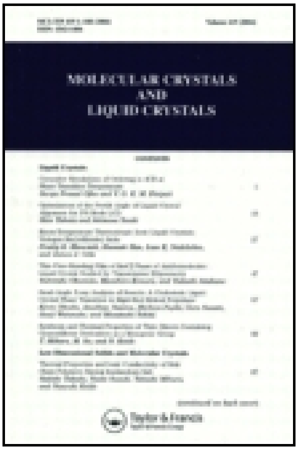

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Intermolecular Structure in Organic Crystals Shown by High Resolution Electron Microscopy

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Version of record first published: 13 Dec 2006.

To cite this article: J. R. Fryer (1986): Intermolecular Structure in Organic Crystals Shown by High Resolution Electron Microscopy, Molecular Crystals and Liquid Crystals, 137:1, 49-65

To link to this article: http://dx.doi.org/10.1080/00268948608070912

Mol. Cryst. Liq. Cryst., 1986, Vol. 137, pp. 49-65
0026-8941/86/1374-0049$20.00/0

Printed in the United States of America

INTERMOLECULAR STRUCTURE IN ORGANIC CRYSTALS SHOWN BY HIGH RESOLUTION ELECTRON MICROSCOPY

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Abstract High resolution electron microscopy at the molecular level has been applied to phthalocyanine polymers, Langmuir-Blodgett films and long chain aliphatic hydrocarbons.

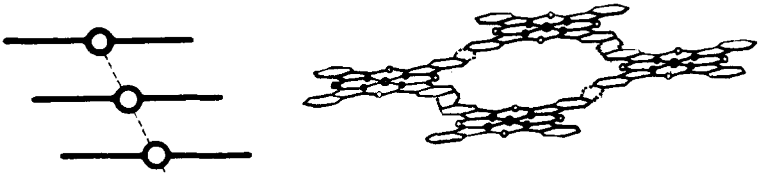
At the previous meeting I showed[1] how electron microscopy can resolve discrete molecular shapes and crystal lattice periodicities in a range of crystals of aromatic molecules.In addition the growth of thin films by vacuum deposition and the parameters controlling the resolvable distances in the microscope were described.The present work is concerned with the structures of materials of potential technological importance and in the case of three of them extends the application of the microscope to crystals hitherto thought to be too electron beam sensitive to yield high resolution images.

The compounds studied were polymeric phthalocyanines,t-butyl phthalocyanine Langmuir Blodgett films,paraffins and phospholipids.

POLYMERIC PHTHALOCYANINES

Phthalocyanine can be polymerised to give either vertically or planar polymerised products as shown in Fig.1.The formation of planar polymers of various metal phthalocyanines according to the reaction scheme shown in Fig.2 has been described by Whorle[2].The products reported by him were fine polycrystalline powders unsuitable for single crystal X-ray analysis.

Tetracyanobenzene was placed in a glass tube with excess copper chloride and heated under vacuum.



Vertical Horizontal

FIGURE 1 Polymerisation structures for phthalocyanine

Initially it was heated to 150C to remove water and then the tube was sealed off and heated at temperatures up to 450C for up to 6hrs.The best products in terms of crystal perfection were those heated at 400C or 450C.Both copper chloride and metallic copper were used as a source of metal with no obvious difference in results.The copper metal was used as a powder and also epitaxial films[3] in both (100) and (111) orientations.No corresponding epitaxy or increased crystal dimensions of the polymeric product were observed. After heating the contents of the tube were dispersed in water and the polymer powder dried down on to a carbon film on an electron microscope grid. Direct mounting of the powder was also employed but produced a less even dispersion.

In some cases the powder was placed in a molybdenum boat and evaporated under vacuum on to a KCl substrate maintained at 220C. After evaporation the polymer film was coated with carbon by evaporation[1] and floated off on to water where it could be picked up by an electron microscope grid.

Microscopy was done on JEOL 100C or JEOL 1200EX microscopes operated at 100keV and 120keV respectively. Minimal exposure techniques were used to minimise electron beam damage to the specimen and the images recorded on X-ray film.

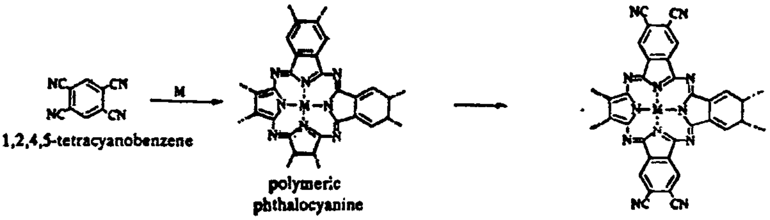


FIGURE 2 Polymerisation and termination.

Results.

The powdered product obtained after heating is shown in Fig.3. There is evidence of ribbon development which indicates that the polymerisation proceeded via a chain process but the crystal development is small and there is a large amount of disorder.The prominent (15A) lattice fringes lie across the ribbons indicating that the growth of the ribbon involved a crystallisation type mechanism with single molecules, i.e., that monomeric species of the polymeric phthalocyanine as shown in Fig.2 condensed on the leading tip of the ribbon and there polymerised with the preceding layer and adjacent molecules in the tip layer rather than growing as a two dimensional raft that would demand equivalent molecular structure and reactivity in both dimensions.Thus the monomeric structures have a considerable lifetime during the reaction.

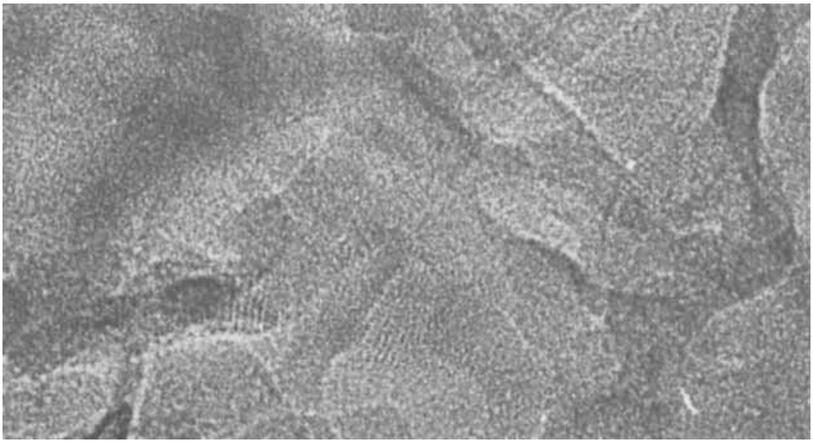


FIGURE 3 Ribbon structure showing lattice fringes

The film obtained by evaporation of the product on to KCl has a much higher crystallinity as shown in Fig.4.No efforts were made to optimise order in this film so that much larger crystalline areas are potentially feasible.Clear definition of the molecules is seen in this micrograph such that it is probably several molecules thick and it is the molecular projection of a column that is imaged.The high symmetry in this projection suggests that the molecules are not tilted and this is supported by the fact that clear definition of the molecular columns is obtained without tilting the specimen.(NB when epitaxial films of a phthalocyanine whose molecules are tilted is made,it is normally necessary to tilt the specimen through the molecular tilt angle to obtain a clear projection as the molecules lie parallel to the substrate[5].)

The lateral extent of this polymer is approximately 20 molecules.This could probably be increased by careful epitaxial growth but it is unlikely that large continuous films would be obtained.

The vertically polymerised phthalocyanine has stemmed from the work of Kenney[6,7,8] and the structural studies reported here are on samples synthesised by him.Of particular interest was the polymer $(AlPcF)_n$[9,10].

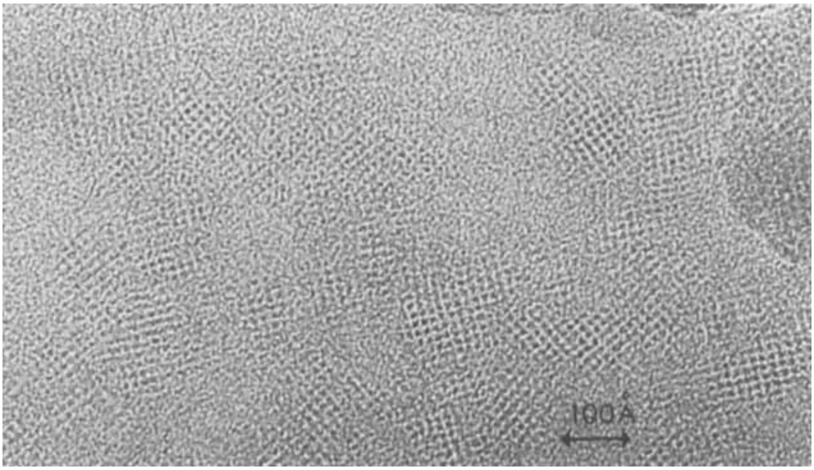


FIGURE 4 Horizontally polymerised copper phthalocyanine

A diagrammatic structure is shown in Fig.5. Examination of the powdered polymer showed extended crystals-Fig.6-that had breaks or discontinuities at 120A intervals or multiples of this value.This suggests that the chain length is of this order with the polymerisation

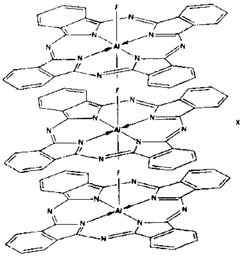


FIGURE 5 Diagrammatic structure of $(AlPcF)_n$

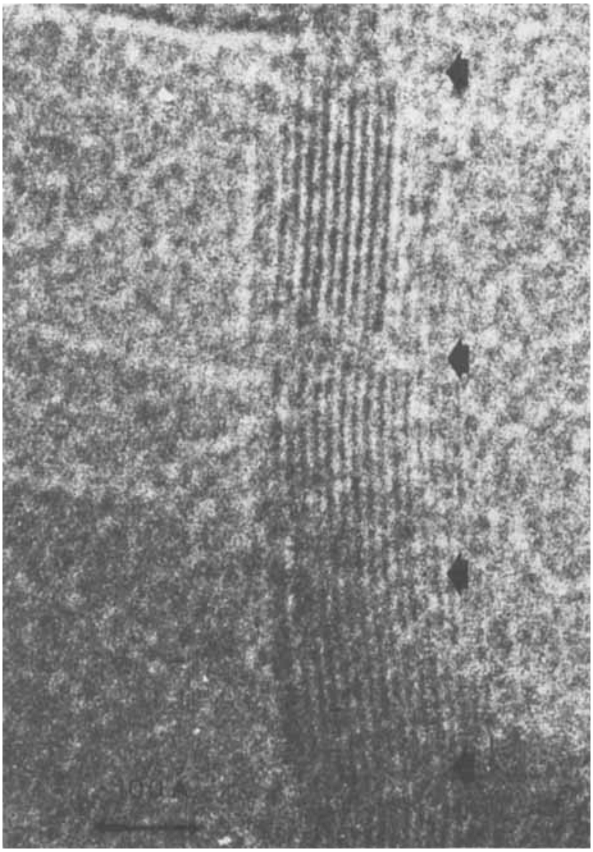


FIGURE 6 Extended crystals of "as synthesised"$(AlPcF)_n$.Breaks are marked by arrows.

extending up the major axis of the crystals.Vacuum evaporation of this material on to KCl maintained at 220C produced epitaxial films of the polymer as shown in Fig.7.

The polymeric chain was perpendicular to the substrate with the molecular plane parallel to the substrate.These images and the electron diffraction patterns indicate that the unit cell is tetragonal with a=b=13.37A and c=3.6xA where x corresponds to the number of phthalocyanine units in the chain (33). Higher resolution micrographs-Fig.8-show the presence of defects which is understandable in terms of the nonpolar,rigid,essentially cylindrical nature of the molecules.

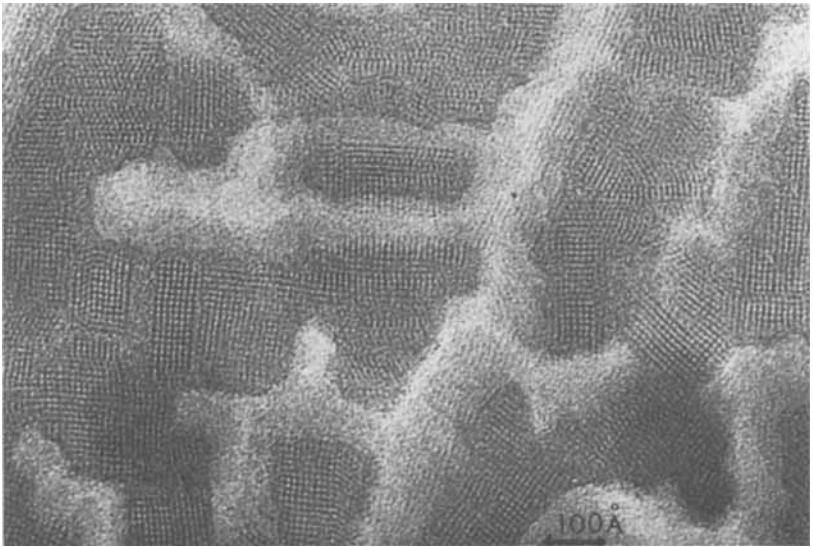


FIGURE 7 Epitaxial film of $(AlPcF)_n$.

Comparison of the vertically and horizontally polymerised phthalocyanines shows surprising similarities.The projection of the structures normal to the molecular plane is similar with the only significant difference being in molecular

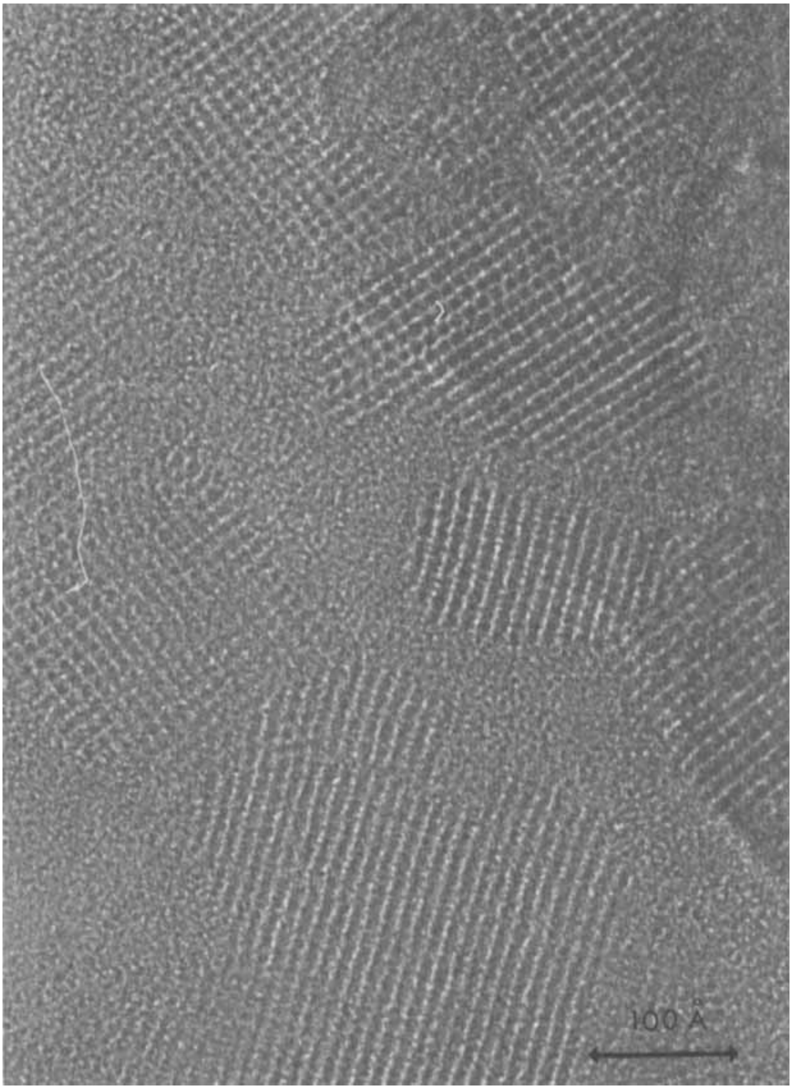


FIGURE 8 High resolution micrograph of epitaxially grown crystals of $(AlPcF)_n$.

separation (i.e.slightly larger in the horizontally polymerised material).The chain lengths are of similar order and their physical behaviour with regard to vacuum sublimation also agrees.The behaviour and structure of $(AlPcF)_n$ is typical of vertically polymerised phthalocyanines and very little structural difference is observed between images of $(SiPcO)_n$,$(SiNcO)_n$ or $(GaPcO)_n$.(Nc is the naphtho-cyanine).

LANGMUIR-BLODGETT FILMS.

This work was done in conjunction with R.Hann, B.L.Eyres and C.McConnell and initial results have been reported[11].

Monolayers of copper tetra-t-butyl phthalocyanine were spread at 20C from a solution in xylene on to the surface of an ICI Langmuir trough[12] whose barriers were compressed to obtain a surface pressure of $20mNm^{-1}$.The monolayer was then mounted on to an amorphous carbon film on an electron microscope grid by lifting the grid through the monolayer.Initial results lifted the grid horizontally but the film often lost its crystalline order in the preparation (i.e.no diffraction pattern was observed).Vertical lifting of the film whilst masking one side(to prevent bilayers) gave more reproducible results.Arced diffraction patterns as reported previously[11] showed the presence of crystallinity (note the 18A reflections are very close to the zero order beam) and lattice imaging under minimal exposure conditions using X-ray film gave satisfactory results-Fig.9.Suitable areas for imaging were determined from the electron diffraction patterns at very low beam intensity and the image recorded at a magnification of 50,000X.

Our previous conclusions that the film has crystalline areas embedded in an amorphous matrix has been supported by our present results.

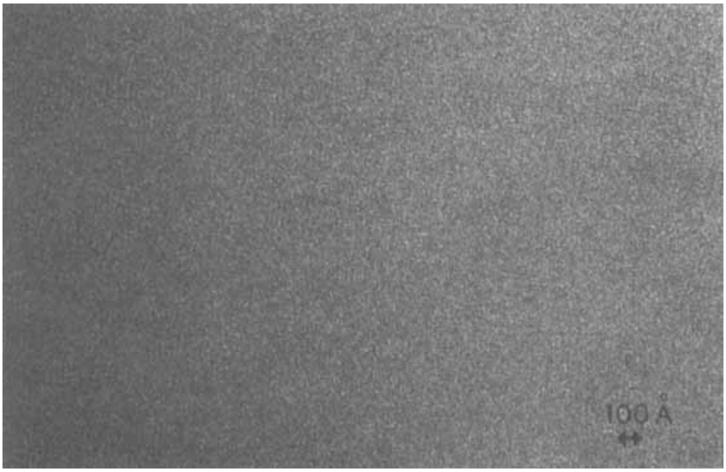


FIGURE 9 Copper tetra-t-butylphthalocyanine monolayer Langmuir-Blodgett film.18A lattice fringes are present.

PARAFFINS AND PHOSPHOLIPIDS.

This study has been done in collaboration with D.Dorset and C.McConnell.The radiation stability of aromatic molecules is such that there is a reasonable expectation of obtaining direct lattice or molecular images[1].Aliphatic molecules have stabilities several orders of magnitude less and for a paraffin the theoretical maximum resolution at room temperature that could be obtained is 40A to give reasonable contrast on photographic film.At much lower doses,however,there is still grain development in the film so that optical processing or digitisation and computer processing can reveal the image[13].The processing system used has been IMAGIC[14]. Electron beam damage stability can also be enhanced by examining the specimen at low temperatures and in this work we have used the cryomicroscope at the Fritz-Haber Institute in Berlin to enable us to study specimens at 4K.

Monolayer crystals of various n-paraffins were prepared from hexane on water surfaces and the crystals picked up on carbon films on electron microscope grids.

Fig.11 shows the reconstructed image of n-$C_{36}H_{74}$ viewed in a direction parallel to the chain axis.Edge defects are visible and the resolution of this image is 2.5A.The type of image and disorder within it are similar to that observed by Dorset et al[15].

This image gives no information as to the third dimension. To resolve this third dimension specimens were expitaxially crystallised on to benzoic acid or naphthalene[16] so that the c-axis was parallel

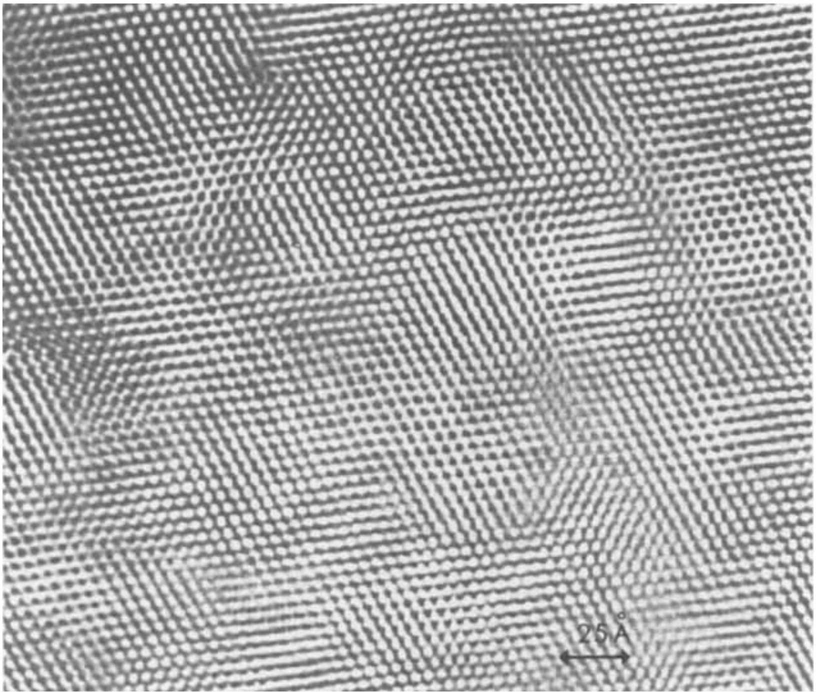


FIGURE 11. Reconstructed image of $C_{36}H_{74}$ viewed down the molecular axis. The crystal is one molecule thick (50A).

to the substrate. The lattice periodicity in this direction is larger than 40A so that direct imaging can be performed at room temperature[17]. A large crystal of $C_{36}H_{74}$ is shown in Fig.12a with enlargements of various areas shown in Figs.12b,12c and 12d. These enlargements show the disorder present in the crystal and in conjunction with the image down the major axis shown in Fig.11 confirm that the disorder is a three dimensional phenomenon. The flexibility in the crystal necessary to accomodate such disorder supports the postulations on thermal and radiation damage behaviour that invoke the presence of chain end voids in the structure[18].

A series of solid solutions of paraffins ranging from $C_{19}H_{40}$ to $C_{60}H_{122}$ mixed with $C_{36}H_{74}$ show a linear dependence of (001) distance with mole fraction as measured from images of the epitaxially grown samples.

Phospholipids are examples of long chain molecules that occur in biological systems and a reported feature of stained and frozen preparations was that undulations appeared in the long distance lattice repeat distances. It was not clear, however, whether the undulations were an artifact of specimen preparation. Using the epitaxial growth techniques described for the paraffins it has been possible to image unstained crystalline 1,2-dihexadecyl-sn glycerophosphoethanolamine directly at room temperature[18]. The images obtained-Fig.13-show

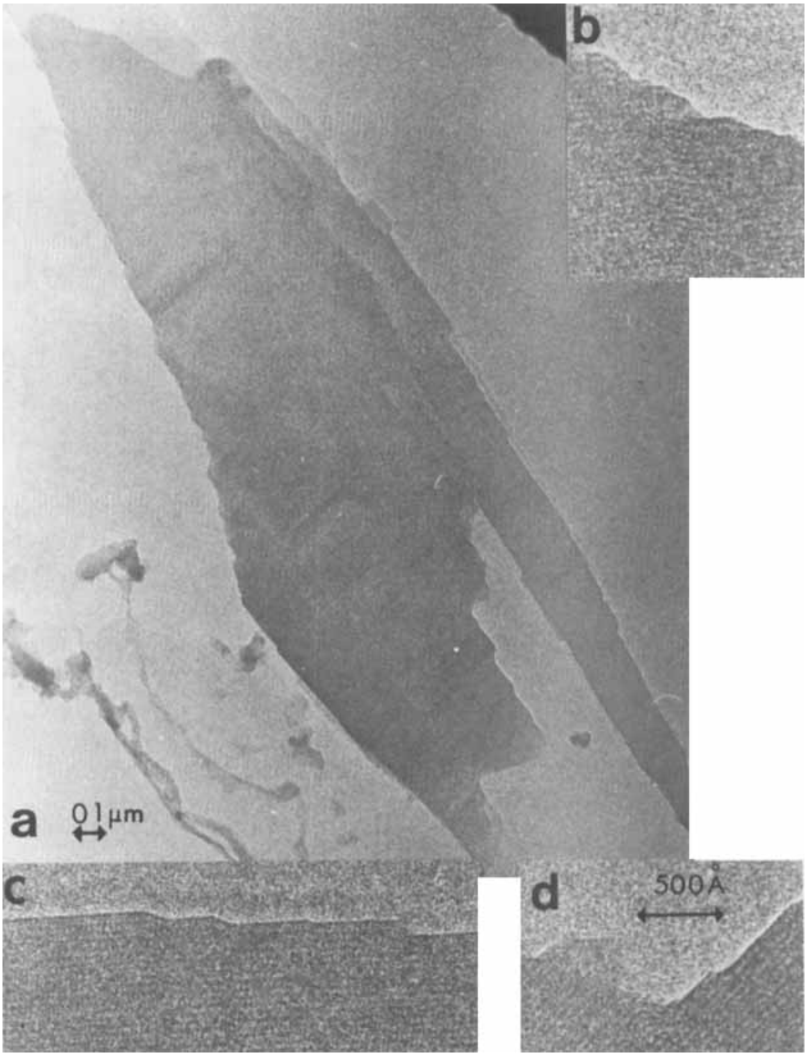


FIGURE 12 Epitaxially grown crystal of $C_{36}H_{74}$ with the (001) axis(chain axis) parallel to the imaging beam. Figs.12a-d show various regions of disorder in the crystal

the 55.6A(001) lattice fringes and confirm that the undulations are an inherent property of these crystals.

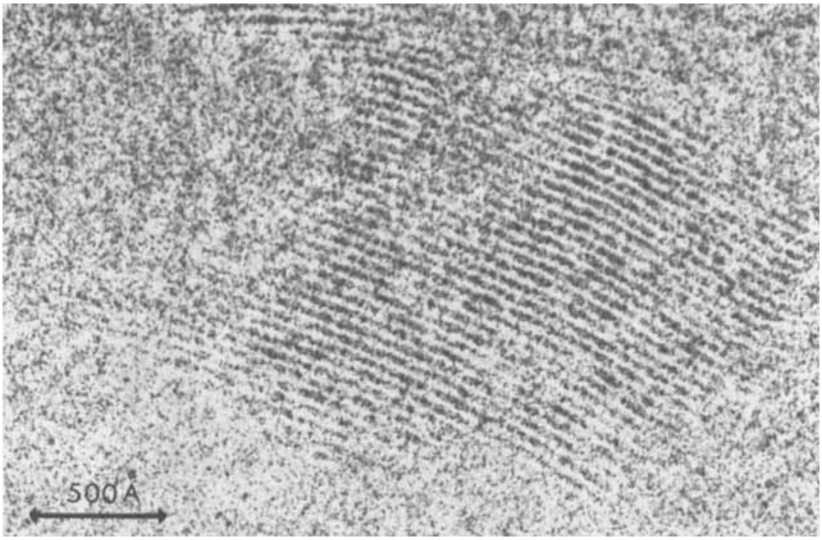


FIGURE 13 Phospholipid crystal lattice -unstained and at room temperature- showing undulations.

This survey of recent results obtained by high resolution electron microscopy extends the technique to all organic crystals which are stable within the vacuum of the microscope. There is much more information in these micrographs and supporting images of the various specimens than has been mentioned and these will be the subject of separate reports that will be published in the near future.This paper and its predecessor at the previous conference[1] have shown that a combination of the epitaxial growth techniques and low dose high resolution electron microscopy permit the growth of crystals of large lateral extent,in a variety of orientations,and their structural characterisation at the molecular level.

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