

Amorphous linear polyethylene

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A technique was developed which is capable of quenching thin linear polyethylene films (100–1000 Å) to an apparently amorphous state. Electron microscopy of samples kept at liquid nitrogen temperature before and during platinum–carbon shadowing indicated that the glass has a morphology consisting of nodules approximately 100 Å in size superimposed upon irregularities 1000 Å or more in diameter. This morphology did not rearrange to form lamellae as the sample was warmed rapidly and recrystallized; instead the chains seemed to reorganize locally to develop three-dimensional crystallinity. In most of the quenched samples some localized areas of varying sizes and numbers were seen which had a lamellar or spherulitic morphology which seemed to have formed during cooling due to local variations in the quench rate. Electron diffraction from well-quenched areas of samples inserted into the microscope without warming them sufficiently that they crystallized showed only amorphous halos. Upon warming, crystallinity in the orthorhombic unit cell form appeared at temperatures above 180–190K. Differential scanning calorimetry revealed a broad exotherm between 160 and 180 or 200K from samples that were kept under liquid nitrogen before and during insertion into the d.s.o.

INTRODUCTION

Linear polyethylene (LPE) is a unique polymer, having an all-carbon backbone and, ideally, no substituents or side groups. This simplicity has made it well suited for investigations of the nature of crystallization in polymeric materials. Yet the ease of crystallization responsible for its availability in highly crystalline forms, has, until recently, made it impossible to quench to a glass.

One of the results of the lack of amorphous polyethylene samples has been a long standing controversy over the location of the glass temperature (T_g) of PE. For details the reader is referred to several review articles by Boyer^{1–4}. The basic difficulty is that convincing experimental evidence, from several techniques, exists for T_g to be at any of three temperature ranges 145 ± 10 , 195 ± 10 and 240 ± 20 K. Boyer has attempted to resolve the problems by suggesting that 145K is the γ -transition where motions of segments 4–5 carbon atoms long begin, 195K is a lower T_g [T_g (L)] where motion of long chain segments unconstrained by crystallites occurs, and 240K is T_g (U), where long segment motion occurs in chains held in tension or otherwise constrained by the lamellae.

In view of the long-standing disagreements on the subject, a sample of amorphous linear polyethylene could provide information on the point at which the molecules became mobile enough to crystallize. Larger samples, if they could be used in dynamic mechanical experiments, might reveal the nature of the molecular motion occurring at each temperature. They should also be useful for studying questions concerning the nature of the nodules seen in electron micrographs of glassy polymers⁵ and the process of crystallization from the glass^{5–10}. Rapid quenching tech-

niques would also prove to be useful in examining the crystallization of LPE and other polymers at high undercoolings. This would provide a check of theories of polymer crystallization, many of which predict a rapid increase in fold period at high undercoolings¹¹. In response to evidence for some polymers that this long period blow-up does not occur^{12–15}, Lauritzen and Hoffman have formulated a revised theory¹⁶ which eliminates the increase at high undercoolings. However, the question has not been answered completely.

In spite of its potential usefulness, it was not until 1975 that successful quenching of LPE to the amorphous state was reported. According to a paper by Hendra, Jobic and Holland-Moritz¹⁷, films 30 μ m thick were prepared between aluminium foil, melted in a furnace, and then dropped into a Dewar flask containing liquid nitrogen which had been set inside the furnace. They published infra-red and Raman spectra taken from quenched samples which had been kept cold continuously up to and during insertion into the spectrometers. Up to 160K, the infra-red spectra were similar to the spectrum of the melt. As the samples warmed up above this temperature features characteristic of crystallinity gradually appeared in the i.r. spectra. A longitudinal acoustic mode appeared in the Raman spectra and was interpreted as being due to the formation of lamellae during crystallization from the glass. Hendra *et al.* commented that their infra-red spectra indicated that T_g for the amorphous polyethylene was below 180K, the implication being that large scale molecular motions above T_g were sufficient to permit crystallization in the form of chain-folded lamellae. In a subsequent paper¹⁸ it was claimed that the lamellar thickness is dependent on the melt temperature, decreasing with increasing melt temperature from which the sample was rapidly cooled or quenched. The samples did not have to be crystallized from the glass to exhibit the claimed correlation. They stated that the structure of the polyethylene melt is related to that of the crystalline solid produced from it by rapid cooling. This would seem to imply some sort of pre-folding in the melt.

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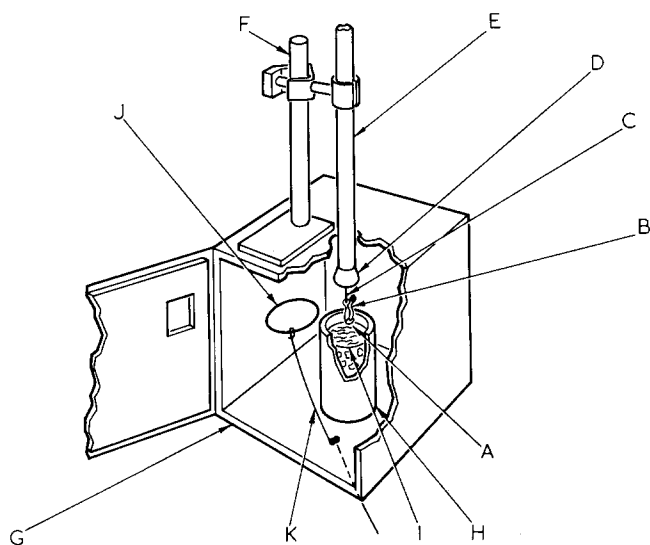


Figure 1 Nitrogen quench apparatus. A, Sample; B, clip; C, wire; D, cork; E, B-B gun; F, ring stand; G, furnace; H, dewar; I, quenchant; J, dewar cover; and K, cover wire

Unfortunately, as far as the authors know, no one has been able to duplicate Hendra's experiment. More than a year was devoted to the problem in this department and the personnel involved were unable to produce amorphous polyethylene using either liquid nitrogen or liquid UCON-12* as the quenchant. Furthermore, Hendra himself admitted¹⁹ that his group had difficulty in reproducing the quench.

When we began our work, we decided that, despite the claims of Hendra, *et al.*¹⁷, it would be useless to try a straight liquid nitrogen quench since it is well known that a film of gaseous nitrogen forms on the surface of the samples and impedes heat transfer¹⁰. Our initial experiments were done using UCON-12 (dichlorodifluoromethane) at its melting point of 118K. This has been successfully used as a medium for rapidly quenching biological samples for freeze-etching experiments². The quench is so rapid that water in the samples is frozen into a glass, which largely eliminates damage to the cellular structure caused by ice crystal growth.

When it was established that the fluorocarbon quench was not fast enough (see below), a new quench scheme was developed by Hart and the present authors. It was first used in practice by Hart and Pineri, though they used samples which were too thick (~20 μm) to become amorphous. Hart's idea of using a bath containing a mixture of solid and liquid nitrogen was crucial to the success of the method.

In order to obtain optimum quenching with minimum subsequent handling of the samples, solution-cast films several hundred Angstroms thick were mounted on electron microscope grids. The suspicion that substantially thicker films could not be quenched successfully was later verified (see below). It became clear early in the work that a support film would be necessary to support the polymer across the holes of the grid. The small sample size places clear limitations on the experiments that could be performed on the quenched material once it had been obtained. The samples were inherently suitable for electron microscopy and electron diffraction, assuming a means could be found for inserting the samples, while cold, into the evaporator or microscope. In addition it was found possible to use differential scanning calorimetry, again using samples on grids which were kept at

* Registered trademark of Union Carbide Corp. for refrigerant-12, dichlorodifluoromethane

liquid nitrogen temperature while in the instrument. The majority of the d.s.c. results were obtained in cooperation with C. J. Singleton and J. L. Savoca at the B. F. Goodrich Co., Brecksville, Ohio, USA.

EXPERIMENTAL

Sample preparation

The polyethylene used in these experiments was Marlex 6015 ($M_n = 7500$, $M_w = 130\,000$) linear polyethylene supplied by the Phillips Petroleum Company. A thin film sample was needed to minimize heat transfer problems. For most purposes the film was supported on a carbon-coated electron microscope grid. Not only did this support the polymer film while it was molten, but after the quench the samples were ready for the electron microscope without subsequent mounting procedures which would have been difficult at cryogenic temperatures. This method did present some unavoidable difficulties in the d.s.c. work, but for the most part these were satisfactorily overcome.

The films were cast from 0.5% solution in reagent grade xylene. The hot solution was allowed to dry on a glass microscope slide that had first been coated using standard evaporation procedure²¹ with a thin layer of evaporated carbon. The carbon-polyethylene layer was then floated off the slide onto distilled water and picked up on 200 mesh copper electron microscope grids.

For the diffraction work, a few samples were prepared on aluminium substrates. These were prepared by evaporating pieces of aluminium foil from a tungsten spiral basket at pressures of the order of 3×10^{-1} torr. on to the (100) cleavage faces of large sodium chloride crystals (from the Harshaw Chemical Company, Cleveland, Ohio) which had been polished by dipping the crystals quickly into distilled water. In order to survive the violence of the quench, the aluminium films had to be thicker than the carbon films; the films used were thick enough to be metallic silver in colour. The rest of the film-casting process was the same as that for carbon substrates.

Nitrogen quench method

A schematic diagram of the quench apparatus is shown in Figure 1. The sample on its grid (A) was suspended vertically by a small steel alligator clip (B) attached to a 3-4 in. copper wire (C), the end of which was inserted into the large end of a cork (D). The cork was properly sized to fit into the end of the barrel of a Daisy Model 1105-BB gun (E) which had been sawed off 1.5 cm above the maximum extension of the plunger. The gun was clamped vertically to a ringstand (F) on the top of the furnace (G) in such a manner that the barrel extended through a hole in the top of the furnace. The height of the gun along the ringstand determined how far the sample hung above the tall Dewar (H) contained the quenchant. About one inch from the sample to the top of the Dewar seemed to be a satisfactory distance.

The quenchant (I) in the Dewar flask was liquid nitrogen containing between 10 and 20% solid nitrogen. The amount of solid varied from run to run, but amounts below about 10% seemed to result in less satisfactory quenches than did greater amounts of solid. The solid nitrogen was produced by bubbling liquid helium directly into the liquid nitrogen in the Dewar. The mixture thus formed was a cloudy liquid with large chunks of solid at the bottom.

After the Dewar was placed in the oven, it was covered

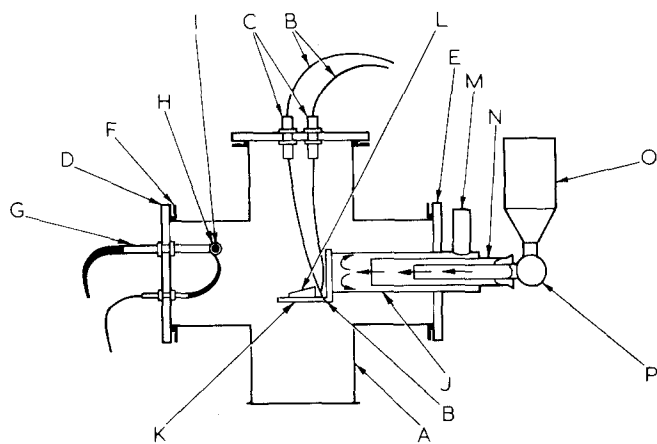


Figure 2 Cold shadowing apparatus. A, Pyrex cross; B, thermocouple; C, terminals; D, E, end plates; F, collars; G, terminals; H, rod holders; I, carbon rod; J, large brass tube; K, brass stage; L, Al dish with sample; M, LN₂ exit tube; N, LN₂ entry tube; O, LN₂ funnel; and P, LN₂ flow valve

with a cardboard cover (J). A wire (K) from one corner of the cardboard through a hole in the bottom of the furnace permitted the cover to be removed from the Dewar before the quench without disturbing the molten sample.

The first step of the quench procedure was to insert the cork bearing the wire and sample into the cocked BB gun so that the sample would be propelled straight down onto the quenchant. Alignment was critical for a fast quench. The sample was allowed to melt at 180°C for 5–10 min while the quenchant was prepared. The Dewar, filled with the nitrogen mixture to within 1 cm of the top, was placed quickly in the furnace directly under the sample. The cover was then set in place and the furnace was again closed. When the temperature in the furnace reached about 155K, the cover on the Dewar was removed. Care was taken to minimize vibrations of the gun that might keep the cork from going straight to the bottom of the Dewar. The cork permitted easy removal of the sample. The sample was kept inside a small beaker of liquid nitrogen during subsequent handling to keep it from warming.

Platinum shadowing

In order to keep the sample cold during the shadowing operating, the cold stage shown schematically in Figure 2 was constructed for the standard high vacuum evaporation apparatus²¹ in our laboratory. The device was built inside a 4 in. o.d. pyrex cross, each end of which had flanges and o-ring grooves to accommodate vacuum-tight end plates. A thermocouple permitted the temperature of the stage attached to the right end plate (K) to be determined to within a few degrees.

A shallow aluminium dish (L) containing the sample grids and liquid nitrogen could be placed on the cold stage. The left end plate had a holder permitting evaporation of platinum-carbon shadowing material onto the samples.

Before cooling the stage, the unit was completely assembled and evacuated to a pressure of 3×10^{-6} torr or better, to permit it to outgas sufficiently well that pump-down after sample insertion would be rapid. The stage was then cooled to liquid nitrogen temperature. Meanwhile, several grids were transferred polymer-side-up under liquid nitrogen to a shallow dish made of folded aluminium foil. When the stage was cold, the chamber was backfilled with dry nitrogen to minimize frost formation. Then the top

plate was lifted and long tweezers were used to lift the dish out of the liquid nitrogen Dewar and position it on the stage. By doing this quickly the top could be replaced and rough pumping begun while nitrogen remained in the aluminium dish. The remaining nitrogen solidified and then slowly sublimed as pumping continued. Liquid nitrogen was continually run through the stage until the shadowing material had been applied. The platinum-carbon was deposited within a second or two onto the samples. The thermocouple showed no evidence of a change in temperature during the evaporation. Experience with polymers with low melting temperatures suggests that during shadowing at room temperatures the surface temperature is raised less than ~30°C. After shadowing, the stage was warmed up to room temperature and the samples were removed for examination in the transmission electron microscope (TEM).

Cold electron diffraction

The JEM 100B microscope has a side-entry liquid nitrogen-cooled cold stage capable of keeping specimens at a temperature of ~-130°C in the microscope column. The primary difficulty in cold diffraction is in keeping the sample cold during removal from its liquid nitrogen storage bath and insertion into the evacuated column. Not having a transfer device available, the grids were coated with solid distilled UCON 12 ($T_M = -155^\circ\text{C}$) to keep them out of contact with the atmosphere for the few seconds necessary for the insertion. Details of the UCON coating technique, which was carried out under liquid nitrogen, are described in ref 22. Visual observation showed that it took 5–10 s for the UCON to melt after the stage with a UCON-coated grid was removed from liquid nitrogen. This proved to be enough time to get the stage into the column by inserting it directly through the airlock. After insertion, the stage was kept full of liquid nitrogen while the vacuum system of the microscope recovered from the sudden entry of air and frost. At the same time the UCON was also pumped away.

Unfortunately, there were a number of opportunities during the required procedure for the grid to warm up enough to cause crystallization. Even after practice a greater portion of the samples were crystalline, as indicated by electron diffraction, than those prepared for the other characterization techniques simply because one step or another in the insertion was too slow. Yet this technique was successful many times in keeping the samples cold and amorphous during insertion into the column of the EM.

Electron diffraction patterns from the samples were photographed onto Kodak medical no-screen X-ray film, which offered greater sensitivity than conventional electron image film at the expense of greater graininess. The beam conditions used (beam current less than 5 μA , small spot size and condenser aperture) gave a beam approximately 1000 Å in diameter at the sample and resulted in some crystallinity being left after a 30 sec exposure of a crystalline area.

Destruction of the polymer by the electron beam made it impossible to obtain both cold and warm patterns from the same region as the sample was warmed to room temperature. For some samples diffraction patterns were taken from a few selected small areas of a grid as marked on a cathode ray tube which displayed the position being examined on the grid. Patterns were taken from different selected areas while the grid was cold, and during and after warming. For several other samples the grid was scanned systematically by quadrants during warming so that, as far as possible, fresh polymer was available for each diffraction pattern photograph. This

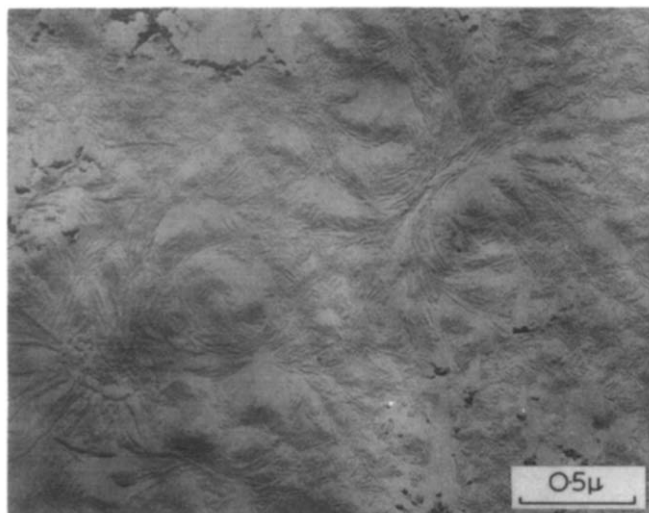


Figure 3 Spherulites in LPE film quenched from melt into Ucon-12. Sample was kept cold before and during shadowing

procedure was followed to ensure that amorphous patterns had not been produced by previous irradiation of an area. It also lessened the chances for previous irradiation to observe the crystallinity as it developed.

The temperature of the sample was read using a copper–constantan thermocouple embedded in the brass block that contained the sample. For most runs a millivoltmeter provided with the stage was used, but the temperature could be read to only $\pm 10\text{K}$ by this method. The cold junction of the thermocouple was kept at room temperature. Because of concern over the accuracy of this unit, for several of the last runs a well-calibrated digital voltmeter and an ice–water cold junction were used. The accuracy of the thermocouple was verified by noting the temperature at which ice diffraction disappeared when a grid containing frozen water was allowed to warm up in the column. A table of the sublimation temperature of water against vacuum was kindly provided by Dr L. W. Hobbs of the CWRU Department of Metallurgy²³.

Differential scanning calorimetry

The d.s.c. experiments in which the sample was kept cold before insertion were performed on a Perkin–Elmer DSC-2 equipped with a Scanning Autozero unit. The sensitivity setting of 0.5 mcal/s that was necessary to see the transitions in the tiny samples resulted in problems with noise and with baseline shape. These, however, did not obscure the information that was contained in the thermograms of the cold samples. The instrument had a subambient cooler with a liquid nitrogen heat sink which was capable of controlling the temperature of the sample down to 100K. Its calibration was checked periodically.

Each sample was placed including its grid inside an aluminium d.s.c. pan under liquid nitrogen. The grids were flattened as much as possible and laid in the pan polymer-side-down. An identical carbon-coated grid was set in the reference pan. A flat lid was then set on the pan and pushed as flat as possible using tweezers. The pan was not crimped for two reasons: the crimper did not operate well under liquid nitrogen, and the uncrimped pan held enough liquid nitrogen in it to keep the sample cold for the several seconds needed to move it from a dish of liquid nitrogen to the sample holder of the d.s.c. However, there were problems in the lack of thermal contact between the sample and the pan that

appeared primarily as a slope in the baseline. The Scanning Autozero was used to subtract from the data for each sample any peculiar shapes the instrument put in the low-temperature baseline. However, it could not compensate for the changes in baseline slope from sample to sample. The head of the d.s.c. is inside a helium-purge glove box which minimizes frost formation. Each sample was transferred through the air lock of the glove box in a Petri dish of liquid nitrogen. The nitrogen-filled sample pan was removed from the dish and inserted into the cell in the usual manner for the instrument. The temperature controller was able to maintain a temperature of 100K for all but the few minutes after the nitrogen in the sample pan ran out. The temperature rise then was almost always less than 10K.

Each sample was scanned at 40K/min between 100K and room temperature to check for crystallization effects. A wider temperature range was not obtainable due to baseline difficulties. Then the temperature was lowered again and two repeat scans were made of the same sample through that temperature interval. The scans above room temperature were taken later under the same scan conditions and with the same samples in crimped pans on another DSC-2.

UCON-12 quench method

Some preliminary work was done in which molten polyethylene was quenched into UCON-12 at its melting point, -155°C . This is a standard rapid quench used in the preparation of biological samples. The samples were grids with carbon-backed polyethylene identical to those used in the nitrogen quench work. For some runs the UCON was distilled. The polyethylene on the grids was melted in an oven and then dropped rapidly into a dish of UCON placed in the furnace. The UCON was solid except for a small puddle of liquid in the centre. For platinum shadowing, the samples were placed on the evaporation cold stage in the block of UCON. After pumpdown, the stage temperature had to be raised slightly, long enough to permit the UCON to melt and boil away. The thermocouple stage was used to be sure the temperature did not rise too far.

RESULTS

UCON quench

Figure 3 is a micrograph of LPE which was quenched into undistilled UCON-12 and shadowed cold. The lamellar structure is clear, with occasional poorly-formed spherulites being present. The regions between the spherulites also contain small lamellae. Other areas in this and other samples had broad, flat lamellae. The lamella thickness is of the order of 100 Angstroms, although this estimate is crude because the angle of inclination of the lamellae to the plane of the specimen is unknown. Other specimens had lamellae with thicknesses between 60 and 100 Å. The film is not uniform in thickness; a surface roughness on the 1000 Å scale exists. These mounds have the same lamellar texture as the rest of the film. The small dark particles and the nodular texture in the centre of the spherulite on the left side of this Figure are artefacts from the undistilled UCON. Needless to say, UCON quenched samples kept cold before and during electron diffraction showed well-developed crystallinity with individual reflections being observed on the various rings.

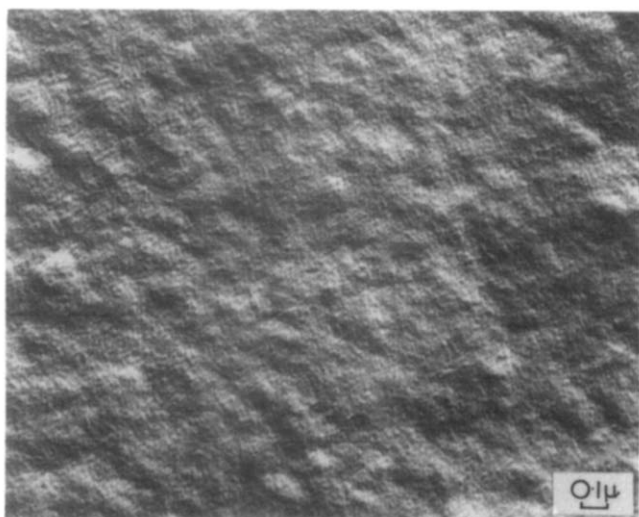


Figure 4 Thicker area of LPE film quenched into liquid–solid nitrogen. Sample was kept cold before and during Pt/C shadowing

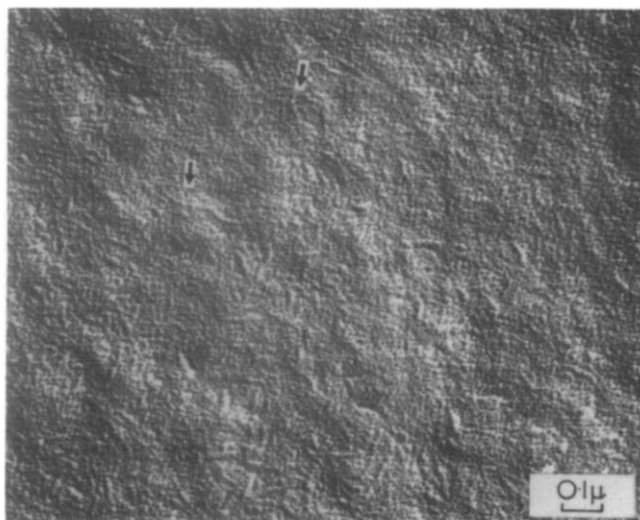


Figure 5 Nitrogen-quenched LPE film containing lamellae with appear to be formed from coalescence of nodules. Sample was kept cold before and during Pt/C shadowing

Nitrogen quench

Figure 4 is a micrograph of a sample which was quenched in a liquid/solid nitrogen mixture and then kept cold before and during platinum–carbon shadowing. Slight surface irregularities on the scale of 1000 Å can be seen. Superimposed upon these irregularities are round nodules, ~100 Å in diameter, which cast well-defined shadows and are too large to be due to platinum granulation. A plain carbon grid run through the same quench and shadow procedure had much finer, uniform granulation. The size of the nodules and irregularities in the polymer varied somewhat with the thickness of the film. A previously published micrograph²⁴ of a thinner film had smaller irregularities and 50–70 Å nodules. In other films where the polymer had collected more thickly around the edges of the grid square, the size of both structures could be seen to increase as the polymer became thicker²².

Figure 5 is a micrograph of an area that is believed to be reasonably thin but that was not quenched quite rapidly enough to prevent the formation of a few lamellae. The lamellae are of similar width to the surrounding nodules, i.e.

~100 Å. Some of the lamellae, such as those marked with the arrows, look like rows of nodules that have not quite coalesced completely into a smooth lamella. On the other hand, in other micrographs²², the transition between poorly quenched and presumably well-quenched areas was quite abrupt.

Figure 6 shows two types of morphologies seen in poorly quenched areas. To the right of the picture are irregularities and lamellae. To the left can be seen several very badly-formed spherulites. Some surface irregularities are still visible, but they may simply be products of the crystallization processes in the spherulites. Within the spherulites there is a radial arrangement of the lamellae and the spherulite boundaries are plainly defined. The 100 Å nodules visible in the well-quenched samples are almost completely absent even outside the spherulites, having been replaced by the lamellae.

Better, but still badly-formed, spherulites can be seen in *Figure 7*. The lamellae seem to be predominantly radial in the spherulites. The spherulite at the lower left seems to have

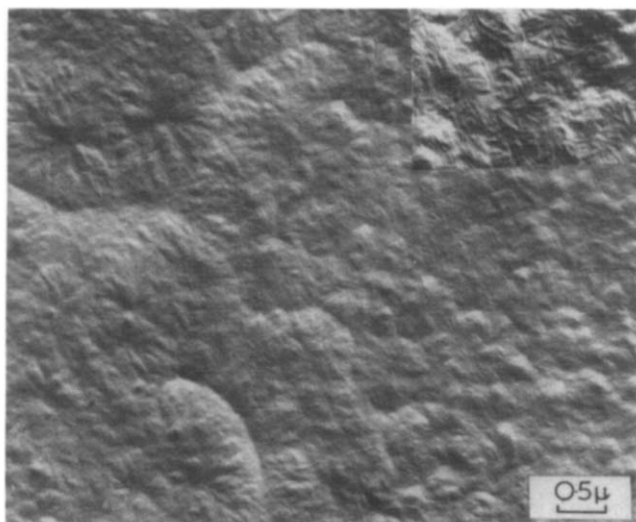


Figure 6 Nitrogen-quenched LPE film showing lamellae and crude spherulites formed in badly quenched areas. Sample was kept cold before and during Pt/C shadowing

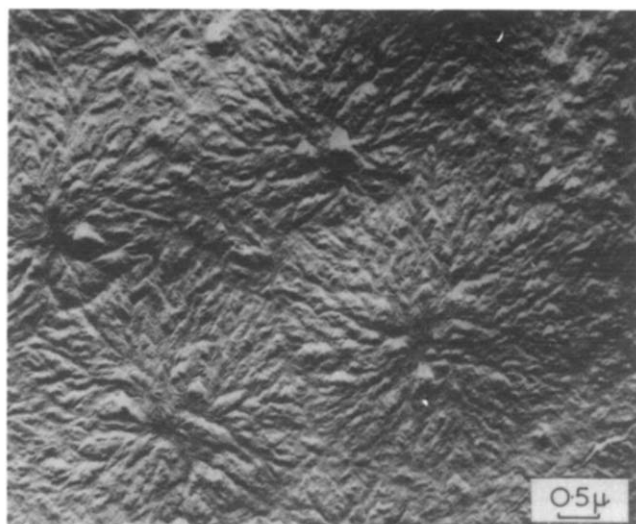


Figure 7 Spherulites in badly nitrogen-quenched LPE film. Sample was kept cold before and during Pt/C shadowing

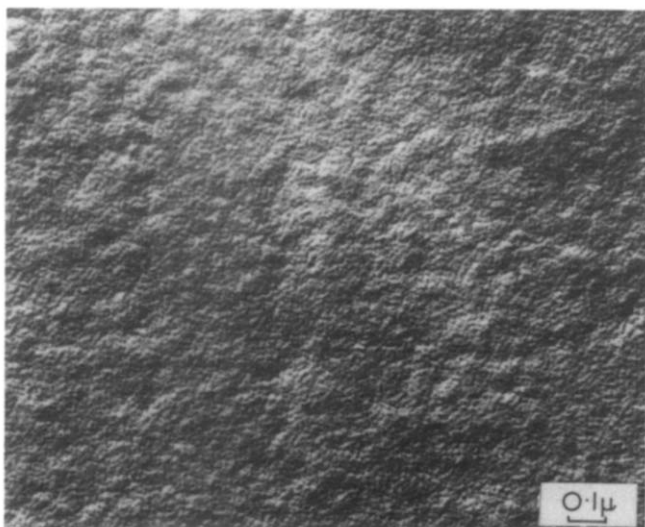


Figure 8 Nitrogen-quenched LPE film that gave predominantly amorphous diffraction when cold. Sample was kept cold before and during insertion and observation in the EM. Upon warming it was entirely crystalline. Pt/C shadowed after warming

developed from a central sheaf. Again, it is not known whether the lumpiness within the spherulites is related to the irregularities seen in non-spherulitic areas.

The above micrographs (Figures 5–8) indicate the range of morphologies visible from well-quenched to poorly-quenched samples that were kept cold before and during platinum–carbon shadowing. It should be pointed out that the proportion of the various structures (and thus presumably the quench speeds) varied greatly from sample to sample. In the ‘best’ samples the entire grid had a surface structure corresponding to Figures 4 and 5. In most samples less than 30% of the material was conspicuously crystalline; however, many of the samples had small areas that were crystalline, especially near grid bars. There were some samples, however, in which half or more seemed to be crystalline. It was not possible to relate these observations to known variations in the quench; presumably, however, the quench rate must have varied both in and between grids.

In an effort to determine whether the nodular structure reorganized upon warming, a number of grids which had been examined by diffraction while cold were shadowed at room temperature with platinum–carbon. These films warmed up rapidly upon removal from the cold stage. Figure 8 shows an area from a grid which was predominantly amorphous while cold and crystalline after warming. The structure has not reorganized into lamellae or spherulites. Instead the chains seem to have crystallized locally, retaining the same morphology which existed in the glass. In other micrographs from this grid polymer pulled across cracks in the carbon substrate confirmed the presence of polyethylene. When the rest of the grid was examined, only a few slightly spherulitic areas were found, confirming the diffraction evidence.

Figure 9, on the other hand, shows a portion of a grid which was partly crystalline while cold and entirely crystalline when warmed. This is a portion of a large, well-formed spherulite embedded in material which presumably was not initially crystalline. Lamellae appear to be growing out into the nodular region; however, it is not possible to determine if the growth occurred during quenching or warming. Occasionally, in lamellae such as those marked with arrows, the nodules do not seem to have merged completely.

One question which arose during this work is whether the degradation of the polymer which undoubtedly occurred while the thin film was hanging in the oven might be severe enough to affect the results which have been obtained. Test samples were held in the oven for up to 25 min and then air-cooled, Pt/C shadowed, and examined by TEM. After 25 min in the oven, the samples still crystallized in the normal lamellar or spherulitic manner. These samples were molten for nearly three times the maximum length of time used for any of the quenched samples. In addition, in current work²⁵, the melting is carried out in an N₂ atmosphere, with identical results being obtained. The results of d.s.c. tests for degradation will be reported below.

Electron diffraction

Figure 10a shows a diffraction pattern from an early ultra-quenched polyethylene sample which was kept cold during insertion and observation in the microscope. The polyethylene film is on a carbon substrate. The pattern is a diffuse halo, though some other patterns from the same sample were definitely crystalline even before the grid was warmed. However, after warming, the entire grid gave crystalline diffraction such as that seen in Figure 10b. This particular pattern is from an area near that used for Figure 10a, but it is not known if this area was originally amorphous. It is noted, that only a few discrete reflections can be seen. Even though the incident beam was only ~1000 Å in diameter; the pattern is essentially ‘powder-like’.

Several grids containing predominantly amorphous polyethylene on carbon were examined and verified the reproducibility of these observations. A number of others were found, however, which were entirely crystalline, and are believed to have warmed up during the cold insertion process.

While carbon films were excellent substrates for the polyethylene films, amorphous carbon films show a diffuse halo in the same location as amorphous polyethylene. This made it impossible to confirm the presence of polyethylene at any given point by anything more than arguments based on the presence of polymer everywhere on shadowed samples and the absence of diffraction-free areas on the warmed grids.

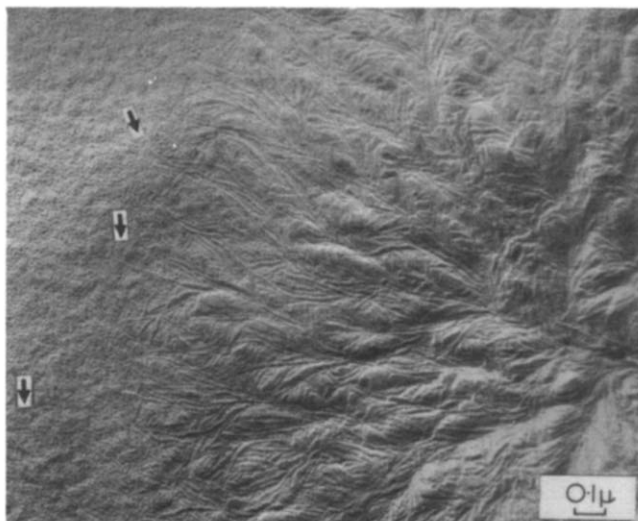


Figure 9 Boundary between crystalline and presumably amorphous areas of nitrogen-quenched LPE film. Arrows mark lamellae in which the nodules do not seem to have coalesced completely. Pt/C shadowed after warming

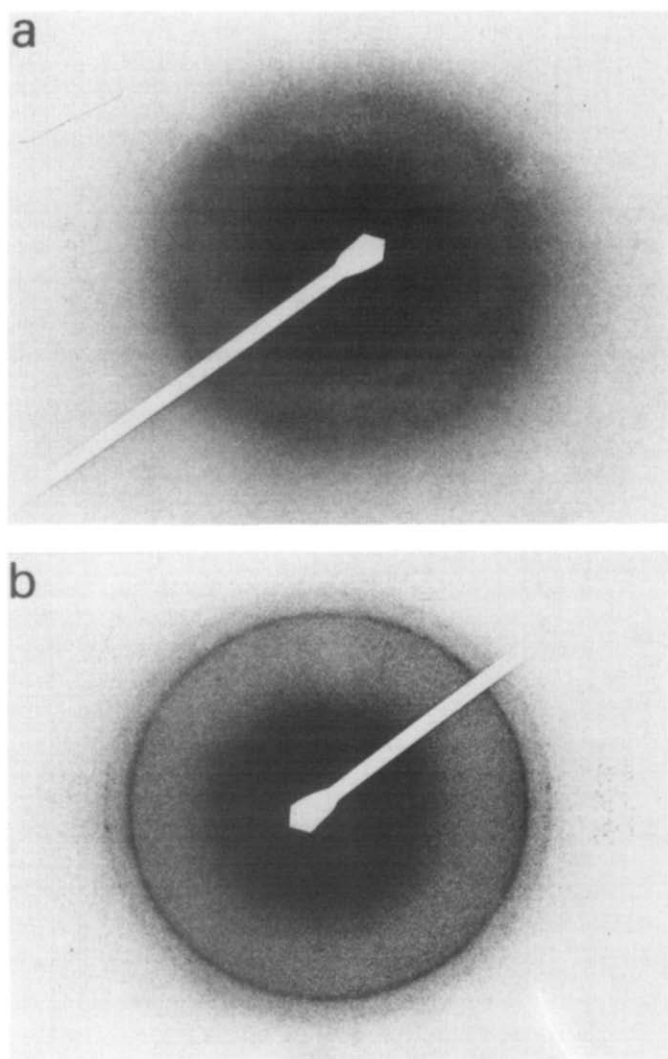


Figure 10 (a) Electron diffraction pattern of nitrogen-quenched LPE film kept cold before and during insertion and observation in EM. Carbon substrate. (b) Diffraction pattern from same film after warming to room temperature

Furthermore, it complicated any hopes of a quantitative study of the intensity profile of the halo or the crystalline peaks.

The use of aluminium substrates for the cast PE films eliminated the extra diffuse halo. The proper thickness for the evaporated metal had to be determined by trial and error because of the brittleness of the aluminium films. The line was very fine between films too thick for easy electron transmission and those too thin for mechanical strength during the quench. The visibility of crystalline A1 diffraction on many of the patterns also provided calibration of the camera constant for individual patterns. This was needed because the grids were crumpled by the quenching procedure and thus did not lie flat on the specimen stage.

Figure 11 is a typical cold diffraction pattern from a sample in which both the polyethylene and aluminium were of proper thickness for good quenching and diffraction. Polyethylene exhibits a diffuse amorphous halo, while the sharp rings are aluminium diffraction. Only one sharp pattern out of 24, chosen randomly while the sample was cold, had a slight amount of crystallinity.

These patterns were taken at $\sim 130\text{K}$. In order to calibrate the camera length we assumed an average thermal expansion

for aluminium below room temperature of $2.2 \times 10^{-6} \text{ K}^{-1}$, the 111 and 200 aluminium spacings would be 2.33 and 2.02 Å, yielding a value of 4.33 Å for the 'Bragg spacing' of the polyethylene diffuse halo. On only one unoriented pattern were other polyethylene spacings seen, these had values of 2.2 and 1.2 Å.

Figure 12 is interpreted as the diffraction pattern from oriented amorphous material stretched across a crack in the aluminium. This sample contained many polymer-bridged cracks, but it is not known whether the material was stretched across the cracks during the quench or during the subsequent handling under liquid nitrogen. The oriented portion of the pattern corresponds to the Fourier transform of an isolated *trans*-planar zig-zag or 2_1 helix. The strong equatorial spots have not split into the (110) and (200) reflections seen in the normal PE fibre pattern. Only in the one case mentioned above were the patterns from unoriented portions of the sample of sufficient intensity to determine if they also could be interpreted as being due to isolated 2_1 helical segments; the spacings in that pattern agree with the quadrant and meridional reflections of the oriented patterns.

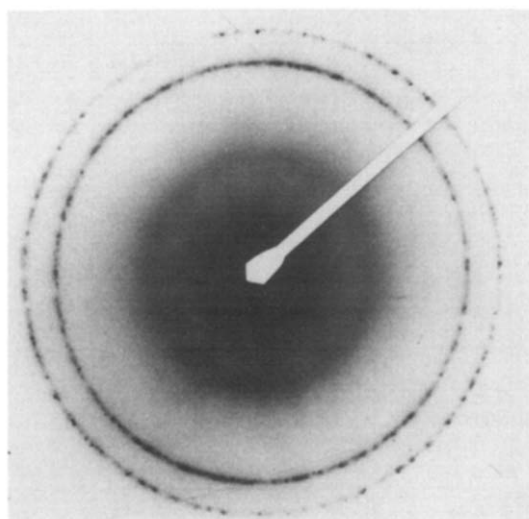


Figure 11 Electron diffraction pattern of nitrogen-quenched LPE film on Al1 diffraction. Sample was kept cold before and during insertion and observation in the EM

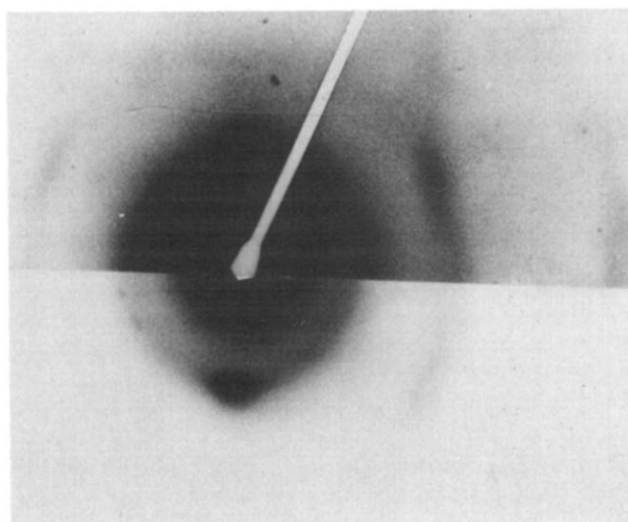


Figure 12 Diffraction pattern before warming of oriented portion of sample used for Figure 11

An attempt was made to note the systematic changes in the diffraction pattern as this sample was warmed. Unfortunately, this was complicated by two factors; the presence of so much oriented material in this sample and the non-uniformity of the sample. A sequence of patterns and the temperatures at which they were taken are shown in *Figure 13*. Temperatures were read from the millivoltmeter provided with the stage and while relatively correct, are only accurate to $\pm 10\text{K}$.

The first pattern, *Figure 13a* shows some orientation but no evidence of crystallinity (no splitting of the 110–200 equatorial reflection) at $\sim 180\text{K}$. The areas used for the next four patterns all contained highly oriented material, as indicated by the small amount of arcing seen in the equatorial spots. However, the equatorial spots which appeared as single spots in *Figure 12* gradually became more sharply split into the (110) and (200) reflections as the temperature was raised from 180 to 210K. The unoriented portion (visible on the original) of the pattern still shows little or no crystallinity. The arcs of sharp spots in *Figure 13d* are believed to be low molecular weight contaminants. In *Figure 13f* a well developed crystalline ring extends from the slightly oriented arcs around some of the rest of the halo. *Figure 13g* continues the trend for sharpening of the oriented equatorial spots as the temperature is raised.

Figure 13h illustrates a problem that occurred for many of the unoriented patterns in this series taken from regions in which the aluminium was thick and difficult to penetrate with electrons. The diffraction pattern is that of an amorphous or very poorly crystalline material. Whereas the sharpness of the spots in the oriented patterns increased as the specimen temperature was raised, this was not generally true of the unoriented material. Although this may be due to some non-uniformity of the sample it is most likely due, as discussed below, to degradation of the polymer from contact with the aluminium.

Other attempts to refine the temperature sequence experiment were not successful, and further work is continuing. However, direct observations of the quenched films on carbon substrates in the microscope indicated that crystallinity was easily visible as the sample was warmed through -80°C . The patterns appeared to become more pronounced as the temperature was raised still further, but this was not confirmed by photography. The samples on carbon were more consistent as far as the visibility of sharp (110) and (200) rings over the entire warmed sample than were the samples on aluminium.

Samples which were too thick could not be quenched successfully at all. Cold diffraction from a typical thick film is shown in *Figure 14*. Judging from the large amount of diffuse scattering which was visible, the film was probably a few thousand Angstroms thick. The uneven intensity of the rings shows that the crystallites are larger than those seen in thinner films which had been quenched and then crystallized from the glass. Further characterization of the variation in quench with thickness is still in progress.

Differential scanning calorimetry

In spite of the experimental difficulties mentioned previously, it was possible to detect what was apparently amorphous polyethylene by d.s.c. *Figure 15* shows the first three d.s.c. scans of an ultraquenched sample which was kept under liquid nitrogen during insertion into the d.s.c. The second and third scans were taken after the sample was

warmed to room temperature. The peculiar shape of the baseline is due to the use of the scan from a previous warmed sample as the instrumental baseline in the Autoscan.

The most prominent feature of the first scan is an exotherm with its peak between 160 and 170K. Depending upon how the relative heights of the scans are adjusted there may be endotherms centred around 150 and 190K, but this is questionable due to uncertainties in the baseline shape. There also may be some exothermic activity above 190K. Heat given off about 190K would almost certainly be due to crystallization continuing above this temperature.

The scans shown in *Figure 16* are for a quenched sample from a different quench batch but one which was supposedly identical to the sample shown in *Figure 5*. However, the shape of the baseline was not adjusted; with a flat empty carbon-coated grid in the sample side, the baseline which was electronically subtracted from the data was the gentle curve indicated by the dotted line below the sample scans. Again an exothermic peak at 160–170K can be seen, but the possible endotherms seen in *Figure 15* do not seem to be present in this case. It is believed that the first scan falls below the second one at temperatures greater than 200K because of a shift in the baseline slope due to a change in thermal contact between the sample and the pan. Such a shift is also seen between the second and third scans. The change in baseline slope between the first two scans makes it impossible to determine whether there is an exotherm above 190K.

The size of the samples naturally raises questions about the possibility that the d.s.c. results are due to contamination. This was investigated by several experiments. The first was to scan a grid containing a solution-cast Marlex film which had not been melted or quenched. It was immersed in liquid nitrogen and inserted into the d.s.c. in the same manner as the quenched specimens. The three scans were not exactly superimposable on each other, but there was no trace of the 160–170K peak. A second check was run using a plain carbon-coated grid which was heated and run through the same quench, storage and insertion as the grids with polyethylene. The first and second d.s.c. scans were exactly superimposable on each other. Also, a polyethylene-containing grid which had been quenched, warmed enough for the polyethylene to crystallize, and then inserted under liquid nitrogen, produced d.s.c. scans which were superimposable on each other except for a minor baseline tilt.

Based on these experiments, it is believed that the exothermic peak between ~ 160 and 180K is real and unique to the ultraquenched polyethylene specimens. Evidence favouring a broad, low, crystallization exotherm above 200K occurred in several samples, but is not conclusive. The evidence for an endotherm such as a glass-relaxation endotherm²⁷ around 150 or 190K is even more questionable due to the peculiar shape of the baseline in those scans in which they were seen.

The impossibility of getting a flat baseline over the entire range between 100 and 400K at this sensitivity required that the samples be saved after the low temperature runs so that the melting behaviour of the crystals formed from the glass could be examined. Furthermore, a different instrument was used, which had more noise at the required sensitivity and temperatures. The pans were crimped around the samples to eliminate the thermal contact problem.

The three heating curves run on each sample did not have well-defined melting endotherms. Instead, they had a number of peaks which could have been endotherms from small,

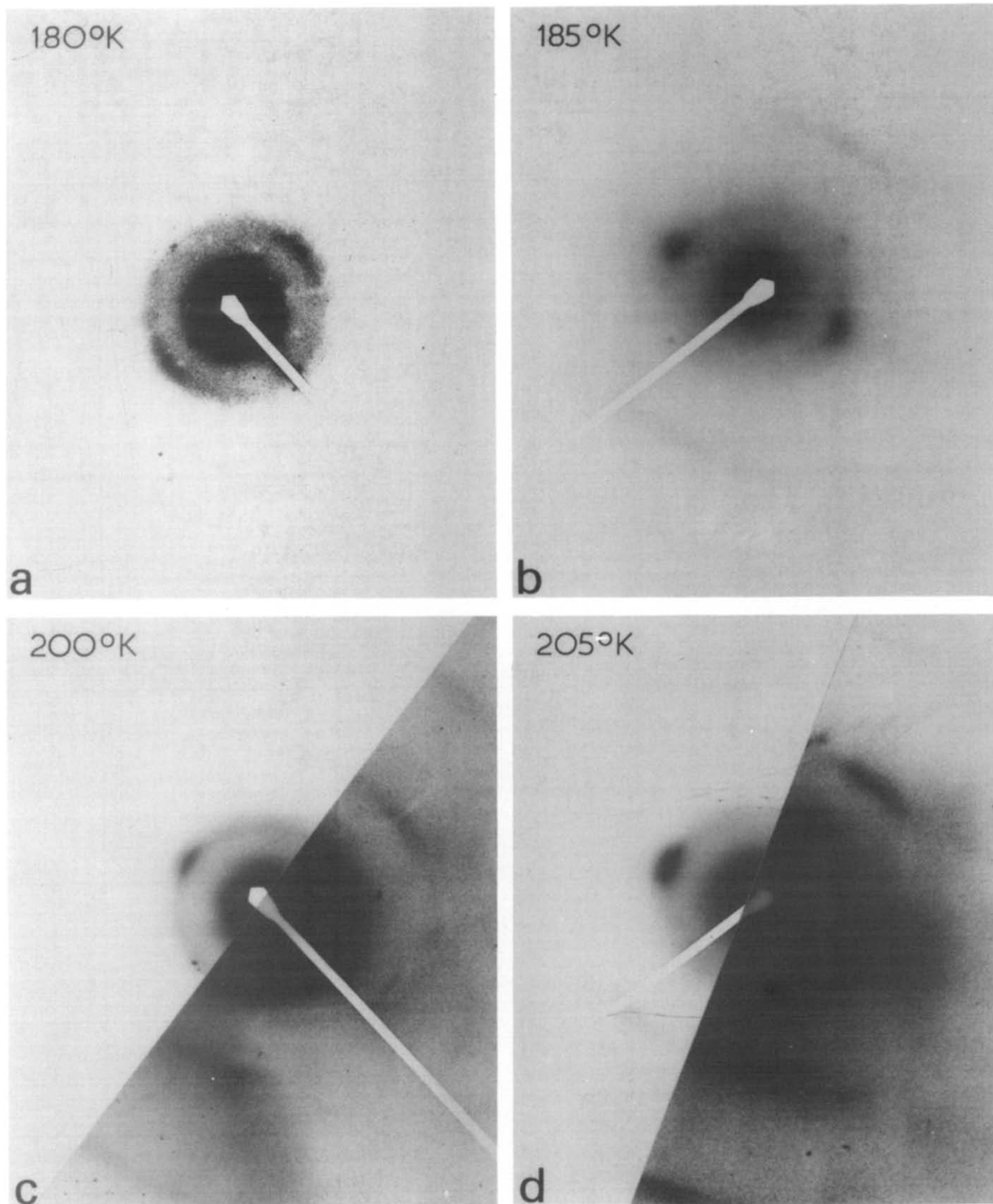
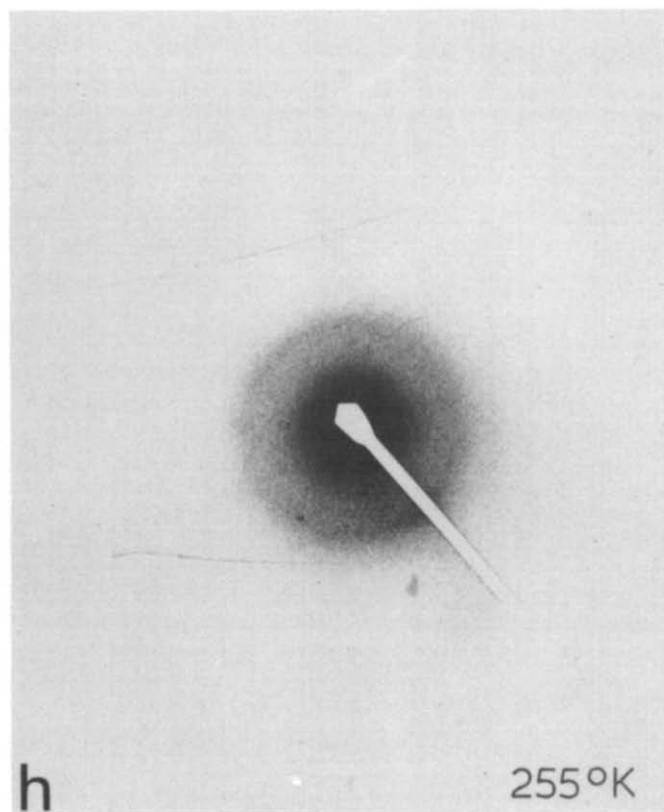
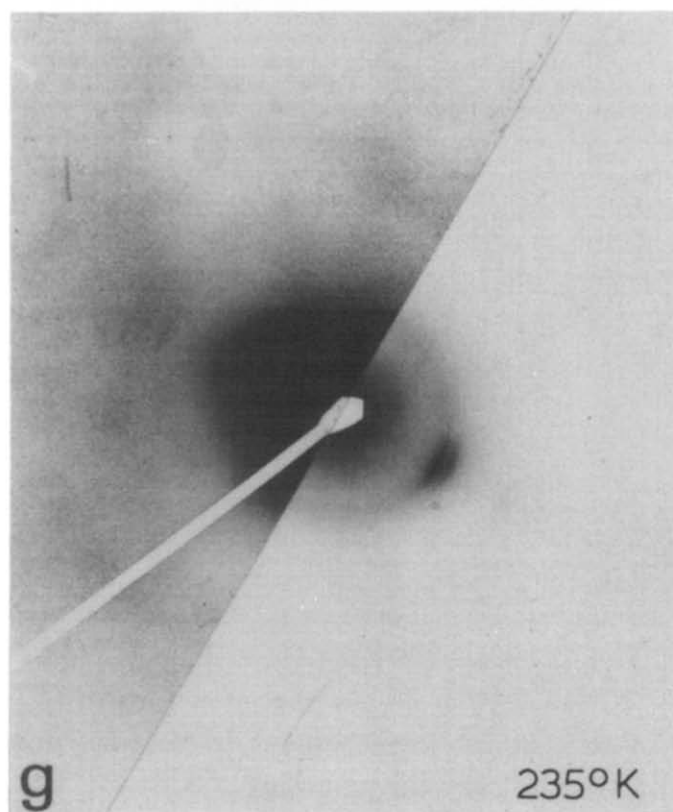
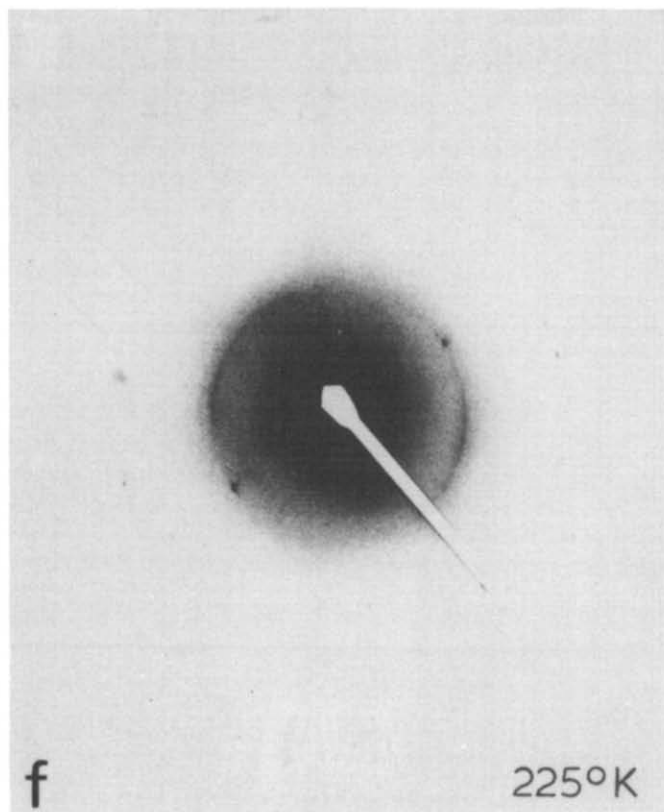
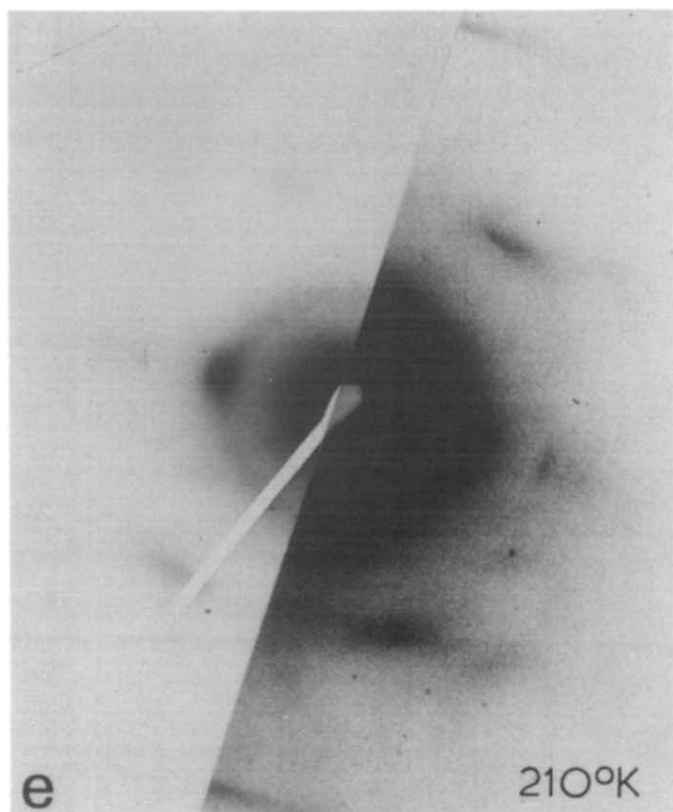


Figure 13 Diffraction patterns taken as sample used in Figure 11 and 12 warmed up in the electron microscopes indicated temperatures are good to ± 10 K. (a) 180K; (b) 185K; (c) 200K; (d) 205K; (e) 210K; (f) 225K; (g) 235K; (h) 255K



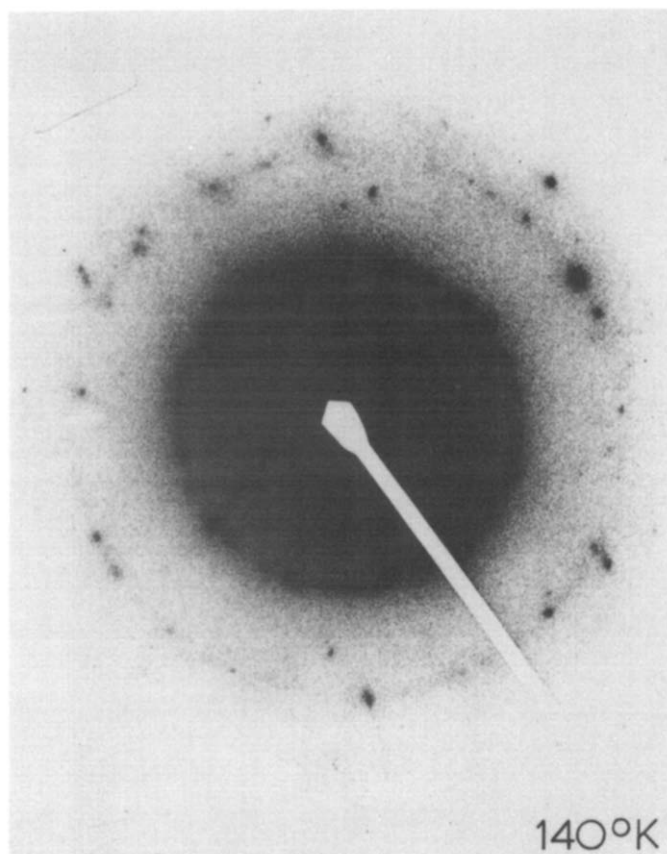


Figure 14 Diffraction pattern of very thick nitrogen-quenched LPE film on Al substrate at 140K. Sample was kept cold before and during observation

imperfect crystals. Unfortunately, these were about the same size as the noise peaks in baseline scans. The reproducibility between scans was only fair, but there was no evidence for annealing of small crystallites into larger, more uniform ones. Cooling curves between the heating scans also had little or no useful information. At this sensitivity it was possible to see a small but clear melting endotherm for a grid containing an equal amount of solution-cast polyethylene. Thus, if these multiple, small peaks are real, they suggest that the quenched and crystallized samples contain a distribution of crystallite sizes. Furthermore, these crystallites do not anneal to form more uniform crystals under the conditions used in this experiment.

DISCUSSION

The first question for consideration is the nature of the polyethylene glass. The micrographs reveal the existence of two levels of structure in the material shadowed before warming. It is believed that all or most of the shadowing material was applied before the polyethylene had a chance to crystallize. Previous observations by Gezovich and Geil¹⁰ of cold-shadowed amorphous polypropylene ($T_g \sim 273\text{K}$) revealed the shadowed nodules of the quenched material on the surface but round, darker (thicker) areas underneath. These dark areas were spherulites which had formed out of the glass. This indicated that the first platinum which evaporated 'froze' the structure of the glass before the sample warmed enough to crystallize. Since the T_g of polyethylene is lower than that of polypropylene the possibility cannot be ruled out that the PE samples crystallized before much of

the shadowing had been applied. However, previous experience with low melting point samples and the polypropylene indicates that shadowing material faithfully reveals the initial surface structure of the quenched material.

The 100 Å nodules seen in well-quenched samples were relatively constant in size and prominence in all but the thinnest areas. In some areas which had not been quenched quite as well, the nodules seemed to have aggregated partly into spotty lamella-like rows. In poorly quenched areas, the nodules were replaced by lamellae whose thickness approximated to the nodule diameter. It is suggested that these nodules are locally ordered regions similar to those proposed^{5,7,8} for other amorphous polymers. It would seem reasonable, due to the partial coalescence of some nodules into lamellae, that appreciable amounts of chain-folding (presumably irregular) might occur in them.

We cannot explain the larger, ~ 1000 Å irregularities. They were seen most distinctly in thicker films; presumably nodules would be the only texture that would be seen in sufficiently thin films. They are not small spherulites which crystallized during the shadowing process because samples shadowed after being warmed slowly to room temperature had the same morphology as the samples shadowed while cold, with nodules superimposed upon the larger irregularities. They may possibly be related to uneven thermal contraction of the film during the quench.

A general trend was noticed in which the thicker regions seemed to have more lamellae and spherulites than did thinner areas. This is not surprising since thicker regions would have required more time to reach the quench bath temperature. However, in some micrographs, thick regions were well quenched, in others thin regions were crystalline, and in some boundaries between poorly and well-quenched areas were quite sharp. We must attribute this variability to the unpredictable nature of the quench, both between samples and within one sample. Pockets of nitrogen bubbles collecting

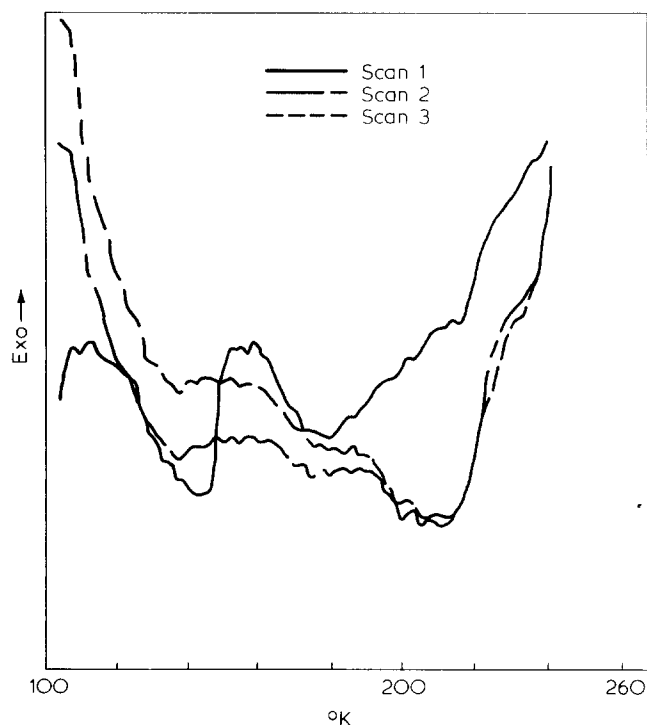


Figure 15 First three d.s.c. scans of nitrogen-quenched LPE sample kept under LN_2 before and during insertion into d.s.c. Scan rate, $40^\circ\text{C}/\text{min}$

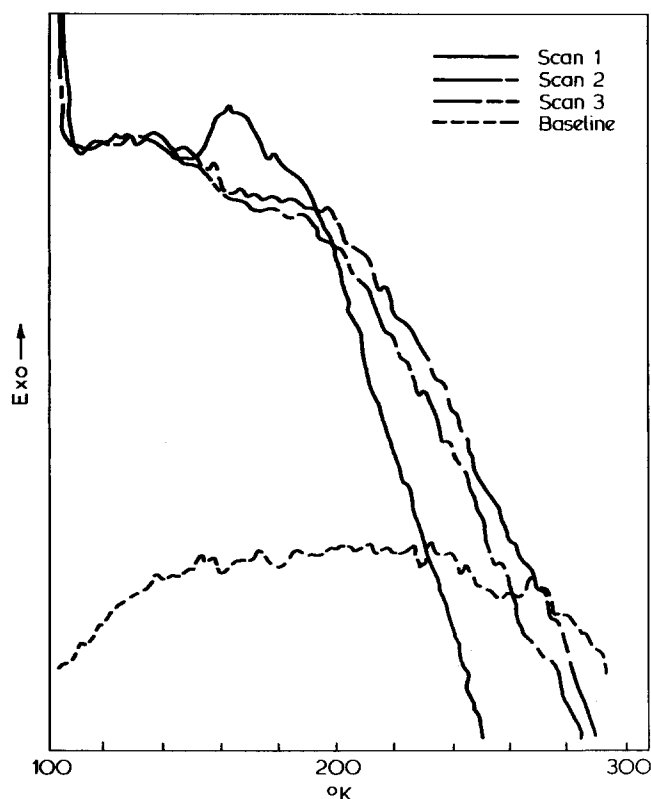


Figure 16 First three scans of nitrogen-quenched LPE sample from different quench batch. Scan rate, 40°C/min

on the surface could have resulted in extreme local variations in heat transfer efficiency and thus in the crystallinity as well.

The most remarkable feature about polyethylene in the glassy state is the fact that no large-scale change in structure occurred as it crystallized. Instead, when rapidly heated to room temperature, the molecules within the nodules, presumably, became the basic crystalline units. This agrees with the observation of the continuous crystalline rings seen by electron diffraction using a beam approximately 1000 Å in diameter. Since the rings are continuous, rather than spotty, a large number of crystals must be in the beam. Each crystal, however, is large enough for its diffraction to be only slightly broadened in comparison to solution-cast crystals. Examination of solution-cast films under identical beam conditions which gave sharp diffraction spots suggests that around 100 slightly diffuse spots would produce a reasonably smooth ring. As a rough estimate, if we imagine a 50% crystalline film, 500 Å in thickness, a circular beam of 500 Å radius, and crystallites 50 × 50 × 50 Å in size, then around 1500 crystals would be in the beam. If 5% of those were in a diffracting position, then, with multiple reflections from each of 75 randomly-oriented crystallites, that ring would appear to be continuous.

The near indistinguishability of the morphologies of samples shadowed while cold and samples shadowed after rapid warming is the reason for believing that the areas of poor crystallinity developed while the temperature was dropping during the quench rather than while the sample was being warmed. This may offer some insight into the melt crystallization process. For example, the apparent aggregation of nodules to form lamellae has been observed to occur during the formation of spherulites from the glass in polymers such as poly(ethylene terephthalate)⁵, polycarbonate⁷, and isotactic polystyrene⁸. Figures 5 and 9 suggest

that this also occurs during rapid crystallization from the melt. This may be an extreme form of the Regime II crystallization which Lauritzen and Hoffman¹⁶ suggested might occur at high undercoolings.

A reasonable extension of the presence of nodules in the glass and in rapidly crystallizing polymer is to speculate that they may be present in the melt as well. It hardly seems likely that a random coil in the melt would have time to form a partly-folded or at least locally parallel structure during quenching which would subsequently form a crystal during warming. This would be in basic agreement with Aharoni's model of crystallization by the merging of domains present in the melt²⁸.

One of the most important pieces of information to be obtained from the morphological study of the crystallization of polyethylene from the glass is the temperature at which this occurs. The series of diffraction patterns in Figure 13 suggests that in well-oriented areas, crystallization begins to appear at around 185 ± 10K (−88°C) and becomes progressively better developed as the temperature is raised. It will be recalled that this particular set of observations was not duplicated, and some of the patterns for unoriented regions taken at higher temperatures seemed to have less well-developed crystallinity than oriented patterns taken at lower temperatures. The temperature dependence of the unoriented patterns was somewhat more variable than that of the oriented ones. In general, however, it is believed, based on these patterns and on direct observations in the microscope of the carbon-backed, quenched films, that crystalline diffraction becomes visible in the neighbourhood of 180–190K (−80° to −90°C).

The d.s.c. results are in basic agreement with the electron diffraction results. For a heating rate of 40°C/min, which is considerably faster than that used for the diffraction work, the scans indicate that an exothermic process begins just below 160K (−113°C) and continues at least through 180K. Quantitative study of the peak area was not possible due to the unknown sample weights. Two possible processes are envisioned for this exotherm: crystallization and relaxation of the excess free volume frozen into the glass by the drastic quench²⁹. Such relaxation or densification of glasses at temperatures just below the glass transition has been observed to produce an exotherm³⁰. Large amounts of frozen-in free volume would certainly be expected to result from the drastic quench used here. Crystallization, on the other hand, would be expected to occur just above T_g . Both processes may be occurring, either in succession or simultaneously (see below). There was also some indication that further crystallization occurred above 200K.

The presence of a contribution from glass relaxation to the peak is suggested by the absence of a well-defined, simple melting endotherm of size comparable to the crystallization exotherm. If multiple small melting endotherms are present, the fact that the crystals do not reorganize appreciably on melting and recrystallization merits further investigation.

A question of concern, however, is whether the samples, especially those on aluminium, oxidized to an appreciable extent before quenching. If the films on carbon were cooled by removal from the oven rather than quenching, well-formed lamellae and spherulites were observed; likewise, samples warmed up after quenching were always crystalline. However, samples prepared on aluminium frequently had areas which did not crystallize upon warming. Furthermore, following this work, a paper was published in which X-ray photoelectron spectroscopy results confirmed that large amounts of oxidation occur on the surfaces of samples of

linear and branched polyethylene melted and crystallized against clean aluminium foils³¹. Thus, although oxidation may have affected the crystallization behaviour, it is not believed to have been sufficient to invalidate the conclusions. The carbon substrate samples always yielded polyethylene diffraction patterns, as did the material drawn across the cracks in the aluminium substrates. Furthermore, the primary effect of oxidation would be expected to be a reduction in molecular weight, which should result in faster crystallization during cooling.

The question of the validity of the results of Hendra *et al.*¹⁷ must now be raised. It does not seem possible that they were able to use liquid nitrogen at its boiling point to quench 30 μm films to the glass. Even the technique we have used was unable to produce amorphous polyethylene from films which were only several thousand Angstroms thick. Our quench, however, should be much superior to liquid nitrogen at its boiling point, due to the reduction in the amount of gas formation on the sample surface. The published description of their quench must therefore be questioned. In addition, even if a better quenchant had been used, one still needs to question whether it is possible to quench 30 μm films to a glass by any quench method. Nevertheless, Hendra's i.r. scans clearly do not resemble those of crystalline polyethylene. Boyer and Snyder, however (see below), have questioned Hendra's interpretation of the spectra³².

We suggest that the interpretation of the longitudinal acoustic mode (*LAM*) band in Hendra's Raman spectra as a lamellar fold thickness may also need revision. Our results indicated that truly amorphous linear polyethylene crystallizes within the nodules during rapid heating, rather than as lamellae, whereas less well-quenched material or amorphous material that crystallizes slowly near 190K²⁵ can be lamellar. The *LAM* only gives the average straight chain segment length and does not indicate whether these are in a nodular or lamellar structure. Detailed interpretation would require morphological examination of Hendra's samples.

The temperature of 180K which Hendra *et al.* suggest for the onset of crystallinity is in good agreement with the present results. It was not possible to determine whether the gradual increase in crystal perfection above 180K which they observed was also occurring in the samples used here for electron diffraction. Measurements of line broadening as a function of temperature would be desirable.

The problem where crystallization begins raises the classic question of the location of T_g for linear polyethylene. Two criteria, among others², have been used to describe T_g : the temperature at which motion occurs in chain segments twenty or more carbon atoms long, and the transition above which crystallization from the glass can occur. The second criterion has been assumed to be a consequence of the first. However, depending on the morphology of the glass, crystallization may occur without large scale segmental motion. For instance, if the glass has domains of local, liquid-crystalline-like order (i.e. nodules) in which chain segments are locally parallel, all that would be required for development of three-dimensional order would be relatively small scale motions. This is strongly suggested by our observations that the nodular morphology did not reorganize to form lamellae or spherulites, while it was warmed to room temperature. Such motions could be provided, for example, by the propagation of kinks³³ or other defects down the chain. Even a γ transition involving motions of segments about four carbons long, as has been proposed by

Boyer¹ and others³⁴⁻³⁶ would be sufficient for both the relaxation of free volume and the development of three-dimensional crystallinity. Thus, using the data presented here, we cannot define T_g for polyethylene.

It has recently come to our attention that Boyer and Snyder³² have independently proposed that crystallization can occur in ultraquenched polyethylene at temperatures above the γ transition but below T_g . They base their arguments on an analysis of the infra-red spectra published in the original paper of Hendra *et al.*¹⁷. They believe that the spectrum of the quenched solid indicates the presence of local ordering in the form of significant amounts of extended *trans* sequences. These *trans* sequences crystallize between 160K and 180K. Above 180K the amorphous portions of the spectrum are gradually converted to crystalline bands, suggesting that the true T_g lies around 180K.

CONCLUSIONS

The evidence indicates that the liquid/solid nitrogen quench is capable of quenching linear polyethylene to a glass which contains some local order but no detectable crystallinity. Electron diffraction indicates that the onset of crystallization occurs at temperatures as low as 185K, especially in oriented areas, and most samples show well-developed crystalline diffraction corresponding to the normal orthorhombic structure at room temperature. Differential scanning calorimetry of unwarmed samples indicates the presence of an exotherm between 160 and 180K to 200K which is probably due to both crystallization and relaxation of free volume frozen into the glass. Further exothermic activity may occur above 200K, indicating the possibility of more crystallization. Electron micrographs of the glass show nodules around 100 \AA in diameter superimposed upon larger irregularities on the order of 1000 \AA or more in size. Upon rapid crystallization the morphology of the quenched material remains unchanged.

Although some oxidative degradation may occur in the molten samples before quenching, it is not believed that it is sufficient to invalidate the work reported here. This is one area which needs further investigation. Work is continuing in this laboratory on methods of protection from oxidation, improved substrates for diffraction, and more precise temperature measurement in the electron microscope.

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