologies in such systems (e.g. lamellar twist) may raise challenging problems of interpretation, in the absence of definite structural features.

Chemical 'tagging' of polymer chains may add further constraints, as illustrated by quantized folding and unfolding of polyamides (Dreyfuss *et al.* 1972). In a different register, side chains in polyolefins impose helical conformations (defined here, for simplicity, as different from strict or nearly *trans–trans* conformation, as in PE and PTFE). In such systems, stringent rules govern packing of right- and left-handed helices, or limit possible folds between helical stems depending on their handedness (Petraccone *et al.* 1986). Contrary to PE, crystallographic, lamellar and spatial organization of these systems may have to take into account the organization of helical paths of the side chains, which introduces a new challenge when it comes to relating morphological features and helical hand.

The present article reviews several topics in polymer science for which the crystallographic or structural roots of specific morphologies could be traced down,

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and attempts to illustrate the use of various techniques which make it possible to gain molecular level insights into polymer morphology and structure. Most examples deal with PE and two helical polyolefins: polypropylene (both iso and syndiotactic) and isotactic poly(1-butene). Experimental techniques concentrate on electron microscopy, electron diffraction, and atomic force microscopy which are best suited for investigations ranging from unit cell to lamellar organization. Keeping in line with the progression along the hierarchical levels of polymer structure and morphology used in this meeting, we limit ourselves to the impact of fold and crystal structure on the morphology of individual lamellae.

2. Folds and lamellar morphology

(*a*) *Fold orientation*

Early observations and analyses have associated the sectorization of lamellae with existence of the folds, and change of their average orientation in the different growth sectors. Difficulties associated with the investigation of a thin (*ca.* 20 Å), poorly organized layer of amorphous material have precluded local analysis of fold orientation, and therefore correlation between fold structure and morphology or physical properties.

Development of the polymer decoration technique (Wittmann & Lotz 1985) which rests on condensation and crystallization of polymer vapours (notably of PE) has made such local analyses possible. The PE vapours crystallize in the form of elongated rods which are small PE lamellae standing edge on (figure 1). The orientation of rods is nearly at right angles to the fold direction, and differences of organization (density, pattern of rods, …) may give a qualitative indication on variations in fold structure, as illustrated here by the transition from ‘paraffinic’ to ‘polymeric’ lamellar morphology in cyclic alcanes, and the impact of fold structure on lamellar twist.

Ihn *et al.* (1990) have examined cyclic $(CH_2)_{60}$ and $(CH_2)_{120}$. The former crystallizes in the form of rectangular crystals, the latter as ‘conventional’ lozenge shaped PE crystals. Polymer decoration reveals that fold orientation switches from an orientation parallel to the *b*-axis (short edge of the rectangular crystals) characteristic of short cyclic paraffins, to the conventional [1 1 0] orientation for tight folds in PE crystals.

Twisting of lamellae in spherulites is well known for several polymers (polyethylene, polyamides, polyesters, etc.). Its structural origin has eluded analysis for many years, but recent progress in observation of internal structure of polymer spherulites by etching techniques has provided new insights (Bassett 1988). At present, two views, which rest on the same lamellar anisotropy and are actually complementary, have received significant experimental support. As developed in his contribution, Pr. Bassett emphasizes the splaying of lamellae at screw dislocations and points out that the sense of splaying is determined by the direction of chain tilt in the lamellar crystal. Keith & Padden (1984) stress a possible intralamellar origin and suggest that, due to this same chain tilt the fold structure is different on opposite surfaces of a lamellar crystal. Different stresses are created on the surface, and therefore generate a bending moment (longitudinal relative to spherulite radius). Since a lamellar crystal is built of two symmetric halves, opposite bending moments are partly relieved by overall twist of the whole lamella.

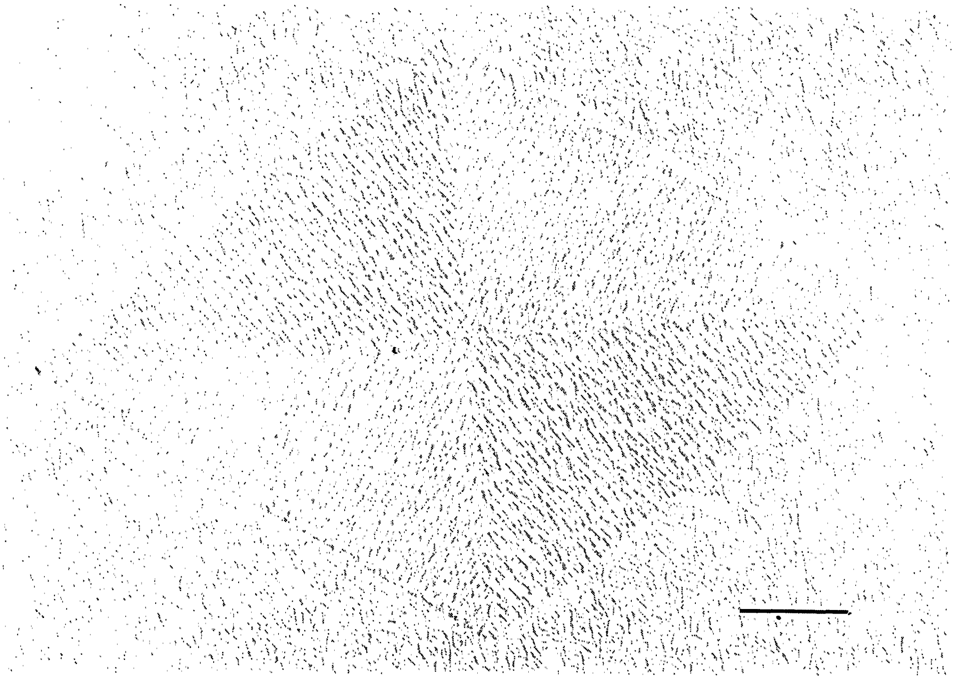

Figure 1. Solution grown polyethylene single crystal decorated with polyethylene vapours. On condensation, these vapours produce crystalline rods which are oriented at random on the glass substrate (background) but are oriented by the folds in the different growth sectors of the lozenge-shaped polyethylene single crystals. Scale bar: 1 μm. (After Wittmann & Lotz 1985.)

This scheme rests on two assumptions: fold structure differences and bending of lamellar halves if split along the axis of growth.

Both hypotheses could be checked in later work on single crystals grown in thin films at high temperatures (Keith *et al.* 1989). Under such growth conditions, some flat-on lamellae produce on one of their lateral edges offshoots which are lamellae growing edge-on. These are half-lamellae; they are always bent (radius *ca.* 5 μmm), and bending depends on growth direction: they illustrate the two crystal halves which are associated in melt-grown lamellae.

Further, for flat-on lamellae, polymer decoration shows differences in surface structure in the two lamellar halves which differ by the chain dip during growth. The nature of these differences is unknown but their existence appears to be at the root of lamellar twist in PE. The above explanation may not apply for other polymers with more complicated constitutions and structures. It illustrates, however, how development of an original surface decoration technique makes it possible to reveal small scale, local structural features and therefore reach the micromechanics of polymer lamellae.

(*b*) *Crystal transformation in poly(1-butene)*

A possible influence of fold orientation on the mechanism of crystal transformation was reported by Holland & Miller (1965). These authors investigated solution grown single crystals of polybutene-1 in its crystal form II (tetragonal unit-cell, 11_3 helices), and could follow the spontaneous transformation to form I (hexagonal unit-cell, 3_1 helices). They report that the orientation of form I is sector-dependent, i.e. the initial square crystal yields two orientations of form I at right angles, in 'twin' relationship, the various components being limited by the initial crystal sector boundaries. This would be a highly original example where fold structure influences the lamellar core crystal transformation.

We have recently reinvestigated this transformation, using the methods and techniques of Holland & Miller, but with quite opposite results (Kopp *et al.* 1994). Indeed, whole square crystals of form II sometimes display after transformation, a unique orientation of form I. Further, dark field imaging shows elongated domains parallel to one diagonal of the crystal, rather than its growth faces. Analysis of the transformation mechanism confirms that it is governed by the crystal structures of form II and form I: since the two structures are made of alternating layers of right- and left-handed helices, transformation progresses along these planes, according to a scheme first proposed by Fujiwara (1985). The resulting lateral shrinkage induces cracks parallel to these planes; fold orientation which was shown in the two prior examples to affect lamellar morphology during its build-up, appears to be of secondary importance in the transformation of a 'developed' lamella. Conversely, this crystal transformation illustrates, in an expanded timescale, possible mechanisms taking place when crystallization involves formation of a 'transient' crystal phase before conversion into the stable form, as illustrated by hexagonal and orthohombic phases of PE (Di Corleto & Bassett 1990).

3. Crystal structure and lamellar organization of tactic polypropylenes

Isotactic (iPP) and syndiotactic (sPP) polypropylenes have provided in recent years a wealth of information on mutual organization of right- and left-handed helices. Although the detailed molecular structure of the β form of iPP is not known (hexagonal unit cell, 3_1 helical conformation), the crystal structure and spherulite morphology of the α and γ phases are highly dependent on packing and stacking of helices of different hand, whereas a 'smectic' form produced at very low T_c is probably characterized by more or less statistical packing of helices of both hands (Brückner *et al.* 1991).

The β form of iPP produces 'conventional' spherulites with radial, sometimes twisting lamellae. α form crystals are always elongated laths. In both solution and bulk crystallization, the α form produces a highly original structure, described as 'cross hatched', in which lamellae give rise to daughter lamellae at an angle of *ca.* 80°. In bulk, the impact of this branching is maximum at *ca.* 135 °C, i.e. in the conventional crystallization range, but decreases to nearly zero at very high crystallization temperatures (*ca.* 150 °C). Coexistence in different proportions of radial and tangential chains within the spherulite results in unusual optical properties (overall positive, or mixed, or negative birefringence depending on T_c) (Padden & Keith 1959).

The origin of this behaviour has been traced down to a case of homoepitaxy (Lotz & Wittmann 1986), or of rotation twin, as first mentioned by Khoury (1966) in his pionneering work. The lateral faces of α phase iPP are alternately made of all right- and of all left-handed helices. The pattern of exposed methyl groups (alternately two and one per unit cell) is highly symmetrical: when two successive methyl groups along the chain are exposed, they are aligned along ⟨1 0 1⟩, or the short diagonal of the lozenge-shaped, exposed lateral (0 1 0) plane of the unit cell. This diagonal therefore corresponds to the outside helical path. When one methyl side chain only is exposed, a lozenge pattern of methyl groups, *ca.* 6.5 Å apart, is created.

The physical origin of the epitaxy or rotation twin is best understood when considering faces with two methyl groups. The rows of methyl groups build up a grating (of spacing *ca.* 5 Å) tilted at a significant angle (50°) to the helix axis: this angle is actually the so-called pitch angle of the helix. In the normal crystal structure, interactions between consecutive layers involve helices of opposite hand related by a glide plane, which ensures interdigitation of the two parallel gratings, and maintains parallelism of helix axes. If, however, helices of the next layer are of the same hand as the substrate ones, parallelism of the two gratings can only be achieved if chain axes are at an angle equal to twice the pitch angle. This situation is formally described as a rotation twin, with the twin axis parallel to the grating direction – in the present case ⟨1 0 1⟩, i.e. the bisector of the monoclinic angle β of the unit cell.

Later work on the γ phase of iPP showed, however, that lamellar branching in α iPP rests actually on interdigitation of lozenge patterns of single methyl groups. The γ phase is a minor phase which exists in crystallographic association with the α phase: it grows epitaxially on the lateral (0 1 0) α faces involved in lamellar branching (Padden & Keith 1973). Brückner & Meille (1989) proposed for this structure a highly innovative cell in which bilayers of polymer chains with non-parallel axes coexist. The structure is best described as a systematization of the lamellar branching pattern described for the α phase: in particular, the rotation twin axis becomes in the present unit cell a conventional element of symmetry (2_1 axis). Brückner & Meille also showed that out of two possible structural models, only the one in which chain axis rotation is achieved via the face with one methyl group fits best the X-ray intensity data.

This highly innovative structure has been further investigated by single crystal electron diffraction, which confirms that it lacks a 'fibre' pattern as in conventional polymer crystal structures (Lotz *et al.* 1991). The morphology differs significantly from the α phase one. Fastest growth direction is at right angles to the α phase, along the c-axis: chain deposition appear to take place mainly on the end, 'flat' surface, rather than on the indented, lateral faces. High molecular mass iPP in γ phase in particular grows in the form of elongated filaments (figure 2).

The folding pattern is most certainly original, as it must reconcile constraints on helical hand and geometrical constraints linked with the different chain orientations. It must be noted that γ phase formation is favoured when these constraints are relaxed, e.g. for very low molecular mass and when ethylene comonomers are included in the iPP.

The α and γ phases of iPP provide an extreme case of interrelationship between crystal structure and lamellar morphology. The latter is so informative that it helps characterize not only the crystal phase (α or γ) but also the organization of building helices. As best shown on epitaxially crystallized films (figure 3), α lamellae are characterized by their *ca.* 80° (or 100°) branching and γ phase by their *ca.* 40° branching to the parent α phase lamella. This γ phase orientation parallel to the bisector of the two α phase lamellar orientation stems from the coexistence of two chain orientations to which the fold surface must be symmet-

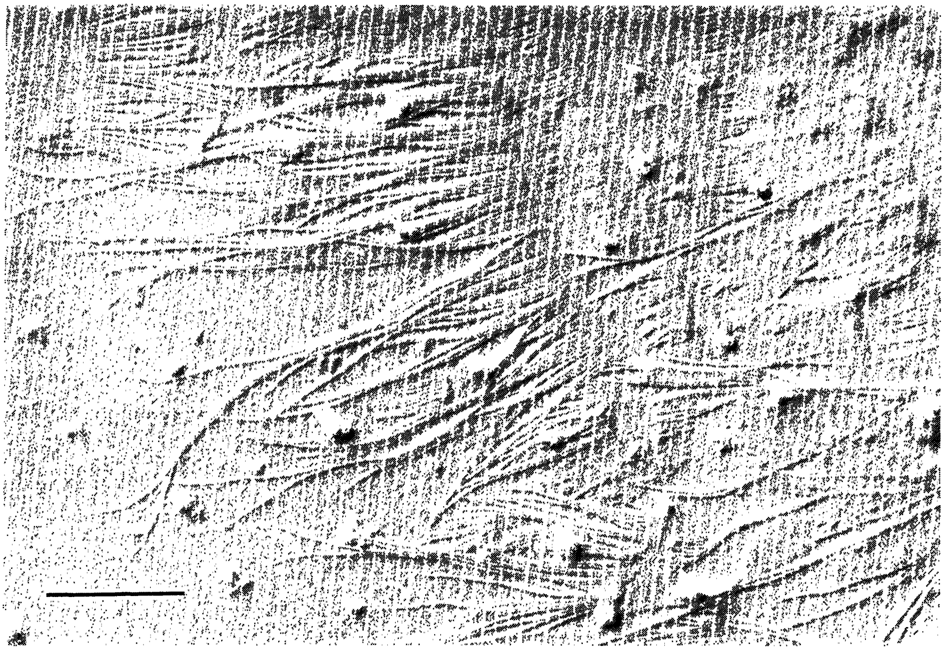

Figure 2. Thin, filamentous crystals of γ-iPP (oriented at 8 and 9 o'clock on the left-hand side of the figure) nucleated on the lateral edges of mostly buried α phase laths (oriented at 11 o'clock): faster growth rates are at right angles in the two phases in spite of similar structure of constituting layers. (After Stocker *et al.* 1993.) Scale bar: 1 μm.

rically related (Meille *et al.* 1990). Further, the α phase or γ phase branches are morphological indicators which materialize the a and $\langle 1\,0\,1 \rangle$ crystallographic direction of parent α crystals. It is thus possible to determine the helical hand and azimuthal setting of all chains (Lotz *et al.* 1991) in the composite crystalline entity, with the sole exception of the exposed layer, to be considered later on.

Before closing this section, it is appropriate to note that since homoepitaxy introduces a different, new lamellar orientation, presence of repeated lamellar branching is a good morphological indicator of homoepitaxy, and suggests the existence of highly symmetrical contact planes. Pr. Munoz Guerra pointed out to us such a situation in solution crystallization of polyamide 3 which indeed has nearly equal a and c parameters of the unit cell. A similar situation has been observed recently, but with more limited impact, for syndiotactic polypropylene and has been linked with the existence, in the bc contact face, of rows or regular patterns of pseudo n-pentane units (Schumacher *et al.* 1994).

4. Epitaxially crystallized films and chain conformation

Whereas polymer decoration helps get insight into the fold surface structure, analysis of the crystal core structure often requires observation of lamellae 'side ways', i.e. on their edges. This is often easily achieved by epitaxial crystallization on a variety of organic and polymeric substrates: low molecular mass organic molecules (e.g. benzoic acid, polyphenyls, condensed aromatic hydrocarbons, ...),

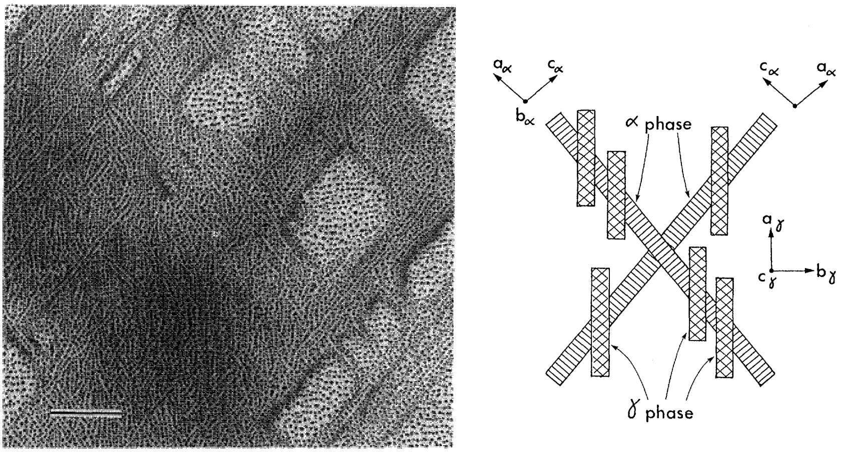

Figure 3. Thin film of isotactic polypropylene epitaxially crystallized on benzoic acid and gold decorated after removal of the substrate (left; scale bar 200 nm), and sketch of lamellar and chain orientations of α and γ phases. (After Stocker *et al.* 1993.)

oriented PTFE films produced by the friction-deposition technique of Wittmann & Smith (1991) (cf. Wittmann & Lotz 1990).

Epitaxial crystallization rests on a one- or two-dimensional lattice match between substrate and (usually) polymer interchain distance in the contact plane. Use of appropriate substrates may permit selection of different contact planes, or initiation of different crystalline forms. Epitaxially crystallized films are well adapted to get better insight into lamellar and crystal structure. They are in particular highly suited for examination of the crystal structure 'in real space' by atomic force microscopy (AFM). Our recent work in this field has concentrated on helical polymers, notably isotactic and syndiotactic (sPP) polypropylenes, with a view to gain direct insight into the contact face structure and visualize helical hand. The structure of epitaxially crystallized iPP is known in quite detail, except for the exact nature of the contact face which, from the setting of chains in the α and γ phase, can expose either one methyl group per unit cell, or two, thus reproducing the 'four' and 'five' patterns of dices. AFM of the contact face reveals the lamellar organization and demonstrates conclusively that the exposed pattern is the 'four', with a single methyl group exposed. Combined with lamellar orientation, it is again possible to determine locally, but in an indirect way, the right or left hand of helices in spite of the symmetry of the AFM pictures (Stocker *et al.* 1993).

Quite recently, we have examined the contact surface of sPP epitaxially crystallized on paraterphenyl. The sPP structure is of special interest with regards to helix chirality since different structural models have been proposed, which involve either helices of only one hand (Corradini *et al.* 1967) or an alternation of right- and left-handed helices (Lotz *et al.* 1988). Furthermore, its t_2g_2 molecular conformation is highly suitable for AFM: in the *bc* plane, due to the gg conformation, a stretch of $CH_3CH_2CH_3$ groups is exposed which is parallel to and actually highlights the (partly burried) helical path. AFM pictures with high resolution could be obtained when using a 'liquid' cell and probing the sample immersed in water. Lamellar and molecular resolution were reached together. The pictures (figure 4)

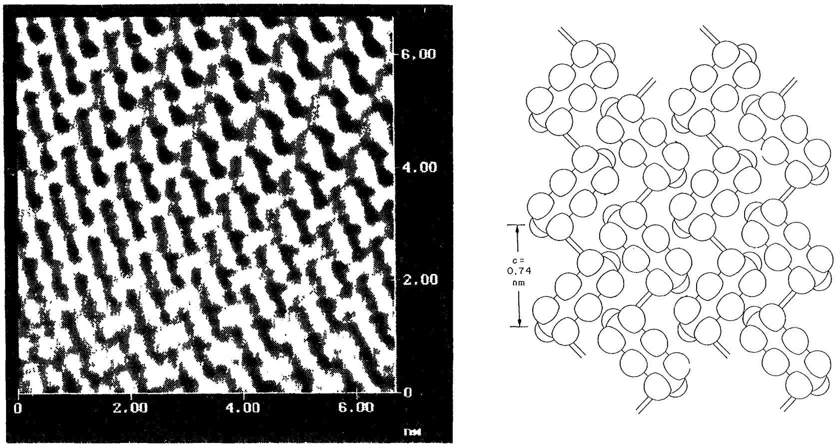

Figure 4. Fourier-filtered atomic force microscope image of the contact face of a syndiotactic polypropylene film epitaxially crystallized on paraterphenyl (left) and schematic representation of the structure of the face (right). The chain axis is oriented at one o'clock in the AFM image, which shows an area of 6.5×6.5 nm^2. (After Stocker *et al.* 1994.)

show conclusively two alternating orientations of the $CH_3CH_2CH_3$ stretches, i.e. make it possible to visualize directly the hand of individual helices, and their respective organization (Stocker *et al.* 1994). Our next objective, using these same systems, is to observe 'mistakes' in the alternation of antichiral helices which, from diffraction evidence (Lovinger *et al.* 1993; Auriemma *et al.* 1993) are known to occur, although with (probably) a low frequency – at least by AFM standards.

5. Conclusion

The morphology of crystalline polymer lamellae reveals the various constraints and requirements they have to fulfil during formation. Correlation between the latter and the former requires, however, very precise and local investigation techniques. In this respect, the crystalline core structure is easiest to investigate: by diffraction techniques, and more recently directly in real space by near field techniques: scanning tunneling and atomic force microscopy. The fold surface structure is still not directly accessible; the polymer decoration technique helped switch from global to more local analysis, i.e. at the marker's length (100 Å) range level, but not yet at the individual fold level. Within these limitations, a molecular understanding of morphological features has been reached in a variety of systems. Such correlations, established for individual lamellar crystals, appear as necessary prerequisites before tackling the more complex three dimensional lamellar organization of spherulites.

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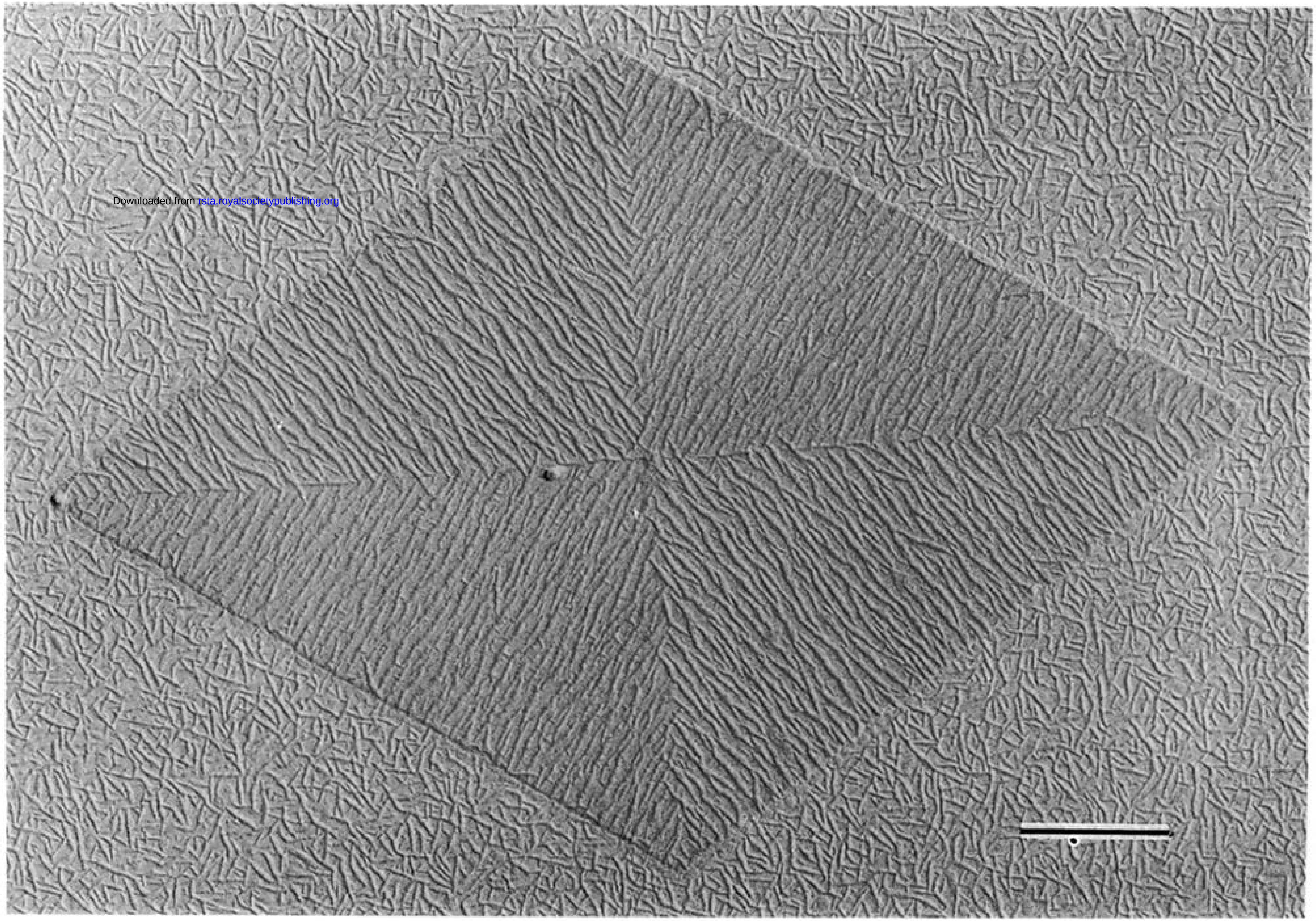
Discussion

E. L. Thomas (*MIT, Cambridge, U.S.A.*). I suggest that because you make the point that the image resolution depends on the scan direction with respect to the chain axis, you include micrographs of the same area taken with different scan directions.

B. Lotz. We have no pictures of the same area taken with different scan directions. Achieving this level of resolution is not trivial matter and, having found the right imaging conditions, we prefered in that experiment to explore other areas of the sample in a search of helix chirality-related structural defects.

E. D. T. Atkins (*University of Bristol, U.K.*). You state that the silk crystals observed by electron microscopy were always twisted. What is the reason for this?

B. Lotz. The origin of the twist lies in the chirality of L-alanine and L-serine residues which alternate with achiral glycine residues to built up the crystalline portion of silk fibroin. As developed in more detail in the original publication (*J. mol. Biol.*, **156**, 345 (1992)), due to the asymmetry of the peptide group conformational map, the most stable conformation of the chain departs slightly from strict 2_1 crystallographic symmetry. Attachement through hydrogen bonding of neighbour chains builds up a β twisted sheet, which is indeed a building element of globular proteins. Twist is very pronounced in proteins, in which individual sheets are free of crystallographic environment. The small thickness of silk crystals (*ca.* 6 nm) allows some relaxation of the crystallographic symmetry. The lamellar twist, although spectacular on a macroscopic scale, implies only very small local deviations from true crystal symmetry: less than 0.1 Å at the ends of the stem, or less than 0.1° rotation from one stem to the next in the hydrogen-bond axis direction. Note that a model poly(D–Ala–Gly) enantiomorphous to silk fibroin was found to produce right rather than left-handed twisted crystals, an observation which definitely links macroscopic twist of the lamellae with configuation of the peptide residues and the specific β sheet strucure. Finally, crystals of the form I of silk fibroin (cf. B. Lotz & H.D. Keith, *J. mol. Biol.*, **61**, 201 (1971)), which are based on a different crankshaft conformation of the chain and sheet structure, do not twist.



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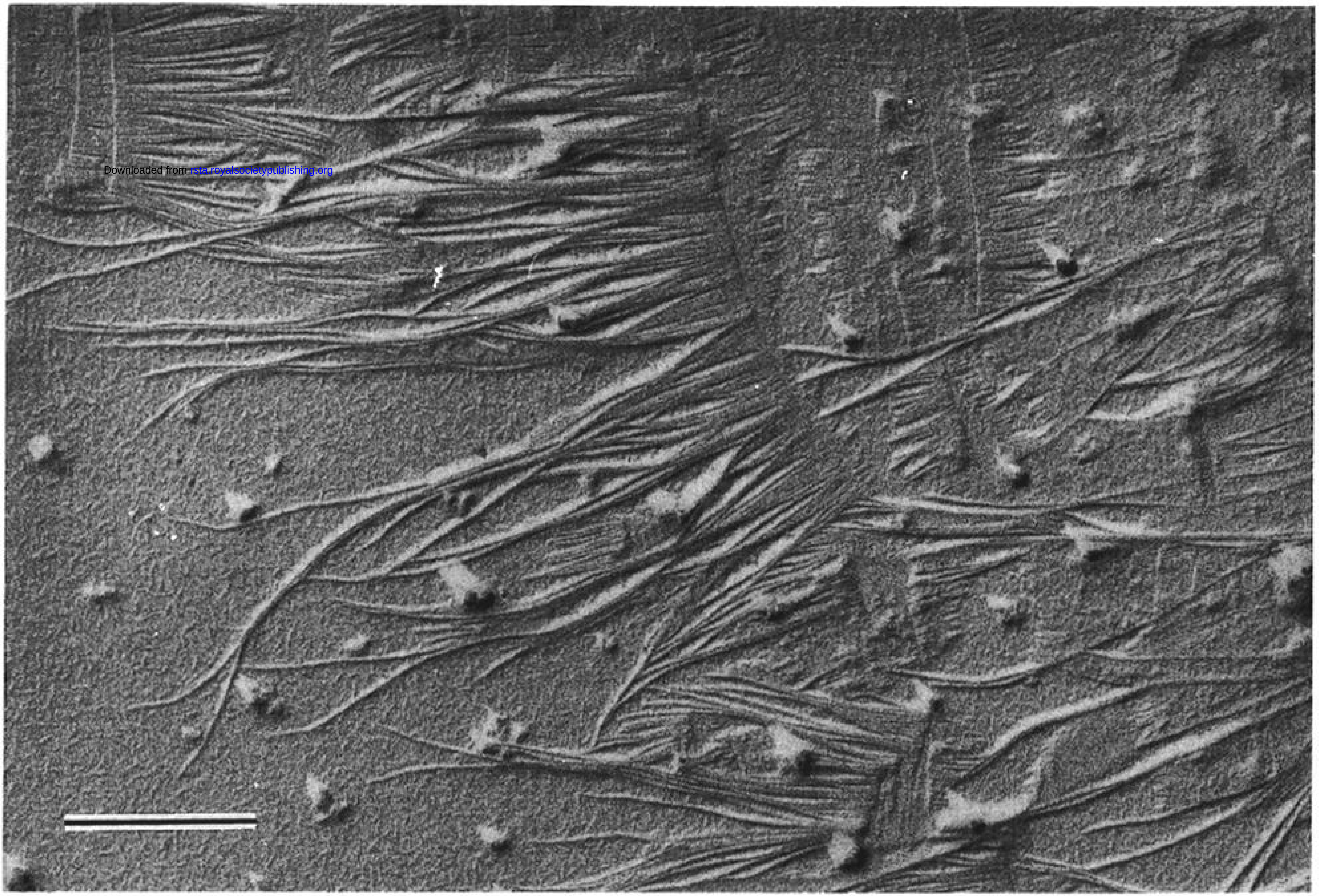

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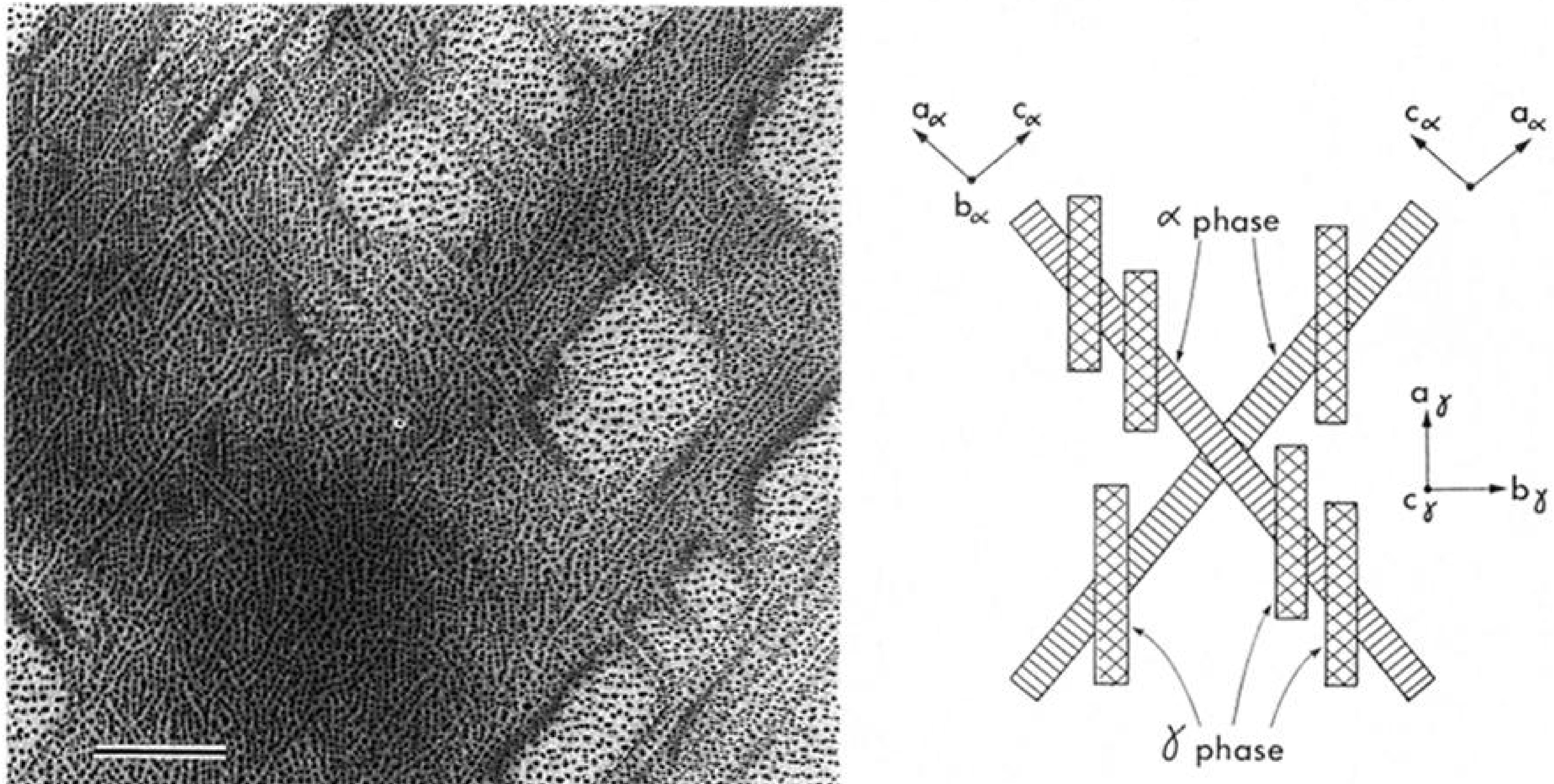

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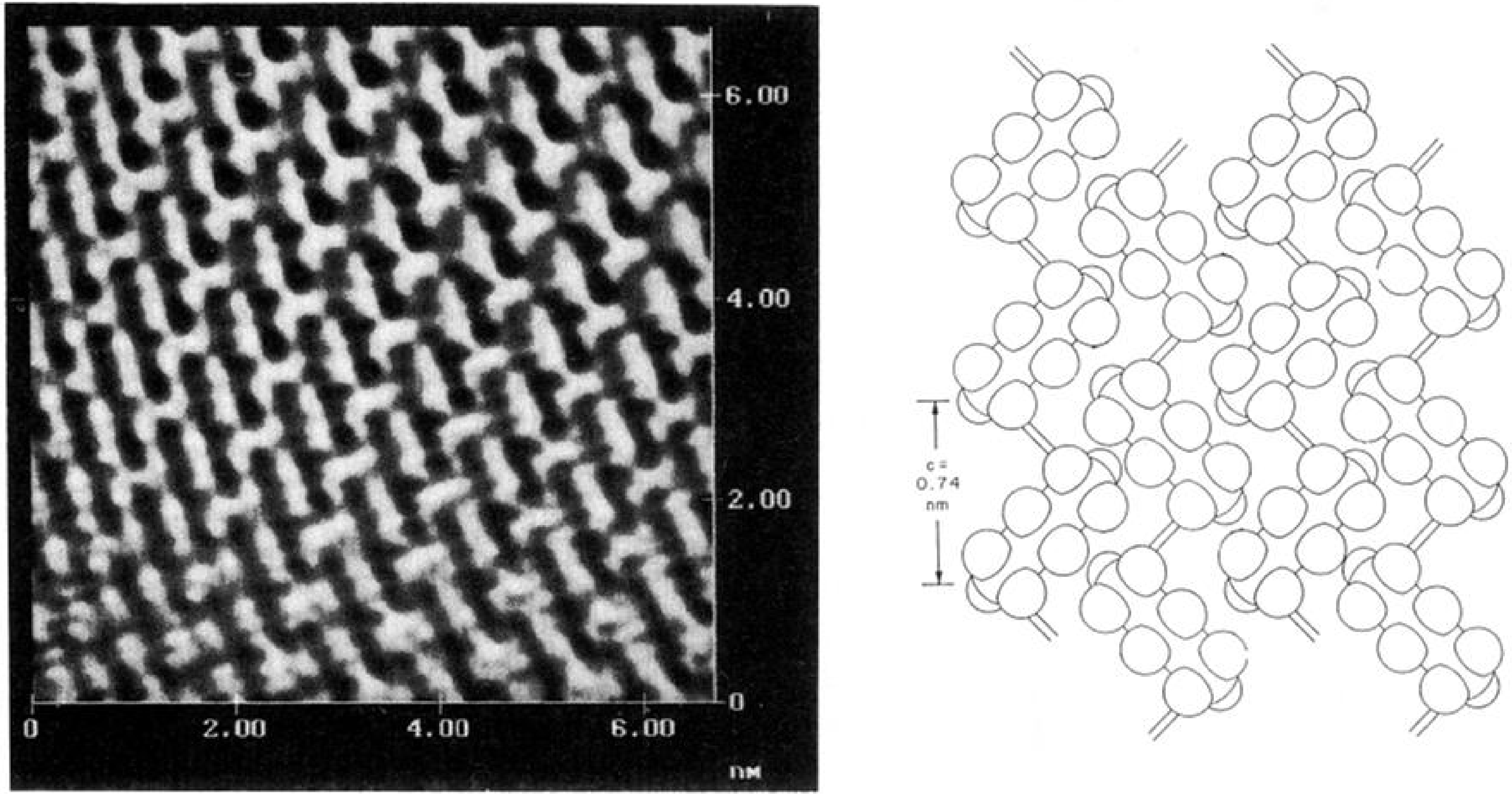

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