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On the morphology of blends of linear and branched polyethylene

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A blend of linear and branched polyethylene was examined in view of establishing conditions of cocrystallization and/or segregation. Two members of the SCLAIR series were used in 1 : 1 proportions. Conditions of segregation on crystallization were first explored by DSC, which was followed by morphological examination of selected samples. This involved optical and electron microscopy, the latter using the permanganate etching technique of Bassett and Hodge. Dependent upon crystallization temperature and time, crystal segregation on different scales was observed revealing that the final product can be regarded as a morphological composite where the ratio and nature of the constituents are determined by the conditions of solidification. The particulars should be relevant to the presently evolving practice of blending different polyethylenes. Examples of the different morphologies will be demonstrated. The individuality of the lamellae of the more readily crystallizable species can become strikingly apparent which incidentally reveals details in the edge on view, such as have not been seen before, and may have relevance to the fundamentals of the structure of lamellar crystals in general.

1. Introduction

The investigation is concerned with the crystallization of a linear and a branched polyethylene in view of establishing conditions of co-crystallization and/or segregation. In addition to being important technologically, the subject is of great interest scientifically for it is relevant to the long standing question of how polyethylene chains with variable branch contents solidify. Two members of the Sclair series were used and eventually a 1:1 proportion blend was chosen. A number of experiments were devised primarily as an exploratory test with regard to the segregation of the blend components. As a first step the crystallization was investigated by differential scanning calorimetry (DSC) correlated with the use of polarized optical microscopy (PM). In cases where segregation became apparent, using the above techniques, the corresponding samples were examined electron microscopically for an assessment of the scale and nature of the segregation. For this purpose the permanganic etching technique [1–4] was utilized. The sequence was always: immiscibility first explored by DSC, followed by the selective choice of samples for PM, and subsequent application of transmission electron microscopy (TEM).

2. Experimental details

A blend of high and low density polyethylene was prepared from two representative Sclair polyethylenes, 2907 and 8105 (Du Pont, Canada, Inc.). The former is essentially linear whilst the other half of this "polymer alloy" is composed of the ethyl branched 8105, the branching of which is on average 14 ethyl branches per 1000 carbon atoms, and believed to be randomly distributed. The blending operation utilized a solvent precipitation technique, because no means of mechanical mixing was available. The blending commenced by making a 1% wt/vol solution of both constituents dissolved into *p*-xylene maintained at 115° C. After an agitation period of four hours, by which time an intimate mix was assumed, a non-solvent was added. The non-solvent, triethylene gycol, was added in sufficient quantity so as to double the original volume and at the same elevated temperature: this caused an instant precipitation of polymer. The blending procedure was successful by virtue of the

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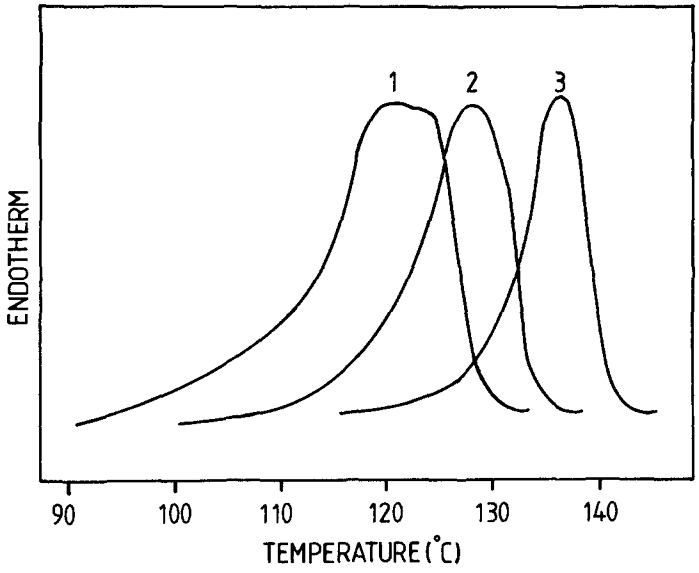


Figure 1 DSC endotherms from melt quenched samples of: curve 1 SCLAIR 8105, curve 2 SCLAIR BLEND 50:50, curve 3 SCLAIR 2907.

fact that all the mass of the polyethylenes were recovered. After cleaning and drying, the blend is subjected to various crystallization experiments, initially explored by DSC followed by morphological examinations on differing scales. Spherulitic morphologies via PM, whilst internal lamellar morphologies were examined by replication and TEM.

DSC proved invaluable in determining the presence and/or absence of segregation and the corresponding differentiation according to lamellar populations by melting point peaks. The study of the corresponding superstructures was carried out on thin-film specimens in a Mettler FP52 hot stage. To view the pertinent bulk morphologies on the lamellar scale the etching method devised by Bassett and Hodge [1] was utilized, the exact preparation being similar to previous works [1–4]. It differs only in that in this work a one-stage replication process is used.

3. Results

Precharacterization via thermal analysis attempted to assess the segregation of the constituents during the various heat treatments. If segregation occurred, by whatever cause, a double or multipeaked endotherm might be expected to appear on subsequent heating in the DSC, owing to the greatly different melting behaviours of the blend components (Fig. 1). Complete compatibility is maintained in the melt up to temperatures of 180° C. This compatibility is maintained upon quenching when a single-peaked endotherm similar to curve 2 in Fig. 1 is attained. The linear Sclair, on its own, possessed a melting peak temperature of 135.1° C with a narrow distribution of melting in its low temperature shoulder (curve 3). The low density Sclair has a melting plateau at around 116–126° C and has a much more diffuse character to its low temperature shoulder (curve 1). As expected, the blend (curve 2) lay somewhere between its two components and its characteristic endotherm peaked at 128° C.

However, during isothermal crystallizations between 121 and 130° C segregations are detectable. Crystallization at all intermediate temperatures produced similar results in overall shape and evolution of the different peaks. Arbitrarily, 124° C was chosen throughout most of this work. This temperature was expedient as it allowed complete interphase segregation on a practicable time scale. The calorimetric information presented in Fig. 2 is compiled from separate measurements obtained on three sample types.

(a) Samples prepared by isothermal crystallization *in situ* within the DSC.

(b) Samples which are portions of thin films, themselves produced for PM.

(c) Products of isothermal crystallizations of bulk blend specimens carried out in silicon oil baths.

The pattern of segregation was identical for sample preparation methods (a), (b) or (c) for any T_c. Fig. 2 illustrates how the pattern of segregation proceeds with time at $T_c = 124°$ C. It is not unreasonable to assume that these peaks corre-

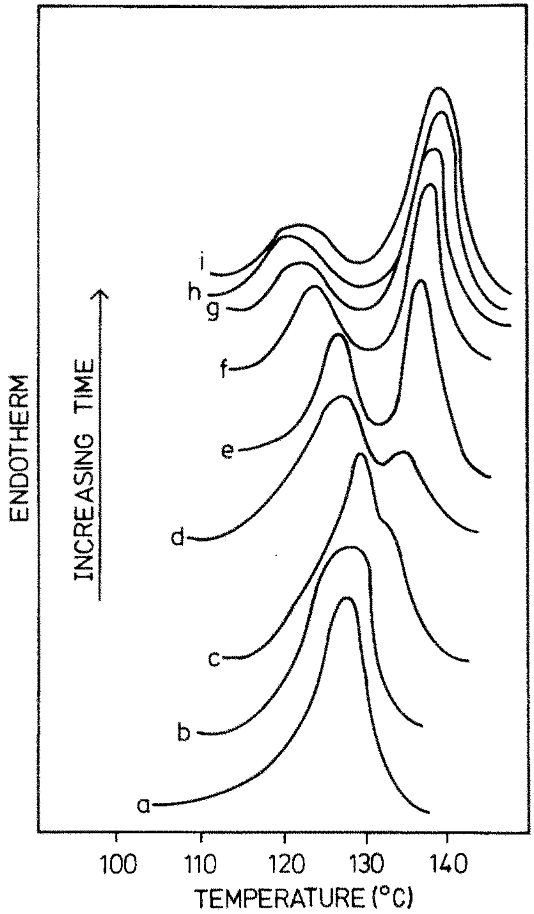


Figure 2 DSC endotherms for the SCLAIR polyethylene blend. The crystallization was at 124° C for the following times: curve a, 1 min; curve b, 30 min; curve c, 60 min; curve d, 140 min; curve e, $7\frac{1}{2}$ h; curve f, 10 h; curve g, 18 h; curve h, 30 h; curve i, 40 h.

spond to each of the constituent polyethylenes. The DSC, as well as indicating the extent of double population proved valuable in the context of correlating the optical observations. Examination of the spherulitic superstructures produced at 124° C followed the DSC analysis. The series of textures illustrated in Fig. 3 refer to the crystallization times in Fig. 2. The photographs taken using PM are of films quenched to room temperature after their respective crystallization times. Fig. 3 clearly gives scale and indication of the distribution of the segregating species, and the manner by which the segregation proceeds during crystallization. We see there must be ejection of material towards the spherulitic boundaries, best observed by reference to Figs. 3g and h. For short times nothing crystallizes at 124° C and what is viewed at room temperature is the whole unsegregated blend crystallized upon cooling (curve a). At longer holding times, curves c, d, e, etc., the linear Sclair starts to crystallize, first giving rise to a coarseness of texture, i.e. the large spherulites formed at the crystallization temperature $T_c = 124°$ C, and the fine grained material formed upon subsequent cooling.

For assessment of segregation on the scale of the individual lamellar thicknesses, selected areas were replicated and examined with TEM. The following micrographs all illustrate how different aspects of the lamellar morphologies can be examined. Fig. 4 illustrates a typical lamellar morphology produced by quenching the blend material after short holding times at the crystallization temperature: i.e. curve 2, Fig. 1, curve a, Fig. 2, where no appreciable segregation as detectable by DSC was apparent. The general appearance is that of a uniform population of smooth, curving lamellae. The sheets grow with large lateral extensions $> 10\,\mu$m. Fig. 4 portrays part of a spherulite where the surface cut is oblique with regard to the *b*-axis. (The *b*-axis is taken to be parallel with the edge-on lamellar view [4].)

Apart from blends crystallized for very short periods such as in Fig. 4, it is a general nature of all blends, irrespective of amount of segregation, to show a bimodal distribution of lamellae, where the constituents are distinct in character and size. This overview is, however, multifaceted, every micrograph containing a wealth of visual information endowing each with some element of uniqueness. The overall appearance, shown by all the subsequent micrographs, is of thick dominant lamellae interspersed with finer material. This is perhaps what we might expect from a two component system and for this reason we can assign their origins thus.

1. The high density linear SCLAIR 2907 produces the large and regular sheets that have crystallized isothermally before quenching.

2. The branched component, 8105 is for the most part molten during crystallization. Upon cooling it crystallizes into inter-lamellar fine textures.

Fig. 5 provides an overview of the general pattern of growth associated with these two component systems: smooth areas, marked S, (for higher magnification view, Fig. 6, see below), which are located between the boundaries and within the arms of the fanning sheaf-like structures marked A and B. These sheaves are com-

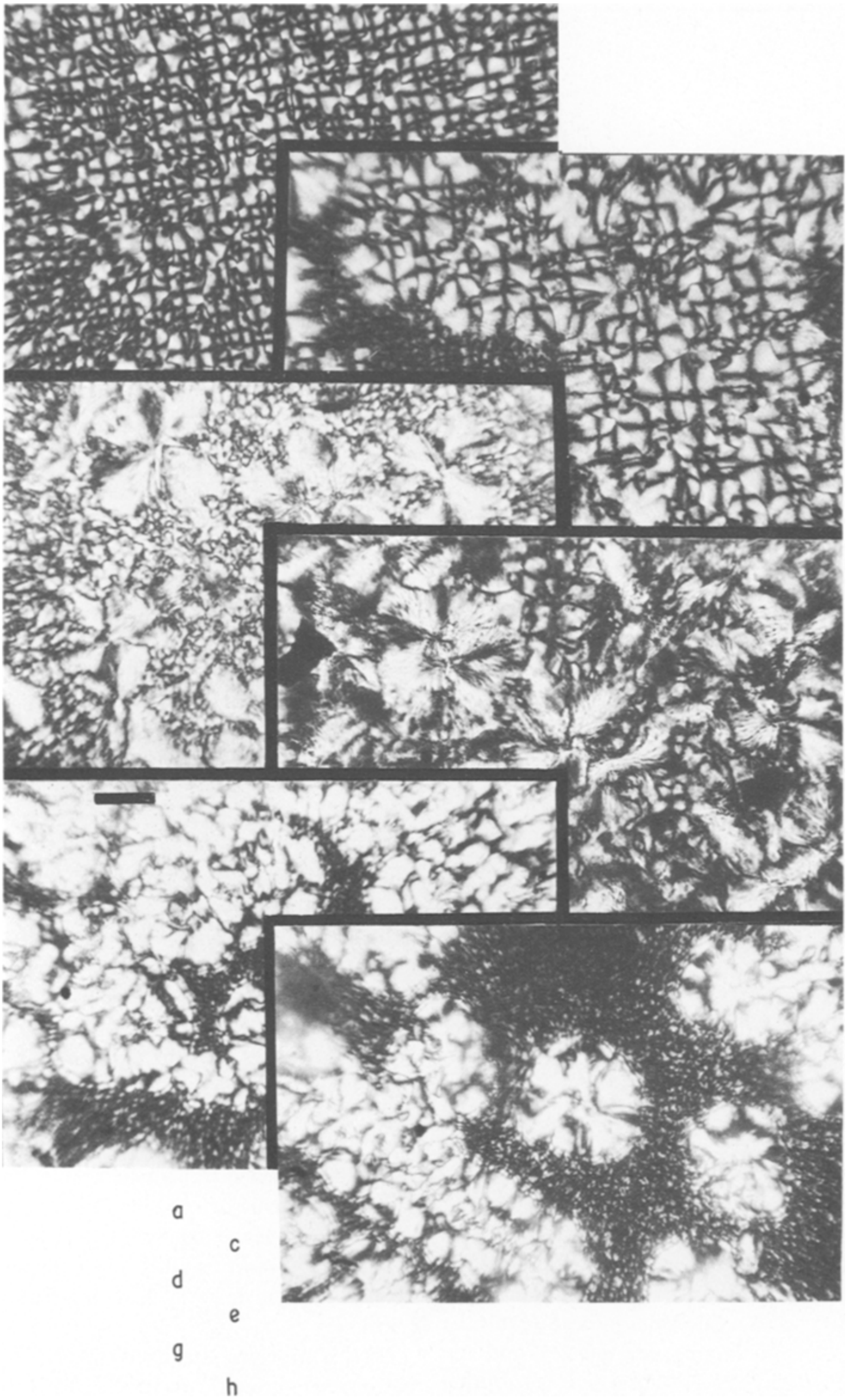
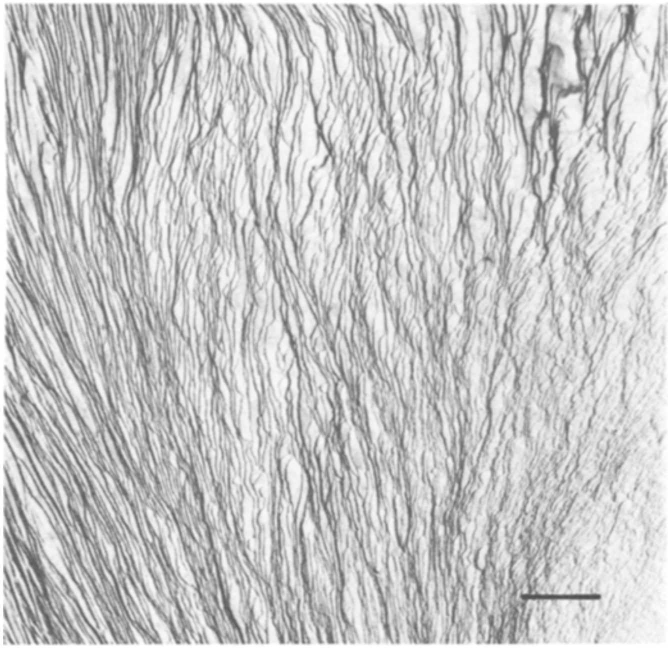


Figure 3 Corresponding spherulite morphologies selected from crystallization times in Fig. 2. Note how the spherulitic texture changes with degree of segregation. Scale bar = 50 μm.



igure 4 Lamellar morphology of melt-quenched blend (curve 2, Fig. 1). The microstructure is single phase. The scale bar = 1 μm.

monly associated with immature spherulites and we are, in fact, observing the extent of spherulite development up to the point where isothermal crystallization was halted. Two types of segregation therefore, could be inferred; that type where material is ejected to the spherulite or sheaf growth front, and that type where molten material is found within the growing sheaf or spherulite. Figs. 7 and 8 illustrate the two different cases. The former has permitted the apparent view of a growth interface relevant to three growth directions (arrowed), due to the impinge-

Figure 5 General growth pattern of crystallizing blend. Areas marked A and B, fanning sheaves, are isothermally growing thick lamellae. The smooth areas, marked S, crystallized on cooling (see Fig. 6). The scale bar = 2 μm.

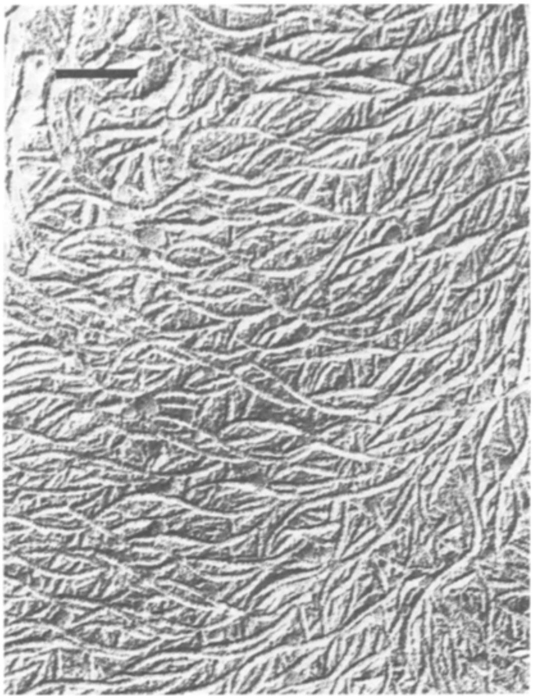


Figure 6 Magnification of similar area to those marked "S" in Fig. 5. The quenched material takes the form of S-shaped sheets. The scale bar = 250 nm. T_c = 124° C for 10 h.

ment of three different spherulites. This has given rise to the central "void", and complex overgrowths occur where the thick crystallizing lamellae have competed for dominance. Fig. 8 shows the structure inside the spherulite. Here, dominant lamellae, running top to bottom, are connected by subsidiary rod-like platelets, (as seen edge-on) conferring a "spider's web" morphology isolating gaps of the then, still molten material. The material in the spaces between the lamellar web crystallizes upon cooling into the proliferous S-shaped sheets; (the structure highlighted in Fig. 6) again marked S. It is shown that the areas of poor contrast in Fig. 5, marked S, are composed of regular arrays of the connected, well-defined, S-shaped habit lamellae (Fig. 6).

The overall picture of morphology that could be described as being typical then, is one of interpenetrating regions of the two components. A web of coarse lamellae constituting sheaves of spherulites which has formed isothermally at the extended crystallization temperature enclosing (or separated by) regions of much finer scale texture formed on solidification during cooling. The latter consists of S-shaped sheets being found at either spherulite boundaries, or, where favourable orien-

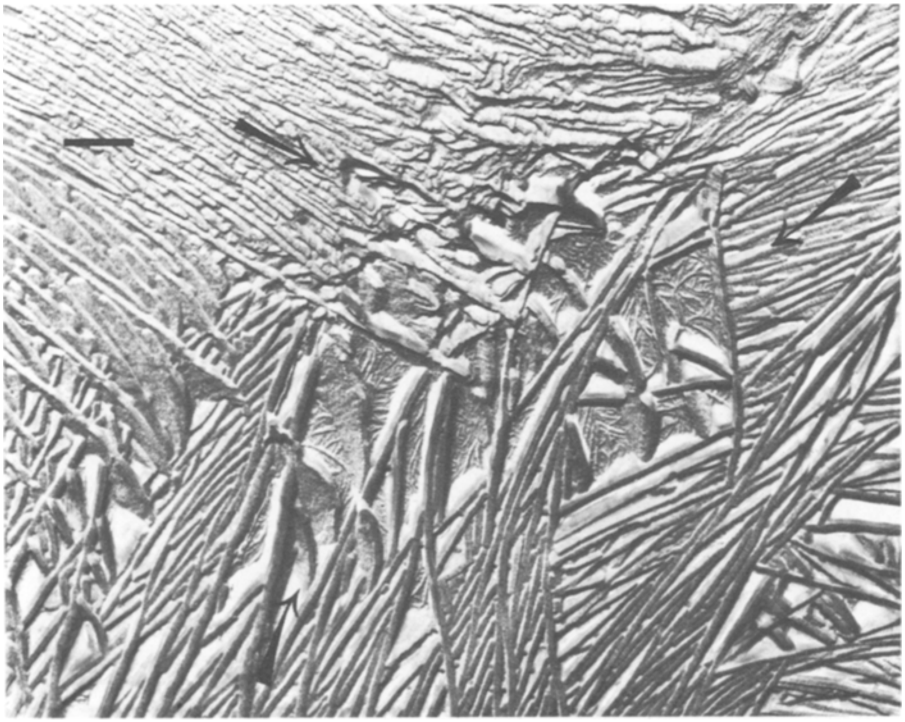


Figure 7 Two phase microstructure at spherulite boundary. The scale bar = 500 nm. T_c = 124° C for 40 h.

Figure 8 Highly complex composite of the two phases within a spherulite. Quenched material is marked S. Scale bar = 500 nm. $T_c = 124°$ C for 50 h.

tation permits, as lying between the stacks of thick lamellae, within the spherulite.

As a bonus to the overall morphological examination fine lamellar details were disclosed in a variety of the samples. This detail took the form of contrast differences within the lamellae revealed when in edge-on or near edge-on orientations. Fig. 9 shows thick, stepped lamellae which appears as doublets when viewed along the lamellar edge (arrowed). More precisely the individual lamellae appear to split along a central divide either side of which the contrast difference occurs. Figs. 10 and 11 show variants of such intra-lamellar subdivisions.

In the case of Fig. 10, which shows details from within a spherulite, this contrast appears to be non-symmetric about the middle of the lamellar thickness. Whilst in the case of Fig. 11, showing detail at a spherulite boundary, the contrast is symmetric. It takes the form of dark contrast

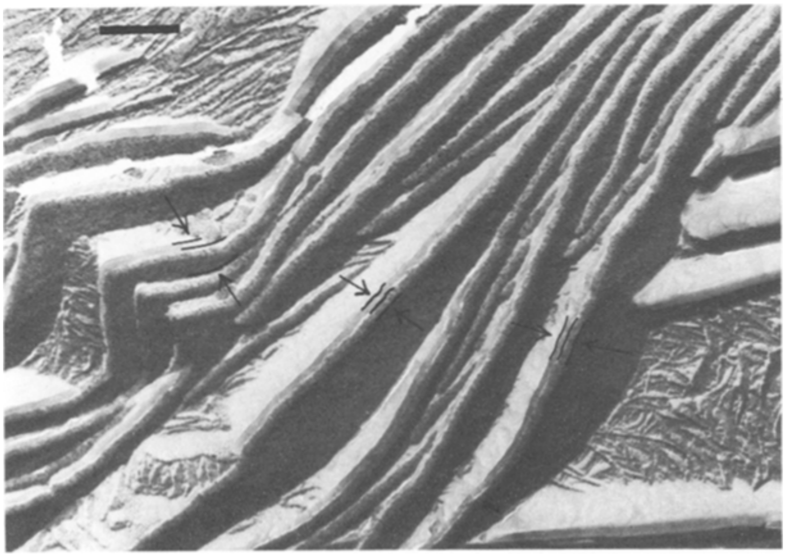


Figure 9 Doublet appearance of isothermally grown thick lamellae. Scale bar = 125 nm. $T_c = 124°$ C for 40 h.

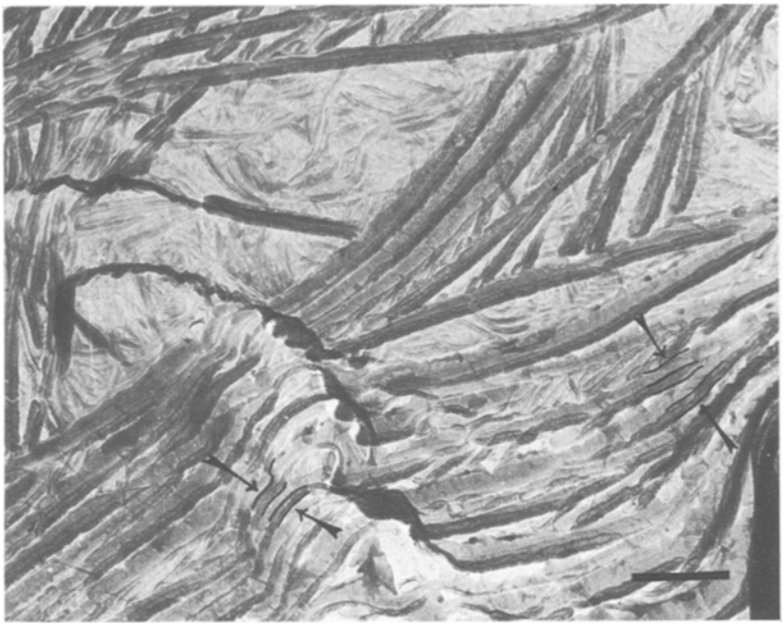


Figure 10 Contrast variations showing fine lamellar features; doublets and triplets. Scale bar = 1 μm. $T_c = 124°$ C for 30 h.

sandwiching a central lighter portion of equal width (arrowed). Whatever their cause, the existence of such fine details in themselves suffices to stimulate discussion, as they are likely to relate to a more intimate mechanism of crystallization.

4. Discussion

The exploratory tests have revealed conditions for segregation in a blend of linear and ethyl branched polyethylene through correlated calorimetric and morphological examination. The electron microscopic examination itself produced irrefutable evidence as to the existence of a two-phase structure down to the level of the individual lamellae. The correlation of these observations with other techniques, namely DSC and PM, add further weight to these effects and affords an opportunity for additional analysis. The coarser spherulites

Figure 11 Contrast variations showing fine lamellar features; doublets and triplets. Scale bar = 1 μm. $T_c = 124°$ C for 30 h.

observed in PM, themselves a product of large scale segregation, are envisaged as consisting of isothermally growing thick lamellae, whilst the quenched material is consistently observed as much thinner lamellae being S-shaped in form. Such differences already revealed on the optical scale became much more conspicuous when resolution is increased; the Bassett–Hodge technique has provided us with the means with which to do so. This reveals the wide variety of structures emanating from one particular sample, the appearance of which is, of course, much dependent upon the precise crystalline orientation in which the particular entity happens to be viewed.

The structures themselves represent a complex arrangement of dominant lamellae embedded in an assembly of finer lamellae, which at low resolution may appear as a featureless matrix (Fig. 5). This two component texture is evidently the result of segregation, or at least incorporates segregation. Qualitative evaluation indicates that this segregation, as revealed by the above symptoms, increases with the time held at the crystallization temperature T_c, consistent with the self-evident expectation that with increasing time the initially compatible mixture has more time to separate into the two individual constituents. In a given sample, what fraction of the mixture crystallizes isothermally and how much upon subsequent quenching, depends upon both the temperature of crystallization and time held at that temperature. At lower crystallization temperatures within the segregation range (121–130°) some of the non-linear component is expected to crystallize and may possibly co-crystallize with the linear material to a certain extent. The appropriate ratios and compositions involved would require an investigation on its own. Some of this is in progress and will be reported separately [6]. The present report will be confined to morphological factors alone.

The dominant lamellar structure formed at T_c develops by growth from specific centres, while as stated before, the segregated material is ejected both sideways, between the lamellae and along the growth fronts of the larger scale sheaves or spherulites constituted by their lamellae. Eventually the lamellae originating from the different centres interpenetrate along with a certain amount of interpenetration between the branching units belonging to the same centre. At this stage the whole sample can be considered as a continuous lamellar network embedded in a matrix of finer texture where the network itself has a larger scale structure on its own (singularities at the spherulite centres from which the lamellae emanate). The whole process giving rise to the texture may be considered as crystallization from a solvent where the solvent now is a polymer in itself and can be frozen in by cooling.

In widest generality the resulting phase segregated system can be regarded as a composite consisting of dominant lamellae of the linear component and the matrix (itself consisting of finer lamellae) of the branched material, (allowing for the possibility of a certain amount of cocrystallization of the two molecular species within the two components). As in every composite the resulting properties will depend upon the nature of the individual components, the relative amounts of components, on their geometry (morphology) and finally, on their mode of interconnectivity. In this respect the stage where the lamellae interpenetrate should be particularly significant because at this point a transition from a composite containing isolated lamellar aggregates to that of a continuous lamellar network sets in. This has potentially significant consequences for the mechanical, or any other property of the material. In final analysis therefore the most important consequence of the phase segregation should lie in the creation of this composite with all its variants.

We can now turn our attention to the fine detail produced within the individual lamellae. The possibility of seeing such fine details could evolve from a variety of causes. The first could be due to an improvement in the technique of replication producing higher quality specimens, coupled with the enhanced microscopic detail apparently afforded by the isolated lamellae produced in blend samples. Any genuine detail seen within a lamellar cross-section is bound to be significant as it relates to the perfection of the crystal and to the nature of chain folding. The details now revealed would, therefore, imply discontinuities within the lamellar sheets; this may be general or perhaps, confined only to the blend material. In the latter case it may involve some form of intralamellar segregation, such as branched material becoming part of the lamellae as a whole but becoming ejected to the fold surfaces. We know that if the melt is quenched (or is subjected to a brief isothermal crystallization (Figs. 1 and 4) no distribution of lamellar species occurs, as indicated by

DSC or TEM. However, we need to know more exactly the part played by crystallization from a diluent phase before we might guess at the cause of these discontinuities. Even if such an intralamellar segregation were at play it does not exclude the existence of the first possibility, namely the generality of an intra-lamellar subdivision with all its important potential implications, particularly as in this work, subdivisions of different kinds, e.g. doublets and triplets can be seen.

We are, of course, aware of the danger of artefacts when viewing such fine details in samples which have been etched, shadowed and replicated. Nevertheless a discontinuity does by its very nature imply the existence of some structure feature, which in turn indicates again some local disorder enabling the action of the etch to be more substantial at the specific locality involved. The subsequent preparation stage of vapour deposition gives ground to some caution. Cryer *et al.* [5] have found artefacts produced by vapour phase deposition of carbon and carbon/platinum. A "fir-tree" deposition was found to occur on coated fibres, and perhaps the way the lamellae are isolated within the blend may be inducive to such artefacts. Still unexplained in this case though are the various straight line contrast differences that divide the lamellae. One may think that doublet and triplet could be different perspectives of similar effects. For example, if the lamellae are not in exact edge-on orientation, then this oblique cut would expose some degree of side surface, which perhaps could give rise to the triplet appearance. On the other hand, no clear correlation between the effects seen and the direction of the vapour deposition relative to the lamellar (edge) direction was observed such as in the artefact source of [5]. On balance, in view of the potential importance of the issues ensuing from a genuine cross-sectional subdivision of the lamellae, no really conclusive evidence can be cited until a more quantitative analysis of the etching and replication techniques is produced.

In conclusion we have shown when and how segregation can occur when a compatible mixture of polyethylenes of different branch content crystallize and we displayed some of the morphological consequences of such a segregation. The experiments followed the logical course; first identifying the conditions when segregation occurs by DSC calorimetry, and secondly to examine the morphological form of this segregation on specimens selected according to DSC results. The latter was pursued on two successive levels: on the level of the spherulites by polarizing microscopy and on that of lamellae by transmission electron microscopy, the latter case utilizing the Bassett–Hodge etching technique demonstrating its applicability for this purpose. The morphological examination clearly revealed the development of a two component texture corresponding to the calorimetrically identified segregation, together with a number of particular textural details of potential interest (also for its potential composite–mechanical behaviour). In addition, at the highest resolution new unexpected features within the segregated lamellae themselves have become apparent, which if found to be genuine (yet to be conclusively ascertained) could be of potential significance to polymer crystallization in general and to that of blended material in particular. In the latter context the prospects opened up by present work could be looked at in another way: namely, by crystallizing polyethylene in blend form offers a new approach for the study of the morphology of the primary entities of the crystalline structure, where the less readily crystallizable component acts as a solvent (which itself is a polymer and of comparable chemical constitution) for the more crystallizable one. Finally the limited nature of this study will be emphasized: it involved only one pair of polyethylenes and this in a single mixing ratio. Extension over a wider range of sample pairs is clearly invited together with a more explicit identification of the components which have segregated. The next stage of this work will present extension along the above directions [6].

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