

# Crystallinity in chemically crosslinked low density polyethylenes: 4. Influence of crosslink density on morphology

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Electron microscopy studies of crosslinked polyethylenes show that with increasing crosslinking conventional superstructures, their nucleation density and the nature of lamellae are greatly modified. With increasing crosslinking, the growth of spherulites is suppressed producing sheaves and ultimately bundles of lamellae. Lamellar organization prevails at all levels of crosslinking studied. Crosslinks exert a profound effect on the nature of the nucleation process as well as on nucleation density, it being mainly heterogenous in nature. The growth features indicate the presence of orienting effects, similar to those induced by externally applied stresses, at high crosslinking levels and temperatures. The values of the Avrami exponent obtained from kinetics studies are correlated with the observed morphologies. An increasing resistance to attack by the etchant on crosslinked polyethylene samples is attributed to the growth of compact bundles of lamellae as well as to the crosslinks themselves. The major causes of multiple melting peaks observed at low and high temperatures are due to (a) considerable change in the interfacial structure of lamellar crystals and the interlamellar material (b) reorganization of lamellar crystals as well as the presence of compact bundles of lamellae.

**(Keywords: morphology; polyethylene; crosslinking; spherulites; lamellae)**

## INTRODUCTION

In the earlier papers in this series the influence of increasing crosslink density on the crystal structure, crystallinity, melting<sup>1</sup> and crystallization kinetics<sup>2</sup> of crosslinked low density polyethylenes have been discussed. In the previous paper<sup>3</sup> the morphology of the commercially available system (XLPE-2) was reported and compared with its component fractions and the non-crosslinked system. In this communication the influence of crosslink density on morphology will be reported for the entire series (whose kinetics of crystallization were already reported<sup>2</sup>). It will be recalled that Avrami analysis of bulk kinetics indicated a clear transition from sheaf-like structures to rod-like structures as crosslink density was increased. For XLPE-0.9 and XLPE-2 and their gel fractions Avrami exponents suggested sheaves for all supercoolings. Intermediate levels of crosslinking gave transitional behaviour in which the Avrami exponent was temperature dependent. Since few correlations exist in the literature for non-spherulitic systems, this study provides a valuable test of the applicability of Avrami exponents to anisotropic morphologies. Of course, the major incentive for this study is to discover the true morphologies of crosslinked polyethylenes. The study of the XLPE-2 system clearly demonstrated the effect of light crosslinking on morphology as well as the important influence of the non-crosslinked short molecules. It was also noted that in addition to preventing true spherulitic growth, the

crosslinks produced a major increase in nucleation density.

Nucleation density is generally influenced by the addition of finely-divided powders of nucleating agents. The detailed mechanisms of nucleation are not clearly understood; however, the mechanisms of self-seeding<sup>4</sup> and the principles of epitaxial growth<sup>5-7</sup> are relatively well understood. Recently, it was shown that the addition of ionic end groups to poly(ethylene terephthalate)<sup>8</sup> produces a nucleating effect. Additionally external stresses are known to influence or change the nucleation process in polymers<sup>9</sup>, and it is likely that inhomogeneities in crosslink density could produce internal stresses on a local scale, thereby influencing the nucleation process and the ensuing growth process. As mentioned above, in our studies of the XLPE-2 system it was realized that a nucleation effect was occurring. It is therefore also our intention to shed some light on the potential role of crosslinks as a nucleating agent.

## EXPERIMENTAL

The preparation and characterization of specimens has already been described<sup>1-3</sup> and will not be repeated here. The permanganic etching technique and the method of preparation of carbon replicas, which are very critical, have already been described for XLPE-2<sup>3</sup>. For these materials, especially the gel fractions, where the crystallinity can be as low as 25% and the crystals thin and imperfect, care is needed. The optimal conditions of 0.2% (w/w) permanganic reagent and direct replication were found to be essential. Electron microscopic studies were carried out using a JEOL JEM 200CX transmission

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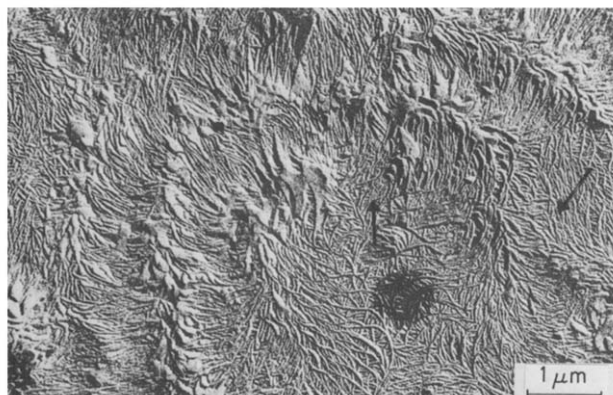
electron microscope. Thermal analyses were conducted on a Perkin-Elmer DSC II instrument.

## RESULTS

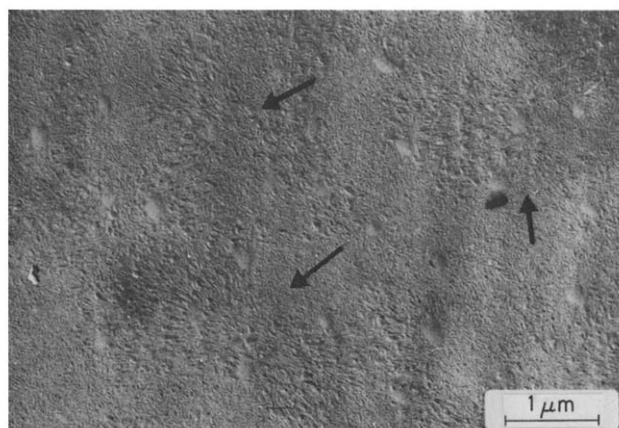
In order to uncover the effect of degree of crosslinking on morphology, all the samples were crystallized at 92°C. For comparison, we have also crystallized the original branched polyethylene at 92°C. *Figure 1* shows an electron micrograph of a typical banded spherulite. The studies show that similar spherulites grow over a wide range of temperature (88°C to 104°C)<sup>3</sup>. The band periodicity, however, was found to increase with crystallization temperature. The size of spherulites at 92°C was in the range 10–12 μm. There were also occasional areas within the spherulites in which banding could not be observed (arrows in *Figure 1*). These non-banded regions were observed more often for higher crystallization temperatures.

Crystallization of GEL-0.9 at 92°C produces the growth of banded sheaves (arrows in *Figure 2*). These may be an advanced intermediate stage of spherulite growth; however *de facto* spherulites could not be produced under any circumstances. The electron micrograph (*Figure 2*) clearly shows that introduction of very slight crosslinking does not eliminate the banding nature of lamellae in the sheaf, but there is a considerable decrease in size, 10–12 μm spherulites being replaced by 2.5–4.5 μm sheaves. The banding retained by the sheaves has a much finer spacing than in the original branched polymer and is, in general, less perfect.

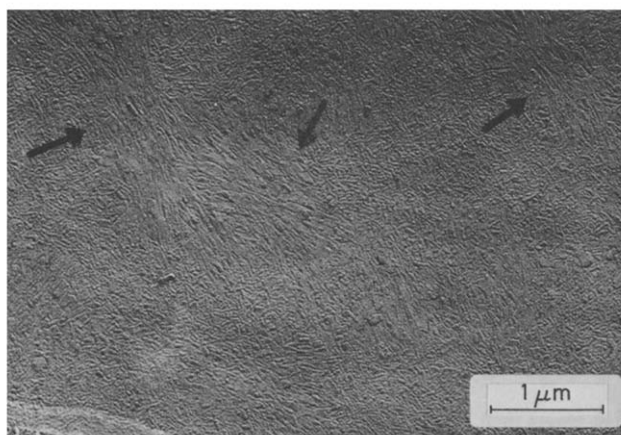
Very noticeable is the major decrease in contrast in the micrographs occurring as a result of crosslinking. This



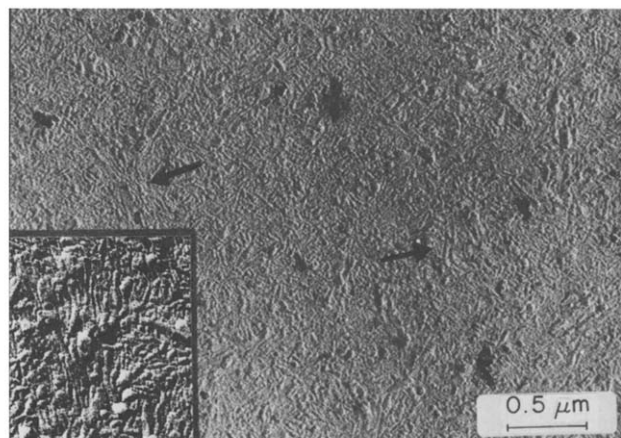
**Figure 1** Banded spherulite in NXLPE;  $T_c = 103.8^\circ\text{C}$



**Figure 2** Banded sheaves of GEL-0.9;  $T_c = 92^\circ\text{C}$



**Figure 3** Non-banded sheaves of GEL-2;  $T_c = 92^\circ\text{C}$



**Figure 4** Growth of bundles of lamellae in GEL-4;  $T_c = 92^\circ\text{C}$ . Inset shows a sheaf and to its left a region of oriented lamellae

can be seen as a direct result of the influence of crosslinking on etching rates since *Figures 1* and *2* are of similar magnifications. In the case of the branched polyethylene, although the depth of attack between bands is major it is more than one order of magnitude lower than that observed in linear polyethylene<sup>10</sup> and the features are barely visible at low magnifications in a scanning electron microscope. In *Figure 2* lamellae in the gel can be detected but they protrude only slightly above the amorphous phase whereas in the branched polyethylene (*Figure 1*) all lamellae can be observed in detail. *Figure 3* is an electron micrograph of GEL-2 crystallized at 92°C where the growth of sheaves again occurs (arrows). In this case, however, the lamellae in the sheaf show no sign of banding. Additionally the size of the sheaves is in the range of 1.4–1.6 μm, i.e. one third to a half of the sheaf size for GEL-0.9. Not only are sheaves smaller but they are less splayed out. At an equivalent stage in their growth the sheaves in GEL-0.9 occupy 90° sectors whereas in GEL-2 they resemble a collection of parallel short lamellae with only a slight tendency to spread apart toward their extremities. This is somewhat reminiscent of the earliest stages of growth of spherulites in polymers such as *cis*-polyisoprene (*Figure 2* in ref. 11) and amylose acetate<sup>12</sup>. *Figure 4* is an electron micrograph of GEL-4 crystallized at 92°C. Although the micrograph clearly shows the presence of well-defined lamellae, it becomes increasingly difficult to detect well-developed sheaves. However, occasionally lamellar organization could be found with sheaves consisting of only a few lamellae (arrows). The

size of the sheaves is in the range 1.2 to 1.4  $\mu\text{m}$ , slightly smaller than in GEL-2. GEL-6.8 at 92°C does not show any well-developed superstructures (such as sheaves). The electron micrograph (Figure 5) does, however, show the presence of oriented lamellae over the entire field. The oriented lamellae occupy regions several microns in size. The orientation does, however, vary from region to region, showing that the structure is basically one of oriented lamellar domains on a scale of several microns. There does not appear to be any correlation in orientation between adjacent domains, the overall superstructure resembling that of nematic grains in liquid crystalline polymers<sup>13</sup>. This morphology could have resulted from growth of a large number of sheaves oriented in the same direction. Such growth is well known in polyisoprenes, having been first noted by Andrews<sup>9</sup> for *cis*-polyisoprene stretched by *ca.* 50% prior to crystallization. Since carbon replicas were being studied here, no information could be obtained on the orientation of the unit cells relative to the lamellar dimension.

Growth of oriented lamellae is generally to be expected when the samples are crystallized under strain. In order to see if an applied strain might produce similar morphologies, a sample of GEL-4 was stretched to 50–60% at 120°C and then immediately cooled to room temperature. Such samples did indeed exhibit a morphology similar to that shown in Figure 5 for GEL-6.8, however, without any domain walls being apparent.

In all samples exhibiting the oriented lamellar structures the appearance of the lamellae is distinctly nodular. It will be recalled that this behaviour was characteristic of overetching in the case of XLPE-2 system<sup>3</sup> and was often difficult to avoid. In the systems being discussed here it was always present. Since we are dealing with gels of crystallinities as low as 25% and with clearly perturbed crystals<sup>1</sup> manifest by large amounts of WAXS line-broadening, it is possible that these nodules are not simply artifacts but may be reflections of internal lamellar structure. Their dimensions are in the range of the 'domain' parameters obtained by Gielenz and Jungnickel<sup>14</sup> for crosslinked linear polyethylenes (100–200 Å). On the other hand, it is necessary to remember that carbon replicas of chemically modified surfaces are being studied here, and such structure, which undoubtedly reflects differences in the rate of chemical attack, need not be caused by physical variables.

Studies of the gel fractions discussed above give information on the behaviour of crosslinked networks. A further question which arises is how the sol fractions affect

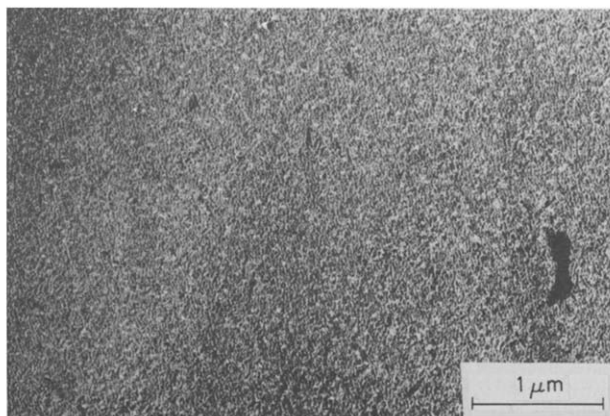


Figure 5 Oriented lamellar growth in GEL-6.8;  $T_c=92^\circ\text{C}$ . Lamellar direction approximately vertical

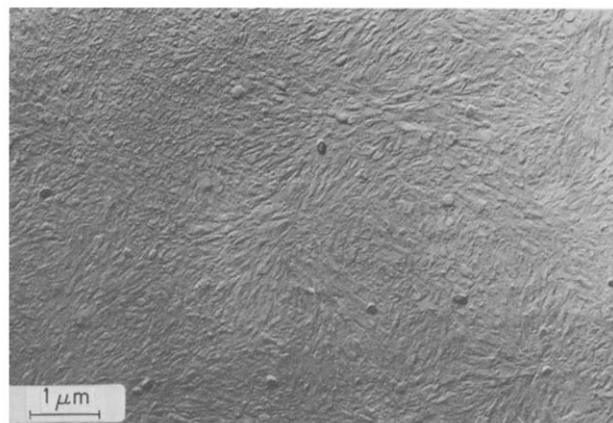


Figure 6 Non-banded sheaves of XLPE-2;  $T_c=92^\circ\text{C}$

the crystallization behaviour of the crosslinked networks when they are present in unextracted polymers, which are *de facto* blends. This is a problem which, while being of scientific interest, is of relevance to the properties and end-uses of crosslinked polymers, which invariably are used commercially in the unextracted form. It will be recalled from information presented in the earlier publications<sup>1,2</sup> that the sol fractions are low molecular weight, perhaps linear, molecules that have a considerable influence on crystallization kinetics and melting behaviour. They crystallize in the form of large banded spherulites having a melting point several degrees above the melting points of the gels. There is evidence pointing to possible segregation of the species on a local level when crystallization is carried out at low supercoolings leading to two melting endotherms, a sharp peak combined with a broad peak occurring at lower temperatures. In the gel fractions just discussed a major change in morphology in which sheaves were replaced by domains of oriented thin lamellae was observed as crosslink density was increased. Kinetic studies<sup>2</sup> have indicated similar behaviour for unextracted materials; however, growth rates were faster than those of gel fractions and Avrami exponents somewhat different. The transition in XLPE-4 resulted in Avrami exponents similar to those of gel fractions; however, the Avrami exponents at high supercoolings were not typical of sheaves, being intermediate and typical of spherulites, which could not have been present. It will be recalled that the influence of SOL-6.8 on the melting behaviour of XLPE-6.8 was very large for such a small component (6%) of the system. Figures 6, 7 and 8 are electron micrographs showing the morphologies of XLPE-2, XLPE-4 and XLPE-6.8, respectively, all crystallized at 92°C.

A comparison of Figures 3 (GEL-2) and 6 (XLPE-2) shows that the 20% sol fraction of XLPE-2 significantly influences the growth of the sheaves. The lamellae are easily resolved in Figure 6, presumably reflecting a resistance to etching much greater than in the gel. They are better formed, wider and splay apart more easily, leading to sheaves of large sector angles. The lamellae in the sheaves of the gel are apparently constrained to the direction of growth. The sheaves appear to occupy a larger volume fraction than in the gel and it is more difficult to detect lamellar growth that is not obviously associated with the sheaves.

Comparing Figures 4 (GEL-4) and 7 (XLPE-4) it can be seen that the most obvious difference lies in the clarity

of the features. Small sheaf-like clusters or bundles (arrows) are present in each case; however, in the case of XLPE-4 the lamellae are better defined and slightly thicker (Figure 7). The material between the sheaves is also better defined but of similar appearance. In both cases this material has a directionality to it similar to the oriented lamellae present in GEL-6.8. There is a clear absence of any morphologies that could give rise to Avrami exponents in the range of 3 to 4. It therefore appears that Avrami exponents obtained for both GEL-4 and XLPE-4 for crystallization at high supercoolings<sup>2</sup> are the result of a combination of a sheaf-like morphology producing an Avrami exponent of 5 to 6 and the background lamellae giving a value of about 2. A clear implication from this conclusion is that both sheaves and matrix lamellae form concurrently.

A comparison of Figures 5 (GEL-6.8) and 8 (XLPE-6.8) shows a major change in lamellar features. Occasional small sheaves can be observed in XLPE-6.8, a good example being close to the centre of Figure 8; however the most significant change lies in the character of the background lamellae. Instead of being perfectly aligned, thin and showing a distinctly 'nodular' appearance, they are oriented in many directions and clearly thicker, the amorphous material being relatively well etched. It will be recalled that the observed Avrami exponent for XLPE-6.8 was slightly larger than for GEL-6.8. Careful observation of Figure 8 reveals that a large fraction of the background lamellae are oriented in a NNW-SSE direction. This effect demonstrates that such lamellae are not generated in a random manner.

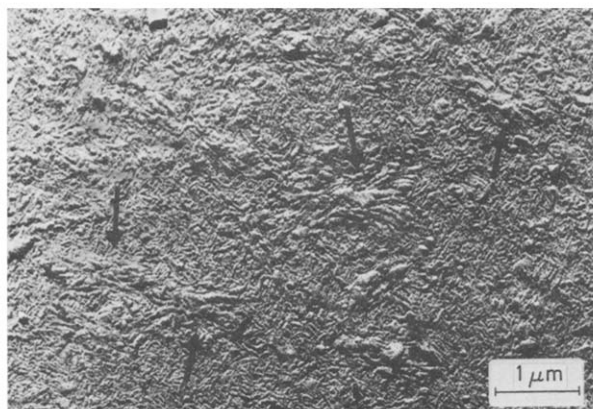


Figure 7 Growth of bundles of lamellae (rods) in XLPE-4;  $T_c = 92^\circ\text{C}$

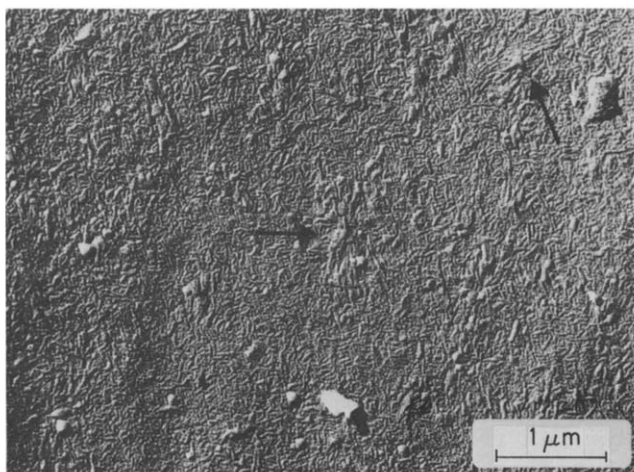


Figure 8 Growth of bundles of lamellae (rods) in XLPE-6.8;  $T_c = 92^\circ\text{C}$

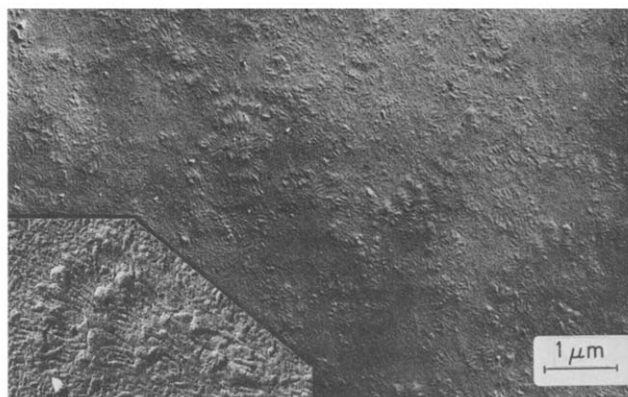


Figure 9 Growth of banded sheaves in XLPE-0.9;  $92^\circ\text{C}$

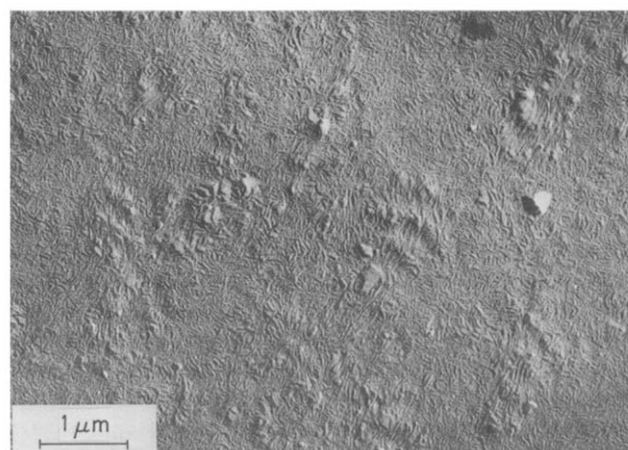


Figure 10 Growth of banded sheaves in XLPE-0.9;  $96^\circ\text{C}$

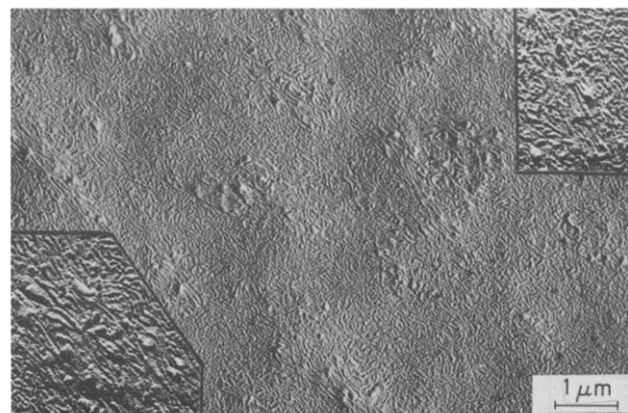


Figure 11 Growth of oriented bundles of lamellae in XLPE-0.9;  $103.8^\circ\text{C}$ . Inset photographs are higher magnification pictures of representative oriented sheaves

In order to obtain further information on the nature of the crystallization process specimens of XLPE and GEL have been crystallized at several temperatures. Typical morphologies of XLPE-0.9 crystallized at  $92^\circ\text{C}$ ,  $96^\circ\text{C}$  and  $103.8^\circ\text{C}$  are shown in Figures 9, 10 and 11. In all instances, lamellar banding occurs. The ultimate sheaf size is essentially independent of crystallization temperature. Additionally, at higher crystallization temperatures (e.g. Figure 11) the sheaves tend to orient in a particular direction. These results clearly indicate the presence of localized stresses even in a lightly crosslinked system. Studies of GEL-2 reported in the preceding paper<sup>3</sup> showed a similar effect. Why this effect should occur at higher temperatures is not known; however, it

must be remembered that a crosslinked network has a higher stiffness at elevated temperatures and hence localized stresses due to inhomogeneities in the network are likely to be higher.

In GEL-2 major effects are produced on a lamellar scale by crystallizing at 103.8°C, very close to the upper temperature limit of crystallization. Here it can be seen (Figure 12) that all features are well developed, whether in sheaves or matrix. Preferential orientation of growth features occurs, similar to the effect mentioned for XLPE-0.9 (Figure 11). It is, however, surprising to observe that the sheaves are composed of the thinnest lamellae, which are also linear, since better organized structures are generally associated with better formed, i.e. thicker, crystals. The inter-sheaf material contains S-shaped lamellae (arrows) similar to those reported by Bassett *et al.*<sup>15</sup> for linear polyethylene, which are presumably of similar origin. Although occasional groupings of these S-shaped lamellae have similar orientations there is generally no orientational correlation. They are generally separated by thinner lamellae of non-correlated orientation. The thinnest lamellae, i.e. those in the sheaves, often have a 'nodular' appearance, perhaps indicative of an over-etch relative to the thicker, more stable lamellae.

Morphological studies were carried out on specimens of the more highly crosslinked materials which had been crystallized at 96°C. The choice of this particular temperature was determined by the transition in Avrami coefficient noted in the kinetic studies<sup>2</sup>. Electron micrographs of GEL-4 clearly indicate the presence of sheaves (Figure 13, arrows). Most of the features observed

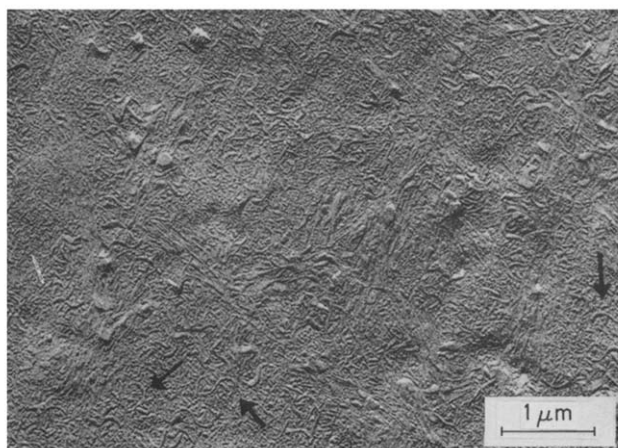


Figure 12 Growth of bundles of lamellae in GEL-2;  $T_c = 103.8^\circ\text{C}$

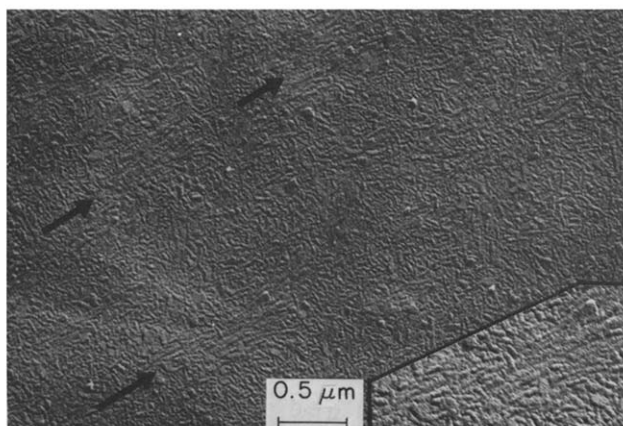


Figure 13 Growth of bundles of lamellae in GEL-4;  $T_c = 96^\circ\text{C}$

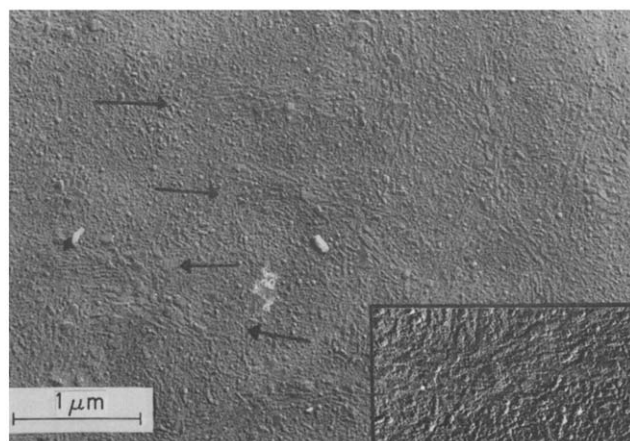


Figure 14 Growth of bundles of lamellae in GEL-6.8;  $T_c = 96^\circ\text{C}$ . Arrows indicate lamellar bundles and their orientation; the inset is a higher magnification picture of an oriented bundle

are essentially oriented bundles of a few lamellae. The background morphology is similar to that observed in Figure 4. GEL 6.8 also produces lamellar bundles (Figure 14), which also tend to be oriented in a particular direction. The background lamellae do not show a preferred orientation, but are also much more highly etched. For XLPE-4 and XLPE-6.8 crystallized at 96°C the morphologies are similar to those of the gel fractions. When XLPE-6.8 is crystallized at 103.8°C distinct randomly sited thick lamellae are produced.

A noticeable effect lies in the background structure of GEL-4, GEL6.8, XLPE-4 and XLPE-6.8. As already noted for lower crosslink density materials the lamellae appear to have a nodular appearance even under optimal etching conditions. This effect is much more pronounced in these higher crosslink density materials. It is presumably reflecting a change in the nature of the lamellar crystals with increasing crosslink density. In the hope that such a change might be monitored through their thermal behaviour, d.s.c. studies have been carried out. The results obtained are compiled in Figures 15 and 16. The major melting peaks for crystallization at 92°C are 107°C, 104°C, 103°C and 100°C for OPE, GEL-2, GEL-4 and GEL-6.8, respectively. For crystallization at 96°C they are 105°C, 103°C, 106°C and 104°C for GEL-4, GEL-6.8, XLPE-4 and XLPE-6.8, respectively. With increasing crystallization temperature and increasing crosslink density the area of the initial lower temperature peak increases.

## DISCUSSION

An initial comprehensive study such as this one has generated much new data together with several new problems which require considerably more in-depth study. It is possible to begin to understand some of the several major effects which have been observed. An attempt will now be made to describe and explain individual effects; however, it must be remembered that all explanations must be regarded as tentative until the whole is understood. First, we will consider two major effects: (a) crosslinking modifies and inhibits conventional superstructures but at the same time increases nucleation density; (b) a new type of morphology consisting of oriented lamellar domains is introduced. Secondly, it is possible to comment on lamellar details and multiple melting phenomena. Finally, Avrami exponents can now be correlated with the known morphologies.

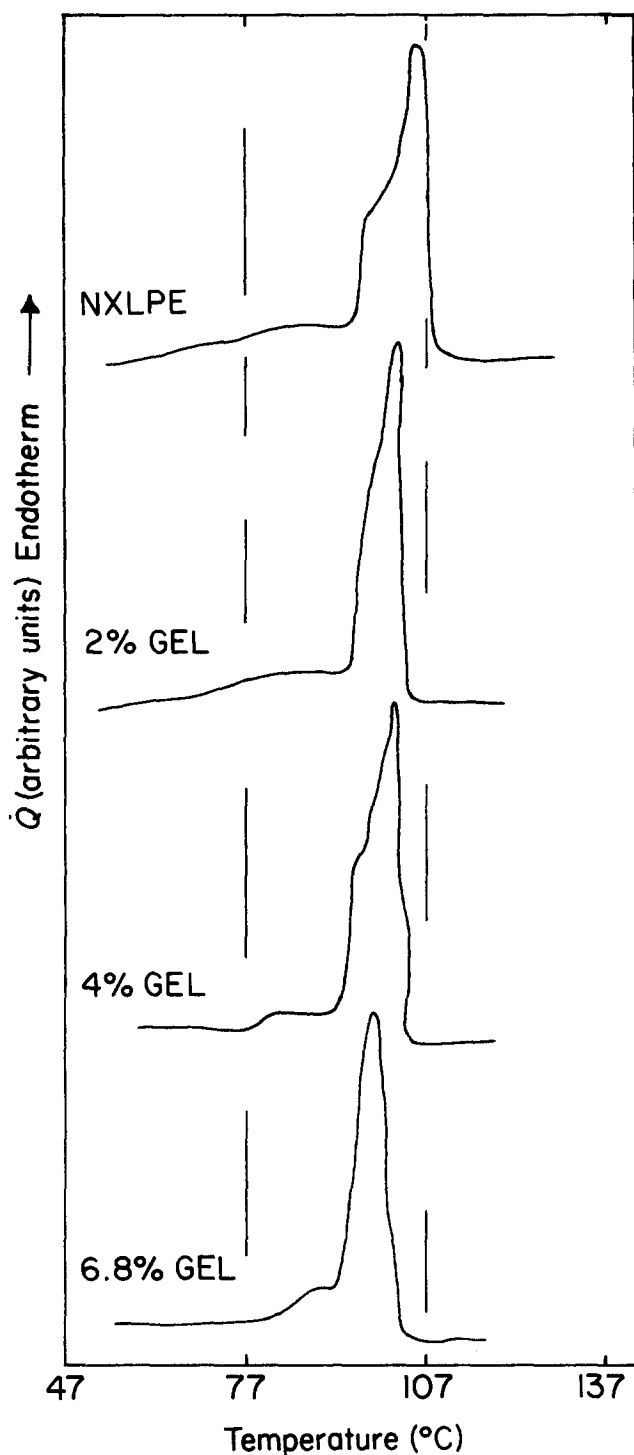


Figure 15 D.s.c. traces of NXLPE, GEL-2, GEL-4, GEL-6.8 crystallized at 92°C. Heating rate, 10°C/min

*Conventional superstructure*

Let us first consider the modification and ultimate suppression of superstructure. The branched polyethylene from which the crosslinked polymers were made showed well developed banded spherulites, 10–12  $\mu\text{m}$  in size. The introduction of light crosslinking (0.9% w/w dicumyl peroxide) eliminates spherulitic growth and produces sheaves composed of lamellae occupying two diametrically opposite 90° sectors. The sheaf length is approximately one quarter the size of the spherulite diameter in the non-crosslinked polymer. Banding is retained in the sheaves but of less perfect construction and

with a finer spacing than in spherulites. Doubling the crosslink density (2% w/w dicumyl peroxide) eliminates the banding completely and the sheaves are composed of sectors of about 45° in size. They are no longer volume-filling and areas between sheaves, if about the same size as the sheaves, contain what appear to be randomly oriented lamellae. The crystallinity has, however, been reduced by only a few per cent. It should be pointed out that the detailed structure varies somewhat with crystallization temperature. For instance, crystallizing at a higher temperature (in this case 103.8°C) produces little change in the character of the sheaves themselves but causes major thickening and better formed lamellae in the intersheaf material, and S-shaped lamellae were observed.

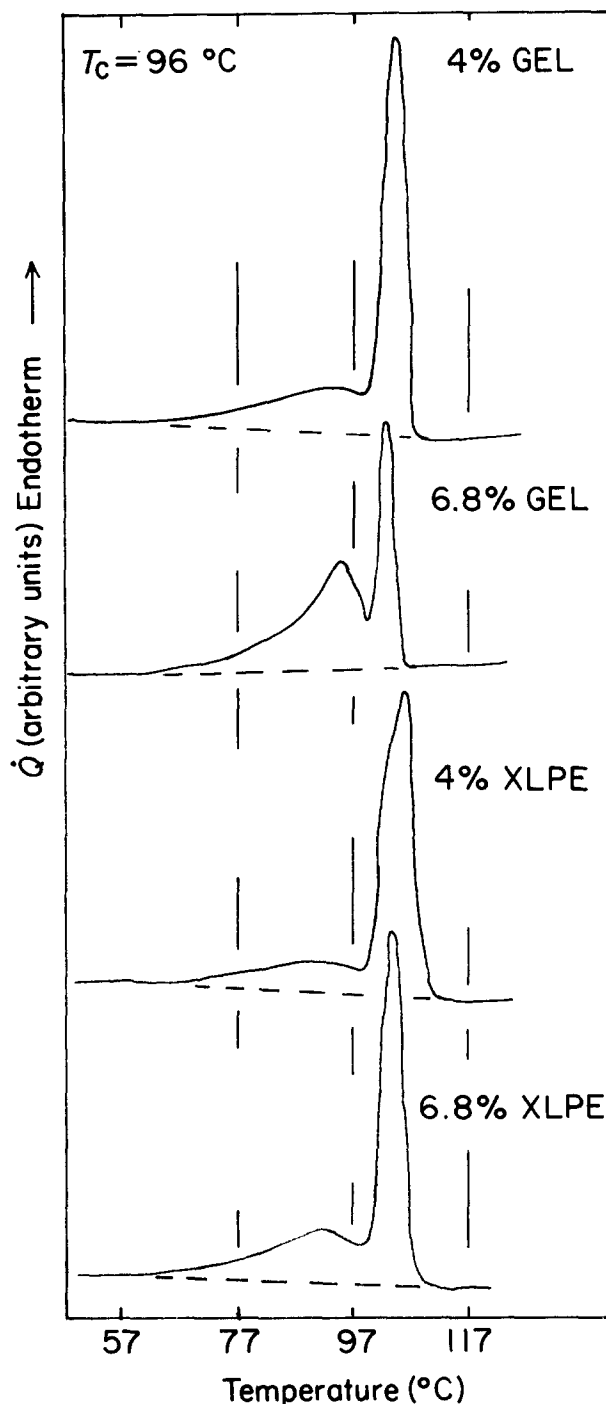


Figure 16 Comparison of d.s.c. traces of GEL and XLPE, crystallized at 96°C. Heating rate, 10°C/min

Beyond the critical loading<sup>2</sup> of 3% w/w dicumyl peroxide, the growth of sheaves becomes severely inhibited and oriented lamellar domains begin to appear. This effect was most pronounced in GEL-6.8 (*Figure 5*). In some areas oriented bundle-like sheaves can also be detected. These results indicate that as crosslink density increases spherulitic growth is gradually suppressed, although they are still nucleated. For the more highly crosslinked systems the growth does not proceed beyond the initial stage of parallel compact lamellar bundles. With decreasing crosslink density the lamellae have a tendency to splay apart and form sheaf-like structures. For the lightest crosslinking sheaves are well-formed and banded.

It is possible therefore to identify three specific influences of increasing crosslink density on the conventional superstructures. First, lamellar bundles are always produced, being similar in appearance to the early stages of spherulite growth. The lamellae are thin and closely stacked together. The nucleation density of these bundles increases with crosslink density. Secondly, for lower levels of crosslinking the lamellae in the bundles are able to grow and, in doing so, form sheaves. The lamellae are also able to splay apart forming sheaves of increasingly large sector size. Thirdly, the lamellae are able to form banded sheaves on further lowering of the crosslink density, but are able to do so even before the lamellae are able to splay out.

The influence of crosslinks on primary nucleation is interesting. Similar effects are normally produced using nucleating agents, for which there are often problems regarding the lack of uniform mixing. The introduction of light crosslinking may therefore provide a novel practical method for the production of relatively uniform nucleation densities, dense clustering being impossible. Mechanical properties and resistance to chemical attack are both improved for light crosslinking of a branched polymer, since crystallinity is barely affected.

#### *Oriented lamellar growth*

It is important to consider the possible mechanisms generating the oriented lamellar growth, but in the context of the general behaviour of the system as a whole. First let us review the important trends and their implications. Morphological studies of specimens crystallized at 92°C showed that the size of the growth feature decreases with increasing crosslink density. The effect is similar to that brought about by a deliberate increase in the nucleation density through the use of foreign nucleating agents, but differs in that the ultimate size is not simply controlled by the nucleation density since impingement does not occur for higher crosslink densities. The size of the morphological features is essentially independent of temperature, indicating a temperature-independent number of nuclei. The presence of oriented sheaves and bundles at higher crosslink densities suggests the likelihood of crystallization under stress. The mechanism of stress generation is not known; however, it is clear that the stress is increasing with crosslink density. The observation that sheaves are often oriented implies that the stresses are operating even in the lightly crosslinked polymers, being most noticeable at higher temperatures. It is likely that the magnitude of local stresses developed will be determined by local non-uniformity of crosslink density although the overall crosslink density and temperature will be important. The

fact that the sheaves developed their orientation at elevated temperatures, where stresses should intensify because of rubber elastic effects, supports this hypothesis. Various growth morphologies are of course possible, dependent on stress level; local variations could produce a variety of features concurrently. The predominance of any particular feature will be determined by the magnitude of local stresses. For intermediate levels of crosslinking oriented growth of lamellar bundles similar to that shown in *Figure 11* can occur. An indication of the range over which these local stresses operate can be obtained from the size of the oriented domains present at the higher levels of crosslinking. Domain orientation was retained over distances of up to a few microns. Localized variations in crosslink density could arise from various mechanisms. Most obvious is local variation in dicumyl peroxide content. It is well known that over a period of several months the peroxide, although in crystalline form, can migrate to the surfaces of pellets. Such major variations could not be applicable to the present study, with the possible exception of XLPE-2; however, holding the sample in the melt just above the melting point for several minutes eliminates any potential problem. It is, however, likely that the peroxide crystals are preferentially located in the spherulite boundaries of the non-crosslinked polymer. In a quenched sample these would be of the order of a few microns. During preparation specimens were held in the melt for at least fifteen minutes at a temperature sufficiently low to ensure only a minor amount of peroxide decomposition prior to raising the temperature to 200°C. This procedure should have been adequate to permit uniformity of peroxide concentration. Alternative sources would be variations in branching or molecular weight on a local level. The latter is possible since commercial polymers are often blends of homopolymers of different molecular weight. Branching is complex in a low density polyethylene and the detailed structure can vary with molecular weight.

#### *Lamellar detail*

An important point to note from this study is that, for all materials considered, lamellar growth occurred and this growth was not random. Lamellae invariably occur as bundles and there is no major variation in lamellar thickness with crosslink density noticeable in the micrographs. It is known from a correlative study using Raman spectroscopy<sup>17</sup> that for a constant crystallization temperature of 92°C the average stem length remains close to the value for the branched polymer over the entire range of crosslink densities studied. This is in contrast to recent data of Gielenz and Jungnickel<sup>14</sup> for melt irradiated linear polyethylene crystallized at 130°C. They observed a drop in lamellar thickness from 550 Å to 80 Å over the first 10 mrad of radiation, which is approximately equivalent to the range of dicumyl peroxide concentrations used here. In the case being considered here the lamellar thickness is already limited to ca. 140 Å by the branching levels so that the effect of crosslinking is quite minor. The original polyethylene is a typical branched polymer having 16 methyl groups per 1000 carbon atoms. Only for the highest crosslink density does the number of crosslinks become comparable at 4 per 1000 carbon atoms.

There are, however, several finer points to be considered, especially when the effects of temperature and

sol content are noted. As already stated, for the unextracted polymer XLPE-2 (20% sol fraction) the sheaves are large and well-formed when crystallized at 92°C. The lamellae are not constrained to grow parallel to one another and they are volume filling. Co-crystallization of the sol and gel fractions is clearly occurring, the sol serving to swell the network and to offset the inhibiting effect of abnormally high local concentrations of crosslinks. For higher crystallization temperatures both XLPE-0.9 and XLPE-2.0 show banded sheaves; however, the sheaves are very linear and show little tendency to splay apart. The background lamellae are also thicker and better defined, indicating thickening of many species. There are also fewer sheaves present, whereas when crystallized at 92°C the non-banded sheaves were volume filling. It therefore appears that crystallization at the higher temperatures permits a better separation of the sol together with the more linear portions of the gel. Sheaf-like superstructures are more difficult to find in GEL-2.0 crystallized at 103.8°C and they are non-banded. Many of the crystals are in the form of S-shaped lamellae. (Two forms of crystals therefore exist, one in the form of groups of parallel lamellae of unsplayed sheaf-like form and the second as thicker S-shaped lamellae which are sometimes aligned in groups.) It seems clear that these are not simply two orientations of one type of lamella.

It will be recalled that beyond the critical loading of 3% dicumyl peroxide the value of the sol fraction levelled off, as did the X-ray line broadening. Indeed the region of 3–4% dicumyl peroxide loading is a watershed in terms of structural variables. In the region prior to this the sol fraction, molecular weight between crosslinks, line broadening and many other variables change significantly as dicumyl peroxide loading is increased. Beyond it variables change slowly. It is in this region that growth of sheaves becomes severely inhibited and in which oriented lamellar domains begin to appear. As dicumyl peroxide loading is increased additional molecules are incorporated into the network at the expense of the sol fraction. Since the probability of attack by the free radical is proportional to molecular length, those being incorporated into the network at higher dicumyl peroxide loadings will be, on average, shorter than those incorporated at low loadings. They can be attached to the network as branches or properly incorporated as network sub-chains. Since the molecular weight between crosslinks continues to decrease with increasing loading undoubtedly the network is becoming tighter. It was recently determined<sup>18</sup> from a study of the relation between sol fraction and dicumyl peroxide loading that 5% of the free radical reactions result in chain scission. The minimum sol fraction achievable should be in the neighbourhood of that figure. The chemical microstructure and molecular weight of the sol need not therefore be constant as loading is increased, nor need they be related to the initial molecular weight distribution. Such changes in the molecular weight and microstructure of the sol may influence its ability to co-crystallize with the gel because of diffusional effects and introduce an additional complicating factor. When crystallized at 92°C both GEL-4 and XLPE-4 show the presence of a fair number of poorly formed sheaves, although the lamellae are better defined in XLPE-4. This indicates inhomogeneities in crosslink density even at such a level of crosslinking. The background lamellae are

in both cases very thin but exhibit a lack of preferential orientation. When crystallized at a higher temperature (96°C) the morphology is well defined in the gel, where relatively well-developed stacks of parallel lamellae can be seen separated by large background areas. In the unfractionated polymer, morphology is not so clear cut since the sol exerts a considerable influence in that isolated groups of thick lamellae are produced. Although areas of oriented parallel thin lamellae still can be discerned they are not as well developed as in the gel. It therefore appears that the production of thicker crystals of high sol content in the early stages of crystallization interferes with formation of superstructures in the gel.

In GEL-6.8 crystallized at 92°C the morphology is clearly that of domains of oriented lamellae; however, in XLPE-6.8 the orientation is less well developed and occasional thicker lamellae, as well as occasional groups of them, can be discerned. At 96°C the appearance of XLPE-6.8 is similar to that at 92°C but is different for the gel. Although the appearance is similar to that of GEL-4 the thinner background lamellae occur in better organized groupings. GEL-6.8 does not crystallize at 103.8°C; however, part of XLPE-6.8 does, followed by the rest of the polymer on cooling. Isolated, very thick lamellae can easily be discerned, with the bulk of the material consisting of groups of oriented lamellae. It does, therefore, seem clear that although two lamellar forms can be discerned in all materials, the possible separation of sol at high temperature is an additional complication.

In studies of the XLPE-2 system involving chlorosulphonation at 102°C it was clear that the part of the morphology most resistant to the reagent was the central core of the sheaf or bundle. It will be recalled that the lamellae composing those entities are always thin and closely stacked. On lamellar thickness grounds they would be expected to form the lower melting fraction rather than the higher melting form.

#### *Multiple melting behaviour*

D.s.c. traces provide evidence of multiple melting even for the gel fractions. For crystallization under most conditions being considered here no major variations in lamellar thickness occurred and hence other mechanisms need to be considered. The mechanisms of melting for non-crosslinked systems have been extensively discussed by other authors<sup>19,20</sup>. Likely causes for such materials would be variations in (a) lattice perfection, (b) fold surface structure, (c) ability to perfect the lattice during the experiment, (d) ability to thicken during the experiment, (e) local strain energy due to bent parts of the lamellae. For a crosslinked polymer all of these mechanisms are likely to be modified. Most influential might be inhibition of the thickening mechanism since many emerging stems would interconnect as four-armed stars at crosslinks. During both crystallization and annealing procedures any tendency for more of the chain to be pulled into the crystal would be resisted by the rubber elastic network.

It has been pointed out previously<sup>1</sup> that, for crystallization at a low constant temperature, the melting point decreases with crosslink density. This effect can be seen in *Figure 15* for crystallization at 92°C; however, lamellar thickness remains constant<sup>17</sup>. It seems unlikely that crosslinking would introduce a large number of imperfections into the crystals themselves. Changes in surface structure combined with mobility limitations in



the vicinity of the fold surface would probably induce local melting. When combined with other factors this produces a second lower melting peak (Figures 15 and 16), which is more evident for higher crystallization temperatures and crosslink densities. It can also be seen from Figure 16 that the major portion of the low melting peak occurs below the crystallization temperature of 96°C. This must mean that either the material involved was rejected at that temperature and crystallized during cooling or its crystallization rate was extremely slow. It also shows that the same material was unable to perfect or thicken during the d.s.c. experiment. The higher temperature peak is also likely to be a result of several factors. As discussed in the previous paper<sup>3</sup> a major contribution comes from the tendency of certain crystals to thicken during the d.s.c. experiment. As was pointed out earlier the central core of a sheaf composed of closely stacked thick lamellae is resistant to etches and remained untouched by chlorosulphonation at 102°C. These bundles must therefore be contributing to the high melting peak despite their low lamellar thickness. It is known that the central parts of spherulites can be superheated because of their compactness<sup>21,22</sup>. This mechanism may be contributory in a d.s.c. experiment; however, in the lengthy chlorosulphonation procedure it should not have been operative. It is possible that the compactness of the bundle caused diffusion problems for the reagent; however, the amorphous material within the bundles is also resistant to permanganic etch. It has already been pointed out<sup>10</sup> that crosslinked polyethylene is more resistant to etching than the linear or branched polymers. A further possibility remaining is, therefore, that the crosslink density in the bundles is relatively uniform.

#### Avrami coefficients

It is now possible to correlate the known morphologies with the Avrami exponents obtained from kinetic studies<sup>2</sup>. The existence of sheaves at lower crosslink densities directly confirms the validity of the assignment of Avrami coefficients of 5–6 to a sheaf-like morphology. For high crosslink densities Avrami coefficients 1–2 were obtained, which should be applicable to rodlike morphologies. The morphologies observed are generally oriented lamellar domains. If the individual lamellae grow independently, then indeed they would correspond to rods, but obviously not of circular cross-section. The presence of central nuclei and 'shish-kebab' type growth would have produced a different value of the exponent. Crystallization is slow so that row nucleation, which would be very fast, cannot influence the measured Avrami exponents. Growth would, therefore, correspond to radial growth of cylinders, which could be regarded as stacked discs. An Avrami exponent of 2 is characteristic of the growth of heterogeneously nucleated discs. Intermediate exponents of 3–4 for crosslinked material must be indicative of mixed morphologies, i.e. sheaves and 'rods'.

## CONCLUSIONS

Conventional crystalline superstructure formation is inhibited by crosslinking. The morphology of both extracted and unextracted crosslinked low density polyethylenes is sheaflike at low crosslink densities. For high crosslink densities the morphology consists of oriented lamellar domains, which may be dependent on local stress levels. At intermediate levels of crosslinking mixed morphologies exist. Observed morphologies are consistent with previously determined Avrami coefficients. Nucleation densities increase with crosslink density but the superstructures resulting do not approach impingement due to inhibiting effects.

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