THE ELECTRON MICROSCOPY OF CRYSTALLINE POLYMERS

By

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"Change and decay in all around I see;"

H. F. Lyte, 1793-1847

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ABSTRACT

This thesis describes the micro-structure of crystalline polymers, particularly as revealed by electron microscopy, and also the effect of the electron beam on the radiation sensitive specimens under various conditions.

Polymer single crystals grown from dilute solution were used for the radiation damage studies, as they are thin ($100 \text{ \AA}$), and a single preparation may contain 10^8 crystals of uniform properties. Preparations of polyethylene (PE), polyoxymethylene (POM), poly-4-methylpentene-1 (P4MP), nylon 6 and polyethyleneoxide were characterized in the transmission electron microscope, confirming previous work for the most part. The scanning electron microscope, operating in its normal mode, showed even the thinnest single crystals clearly, when they were sedimented onto a metal coated substrate. Attempts to observe the 3-D pyramidal structure of PE single crystals were unsuccessful. The crumpling seen when crystals floating on glycerol, or freely suspended from a fine mesh, are irradiated in an electron microscope indicates that even if the structure were preserved, by freeze drying or however, it would be difficult to observe. Thicker, complex, crystals seemed more stable in the scanning electron microscope, and cannot be seen well in the transmission microscope.

A chart recorder, picoammeter and special faraday cup were fitted to a Siemens Elmiskop 1 for accurate beam current measurements, and dynamic recording of the varying intensity of polymer crystal images.

Reproducible curves for the variation of intensity of one spot in the diffraction pattern were obtained for POM and PE. There was a period, p , of very variable intensity, followed by an exponential decay. The very variable intensity is due to the diffraction contrast of detail, so after ^{p} no information could be gained from the crystal, although the diffraction pattern shows it to be largely crystalline at that point. For the particular preparations described, at 100 kV,

	PE	POM	
p	43 ± 5	34 ± 4	values in Coulombs/sq. m.
<hr/>			
Diff. Pattern			
Decayed	92 ± 10	70 ± 7	

It is shown that in the electron microscope, heating and ionic bombardment are negligible effects compared to the electron irradiation.

An energy loss analysing microscope applied to PE crystals showed that

- 1) 1 Coulomb/sq. m. is equivalent to 42 Mrads, at 100 kV in agreement with theory.
- 2) The density of PE increases sharply on irradiation, and the final product seems much like amorphous carbon.

Radiation damage mechanisms are discussed, with special reference to polymers and to conditions in an electron microscope.

For POM, PE and P4MP the variation in radiation damage rate with beam voltage between 30kV and 100 kV was found to be accurately

$\propto (\text{electron velocity})^{-2}$ as predicted by theory, both simple and complex. With exactly similar samples of PE and POM in the 1MV electron microscope at U.S. Steel, the trend was the same up to 1MV. Between 700kV and 1MV there was a deviation from proportionality towards even slower damage. Absolute measurements differed by 30 - 50%.

Adapting the scanning electron microscope to transmission, the damage of POM could be studied down to 3kV. There was a steady increase of damage rate as the voltage was reduced, but it was not possible to compare the results with those at higher voltages.

The effect of specimen temperature on damage rate was investigated with a liquid helium cooled specimen stage. In going from room temperature to $< 30^{\circ}\text{K}$ the rate was reduced by a factor of 2 (2.2 ± 0.8). This is not enough to outweigh practical difficulties.

There is a fundamental noise limit to resolution with a decaying crystal. This has been calculated, and found to be well below anything practically realized. For example random structure $50\text{ \AA}$ across, and periodic structure of $20\text{ \AA}$ should be resolvable in a POM crystal, $85\text{ \AA}$ thick imaged in bright field at 100 kV and 13,000 times magnification. The real limits are image instability and focus, and there is no good way round either. There is no advantage to be gained from higher beam voltages. Ease of rapid operation of the microscope is the most important factor. Image intensifiers, if easy to use, may be a great help, allowing more manipulation of specimens, and presenting more of the information to be made.

that is obtained.

Thin films of PE and POM were cast from slurry and observed in the electron microscope. PE gives complex crystallographic diffraction contrast which rapidly disappears but another, stronger, contrast builds up showing another structure, and this is retained however large the dose. This beam-induced image looks just like what one might expect from undamaged material, in this case, banded spherulites. Detailed study of the changes, combined with optical microscopy and experiments on single crystals leads to the following conclusion:

The beam-induced contrast is due to anisotropic deformation caused by radiation damage. Each crystalline unit expands along a and contracts along c, while the third dimension, along b, remains constant.

This explanation supports the current view of spherulite structure, a collection of radiating twisting lamellae, and may well apply to other polymers and structures.

Thin films of PE were drawn at room temperature and annealed at 120°C . On irradiation, the drawn regions retracted by around 30%, but this is not a measure of contraction along c (predicted as $> 25\%$) because of the unknown behaviour of interlamellar material. The fibrils seen in drawn PE after irradiation were found to be the radial lamellae, homogeneously deformed, whenever the spherulite structure persisted enough for measurements to be made.

An ultra-thin PE film which became in the limit, an open network, was produced in an uncontrolled way. Normal spherulite structure was not observed. Areas seemingly undrawn gave a single crystal type of diffraction pattern, and drawn ribbons looked like a 'shish-kebab', transverse platelets on a fine thread. The plates were $200 \pm 25\text{\AA}$ thick, separated by $200 \pm 75\text{\AA}$. The centre to centre period was $380 \pm 40\text{\AA}$. Diffraction indicated that the orientation was very good, with b and c in the specimen plane, and c along the ribbon. The film was quite stable, and diffracting units could be identified with individual platelets. This was a fascinating demonstration of an ideal drawn PE, but it could not be made to order, or investigated systematically.

The POM films degraded to a featureless film in the electron microscope with $< 20\%$ of the mass remaining. Optical microscopy showed coarse textured spherulites, beginning to organise into banded spherulites with radial period $> 10\mu$. Initial contrast in the electron microscope showed a radiating structure from well spaced centres. The radiating units gave a single crystal type of diffraction pattern, with a $\{10\bar{1}0\}$ growth direction. It seems that because of the coarse texture of POM spherulites, a thicker film is needed to give information about the bulk. This would need a high voltage microscope.

PREFACE

The work described in this thesis was carried out between October 1966 and October 1969 under the supervision of Professor P.B. Hirsch, F.R.S. initially, and then of Dr. G.W. Groves. None of this work has been, or is being, submitted in any other degree thesis.

The thesis is divided into seven chapters, and the sections and sub-sections are listed on title pages at the head of each chapter. Figures have been placed near the text where they are described, so that figure captions have been reduced to a minimum. When the work of others is mentioned, reference is given to the name of the author and the date of publication. An alphabetical list of complete references is at the end of the thesis. A computer program is included as an appendix because it can be applied generally, although it is an adaptation of a program by Dr. M.J. Whelan.

I am indebted to Professor Hirsch for the provision of laboratory facilities, and to both my supervisors for their guidance, help and criticism.

The energy loss analysis described in section 3.5 was performed in collaboration with Mr. R.W. Ditchfield. Both of us were needed for fast operation of the complex instrument, which was aligned and calibrated by Mr. Ditchfield. His views on interpretation have been valuable, and the work is continuing at present.

The experiments in the high voltage electron microscope (section 4.4) were done at the U.S. Steel Co. research centre, by Dr. C.J. Humphreys, Dr. L.E. Thomas and Mr. W.R. Duff and are attributed to them in the text. I must thank all three, and especially Dr. Humphreys for his effective liaison.

The low temperature electron microscopy (chapter 5) would have been impossible without the instruction and help of Dr. M.J. Goringe, whose continuing interest and discussions have been invaluable.

I would like to thank Mr. R.H. Donaghay and Mr. A. Davis for their technical assistance on the electron microscopes, and Dr. G. McCrum for providing several polymers as starting material.

Special thanks to Miss J.L. Robinson for her perfectionist attitude to the photographic work in this thesis, to Miss J.E. Blomfield for rapid and accurate typing, and to Mrs. N. Kurton for the drawings.

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INTRODUCTION

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INTRODUCTION

Plastics are very important materials today, and the technology of their production and use is well advanced. Detailed understanding of the structures which lead to their desirable properties lags far behind. Statistical models deal with rubbers and amorphous glassy polymers, but not highly crystalline materials. X-ray diffraction shows that the crystalline regions in polymers are only a few hundred Angstroms across, so the transmission electron microscope should be a very powerful instrument for studying polymer morphology. It is difficult to make thin specimens from bulk material, but apart from this, the major difficulty in the electron microscopy of crystalline polymers is the degradation of the specimen by the electron beam. The crystalline order and sometimes the whole structure of the irradiated part is quickly destroyed.

The present work has been concerned with describing and measuring the effects of radiation on polymers in the electron microscope, under various conditions. Using solution grown single crystals as specimens, both the theoretical limits and the practical problems can be taken into account in deriving the optimum conditions for resolving crystalline detail. The scanning electron microscope does not require thin specimens, but polymer single crystal specimens show the radiation damage is still a serious problem.

Polyethylene films cast to less than $1,000 \overset{\circ}{\text{A}}$ thick

show the rapid loss of order in the transmission electron microscope, but then contrast reappears when crystallinity has gone. Dlugosz and Keller (1968) found this effect in microtomed sections of bulk polyethylene, so it is representative behaviour. Combined optical and electron microscopy of thin films, as cast and highly drawn, provides evidence for a simple mechanism for beam induced contrast. It is hoped that electron micrographs of other melt crystallised polymer structures may be better interpreted in the light of these results. Cast films of polyoxymethylene were observed, and their initial structure is described, but there is no beam induced contrast in this material.

CHAPTER 1

CRYSTALLINE POLYMERS

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structure, and this is why it has been called a *comb*. This polymer is an ideal one, for every unit polymer contains a proportion of defects in its configuration. A very great difference exists between the linear polymers and those synthesized from monomers of greater functionality. These latterly form a net or three dimensional network, and are not crystallizable.

Some linear high polymers are amorphous. This is due to a lack of regularity in the molecular structure of the chain. For example, polystyrene and polyvinylcarbazole are amorphous.

CHAPTER I

CRYSTALLINE POLYMERS

1.1 General

The crystalline polymers referred to are all organic linear polymers. They have a high degree of polymerization, that is, each molecule is made up of many thousands of simple chemical repeat units, and the molecular weight is high, 10^4 to 10^7 . Linear polymers are synthesized from difunctional monomers, forming a long chain. Any branches from the main chain are due to branch points within the repeat units. For example, poly-4-methylpentene-1 (P4MP) has a repeat unit of:

structure, and this is why it has been studied so much. This picture is an idealized one, for every real polymer contains a proportion of defects in its configuration. A very real difference exists between the linear polymers and those synthesized from monomers of greater polyfunctionality. These naturally form a two or three dimensional network, and are not crystallizable.

Some linear high polymers are amorphous. This is due to a lack of regularity in the molecular structure of the chain. For example, polystyrene and polymethylmethacrylate are amorphous,

but the regular isotactic isomers, synthesized with stereoregular catalysts, can be crystalline (Natta et al. 1958).

Although the presence of crystallinity is detectable in many ways, the X-ray diffraction pattern gives the most direct evidence. Generally the X-ray diffraction pattern from a bulk crystalline polymer contains a number of sharp rings and a more slowly varying background, called the amorphous halo. The sharp rings have a definite width, which is appropriate to crystals less than a few hundred Angstroms across in any direction. This type of pattern was naturally interpreted as due to a two phase structure of small crystalline units embedded in an amorphous matrix. The relative intensities of rings and halo gave the relative proportions of the two phases, that is, the degree of crystallinity (see Miller 1966). Study of diffraction (Hosemann, Bonart et al. quoted in Geil 1963, p. 23 et seq.) showed that an amorphous halo did not necessarily imply an amorphous phase. The same pattern could be obtained from defects distributed throughout a crystal. However, a periodic density variation was observed by low angle X-ray diffraction (e.g. Keller and O'Connor 1957) with a period of a few hundred Angstroms. This means that the defects must be highly segregated. For most polymer structures, the amount of disorder is large, and the two phase model is a good approximation (Takayanagi et al. 1966).

The polymer molecules are individually over $1,000 \text{ \AA}$ long, if stretched out. It was thought that each crystalline region contained

portions of molecules packed parallel, and that each molecule passed through a number of crystallites. The portions of the molecules between the crystalline regions constituted the amorphous matrix. This was the fringed micelle model, developed in 1930, (Gerngross, Hermann and Abitz 1930) the micelles being the crystalline bundles, and the fringes the intermediate regions at the ends of the bundles.

Radially symmetric arrays of oriented crystallites, ten microns or more across, were observed in the more highly crystalline polymers. These arrays, called spherulites, and recognized by a maltese cross extinction pattern in the polarizing microscope, are discussed in detail in section 7.3. It was difficult to explain why micelles, essentially random, should form such arrays, but the explanation was attempted. (Bunn 1953). The discovery that many polymers form distinct single crystals from dilute solution proved the fringed micelle model to be insufficient. It was in 1957 that detailed studies of single crystals of PE were published (e.g. Till 1957). These showed that the basic crystal form was a plate about 100 Å thick and a few microns across, e.g. fig. 2.8, with the molecular chains parallel to each other and perpendicular to the plane of the plate. Since the crystals are discrete units, the molecules must fold back on themselves.

1.2 Polymer Single Crystals

The PE chain can distort with a relatively small increase in energy to fold back on itself, with about 5 carbon atoms in the

fold (Keller 1962). The model of abrupt regular folds with adjacent re-entry was put forward from the first (Keller 1957). There is plenty of evidence for this model, all gained from the observation of individual single crystals. The observation of dislocation networks at the interface in a crystal made up of two layers (Holland and Lindenmeyer 1965) shows directly that the fold surfaces are highly regular. Moiré fringes are more commonly observed in such cases (eg. fig. 6.4) and imply no interaction between the surfaces. A detailed analysis of the networks and the conditions under which they are formed (Sadler 1969) points to regular folds in a rough fold surface.

As each molecule adds itself to a growing crystal, it forms a ribbon on the growth face. Each prism face should define a distinct sector, where most of the folds are in planes parallel to that face (fig. 1.1). Different sectors do have different mechanical (Geil 1964) and thermal (Bassett, Frank and Keller 1959) properties and the distorting effect of all the folds on the crystal interior has been demonstrated by diffraction and moiré effects (Bassett 1964). Beyond these observations, there is the fact that PE single crystals are not planar. In the simplest crystals, each sector is flat, and together they make up a hollow pyramid, (fig. 2.11a). Crystals which have collapsed onto a substrate show several indications of this, (Section 2.2.3) but the effect has been observed directly on large crystals suspended in liquid, using dark field optical microscopy (Bassett, Frank and Keller 1963a). In the pyramidal

sharp fold model

Fi g. 1.1

crystals, the chain axis has the same direction throughout. The asymmetry and lower packing density of sharp folds is used to explain the obliquity of the sectors. The folds need to be staggered to pack together. This explanation implies an absolutely smooth fold surface, which was supposed to form after the crystal had grown (Keller 1967).

It is more difficult to imagine sharp folding in complex molecules. Many, such as the polyamides, will have chemical effects limiting the possibilities, and all molecules with a spiral form must be restricted. A model for polypropylene has been proposed (Sauer, Morrow and Richardson 1965), where only one fold plane is permitted. Evidence for regular folds has been obtained both for polyoxymethylene (POM) and for P4MP. (Bassett, Dammont and Salovey 1964).

At the same time, evidence from aggregates of crystals supported the view that the fold surface was disordered, and essentially amorphous. The density and heat of fusion of PE single crystal mats show a crystalline deficiency of 10-20%. (Martin and Passaglia 1966, Mandelkern et al. 1965). X-ray diffraction gives the same sort of result, though the interpretation is difficult. The line broadening of $\{hk0\}$ reflections remains, indicating that some disorder is within the lattice. Chemical attack indicates a $10\text{\AA}$ surface layer which is more reactive. (Blundell, Keller and Connor 1967). Similar methods have shown that most chain ends are excluded from the lattice, and may be

enough to make up the amorphous layer. (Keller and Priest 1968).

Different sample types give these conflicting results. Since even a perfect fold surface is disordered, compared to the perfect crystal, and its regularity may not be impaired by a few chain ends, the conflict may be resolved to some extent.

It is generally accepted that the lamellar mode of growth is kinetically favoured. The thermodynamically stable state is a crystal of extended chains. The lamellar thickness (fold length) depends on the supercooling and changes sharply if growth conditions are altered. The fold length is therefore controlled by the secondary nucleation process. Various detailed theories of different sophistication have been developed. They are sufficiently similar for them all to agree with experiment. The most recent predicts a rough fold surface, with a standard deviation of $10\text{\AA}$. (Lauritzen and Passaglia, 1967).

Most polymer single crystals are not simple single lamellae as described above. They may be dendritic (fig. 2.1a), as happens at high supercoolings, or twinned. Both these habits occur in ordinary crystals, but the extra complications possible with folded chains are described at length in Burbank (1960). Much more common in most preparations is the spiral growth by which lamellae grow in the perpendicular direction (figs. 2.2a, 2.9). The spirals are like those associated with a screw dislocation in non polymeric substances. The Burgers vector of the dislocation in this case is the thickness of the crystal, some $100\text{\AA}$. Generally the layers are not in good contact, except near the centre of the spiral.

1.3 Melt Crystallized Polymer

It is important to know how far single crystals can be taken as representing some subunit of bulk material. Replicas of freely crystallized surfaces and of fracture surfaces show lamellar detail. Low angle X-ray diffraction from bulk and oriented polymers shows that there is a density variation on the scale of a few hundred angstroms, but exact interpretation is not always easy (Geil 1966). Infra red spectroscopy has been used in the case of Nylon 6,6, certain bands being identified with chain folds. (Koenig and Agboatwalla 1968). The best evidence comes from PE. Hot fuming nitric acid breaks up bulk PE, by oxidizing the amorphous material (Palmer and Cobbold 1964). The crystalline fragments which remain are lamellae, elongated along the b direction, and bounded by recognisable $\{110\}$ and $\{100\}$ faces (Keller and Sawada 1964). This agrees with the behaviour of PE crystallized from solution in paraffinic solvents which are similar to the environment of the melt (Keith 1964). Thus in PE at least, the crystalline units in the melt are very like single crystals.

1.4 Crystallization under Stress

Statistically, a loose coil is the most likely confirmation for a free polymer molecule. Hydrodynamic forces in an agitated solution can help straighten out some molecules, especially the longest ones. In a stirred solution, some partially extended chains act as nuclei, and a large oriented structure, called a 'shish-kebab',

can form (Pennings 1965). The name is descriptive; there is a string of platelets, connected by a central core. The core is more stable, the lamellar overgrowths can be dissolved away. Etching of the core (Willmouth et al. 1968) reveals a composite structure, with extremely fine threads of extended material.

A similar structure is formed from the melt, when it is crystallized under stress (Keller and Machin 1967). Nuclei form along lines in the stress direction, and crystallization proceeds outwards from these lines. The nucleating line has not yet been identified.

1.5 Lattice Structure of Some Polymers

Polyethylene

The structure of PE was determined by C. W. Bunn (1939) from X-ray analysis of rolled sheets. The unit cell is orthorhombic, with $a = 7.40\text{\AA}$, $b = 4.93\text{\AA}$, $c = 2.534\text{\AA}$. Each molecule is extended in a planar zig zag along the c axis, Fig. 1.2. The positions of the carbon atoms in the unit cell are .038, .935, .250; .962, .065, .750; .462, .435, .750; .538, .565, .250. The positions of the hydrogen atoms are not defined by the diffraction pattern, which shows the CH_2 group as a non-spherical scattering unit. The hydrogen atoms in the figure are placed by assuming a tetrahedral bond configuration, and a C-H distance of $1.08\text{\AA}$.

Polyoxymethylene

There was an early structure determination by Sauter (1933).

Fig. 1.2

Unit cell of
Polyethylene

Model of packing of molecules in the unit cell of polyoxymethylene

Fig. 1.3

He used single crystals of POM, hexagonal prisms up to a millimeter across, which formed during slow polymerization of formaldehyde. He found a hexagonal unit cell, $a = 4.45\overset{\circ}{\text{\AA}}$, $c = 17.3\overset{\circ}{\text{\AA}}$, containing nine chemical repeat units ($-\text{CH}_2\overset{\circ}{\text{O}}-$) arranged in a spiral with five complete turns. This work was refined by Uchida and Tadokoru (1967), using a highly oriented POM specimen, prepared by the solid state polymerization of a single crystal of tetraoxane. They found $a = 4.47\overset{\circ}{\text{\AA}}$, $c = 17.39\overset{\circ}{\text{\AA}}$, and the same five turn helical conformation. They describe the atomic positions in terms of cylindrical polar co-ordinates centred on the axis of the helix, so that only one repeat unit needs to be described:

	$r, \overset{\circ}{\text{\AA}}$	ϕ	$z, \overset{\circ}{\text{\AA}}$
C	0.691	0	0
O	0.671	100°	0.966
H	1.507	$-28^\circ 48'$	0.515
H	1.507	$+28^\circ 48'$	-0.515

The analysis also shows that all the helices are of the same hand. An atomic model, fig. 1.3, from Geil (1963), p. 59, shows that the molecules mesh tightly together, and this means the helices are all of the same hand.

Poly-4-methylpentene-1

The structure of this polymer has been determined from solution grown crystals, by electron diffraction from individual crystals, and X-ray diffraction from sedimented mats (Frank, Keller and O'Connor 1959). The unit cell is tetragonal, $a=b=18.66\overset{\circ}{\text{\AA}}$,

Fig. 1.4

$c = 13.80 \text{ \AA}$. The molecular conformation is helical, with seven chemical repeat units to two turns of the helix, fig. 1.4. The packing of spirals with such large side branches is difficult. There are four spirals in the unit cell, and it is believed that :

- 1) their centres are at .27, .27, .27, .73, .73, .27, .73, .73
 - 2) adjacent spirals have opposite hands
 - 3) spirals of the same hand in the unit cell are half a turn out of phase.
- These three points are not certain, and even if they were, the structure is not completely defined, because the configuration of the side branches is unknown.

1.2.1 Spectroscopic Methods

1.2.2 General

1.2.3 2-D Structure of Polyethylene

1.2.4 3-D Structure of Polyethylene

2.3 Scanning Electron Microscopy

2.3.1 General

2.3.2 Solid Substrates

2.3.3 Liquid Substrates

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2.3.5 Dissection

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CHAPTER 2

PREPARATION AND OBSERVATION OF POLYMER SINGLE CRYSTALS

2.1 Preparation of Single Crystals

2.1.1 General

As has been described in Chapter 1, polymer single crystals are formed from dilute solution. To make perfect crystals the crystallization must be slow, and must occur fairly near the melting point of the polymer, so that the molecules are highly mobile. A suitable solvent must have a sufficiently high boiling point, and must be a very poor solvent of the polymer until well above room temperature.

The self-nucleation process, first described by Blundell et al. (1966) has been used to make homogeneous preparations of single crystals. In practice the process involves slowly heating a suspension of polymer crystals until it has almost entirely dissolved, then cooling the suspension sharply to a lower temperature where recrystallization occurs. The process uses the molecular weight distribution which is present in all polymers unless specially prepared. The equilibrium dissolution temperature of a polymer increases with its molecular weight. As a suspension is heated, the lower molecular weight material dissolves and the higher molecular weight material re-orders to form stable crystals. Just before the polymer dissolves entirely, only extremely high molecular weight material remains in suspension. These tiny crystalline residues act as nuclei for the crystallization of the rest of the polymer when the solution is cooled. Crystallization starts on all these nuclei at the same time, so the crystals are of uniform size.

Fig. 2.1 a) 4,500x

Fig. 2.1b) 10,700x

There are many nuclei, so the crystals formed are small and simple.

In fig. 2.1, both the crystals shown were grown at 78°C from an 0.13% w/v solution of PE in xylene. However (a) was cooled directly from near the boiling point, while (b) was cooled to below 70°C , slowly heated to 101.5°C and then cooled to 78°C . (a) is massively dendritic, (b) is much simpler, though it still has many spiral overgrowths. Poor temperature control during heating was the reason for imperfect crystals, such as in fig. 2.1(b). The suspensions had at first been heated in a 2 gallon oil bath, using a Tecam 'Tempunit' controller. To improve temperature control the bath was subsequently covered, and a 'simmerstat' type energy controller put on the heater power supply. The temperature controller was set to the maximum temperature required, and the energy controller was set to give a heater duty cycle which would heat the bath at about 10°C per hour from the starting temperature. The rate of heating fell as the temperature rose, but it was not usually necessary to re-adjust the energy controller to reach the required temperature in reasonable time.

For each solvent and polymer used, a strong solution was made at the boiling point of the solvent as a first step. The hot solution was decanted from the excess polymer and a slurry formed on cooling. The concentration of the slurry was measured by weighing the solid residue of a known volume, dried in an oven. Portions of the slurry were diluted, by up to 150 times, to make

Fig. 2.2a) 10,300x

Fig. 2.2b) 10,500x

the suspensions which were recrystallized as single crystals. The single crystal preparations were on a small scale, 150cc at most, so there was too little for low angle X-ray analysis. Some preparations were made under conditions corresponding to previous X-ray work, to check the thickness determined by microscopy, which is not accurate.

2.1.2 Polyethylene

The starting material was Rigidex type 9, supplied by I. C. I. Ltd., a PE of above average molecular weight, having one branch every 2,000 or more carbon atoms. The commercial product contains 200 p.p.m. antioxidant and a similar quantity of catalyst residues.

First preparations were made following the method of Niegish and Swan (1960). For example; PE 1) A 0.1% w/v solution in trichloroethylene was allowed to cool at about 20°C per hour from the boiling point. Diamond shaped platelets $10\text{-}15\mu$ long were seen in the optical microscope. Transmission electron microscopy showed that the objects which had been easily visible in the optical microscope were complex, and had very many layers, fig. 2.2a. There were some single layer crystals, about 3μ long and poorly formed. Fig. 2.2b shows atypically regular small crystals, which still have some overgrowths, and have projections in the b direction.

Subsequent preparations from xylene were better:

PE 2) A 0.05% w/v solution in xylene heated slowly to 101.8°C and crystallized at 80°C gave the crystals shown in fig. 2.3. About 5μ

Fig. 2.3 15,400x

Fig. 2.4 4,500x

Fig. 2.5 3,750x

long, they have some spiral growths, and many of the effects, noted by Blundell and Keller (1966), caused by crystals growing into one another.

PE 3) Reducing the concentration to 0.008% w/v, reducing the maximum temperature to 100.8°C and crystallizing at 83°C gave the crystals shown in fig. 2.4. These are about 10μ long, almost entirely single layer, and distinct, though there is the usual tendency to clump together on deposition. The lozenges are slightly truncated, with $\{100\}$ sectors subtending 8° at the centre of the crystal.

Several other solvents were tried. Tetrachloroethylene, as used by Reneker and Geil (1960), bromobenzene, and amyl acetate all gave results similar to those already described and generally poorer. One preparation using mixed solvents turned out to be particularly useful.

PE 4) A solution containing 60cc xylene, 40cc bromobenzene and 0.08gm of PE per 100 ccs total was made up, using a PE suspension in xylene. The mixture was heated to the boiling point and then crystallized at 85°C . The resulting crystals, shown in fig. 2.5 are single layer lozenges, of length between 0.5 and 10μ .

2.1.3 Polyoxymethylene

The starting material was Delrin 900, supplied by Du Pont Inc. This is the low molecular weight blend of their range, produced by polymerization of formaldehyde and stabilized with acetyl end groups.

POM 1) A slurry of POM in bromobenzene was diluted 120 times

Fig. 2.6 4,050x

Fig. 2.7 8,250x

to about 0.02% w/v. This was boiled for a minute or so, and crystallized at 125°C. Hexagonal crystals formed, up to 50 μ across, often with some central spiral growths, Fig. 2.6.

POM 2) A 0.015% w/v suspension of POM in cyclohexanol was heated slowly till the suspension cleared, at 151°C, then crystallized at 140°C (Carter and Baer, 1966). These crystals, fig. 2.7 are much smaller (2-3 μ across) and simpler than the previous preparation.

POM 3) A 0.1% w/v solution in phenol was allowed to cool slowly from the boiling point. The solution grew turbid at 62°C. The crystals formed were very complex, though some hexagonal shapes were seen in the optical microscope.

Alsup et al., (1958), gives dissolution and recrystallization temperatures for 1% w/v of a POM in 200 various solvents. *O*-toluidene and *m*-bromotoluene gave excellent single crystals when a solution was slowly cooled. The form and habit of the crystals was very similar to those grown from bromobenzene.

2.1.4 Poly-4-methylpentene-1

The starting material was supplied by I.C.I. Ltd., under its commercial name of TPX.

P4MP, 1) A 0.1% w/v suspension in xylene was heated to the boiling point, and crystallized at 80°C. Large masses of crystalline material precipitated, which were clumps of simple square lamellae, fig. 2.8.

P4MP, 2) A 50/50 mixture by volume of amyl acetate and xylene was

Fig. 2.8 7,060x

Fig. 2.9 2,110x

Fig. 2.10 4,820x

used as a solvent (Barnes and Khoury 1964) at a concentration of 0.02% w/v. The solution was crystallized at 88°C for 12 hrs., then cooled to room temperature. The crystals are large squares with a narrow thinner edge. Spiral growths have formed along the step, and there is occasionally a large central spiral, fig. 2.9.

P4MP, 3) A 50/50 mixture by volume of amyl acetate and bromobenzene containing 0.1% w/v of P4MP was left to cool slowly from the boiling point. The complex crystals formed, fig. 2.10, hardly show the basic square shape.

It was not possible to repeat the work of Morrow et al. (1967), growing crystals by cooling "pentyl acetate" from 165°C to 115°C because the solvent is not adequately described. The usual "pentyl acetate" is "amyl acetate" mentioned above, which strictly speaking is 70% 3-methyl butyl acetate and 30% 2-methyl butyl acetate, and boils at $130\text{--}142^{\circ}\text{C}$. A suspension of P4MP1 slowly heated in amyl acetate dissolved at $\sim 140^{\circ}\text{C}$, and slow cooling did not give good crystals.

2.1.5 Other Polymers

A polyethylene oxide, Carbowax 6,000, supplied by Union Carbide Co., was crystallized by slowly cooling a solution in 2-butoxyethanol, the method described by Kobayashi and Sakaoku, (1965). Very poor crystals were obtained. Using amyl acetate (Lotz 1966) complex but distinct single crystals were obtained on cooling very slowly from 70°C , even at 2.5% w/v. At 0.3% w/v

the crystals were much better and at 0.02% w/v square lamellae 10μ across were formed.

Another attempt to repeat a preparation of Kobayashi and Sakaoku (1965) was made by slowly cooling a solution of Nylon 6 in glycerol. It was a failure. 2-4 xylidene was a better solvent for the purpose, but the crystals, leaf shaped lamellae, were not used.

'Kematal' supplied by I.C.I. Ltd., was crystallized in the same manner as preparation POM, 1). This material is a copolymer of $-\text{CH}_2\text{OCH}_2\text{OCH}_2\text{O}-$ and $-\text{CH}_2\text{CH}_2-$ made by ring opening trioxane in the presence of ethylene. It is very similar to POM; the ethylene addition is a stabilizer.

2.2 Transmission Electron Microscopy

2.2.1 Specimen Mounting

Nearly all the single crystal specimens were mounted on a thin film of evaporated carbon, by allowing a drop of suspension to dry on a carbon coated glass slide. To make the carbon strip off easily onto a water surface, Bradley (1965) suggests adding detergent to the glass, then polishing it to leave a thin film. Siddall, (1960) recommended contaminating the glass in the evaporation chamber with hydrocarbon oil vapour. It was found that reliable stripping could be achieved by using the layer of contamination already present on the slide, merely wiping it with a dry cloth to remove dirt before use. Application and evaporation of organic solvents seemed to make the carbon adhere more firmly to the glass. The film was therefore

stripped first, picked up on another slide and allowed to dry before adding the polymer crystal suspension. Once stripped, the film would nearly always strip again.

The thickness of the carbon film was poorly controlled, as it was deposited in 3 or 4 short bursts from a powerful 30v arc. Consistent results, in terms of electron absorption, were obtained with experience. The published calibration of the optical density of evaporated carbon film as a function of thickness, Cosslett and Cosslett (1957), is unfortunately particularly difficult to interpret in the region of interest, $D \sim 0.1$, thickness $\sim 100 \text{ \AA}$.

For general purposes, and even for high resolution work (Sugihara et al. 1968) a thin specimen support film makes little difference to the image. For the energy loss analysis, and some radiation damage studies, a freely suspended crystal is required. In 1969 a suitable support became available, a fine mesh copper grid kindly supplied by the English Electric Valve Co. The grid has bars 7.5μ across, and square holes 9.2μ across. It is supplied in four inch square sheets. 2.3mm diameter circles were cut out using a punch which was designed to make metal specimen blanks from sheet metal. The delicate mesh had to be supported on both sides by steel foil while it was being punched. The bare grid is mounted in the microscope specimen holder, a drop of polymer crystal suspension is applied and the excess is quickly removed with filter paper. If the crystals are 10μ across or greater, individual crystals are laid across the holes. If the concentration

is high, a crystal mat begins to form. A convenient check on this process is holding the specimen up to a light. The normally sharp cross grating optical diffraction pattern becomes blurred as the holes are covered.

2.2.2 General

All the electron micrographs included in section 2.1 were of crystals sedimented on to a carbon film. They demonstrate the morphological detail available from such preparations when diffraction information is not obtainable - that is, after a good deal of radiation damage. Size, perfection, habit and growth features can all be seen directly, and form the basis of a lot of work. (e.g. Orsini, Marchese and Mazzarella 1963). There is no very fine scale detail in these crystals, and unless it is added, by gold decoration for example (Bassett, Blundell and Keller 1967) there is no need for resolution much better than 100Å.

2.2.3 3-D Structure of PE

Bassett, Frank and Keller (1963 a,b) made a detailed analysis of the 3-D structure of PE single crystals on the basis of optical observation, supported by transmission electron microscopy of sedimented crystals. These authors concluded that the simple truncated lozenges grown from xylene at low supercoolings were non flat based hollow pyramids, the fold surface in each $\{110\}$ sector being (312) (fig. 2.11 a). Some crystals, called 'chair' crystals had one half of the pyramid upside down, connected to the

a)

b) Fig. 2.11

other half by a flattened, distorted, area around the short diagonal, (fig. 2.11b). Only a few values for the size of the $\{100\}$ sectors allow a low index face to be their fold surface, while the crystal is continuous. These sectors merely fit in with the others. It was also concluded that these crystals collapse primarily by tilt. That is, each sector is undeformed and rotates as a unit to give a flat crystal. The other possibility considered was collapse by shear of the molecules along $\underline{c}$.

The truncated lozenges of preparation PE 3) normally collapse as in fig. 2.4, with a triangular pleat along the $\underline{b}$ axis. On a few occasions the crystal collapses by folding across the short diagonal (fig. 2.12). The oblique angle in the centre of the fold is 169° in fig. 2.12 compared to 170° and $170\frac{1}{2}^\circ$ in observations by Reneker and Geil, (1960) and Niegish and Swan (1960) respectively. This angle agrees with the (312) obliquity (Bassett, Frank and Keller 1963b) but is independent of the size of the $\{100\}$ sectors. Collapse of a truncated crystal must be complex. Distorted sector boundaries and wrinkles in the $\{100\}$ sectors confirm this.

Collapse by tilt should give different lattice orientations in each sector. Bassett, Frank and Keller (1963b) showed that the specimen tilts required to bring each sector to the reflecting position agreed with the calculated angles between the reflecting planes and the fold surface in that sector. The same effects were seen in the crystals of preparation PE3), but it was not possible to measure the various angles.

Descriptions and models of pyramidal crystals usually have the apex uppermost. If the crystal is falling through a fluid, apex down is the stable position, as tossing a simple model through the air soon shows. The greater viscosity and density of a liquid may reduce this effect, but then there should be equal numbers, up and down. The two different attitudes have been associated with different collapse features, but this depends on models for the collapse process. There is a difference in the final lattice orientation, as long as collapse is by tilt. If the point was up before collapse, the c axis directions in the various sectors lean inwards to a point above the specimen. Conversely, point down leads to c axes leaning outwards, coming from a point below the specimen. Thus tilting in dark field can distinguish the two attitudes, and identify them if it is known which way up the specimen is in the microscope. The qualitative investigations mentioned above showed all three possibilities; chair, pyramid up and pyramid down. There were not enough observations to say how relatively abundant the three are.

2.2.4 3-D Structure of POM

Some preparations of POM crystals have been seen to be hollow flat based pyramids (Bassett Dammont and Salovey 1964). Since the sectors of sedimented POM crystals diffract uniformly, the collapse must be by molecular shear. There are non reflecting streaks perpendicular to the fold planes associated with relief of the dishing due to lattice distortion. There are often large wrinkles as well, fig. 2.6. The intensity variations of crystallographic

Fig. 2.12 9,280x

Fig. 2.13 11,400x

FIG.2-14.

diffraction across these areas is easily explained by the tilting of the crystal.

In one particular preparation, which had been left for a long time after sedimentation, a much finer texture was visible. Fig. 2.13 shows bright lines, $200 \text{ \AA}$ across, in a dark field image, making closed loops as little as $1,000 \text{ \AA}$ in diameter. Fig. 2.14 shows how such loops can be caused by a dome shaped distortion of the crystal. The plots a)-c) are taken through the distorted crystal perpendicular to the reflecting planes. Moving parallel to these planes the distortion is reduced, so the intensity peaks in fig. 2.14(c) move together. Thus, looking down on the specimen, fig. 2.14(d) shows a contour map of the pimple and the position of the bright ring in this case. When the undistorted crystal is in the reflecting position, (dotted lines (a)-(c)) the bump shows up as a dark circle with a bright line straight across it.

For a perfect crystal $80 \text{ \AA}$ thick, the reflecting position covers $0.05r$. If the true width of the lines is $200 \text{ \AA}$, the radius of curvature of the crystal is $4,000 \text{ \AA}$, not excessive for a foil $80 \text{ \AA}$ thick. If that is the sharpest permissible bend, a dark circle $1,000 \text{ \AA}$ across means the crystal is raised $120 \text{ \AA}$ at the height of the bump. After the crystal in fig. 2.13 had been destroyed by the beam, the area it had covered was spotty. Some of the spots were only $300 \text{ \AA}$ across, and where they were sufficiently well separated, there was a good correlation between the original rings and the remaining spots. The rest of the carbon film was not so spotty, so it seems that the particles were products of the crystal itself, perhaps products of oxidative degradation. These artefacts show that much care in interpretation is always required.

2.3 Scanning Electron Microscopy

2.3.1 General

The scanning electron microscope has an ultimate resolution of about $100 \text{ \AA}$ in the reflection mode, and it is not normally so good. Specimen preparation is easy, the instrument has a great depth of focus, and each micrograph gives an impression of the 3-D structure of the specimen. These advantages have made the instrument particularly useful for bulk polymer structures such as fibres, though there may be artefacts from radiation damage. (Heavens et al. 1970) from electrostatic charges, or from the coatings used to prevent charging. Reducing the beam voltage to 2-3 kV eliminates charging, as the secondary electron emission coefficient exceeds unity, but the source intensity falls, and so the resolution gets worse. The direct presentation of 3-D information makes scanning microscopy worthwhile even on transmission specimens (e.g. Dlugosz and Keller 1968). The PE single crystals characterized in sections 2.1.2 and 2.2.3 were used as test specimens to see if their 3-D structure could be preserved as the mother liquor was removed, and in the radiation flux of the microscope.

2.3.2 Solid Substrates

The radiation enhanced conductivity of the very thin polymer crystals is sufficient to prevent charging when the specimen is in good contact with an earthed support. Crystals deposited from suspension by evaporation of the solvent are pressed closely to the support, so the contact is good, and the support surface must be

very smooth. Glass was found to be best, pieces of microscope slide or cover slip, stuck to the normal specimen stub and then well coated with gold by evaporation.

Single layers have little contrast at 20kV, and their collapse is almost complete. Fig. 2.15, (a) and (b) are a stereo pair of micrographs of a crystal of PE 3), taken at 15kV, with a 6° tilt between exposures. Note the sharp discontinuity along the short diagonal, and the large wrinkles distributed over the crystal. There is no visible change in such preparations during irradiation.

2.3.3 Liquid Substrates

Carbon replicas of single crystals sedimented on to glycerol have shown that the crystals are not completely flattened (Bassett, Frank and Keller 1963b). The saturated vapour pressure of glycerol is low at room temperature. Extrapolation from high temperatures leads to 10^{-5} torr, low enough for electron beam equipment to work in. Crystals were therefore sedimented on glycerol and observed in the scanning electron microscope while floating on a liquid surface. The beam voltage was reduced to prevent charging.

The results were limited but surprising. Limitations were that the specimen would flow away at tilts of over 10° , and at magnifications over 5,000 x, the glycerol boiled. The work was done in periods just before the regular cleaning of the microscope. The crystals were generally flat, surface features stood out well and there were bands of inexplicable contrast across the crystal.

Fig. 2.16 shows all of this. It was taken at 3kV, with only one previous scan for focussing. On subsequent scans, the crystals crumpled up, mostly folding along lines parallel to the short diagonal.

2.3.4 Freeze Drying

A rough calculation based on figures from Odajima and Maeda (1966) indicates that a PE crystal would not collapse far under its own weight. Air pressure and surface tension are much stronger forces leading to collapse. Freeze drying, that is, removing the mother liquor by sublimation instead of evaporation, cuts out both of these strong forces and so might preserve the original structure. Sublimation has been carried out in the microscope itself, by Cross and Cross (1968). Their purpose was not to sublime but to preserve water bound structures. An isolated specimen of low thermal capacity can be kept frozen by a low sublimation rate, and a low sublimation rate allows the instrument to operate. With xylene instead of water this technique was not successful. Although the specimen was thermally isolated on a glass support, it warmed up and the pressure rose above the operating limit.

A separate freeze dryer was constructed, simply a pump, a liquid nitrogen cold trap and a cooled specimen chamber. To get a good rate of sublimation, the solid should be kept near its melting point. The freezing points of the xylene isomers are: o, -25°C ; m, -47°C ; p 13°C . The mixed isomers of the preparation were replaced by p-xylene, and ice was used as coolant. After all signs of the subliming solid had disappeared from the specimen, the

a) Fig. 2.15

b)

Fig. 2.16

Fig. 2.17

pumping was continued for another 12 hours. The specimen was then allowed to warm up, and air was very gradually let in. Examination of these specimens in the scanning electron microscope was disappointing. Only collapsed crystals were seen, for the most part. Either the crystals had all collapsed, or those which did not had so little contact with the substrate that they had blown away. Some objects were seen, too large and complex to have been single layer crystals, fig. 2.17. They agreed very well with the description given by Dr. Priest (1968) of crystals that he had freeze dried in quantity for surface reaction studies - "like cornflakes".

2.3.5 Discussion

Freeze drying did not preserve the structure of PE crystals, but this could have been due to inadequate apparatus. Drying in the microscope with a cold stage, or drying in a commercial freeze etcher, and coating with carbon immediately afterwards without breaking the vacuum, could give good results. The second seems more promising, since the experiments with a liquid substrate showed that an uncoated free crystal would quickly distort in the beam.

Even though the preparation is imperfect, the instrument can give useful information, especially about more complex crystals. Multilayer crystals, PE 1), were deposited from suspension onto an ordinary specimen stub, and were not coated. Fig. 2.18 shows three pictures out of a series of eight taken at intervals of 10° of tilt. Some of the splayed layers of the crystal in the foreground have remained upright. The charging of this part makes it bright,

a) 15° tilt

b) 65° tilt

c) 75° tilt

Fig. 2.18

but does not prevent a clear image forming. It must be very thin, because it appears partially transparent. This means that it was partially transparent to the 20kV electrons of the beam. Radiation damage has given the crystal a crumpled appearance, but the structure has not been destroyed.

Exploratory work such as described in this section should be extended to more complex structure, such as the axialites of Bassett, Keller and Mitsuhashi (1963).

4.2.6 Calibration of Picoammeter

4.3 Dynamic Observation of Decay

4.3.1 General

4.3.2 Polymers: Polyethylene, Total Diffraction

4.3.3 Polymers: Polyethylene, One Beam

4.3.4 Polymers: Polyethylene, Interference

4.3.5 Polymers: Polyethylene

4.3.6 Summary

4.4 States of Damage

4.4.1 Electrons

4.4.2 Heat

4.4.3 Other Ionizing Radiation

4.4.4 Residual Gas

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CHAPTER 3

RADIATION DAMAGE OF POLYMERS

3.1 Damage in the Electron Microscope

In the preceding chapter, mention of changes occurring in the electron microscope has been mostly avoided. The interaction between electron microscope and specimen cannot be neglected. The specimen is in a strong radiation flux, a strong magnetic field, and an atmosphere of $\sim 10^{-4}$ torr of water and hydrocarbon vapours. Even those inert materials which are not directly affected, such as silicon or gold, are covered by a contaminating layer during observation, which reduces resolution. (Ruska 1966). Defects appear in alkali halide crystals (Yagi and Honjo 1967) and vanadium carbide becomes disordered (Venables and Lye 1969) in the electron beam. But covalently bonded molecules such as synthetic polymers are affected much more rapidly and drastically (Agar, Frank and Keller 1959).

If a PE specimen, for example, were to be examined in the electron microscope at a normal beam current and at a magnification of 10,000 x, all the crystalline order would be destroyed in 2 seconds. This loss of order is shown by the changing diffraction pattern. An initial pattern of sharp spots changes to broad spots and to a ring pattern, fading all the time. The sequence is shown in fig. 3.1. The electron dose at the beginning and at the end of each exposure is given in coulombs per square metre, Cm^{-2} . The beam current density at the specimen was 0.18 Am^{-2} , at 80kV. 3.1. a) 35-37,

a) $35-37 \text{ Cm}^{-2}$

b) $53-55\frac{1}{2} \text{ Cm}^{-2}$

c) $70\frac{1}{2}-74 \text{ Cm}^{-2}$

d) $123-130 \text{ Cm}^{-2}$

Fig. 3.1

a) $2.0 - 5.1 \text{ Cm}^{-2}$

b) $5.7 - 9.3 \text{ Cm}^{-2}$

c) $9.6 - 14.5 \text{ Cm}^{-2}$

d) $16 - 26 \text{ Cm}^{-2}$

Fig. 3.2 all at 1,880x, 80 kV

a) Low dose

b) High dose

b) $53-55\frac{1}{2}$, c) $70\frac{1}{2} - 74$, d) $123-130 \text{ Cm}^{-2}$. The initial pattern is made slightly more complex by a $\langle 110 \rangle$ twin. These diffraction patterns come from a PE crystal supported on a fine mesh grid. The diffraction pattern of the usual carbon support film lies just where the ring pattern appears, which is confusing. Fig. 3.1a is a fairly sharp pattern, with no trace of a halo. The diffraction pattern is thus insensitive to the early stages of damage. A dark field image of PE shows the effects more clearly; bright bend contours move, broaden, and dim. Fig. 3.2 is a dark field sequence taken at $680\times$ magnification, with a beam current density of 0.40 Am^{-2} at 80kV. 3.2 a) $2.0 - 5.1$, b) $5.7 - 9.3$, c) $9.6 - 14.5$, d) $16 - 26 \text{ Cm}^{-2}$. The exposures increase, to give a similar brightness on the plate, and the final exposure is taken well before the dose equivalent to fig. 3.1 a).

The micrographs of PE in Chapter 2 were taken after large doses, so the objects are not PE crystals, but replicas of crystals. They appear to be good replicas, but there is no way of telling in detail without reference to pictures of undamaged crystals. When micrographs are taken of PE crystals supported on a fine grid, the extreme nature of the damage is seen more clearly. The crystals distort grossly, buckling and twisting.

The motion is often seen to include considerable expansion along the a axis. Fig. 3.3a shows, in bright field, two crystals of nearly the same orientation supporting each other at the tips. Dark bend contours show that the crystals are not badly damaged. Fig. 3.3 b shows the same scene after a long irradiation; the crystals have pushed into each other. From such sequences it is clear that irradiation

causes little expansion along b and at least 10% along a. The a lattice spacing in PE increases by some 15% on irradiation (Orth and Fischer 1965). Kobayashi and Sakaoku (1965) commented on the lack of visible expansion of their crystals as the lattice spacing increased. It appears that the lack of visible expansion is due to the good adhesion of the crystals to the strong carbon film. When thick PE crystals are irradiated, the carbon film sometimes cracks along the short diagonal, that is, perpendicular to a. (Fig. 2.2, for example.)

In the case of POM, the diffraction pattern decays by losing intensity until it disappears, keeping the same pattern of sharp spots throughout. Only when a cast film or a very thick crystal is irradiated and there is no carbon film support is any final ring pattern visible. The dark field image of a crystal shows a loss of detail similar to that in PE, but the overall brightness drops much more. Fig. 3.4a shows a crystal taken in bright field at 80kV between 1.2 and 2.5 Cm^{-2} . Figs. 3.4b and 3.4c are subsequent dark field images, at 10-17 and 25-34 Cm^{-2} respectively. In bright field the crystal leaves a hardly visible trace of its presence on the support film. Here the replica formed by radiation damage is very poor and any micrograph, such as fig. 2.6, must be taken before damage is complete.

When POM crystals are suspended on a fine grid, the changes on irradiation are very drastic indeed. In a crystal well held by the grid bars on all sides, voids appear and spread, and may cover over half the original crystal area eventually. A crystal not so well supported crumples up completely into a featureless mass.

a) Bright field
 $1.2 - 2.5 \text{ Cm}^{-2}$

b) Dark field
 $10 - 17 \text{ Cm}^{-2}$

c) Dark field
 $25 - 34 \text{ Cm}^{-2}$

Fig. 3.4 1,780x

Obviously if the process of damage could be eliminated or slowed down, the usefulness of electron microscopy for polymers would be greatly increased.

3.2 Measurement of Damage Rates

3.2.1 Visual Criteria

How is the rate of damage to be measured? The changing diffraction pattern is a good measure of damage, as it does not depend on the precise nature of the specimen. Some criterion must be used to describe a definite point in the decay sequence. Kobayashi and Sakaoku (1965) determined the "end point", that is the electron dosage "by which the pattern changed into halo rings". Venables and Bassett (1967) measured times taken for the pattern to become "(a), perceptibly altered; (b), largely amorphous".

If the general form of the decay is exponential with dose, R , as it is later shown to be, then the brightness, Y , of some crystalline effect will be given by

$$Y = A \exp(-aR)$$

$$dY = -Aa \exp(-aR) dR$$

$$\frac{dY}{Y} = -aR \frac{dR}{R}$$

Since the eye compares intensities, rather than giving an absolute measure, the fractional error in brightness measurements, $\delta Y/Y$, will tend to be constant. Therefore the fractional error in dose, $\delta R/R$, is inversely proportional to dose, when measured visually.

Measurements near the end of the decay will be more accurate. With this in mind, the visual criterion used here was that at the measured dose, there should be no further distinct change in the image. This is equivalent to the criterion of Kobayashi and Sakaoku (1965) for those polymers which give a ring pattern on decay, and their name for it is a good one. The criterion is also applicable to POM - it is then the dose at which the pattern becomes invisible - and to the decay of image contrast.

Kobayashi and Sakaoku (1965) took a series of plates as the decay progressed, like fig. 3.1, then somehow interpolated the end point from the series. Direct visual observation was used in this work, as it was found to be individually almost as accurate, and many more observations could be made to give one averaged result.

3.2.2 Dose Measurement

To find the dose, it is necessary to measure the beam current density at the specimen plane, and the time of irradiation. The time is usually between 20 and 200 seconds, so a stop watch is more than adequate. The current density is not so easy to measure. The Siemens microscopes were fitted with an exposure meter and special viewing screens. The meter consists of a picoammeter and a shutter timing device not used in these experiments. One screen is mushroom shaped, with a flat circular top 0.79 cm diameter. The other is the usual 10 cm diameter, with circles scribed at 7.4 and 8.75 mm, but has a hole, off centre and 0.82 cm diameter. In the microscope the two screens fit in a special holder

to lie in a plane, one fitting in the hole in the other. They are well insulated from earth and from each other. The picoammeter has two inputs, one 100 times more sensitive than the other. In normal use the sensitive input is connected to the small screen and the less sensitive input to both screens. Thus the beam current, or some part of it, can be monitored continuously as the microscope is operated, except when photographic exposures are being made.

To find the dose, the measured beam must pass through a defined area on the specimen. If the magnification is known, the small screen or another area in that plane defines an area on the specimen. It is more accurate to set the microscope to the 'selected area diffraction' condition, when an intermediate aperture defines an area on the specimen, and only the objective magnification needs to be known.

It is most convenient to observe the image formed by the electrons as they are collected, but the flat screens cannot be 100% efficient collectors. Some of the incident electrons will be reflected away, some will cause secondary emission, and stray electrons from other sources may arrive at the surface. To reduce these effects to a minimum, a shielded collector is required.

3.2.3 Faraday Cup: Construction

Fig. 3.5 shows a detailed cross section of a faraday cup built to work in the microscope viewing chamber, between the projector and the final screen. The main structure of the cup is a block of nylon. The collector electrode is the inside surface,

FIG.3.5.

coated with colloidal graphite (Aquadag). This coating is keyed well into the nylon by adding 10% formic acid to the suspension, just before brushing it on. The earthed shield is the outer surface of the nylon, coated with colloidal silver. This adheres well to nylon; graphite was chosen for the inner surface because carbon has a lower backscatter coefficient than silver. Two brass caps, both tight push fits onto the nylon, limit the aperture to 4 mm diameter. A very deep groove has been cut in the nylon between the two caps to reduce surface conduction. The outer cap has a fluorescent coating on its top surface, to help in aligning the beam. In use the cup is suspended from a wire loop held in a groove in the outer cap. After baking the cup in an oven for 24 hours the leakage resistance was measured by applying a d.c. voltage across the cup and a microvoltmeter held in series. The microvoltmeter, a Philips model PM2440, has an input impedance of $1\text{ M}\Omega \pm 1\%$, when its most sensitive range is $100\text{ }\mu\text{V f.s.d.}$ The cup and voltmeter act as a potential divider, so that leakage resistance equals $10^6 \times$ applied voltage/indicated voltage. When 120v was applied, the meter deflection was just detectable, less than $1\text{ }\mu\text{V}$, so the leakage resistance between 10^{14} and 10^{15} ohms.

3.2.4 Faraday Cup: Collection Efficiency

Because the collection surface of the faraday cup cannot be completely enclosed, some electrons will escape. The critical dimensions of the cup are shown in fig. 3.6. The solid angle subtended by the hole at the centre of the base, θ , is approximately

$R = 5\text{mm}$
 $l = 15\text{mm}$
 $r = 2\text{mm}$

FIG.3.6.

$\pi r^2 / l^2$. A matt surface acts as a diffuse reflector for electrons, that is, the proportion emitted into any solid angle depends only on the magnitude of the solid angle. If the total reflection coefficient, including secondary emission, is a , the fraction of the incident electron flux that escapes will be $(\pi r^2 / l^2)(a/2\pi)$.

Consider now the second reflections of electrons from the walls of the cup. The ring between x and $x + dx$ has a projected area at O of $2\pi R dx \cos\theta$, and so subtends a solid angle, W , of $2\pi r dx \cos\theta / (R^2 + x^2)$.

$$\cos\theta = R / (R^2 + x^2)^{1/2}$$

$$W = \frac{2\pi R^2}{(R^2 + x^2)^{3/2}} dx$$

The number of electrons arriving at the ring will be $W \cdot a/2\pi$, and if the same reflection coefficient applies, a pessimistic assumption, $W \cdot a^2/2\pi$ will leave. At any point on the ring, the hole in the cup subtends a solid angle of

$$\pi r^2 \cdot \frac{l-x}{\{R^2 + (l-x)^2\}^{3/2}} \cdot \frac{1}{R^2 + (l-x)^2}$$

The number of electrons escaping via this ring will be:

$$\begin{aligned} \frac{\pi r^2 (l-x)}{\{R^2 + (l-x)^2\}^{3/2}} \cdot \frac{W a^2}{(2\pi)^2} &= \frac{\pi r^2 (l-x) 2\pi R^2 a^2 dx}{\{R^2 + (l-x)^2\}^{3/2} (R^2 + x^2)^{3/2} (2\pi)^2} \\ &= \frac{a^2 r^2 R^2}{2} \cdot \frac{(l-x) dx}{\{R^2 + (l-x)^2\}^{3/2} (R^2 + x^2)^{3/2}} \end{aligned}$$

The total number of twice reflected electrons which escape is given by

$$I = \frac{a^2 r^2 R^2}{2} \int_0^l \frac{(l-x) dx}{\{R^2 + (l-x)^2\}^{3/2} (R^2 + x^2)^{3/2}} = \frac{la^2 r^2 R^2}{2} \int_0^l \frac{dx}{\{R^2 + (l-x)^2\}^{3/2} (R^2 + x^2)^{3/2}}$$

The somewhat intractable function under the integral sign is in fact a slowly varying function of x , which on putting $l = 3R$, has a mean value of $0.086.R^{-6}$

$$I = \frac{3R}{4} \frac{a^2 r^2 R^2}{R^6} \times \frac{3R \cdot 0.086}{R^6} = \frac{0.19}{R^2} \cdot a^2 r^2$$

Thus the total fraction of electrons escaping is $0.055 \frac{r^2}{R^2} a + 0.19 \frac{r^2}{R^2} a^2 + \dots$

$r/R = 0.4$ in this case, so the fraction is $0.009a + 0.03a^2 + \dots$

For a light element such as carbon, and with incident electron of 30kV or greater, a is certainly less than 0.5, so the collection efficiency is over 99%, and losses can be neglected.

3.2.5 Screen Collection Efficiency

A finely focussed beam was directed into the cup, then shifted on to the screen by moving the projector pole piece. The cup is wired in place of the small screen, so that on the less sensitive input of the picoammeter, both cup and large screen act as detectors all the time. The ratio between the currents indicated by the two detectors was

found to depend on the beam voltage, but not on the beam current. The exact position of the spot on the screen was not important, and the two Siemens microscopes, 1 and 1A, gave the same results. The collection efficiency of the screen as compared to the faraday cup is shown in fig. 3.7. The efficiency increases with increasing beam voltage, as expected, since the secondary emission coefficient falls. The observed variation is linear, within the limits of random error, and values from the best straight line were used at all times.

For a flat plate, the collection efficiency expected is $1-a$. The lowest efficiency, at 40kV, is 55.5%, so the assumption that $a < 0.5$ in the previous section is justified.

3.2.6 Calibration of Picoammeter

It was found that there was a small potential difference, some $230\mu\text{V}$, across the input terminals of the picoammeter, presumably due to imbalance in the amplifier. When the microvoltmeter, with $1\text{M}\Omega$ input impedance, was put across the input terminals it registered about $200\mu\text{V}$, and the ammeter read about $2 \cdot 10^{-10}$ amps. By putting various resistors in series and parallel with the voltmeter, the resistance presented to the picoammeter was varied from $2\text{K}\Omega$ to $100\text{M}\Omega$, and the indicated current was compared to the calculated current. There was a zero setting error of 4% of f.s.d., and when that was corrected, a similar random error. To cut down reading errors on the meter, the output of the ammeter was connected to a potentiometric chart recorder. The a.c. component of the output, 25mV at 50Hz , badly affected the response of the chart recorder,

FIG.3.7.

FIG. 3-8.

and so had to be filtered out. A double T filter was used, with an extra $3\mu\text{F}$ condenser across the output to remove high frequency components. (Fig. 3.8.) The rejection of this system was over 98% at 50Hz, and the recorder returned to specification when it was fitted. Using the chart as a ten inch meter scale, the random error dropped to nearly 1%. It was concluded that the picoammeter indicated the current collected by the faraday cup to within the limits of measurement.

3.3 Dynamic Observation of Decay

3.3.1 General

The subjective visual basis of the decay measurement described in 3.2.1 seemed to be inadequate considering the possible accuracy of dose measurement. To make quantitative measurements, it is necessary to record the changing diffraction pattern, either by a series of photographic exposures, as Orth and Fischer (1965) or by collecting the electrons at the image plane, amplifying, and recording the signals. The first method retains spatial information, at the loss of some temporal information, since each plate is a time average. The second is more applicable to the later stages of decay, when the spots are weak, and may be diffuse. Indeed Orth and Fischer (1965) took their results only one quarter of the way to the visual end point, in the case of PE. Using the detector system and chart recorder described in section 3.2, traces were made of the variation of the intensity of diffracted beams with electron dose, for POM single crystals and two preparations of PE single crystals.

3.3.2 Polyoxymethylene: Total Diffraction

The microscope was adjusted to give a selected area diffraction pattern with a POM single crystal specimen at the 6mm position. The crystals were mounted on a carbon support film, as were the PE crystals in section 3.3.5. The presence of carbon complicates the results, but preparations with no support film were not stable enough. Pole piece two was selected, to give a camera length of 642mm at 100kV, and adjusted, to make the direct beam fall on the centre of the small screen. The leads to the picoammeter were reversed so that the sensitive input was fed from the large annular screen. The hole in this screen is 8.2mm in diameter, so under these conditions, the ammeter detects electrons scattered from the selected area by an angle greater than $4.1/.642 = 6.4$ mr and less than about $30/.642 = 47$ mr. For comparison, at 100 kV, the first order diffraction of POM occurs at 9.5 mr. It was found that altering the cut off limits, by altering the projector lens current, had no effect on the form of the results. The measured output is therefore referred to as 'total diffracted intensity', I_D .

Fig. 3.9 shows the variation of I_D with radiation dose, on a linear and on a logarithmic plot. The form of the curve is an exponential decay, $I_D - I_2 = B \exp(-R/m)$. At 100kV, $m = 41 \pm 6 \text{ Cm}^{-2}$. The error quoted here and in the rest of this chapter is the total error in the absolute measurement, including that due to magnification calibration. Comparative values are more accurate. The constant B varies at each measurement, because the selected area may not be

FIG. 3.9.

a)

b)

FIG.3.10.

completely covered by crystal, or may be covered by more than one layer. I_1 depends upon the thickness of the carbon film support. $I_2 - I_1$ is due to the amorphous remains of the POM, and for a single crystal this is slight. Typically, for a carbon film about 100 Å thick, I_1 is 16% of the total beam, and $I_2 - I_1$ is 1% for a single layer. The time of the end point as judged visually was marked on the decay curve as it was being drawn. It was found that this point was arbitrary, as there was no special feature in the curve at the end point.

The end point did tend to occur at a particular intensity level, in that a multilayer crystal giving strong reflections appeared to last longer. The exponential decay was slightly slower with these crystals. Choosing only simple patterns of moderate intensity, corresponding to one or two layers the end point occurred at a fixed dose, $70 \pm 7 \text{ Cm}^{-2}$ for 100 kV electrons. However, another microscope in another building gave a different result, $113 \pm 14 \text{ Cm}^{-2}$.

The trace as in fig. 3.9 did not exactly follow the exponential decay for the first part of the irradiation, it always fell short to some extent. The effect is shown up more sensitively by recording the intensity of only one diffracted beam.

3.3.3 Polyoxymethylene: One Beam

The microscope was adjusted to form a low magnification ($\sim 1,000\times$) dark field image of the specimen. The leads to the picoammeter were returned to their normal position, the sensitive input connected to the small screen. Before, the intermediate

aperture selected an area on the specimen and the viewing screen selected a solid angle. Now the objective aperture is used to select a solid angle and the screen selects an area on the specimen. The measured quantity is the average intensity of the dark field image.

Results for $\{10\bar{1}0\}$ reflections are shown in fig. 3.10. The form is quite similar to the total diffracted intensity variation. There is a background due to the carbon film, I_3 , but for the same thickness this is now less than 0.5% of the total beam. The actual value depends on the size of the objective aperture. The effect of the polymer residue, $I_4 - I_3$, is now very slight, 0.03% or less of the total beam. In this experiment the beam current, as measured at the small screen, is about 100 pA, so $I_4 - I_3$ is about 30 fA. The full sensitivity of the amplifier at which 13 fA gives 1% of full scale deflection, is required.

The intensity decays exponentially, with the same decay constant as before, measured in this way as $43 \pm 5 \text{ Cm}^{-2}$ at 100 kV. Again there is an initial period when the decay is not exponential, but the variation is now pronounced, and it is possible to measure the dose, p , at which the exponential form begins. At 100 kV this is $34 \pm 4 \text{ Cm}^{-2}$. Curve A corresponds to the case where the image of the crystal appears generally bright at first. In case B the crystal had just a bright contour across it. The dotted lines in fig. 3.10b show the observed limits of this variation, from a constant intensity, to one decaying exponentially at twice the rate of later decay.

The point p can be picked out quite well visually. As shown in fig. 3.4 the diffraction contrast effects weaken as irradiation proceeds, and after a time they disappear. The process is gradual, but the point after which the crystal seems to diffract with uniform intensity is distinct, and was measured at 100 kV to be $32.5 \pm 4 \text{ Cm}^{-2}$, essentially the same as p measured graphically.

Over ten measurements on a varied selection of crystals, the r.m.s. deviation of the decay constant m and of the end point was $\pm 20\%$. The r.m.s. deviation of p , measured graphically, was $\pm 6\%$. When a similar group of measurements were made on single or double layer crystals only, the r.m.s. deviations of visual measurements of p and the end point were both about $\pm 8\%$. The graphical measurement of m had $\pm 8\%$ deviations, but the accuracy of p , measured graphically, was only slightly better than before. When the whole specimen was tilted, in a tilting holder, p increased markedly and became more variable. Graphical measurements on different microscopes agreed within the limits of error.

Thus with care, visual observations give comparative results substantially as accurate as can be obtained from these intensity measurements, but only the graphical methods give a truly reproducible measure of decay.

3.3.4 Polyoxymethylene: Interpretation

All diffraction contrast of detail is due to slight tilts and rotations of parts of the crystal, due to the strain fields surrounding

a defect or, as in fig. 3.4, due to bends and wrinkles in a thin crystal. A rocking curve is the name given to the variation in intensity of the diffracted beam as a function of crystal orientation, in particular as a function of s , the deviation from the exact reflecting position. For a very thin perfect crystal, thickness t , and when s refers to a tilt of the plane of the crystals, simple (kinematical) electron diffraction theory predicts that the curve has the form

$$I_G(s) = \frac{C \cdot \sin^2(\pi t s)}{(\pi s)^2} \quad (\text{Hirsch et al. 1965, p.158}) \quad (3.1)$$

This has a maximum at $s = 0$, $I_G(0) = Ct^2$ and it is zero at $s = n/t$, n , integer. The half width of the central peak is $1/t$ and the total area under the curve is:

$$2 \int_0^\infty I_G(s) ds = 2Ct/\pi \int_0^\infty \frac{\sin^2 x}{x^2} dx = 2C \frac{t}{\pi} \cdot \frac{\pi}{2} = Ct \quad (3.2)$$

As damage progresses, the POM crystal loses mass. Since falling density has the same effect as falling thickness, (through the extinction distance, section 6.3) whatever happens, the rocking curve broadens out. Thus the image of any detail will broaden as well as lose contrast. When the contrast caused by the largest tilt which is present to an appreciable extent falls below the visibility level, the crystal will appear to diffract uniformly. This occurs at dose p , by observation of the image. At this point, and beyond it, the

rocking curve is essentially flat, so the measured intensity will be the same as the maximum intensity. (Fig. 6.5). Disruption of the remaining crystal will also play a part in this process.

Since radiation damage causes the loss of mass, it is to be expected that $t(R) = t(0) \exp(-\alpha R)$

so the maximum diffracted intensity will vary as

$$C [t(0) \exp(-\alpha R)]^2 = C' \exp(-2\alpha R) \quad (3.3)$$

This agrees with the observed exponential decay after p if $m = 1/2\alpha$.

When the irradiation dose is less than p , the diffracted intensity depends on the orientation distribution in the crystal. If, for example, there is a preferred orientation at a deviation s , $s = 1/2t$ the intensity will at first rise, then fall, as curve B in fig. 3.10. This cannot explain any excess over the exponential decay, such as curve A, for the exponential refers to the perfectly oriented crystal. The fault lies in an over simplified assumption. It has been assumed that only one reflection is excited by the crystal. This is not true; even for a perfect crystal $100 \text{ \AA}$ thick, when the c axis is exactly parallel to the beam, all 6 $\{10\bar{1}0\}$ spots are strongly excited. By the time that the rocking curve has got so broad that the precise orientation of the crystal is immaterial, very many reflections must be excited. The extrapolation of the exponential back to zero dose corresponds to the behaviour of a crystal which is somehow equally well aligned for a large number of reflections. The measured

intensity will exceed this if the crystal is well aligned for the collected beam, and therefore poorly aligned for the others. The total diffracted intensity averages over a number of reflections, and the curve always lies slightly below the extrapolated exponential at low doses.

The fact that the decay of both types of measured intensity has the same decay constant at high doses shows that the spots do not broaden beyond the limits of the objective aperture, even when they are invisible. Since the spots were not always centred in the aperture, this means that they did not broaden at all. The increased value of p when the specimen was tilted was due to the abnormally large deviations which had to be accommodated. Thus the dynamic results point to an exponential loss of mass of POM

$$M(r) = M(0) \exp(-R/2m) \quad (3.4)$$

where $m = 42 \text{ Cm}^{-2} \pm 12\%$ at 100 kV.

The dose p , after which no diffraction contrast can be observed is $34 = 4 \text{ Cm}^{-2}$, so

$$M(p) = M(0) \exp(-p/2m) = M(0) \exp(-34/84)$$

$$M(p)/M(0) = 67 \pm 8\%$$

3.3.5 Polyethylene

First measurements were made on crystals of preparation PE 3), which, as described in chapter 2, have a different orientation in each sector. A decay of the total diffracted intensity as irradiation

FIG. 3.11.

proceeds is shown in fig. 3.11. The intensity due to the completely damaged crystal is large compared to the POM crystal remains, at about $7\frac{1}{2}\%$ of the total beam for a single layer. The basic form is very similar; there is initially a somewhat variable curve which later becomes exponential. The decay constant of the exponential was found to be $40 \pm 6 \text{ Cm}^{-2}$, and it began at a dose of $72 \pm 12 \text{ Cm}^{-2}$ usually, though occasionally much sooner. The visual end point was found to occur at some arbitrary point in the decay, actually at $99 \pm 8 \text{ Cm}^{-2}$. (All at 100 kV). The end point did not vary from microscope to microscope, or with the overall brightness in the way it did with POM. Measurement of the intensity of one diffracted beam gave very variable results, often with sharp changes one way or the other. Watching the dark field image as this occurred, a bend contour shifted suddenly, or swept right across the crystal.

To get results more comparable with POM, it is necessary to have crystals in which deviations of the c axis direction across the collapsed crystal are much less. Such crystals have been grown using low molecular weight PE. Preparation PE4) had this property, using the same high molecular weight starting material as PE3). It may have been degraded in the preparation.

The variation with dose of the total diffracted intensity from PE4) is much more like that of POM. There is little deviation from the exponential decay. The decay constant and end point were the same as for the other PE sample, measured as $42 \pm 4 \text{ Cm}^{-2}$ and $92 \pm 10 \text{ Cm}^{-2}$ respectively. The preparation contains many very small crystals, which with their random orientation produce a

spotty ring pattern. If the intensity of this ring was appreciable, the visual end point appeared to be sooner, at as little as 50 Cm^{-2} , because of the increased background.

Measurement of one beam shows an initial variable period, followed by exponential decay. $p = 43 \pm 5 \text{ Cm}^{-2}$ and $m = 26 \pm 3 \text{ Cm}^{-2}$. The intensity falls more rapidly because the spots are broadening out. There is a deviation from the exponential towards the end of the decay, hardly significant with single layer crystals. The occasional multilayer crystal which diffracts very strongly gives enough signal to pick out this portion as an exponential decay beginning at about 80 Cm^{-2} and having a decay constant of about 50 Cm^{-2} . This corresponds to the decay after the spots have broadened to an arc of almost uniform intensity across the objective aperture. This should happen just before the diffraction end point (92 Cm^{-2}) and the decay should then proceed with the same decay constant as in the total diffracted intensity case (42 Cm^{-2}).

PE does not lose much mass on damage. Instead the lattice distorts and orientation becomes indistinct. The effect of superimposing a number of narrow rocking curves, each slightly displaced and corresponding to the portion of the crystal oriented in a particular direction, is very like the simple broadening that occurs with POM. Direct derivation of a simple exponential is not possible in this case.

3.3.6 Summary

The visual end point has no special significance, and it is

not generally reproducible. Only by selecting simple crystals and similar viewing conditions can reproducible results be obtained by one operator. Intensity measurements show two distinct quantitative features, an exponential decay and an induction period before the exponential decay sets in. The induction period is more accurately reproducible, and can be checked visually, though this may depend on the operator. The induction period does not vary with the crystal thickness and as it is the time over which diffraction information can be obtained, it is a directly useful measure. It is only constant for a given preparation of crystals, and depends on how flat they lie. There is no accurate absolute measure of damage. Numerical results from section 3.3 are summarized in the table.

	End Point	$P(I_D)$	$P(I_G)$	$m(I_D)$	$m(I_G)$	
PE ³	99±8	72±12	-	40±6	-	all in Cm^{-2} and at 100kV
⁴	92±10	-	43±5	42±4	26±3	
POM	70±7	-	34±4	41±6	43±5	

3.4 Modes of Damage

3.4.1 Electrons

Polymeric materials are severely damaged by exposure to ionizing radiations, in an accelerator or a nuclear pile (Little 1954, 1957), and the electron microscope is an intense source for electron irradiation. Measurements of the damage caused in the microscope show that it depends only on the dose, not the dose rate, and that it

varies with the beam voltage in the same way as electron-electron interactions (chapter 4). It is clear that the primary cause of damage in the electron microscope is the ionization caused by electrons. However, other possible causes must not be dismissed.

3.4.2 Heat

The energy absorbed by the specimen from the beam will cause some rise in temperature in the illuminated area, whatever the direct interactions are. It has been considered by Honjo and Watanabe (1958) and Premisela (1968) that this heating could be a major factor promoting damage in organic and polymeric systems, but the effect of irradiation is very different from the effect of heat alone, as was pointed out by Little (1954). Orth and Fischer (1965) showed that heating the specimen, with a hot stage, in the electron microscope caused a sharp rise in the rate of damage, even when the increase was only 30°C . Thus even though heating is not the primary cause of damage, it is necessary to ensure that there is only a very small temperature rise, especially when comparing damage rates.

Consider a circularly symmetric situation (following Goringe, 1966), a uniform specimen in contact with a circular heat sink, radius b and temperature θ_b . If the heat input is $f(r)$ per unit area, then for a ring of radius r :

$$\int_0^r f(r') 2\pi r' dr' = -2\pi r t K d\theta/dr \quad (3.5)$$

where t , K are the thickness and thermal conductivity of the specimen.

Integrating

$$\theta_R - \theta_G = \int_G^R \frac{\int_0^r r' f(r') dr'}{r t K} dr \quad (3.6)$$

If the illuminating spot is considered as having uniform intensity up to radius a , and none at greater radius, then

$$f(r') = k t I, \quad r' \leq a. \quad f(r') = 0, \quad r' > a.$$

where k is the energy loss rate of the electrons and I the beam current density in Am^{-2} . Eq. 3.6 becomes

$$\begin{aligned} \theta_R - \theta_G &= \frac{I k}{2K} \left\{ \int_G^a \frac{a^2}{r} dr + \int_a^R r dr \right\} \quad (R \leq a) \\ &= \frac{I k a^2}{2K} \left(\log_e(b/a) + \frac{a^2 - R^2}{2a^2} \right) \end{aligned}$$

The temperature rise will be greatest at $R = 0$

$$\theta_0 - \theta_G = \frac{I k a^2}{2K} \left(\frac{1}{2} + \log_e b/a \right) \quad (3.7)$$

For an evaporated carbon film, $k \approx 8.10^8 \text{ Vm}^{-1}$ (Lea 1947, 100kV beam) $K \approx 1.6 \text{ J m}^{-1} (\text{deg C})^{-1} \text{ sec}^{-1}$

$$\therefore \theta_0 = \theta_G + I a^2 \cdot 2.5 \cdot 10^8 \left(\frac{1}{2} + \log_e b/a \right)$$

For a 200 mesh grid, the grid bars acting as a heat sink, $b \approx 10^{-4}$ m. With a typical illuminating spot, 50μ across, $a = 2.5 \cdot 10^{-5}$ m, $\ln(b/a) = 1.4$. At most, $I = 5 \text{ Am}^{-2}$

$$\begin{aligned}\therefore \theta_o &= \theta_g + 5.6 \cdot 25 \cdot 10^{-10} \cdot 2.5 \cdot 10^8 \cdot 1.9 \quad ^\circ\text{C} \\ &= \theta_g + 1.5^\circ\text{C}\end{aligned}$$

From fig. 10 in Orth and Fischer (1965), such a difference could increase the decay rate by only 2%. However, the energy loss rate will increase at lower beam voltages, and the effect of the polymer crystal has been neglected. The expression 3.7 is independent of specimen thickness, but only so long as the specimen is uniform. If a crystal in the beam does not extend to the heat sink, the temperature rise will be enhanced. In particular, take a crystal n times thicker than the substrate, with a stopping power $k/2$. In the worst case, the crystal covers the illuminated area exactly, and

$$\theta_o \approx \theta_g + \frac{Ia^2k}{2K} \left[\frac{1}{2} + \log_e \left\{ (1+n/2) b/a \right\} \right]$$

If $n = 1$, and the other conditions are as above,

$$\theta_o = \theta_g + 2^\circ\text{C}$$

and there is an extra $\frac{1}{2}^\circ\text{C}$ for each layer.

Kobayashi and Sakaoku (1965) and Ruska (1966) have mentioned intense heating caused by allowing the beam to fall on part of the support grid. The copper grids are normally 15μ thick, so there is

no transmission. Pessimistically, assume that all the energy of the beam is absorbed. Adapting equation 3.5 to the case of a uniform bar, width d , with heat sinks at $x = \pm b$.

$$\int_0^x f(x') dx' = -d.t.K. d\theta/dx \quad (3.8)$$

If the bar is illuminated between $-a$ and $+a$, with energy in flow I watts m^{-2}

$$\begin{aligned} \theta_x - \theta_G &= \int_b^a \frac{Iad}{tKd} dx + \int_a^X \frac{Ixd}{tKd} dx \\ &= \frac{Ia^2}{tK} \left(\frac{b}{a} - 1 + \frac{a^2 - X^2}{2} \right) \quad (X \leq a) \end{aligned} \quad (3.9)$$

at the centre, $\theta_0 = \theta_G + \frac{Ia^2}{tK} \left(\frac{b}{a} - \frac{1}{2} \right)$

here $K = 385 \text{ } \mu\text{m}^{-1} \text{sec}^{-1} \text{degC}^{-1}$

$$t = 15.10^{-6} \text{ m}$$

$$I = 5.10^5 \text{ j sec}^{-1} \text{ m}^{-2}$$

$$a = 25.10^{-6} \text{ m}$$

Take as the worst case, $b = 0.5\text{mm}$. The conduction due to a

single bar is obviously much less than that due to a grid

$$\theta_0 = \theta_b + \frac{5 \cdot 10^5 \cdot 625 \cdot 10^{-12}}{15 \cdot 15^{-6} \cdot 385} \left(\frac{0.5 \cdot 10^{-3}}{25 \cdot 10^{-6}} - \frac{1}{2} \right)$$

$$= \theta_b + 0.5 \cdot 20$$

$$= \theta_b + 10^\circ \text{C}$$

Thus there may easily be significant heating of multilayer crystals, but for the simpler crystals the temperature rise will be negligible at low beam current densities, even when some grid bar is illuminated.

3.4.3 Other Ionizing Radiation

There is a considerable X-ray flux in electron microscopes, particularly in the high voltage microscope, but the mass thickness of a polymer crystal is so slight that there could be no appreciable effect. Negative ions are also present, sputtered from the filament surface. The number of ions produced depends on the condition of the filament, on the current drawn from it, and most critically on the vacuum around the gun. In the Siemens Elmiskop 1 ^{and} 1A this vacuum is poor because of the sliding seals used for traversing and tilting the gun. Pashley and Presland (1961) found that under normal operating conditions in the Elmiskop 1, defects due to ions appeared in gold foil at $10^7 - 10^9 \text{ cm}^{-2} \text{ sec}^{-1}$. The range of oxygen ions in graphite, calculated from the formulae and tables in

Matthews and Holloway (1967) is about 1μ at 100 kV, only 1% of the equivalent electron range. They might therefore have an effect out of proportion to their number.

Ions are much more massive than electrons, so the lens fields affect them hardly at all, and the irradiated area on the specimen is the geometrical projection of the condenser aperture from the filament. In the Elmiskop 1, this is about $1\frac{1}{2}$ times the diameter of the aperture, 100 or 200μ . Thus if the condenser lenses are used to vary the beam current density, ionic damage should cause a dose rate dependence, noticeable at low dose rates. No dose rate dependence was found, but a combination of condenser and bias adjustment was normally used. When the condenser aperture is removed, the whole specimen is irradiated by ions. With condenser 2 switched off the electron dose rate is very small, and the ion dose rate unchanged. Crystal lifetimes were unaffected by 5 mins exposure.

As a final test, an electrostatic beam shifter, described in chapter 6, was used in conjunction with the beam intensity recorder of the previous section. While the decay of a PE crystal was being recorded, the spot was shifted off the crystal, and the recorder stopped. After a delay of up to ten times the normal decay time, the beam was moved back, and the recorder re-started. The two parts of the curve fitted together accurately. This is in direct comparison with Pashley's work, when shifting the beam away made little difference to the damage rate.

It is concluded from these experiments that there is a

negligible ionic contribution to radiation damage of polymers in the electron microscope.

3.4.4 Residual Gas

Even in a vacuum of 10^{-5} torr, rarely achieved, the specimen surface is struck by large amounts of hydrocarbons and water vapour. Both of these can, in conjunction with radiation, affect the specimen (Heide 1963). The hydrocarbons become damaged while adsorbed and a layer of carbon builds up. Any adsorbed water which is ionized is likely to oxidize and remove carbon. Only a very slow addition of carbon was seen because both effects depend on the beam current density, always very low. There was therefore no need to use the available anti-contamination devices.

3.5 Energy Loss Analysis

To find out more about the inelastic processes causing damage, the electron energy losses in polymer specimens have been studied.

3.5.1 The Energy Analysing Microscope

This is an unusual instrument, able to show how many electrons suffer a specific energy loss in passing through an identifiable small area of a specimen. This particular instrument (fig. 3.12) consists of a Mollenstedt electrostatic energy analyser placed below the final viewing screen of a Siemens Elmiskop 1, and it is described in detail by Gundy (1967). The microscope is unmodified above the final screen. Below it there is a fine slit which selects a line in the specimen. The analyser disperses the electrons perpendicularly

Fig. 3.12

to this slit. The result is an energy loss spectrum, a two dimensional display of energy loss against position along the line in the specimen. To observe and record this spectrum, there is a standard Siemens screen, airlock and plate camera below the analyser. A 35 mm camera in the projector tube of the microscope is used to record a normal image of the specimen. The bulky analyser chamber has required the removal of the control table to a separate trolley, and the addition of extra vacuum pumps.

The slit can be translated and rotated, and its width can be altered, all by external micrometers. The blades of the slit have to be straight and parallel to within 2μ over 2cm. Edges cut from razor blades are used in this instrument, but they must be thoroughly demagnetized.

The analyser electrodes must be at exactly the same potential as the tip of the filament. The filament is heated with a.c., so the analyser voltage is taken from the centre point of two equal resistances in parallel with the filament. This is done in an auxiliary oil tank, which also contains a protective spark gap and the calibration unit. The calibration unit adds accurately known voltages to the analyser electrodes. These voltages simulate a decrease in energy of the electrons, so with no specimen in position, sharp calibration lines are obtained. The unit is at the accelerating potential, inside the oil tank, and so uses a bank of mercury cells to provide the voltages. The E.H.T. must be switched off each time a calibration voltage is switched in or out.

The Möllenstedt analyser is a cylindrical electrostatic lens, designed as a compromise between high dispersive power and high resolution on the basis of calculations by Metherall (1965), and Metherall and Whelan (1966). The standard configuration of this instrument gave a dispersion such that an energy loss of about 70 volts was just recorded on the edge of the plate. It was not possible to fit the beam current measuring device to this special apparatus, the PE crystals themselves were used as dosimeters.

3.5.2 Experimental Procedure

Crystals of PE 3) were mounted on the fine mesh support (section 2.2.1) to cut out the confusing effect of a carbon support film. Three series of experiments were performed.

1) A single crystal was examined in direct transmission at a magnification of 10,000x, with a nominal beam current of 20 μ A at 80kV. The energy loss spectrum was recorded on a slow (N 60) plate to give a good signal to noise ratio. The thin crystal gives a spectrum which is very weak compared to the intense elastically scattered peak. Peak intensities were measured with the Joyce Loebel integrating attachment on the microdensitometer.

2) The 15 μ diameter objective aperture was displaced from the central spot of the diffraction pattern to a region close by. This cuts down the proportion of elastically scattered electrons entering the analyser, so a more even distribution is obtained, giving better detail in the spectrum.

3) The above experiments give information on the damaged polymer only. To indicate the magnitude of the transformation, the direct transmission spectrum was taken quickly. Fast (LN blue sensitive) plates were used, and the specimen was imaged at 1,000 - 1,500x. An exposure of 4 seconds was required, at a beam current which reduced the diffraction pattern to rings in 12 seconds. The apparatus was completely set up, and the specimen moved into the beam, so that no more than 1 or 2 seconds of irradiation elapsed before the exposure started.

Displaced aperture spectra, as in 2), were obtained for comparison from thicker PE, from a single crystal flake of graphite, and from evaporated carbon film, as normally used for a substrate.

3.5.3 Results

The PE crystal scatters 20-30% of the incident electrons inelastically, between 5 and 70eV loss. The variation is mostly due to variations in the projected thickness of the crystal. Since the thickness of a single layer is known to be a constant $120 \text{ \AA}$, tilting and folding can only increase the projected thickness and thus the percentage of electrons scattered. The lower limit, 20%, is therefore taken as the best value.

The displaced aperture spectra of evaporated carbon and of a damaged PE crystal are shown in figs. 3.13 a) and b). The curves are very similar; the extra peak at about 50eV in the evaporated carbon spectrum is due to multiple scattering in a thicker specimen. The spectrum of graphite is also

Fig. 3.13

Evaporated carbon

Fig. 3.13

Damaged PE crystal

very similar with main peak at $26.8 \pm 0.4 \text{ eV}$. The PE spectra obtained at low doses were very noisy, but again showed the same form with similar peak heights as found after higher doses, and a peak energy loss only slightly lower.

3.5.4 Discussion

The energy loss spectra are all so similar that it seems that all the specimens may be well described as different forms of carbon. Burge and Misell (1968) found that the energy losses between 10 eV and 200 eV from films of evaporated carbon could be well fitted by a theoretical curve based on a single loss process, a volume plasma loss at about 25 eV. In this case, the energy loss is proportional to the square root of the participating electron density. If the composition and loss mechanism is the same for a number of specimens, then the peak energy loss will be proportional to the square root of the mass density. Leder and Suddeth (1960) used this relation in experiments on annealing evaporated carbon. Here, using the known density of graphite, the density of the various specimens can be derived.

Material	Energy loss eV	density, gm/cc
Graphite	26.8	(2.25)
Evaporated Carbon	24.5	1.86
Irradiated PE	23.7	1.76
Lightly Irradiated PE	21.3	1.42

The density of crystalline PE is 0.98-1.00, so something is wrong with the last figure. The 'lightly irradiated' spectrum was exposed between 10 and 40 Cm^{-2} approximately. Bahr, Johnson

and Zeitler (1965) irradiated polymers at 10^{-2} Am^{-2} and 75 kV, in an electron microscope analogue which would accept large specimens, and found that:

- 1) Most of the mass loss from PE occurred before 20 Cm^{-2} (about 4%)
- 2) Even at 250 Cm^{-2} , 75% of the hydrogen remained, as well as 90% of the carbon, i.e. $2/3$ of the material is still CH_2 , and $1/3$ CH.

Thus the 'lightly irradiated' PE is damaged, and a different technique will be required in order to find the energy loss spectrum of undamaged PE. A lower magnification is needed, but the single crystals are then too small to give a uniform image of reasonable length on the slit. However alike the spectra, the hydrogen retention makes the calculated densities unreliable. It still seems reasonable to infer a significant density increase between the two stages of irradiation of PE. Irradiation of bulk PE in a reactor causes an initial decrease in density, followed by a rise of at least 10%.

It would be surprising if undamaged PE, which is fully saturated, gave a π band peak, and that is the interpretation of the lower energy peak in carbon. Swanson and Powell (1963) found such a peak in the energy loss spectrum of polystyrene, and found that it shifted as irradiation proceeded. They were using lower beam current densities on a polymer which contains phenyl groups, giving π valence electrons and also more stability against radiation.

3.5.5 Absorbed Dose

Dosage in the previous section has been measured as incident radiation, in Coulombs/sq Metre, but the usual measure is absorbed

energy/unit mass. The unit is the rad. $1 \text{ rad} = 100 \text{ ergs per gram}$. The advantage of this system is that different forms of radiation have very similar effects, when measured this way. To convert from Cm^{-2} to rads for a particular system, the mean energy loss of the primary particle must be known. From the energy loss results, at 80 kV, a PE crystal $120 \text{ \AA}$ thick, density 1, scatters 20% of the incident electrons. The average energy loss as measured was about 30 eV, but this depends on the arbitrary cut off at high losses. Burge and Missell (1968) found the mean energy loss for one excitation to be 30 eV. Rauth and Simpson (1964) took into account the high energy tail of the spectrum, which is due to single electron processes, and found a mean energy loss per inelastic event of $60 \pm 10 \text{ eV}$. Because the specimen is very thin, and the dose refers to energy absorbed in the specimen, the lower value is more appropriate. This point is covered in more detail in section 4.2.

20% lose 30 eV each, mean loss 6 eV in $120 \text{ \AA}$
 1 Am^{-2} , loss is 6 watts m^{-2}

$$\begin{aligned}
 &= 6 \cdot 10^7 \text{ ergs m}^{-2} \text{ sec}^{-1} \\
 &= \frac{6 \cdot 10^7}{120 \cdot 10^{-8} \cdot 10^4} \text{ ergs gm}^{-1} \text{ sec}^{-1} \\
 &= 5 \cdot 10^7 \text{ rads sec}^{-1}
 \end{aligned}$$

$$1 \text{ Coulomb m}^{-2} \equiv 50 \text{ Mrads at } 80 \text{ kV}$$

$$1 \text{ Coulomb m}^{-2} \equiv 42 \text{ Mrads at } 100 \text{ kV} \quad (\propto 1/\beta^2, \text{ chapter 4})$$

This can only be an estimate, with an estimated maximum

error of $\pm 50\%$, and it is based on data from damaged PE. Let us compare the value with other results.

Orth and Fischer (1965) use the semi empirical Thomson Whiddington law:

$$\Delta E = C \cdot \frac{f \cdot x}{E_p}$$

ΔE 'most probable energy loss'
 f density of specimen
 x thickness of specimen
 E_p primary electron energy
 C constant
 $C \simeq 10^{11}$
 (Ardenne 1956)

and they get $\Delta E = 3.2 \text{ eV}$ at $E_p, 40 \text{ kV}$; $x, 120 \text{ \AA}$.

Kiho and Ingram (1968) use the same formula and value for x and get $\Delta E = 1.3 \text{ eV}$ at $E_p, 80 \text{ kV}$.

They discard this value because it is so different from the energy loss peak in carbon, 25 eV. This is a slip, the Thomson-Whiddington law can only refer to the mean energy loss, since the true 'most probable energy loss' is zero for a thin specimen. Thus although the empirical law gives

$$\underline{1 \text{ Cm}^{-2} \equiv 10 \text{ Mrads at } 100 \text{ kV}}$$

Kiho and Ingram (1968) somehow arrive at

$$27 \text{ Mrad} < 1 \text{ Cm}^{-2} < 270 \text{ Mrads at } 80 \text{ kV}$$

$$\text{i.e. } \underline{23 \text{ Mrad} < 1 \text{ Cm}^{-2} < 230 \text{ Mrads at } 100 \text{ kV}}$$

Reimer (1965) quotes

$$\underline{1 \text{ Cm}^{-2} \equiv 40 \text{ Mrad at } 110 \text{ kV}}$$

$$\text{and } 1 \text{ Cm}^{-2} \equiv 70 \text{ Mrad at } 50 \text{ kV}$$

using a single scattering theory.

The usual non relativistic formula for energy loss rate (Burcham, 1963, p.153) must be modified for electron-electron collisions, giving:

$$-\frac{dE}{dx} = \frac{4\pi z^2 e^4}{M_0 v_1^2} N Z \log_e \left(\frac{M_0 v_1^2}{4I} \right) \quad (3.10)$$

I is set at 20 eV.

$$I = 3 \cdot 2 \cdot 10^{-11} \text{ erg}$$

$$Z = 6$$

$$z = 1$$

$$v_1 = 0.548c$$

$$M_0 = 9 \cdot 1 \cdot 10^{-28} \text{ gm}$$

$$e = 5 \cdot 10^{-10} \text{ e.s.u.}$$

$$c = 3 \cdot 10^{10} \text{ cm sec}^{-1}$$

$$N = 5 \cdot 10^{22} \text{ cm}^{-3}$$

for carbon, density 1,

and 100kV electrons

$$\frac{M_0 v_1^2}{4I} = \frac{9 \cdot 1 \cdot 10^{-28} \cdot 0.548^2 \cdot 9 \cdot 10^{-20}}{4 \cdot 3 \cdot 2 \cdot 10^{-11}} = 1 \cdot 7 \cdot 10^3$$

$$\frac{dE}{dx} = \frac{4 \cdot 3 \cdot 1 \cdot 625 \cdot 10^{-40} \cdot 5 \cdot 10^{22}}{9 \cdot 1 \cdot 10^{-28} \cdot 0.548^2 \cdot 9 \cdot 10^{20}} \cdot 6.75 \text{ erg cm}^{-1}$$

$$= 7 \cdot 10^{-6} \text{ erg cm}^{-1}$$

$$= 450 \text{ eV}/\mu$$

mean energy loss in $120\text{\AA}$ is 5.4 eV

$$\text{and } 1 \text{ Cm}^{-2} \approx 45 \text{ Mrads at 100 kV}$$

Thus the Thomson Whiddington law gives a lower result, but other calculations agree very well with the experimental result.

Since the beam current density in the microscope can approach

1 A cm^{-2} , that is, over 10^{11} rads/sec, the 'strong radiation flux' mentioned at the beginning of the chapter is immensely powerful. Only a nearby nuclear explosion could give such a dose rate to bulk material. PE has been used as a dosimeter at nuclear tests (Fydelor 1969).

3.6 Damage Mechanisms

3.6.1 Physics

Most studies of radiation mechanisms have been done with low doses on fluid targets. There the molecules are isolated, and any energy transfer over the ionization potential is likely to result in an ion pair. The expelled electron carries away the excess energy, and it will cause further ionizations nearby before capture if it has enough energy. Ions appear along the track of the primary particle not randomly spaced but in clumps.

No. of ion pairs per cluster	1	2	3	4	>4
% of total number of clusters	43	22	12	10	13

(From Lea 1947)

About half the energy loss is accounted for by ionization, the rest is assumed to excite molecules, but not sufficiently to ionize them.

In solid materials it is not possible to follow the primary processes, and they are different, because the molecules are no longer isolated and the electrons may be excited collectively. In the case of a metal crystal, conduction band electrons are completely delocalized, ionization has little meaning, and well defined collective

excitations called plasmons are excited (Pines 1956). The solid need be neither ordered nor conducting to show collective effects, the requirement is that there must be enough electron interaction to form a band structure.

The results of Burge and Misell (1968) show that in organic materials there should be some delocalized electron excitations, dissipating energy as heat, and perhaps transferring it to inhomogeneities in the crystal, and some clusters of ions and radicals at the randomly distributed localized interaction. The distinction is not really so clear. Alexander and Charlesby (1954), irradiating substituted hydrocarbons, showed that energy could be transferred up to 20 Å along an isolated molecule, and plasmons extend no more than 100 Å around the primary electron path.

3.6.2 Chemistry

Since ions were observed, ("ionizing radiation") chemical effects were at first explained by ionic reactions. Later, free radicals were detected by electron spin resonance, and radical reactions were found to dominate in fluid systems. Radicals are believed to form from excited molecules, perhaps through ionization and recombination.

In solids, radicals tend to lose their reactivity, becoming "frozen in" and ionic lifetimes increase.

There are two typical reactions of irradiated polymers,

cross-linking and chain scission. In the first, chemical bonds are formed between molecules so that the molecular weight increases. When there is on average one link per molecule an infinite network begins to form. This network is observed as an insoluble gel. In the second, the main chains of the linear polymers are broken so that the molecular weight goes down. Polymers are usually characterized as 'cross-linking' or 'degrading' depending upon which reaction is dominant, for there are often components of both. Theoretical calculation of the effects of both reactions is simple in principle, but complex when applied to polydisperse polymer, especially at high doses. PE cross-links, POM degrades, P4MP is intermediate.

Chain scission involves one undamaged molecule, and obeys first order kinetics, so can be explained by localized deposition of energy, whatever the processes. Cross-linking involves two molecules, and is intrinsically more complex. Cross-linking in PE is a commercially useful process and much data has been obtained (Chapiro 1962).

3.6.3 Cross-linking of Polyolefins

The simplest mechanism is the combination of two alkyl free radicals in adjacent positions

Alkyl free radicals are produced by irradiation but the efficiency of cross-linking is too high to be accounted for by random encounters. It has been proposed that the radicals can migrate (Dole and Keeling 1953, Charlesby, Libby and Ormerod 1961) although the energy barrier to hydrogen transfer is about 0.5eV. Alternatively, the proton produced with the first radical was supposed (Miller et al. 1956) to have enough kinetic energy to cause another reaction in the adjacent chain. This idea can only have arisen through thinking in terms of radicals only. An electron is very likely to cause a second reaction, even if it rapidly recombines with the ion. (Samuel and Magee 1953). The clusters described in the previous section are so small ($< 10\text{\AA}$ radius, Bolt and Carroll 1963) that radical combination is extremely likely. In this way cross-link formation would be a single process, with very short lived intermediates.

However, Geymer (1967) irradiating as polymerized polypropylene with γ rays, at 0.8 Mrads/hr., was able to inhibit cross-linking completely with a very low concentration of a free radical scavenger, methyl mercaptan. Further, by irradiating samples to 40 Mrads at -196°C , then flooding with mercaptan he showed that very little cross-linking occurred at low temperature. If the specimen was annealed before flooding, there was a sharp rise in the number of cross-links, then a slow rise, for several hours at room temperature. Cross-links therefore form by a slow interaction of thermal free radicals. The initial rapid formation was visualized by Geymer as being due to the clustered production of radicals.

Kawai et al. (1964, 1965) irradiated a PE crystallized from bulk, and the same material as single crystal mats and as single crystals in suspension. They found that hydrogen and radical production was unaffected, but single crystal preparations did not gel so readily as the bulk. They concluded that there is always a proportion of "ineffective" cross-links, mostly intramolecular, which do not help form a gel, and that all cross-links are concentrated at the fold surfaces of lamellae. This supports a migration model again, but does not allow cross-linking in randomly spaced clusters. The concentration of radicals formed at -196°C and the final concentration of cross-links found by these authors imply that some cross-links form without stable radical precursors. The effect of radical scavengers on PE is to reduce but not eliminate cross-linking (Prober, 1958). Electrons or excitation may migrate as well as radicals (Weiss, 1958). For example, the U.V. absorption of PE single crystals at 4.2°K (George 1969) shows an absorption edge at 8.3 eV, corresponding to the predicted C-C bond excitation energy. This excitation is strongly coupled, and can be easily transferred along the chain.

3.6.4 Application to Electron Microscopy

The electron microscope, with its tiny irradiated volume and enormous dose rate, is particularly unsuited to study of damage mechanisms. Only the changing diffraction pattern can be measured, and this is very indirect. (e.g. Kiko and Ingram, 1968). With regard to the possible reduction of damage, any process should be affected by the voltage of the beam, through the primary electron-electron

interaction. This is dealt with in chapter 4. There is no other way to affect any 'fast' process which may occur. If slow migration of radicals is the mechanism of cross-linking, low specimen temperatures or chemical additives might retard the damage of PE. The effect of temperature on PE in the electron microscope is considered in chapter 5. The stabilizers described by Geymer (1967) are volatile and could not be used in the microscope. The effect of a stabilizer on a 'degrading' polymer was tested. The stabilizer was intrinsic to the polymer, so diffusion is impossible and the speed of the scission reaction is unimportant.

Polyformaldehyde depolymerizes spontaneously.

It was not commercially produced until it was discovered that an acetyl group added to the ends of the chain stabilized it. Thus Delrin carries its own stabilizer, but it is ineffective against radiation. Chain scission produces two new ends, so the whole molecule may 'unzip'. In Kematal (section 2.1.5) the ethylene groups will not 'unzip' and so protect the rest of the molecule. Measuring the decay of the two materials under the same conditions in the microscope, the radiation was $15 \pm 5\%$ less effective on Kematal. This is only a small difference, indicating that the material is removed by many small reactions, rather than a few chain reactions. From eq. 3.3, the initial rate of mass loss of POM is such that all would be removed after 84 Cm^{-2} , or $5.3 \text{ electrons}/\text{\AA}^2$. Using the data on inelastic

scattering in PE, this means that on average 4 monomer units are depolymerized by each inelastic event. In Kematal it is $3\frac{1}{2}$ units. Unfortunately the degree of copolymerization, that is, the stabilizer concentration in Kematal is a trade secret.

4.1 Theory

4.2 20 - 115 kV, Experimental

4.3 100 - 1,000 kV, Experimental

4.4 5 - 25 kV, Experimental

4.5 Conclusions

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Belavitskaya (1957) observed the degradation of amorphous carbon granules C at 50, 55 and 100 kV. She found a strong dose rate dependence which suggests that specimen heating should also have been important. Stepanovsk and Shchegolev (1957) and Shchegolev (1958) used PM single crystals as a model substance for the study of electron effects at 50 and 100 kV, but the results obtained are very different. The effect of the amorphous phase on electron-induced damage is not clear. They found that an amorphous phase in polymers is more resistant to radiation and that the rate of damage is a factor of two.

4.2 Theory

The observed degradation of polymers is a function of the electron

CHAPTER 4

RADIATION DAMAGE AS A FUNCTION OF BEAM VOLTAGE

4.1 Introduction

Professor Kobayashi, in Kobayashi and Sakaoku (1965) and in Kobayashi and Ohara (1966), strongly puts forward the view that the way to reduce radiation damage in polymers is to use electron microscopes with higher accelerating voltages. His papers demonstrate that there is a considerable improvement in going from 100 to 500 kV, but he finds a functional dependence on beam voltage which is difficult to explain theoretically, and the results in the two papers are inconsistent. It was decided to repeat and extend this work as far as possible, to voltages above 500 kV and below 100 kV, where no systematic study has been published.

Belavtseva (1959) observed the degradation of β -carotene and gramicidin C at 40, 60 and 100 kV. He found a strong dose rate dependence which suggests that specimen heating effects may have been important. Stoyanova and Morozova (1963) and Stoyanova (1966) used PE single crystals as a model substance for electron damage studies at 50 and 100 kV, but the main interest of these authors was the effect of the atmosphere in an environmental cell. Incidentally, they found that an atmosphere of helium at 0.3 mm Hg pressure reduced the rate of damage by a factor of two.

4.2 Theory

The observed degradation of polymer crystals in the electron

microscope is ascribed to the secondary chemical effects of electron bombardment, particularly cross-linking and chain scission. The primary effect of the fast electron is to excite electrons in the target, collectively or individually, and there will be competitive processes of de-excitation which do not leave a chemically different end product. If the rates of production and decay of the initial excitations and intermediate products are such that an equilibrium concentration for each is quickly approached, then the damage at a given dose during irradiation will not depend on the dose rate.

At equilibrium, the rate of secondary reactions will be linearly proportional to the concentration of excitations, when they decay singly, or proportional to the square of the concentration when two decay together. In both cases the rate of secondary reactions is simply proportional to the rate of primary reactions, but things are not so simple in the general case. Assume for example that the initial ions can decay in two ways, (a) individually, giving an unchanged product and (b) in pairs, to give cross-links. Then the proportion of channel (b) would increase with increasing rate of primary reactions.

This is presumably what Kobayashi and Ohara (1966) were getting at in paragraph four of their paper, the English is too opaque to be certain. There are two objections to their suggestion. Firstly, the resultant dependence will be a complicated function in general, not the three halves power law they suggest. Secondly, the effect should show up as a dose rate dependence at any voltage, as well

as a voltage dependence at one dose rate. Since no dose rate dependence has been observed in this study, initial excitation and damage can be taken as linearly proportional. We must now connect the initial excitation with the measured dose.

Primary ionization, that caused directly by the collision of a fast electron, can be calculated in a straightforward manner, but it is not the same as the total ionization. If the primary electron transfers a significant amount of energy to the electron which is hit, conventionally 100eV or more, this electron is called a delta ray. The delta ray may cause other ionizations in the material, and these are just as likely to initiate chemical processes as the primary ionizations are. Even if less energy than 100eV is transferred, a second ionization may be caused, very near to the first.

It is usual to assume, reasonably, that the number of ionizations caused by a delta ray is proportional to its energy E_δ . Since the energy lost by the primary electron, W , is just that required for one ionization I , plus E_δ , the total ionization will be proportional to the energy loss W . Since at collision, the primary and the target electron are indistinguishable, the possible range of energy loss is up to half the primary energy E_p . The range causing ionization will be from the threshold I to $E_p/2$. The number of collisions which occur with energy loss W is a known function F of E_p and W , so the total energy loss rate will be

$$\int_0^{E_p/2} F(E_p, W) \cdot W dW$$

Then the total ionization will be proportional to

$$\int_0^{E_p/2} F(E_p, W) \cdot W dW$$

This is true for bulk material, where none of the delta rays escape. Since the projected range of a 50 kV electron in material of density 1 is about 30 microns (Lea, 1947) and the polymer crystals are only 100 Å thick, the expression will not hold in this case. To find how many ions are produced in the specimen per primary ionization would require complex numerical calculation for each value of E_δ and E_p . An estimate can be made from simpler considerations.

The tables of electronic ranges and ionization rates in Lea (1947) relate primarily to body tissues, but these are not too far removed from the polymers studied in terms of density and mean atomic weight. Neglecting any specific structural effects, then, we have from Lea:

E_δ , keV	Range μ	Total number of ions produced by delta ray	Ions produced in specimen by delta ray
0.1	0.0030	5	5
0.4	0.0145	15	7
1.0	0.0535	34	4

The figures in the last column assume that

- 1) the specimen is a sheet 100 Å thick, and the primary collision

occurs at the centre

2) the delta rays have an isotropic distribution, and straight paths.

Allowing 20eV as the energy absorbed by the primary ionization, and calling the number of ions produced in the specimen for each primary ionization f , gives

Energy loss, WkeV	f
0.12	6
0.42	8
1.02	5

by adding the primary ionization to the delta rays in the previous table.

Unfortunately, both the assumptions under heading 2), above, are wrong. In particular, because the primary collision is a two body problem, the angle at which a delta ray is emitted can be specified in terms of E_p and E_δ . Let the initial velocity of the primary electron be v_1 , and its mass m , where $m = M_0(1-v^2/c^2)^{-\frac{1}{2}} = (1-\beta^2)^{-\frac{1}{2}}M_0 = \alpha M_0$. Let the final velocity of the delta ray be v_2 , its initial velocity zero, and its mass the rest mass of the electron, M_0 .

$$\text{Then } E_p = \frac{1}{2} \alpha M_0 v_1^2 \text{ and } E_\delta = \frac{1}{2} M_0 v_2^2$$

From kinematics, by drawing out the vector momentum diagram for centre of mass and laboratory co-ordinates we get directly:

$$\cos \phi = \frac{M_0 v_2}{2} \cdot \frac{1 + \alpha}{\alpha M_0 v_1}$$

where ϕ is the angle between $\underline{v_1}$ and $\underline{v_2}$ in laboratory co-ordinates.

$$\begin{aligned}
 \cos \phi &= \frac{1+a}{2a} \cdot \frac{v_2}{v_1} \\
 &= \frac{1+a}{2a} \left(\frac{2E_\delta}{M_o} \cdot \frac{aM_o}{2E_p} \right)^{\frac{1}{2}} \\
 \therefore \cos \phi &= \left(\frac{E_\delta}{E_p} \right)^{\frac{1}{2}} \cdot \frac{1+a}{2/a} \quad (4.1)
 \end{aligned}$$

Normally $E_\delta \ll E_p$, so $\cos \phi \approx 0$, $\phi \approx 90^\circ$. As the primary beam is usually normal to the specimen plane, delta rays are emitted preferentially in the specimen plane. The number which do not escape and hence the value of f has been underestimated. However, the fact that the path of a delta ray is not at all straight tends to reduce any effect caused by an originally anisotropic distribution. The lower the energy of the delta ray, the more likely it is to have large angle deviations at each collision.

As an example, consider a delta ray of energy 1 KeV. If the primary electron has an energy of 100 KeV, then from eq. 4.1 ϕ equals 89.5° . Now using eq. 4.1 with the delta ray as 'primary' electron, and putting E_δ at 20eV, the minimum energy transfer for ionization, ϕ equals 82° . This itself means little, since the target electron will not get very far, but as $a \approx 1$, the masses of the particles are the same, so the angle between their final directions is 90° . Thus the deviation of the delta ray at each ionization is at least 8° . Assume that all ionizations involve just this deflection, and that they occur

regularly at intervals equal to their mean separation. From tables, in Lea (1947), this is $40\text{\AA}$. Then the magnitude of the deviation after n ionizations will on average be $\sqrt{n} \cdot 8^\circ$. $n = x/40$ where x is the track length in Angstrom units. If the total deviation is never large, x is approximately equal to the distance travelled in the plane of the specimen. Let y be the distance travelled normal to this plane. Then approximating to a continuous deviation,

$$\frac{dy}{dx} = \tan 8^\circ \cdot (x/40)^{\frac{1}{2}}$$

$$y = \frac{\tan 8^\circ}{(40)^{\frac{1}{2}}} \cdot \frac{2}{3} \cdot x^{3/2} + C$$

setting $y = 0$ at $x = 0$, $C = 0$

$$y = x^{3/2}/70$$

Assuming as before that the specimen is $100\text{\AA}$ thick, and the delta ray is formed in the centre, it will escape at $y = 50\text{\AA}$.

$$\text{At } y = 50, x = (50 \cdot 70)^{2/3} = 230\text{\AA}. n = x/40 \approx 6.$$

Thus the new considerations and approximations only alter the estimated value of f for $W = 1.02 \text{ keV}$ from 5 to 7.

The specific direction at which a delta ray is emitted can give a better estimate for f at the high energy end of the delta ray spectrum. For each primary energy, there will be a delta ray, energy E'_6 which on average has just reached the specimen surface

when an ionization event is due. By trial and error, using tables and eq. 4.1 it is found that:

E_p , keV	10	100	1,000
E'_δ , keV	3	6	12

These delta rays will form on average almost 0.5 ions in the specimen. That is, at $W = E'_\delta$, $f = 1.5$, and for $E'_\delta < W < E_p/2$, $1.5 \geq f \geq 1.0$.

A plot of the estimated variation of f with W , for a primary energy of 100 keV is shown in fig. 4.1a, and a plot assuming that no energy escapes in fig. 4.1b. As the plots are log-log, the curves are very different. A better approximation to the curve in fig. 4.1a is to set f equal to a constant, as in fig. 4.1c. Fig. 4.1b is equivalent to applying the energy loss rate formula, and fig. 4.1c to counting primary ionization only. The latter is better, but neither is correct.

The function $F(E_p, W)$ is approximately equal to $\frac{A}{\beta^2 \cdot W^2}$, where A is a constant. (e.g. Burcham, (1963) chapter 5). The different weighting given above to large values of W are thus less important than they might appear.

The energy loss rate formula is

$$\int_I^{E_p/2} F(E_p, W) \cdot W dW \simeq \frac{A}{\beta^2} \cdot \log_e \left(\frac{E_p}{2I} \right) \quad (\text{c.f. eq. 3.9})$$

$\log_e \left(E_p / 2I \right)$ is a slowly varying function of E_p .

FIG. 4.1.

The primary ionization rate is

$$\int_I^{E_p/2} F(E_p, W) dW \approx \frac{A}{\beta^2} \left(\frac{1}{I} - \frac{2}{E_p} \right)$$

$$\approx \frac{A}{I\beta^2} \quad \text{since } I \ll E_p$$

To a first approximation, then the two formulae which seemed so different are both equivalent to C/β^2 . At high primary energies relativistic corrections become important, and the functions diverge. The relativistically correct formulae are given in Bethe, (1933) and are:

$$F(E_p, W) = \frac{2\pi e^4 N Z}{M_0 c^2 \beta^2} \left(\frac{1}{W^2} - \frac{M_0 c^2 (2E_p + M_0 c^2)}{(E_p + M_0 c^2)^2} \cdot \frac{1}{W(E_p - W)} \right. \\ \left. + \frac{1}{(E_p - W)^2} + \frac{1}{(E_p + M_0 c^2)^2} \right) \quad (4.2)$$

Integrating term by term gives

$$\int_I^{E_p/2} F(E_p, W) dW = \frac{2\pi e^4 N Z}{M_0 c^2 \beta^2} \left\{ \frac{1}{I} - \frac{2}{E_p} - \frac{M_0 c^2 (2E_p + M_0 c^2)}{E_p (E_p + M_0 c^2)^2} \log_e \left(\frac{E_p^2}{4I(E_p - I)} \right) \right. \\ \left. + \frac{E_p - 2I}{E_p (E_p - I)} + \frac{E_p - 2I}{2(E_p + M_0 c^2)^2} \right\}$$

$$\int_I^{E_p/2} F(E_p, w) w dw = \frac{2\pi e^4 N Z}{M_0 c^2 \beta^2} \left[\log_e \left\{ \frac{M_0 c^2 E_p \beta^2}{2 I^2 (1 - \beta^2)} \right\} - \left\{ 2\sqrt{1 - \beta^2} - (1 - \beta^2) \right\} \log_e 2 + 1 - \beta^2 + \frac{1}{8} (1 - \sqrt{1 - \beta^2})^2 \right] \quad (4.4)$$

Equation 4.3 has been calculated with I set to 20eV, for values of E_p between 30 KeV and 1 MeV. It was found that at most, the deviation from C/β^2 caused by the last four terms was less than 1%. This is negligible.

Equation 4.4 has been calculated with I equal to 1, 20 and 76 eV, over the same range of primary energies. The value of I has little effect on the shape of the curve, 20eV was used in the curve fitted to the data.

Thus as the beam voltage is altered, the damage at a given dosage should vary as $1/\beta^2$. This is true even if ionization is not a necessary precursor to the damage process, as long as there must be an energy transfer greater than some threshold value.

4.3 30 - 125KV, Experimental

This is the range of beam voltages available on standard transmission electron microscopes. Two microscopes were used

for the most part, a Siemens Elmiskop I and an E.M.6.G. A Siemens Elmiskop IA was also used, a microscope with the same construction as the I, but operating voltages of 50, 75, 100 and 125 kV instead of 40, 60, 80 and 100 kV. The voltages available on the E.M.6G were 30, 40, 60, 80 and 100 kV.

The faraday cup described in the previous chapter was used to measure the beam current, and the visual criterion for degradation was also used. That is, that the diffraction pattern, or in one case the dark field image, should show no further change. The test area was defined by an intermediate aperture, the same defining the area for beam current measurement. This was 2.5 to 4 microns in diameter on the specimen, depending on the microscope used. The objective lens was focussed on the specimen at the selected area diffraction condition, and this gave a fixed objective magnification, which was calibrated with latex spheres. The illumination was adjusted to give a spot 2 to 3 times larger than the test area, so that illumination within the area was uniform, while as little as possible of the rest of the specimen was irradiated.

With this simple technique, between 15 and 25 time measurements were made for each voltage and material. Beam current measurements were made every few minutes throughout the runs. Single crystals of PE 3), POM(1) and P4MP2), mounted on evaporated carbon films were the specimens, and the results are summarised in figs. 4.2 and 4.3. These figures are plots of $\log_e$ (dose required to fulfill damage criterion) against $\log_e(\beta)$. The previous section predicts a damage rate proportional to $1/\beta^2$, and

Polyethylene & Poly-4-methylpentene 1.

FIG. 4.2.

Polyoxyethylene
FIG. 4.3.

so a dose proportional to β^2 is to be expected. The straight lines drawn in the figures have been fitted to each set of points by the least squares method, and the gradients are as follows:

Substance	Microscope	Gradient
PE	Elmiskop 1	2.1
PE	EM6	2.04
PE	Elmiskop 1A	2.2
POM	Elmiskop 1	1.9
POM	EM6	1.8
POM	EM6 (Dark Field)	1.7
P4MP	Elmiskop 1A	1.7

As a whole this is very strong evidence for the damage at a given dose being proportional to $1/\beta^2$ in this range of beam voltages. Although the deviations from $1/\beta^2$ in equation 4.4 are not very great below 100 kV, the PE results are sufficiently accurate to pick them out. A trial and error least squares fit of the curve of eq. 4.4 gives a minimum $\leq 6^2$ twice as great as that obtained on fitting $1/\beta^2$.

An important point is that the results from the various microscopes are so similar. The error bars marked on the figures cover the random errors only, the possible systematic error due to error in the magnification calibration has been ignored to show the shape of each curve. This systematic error could produce a difference in results from two different microscopes of up to 13%.

The observed difference is only 10% in the case of PE and for POM, where the 'end point' is more difficult to judge it is 30%. This shows that the results are a property of the specimens, and not of the microscopes used. Apparent differences between microscopes must be a matter of speed of operation, fluorescent screen efficiency or background light level.

4.4 100-1,000 kV, Experimental

This work was carried out at the U.S. Steel Co. research centre, by Drs. L.E. Thomas and C.J. Humphreys assisted by W.R. Duff. I provided specimens and experimental design to be exactly the same as in the previous section and aided the analysis of results. The beam current density in the high voltage electron microscope was measured with a faraday cup below the projector lens, just as at lower voltages, measuring the current passing through an intermediate aperture. The beam current density was adjusted to a standard 1 Am^{-2} at the specimen plane. As at lower voltages, again, a small selected area, 4 microns in diameter, was used with an illuminating spot three times as big. About ten measurements of the time taken for the diffraction pattern to decay were made at each voltage. There was no trouble in getting results which were reproducible from day to day.

The results for PE and POM are shown in fig. 4.4, the same kind of plot as figs 4.2 and 4.3. Again the best straight lines have been drawn, and the gradients are for PE 2.1, for POM 2.25. This agrees very well with a $1/\beta^2$ dose rate dependence, but it is clear

High Voltage Electron Microscope
FIG. 4.4.

Polyethylene
FIG. 4.5a.

Polyoxymethylene

FIG. 4.5b.

that there is a systematic trend, to higher doses, i.e. to higher resistance to radiation, at higher beam voltages. Attempting to fit the energy loss rate curve gives a much worse result, since the effect of the corrections is to reduce resistance to radiation at high voltages (Fig. 4.5a).

Fig. 4.5 shows the low and high voltage range results together, on a plot of (dose required to fulfill damage criterion) against β^2 . For PE, fig. 4.5a the absolute dose differs by 30%; for POM, fig. 4.5b by 50%. This is more than can be covered by possible errors in magnification calibration, $\pm 15\%$, but since the basis of measurement is a subjective visual one, it is not surprising that two operators who have never met should get different results. The 'dark field end point' has been associated, in section 3.5.2, with a distinct point on the image intensity decay curve. Another operator might not see the end point at the same state of degradation, only the intensity decay gives an objective record which should be fully reproducible.

4.5 5-20 kV, Experimental

To investigate this range of accelerating voltages, a 'Stereoscan' scanning electron microscope, which can operate from 3 to 20 kV, was adapted to work in transmission. A specimen holder to take four 2.3 mm diameter grids was made, with a pin to fit into the scanning electron microscope specimen mount. This pin was angled, so that when the specimen carriage was tilted to about 60° , the grids were horizontal with a clear space below. Into this space was put a detector,

essentially the same as the normal detector, merely a perspex rod and plastic scintillator cap. The rod was longer than normal, and bent to a swan neck to get below the specimen. Since the transmitted beam is hitting the detector, there is no need for a faraday cup, or for the biasing voltages normally used.

The direct beam at high magnifications scans a small area on the specimen, and thus on the detector beneath. The abnormally high current density in this area quickly ruined the scintillator there, giving an uncontrollable dark field effect. A more permanent detector, with a slower response, was made using a fluorescent powder coating for the perspex rod.

At such low beam voltages, even the thinnest specimens show strong absorption contrast with no aperture in the system. With a 100μ diameter aperture between specimen and detector, poor quality bright and dark field pictures of bend contours were obtained with a test specimen of cleaved molybdenum disulphide. Unfortunately it was not possible to move the aperture independently of the specimen, and no specific diffraction effects were seen in polymer crystals. Attempts were made to form selected area diffraction patterns from the polymer and test specimens, by combining the transmission technique with the selected area channelling pattern technique. (Van Essen et al., 1970). The latter was still in process of establishment, and the extra complications were too much. No diffraction patterns were seen, so there could be no direct comparison with the observations of damage made at higher voltages.

a) After 3 scans

Fig. 4.6 5,200x

b) After 20 part scans

The degradation of POM crystals could be followed by the reduction of absorption contrast. Fig. 4.6 shows a crystal which has been heavily scanned on the right hand side. The vertical light band is caused by dwell of the spot before the start of each line scan. The oblique bands could be caused by the changing orientation of the lowest crystal layer, even though there is no aperture in the system. By setting the microscope to scan a line crossing the edge of a crystal, the absorption contrast could be measured directly from the signal level oscilloscope. Measured every tenth scan, it showed an approximately exponential decrease, and the decay rate was, at 10 kV, between 2 and $2\frac{1}{2}$ times the rate at 20 kV. To get this comparative measurement, the amplifier controls were kept at the same setting when the beam voltage was changed. The final condenser was adjusted to give the same size of spot. After each sequence, the average signal level was measured on the meter with the black level control set to zero, and the change was corrected for. It was assumed that the detector efficiency remained constant. Damage still took place at 5 kV and 3 kV, no threshold was detected; indeed the damage at these voltages was so rapid, that the rate could not be properly measured.

4.6 Conclusions

In the range 30 kV to 1 MV the damage at a given electron dosage is, to a good approximation, proportional to the inverse square of the electron velocity ($1/\beta^2$). This is true for both cross linking (PE) and chain scission (POM) polymers. In POM at least

this trend continues down to 10 kV. A deviation from proportionality is just detectable in the results at 0.7 to 1.0 MV. It is impossible to give a really accurate theoretical estimate of the damage to be expected. Too little is known about the production of ions and other excitations by electrons in solid materials, and a polymer crystal in process of degrading to a carbon glass is not a simple substance. Elementary theory says that the electronicinelastic cross section is proportional to $1/\beta^2$, and it has been shown above that much more complicated considerations make very little difference. Replacing the primary ionization density by the total energy lost by the fast electrons gives roughly the same result. Further experiments at very high voltages to investigate the departure from simple proportionality would hardly be justified unless a better theoretical analysis was available.

5.2 Discussion

CHAPTER 5

CHAPTER 5 LOW TEMPERATURE ELECTRON MICROSCOPY OF POLYETHYLENE

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This chapter describes a method for studying the structure of single crystals of polyethylene at liquid helium temperatures by electron microscopy.

5.1 Apparatus

5.1.1 General

A liquid helium cooled specimen stage designed for a Siemens Elmiskop I by Drs. Garling and Valdre in Copenhagen (Garling and Valdre 1963) was available, and was fitted to a Siemens Elmiskop I at this laboratory with little adaptation. The design is shown

CHAPTER 5

LOW TEMPERATURE ELECTRON MICROSCOPY OF POLYETHYLENE

5.1 Introduction

The loss of crystallinity of PE specimens in the electron microscope is attributed to lattice distortion due to cross-linking. If the cross-linking could be impeded, even though the concentration of active species builds up, the damage would be slowed. As described in section 3.6, it is possible that a low specimen temperature, halting the decay or migration of alkyl free radicals, might bring this about.

Kobayashi and Sakaoku (1965), using PE single crystal specimens, found that the radiation damage rate did not vary as the specimen temperature was lowered from 20°C to -150°C . The free radicals are completely stable at -196°C , so this is not a hopeful indication. However, an experiment on cellulosic materials (Honjo and Watanabe 1958) indicated that there was a considerable improvement on cooling the specimen with liquid nitrogen (-196°C).

This chapter describes a study of radiation damage of PE single crystals at liquid helium temperatures in the electron microscope.

5.2 Apparatus

5.2.1 General

A liquid helium cooled specimen stage designed for a Siemens Elmiskop I by Drs. Goringe and Valdre in Cambridge (Goringe and Valdre 1965) was available, and was fitted to a similar instrument at this laboratory with little adaptation. The apparatus is shown

FIG. 5.1a.

Fig 5.16

schematically in fig. 5.1a. The specimen holder A is on the end of two long flexible tubes B. These tubes carry the liquid helium and at the same time allow the specimen to move and to tilt a little. The liquid helium is forced through the system by an overpressure of helium gas applied at C. The cold helium gas at D passes through a control valve and flow gauge (not shown) and is then allowed to escape. Helium recovery from such a small isolated system is uneconomical. Note that there is no liquid nitrogen system. The advantages of simple construction and lower thermal capacities outweigh the lack of thermal shielding.

Fig. 5.1b shows the apparatus in position. A trolley carries the helium storage dewar, the transfer lines and associated vacuum equipment. On the electron microscope, the standard specimen airlock section has been replaced by a new specimen chamber. To change specimens the microscope column is let up to atmospheric pressure, and split below the condenser lenses. The specimen holder is raised out of the objective stage, the transfer line casing is disconnected from the microscope, and the trolley is rolled back.

5.2.2 The Specimen Holder

Detail of the specimen holder is shown in fig. 5.2a. The specimen is located in a diametral plane of the copper ball B. Liquid helium flows around the cavity in the upper hemisphere. The clamping ring T holds the specimen in position, and acts as a contamination and radiation shield. The hole in it is 0.3mm dia., limiting the visible area of the specimen. A thin nylon socket holds the ball

Fig. 5.2

in the stage, and has sufficient 'give' for the ball to be pressed in from above when the stage is in position, entered into the objective lens pole piece. The nylon is coated with colloidal graphite (Aquadag) to prevent charging.

5.3 Measurement of Specimen Temperature

The flexible tubing which transfers the liquid helium has a very large surface area, so when helium is flowing, the cryogenic pumping action rapidly reduces the pressure of residual vapours in that region of the microscope. The ion gauge in the specimen chamber gave a reasonably steady reading of 10^{-5} torr when helium was flowing properly. This was taken as a reliable indication that the lowest temperatures had been reached. However, this does not help to determine what these low temperatures are. In particular, it is difficult to find the temperature of the small area of the specimen which is being illuminated by the electron beam.

The method of Piercy, Gilbert and Howe (1963) was used. This consists of allowing a little pure gas into the microscope specimen chamber, and detecting the deposition of the gas as a solid on the specimen surface. If deposition occurs, the specimen temperature must be less than the equilibrium sublimation temperature of the solidified gas at the pressure in the specimen chamber. The pressure cannot be much below 10^{-5} torr, and it must be below 10^{-3} torr, to allow the microscope to operate. Unfortunately the only suitable gases are nitrogen, sublimation temperature at 10^{-4} torr 31°K , and neon, sublimation temperature at 10^{-4} torr 10°K .

Nitrogen was condensed onto the specimen under the conditions used in these experiments. The nitrogen was recognized by its diffraction pattern, and the polycrystalline layer which condensed could be annealed by raising the beam current. A great increase in beam current caused the nitrogen to sublime. Neon has been condensed on carbon films in the same specimen stage under similar conditions, but not in this series of experiments. Thus the specimen temperatures during the liquid helium runs was above 10°K , but well below 30°K .

5.4 Radiation Damage Experiments

5.4.1 Procedure

These experiments were early ones, completed before a means to measure beam current density was available. There could therefore be no absolute measurement of radiation sensitivity. Measurements were made at low temperature and at room temperature, keeping every other condition of observation as similar as possible.

Changing the specimen temperature took some time, and on warming, the H.T. had to be switched off, because of the sudden release of cryogenically pumped vapours. For the first trials, the illumination controls were left untouched throughout, but the illumination was not sufficiently stable. After this, the condenser lens and the anode bias controller were set to known values, and the microscope was allowed to settle down for 1 or 2 hours. During the experiment, the filament and anode alignment controls were adjusted at intervals, to give centred illumination of maximum brightness.

This procedure was checked by making standard photographic exposures during each run, as the density of the developed plate is proportional to the dosage received. The development was not sufficiently standardized to allow these plates to be used later as dosimeters, but this does not affect the accuracy of comparison. It was found that with frequent adjustment, the beam intensity could be kept within 15% of its maximum.

A small condenser aperture, 50μ in diameter, was used in these experiments to allow a spot of low intensity and small extent to be formed. It was this that made the gun alignment so critical, and made it imperative that the operator should never lean his elbows on the microscope table.

The damage criterion was the visual one used in the voltage dependence experiments in chapter 4, that of no further change in the diffraction pattern. The specimens were PE crystals grown from xylene, as in fig. 2.1b. The beam voltage was 80kV throughout.

5.4.2 Results

The results of each pair of runs could not be combined, except to form an average. However, it was assumed that the actual current on the specimen was proportional to the indicated H.T. current, less the leakage current. The leakage current is the indicated H.T. current when the filament is cold. This allowed consecutive groups of runs to be combined. Later calibration with a faraday cup showed that the assumption was correct, in the range considered. Fig. 5.3 shows the results of two pairs of runs combined on this basis. The factor of interest is the improvement in the lifetime of PE, that is, the ratio of the gradient of the line through the low temperature results and the

FIG. 5.3.

line through the room temperature results. In fig. 5.3 this is 1.6 ± 0.5 . In other sets of runs it was 3.7 ± 2.3 , 2.2 ± 1.1 , and 1.4 ± 0.7 . The average of all eight determinations is 2.2 ± 0.8 .

While these experiments were in progress, results of an almost exactly similar experiment were published. (Venables and Bassett, 1967). These authors observed no systematic variation of damage rate with temperature, and said that the lifetime of PE in the electron microscope is constant between 20°K and 300°K to within a factor of two.

5.5 Discussion

The procedures described in section 5.2 make it clear that from a practical point of view, at least an order of magnitude improvement would be required to offset the difficulty and restrictions of working at liquid helium temperatures. It is clear that for PE, cooling is not advantageous.

To explain why they found that cooling had no effect, Venables and Bassett (1967) suggested that at the high doses used, radical concentration would be high enough to allow cross-linking without migration. Using the dose equivalence derived in chapter 3, crystallinity is lost in PE by 4,000 Mrads. 1 rad produces $1.4 \cdot 10^{12}$ alkyl radicals/gm (Kawai et al. 1965) so at $4 \cdot 10^9$ rads there are $6 \cdot 10^{21}$ radical/gm, or 1 alkyl radical per 7CH_2 groups. This is a high concentration, equivalent to a mean separation of only $15\text{\AA}$, if the distribution is random. Studies which support migration models have used doses 100 times less.

CHAPTER 4 LIMITS OF ELECTRON MICROSCOPY

This mechanism should also apply to cross-linking at room temperature, if the dose rate is high enough. Ormerod (1965) found that on warming PE single crystals irradiated to 10 Mrads, $2/3$ of the radicals decayed in less than 10 mins., the rest took much longer. If cross-linking without migration becomes efficient at 10^9 rads, (fig. 3.1) migration should be an effective competitive process at dose rates below 10^9 rads/5 mins i.e. 3 Mrads/sec or about 0.1 Am^{-2} . Observed damage was found to be independent of dose rate in the range 0.4 to 4 Am^{-2} . (chapter 4), and the beam current densities used in the experiments in this chapter were within this range. The factor of two improvement observed in these experiments cannot be explained on this basis.

4.1 Introduction

4.2 Localized Damage

4.3 Practical Points

4.3.1 Focus

4.3.2 Electron Diffraction

4.3.3 Beam Stops

4.3.4 Microscope Operation

4.4 Summary

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4.5.1 The Present

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CHAPTER 6

LIMITS OF ELECTRON MICROSCOPY

There is a basic limitation on the resolution of detail in polymer crystals. This is due to the limited number of electrons which carry information from the specimen before it has changed from its original state. In this chapter the theoretical limits are worked out for some cases, and compared to practical limits.

6.1 Photographic Response

All information from the electron microscope is normally obtained via a photographic emulsion. Valentine and Wrigby (1964) have shown that emulsions, when they are fully developed, are almost perfect noise-free detectors of electrons. Because the passage of only one electron is required to form a latent image in a grain, the optical density D of the developed emulsion is proportional to the incident electron density I , until saturation approaches (Valentine 1966). Optical density is defined as

$$D = \log_{10} \left(\frac{1}{T} \right) \quad \text{where } T \text{ is the fraction of light transmitted}$$

by the emulsion, measured relative to an unexposed emulsion. For most emulsions, saturation density, with every grain developed, is very high, six or more. $D = 3$, 0.1% transmission, is opaque for most purposes. The relation $D \propto I$ therefore holds accurately over the useful working range, up to densities of two at least.

Consider the r.m.s. fluctuation in the density of an exposed

emulsion, σ_D , due to electron noise. For a perfect detector this will be the only source of random noise. If this fluctuation is measured over an area S on the emulsion, where the mean electron density $I = N/S$, then from Poisson's Law, the fluctuation in N from area to area will be $\sqrt{N}$, and

$$\frac{\sigma_D}{D} = \frac{\sigma_I}{I} = \frac{\sigma_N}{N} = \frac{1}{\sqrt{N}}$$

If an image of area S on the emulsion has a density different from the mean, the fractional difference must be several times the r.m.s. random fluctuation, if the image is to be picked out by eye from noise. A minimum value for this 'several times' has been put at 5 (Valentine 1966), so the detectable limit of fractional density change is $5/\sqrt{N}$. Since $D \approx I$, an object just detectable over noise must cause the number of electrons falling on S to vary by $5/\sqrt{N}$.

6.2 Decaying Crystals

6.2.1 Noise Limits in Bright Field

Consider now the effect of a crystal undergoing damage during observation, assuming that there is an exponential decay in the number of electrons scattered by the lattice, with rate constant h electrons per unit area. Consider a detail, initially scattering a fraction b of the beam incident upon it. After a dose R electrons per unit area, the fraction being scattered will be $b \exp(-R/h)$.

The incident beam current per unit area is dR/dt , so if the

detail is a square of side x , the rate of scattering by the detail will be

$$b \exp(-R/h) \cdot x^2 \cdot dR/dt$$

And the total number of electrons which have been scattered by time t_1 , radiation dose R , is given by

$$N = \int_0^{t_1} x^2 \cdot \frac{dR'}{dt} \cdot b \exp(-R'/h) dt$$

$$= \int_0^R b x^2 \exp(-R'/h) dR'$$

$$\therefore N = h b x^2 [1 - \exp(-R/h)]$$

6.1

The total number of electrons which have been incident on the detail at this time is simply $R x^2$. Neglecting the effect of the substrate, in bright field the background transmits all the electrons. In the image plane an area the same size as the image of the detail will have received $R x^2$ electrons ($N = R x^2$) For the detail to be visible:

$$N \geq 5(R x^2)^{\frac{1}{2}}$$

from 6.1

$$\therefore x \geq \frac{5\sqrt{R}}{h b} [1 - \exp(-R/h)]^{-1}$$

At the limit,

$$x = \frac{5\sqrt{R}}{h b} [1 - \exp(-R/h)]^{-1}$$

Putting $r = R/h$, $s = \frac{62^2}{25} r^2$ and squaring, this becomes:

$$s = r (1 - e^{-r})^{-2} \quad 6.2$$

This is curve A, fig. 6.1. As $r \rightarrow 0$, $s \rightarrow 1/r$; as $r \rightarrow \infty$, $s \rightarrow r$.

There is a minimum of s at $r = 1.25$; $s_{\min} = 2.46$

Therefore optimum dosage is $R_{\min} = 1.25h$, at which the smallest visible detail is $x_{\min} = (62/h)^{1/2}/b$ on a side.

For a plate of given sensitivity, this requires a specific magnification M . If P electrons per unit area are required for correct overall exposure, then

$$R_{\min} = PM^2; \quad M = (R_{\min}/P)^{1/2}$$

Since doses are measured in coulombs per square metre, and resolution in Angstrom units, and 1 electron $\text{\AA}^{-2}$ is equivalent to 16.0 Cm^{-2} ,

$$x_{\min} = (985/h)^{1/2}/b \text{ \AA} \text{ with } h \text{ in } \text{Cm}^{-2}$$

6.2.2 Contrast Limits in Bright Field

The calculations above take no account of contrast. If this is very small, the detail may be quite invisible, despite being separated from noise. Contrast C , defined as $\frac{D_{\max} - D_{\min}}{D_{\max} + D_{\min}}$

is, at low values, approximately equal to $\Delta D/2D$.

FIG. 6.1.

from eq. 6.1

$$C \approx \frac{hb^2x^2[1-e^{-R/k}]}{2Rx^2}$$

$$\therefore C \approx \frac{b}{2} \cdot \frac{1-e^{-r}}{r}$$

This function decreases continuously as r increases.

at $r = 0$ $C = 0.5b$

at $r = 1.25$, $C = 0.28b$

The lowest contrast at which a feature is visible is usually given as 5%. Thus for $b < 0.1$, the feature cannot be seen. If $b > 0.17$, the feature can be seen at the optimum dose. Only when $0.1 \leq b \leq 0.17$ does the resolution depend on the contrast.

This is true for a small detail, but in practice, the feature is usually part of a simple pattern, such as a line. The pattern recognition capability of the human eye means that features of lower contrast, and smaller separation from noise can then be picked out. Thus the limit of visibility depends on the shape and form of the feature as well as its size.

Since the contrast diminishes as dose increases, the dose should be kept as low as possible when forming an image of a detail which is larger than the smallest detectable. The greatest contrast compatible with noise considerations will be on the left hand side of curve A in fig. 6.1. The best conditions will lie between this and

the condition of maximum separation from noise, curve B in fig. 6.1, in the shaded area.

Curve B is obtained as follows:

let the separation be E . E is to be maximized.

$$E = kbx^2(1 - e^{-R/k}) - 5x\sqrt{R}$$

$$\frac{dE}{dR} = bx^2e^{-R/k} - \frac{5x}{2\sqrt{R}}$$

$$\frac{dE}{dR} = 0 \quad \text{at} \quad be^{-R/k} = \frac{5}{2x\sqrt{R}}$$

or in terms of r and s , at

$$s = \frac{2r}{4r}$$

This is curve B.

6.4

The maximum value of E , which corresponds to the right hand portion of the curve, becomes positive where it intersects A. The left hand part corresponds to a minimum which is always negative.

6.2.3 Dark Field

The background in a 'dark field' image is very dark, so neither contrast nor background noise should be real limits to resolution. First calculations, assuming no background at all, predicted that an

optimum resolution of $1\text{\AA}$ would be obtained at zero dose and zero magnification. Adding a constant background, such as might be expected from a carbon support film, makes the form of the calculations very similar to those for bright field. If the constant background scattering is the same as that due to the totally damaged crystal, to within an order of magnitude, the optimum dose is near h , $(0.9-1.3h)$, the optimum resolution gets better, and the required magnification gets less.

6.3 Extinction Distance

6.3.1 Definition

Before the preceding formulae can be worked out for any real case, it is necessary to have a value for b . This is equivalent to calculating the image contrast for a specimen which is not affected by the beam. As a starting point for such calculations, an accurate value is needed for the extinction distance, written t_g . This parameter, which has the dimension of length, is a measure of the strength of the interaction which produces a diffracted beam with wave vector $\underline{g}$.

In the kinematical theory of electron diffraction, it is assumed that the energy of the incident beam of electrons is not significantly reduced by the process of diffraction, and scattering of the diffracted beam is neglected. At the exact Bragg reflecting position, the waves scattered from successive planes are exactly in phase, and the kinematical theory predicts that the intensity of the diffracted beam increases as the square of the thickness of the crystal. When the

crystal is not exactly at the reflecting position (deviation s) the phase difference between successive planes builds up, so that the amplitude of the diffracted wave reaches a maximum at a certain depth, falls to zero, and continues to oscillate with a period $1/s$. If the deviation is such that the maximum amplitude equals the amplitude of the incident beam, the depth where the first zero occurs, $1/s$, is called the extinction distance.

If the deviation is less than $1/t_g$, the maximum amplitude of the diffracted beam will be greater than 1, and will occur at a depth $> t_g$, according to kinematical theory. The theory will thus hold only at large deviations, or for crystals much thinner than t_g . The dynamical theory, which takes account of scattering of the diffracted beam, gives formulae in which s is replaced by $s_{\text{eff}} = (s^2 + 1/t_g^2)^{1/2}$. At $s = 0$, $s_{\text{eff}} = 1/t_g$.

For a perfect crystal with no absorption at $s = 0$ the predicted diffracted intensities are shown in fig. 6.2. The two theories differ by 12% for a crystal $t_g/4$ thick. This thickness is usually taken as the upper limit of application of the kinematical theory at $s = 0$.

For any given reflection and unit cell, t_g can be calculated from the following formula, derived from first principles by Hirsch et al. (1965).

$$t_g = \pi V_c \cos \theta / \lambda F_g$$

V_c unit cell volume

θ angle of reflection

($\cos \theta \approx 1$)

λ electron wavelength

F_g structure factor for reflection g .

FIG.6.2.

$$F_g = \sum_j f_j(\theta) e^{-2\pi i g \cdot r_j}$$

$f_j(\theta)$ are the atomic scattering amplitudes of atoms at r_j , and the sum is over all atoms in the unit cell. A computer programme to calculate t_g , due to M.J. Whelan, was adapted for use on a KDF9. This programme (Appendix 1) accepts the data for atomic positions in terms of fractional indices of the unit cell, and uses the analytical representation of $f(\theta)$ due to Smith and Burge (1962). The programme applies to all crystals. The atomic scattering amplitudes are generally the main source of error in calculating extinction distances. Fourier analysis based on X-ray diffraction results have shown that the electron density map of molecular crystals is often poorly represented by atoms at the nominal positions. (Bunn 1939, Kasai and Kakudo 1968).

6.3.2 Extinction Distance, Results of Computation

The atomic coordinates given in chapter 1 were used for PE and POM. Those for POM had to be transformed into fractional indices of the unit cell.

$$X = \frac{r \sin \theta}{a}, \quad Y = \frac{r \cos(\theta - \pi/6)}{a}, \quad Z = z/c$$

Results are given in the table which contains values for most of the reflections seen and indexed in the electron microscope, from single crystals or cast films. Results for PE in Holland et al. (1965),

corrected to 100 kV are tabulated to the right of the new results. The discrepancies, about 10%, are probably due to different atomic scattering factors being used. Ten years ago, the extinction distances for $\{110\}$, $\{200\}$ in PE were estimated to be $1,000 \text{ \AA}$ (Agar, Frank and Keller 1959)

1) Polyethylene at 100kV

Reflection	$t_g^{\circ} \text{ \AA}$		Reflection	$t_g^{\circ} \text{ \AA}$
110	870	975	011	1,880
200	915	960	111	3,220
210	3,720	-	201	2,080
020	1,770	1,580	211	2,820
120	4,380		311	3,120
310	2,530		002	1,870
220	4,950		112	2,960
400	2,160		(100	330,000)
320	3,650			

2) Polyoxymethylene at 100 kV

Reflection	$t_g^{\circ} \text{ \AA}$	Reflection	$t_g^{\circ} \text{ \AA}$
$10\bar{1}0$	812	$10\bar{1}5$	1,840
$11\bar{2}0$	1,110	$20\bar{2}5$	2,050
$20\bar{2}0$	5,230	$11\bar{2}5$	2,400
$12\bar{3}0$	4,100	$12\bar{3}5$	2,740
$30\bar{3}0$	10,200		

The description of P4MP in chapter 1 was assumed to be correct,

and an arbitrary, symmetrical, arrangement of the branches was also assumed. The arrangement conformed with usual bond angles and lengths, and branches of adjacent chains seemed to fit together quite well. The atomic coordinates were measured from a drawing of one spiral. Computation considering only the 168 carbon atoms in the unit cell, and not the 336 hydrogen atoms, gave the following results.

Reflection	$t_g^o A$	Reflection	$t_g^o A$
100	6,500	120	20,000
200	2,100	420	33,000
300	24,000	600	8,200
400	33,000		

The diffraction pattern from a thin crystal, fig. 6.3 shows that $\{100\}$ and $\{300\}$ are not seen, and both $\{400\}$ and $\{420\}$ are much stronger than $\{120\}$. The computed results do not agree with this, so it seems that the guesses of the structure were not good. There is insufficient data to work back to the correct structure.

From the original equation, 6.3, the extinction distance is inversely proportional to the electron wavelength λ and to the structure factor F_g . These terms depend on the electron energy and the results so far have been calculated for 100 kV.

$$F_g \propto m \quad m, \text{ electronic mass}$$

$$\text{and } \lambda = h/mv \quad v, \text{ electronic velocity}$$

$$F_g \lambda \propto 1/v$$

$$\text{and } tg \propto \beta \quad (\beta = v/c)$$

6.4 Numerical Values

6.4.1 Crystal Fragment

With the results of the previous section, and those of chapters 3 and 4, it is possible to calculate values for the parameters described in section 6.2. Consider a small square block of POM crystal, supported on a film of negligible scattering power, and correctly oriented for reflection into $(10\bar{1}0)$. If other reflections can be neglected, and the crystal is $85\text{\AA}$ thick, then the following table applies.

E_p , kV	10	20	50	100	200	500	1,000
t_g , $\text{\AA}$	288	402	610	810	1,030	1,274	1,390
t/t_g	.295	.212	.139	.105	.083	.067	.061
b	.66	.38	.18	.11	.067	.043	.037
C , %	18.5	10.6	5.1	3.1	1.9	1.2	1.0
h , Cm^{-2}	5.3	10.4	24	42	68	104	160
$R_{\min}$, Cm^{-2}	6.6	13	30	53	85	130	200
$x_{\min}$, $\text{\AA}$	21	25	35	44	57	71	67

h , the decay constant of section 6.2 has been set equal to m , the experimental decay constant of chapter 3, at 100 kV. The values at other voltages are derived from the experimental data in chapter 4. Their deviation from the trend at very high voltages causes $x_{\min}$ to fall to $67\text{\AA}$ at 1MV.

If $h \propto \beta^2$ were strictly followed, since $b \propto 1/tg^2$ and $tg \propto \beta$

$$x_{\min} \propto h^{-\frac{1}{2}} b^{-1}$$

$$x_{\min} \propto \beta.$$

According to the calculated values of contrast, C , a POM crystal should not be visible at all at beam voltages much above 100 kV, and between 50 and 100 kV, the minimum size of a resolvable fragment depends on contrast considerations. As mentioned before, pattern recognition makes this calculation pessimistic, but the two beam approximation will also cause C to be underestimated.

Under the development conditions normally used in this laboratory, 3 mins in PQ Universal, diluted 1 + 9, Special Lantern Contrasty Plates require the following doses for optical density $D = 1$.

E kV	P , electrons μ^{-2}	P , Cm^{-2}
50	1.18	$19 \cdot 10^{-8}$
75	1.60	$26 \cdot 10^{-8}$
100	1.95	$31 \cdot 10^{-8}$
125	2.56	$41 \cdot 10^{-8}$

$M = (R_{\min}/P)^{\frac{1}{2}}$ so at 100 kV, $M = 13,000$. The voltage range is not wide enough, but it indicates that $P \propto E$. The photographic processes arise through the energy losses of the fast electrons, so $P \propto \beta^2$ ($P \propto E_p$, non-relativistically) is to be expected. This means that M does not vary with voltage. Below 20kV, the electrons do not fully penetrate the emulsion, and photographic recording is not efficient. For the other plates tested, LN Blue sensitive and N60 photomechanical, $P(100\text{kV})$ is 0.075 and $6.7 \text{ e}\mu^{-2}$ respectively.

Cox (1961) has given a detailed 2-beam dynamical theory

For these plates M would be 65,000 and 7,000. Compare this with the table in Valentine (1965) where, using slightly different criteria and data he calculates the minimum magnification required to show reliably above grain $10\text{\AA}$ random spots of metal. Correcting his figures to 100 kV, and $44\text{\AA}$ spots:

Emulsion	Mag (Valentine)	M	$M \cdot x_{\min}^{\circ}, \mu$
N60	5,000	7,000	15
SLC	11,000	13,500	60
LN	31,000	65,000	290

In each case M is in the region of Valentine's minimum magnification for resolution of a stable object. The last column of the table gives the size of a $44\text{\AA}$ object in the image plane.

For PE, assume a background of scattering power the same as a completely misoriented crystal, so that only crystalline diffraction contributes to the image contrast. A crystal fragment $120\text{\AA}$ thick, imaged in bright field and diffracting into (110) gives almost exactly the same results as those in the table for POM. For example, at 100 kV, $R_{\min} = 50 \text{ Cm}^{-2}$, $x_{\min}^{\circ} = 29\text{\AA}$.

The dark field calculations depend on too many experimental variables for detailed work to be worthwhile, but using reasonable values referring to the PE crystal fragment at 100 kV, $R_{\min} = 44 \text{ Cm}^{-2}$, $x_{\min}^{\circ} = 12\text{\AA}$, $M = 2,500 \times$ (for S.L.C. plates). The voltage dependence of $x_{\min}^{\circ}$ is the same as in bright field.

6.4.2 Moiré Fringe Patterns

Gevers (1962) has given a detailed 2-beam dynamical theory

of the form and contrast of moiré patterns and the effects can be quite complex. In polymer crystals, moiré patterns arise from rotational misalignment of the layers in a multilayer crystal. Taking the simplest case, a bi-layer crystal, two facts allow some simplification.

- 1) The total thickness is much less than the extinction distance, except at very low voltages.
- 2) The two layers are the same thickness.

If I_T and I_G are the transmitted and diffracted intensities at the lower surface of a bilayer crystal, and I'_T and I'_G refer to one layer only,

$$I_T = (I'_T)^2 + (I'_G)^2 + 2I'_G I'_T \cos 2\pi (x-x_0)/\lambda$$

(eq. 22, Gevers 1962)

$$\text{Thus } (I_T)_{\max} = (I'_T + I'_G)^2$$

$$(I_T)_{\min} = (I'_T - I'_G)^2$$

Neglecting absorption, $I'_T = 1 - I'_G$

$$\therefore (I_T)_{\max} = 1$$

$$\text{and } (I_T)_{\min} = (1 - 2I'_G)^2$$

$$(I_T)_{\min} = 0 \quad \text{at} \quad I'_G = \frac{1}{2}$$

$$I'_G = \frac{1}{(s_{\text{eff}} t_g)^2} \sin^2(\pi t s_{\text{eff}}) \quad t, \text{ thickness of 1 layer}$$

At $t > t_g/4$, $I'_G = \frac{1}{2}$ at $s_{\text{eff}} > 1/t_g$, $s > 0$

At $t = t_g/4$, $I'_G = \frac{1}{2}$ at $s_{\text{eff}} = 1/t_g$, $s = 0$

At $t < t_g/4$, $I'_G < \frac{1}{2}$,

and I'_G is max at $s_{\text{eff}} = 1/t_g$, $s = 0$

$$\text{Contrast visibility, } \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} + I_{\text{min}}} = 2I'_G (1 - I'_{G'})$$

Thus for $t < t_g/4$, best contrast is at $s = 0$

$$\text{and } I'_G = \sin^2(\pi t/t_g)$$

$$\approx (\pi t/t_g)^2$$

$$\leq 0.2$$

$$(I_T)_{\text{min}} \approx 1 - 4I'_G$$

Since $I'_G \propto t^2$, in this approximation the maximum diffracted intensity is the same as that from a single crystal $2t$ thick. The equations (23) in Gevers (1962) show that the absolute position of the fringes does not change as t/t_g changes if $s = 0$. As there is a periodic structure with a sinusoidal variation of intensity, the visibility criterion should be altered. Setting the required signal to noise ratio to 2 instead of 5 is equivalent to allowing a phase spread of π (Hirsch et al. 1965, p. 336). Modifying the results for a POM crystal fragment in this way gives, at 100 kV, $R_{\text{min}} = 53 \text{ Cm}^{-2}$,

Fig. 6.3 Diffraction from P4MP crystal

a)

b)

$x_{\min} = 4\frac{1}{2}\overset{\circ}{\text{Å}}$. Applying the same calculations to a PE bilayer,
 $x_{\min} = 3\overset{\circ}{\text{Å}}$.

Resolution of 'moiré patterns' of period $< 5\overset{\circ}{\text{Å}}$ is the same as resolution of the lattice planes themselves. For thin crystals, $x_{\min} \propto 1/t^2$, so the limits for a periodic structure in one crystal layer are POM, $18\overset{\circ}{\text{Å}}$, PE, $12\overset{\circ}{\text{Å}}$ (100 kV).

6.4.3 Discussion

The resolution of moiré patterns is not limited by the decay of the crystals, and the lattice fringes might be resolved from bilayer crystals of PE and POM. This has certainly not been observed experimentally. Agar et al. (1959) reported a moiré pattern with $40\overset{\circ}{\text{Å}}$ spacing in PE. The micrographs were taken in bright field at 5,000x and 80 kV. The exposure was 8Cm^{-2} , i.e. $r = 0.25$. These non-ideal conditions increase $x_{\min}$, but only to $5\overset{\circ}{\text{Å}}$. No one has reported better resolution since, authors (e.g. Bassett 1964) have concentrated on clear, informative, patterns.

There are many good reasons for not attaining the theoretical limit, and one is the assumption in the theory of perfect image stability. Imaging crystals of preparation POM 2) at 13,000x in bright field, exposure 50Cm^{-2} , no moirés finer than $100\overset{\circ}{\text{Å}}$ were recorded. Fig. 6.4 shows two micrographs taken of the same area at 13,000x, 80 kV, with exposures of 22Cm^{-2} each. Under these conditions, the periodicity detectable above noise is larger than the minimum. For exposures from r_0 to r , rather than 0 to r ,

equation 6.2 is corrected to:

$$s = (r - r_0) / (e^{-r_0} - e^{-r})^2$$

For the second exposure, $x/x_{\min}$ is only 2, and since the crystals of this preparation are 120Å thick (Carter and Baer, 1966), theoretical resolution is still around 5Å.

Both pictures are underexposed, but show moiré patterns of 1-200Å spacing. (a) shows a pattern of parallel fringes, (b) is more confused, but a hexagonal network is visible. This means that only one set of planes is contributing in (a), but all are in (b). It may be due to bending, but the trend is always towards better orientation for more beams. It seems more likely that the relaxation of diffraction conditions which occurs as the crystal becomes damaged causes the image to change. The prediction of a stable image in the last section depended on considering two beams only, so that a crystal could be perfectly oriented. The two model images discussed so far were chosen for their stability.

6.5 Localised Detail

As described in section 3.3.4, the image of a crystal defect or of a bent crystal will depend on the rocking curve and on the local variation of orientation. Fig. 6.5 shows the rocking curve of a perfect crystal at crystal thickness t , $t = t_g/10$ to $t_g/40$ from $s_{\text{eff}}^t = 1$ to $s_{\text{eff}}^t = 10$. At $R = R_{\min}$, $t \approx t_g/2$ so the curve has

FIG.6.5.

FIG.6.6.

broadened considerably. A photographic exposure integrates over this variation to give an intermediate result. If the rocking curve is simplified to a triangular peak:

$$I = Ct^2(1 - st) \quad st < 1$$

$$I = 0 \quad st > 1$$

curve 1 on fig. 6.6, then putting $t = t_0 \exp(-R/2m)$ and integrating from 0 to R ,

$$I = mCt_0^2 \left[\left(1 - e^{-R/m}\right) - \frac{2st_0}{3} \left(1 - e^{-3R/2m}\right) \right] \quad st_0 < 1$$

$$I = mCt_0^2 \left[\left\{ \left(\frac{1}{st_0}\right)^2 - e^{-R/m} \right\} - \frac{2st_0}{3} \left\{ \left(\frac{1}{st_0}\right)^3 - e^{-3R/2m} \right\} \right] \quad \begin{matrix} st_0 > 1 \\ st_R < 1 \end{matrix}$$

$$I = 0 \quad st_R > 1$$

This function is plotted for $R = \infty$ and $R = R_{\min}$ in Fig. 6.6. The half width of the peak increases by 40-50%, and there is a broad tail. Fig. 6.6 does not refer to the diffracted intensity variation across a specimen, unless s varies uniformly. This is equivalent to constant curvature, assumed for the bumps in POM crystals described in section 2.2.4. There the bright lines in dark field were 200 Å or more across, at a dose of $1-2 \text{ Cm}^{-2}$ at 80 kV. At such a low dose, the spreading effect is only slight.

Holland et al. (1965) described dislocation networks appearing between two layers of a PE crystal. The dislocations were resolved

in both bright and dark field as lines $200\text{--}300\overset{\circ}{\text{\AA}}$ across. With two beam dynamical theory, the authors predicted that the $\{110\}$ image from an undamaged crystal should have a half width of $0.2 t_g$, that is, $160\overset{\circ}{\text{\AA}}$ at 80 kV. The exposure they used is not known, but since four different dark field images were taken of one area, each exposure must have been small.

At a given dose, spreading will affect all localized details in the same proportion. However, unless the 'true' width of the detail is very small, approaching the resolution limit, lower doses (lower magnifications) can be used. At low doses spreading is slight and contrast high. The effect may still be important in the later pictures of a sequence (e.g. fig. 3.4).

6.6 Practical Points

6.6.1 Focus

Image detail finer than 100μ cannot be seen on the fluorescent screen. Focussing near this limit is only possible with a brightly illuminated screen, about $4 \cdot 10^{-7} \text{ Am}^{-2}$ at 100 kV. If the beam current density at the specimen is limited to 5 Am^{-2} by heating effects, the magnification must be $< 3,500\times$, so the smallest detail which can be focussed is $300\overset{\circ}{\text{\AA}}$. Under these conditions, only 2 or 3 seconds is available for focussing if a good resolution picture is to follow.

The usual procedure is to search for a polymer crystal at low magnification and very low intensity. When one appears, the beam is concentrated nearby, the magnification is increased to the

chosen value and some stable detail is used to focus. The beam intensity is then reduced, the specimen is shifted to bring the crystal into view, and the plate is exposed immediately. This hit or miss method works reasonably well at low magnification ($< 5,000\times$). Even if focus is achieved at high magnification, moving the specimen stage just before exposure is bound to cause the specimen to drift.

6.6.2 Electron Diffusion

Electrons are scattered in the emulsion, causing the developed silver grains to be more dispersed. A large image will get a diffuse edge, but a small one will lose contrast. There have been very different estimates of the size of the effect. (Zeitler and Hayes 1965, Valentine 1966). In fig. 2.13, lines 2-300 $\text{\AA}$ across are recorded in high contrast, and the original exposure was at 715 $\times$. The image on the plate was 15-20 μ , and this supports the lower estimates. Electron diffusion limits the resolution at low magnification, but the limit, 10 times below the focus limit, is rarely approached.

6.6.3 Beam Stops

It is very desirable to be able to stop the irradiation of a specimen during an experiment without altering the settings of the microscope and without switching off the E.H.T. The shutter mechanism of the Siemens (when fitted) is below the plane of the specimen, and therefore no use. Instead, a blank aperture was prepared, by filling in an old aperture with solder. This blank

aperture was put in the condenser aperture slide, between apertures smaller than the usual, so the sequence was 100μ , - , 50μ . Changing to the blank aperture stopped the beam completely. The only problem was that the mechanisms for changing and for adjusting the apertures were not completely independent, so the illumination was occasionally misaligned after an interruption.

To prevent this, an electrostatic beam deflector was designed and built to fit in place of the splash aperture, on the top of the specimen airlock stage of the Siemens Elmiskop 1. A brass rod 6 mm in diameter was set in Araldite casting resin, and a slot 3 mm by 7 mm was milled through its centre. The araldite was turned to the shape of a top hat, 6 mm high and 13 mm wide, and it was held in place by a locking ring acting on the 'brim'. 400 v d.c. applied between the parallel plates made in this way was enough to swing a 100 kV beam off the specimen entirely, but the araldite charged up in the beam. An earthed brass cap with a small central hole was made to fit over the beam deflector, and most of the araldite was coated with gold by evaporation. Charging was much reduced, but it was not eliminated, and the deflector was not left in the microscope permanently.

6.6.4 Microscope Operation

The microscope was usually operated with the specimen raised, and the focal length of the objective lens increased. There is a standard fitting for this in the Siemens, with objective focal length 6 mm instead of 2.3 mm. This has the effect of reducing the magnification by a factor of three and increasing the camera length

of the diffraction setting. At the same time, the resolution of the instrument is considerably reduced. At the '6mm' position, magnifications down to 600x could be obtained with no distortion. This range is important because the specimen does move during irradiation, especially if it is complex (chapter 7), and a series of pictures is very informative. Low doses and therefore low magnifications are required for each.

6.7 Summary

The basic limitations of noise and electron diffusion do not prevent very high resolution in polymer crystals. A detail 50Å square in a monolayer, or lattice planes in a bilayer, may be resolved, although fast plates are required. The resolution due to both effects gets better at lower beam voltages (Wilska 1965). However, the limit due to focussing errors is generally much larger, and does not vary with voltage. Resolution beyond this limit may be achieved, but only by chance. The experimental limits for PE are 150Å for a monolayer and 40Å for a bilayer. Most useful results are obtained from short exposures, for example:

Suitable conditions for monolayers	A 1,500x, S.L.C.		B 5,000x L.N.	
	B.F.	D.F.	B.F.	D.F.
Focus Limit, Å	(600)	(600)	(200)	(200)
El. diffn. Limit, Å	100	60	30	20
Noise limit, Å	200	50	280	70
Exposure, seconds, For decay in 200 sec	2	10	1	5

The advantage of A is that the screen is brightly illuminated. The screen brightness of B is 10 times less, but the resolution is likely to be better. Slower plates give no better resolution in dark fields and need longer exposures.

6.8 Equipment for Electron Microscopy of Polymers

6.8.1 The Present

The resolution and contrast predicted for dark field images is always better than for bright fields, so it is desirable to obtain high resolution dark field conditions easily. The electrical beam tilt equipment supplied with modern microscopes (e.g. Phillips EM 300, Siemens 101) can do this, can be pre-set, and can be adapted to act as beam stops.

Above all, the microscope must be easy to operate quickly in all respects. Specimen manipulation is particularly important. The goniometer stage of the Siemens is bad from this point of view, sacrificing ease of operation for resolution and stability.

6.8.2 The Future

Image intensifiers have been tried, (Anderson 1968, Morrow and Horner 1966) but they have been found wanting. A recent design (Premisela 1968) using fibre optics and a plumbicon seems much more promising. Intensifiers cannot beat the basic noise or focussing problems of high resolution, but searching and specimen manipulation can be done at beam currents as low as $5 \cdot 10^{-4} \text{ Am}^{-2}$ while a low resolution image is displayed on the monitor. This increases the time available by 1,000x or more.

CHAPTER 7 The output of an intensifier is a video signal, and this fact might lead to even greater advantages. A video signal can easily have its contrast enhanced or reversed. It can be differentiated, and the advantages of complex signal processing are being appreciated in the case of the scanning electron microscope. (Fleming 1968). If the signal were recorded on a video tape recorder, different photographic exposures, integrating many scans, could be taken of the same period of decay. Thus micrographs of $0-10 \text{ Cm}^{-2}$, $2-12 \text{ Cm}^{-2}$, $2-16 \text{ Cm}^{-2}$, $6-18 \text{ Cm}^{-2}$, etc., could all be taken and compared. Direct photography permits only one set, say $0-10 \text{ Cm}^{-2}$, $12-22 \text{ Cm}^{-2}$.

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CHAPTER 7

SPHERULITIC STRUCTURES

7.1 Introduction

So far, the polymers have been studied in the form of single crystals. To extend the work to material more representative of bulk crystallized polymer, specimens for electron microscopy were made by allowing a very thin film of molten polymer to cool. Crystallization proceeds in a similar manner to that in the bulk, but is constrained to occur in a plane. Thus each "spherulite" grows outwards with a circular boundary, not a spherical one. They possibly deserve the name "circulite", as "spherulites" with a cylindrical boundary have been called "cylindrites". Each one is like the diametral section of a true spherulite, but not exactly like it. Nucleation will occur at the surface of the film rather than the centre, and radial growth is inclined to the plane of the film. (Keith and Padden 1959b). When the film is so thin that such effects can be neglected, the substructure of the spherulite may be affected by the constraint. All this must be kept in mind while these crystalline units are, for convenience, referred to as spherulites.

Most of the work was done on PE, the same material, Rigidex 9, as was used for the single crystals. Films were also made from POM, Delrin 900.

7.2 Preparation of Thin Specimens

To prepare a sufficiently thin specimen, the polymer is first

made into a slurry in a suitable solvent, and a drop of the slurry is let fall on to a hot surface. The solvent evaporates, the drop spreads, and the polymer melts to give a very thin continuous film. The thickness always varies considerably across the specimen, and usually different parts of the same film are the correct thickness for observation in the optical or electron microscope. A film which is transparent to electrons is almost invisible in an optical microscope.

PE sticks to any solid substrate it is cast on, so a liquid surface is used. Phosphoric acid and glycerol are not solvents and have high enough boiling points. A few drops of the liquid are put on a microscope slide which is on a 'Kofler' hotbench. This device, a Reichert microscope accessory, is a very convenient source of heat, being a metal bar heated at one end so that a stable thermal gradient forms. A drop of PE slurry of about 1% w/v in xylene is dropped onto the hot liquid surface, a film forms, and is solidified by moving the slide down the hotbench, or transferring it to an oven. The solid film is floated off on a water surface and allowed to stand while the support liquid disperses in the water. The film can then be picked up on another slide for observation. If electron microscope specimens are to be made, the film must be cut up before it dries down completely to the glass, and the pieces floated off again, to be picked up on grids, usually 50 mesh. The films can be very tough and must be cut carefully. A small hot wire tip gave the fewest failures.

The films were not metal coated or shadowed, as this could

give rise to artefacts. There was therefore some charging in the electron microscope. This affected the quality of the image only when the objective aperture was withdrawn. Thus bright and dark field images were easy to obtain, but not diffraction patterns or absorption contrast images. It is not at all clear why this was so. A 'through focus' series taken at the edge of a film showed that it was charged negatively. Very few primary electrons could be stopped by such a thin specimen, so the charge must be due to the shower of low energy electrons produced when the beam hits the edge of any defining aperture. The objective aperture holder and aperture must somehow alter the geometry to make a much smaller charge stable, even though at 6mm from the specimen the solid angle they subtend is small.

7.3 Observation in the Optical Microscope

As observed between crossed polars, most of the films comprised banded spherulites, fig. 7.1a. There is a variation in the thickness of the film corresponding to the crystalline structure, visible with phase contrast or with oblique reflected light, fig. 7.1b. Spherulite centres are thicker and the boundaries between spherulites are clearly defined clefts. There is also a variation in thickness corresponding to the bands.

The band periodicity varied from 1 to 4μ . The longest periods occurred in samples crystallized most slowly, as mentioned by Geil (1961), and these films were of generally less uniform thickness. On very rapid cooling, bands were only visible near the thickest spherulite centres. The appearance of the bands thus gives information

a)

b)

Fig. 7.1 360x

Fig. 7.2 1,150x

Fig. 7.3 915x

about the growth conditions. The difficulty of controlling the temperature of a specimen of such small thermal capacity and large surface area is shown in fig. 7.2, where large changes have occurred during crystallization. To show up the band structure, fig. 7.2 is a double exposure, with polarizer and analyser set first at 0° and 90° , then at $\pm 45^\circ$.

Films prepared in the same way, but using branched PE, Alkathene WSG 17, had smaller spherulites with no bands, though occasionally there were sharp circumferential discontinuities, as in fig. 7.3.

7.4 Spherulite Structure

Spherulites, distinguished by the "maltese cross" appearance when observed between crossed polars, have been seen in PE since 1945 (Bunn and Alcock, 1945) and in low molecular weight materials from the beginning of the century (Gaubert, 1909). They are the characteristic mode of crystallization of polymers from the melt. The dark arms of the cross remain parallel and perpendicular to the plane of polarization of the incident light as the specimen is rotated, so the birefringent units are arranged symmetrically. In the dark areas the index ellipsoid axes are parallel to the polarizer and analyser directions. If the long axis of the ellipsoid is radial, the spherulite is called positive; if tangential, negative. PE spherulites are negative, indicating that the molecular chains are tangential.

A system of dark concentric rings or bands is often seen, is too specific, considering that banded spherulites are a general phenomenon.

superimposed on the dark cross, fig. 7.1. A good deal of work was done in the 1950's on the origin of bands in polymeric spherulites. Observations in the optical microscope, on both thin films and cut sections, Keller (1953, 1959) Keith and Padden (1959 a, b,) showed that all the complex effects obtainable required the following model for complete explanation. The birefringent units periodically vary in orientation, twisting about the radial growth direction. The period and phase of the twist is the same along every radius, so there are circumferential bands where the orientation is the same. When the index ellipsoids are positioned so that the section perpendicular to the incident light direction is circular, or nearly so, the band will be dark between crossed polars. In the case of PE, almost uniaxial, and with negative spherulites, the dark bands will correspond to the molecular chains being parallel to the incident light.

Without considering why the structure should be visible, electron micrographs of spherulitic films showing twisting lamellae have been taken as support for this view (Fischer 1957, Keller and Bassett 1960). There is no generally accepted explanation of why the twisting occurs. Keith and Padden (1961) suggested strain in the outer edges of the lamellae, and Hoffman and Lauritzen (1961) suggested that the stressed fold surface were the cause. Neither suggestion properly explains the variation of band period with growth temperature (Lindenmeyer and Holland 1964). It has been suggested that twinning is involved, and recently a specific model for PE was put forward (Burns 1969). This sounds plausible, but is too specific, considering that banded spherulites are a general phenomenon.

The alternative model for the structure of banded spherulites involves a cyclic variation of the amorphous content along a radius, due to impurity rejection. The dark bands appear in the polarizing microscope because the material there is largely amorphous. Claver, Buchdahl, and Miller (1956) wrote that because bands were visible in the electron microscope, their cause could not be birefringence. Their evidence was weakened by the fact that thin films, as cast, do have a periodic variation in thickness corresponding to the band periodicity. The ridges are bright when observed between crossed polars, fig. 7.1 and Geil (1963) p.229. Andrews et al. (1967) revived this model after seeing bands in the electron microscope when viewing ultramicrotomed sections of PE, cut to a uniform thickness. For their specimens, the contrast of a band was consistent with a density difference of about 20%, corresponding to the difference between undamaged crystalline and undamaged amorphous PE. They pointed out that the contrast persisted on irradiation, and was not due to crystallographic diffraction, but they thought that there was no change during exposure to the electron beam.

The idea of concentric structural discontinuities of some sort was supported by Kawai and Matsumoto (1968) following similar observations on extraction replicas of spherulitic surfaces.

Dlugosz and Keller (1968) were the first to recognize the overwhelming importance of beam damage effects in the interpretation of electron micrographs of spherulites. They observed that ultramicrotomed sections of PE had little or no contrast initially,

that the bands and the lamellar detail appeared on irradiation. Using the scanning electron microscope, they showed that the initially smooth cut surface of a section developed undulations corresponding to the band structure after irradiation. Dlugosz and Keller also saw their sections move and distort in the electron beam.

7.5 Observations in the Electron Microscope

Large changes occur in the image as the exposure and irradiation proceeds. Fig. 7.4 shows a sequence of bright field micrographs of the same area of a spherulitic film, without bands, taken at 80 kV. The qualitative features of the decay are as follows:-

- 1) At first, fig. 7.4a, there is a jumble of fine dark lines, some as narrow as $400 \text{ \AA}$. It is difficult to trace a continuous line through this jumble for more than 0.5μ . Detail of much lower contrast defines a radiating fibrous structure. Superimposed on all this is the overall thickness variation of the film, slight here except at the spherulite boundaries, which are thinner.
- 2) The fine lines move, broaden and quickly lose contrast. In fig. 7.4b few traces of this structure remain. The lower contrast detail appears more prominent because of this, but has actually changed little.
- 3) The film is seen to move. Not all the film moves, since it is held by grid bars, or by a surrounding ring of undamaged material.

The motion seems to be towards the spherulite centres, and in fig. 7.4c these are more dense than before. Material near the spherulite boundaries extends radially, and the centres tend to buckle. Micrographs taken during this motion are naturally blurred, but have low contrast anyway.

4) On further irradiation the contrast of the radiating fibrils increases considerably and the structure gains a coarser, shaggy, appearance, fig. 7.4d.

Dark field images show that the fine lines seen at first are due to crystallographic diffraction contrast, and that the other features are not. Fig. 7.5 shows the sequence of decay in 110 and 200 dark field. (The reflections are not separable). The upper left has been heavily pre-irradiated, and the upper right slightly so. Note that there is motion of the film, in this case, while crystallographic contrast is still distinct, at A.

Fig. 7.6 shows a sequence of bright field micrographs from a film which optical microscopy showed to have banded spherulites. The general features are the same as in fig. 7.4, but now the density of the jumble of dark lines varies in circumferential bands of the same period as the extinction bands. On irradiation this contrast disappears, the film seems to shift and the bands appear again, with greater contrast than before. Radiating through the bands are the lamellar sub-units, again in contrast brought up by irradiation.

The area in fig. 7.6 was picked specially because of the

Fig. 7.4 a) $1 - 6 \text{ Cm}^{-2}$ 9,000x

Fig. 7.4 b) $28 - 34 \text{ Cm}^{-2}$ $9,000\times$

Fig. 7.4 c) $69 - 75 \text{ Cm}^{-2}$

9,000 x

Fig. 7.4 d) $240 - 246 \text{ Cm}^{-2}$ 9,000 x

Fig. 7.5 5,400 x

Fig. 7.6a $1 - 14 \text{ Cm}^{-2}$ 6,800 x

Fig. 7.6 b $32 - 44 \text{ Cm}^{-2}$ 6,800 x

Fig. 7.6c $106 - 119 \text{ Cm}^{-2}$ $6,800 \times$

Fig. 7.6d 146 - 160 Cm^{-2} 6,800 x

large number of fragments lying on the surface. Using these as markers it is possible to see that the radial extension near the boundaries is about 10%, and that as the exposure to radiation proceeds, the phase of the bands changes by 180° . Thus the rings which initially diffracted more, and were darker, become light compared to the other parts.

Diffraction patterns from thin films start as a sharp ring pattern, often with a preferred orientation corresponding to the growth direction in the area selected. The ring, superimposed on a strong diffuse background, persisted after the bright field diffraction contrast vanished, as in the analogous case of single crystals. It persisted during the motion of the film, and the beginning of contrast enhancement, but eventually decayed to the broad rings of an amorphous material.

7.6 Discussion

7.6.1 Comparison with Microtomed Sections

These observations agree with those of Dlugosz and Keller (1968) to a great extent. There were two points of difference, explicable in terms of the different specimens used.

- 1) In the cut sections the final contrast was greater, if the initial dose rate was high. This was not observed in thin films. Since generally higher beam currents are required for transmission through sections, what was described as a high dose rate by Dlugosz and Keller was probably sufficient to cause considerable

heating in the specimen. The increased mobility at higher temperatures would allow whatever changes are occurring to proceed further. Following the calculation of the heating effect in chapter 3, the temperature rise is given by:

$$\theta_o - \theta_b = \frac{I\beta a^2}{2K} \left(\frac{1}{2} + \ln b/a \right) ^\circ\text{C}$$

here $\beta \approx 4 \cdot 10^8 \text{ Vm}^{-1}$

$K \approx 0.4 \text{ J m}^{-1} \text{ sec}^{-1} ^\circ\text{C}^{-1}$

$b = 4 \cdot 10^{-4} \text{ m}$

$a = 2.5 \cdot 10^{-5} \text{ m}$, typically

so $\theta_o - \theta_b \approx 1 ^\circ\text{C}$

For the thin film specimens, the beam current density, I , was 5 Am^{-2} or less, so the temperature rise should have been $5 ^\circ\text{C}$ or less.

2) The microtomed sections appeared to lose all crystallinity before the contrast developed. In thin film specimens, there was a distinct sharp ring in the diffraction pattern during the initial stages of the increase of contrast. The cast films are thinner, and the diffraction pattern is easier to see in thinner specimens.

Dlugosz and Keller suggested that the model of alternate amorphous and crystalline zones could explain their results, the electron beam acting like chemical degradation agents and selectively etching the amorphous material. They pointed out, however, that the contrast was too great to be explained in this way, and that a

large amorphous fraction would be required. My observation that those bands which are finally least dense begin by having the greatest crystalline diffraction shows that they cannot be amorphous zones. Selective etching of crystalline material is unlikely.

7.6.2 Interpretation

For contrast to be produced on the twisting lamellae model, the effect of irradiation must be different, depending on the orientation of the crystallites with respect to the specimen plane. It was shown in chapter 4 that secondary electrons are ejected at right angles to the path of the primary electron. This would seem to promote crosslinking on irradiation parallel to $\underline{c}$, and intramolecular defects on irradiation perpendicular to $\underline{c}$. This effect is conjectural, and acts in the wrong direction. The experiment of irradiating unconstrained single crystals in the electron microscope, described in chapter 3, shows the way to a better explanation. On irradiation, the crystals expanded along $\underline{a}$ by some 10 to 15%. Any change along $\underline{b}$ was much less, and the mass thickness of the single crystals was reduced by about 20%. This ties in with an actual mass loss of 7-10%. (Bahr et al. 1965). The thickness change depends on the density of the residual material. The density of PE rises on irradiation; Charlesby and Ross (1953) found a rise of 8% at 4,000 Mrads in a reactor, and the energy loss results (section 3.5) indicate a greater rise in the electron microscope. Thus on irradiation, the thickness of a PE crystal falls to less than three quarters of its original value.

The same lattice structure exists in the lamellae in spherulites,

so the same anisotropy should occur. The radial direction, b, is unaffected by radiation damage, but the lamellae get wider, expanding along a, and thinner, contracting along c. Thus the apparent change depends on the orientation of the lamellae. Those "flat on" to the specimen plane should expand tangentially and become more transparent. Those "edge on" should contract tangentially and become less transparent.

It is difficult to imagine how these dimensional changes are possible in a spherulite. Certainly, if the constraints entirely suppressed the opposing trends no effects could be seen. For the film to remain continuous, the alternating tangential expansion and contraction in the plane of the film must be transformed into radial mass transfer. Since the 'edge on' bands are trying to contract, the interlamellar material there will be under tension. Molecules made mobile by radiation damage could be drawn in to those bands, and they do become more dense. It is not possible to say what the constraints on any individual unit might be, when no one knows how the system of radiating twisted ribbons can fill space in the first place.

Although the diffraction contrast obscures the thickness effect in bright field, it can be seen when the objective aperture is removed. Those parts which become least dense are originally slightly thinner. From optical microscopy, the thinner regions correspond to the extinction bands, where the molecular chain axis, c, is normal to the specimen plane. These bands diffract

more strongly than the rest, before damage begins fig. 7.6a. The strongest reflections excited in the electron microscope are $\{110\}$ and $\{200\}$. These $\{hk0\}$ reflections are most likely to be excited when $\underline{c}$ is nearly parallel to the beam. When $\underline{c}$ is at a large angle to the beam direction, only one pair of these reflections can possibly be excited. Thus using the film thickness variation as a marker, the transmitting bands seen in the electron microscope after irradiation are associated with the extinction bands seen in the optical microscope, and both instruments give evidence for the molecular chain direction $\underline{c}$ being perpendicular to the specimen plane in these bands.

The $\underline{c}$ axis and the lamellar normal are not identical. The difference could not be measured on these specimens, but Hay and Keller (1965), using detachment replicas from a similar preparation, found that there was a tilt of between 10° and 30° about $\underline{b}$. This would mean that the 'flat on' position and the zero birefringence position differ by between $1/18$ and $1/6$ of the band period. Small angle dark field imaging (Yeh and Geil 1968) might possibly pick out those areas where the lamellae are parallel to the electron beam.

The effect of $\underline{c}$ axis tilt on the deformation of lamellae will be slight. An expansion of 20% along $\underline{a}$, if $\underline{a}$ is at 20° to the plane of the lamella, would change the orientation of that plane by only 3° .

The visibility of individual lamellae is reasonable if each one is trying to contract along $\underline{c}$ while the material as a whole has fixed boundaries. In the crystalline lamellae, a broken chain is

likely to reform, as the ends are held in place. In the interlamellar regions, especially when they are under tension, any break is liable to be permanent, so there will be some 'give'. This process will enhance the density difference between those regions originally crystalline and non-crystalline. The lamella will still be invisible in the electron microscope if it is flat on in the film, so it should be difficult to trace a lamella through a complete twist period. It is in fact generally impossible to do so, and fig. 7.6d shows that lamellae are more distinct in the thicker 'edge on' bands. In the PE films crystallized under high stress by Keller and Machin (1967), the lamellae are preferentially oriented with the c axis in the plane of the film ('edge on') and with rare or incomplete twists. Particular mention is made in that paper of the remarkable distances over which a single lamella could be traced.

The mass loss of PE specimens on irradiation is small enough, at 10%, to be explained by loss of hydrogen throughout the material, due to crosslinking. It would be surprising if this loss were not observed, since hydrogen is produced and will diffuse from such thin specimens very rapidly. Still, selective etching of amorphous material could be occurring, in this case in the interlamellar regions. The fine structure which appears in thin films, fig. 7.4d for example, shows clearly that the density in some parts is greater than it originally was. Selective etching cannot explain this, there must be material transferred to these regions.

Dlugosz and Keller (1968) observed some spherulites which

had less contrast, and were generally dark. These they identified with off-diametral sections. A 'small circle' cut on the amorphous rings model would give bands of undiminished contrast, and greater period. On the twisting lamellae model, the 'flat on' portions become more oblique, so the contrast drops as the section approaches an all 'end on', b axis vertical, state.

The buckling and wrinkling of the film in the beam means that its surface area must have increased. There cannot have been an overall expansion, for under compression the film would have given way at the spherulite boundaries, since they are the thinnest parts. Instead, the severe buckling occurs at the thickest parts, the spherulite centres. There is little effect at the edges, and it is a slight radial extension. This implies a tangential contraction. Of the alternate bands in tension and compression, the tension is more effective. This is to be expected in a thin film. The radial extension near the spherulite boundaries is the only source of the increase in area.

7.6.3 Summary

All the observations of spherulites of PE in the electron microscope fit in with the twisting lamellar structure deduced from optical microscopy. The explanation for the persistent contrast, anisotropic deformation on irradiation, is not specific to PE. It could well be the explanation of the visibility of crystalline regions in thin films of gutta percha (Keller and Machin 1967) and polystyrene (Machin 1967) as well as in sections of polyamides (Little, 1968;

Cannon and Harris, 1969). The behaviour of spherulites of natural rubber in the electron microscope (Andrews, 1962) is very similar to the present observations on PE.

Some polymers, such as polypropylene (Andrews et al., 1967) and POM (section 7.8) are featureless after irradiation. POM crystals collapse entirely in the beam, and show anisotropy only when constraints require it. The diffraction pattern of PE shows that the lattice parameter a expands as the crystal does, (fig. 3.1, and Kiho and Ingram 1968) whereas the diffraction pattern of POM is stable. It would be very interesting to make this comparison in other polymers.

7.7 Drawn Films of Polyethylene

7.7.1 Specimen Preparation

Thin films were cast in the usual way, then drawn at room temperature. The films were very difficult to handle and tended to tear. It was found best to float the cast films on water and pick them up with a slide that had been smeared with glycerol. The film was gripped by pressing it firmly to the slide in two places, with needles or with the thumbs, and the gripped points were moved slightly apart. The film always deformed inhomogeneously, but small areas, a few sq. mm. in extent could be seen to have drawn. For electron microscopy, these pieces were cut out and floated off onto water again. If they were to be annealed, they were picked up on another smeared slide for the purpose then floated off and washed again. Finally the specimens were picked

up on 50 mesh grids and allowed to dry.

7.7.2 Observation in the Optical Microscope

Optical microscopy showed that the films had deformed very inhomogeneously on the small scale. Spherulites generally broke up along a diameter perpendicular to the draw direction, and the two regions, little affected within themselves, became separated by a highly drawn part. Sometimes the yielding process began at spherulite boundaries. Usually the highly drawn regions showed no structure in the optical microscope, extinguishing uniformly when the polarizer and analyser were parallel and perpendicular to the draw direction. In the thicker areas of the film, the band structure of the spherulite was seen to persist even at high draw ratios. The contrast in polarised light was normally weak, fig. 7.7a is unusually clear, but reflected light showed that the thickness variation corresponding to the bands became very much more pronounced on drawing, fig. 7.7b. This type of deformation is the same as that described in great detail by Hay and Keller (1965), and explained by them in terms of the twisting lamellae.

7.7.3 Electron Microscopy During Radiation Damage

In the electron microscope, the most obvious effect of irradiation on a drawn film is to make it retract. At moderate beam current densities, the relaxation appears to begin at once. If a limited area is being illuminated, the motion continues for a long time as fresh material is drawn into the beam and contracts in its turn. Using very low beam currents, it can be seen that

a)

b)

Fig. 7.7 477x
Draw direction horizontal

there is an initial short induction period. The motion begins while diffraction contrast is still clearly visible, and does not stop till after evidence of crystallinity has disappeared.

Films annealed for a few minutes at 120°C showed the same behaviour. Measurements were made on pairs of plates, one of each pair showing sharp diffraction contrast, the other taken after long irradiation. In nine pairs, the recovery was between 24 and 37%. In a tenth, where the drawn region was close to a grid bar, and the draw direction was parallel to it, the retraction was less than 10%. Surface marks near the edge of the drawn material were used as reference points, and this could lead to underestimation of the motion. The film as mounted is often not taut, and any slack must be taken up before measurable retraction occurs.

The drawn material is well oriented, with $\underline{c}$ in the plane of the specimen and along the draw direction. Unfortunately, the measured retraction is not the same as the contraction of the crystallites along $\underline{c}$. The stressed amorphous interlamellar material may relax, or, if the material is held firmly, it may give way under tension.

There was little retraction on annealing at 120°C , as measured by optical microscopy. This agrees with Hay and Keller (1966), who found that high density PE which had been deformed retracted only a little on annealing, and only above 130°C . On the other hand, Peterlin (1967) mentions that annealing changes in highly drawn PE take place very quickly, and Peterlin and Sakaoku (1966) showed by

replication that annealing at 120°C caused a complete change of structure in the surface of drawn high density PE (Fortiflex 60/500). This change, a rotation of the lamellae about an axis in the specimen and perpendicular to the draw direction was not observed when a thin film of the same material was drawn at 90°C and then annealed at 120°C (Sakaoku and Peterlin, 1967).

Because of the retraction, and specimen movement generally, it is difficult to get good micrographs of drawn films in the early stages of damage. The diffraction contrast usually seems to come from a peppering of spots, as described by Yeh and Geil (1968). Fig. 7.8 shows a sequence of three micrographs of a drawn region where the spherulite structure has been preserved. Fig. 7.8a is an atypically clear dark field image, taken with $\{110\}$ and $\{200\}$ reflections. Fig. 7.8b was taken under the same conditions as 7.8a, and immediately after it. The motion of the specimen obscures nearly everything, except some diffraction contrast at the lower left. Fig. 7.8c was taken in bright field, after a long irradiation time. In undrawn spherulites (section 7.5) there was less diffraction from those bands which became darker with irradiation. Here, comparing a) and c) the effect is much more extreme, there is no diffraction at all from these bands. The lamellae are edge on to the specimen plane in the dark bands, so $\underline{b}$ and $\underline{c}$ should lie in this plane. If this were exactly so, there would be no $\{110\}$ or $\{200\}$ diffraction from them before drawing. Diffraction occurs because $\underline{b}$ varies sufficiently to allow $\{110\}$ reflections, that is, by $\pm 30^{\circ}$. From equation 7.1, in section 7.7.4, the variation would have to be $\pm 70^{\circ}$

a) $1.5-12 \text{ cm}^{-2}$ D.F.

b) $13.5-40 \text{ cm}^{-2}$ D.F.

c) $162-165 \text{ cm}^{-2}$ B.F.

Fig. 7.8

3,900 x

for there still to be diffraction after a $4\frac{1}{2}x$ extension parallel to b, as in the centre of fig. 7.8.

According to Hay and Keller (1965), when the growth direction (b) is parallel to the draw direction, the c axis is aligned in the draw direction by rotation about a. This preserves the a direction, so in the bright bands, where a is in the specimen plane, diffraction into $\{200\}$ should still occur. When the growth direction is perpendicular to the draw direction, the orientation of c proceeds by rotation about b. This is equivalent to untwisting the lamellae, so the band structure should be suppressed. In fig. 7.8, at an extension of $4\frac{1}{2}x$, the band structure persists in a direction nearly perpendicular to the draw direction.

7.7.4 Electron Microscopy After Radiation Damage

After irradiation, most of the drawn material has an irregular fibrous appearance, with no details that can be related back to the spherulite structure. In the electron microscope as in the optical microscope there were some areas where the band structure of the spherulites was remarkably persistent. Fig. 7.9. These areas were thicker and not so highly drawn as the average. The first of these two characteristics could explain the second, and also why there were few such areas, since the film deforms at its weakest points. The boundary between drawn and undrawn material is very sharp, and it is difficult to follow detail from one region to the other on a micrograph because of the great difference in transmitted intensity. Clearly the dark bands in region A' are continuations of

Fig. 7.9 8,470x

the dark bands in the undrawn spherulite A. The bands act as a marker, giving the magnitude of the extension. The direction is given clearly by the appearance of the necked region. Both magnitude and direction vary over the neck, but an average direction is marked on the figure, and the average draw-ratio is 6 times. This is after the retraction due to irradiation, the original extension would be between 8 and 10 times.

Note that just to the right of the letter A' there is a discontinuity in the bands. Looking along the print, an extra band appears below the discontinuity. The three regions marked A', B' and C' have been drawn from three spherulites A, B and C. A and C have deformed along the diameter perpendicular to the draw direction (the centre of A is on the left hand edge of the figure). Only the tip of B has deformed, so the extension there is nearly radial. The contrast between light and dark bands is greater in the drawn regions A' and C'. The dark bands stay at much the same density, while the light bands get much lighter. This might be expected, since the lamellae in the dark bands, edge on, were originally nearer to the orientation of the drawn material. They should therefore be affected less by the drawing process. In B', where the extension is nearly radial, and the lamellae were equally misoriented throughout their twist period, the bands are hardly visible.

Fig. 7.10 is a picture of the same area as fig. 7.9, at higher magnification and higher contrast. The fibrous structure is clearly visible throughout the material. Some of the dense fibrils can be distinguished by the blobs spaced along them. The blobs are spaced

1 μ

Fig. 7.10 15, 300x

fairly regularly along each fibre, with an average periodicity of 600 to 900 Å. It is difficult to define their size exactly, but they are usually between 150 and 250 Å measured along the fibril and a little larger, up to 400 Å, measured across the fibril. These structures are visible in other regions, where drawing has destroyed all trace of the spherulite structure, and they were also observed by Yeh and Geil (1968). In fig. 7.10, however, there is more information.

If any detail lies at an angle ϕ to the draw direction after it has been deformed, with a draw ratio of n times, and if it was originally at an angle θ to the draw direction, then we can draw a simple diagram connecting ϕ and θ , fig. 7.11.

Fig. 7.11

$$\tan \theta = \frac{PQ}{QR} \quad \tan \phi = \frac{PQ}{QR'} \quad \tan \theta = \frac{QR'}{QR} \quad \tan \phi = n \tan \theta . \quad 7.1$$

QR'/QR is the draw ratio, n , measured along the draw direction, QRR' . In this case $n = 6$.

The bands just below A' in fig. 7.10 run at 12° to the draw direction. They are made up of fibrils, some beaded, which lie at 20° to the band direction, that is, at 8° to the draw direction.

	ϕ	$\tan \phi$	$6 \tan \phi$	θ
fibrils	8	.15	0.90	40
bands	<u>12</u>	.21	1.28	<u>52</u>
	20			92

Since the bands were originally circumferential, the fibrils must have been radial. This has been confirmed in several specimens, and it can be checked further near the boundary of the neck, where the original direction of the bands can also be measured. For example take points X and Y in fig. 7.9.

		ϕ	$\tan^{-1} 6 \tan \phi$	measured θ
at X:	bands	5	28	30
	fibrils	22	$\frac{67}{95}$	
at Y:	bands	20	66	65
	fibrils	$2\frac{1}{2}$	$\frac{15}{81}$	

This confirms that the fibrils in this material are the radial lamellae, homogeneously deformed.

From fig. 7.11, the extension of the detail itself is $R'P/RP$.

$$\cos \phi = R'Q/R'P. \quad \cos \theta = RQ/RP.$$

$$R'P/RP = n \cos \theta / \cos \phi. \quad 7.2$$

For the fibrils in the three cases above, this extension is 4.6, 2.4 and 5.9. Although there is considerable scatter in the

Fig. 7.12 40,700x

Draw direction vertical

measured periodicities along the beaded fibrils, a systematic variation of a factor of two could not be missed. This variation would be expected if the beads were the result of drawing a pre-existent structure. The spacing must be produced by drawing, since this specimen was not annealed. The micrographs of unannealed specimens taken at very low irradiation doses show no signs of beaded fibrils, but the quality is so poor, because of specimen motion, that this proves nothing.

Since the fibrils that are beaded are mostly the darkest in the micrographs, they must protrude from the surface of the drawn film. The free edge may collapse, to form the blobs, but there seems to be no reason for the 600-900 Å spacing. Yeh and Geil (1968), with shadowed samples, described the blobs as being projections spaced along a ridge. They suggested that the beads were sections which had for some reason not been drawn. Since they are 150-250 Å thick, this is possible only up to a draw ratio of six times. At greater extensions, the size and spacing alter little, so there would be no room for a continuous line of the beads in the undrawn material.

Some micrographs of drawn material showed regular cross striations of small period, for example, fig. 7.12, where the period is 195 Å. Pairs of such fringes could be formed from isolated scatterers if there is some defocus, but these fringes are 1,000 Å long and there are long regular sequences. It is possible for defocussing to bring up a weak but real periodic structure in the

material. Fayet et al. (1960) and Albert et al. (1964) describe these effects of phase contrast, though these authors were mainly interested in detail $< 10 \text{ \AA}$ across.

Careful experiment showed that reasonable fringes of $190 \text{ \AA}$, $240 \text{ \AA}$ and $440 \text{ \AA}$ spacing could be obtained, all from the same area of one sample. All must be purely artefacts, a combination of defocus and astigmatism. The use of this observation is to point out that the regularity of periodic structures, such as the beaded fibrils, may be more apparent than real.

7.7.5 Ultra-thin Films

On two occasions, small areas of specimens which had been drawn at room temperature, then annealed at 120°C for a few minutes, showed a peculiar open network structure. The structure is surprisingly stable in the beam. Figs. 7.13 a) and b) are bright field micrographs taken at the start and at the end of the radiation damage process. In fig. 7.13 it is clear that there is a strong cross banding on every strip of material. The thinnest threads are not resolved as a continuous structure, only as a series of transverse plates like a shish-kebab. Measurement of these thin threads gives an accurate description of the transverse structure. The plates are $200 \pm 25 \text{ \AA}$ thick, and have a mean separation of $200 \pm 75 \text{ \AA}$. More measurement on threads where the plates are not so distinctly separate gives a periodicity of $380 \pm 40 \text{ \AA}$. Each of these errors contains $\pm 4\%$ for the magnification error. The error in the thickness may indicate a real variation, or may be due to difficulty in defining

Fig. 7.13a 7,660x

$3-4\frac{1}{2} \text{ Cm}^{-2}$

Fig. 7.13b 7,660x
127 - 130 Cm^{-2}

the edge of the units. The additional error in the separation describes a real variation. The low angle X-ray spacings from Marlex 50 crystallized at 120°C are $190\text{ \AA}$ and $400\text{ \AA}$, (Mandelkern et al. 1961), and the low angle spacing obtained from PE cold drawn and annealed at 120°C by Peterlin (1967) was $250\text{ \AA}$.

The diffracting crystallites in fig. 7.13 a) are the width of the ribbon, unless that is over 2 or 3,000 $\text{\AA}$, and they are $210 \pm 40\text{ \AA}$ thick. In every case the diffracting element is a straight line, diffracting with uniform intensity over its length. A few, on the thinnest threads, can be identified with a particular transverse plate. Fig. 7.14a, a dark field micrograph, shows the diffracting units more clearly. The objective aperture was placed over the brightest arc of the $\{110\}$ and $\{200\}$ rings. This was at right angles to the preferred orientation of the ribbons. There is no diffraction from the finest threads, which are all oblique. Fig. 7.14b is a bright field image, after irradiation, for comparison.

From these pictures it is clear that each ribbon is a stack of vertical lamellae, held together only by the interlamellar ties. Diffraction patterns from the ribbons confirm this, and also show that the $\underline{b}$ axis tends to lie in the specimen plane. Fig. 7.15a) is the diffraction pattern from a very well oriented area, which included a bundle of ribbons like a rope. Many reflections are visible, and the $\{200\}$ are very strong. Fig. 7.15b) is the pattern from an area not nearly so well oriented, where the ribbons were flat. Strong arcs of $\{110\}$ and $\{020\}$ show up, but $\{200\}$ is faint, spotty, and randomly oriented.

Fig. 7.14a 4,270x
4-11 Cm^{-2}

Fig. 7.14b 4,270x
-2
148 - 151 Cm

a) From 'rope'

b) From flat specimen

Fig. 7.15

Unfortunately, it is not clear how this ideal highly drawn structure came about. Fig. 7.16 is at very low magnification, and fig. 7.17 is a detail of the material intermediate between this structure and the normal one. Each hole in fig. 7.17 seems to have been at the nucleus of a sheaf of lamellae. The ribbon structure appears as the holes get larger. It is possible that the holes formed on drawing, but the wrinkles on each side do not match up well. It seems more likely that the holes existed in the molten film, and the edges acted as nucleation centres. Away from the holes the growth is not normal, leaf shaped and dendritic crystals are visible. The diffraction pattern in the corner of fig. 7.17 came from a 2μ diameter selected area of material exactly like that in fig. 7.17. It is a single crystal pattern with two orders visible.

It appears that the area was exceedingly thin, as cast, so that normal spherulitic growth, with twisting lamellae and small angle branching, was impossible. The usual process of deformation and re-orientation would also be impossible. Under these conditions, the 120°C anneal would have a greater effect than was normally observed. By comparison with X-ray measurements, the regular crystallites in the ribbons are formed at 120°C , and same could be true of the single crystal texture. Nothing remotely like this structure was seen in unannealed specimens.

On irradiation, some networks were very stable, with little retraction. Other areas broke up and disappeared completely in the beam. This could be due to some basic difference between the networks and the remainder of the drawn material. However, a

Fig. 7.16 560x Some distortion

Fig. 7.17 12,100x Diffraction pattern from area such as A

very thin film of the same basic properties would behave in this way. The forces generated would be too small to make any impression on the surrounding thicker film, so there could be no retraction unless the thin film broke.

7.8 Thin Films of Polyoxymethylene

POM films were prepared from a suspension of Delrin 900 in bromobenzene, by allowing a single drop to fall directly onto the hot surface of a microscope slide, which was then slowly cooled. The liquids used as substrates for PE were unsuitable for POM, but POM adheres only slightly to glass and the films could be teased off onto a water surface with tweezers. Being much more brittle than PE, the POM films could easily be cut into squares for electron microscopy, but they could not be drawn at room temperature.

As seen in the optical microscope, fig. 7.18, the films were made up of coarsely textured spherulites. There is some trace of a radial periodicity of about 10μ , but it is very poorly ordered. When a specimen was cooled more slowly, the regularity and the spacing of the bands increases. Fig. 7.19 is an extreme example. It is a double exposure like fig. 7.2, taken to show up the bands. They are very clear, with a periodicity of almost 25μ , but there are still many radial faults. Geil, (1963) quotes POM as an example of non-banded spherulites, and only gives one counter-example, of a film cooled over several days, with bands of 100μ spacing.

Fig. 7.18 234x

Fig. 7.19 234x

Clear observations of banding were made only on thick regions of the films. In the thinner parts, all contrast due to birefringence naturally gets less, but it did seem that the visibility of the bands was reduced more quickly than this could explain. That is to say, there appeared to be a real difference, with less well ordered bands in the thin regions.

POM degrades severely in the electron beam (chapter 3) and it was surprising to find that however long the irradiation, a very thin film was left. The final mass thickness was less than 20% of the original mass thickness. The residue gave an amorphous diffraction pattern very similar to that of the residue of PE. In this case the initial contrast faded away, leaving a featureless film. Some thick, electron opaque, regions became partially transparent on irradiation, and voids appeared, radiating from a centre. The material left showed the sheaf like form of a spherulite centre.

In the thin areas, radiating units about a micron wide were visible. The centres of growth were widely spaced, by $\frac{1}{2}$ mm typically, so the nuclei were rarely seen, and the radial divergence in any area was usually slight. Fig. 7.20 shows the appearance in bright field (a) before there has been much damage and (b) near the end of the damage process. The inset diffraction pattern was taken from the area marked by double exposure on (b), between taking the two micrographs. The diffraction pattern shows a surprisingly perfect orientation. It is very similar to the basal pattern obtained from single crystals, with very strong $\{10\bar{1}0\}$ spots. There are

a) $2-9 \text{ Cm}^{-2}$

Fig. 7.20 Diffraction pattern taken at 12 Cm^{-2} 6,450x

b) $22-26 \text{ Cm}^{-2}$

Fig. 7.20 6,450x

a) 2,750x

Fig. 7.21

b) 8,290x Enlargement of central area of a)

weak $\{11\bar{2}0\}$ and $\{20\bar{2}0\}$ spots, and $\{10\bar{1}5\}$ and $\{11\bar{2}5\}$ spots are faintly visible. Fig. 7.21 is a $\{10\bar{1}0\}$ dark field micrograph which shows the detail within the radiating units. Diffraction contrast is confined to a central area in fig. 7.21a because of the very low magnification of the original plate, not because of any property of the specimen. Fig. 7.21b is an enlargement from the central area. Selected area diffraction patterns, such as fig. 7.20 show that the growth direction is $\{10\bar{1}0\}$. This has been confirmed with dark field micrographs, where only a certain sector appears bright.

The twisting of the lamellae in thick films, which is inferred from the banded spherulites, has been suppressed in these thin specimens. The lamellae lie with the c axis perpendicular to the specimen plane. This was observed in PE for even thinner films (section 7.7.5), but since POM spherulites have a coarser structure, the effect should appear sooner. On the other hand, it is possible that the glass substrate affects the structure when the film is thin. This happens when selenium is crystallized, according to Fitton and Griffith (1968). From bulk, and on a like substrate, selenium forms banded spherulites. When crystallized on a glass substrate, it crystallizes faster, with little twist, and a single orientation along a radius. Attempts to cast POM films on a teflon substrate were not successful. However, O'Leary and Geil (1968) cast thin films of POM by a variety of methods and saw spherulites only in the thicker films. The thin regions they described as single crystals, because there was always a well defined 'single crystal' diffraction pattern.

Here is a good case for the application of high voltage microscopy, to get information from thick films, and from any intermediate structures that may exist.

APPENDIX

Extinction Distance Calculation

```

begin          library      A6,A12,A30,A14;
                real    e,a,b,c,h,al,be,ga,beta,vc,lambda,kk,V,
                as,bs,cs,cosas,cosbs,coscs,x,rr,ii;
                integer    f30,f5,n,m,j,q,s,k,i,t;

A0:  open(20);  open(30);
      writetext (30,[[cc] MJW**extinction*distances[cc]]);
      f30:=  format([-nddss]);
      f5:=  format([ss-d.ddddn-nd]);

      h:=4*arctan(1);

A7:  copytext(20,30,[//]);
      e:=read(20);  if e<0 then  goto STOP;
      a:=read(20);  b:=read(20);  c:=read(20);
      al:=(read(20))*xh/180;  be:=(read(20))*xh/180;
      ga:=(read(20))*xh/180;  n:=read(20);  m:=read(20);

begin          integer array  ZZ[1:m], H,K,L[1:n];
                array    FX,A1,A2,A3,B1,B2,B3[1:m];

C0:  t:=0;
      for j:=1 step 1 until m do  begin  ZZ[j]:= read(20);
                                     t:= t+ZZ[j]
                                     end;

begin          array    X,Y,Z[1:t];
                for j:=1 step 1 until n do
                begin    H[j]:=read(20);
                        K[j]:=read(20);
                        L[j]:=read(20);
                end;

C1:  q:=s:=0;
      for j:=1 step 1 until m do
      begin    q:=s+1;  s:=s+ZZ[j];
                A1[j]:=read(20);  B1[j]:=read(20);
                A2[j]:=read(20);  B2[j]:=read(20);
                A3[j]:=read(20);  B3[j]:=read(20);
                for k:=q step 1 until s do
                begin    X[k]:=read(20);
                        Y[k]:=read(20);
                        Z[k]:=read(20)
                end

      end;

```



```

C2:  beta:=1+e/511.0058;
      vc:=sqrt(beta*beta-1)/beta;
      lambda:=.02426206/sqrt(beta*beta-1);
      kk:=1/lambda;
      writetext (30,[[ccc5s]e[11s]lambda[8s]k
                    [11s]beta[11s]v/c[c]]);
      write(30,f5,e);      write(30,f5,lambda);
      write(30,f5,kk);      write(30,f5,beta);
      write(30,f5,vc);

C3:  V:=a*b*c*sqrt(2*cos(al)*cos(be)*cos(ga)+1-cos(al)*cos(al)
                -cos(be)*cos(be)-cos(ga)*cos(ga));
      as:=b*c*sin(al)/V;
      bs:=a*c*sin(be)/V;
      cs:=a*b*sin(ga)/V;

      cosas:=(cos(be)*cos(ga)-cos(al))/sin(be)/sin(ga);
      cosbs:=(cos(ga)*cos(al)-cos(be))/sin(ga)/sin(al);
      coscs:=(cos(al)*cos(be)-cos(ga))/sin(al)/sin(be);

C4:  writetext(30,[[cc3s]h*****k*****l*****x[11s]r(ug)[9s]
                i(ug)*****ext*dist[cc]]);
      for i:=1 step 1 until n do

      begin  x:=(H[i]*H[i]*as*as +K[i]*K[i]*bs*bs
                +L[i]*L[i]*cs*cs +2*K[i]*L[i]*bs*cs*cosas
                +2*L[i]*H[i]*cs*as*cosbs
                +2*H[i]*K[i]*as*bs*coscs)/4;

C5:  rr:=ii:=0;
      q:=s:=0;
      for j:=1 step 1 until m do

      begin  FX[j]:=A1[j]*exp(-B1[j]*xx)
                +A2[j]*exp(-B2[j]*xx)
                +A3[j]*exp(-B3[j]*xx);
                q:=s+1;      s:=s+ZZ[j];
                for k:=q step 1 until s do
                begin  e:=2*xh*(H[i]*X[k]+K[i]*Y[k]
                                +L[i]*Z[k]);

                                rr:=rr +FX[j]*cos(e);
                                ii:=ii +FX[j]*sin(e)

                end
      end;
      end;

```



```

write(30,f30,H[i]);   write(30,f30,K[i]);
write(30,f30,L[i]);   write(30,f5,2*sqrt(x));
write(30,f5,beta*rr/h/V);
write(30,f5,beta*i1/h/V);

```

```

if rr*rr + i1*i1 < 10-10 then goto D4;

```

```

write(30,f5,V*h*kk/beta/sqrt(rr*rr + i1*i1));
goto D5;

```

```

D4: writetext(30,[***forbidden]);

```

```

D5: newline(30,1)

```

```

end

```

```

end

```

```

end;

```

```

writetext(30,[[p]]); goto A7;

```

```

STOP: writetext(30,[[cc]completed[cc]]);
close(20); close(30);

```

```

comment      data in form:  /text/  -ve to stop

```

e	kV
a,b,c,	A
al,be,ga,	angles in degrees
n	no of hkl sets req
m	no of types of atom
ZZ[i]	no of sites of each
	type of atom in order
H[i],K[i],L[i]	reflexions

Smith and Burge parameters followed
by atomic positions for each type of atom;

```

end→

```


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