Crystallinity in chemically crosslinked low density polyethylenes: 3. Morphology of the XLPE-2 system

R. M. Gohil and P. J. Phillips*
Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112, USA
(Received 26 July 1985; revised 19 February 1986)

Studies of the morphology of low density branched polyethylene crosslinked using 2% dicumyl peroxide have been carried out using transmission electron microscopy of replicas of surfaces etched with permanganic reagent. Under optimal etching conditions detailed information regarding the morphologies of bulk crystallized samples of low crystallinity can be obtained. The morphology of crosslinked polyethylene is compared with that of the original branched polyethylene as a function of crystallization temperature. Branched polyethylene crystallizes in the form of banded spherulites from 88°C to 103°C with a temperature dependent band periodicity. Introduction of a small amount of crosslinking produces profound effects with banded sheaf or bundle-like morphologies resulting. The absence of lamellar banding in the sheaves of the gel fraction of the crosslinked polyethylene is attributed to pre-existent tie-molecules which are an inherent feature of network junctions in a crosslinked system. In the case of a typical unextracted crosslinked polyethylene, the morphology is found to vary with crystallization temperature. D.s.c. studies reveal that the thermal behaviour of XLPE-2 is not too different from that of OPE. The cause of multiple melting behaviour in this class of material is discussed and it is suggested that in addition to other processes of reorganization, hindrance to solid state thickening may be important. A method of monitoring different stages of lamellar melting for semicrystalline polymers was developed involving annealing at elevated temperatures in the presence of chlorosulphonic acid.

(Keywords: morphology; polyethylene; crystallization; crosslinking; tie-molecules)

INTRODUCTION

Background information on the systems being studied has been provided in the first two papers of this series[1,2]. A major problem in the elucidation of the detailed morphological structure of polyolefins, particularly those of low crystallinity, has been the lack of an etching or staining technique for transmission electron microscopy.

Recently, the development of etching techniques has permitted the possibility of morphological characterization. The present studies were initiated with the object of adapting the permanganic acid etching technique[3-7] to low crystallinity crosslinked polyethylene and its component parts. Although studies of the crystallization behaviour of crosslinked polymers in the deformed state have been reported, there is a lack of information on direct observation of lamellar organization from the isotropic melt. It is important to understand the character of lamellar organization in a system where mobility is significantly impeded. An essential part of such a study lies in a comparison of the morphology of crosslinked polyethylene with its noncrosslinked precursor, leading to an evaluation of the conditions necessary for inhibition of well-defined superstructures. The information derived from such studies may also be extended to the crystallization behaviour of high molecular weight polymeric materials in which the role of impeded mobility cannot be avoided for other reasons.

EXPERIMENTAL

Specimen preparation

The basic polymer and its characterization procedure have already been described[1,2].

Specimens were crystallized in the form of relatively thick films (*ca.* 1 mm) in a constant temperature bath. They were then etched, washed and re-etched twice more using 0.2% (w/w) potassium permanganate in concentrated sulphuric acid, all treatments being carried out at room temperature in an ultrasonic bath. The above concentration of etchant was found to be optimal for low crystallinity polymers and is very different from the concentration recommended by Bassett *et al.*[3-6] but close to those reported by Naylor and Phillips[7].

In order to explore the various stages of melting, dried etched samples were treated with chlorosulphonic acid at chosen annealing temperatures. As chlorosulphonic acid is very reactive, considerable care was taken during the annealing process. Following annealing treatments, samples were washed with water then acetone and surface replication was carried out.

The replication process involved direct deposition of carbon on the clean etched surface. Chromium shadowing was applied at an angle of 20°. After carbon coating and chromium shadowing, a thin film of polyacrylic acid was deposited from a 1% aqueous solution. Drying of the polyacrylic acid film was carried out at room temperature for two days. Because of the fine morphological textures present in these materials conventional methods such as tape impression were

---

* Present address: Department of Materials Science and Engineering, The University of Tennessee, Knoxville, TN 37996-2200, USA.

0032-3861/86/111687$03.00

found to be unsatisfactory. A JEOL JEM 200 CX transmission electron microscope was used to examine the replicas in morphological studies.

Thermal characterization was carried out using a Perkin Elmer DSC-2 differential scanning calorimeter, temperature calibration being carried out using indium.

RESULTS

Etching technique

The successful application of permanganic etching to polymeric materials having low crystallinities necessitated the establishment of optimal conditions. For branched and crosslinked polyethylenes, this condition was found to be 0.2% (w/w) potassium permanganate in concentrated sulphuric acid. The samples were etched for 25 min and then treated sequentially for one minute with a 7/2 (v/v) water/sulphuric acid mixture followed by hydrogen peroxide, water and lastly acetone[3]. All these treatments were carried out twice in an ultrasonic bath[7]. For these conditions of etching, occurrence of artifacts was either minimized or eliminated.

Even for the above conditions two different kinds of artifacts can be observed, but in small numbers. The first type is similar to that described in detail by Naylor and Phillips[7] for linear polyethylene and in less detail for lower crystallinity polyethylenes. It consists of a series of flat ridges which can split producing 'lamellae' radiating out from the central crater. These 'lamellar' structures will be referred as the second type of artifact. A typical artifact is shown in *Figure 1*. In the second type, the various arm-like structures radiating from the centre produce a spherulitic appearance. In *Figure 1*, only a few radiating arms are seen but generally they form a complete disc. In fact, *Figure 1* illustrates the partial conversion of a type I into a type II artifact. These structures differ from those already reported by Naylor and Phillips[7] for linear polyethylene in their height, being much shallower. They are illustrated here partly because the relation between the artifacts and the lamellar polymer crystals can be seen because of the higher magnifications used in this study. Anomalous banded structures can also be observed, a detailed region of the banded type of structure being shown in *Figure 2*. In this electron micrograph as many as eight bands can easily be seen. Careful observation of the electron micrographs at relatively low magnifications reveals the true representative banded sheaf morphology of crosslinked polyethylene crystallized at 103.8°C. Even at such a magnification, one can observe detailed lamellar crystals. A representative morphology from the same sample is shown in *Figure 3* where it can be seen that artifacts are sufficiently far apart for the true morphology and also the lamellar details to be determined. The same technique was applied to crosslinked polyethylene electrical cable insulation and found to be satisfactory for determining the morphologies at different depths within the insulation[8].

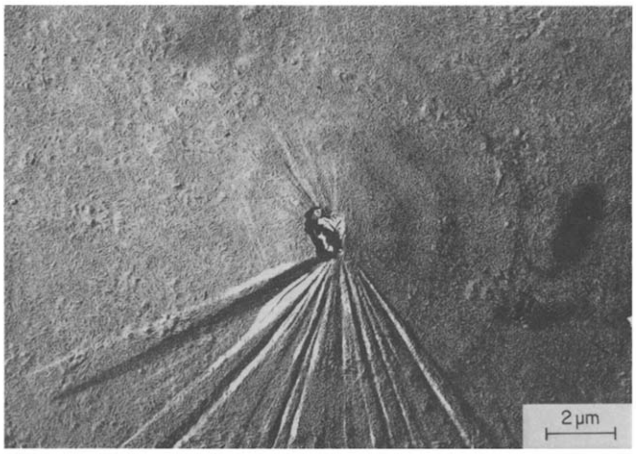

Figure 1 Formation of a typical artifact in XLPE-2; $T_c = 103.8$°C

Figure 2 An enlarged portion of a banded artifact developed in XLPE-2, $T_c = 103.8$°C. Note presence of banded sheaves

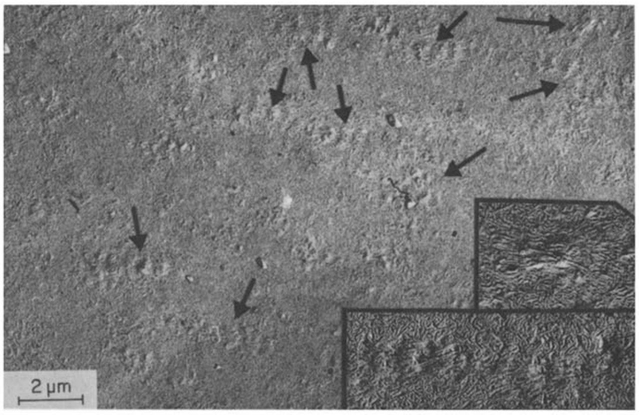

Figure 3 Electron micrograph showing large area devoid of artifacts, and presence of banded sheaves in XLPE-2, $T_c = 103.8$°C. Sheaves are indicated by arrows; insets are higher magnification pictures of representative banded sheaf morphologies, S-shaped lamellae being present in adjacent areas

Increasing the concentration of permanganic acid (0.5% w/w in sulphuric acid) induces a modulated structure along the edge of lamellar crystals (*Figure 4*). Sometimes an advanced stage of such structures gives a globular appearance. Development of this structure may be a result of the nature of lamellae in branched and crosslinked polyethylenes, implications of which will be discussed later.

Branched polyethylenes (NXLPE-2 and SOL-2)

Crystallization of branched polyethylene and the SOL fraction of the crosslinked polymer gives well-developed spherulites over the whole range of crystallization temperatures ($T_c = 88$°C–104°C). *Figures 5* and *6* show banded spherulites of NXLPE-2 grown at 88°C and 103.8°C respectively. It will be noted that there are regions where the regular banding in the spherulites is disrupted (arrows) and relatively linear growth has

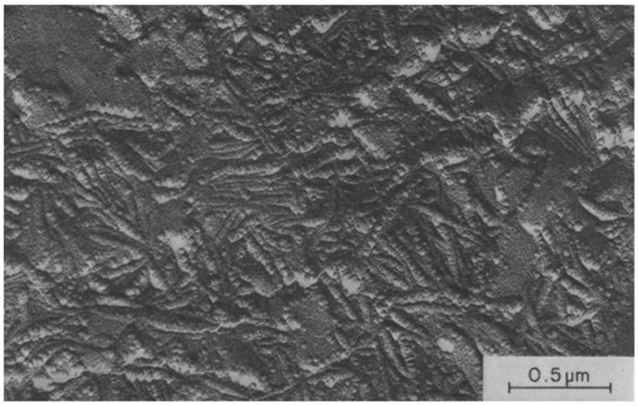

Figure 4 Electron micrograph showing nodular structure in edge-on lamellae of non-crosslinked polyethylene; $T_c = 103.8°C$

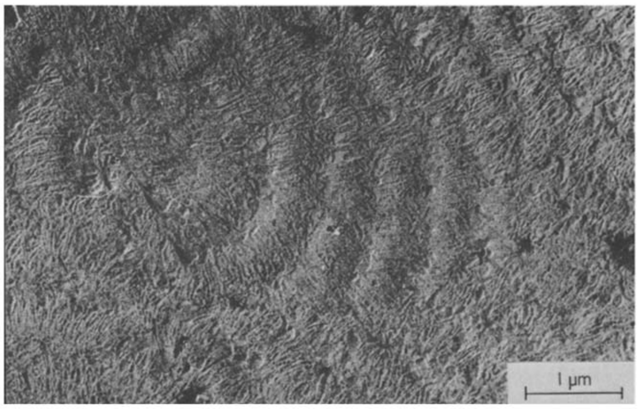

Figure 5 Banded spherulite of non-crosslinked polyethylene; $T_c = 88°C$

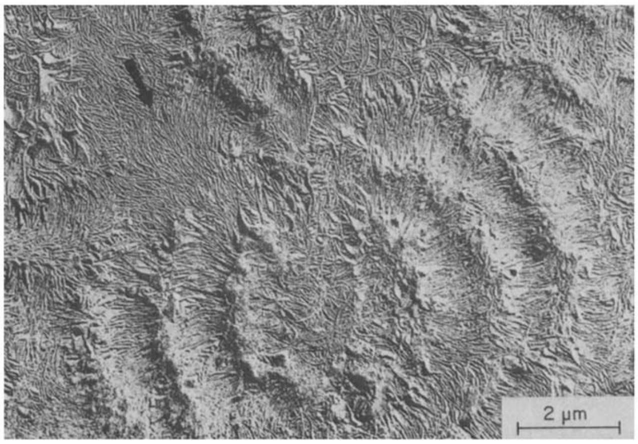

Figure 6 Banded spherulite of non-crosslinked polyethylene; $T_c = 103.8°C$

occurred. This type of irregularity is common and increases in frequency with increasing crystallization temperature. *Figure 7* shows an electron micrograph of spherulites of SOL-2 grown at 92°C. There are no major changes in the spherulites of XLPE-2 and SOL-2 over the entire range of crystallization temperatures studied. The size of the spherulites varies from 10 to 15 μm. The band periodicities in the spherulites are found to be temperature dependent, e.g. for crystallization at 88°C, 94°C and 103.8°C they are respectively 0.6, 0.85 and 1.5 μm. These spherulites appear to be very compact when viewed from certain directions; however, detailed studies of such spherulites with the lamellae in the edge-on position reveals the presence of large numbers of secondary lamellae. Such an area is shown in *Figure 8*, being similar to the central part of the spherulite shown in *Figure 6*. In addition to twisting of primary lamellae, one clearly observes growth of secondary lamellae. These secondary lamellae apparently nucleated on the primary lamellae at a range of angles which are usually fairly constant at a given location; however, no definite crystallographic relationship with the primary lamellae could be defined. Surprisingly, in some cases, the lamellae appear to have nucleated at right angles to the folded lamellar surface. Infilling processes, via growth of secondary lamellae, seem to be common even in the growth of banded spherulites.

Crosslinked polyethylene

As the crosslinked polyethylene (XLPE-2) contains 20% sol fraction, it may be considered as a blend of 80% crosslinked polyethylene (gel fraction) with 20% branched low molecular weight polyethylene. Studies of crosslinked polyethylene over the entire range of crystallization temperature ($T_c = 88°C–104°C$) indicate the presence of a sheaf-like morphology. *Figure 9* shows a typical electron micrograph of sheaves grown at 92°C. The size of the sheaves varies slightly with crystallization temperature and falls within the range of 2–6 μm. The

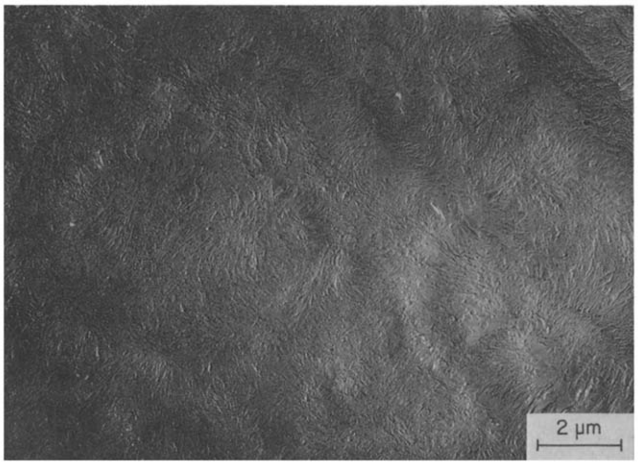

Figure 7 Banded spherulite of sol fraction, $T_c = 92°C$

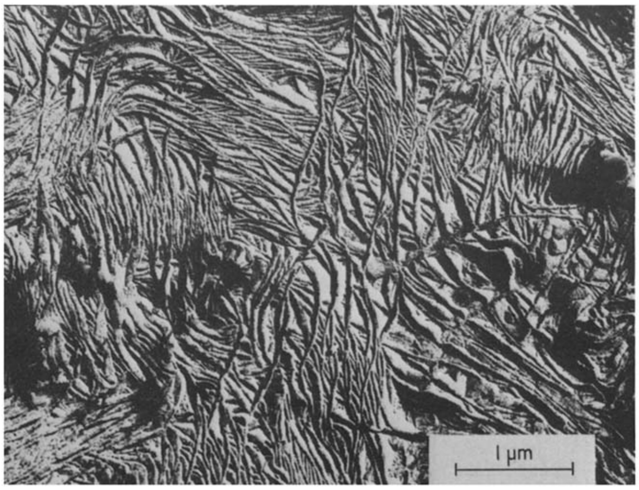

Figure 8 Electron micrograph showing infilling process by the growth of secondary lamellae in a banded spherulite of non-crosslinked polyethylene, $T_c = 103.4°C$

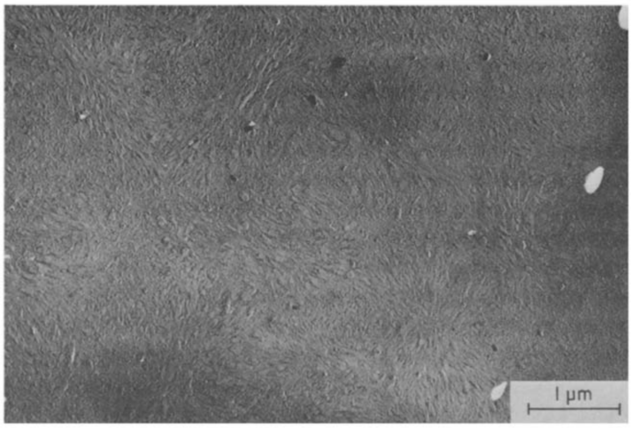

Figure 9 Growth of non-banded sheaves of XLPE-2; $T_c = 92°C$

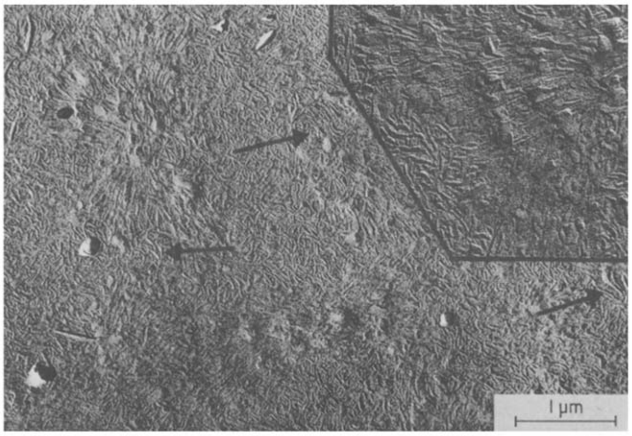

Figure 10 Electron micrograph of enlarged banded sheaves (see *Figure 3*) of XLPE-2, $T_c = 103.8°C$; S-shaped lamellae are indicated by arrows

ultimate size of this growth feature is five times smaller (at 92°C) than the spherulites produced in NXLPE-2 at the same temperature. Crystallization of crosslinked polyethylene above 102°C indicates a change in morphology and one observes banded sheaves (*Figures 3* and *10*). The band periodicity in the sheaf is in the range 0.8 to 1 μm which is considerably smaller than that observed in branched polyethylene at a crystallization temperature of 103.8°C. The sheaves are found to be well separated (*Figures 3* and *10*) and in surrounding regions one clearly observes the presence of 'S' shaped lamellae, being characteristic of the twisting nature of the lamellar crystals. Although S-shaped lamellae occur in the matrix it cannot be seen whether or not they also are twisted. The lamellar thickness of the samples crystallized at 103–5°C is 140 ± 20 Å. The results clearly show that morphology varies with crystallization temperature even though the nucleation density shows little change.

Gel fraction

The gel fraction consists solely of the part of the crosslinked polyethylene which was completely insoluble in xylene. Morphological investigations of the gel fraction over the entire range of crystallization temperature (88°C–104°C) reveals only non-banded sheaf-like structures. *Figures 11*, *12* and *13* are electron micrographs showing the morphology obtained for crystallization temperatures of 88°C, 92°C and 103.8°C respectively. It is clearly evident that the gel fraction can form a definite lamellar organization. The size of the sheaf structures grown at 88°C, 92°C and 103.8°C is respectively 1.2 ± 0.2, 1.3 ± 0.2 and 1.9 ± 0.2 μm. The drastic change in the size of the largest morphological feature compared to that observed in branched polyethylene indicates a major enhancement in nucleation density, although there is no great change in nucleation density with crystallization temperature. In contrast to crosslinked polyethylene, crystallization of the gel fraction above 102°C does not produce periodic banding in the lamellae of the sheaf. In most cases, a sheaf section contains only 8–10 lamellae and at higher crystallization temperatures (102°C–104°C), the growth features appear to be a collection of

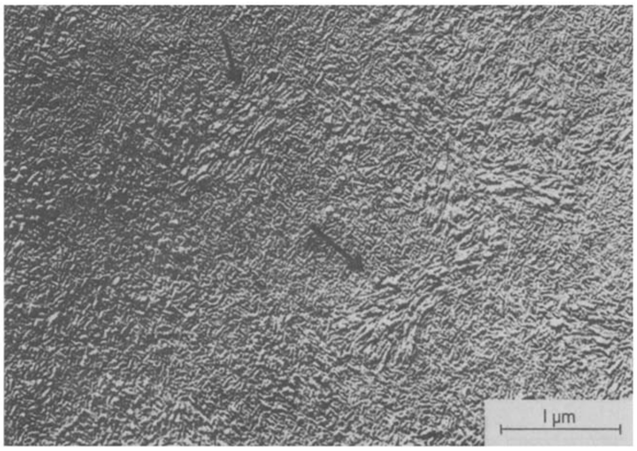

Figure 11 Growth of sheaves in GEL-2; $T_c = 88°C$; representative sheaves are indicated by arrows

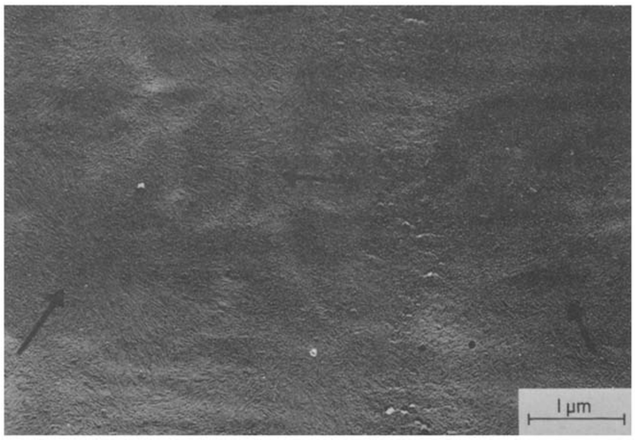

Figure 12 Growth of non-banded sheaves in GEL-2; $T_c = 92°C$

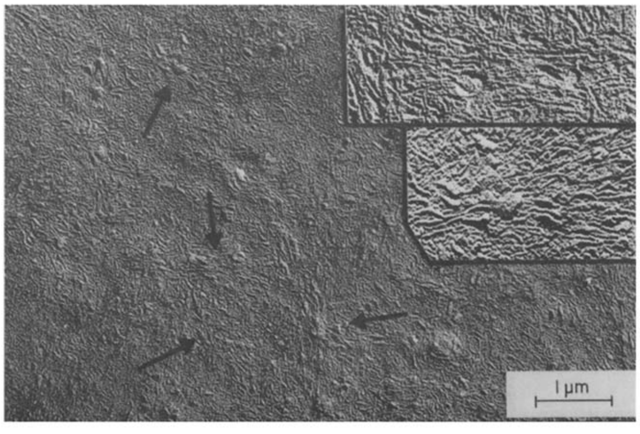

Figure 13 Growth of sheaves in GEL-2; $T_c = 103.8°C$

rods rather than a sheaf. The same morphology was found at concentrations of the permanganic etch as low as 0.1% showing that the sheaves are not a result of selective etching of 'pre-existing' spherulites.

Correlative fusion studies

In addition to the direct study of morphology in crosslinked and branched polyethylenes, it is helpful to have more information on the nature of lamellar crystals in this class of polymers. Hence d.s.c. studies of the samples crystallized and annealed at different temperatures as well as those annealed in the presence of chlorosulphonic acid have been carried out.

General d.s.c. results were presented in the first paper of this series[1] so that only data of direct relevance to the XLPE-2 system will be discussed here. Thermal traces show similar behaviour for all samples and generally two peaks are present (*Figures 14* and *15*). With increasing crystallization temperature, the position of the low melting shoulder (97°C–99°C) remains almost constant. The values of the second (and higher) temperature melting peak for GEL-2, XLPE-2, SOL-2 and NXLPE-2 crystallized at 92°C are 104°, 106°, 110° and 110° respectively. These values remain constant up to a crystallization temperature of 95°C. For a crystallization temperature of 103.8°C, the values of the peak (*Figure 15*) for GEL-2, XLPE-2, SOL-2 and NXLPE-2 are respectively 108°C, 110°C, 112°C and 114°C. Hence the increase in the stability of the crystals with temperature is comparatively lower than is usually observed for linear polyethylene[9].

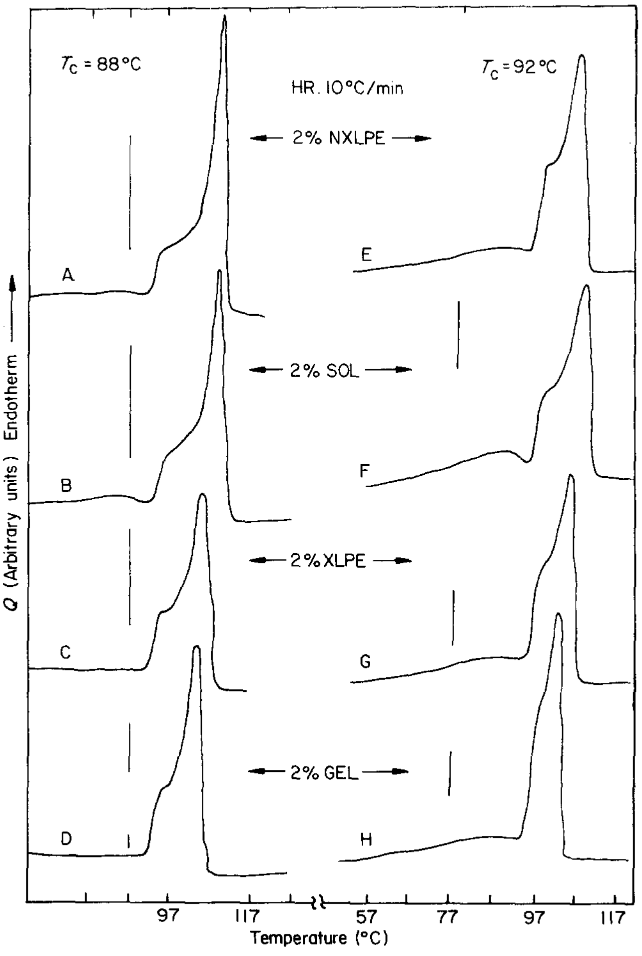

Figure 14 D.s.c. traces of the samples crystallized at 88°C and 92°C

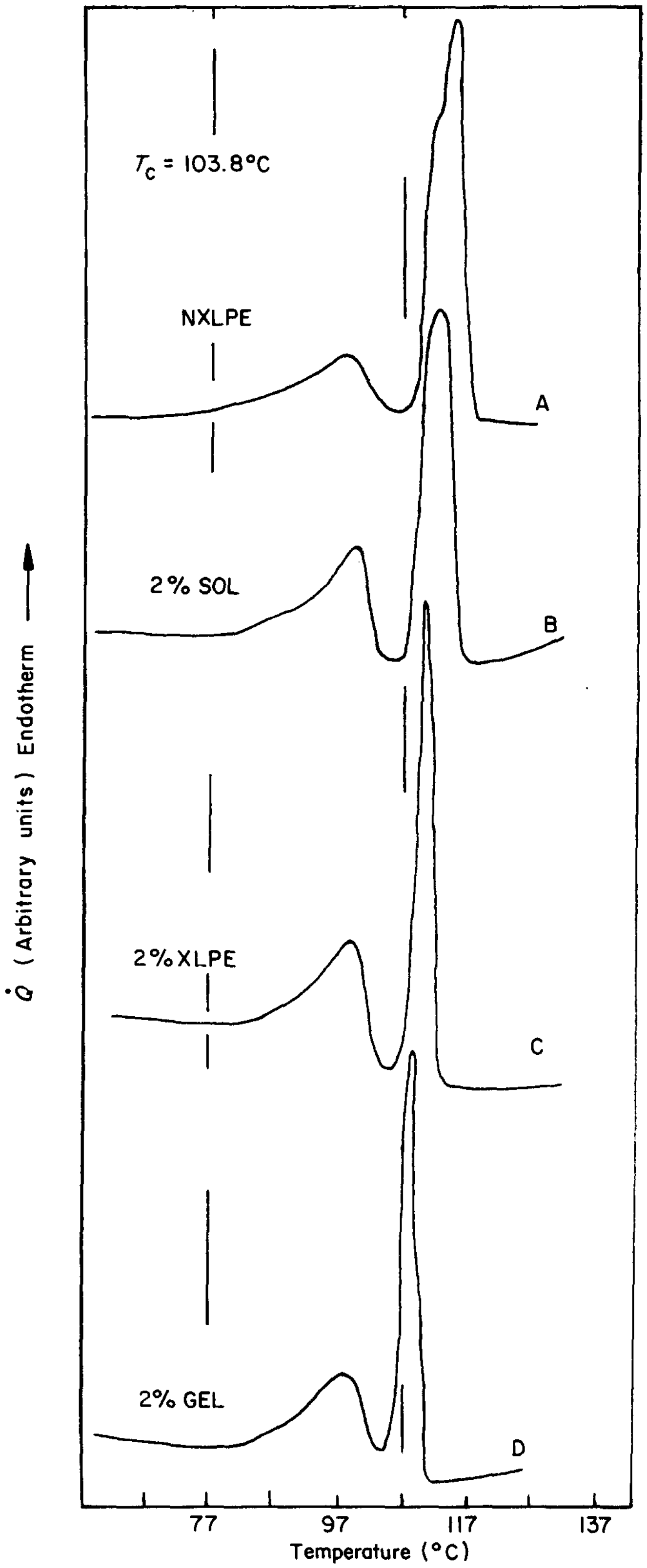

Figure 15 D.s.c. traces of the samples crystallized at 103.8°C

The d.s.c. results discussed above reveal that the temperature of the second melting peak increases slightly, and at the same time the magnitude of the first peak increases, with increasing crystallization temperature. During this process, the low melting peak separates from the higher melting peak. The above situation could occur if there were growing crystals with different crystal structures. However, such a possibility can be ruled out from X-ray studies of branched and crosslinked polyethylenes[1].

In order to determine whether stabilization and/or reorganization of the crystals can occur, samples of sol fractions crystallized at 88°C have been annealed at 97°C for 50 h and 103°C for 6 days. D.s.c. traces of the annealed samples (*Figure 16*) show considerable change in the thermal behaviour. In addition to the increase in the value of the higher melting peak, there is development of a new melting peak at intermediate temperatures producing three well defined melting peaks (*Figure 16c*). Annealing the sample at 103°C shows a shift of the intermediate peak to higher temperatures (*Figure 16C*). This d.s.c. trace is similar to the one observed for the sample crystallized at 103.8°C (*Figure 15*).

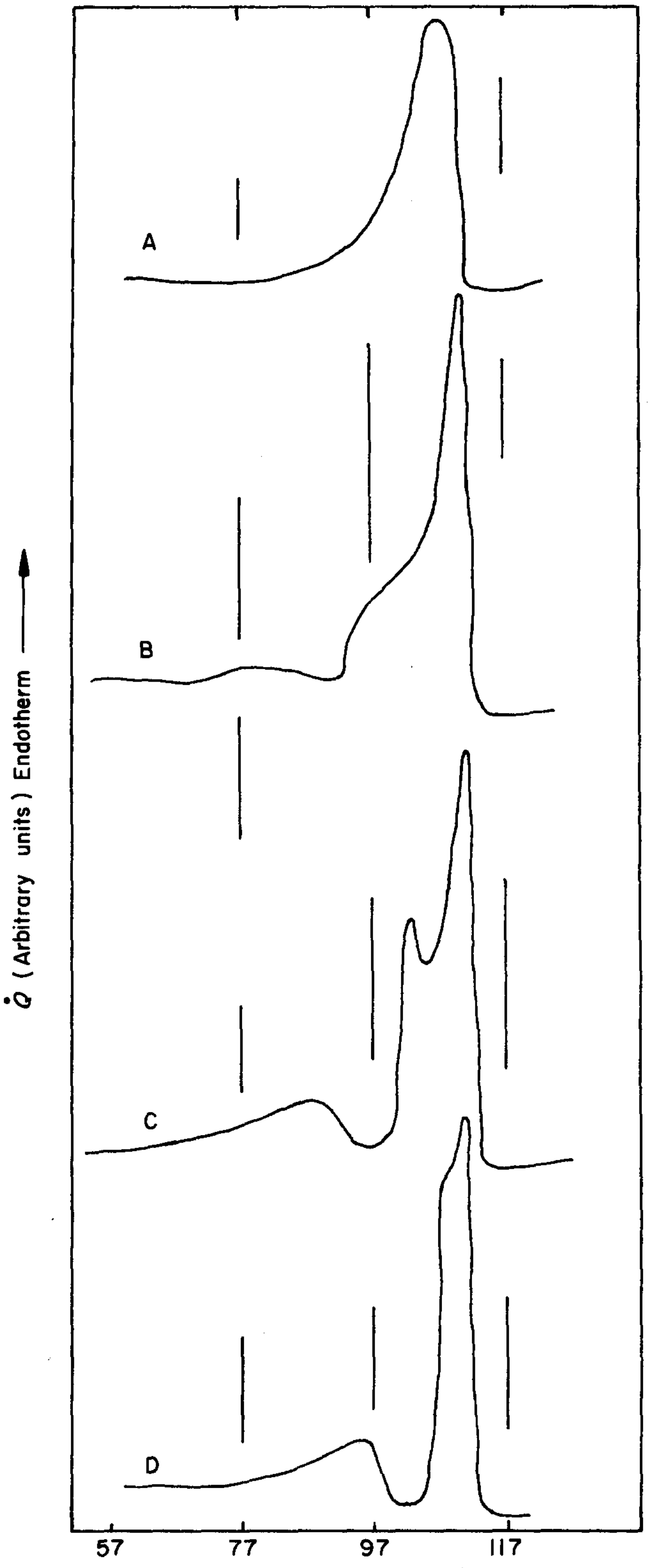

Figure 16 D.s.c. traces showing effect of annealing temperatures on the sol crystal. (A) Sol crystallized during cooling process. (B) Sol crystallized at 88°C. (C) A sample of sol crystallized at 88°C and annealed at 97°C. (D) A sample of sol crystallized at 88°C and annealed at 103.8°C

The samples crystallized at 103°C show a large endotherm at low temperatures (*Figure 17A*). When the samples are heated to 102°C, a considerable volume fraction of the crystals should be in the molten state. In an experiment, a sample was scanned up to 102°C (*Figure 17b*) and then it was quenched in the d.s.c. cell. The same sample was rescanned (*Figure 17C*), the results indicating that, other than a slight reorganization of crystals, the same basic d.s.c. thermogram was obtained (*Figure 17A*). In another experiment, the sample of *Figure 17D* was annealed for five days at 102°C. The d.s.c. trace of the sample showed essentially the same type of thermal behaviour (*Figure 17E*).

The above results indicate that a considerable proportion of the crystals cannot be stabilized by annealing and that regardless of thermal treatment they retain a relatively low melting point. Clearly it would be useful to know which crystals are preferentially melting and then recrystallizing only during the cooling process. As polyethylene cannot be quenched to its glassy state, it is difficult to observe different stages of melting of lamellar crystals using electron microscopic techniques. In order to hinder crystallization during the cooling process, the samples were annealed in chlorosulphonic acid. In this method, annealing the sample at 102°C should crosslink sufficiently the parts of the lamellar crystals which have melted, so preventing their recrystallization during the cooling process. Such annealing studies have been carried out on branched and crosslinked polyethylenes crystallized at 103.8°C. *Figure 18* shows an electron micrograph of crosslinked polyethylene treated in chlorosulphonic acid at 102°C. A d.s.c trace of the same sample (*Figure 17F*) clearly shows the absence of the low melting peak below 102°C, showing that recrystallization did not occur on cooling. The electron micrograph of the crosslinked polyethylene clearly reveals the presence of the banded sheaf which was present prior to the annealing process. The lamellar thickness measured after annealing in chlorosulphonic acid at 102°C was found to be 400±20 Å from the electron micrograph, which is considerably higher than the original lamellar thickness of 140±20 Å. According to the d.s.c. trace (*Figure 17D*) a considerable part of the specimen must be molten at 102°C. There were no areas of the specimen completely devoid of sheaves. These results indicate that the melting process is confirmed to local regions on a lamellar scale and is not on a spherulitic scale. Close observation of lamellar edges shows that the lamellae were locally molten. For side-on lamellae it was impossible to obtain good contrast by replication techniques as the locally molten part was crosslinked and not removed from the lamellae during the annealing process.

DISCUSSION

No experimental method is free from limitations regarding its applicability and for the permanganic etching technique artifact formation cannot be avoided completely under any conditions of etching[7]. It is therefore essential to understand the nature of artifacts for any

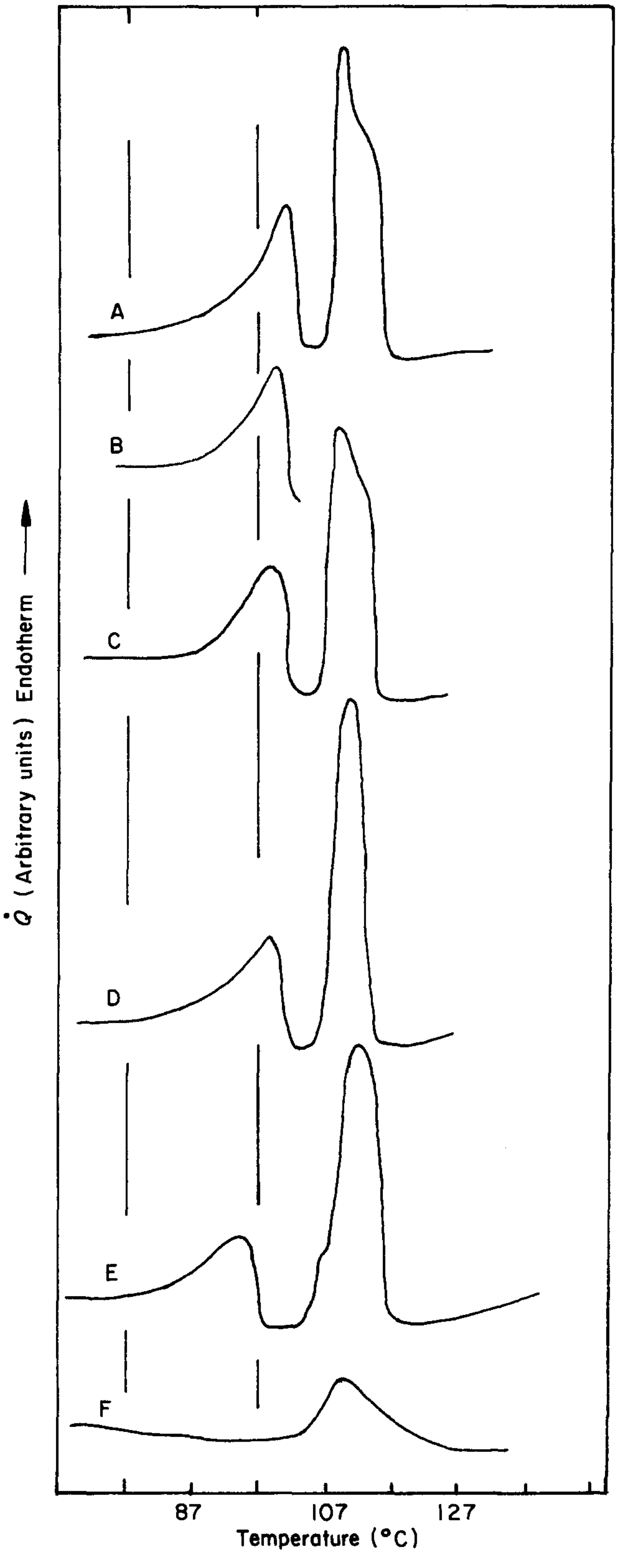

Figure 17 (A) A sample of sol crystallized at $T_c = 103$°C. (B) A sample of (A) scanned up to 102°C and then quenched. (C) The same sample (B) rescanned. (D) Sample of sol crystallized at 103.8°C. (E) The sample of sol (D) annealed at 102°C for 5 days and then scanned. (F) A sample of XLPE-2, $T_c = 103.8$°C, annealed in chlorosulphonic acid at 102°C

particular polymer. Experimentally, the density of the artifacts produced can be minimized by establishing optimal etching conditions. For the polymers studied here having medium crystallinities, *ca.* 50%, at optimal conditions small numbers of two kinds of artifacts occur which resemble spherulites. In one type, the artifact superficially resembles a banded spherulite in which the artificially developed plate-like structures can be resolved radiating from the centres (*Figure 1*). In scanning electron microscopic studies at low magnifications these artifacts can produce misleading results. In transmission electron microscopic studies, these artifacts can easily be recognized as such since the actual lamellae can be resolved. The artifacts are usually larger than representative morphologies of crosslinked and branched polyethylenes. For optimal etching conditions, since their density is low, there are large areas available for observation of the true morphology (*Figure 3*). With a proper understanding of the nature of artifacts and establishment of optimal conditions of etching, it was found that even for these low crystallinity polymers changes in minute morphological details could be observed. Such results are extremely difficult to obtain using other techniques. Chlorosulphonic acid staining[10] has been valuable in the study of drawn samples having edge-on lamellae. However, for samples crystallized from the relaxed melt where side-on lamellae proliferate, contrast is not comparable and observed details do not compare to those obtained by etching.

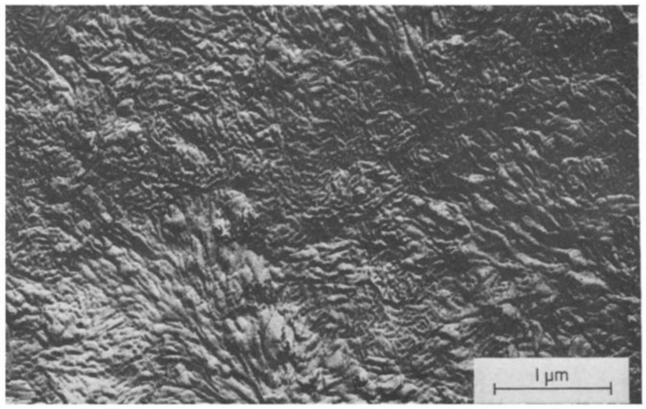

Figure 18 A sample of XLPE-2, $T_c = 103.8$°C annealed in presence of chlorosulphonic acid at 102°C

A comparison of the morphologies of branched polyethylene and crosslinked polyethylene shows that the introduction of a few crosslinks has a marked influence on the crystallization behaviour. The fully developed banded spherulites of branched polyethylene no longer occur, non-banded sheaves being produced. The mechanism responsible for the elimination of banding in crosslinked polyethylene is not known but presumably the lack of long range mobility and the presence of preexisting tie molecules amongst the growing lamellar crystals must be playing an important role. In multilayered crystals of several polymers[11,12], it has been noted that an increasing concentration of tie molecules eliminates the splaying nature of lamellae in spirals and terraces.

From a comparison of the size of the morphological units of branched and crosslinked polyethylenes grown at 92°C, it is evident that introduction of a small number of crosslinks produces a considerable increase in nucleation density. This effect reduces the long dimension of the sheaf and may eventually influence mechanical properties. It is also apparent from the micrographs that the sheaves in the gel do not impinge (*Figures 11–13*), although for the unextracted polymer they do (*Figure 9*). There must therefore be some other effect, as yet not understood, which limits growth but is overcome by the presence of the sol fraction. In short, the study reveals that introduction of crosslinks may be used as a means of controlling nucleation density, obviating the need for foreign nucleating agents. Since the nucleation density of the gel fraction does not vary appreciably with crystallization temperature (88°C–103.8°C) it can be concluded that the nucleation process in such a polymer is largely instantaneous in nature and probably occurs at 103.8°C or above. The precise role of crosslinks in increasing nucleation density is not understood; however, the role of stress development on a microscopic scale may be relevant. Studies of the effect of increasing crosslink density on the phenomenon will be discussed in a later publication.

As indicated earlier, chemically crosslinked polyethylene can be regarded as a blend of 20% sol and 80% gel. Crystallization of such a blend at 92°C (*Figure 9*) shows a non-banded sheaf-like morphology. It should be remembered that branched polyethylene always crystallizes as fully developed banded spherulites (*Figures 5–7*). The absence of banding in the sheaves as well as the lack of banded spherulites indicates that the addition of 20% sol does not greatly change the crystallization behaviour of the gel fraction. There is therefore no direct evidence for phase separation of the fractions at this crystallization temperature. It may be possible that the high rates of crystallization along with high viscosity at low crystallization temperatures suppress fractionation of structurally different molecules and that the components can co-crystallize.

When the blend is crystallized above 102°C, growth of banded sheaves is observed (*Figure 3*). Hence, in this blend, morphology varies with crystallization temperature. There are several possible reasons for the observation of temperature dependent morphology. The major possibilities include phase separation in the melt or segregation of low molecular weight polyethylene molecules during the crystallization process, mainly due to low crystallization rates and increased molecular mobilities at higher crystallization temperatures.

Complete phase separation of gel and sol fractions in the molten polymer blend might have led to two distinct morphologies, viz banded spherulites of the sol fraction and non-banded sheaves of the gel fraction. As only banded sheaves are observed in the blend, the above possibility can be ruled out. In addition, the difference in band periodicities between spherulites (*Figures 5–7*) and sheaves in the blend (*Figure 3*) supports the above conclusion. It seems more likely that during the crystallization process, there may be segregation of molecules on a local level. In the process, structurally more heterogeneous molecules may be crystallizing as secondary lamellae. If this is the case then relative rates of diffusion of the molecules may be playing an important role in the growth process. The possibility of banded lamellar growth in the sheaf due only to temperature effects must also be considered. However, for this to be a likely mechanism the lower growth rates at higher temperatures must facilitate banding. If this were an effect caused by the elasticity of the crosslinked network then the resistance would increase with temperature. It therefore seems likely that reduced mobility of the crystallizing molecules at lower temperatures suppresses banded growth. Since the reasons for banding in polyethylene are not fully understood at the present time further discussion would not be fruitful; however, the observations may assist in understanding the general phenomenon of banding.

An indication of phase separation at higher temperatures or the formation of a solid solution at low crystallization temperatures in the blend can be obtained from the d.s.c. studies provided that both the components of the blend have sufficiently sharp and different melting points. D.s.c. traces of branched and crosslinked polyethylenes, sol and gel fractions crystallized at 103.8°C are found to be complex but superpose considerably. Thus, it is difficult to obtain detailed information regarding any segregation process in the blend merely from d.s.c. studies. An indication of molecular segregation in this system can be obtained only from electron microscopic studies.

The thermal behaviour of semicrystalline polymers is a complex process[13–16] and one can expect additional complexity in the case of crosslinked and branched polymers[17]. As the melting of polymer crystals is governed by many parameters, such as the entropy and the impurity content of surrounding amorphous material, the structure of the crystal surface and its free energy, lattice imperfections, etc., it is difficult to come to any particular conclusions regarding predominant processes. In the present studies, our major intention is to throw some light on the nucleation processes and on the nature of the low melting crystals of branched and crosslinked polyethylenes.

As there is no major change in the melting temperature of lamellar crystals in all samples crystallized at temperatures lower than or equal to 95°C, one expects little change in the nature of the lamellae present. The slight increase in melting temperature (2°C–3°C) at 103.8°C may be due to a slight increase in lamellar thickness or perfection of the crystals.

D.s.c. traces of the samples crystallized at different temperatures demonstrate that the introduction of crosslinks does little to alter the basic nature of the thermal behaviour. It is evident that the nature of the lamellae as well as the distribution of the surrounding amorphous material is not changed drastically. However, the disappearance of the last traces of crystallinity of the gel fraction occurs 5°C lower than in non-crosslinked polyethylene. These results mean that the crystals of the gel fraction are either relatively more imperfect or there is an increase in the entropy of fusion.

D.s.c. studies of the crystals of branched and crosslinked polyethylenes crystallized at 88°C show that some of the metastable crystals have a tendency to rearrange on annealing above the crystallization temperature (*Figure 16*). This type of behaviour is very common in the case of linear semicrystalline polymers and it seems that branched and crosslinked polyethylenes are not exceptional. It is well established that stabilization of crystals can occur either by melting and recrystallization or by a solid state thickening process. The predominance of a particular process depends on its rate compared with heating rates.

The following results are also relevant. With increasing crystallization and annealing temperatures, multiple melting behaviour develops below the major high temperature melting peak. The magnitude of these melting peaks increases with increasing crystallization or annealing temperature; however, a single peak occurs at low temperatures. The endotherm starts at temperatures as low as 60°C. Furthermore, all the samples crystallized above 102°C show only one melting peak below the major higher melting peak. Annealing of these samples for several days below 102°C does not eliminate the lower melting peak.

The results indicate that during the annealing process a fraction of the molten polymer cannot crystallize and does so on cooling. The crystals grown at the lower temperatures during cooling can introduce a wide distribution of lamellar thickness and considerable imperfection. Local variation of lamellar thickness can occur and may be important in crosslinked low density systems because of local variations in branching and crosslink density. Therefore these crystals show low melting peaks in the d.s.c. traces. However, if the conventional explanations apply, then on prolonged annealing treatments of such samples, the peaks observed below annealing temperatures should disappear. It therefore appears that a significant fraction of the lamellar crystals cannot thicken, probably because of the inability of the crystals to accept short chain branches together with resistance from the crosslinked network.

In order to determine which part of the sheaves are preferentially melting, electron microscopy was used to investigate the situation in the samples crystallized above 103.8°C. As discussed above, the samples show a major melting peak below 102°C. To determine the exact location of crystals melting below 102°C the samples were annealed at 102°C in the presence of chlorosulphonic acid. An advantage of annealing in chlorosulphonic acid is that the amorphous phase is crosslinked sufficiently to prevent the reappearance of the lower melting point crystals. D.s.c. confirmed this presumption in that the low melting peak no longer occurred after chlorosulphonation (*Figure 17*). Electron microscopic studies of such a sample clearly reveal the continued presence of the banded sheaf, which is characteristic of samples crystallized above 102°C. From d.s.c. traces a considerable fraction of the crystals is molten at 102°C and one should observe unmolten lamellae or unmolten parts of the sheaves. As there is no great modification in the original banded sheaf morphology on annealing in chlorosulphonic acid, it can be concluded that the melting process is confined to a local level. A similar inference can be made for spherulites of branched polyethylene crystallized at 103.8°C. Careful observation of electron micrographs (*Figure 18*) reveals locally molten parts along the edge-on lamellae. Additional support for this kind of melting process may be culled from the use of slightly more concentrated permanganic etching conditions, whereby nodulation was produced. This may have been caused by the heat of reaction on a local scale. At this point, it should be noted that since the endotherm can start as low as 60°C, a slight increase in local temperature could be sufficient to produce local melting. Examination of *Figure 4* reveals a local melting effect even in the straight part of a lamella. If this is not an artifact, occurrence of local melting in the lamellae could be attributed to hindrance of the solid state thickening process. This hindrance to solid state thickening may arise from surface defects or structural irregularities along the lamellae resulting from network junctions and branch points.

The method discussed above for monitoring different stages of lamellar melting using chlorosulphonic acid may provide a general technique for the study of multiple melting in non-quenchable polyolefins. This method may be very useful in the study of thin polymeric films (*ca.* 1000 Å) directly in the transmission electron microscope. From the study of such films one could obtain information using phase contrast and dark-field electron microscopic techniques. The method may be most useful if the melting point of the polymer selected is less than 80°C.

As mentioned in our earlier discussions, the low melting peak of the samples crystallized at 103.8°C can be eliminated by annealing in the presence of chlorosulphonic acid. This is achieved at the cost of crystallinity. Further, the melting point of the remaining crystals is increased considerably. This arose from an increase in the lamellar thickness of the crystals. The increase in lamellar thickness, more than two-fold, is apparent in the electron micrographs. This increase in the ability of the crystals to thicken below the crystallization temperature in reactive inorganic media warrants further investigation. Hence, the use of the Kanig method for quantitative lamellar thickness or amorphous thickness determination is open to question and requires further evaluation.

CONCLUSIONS

The morphology of unextracted crosslinked polyethylene, XLPE-2, is sheaf-like under all crystallization conditions studied, the sheaves being banded when produced at low supercoolings. Conventional banded spherulites are typical of the sol fraction and small poorly formed non-banded sheaves of the gel fraction. Nucleation densities are increased by crosslinking and multiple melting behaviour becomes more complex. Chlorosulphonation can be carried out during partial melting to determine the location of species giving rise to specific melting peaks.

ACKNOWLEDGEMENT

This research has been supported by the Basic Materials Section of the Department of Energy under contract No. DE-AC02-79ER10421.

REFERENCES

1 Kao, Y. H. and Phillips, P. J. *Polymer* 1986, **27**, 1669

2 Phillips, P. J. and Kao, Y. H. *Polymer* 1986, **27**, 1679

3 Olley, R. H., Hodge, A. M. and Bassett, D. C. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 627

4 Bassett, D. C. and Hodge, A. M. *Proc. Roy. Soc. London Ser. A* 1981, **A377**, 25

5 Bassett, D. C., Hodge, A. M. and Olley, R. H. *Proc. Roy. Soc. London Ser. A* 1981, **A377**, 39

6 Bassett, D. C. and Hodge, A. M. *Proc. Roy. Soc. London Ser. A* 1981, **A377**, 61

7 Naylor, K. L. and Phillips, P. J. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 2100

8 Vatansever, A., Gohil, R. M. and Phillips, P. J., unpublished data

9 Wunderlich, B. 'Macromolecular Physics', Vol. 3, Academic Press, New York, 1980

10 Kanig, G. *Kunststoffe* 1974, **64**, 470

11 Bassett, D. C., Keller, A. and Mitsuhashi, S. *J. Polym. Sci.* 1963, **A1**, 763

12 Gohil, R. M. and Patel, R. D. *Die Starke* 1976, **9**, 293

13 Petermann, J. and Gohil, R. M. *J. Macromol. Sci., Phys.* 1979, **B16**, 177

14 Gohil, R. M. and Patel, R. D. *Makromol. Chem.* 1977, **64**, 43

15 Lemstra, P. J., Kookstra, T. and Challa, G. *J. Polym. Sci., A-2* 1972, **10**, 823

16 Harrison, I. R. and Runt, J. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 321

17 Bassett, D. C. 'Principles of Polymer Morphology', Cambridge University Press, Cambridge, 1981