On morphology and polymer blends: polystyrene and polyethylene*

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This paper compares the morphologies observed in two blend systems, namely blends of isotactic and atactic polystyrene, and blends of linear and branched polyethylene. Crystallization of isotactic polystyrene at high temperatures ($\gtrsim$200°C) produces immature sheaf-like aggregates of lamellae. Addition of atactic polymer results in modified morphologies that are based upon bundles of lamellae, separated from one another by non-crystalline regions. At high atactic contents sheaf-like objects are no longer observed, crystallization occurring to give structures that are better described as multilayered crystals. At temperatures below ~200°C, mature spherulites develop. Addition of atactic polystyrene again results in morphologies in which lamellae are grouped into stacks separated from one another by non-crystalline regions. Again, at high atactic contents a less complex (sheaf-like) overall morphology is observed. In all the above microstructures, lamellae exhibit an inherently hexagonal habit. However, at lower crystallization temperatures observations suggest that lateral lamellar growth may be restricted. Isothermal crystallization of linear polyethylene at temperatures above ~125°C results in morphologies in which a complex lamellar hierarchy exists, as a consequence of molecular fractionation during crystallization. Addition of branched polyethylene, which is unable to crystallize at these temperatures, suppresses fractionation such that the resulting morphologies may be described in terms of only one dominant and one subsidiary lamellar population. When viewed along the crystallographic *b* axis, dominant lamellae appear planar or mildly S-shaped in profile, whilst subsidiary lamellae are planar and inclined at an angle of ~25° to the local dominant population. In blends with a high branched content, apparently non-crystalline regions can be seen between individual lamellae. Thus, in polyethylene blends, the non-crystallizing component is located between individual lamellae rather than between bundles of lamellae, as is the case in polystyrene. This difference arises from the parallel growth of dominant and subsidiary lamellae in polystyrene as opposed to the inclined development of subsidiaries with respect to the dominant lamellae in the polyethylene blends. In all the samples studied, spherulite growth occurs via a dominant/subsidiary mechanism.

(Keywords: blends; polystyrene; polyethylene; transmission electron microscopy; spherulites; dominant/subsidiary growth; molecular fractionation; lamellar bundles; lamellae)

INTRODUCTION

The concept of blending two or more polymers together as a means of modifying macroscopic properties is one that has been widely adopted. Indeed, many commercial plastics are in truth blends, where this term is used to describe: a combination of two or more similar systems, e.g. linear and low-density polyethylene; a formulation containing a number of incompatible polymers, e.g. rubber-toughened materials such as high-impact polystyrene; or even a material that contains a 'polymeric plasticizer', e.g. poly(ethylene-*co*-vinyl acetate) in poly(vinyl chloride) (PVC)[1]. However, polymer blending constitutes much more than a mere technological expedient that enables improved materials to be devised by combining the useful properties of different molecular species in an effort to meet ever more demanding requirements. Indeed, the study of blends has done much to refine the fundamental understanding of polymeric materials and stimulate further research.

In the work considered here, blending is employed primarily as a morphological device, whereby a compatible, non-crystallizing diluent is added to the polymer of interest. Such an approach has a number of advantages compared with the direct examination of a single-component system. First, the morphological study of melt-crystallized polymers at high resolution (i.e. by electron microscopy) almost invariably involves a complex sample preparation procedure. Blending, in some circumstances, may constitute an experimental route that enables useful morphological information to be gained relatively straightforwardly, by, for example, the preferential dissolution of one phase. Such an approach has been employed as part of a study of blends of poly(vinylidene fluoride) (PVF_2) and poly(ethyl acrylate)[2], the non-crystallizable component being removed relatively easily to leave the crystalline PVF_2 microstructure essentially intact[3].

Alternatively, the addition of a suitable diluent may be employed as a means of clarifying morphological features that are otherwise obscured within the dense mass of lamellae that often form during rapid crystallization from the melt. In this case, the non-crystallizable polymeric additive serves to 'open up' the microstructure, leaving the vast amount of

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information that may be present in a micrograph more amenable to interpretation. Finally, in contrast to the previous qualitative uses of blending, this approach may also be employed as a quantitative morphological tool. The addition of a suitable compatible diluent constitutes a potential means of modifying appropriate crystallization parameters (e.g. spherulite or lamellar growth rate, melt diffusion coefficient, etc.) independently of one another, as in the seminal work of Keith and Padden[4–6].

Structural studies of compatible polymer blends composed of a crystallizing and a non-crystallizing component have revealed that, after crystallization, the non-crystallizing polymer may reside either between individual lamellae[7] or at what have been referred to as interfibrillar sites[4]. In this paper the morphology of two blend systems will be considered – blends of isotactic and atactic polystyrene (iPS/aPS blends), and blends of linear and low-density polyethylene – to illustrate these two modes of behaviour. A complete description of all the morphological variations that arise as a result of changes in material parameters, blend composition and crystallization conditions is, however, beyond the scope of one communication and will not, as a result, be attempted. Indeed, rather than concentrating on the observed structural differences, attention here will focus upon the underlying morphological principles and the way in which the differences seen arise as a consequence of the basic mechanism of crystallization.

EXPERIMENTAL

The materials used in this study are as follows. The polystyrene blends were prepared using a sample of iPS purchased from Polymer Laboratories Ltd. From this, polymer fractions were prepared using solvent extraction procedures[8,9]. The aPS was also purchased from Polymer Laboratories Ltd. This was obtained both in the form of narrow fractions of the required molecular mass, and as a whole polymer; appropriate materials were selected as required. The polyethylene blends were prepared using Sclair 2907 (Du Pont) and a typical commercial low-density polyethylene designated LDPE 4 (obtained from the Rubber and Plastics Research Association). Available material parameters are listed in *Table 1*. In all cases blending was performed in solution using appropriate solvents: chloroform in the case of polystyrene, and xylene for the linear/branched polyethylene blends. All samples were crystallized isothermally from the melt at a temperature where only one component of the blend was capable of crystallization. The nomenclature employed when referring to these blends conforms to the following pattern. First, the blend system itself is specified (BPS for blended polystyrene and BPE for blended polyethylene), then the crystallization temperature and, finally, an arbitrary character to indicate the precise sample. Thus, for example, BPS/210 1 represents a polystyrene blend, crystallized at 210°C in which the isotactic component comprises 20% by mass of the blend (see *Table 2*). Isotactic polystyrene is referred to in a similar manner but with IPS in place of BPS.

Table 1 Material parameters

Polymer	Material	$\bar{M}_w$	$\bar{M}_n$	
iPS	PS-E3	1.2×10^6	1.3×10^5	(*a*)
iPS	PS-BI	8.4×10^5	1.8×10^5	(*b*)
iPS	iPS-D	6.0×10^5	2.4×10^5	(*b*)
iPS	iPS-G	1.1×10^6	3.9×10^5	(*b*)
aPS	PS-BA	2.3×10^5	6.6×10^4	(*b*)
aPS	aPS-2	3.62×10^5	3.38×10^5	(*c*)
Linear PE	Sclair 2907	9.8×10^4	2.1×10^4	(*a*)
LDPE	LDPE 4	1.5×10^5	1.9×10^4	(*a*)

[a] G.p.c. – Rubber and Plastics Research Association
[b] G.p.c. – this laboratory
[c] Polymer Laboratories

Table 2 Composition of blends

Sample	Crystallization temperature (°C)	Composition
IPS/220 B	220	100% PS-E3
IPS/220 81	220	100% iPS-G
BPS/210 5	210	50% PS-BI, 50% PS-BA
BPS/210 1	210	20% PB-BI, 80% PS-BA
IPS/190 A	190	100% PS-E4A
BPS/190 5	190	50% PS-BI, 50% PS-BA
BPS/190 1	190	20% PS-BI, 80% PS-BA
IPS/162 A	162	100% PS-BI
BPS/162 1R	162	19% PS-BI, 81% aPS-2
BPE/128 E	128	23% Sclair, 77% LDPE 4
BPE/125 A	125	100% Sclair
BPE/125 B	125	80% Sclair, 20% LDPE 4
BPE/125 C	125	61% Sclair, 39% LDPE 4
BPE/125 E	125	23% Sclair, 77% LDPE 4

Samples were prepared for examination in the transmission electron microscope (TEM), using the procedure outlined below. First, an internal surface was exposed using a microtome. Thin sections removed during this step were routinely examined optically and compared with subsequent TEM data. The microtomed surfaces were then etched using prescribed etchants and procedures[10,11]. After etching, surface replication was performed using a standard two-stage technique. In this, an intermediate replica is first formed in cellulose acetate, which is then shadowed obliquely and coated with carbon. The cellulose acetate is finally dissolved in acetone to leave the shadowed carbon replica sitting on a TEM grid, ready for examination.

RESULTS AND DISCUSSION

iPS/aPS blends

Isotactic polystyrene may be crystallized isothermally from the melt over a wide temperature range. At crystallization temperatures above ~200°C sheaf-like aggregates of lamellar crystals are generally observed and these range in complexity from simple groups composed of only a few layers, to relatively complex structures containing many diverging lamellae. The precise form depends upon both the temperature and the crystallization time[11,12]. Extreme examples can be seen in *Figure 1*. Both the structures shown are composed of inherently hexagonal lamellae and develop by a branching and splaying mechanism to give the range of morphologies indicated. In addition to lamellar branching and subsequent divergence, the other basic principle of polymer crystallization that is evident in *Figure 1a* is that of dominant/subsidiary growth. In this process, a framework of individual (dominant) lamellae is initially formed, and this is followed by subsequent in-filling crystallization (subsidiary lamellae).

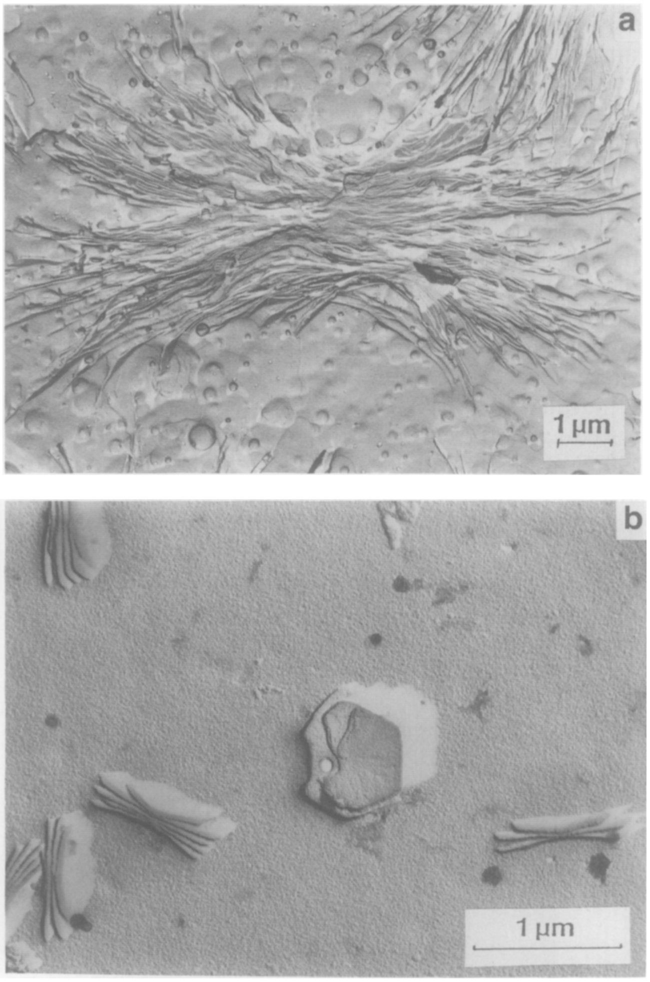

Figure 1 Sheaf-like lamellar aggregates in iPS crystallized at 220°C and then quenched; in (a) the sample (IPS/220 B) was crystallized for 24 h, whereas in (b) the crystallization time was only 81 min (sample IPS/220 81). The latter micrograph also reveals the inherently hexagonal habit of iPS lamellae

Addition of aPS results in morphologies that, at first sight, appear somewhat different from those observed in unblended systems. *Figure 2* shows the effect of varying the atactic concentration on objects grown at 210°C. Two conclusions can be drawn immediately from evidence of this type. First, increasing the amount of atactic polymer present results in objects that are less compact and that are, as a result, less complex. At 80% aPS, the structure shown is more reminiscent of multilayered crystals than axialites (this lattet term is used merely to indicate an object that is sheaf-like in form rather than to imply a morphology in which lamellar divergence is strictly confined to a single axis). This conclusion is consistent with previous studies[13] where crystallization from highly doped melts (e.g. 10% iPs, 90% aPS) has been employed as a means of producing individual lamellae of polystyrene, whereupon such a process has been referred to as crystallization from solution in a polymeric solvent. Of more importance, as far as the general crystallization process is concerned, is the observation that, on addition of aPS, the morphology changes from one based on individual lamellae to one in which the observed structures are composed of bundles of lamellae that are separated from one another by non-crystalline regions presumably containing atactic material. This observation is not unreasonable, bearing in mind the processes involved in dominant/subsidiary crystallization. In the purely isotactic case, an array of individual dominant lamellae is first established and this is then followed by the subsequent crystallization of the intervening material to yield a morphology that varies from single, well separated lamellae at the growth tips to a dense, compact mass of lamellae nearer the centre of the structure (see *Figure 1a*). Now, consider a material composed of 50% iPS and 50% aPS. Examination of such a sample, as in *Figure 2a*, again reveals the presence of individual lamellae at the extreme growth tips. As crystallization proceeds, subsidiary lamellae begin to develop within the existing dominant framework and this process will continue until all the potentially crystallizable, interstitial material has been used up. Thus, bundles of lamellae form and these are separated from one another by predominantly atactic regions. Whilst studies of iPs/aPS blends by optical microscopy[4] and small-angle X-ray scattering[14] have arrived at a similar conclusion concerning the location of the non-crystallizable component in this system, the processes that result in the formation of lamellar stacks in polystyrene (and their absence in many other polymer blends) have not, in the past, been adequately described.

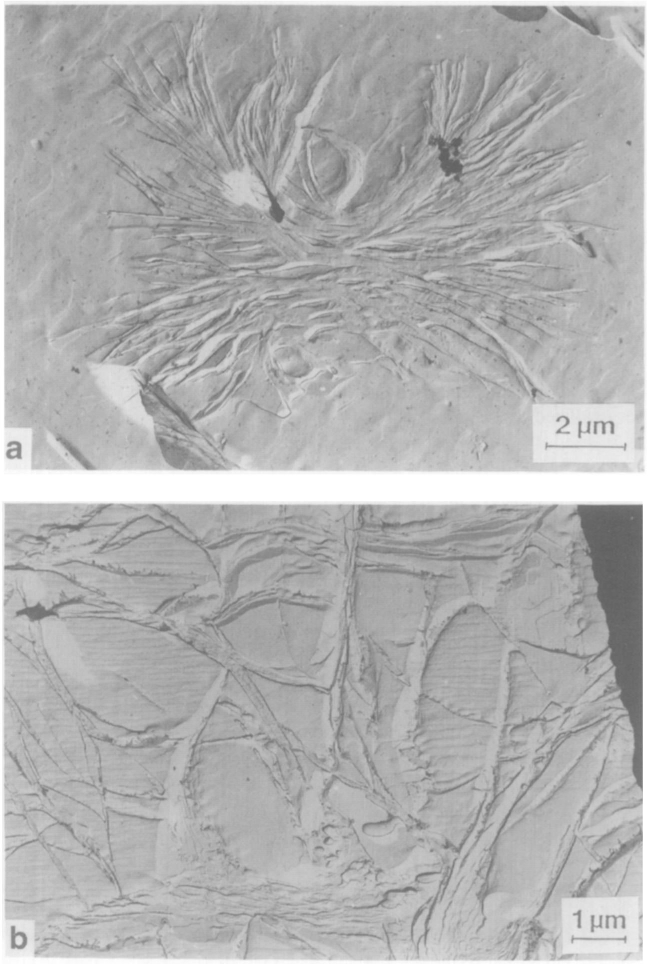

Figure 2 Blends of iPS/aPS crystallized at 210°C. In (a) a sheaf-like object can be seen (blend: BPS/210 5, 50% iPS). This object is composed of bundles of lamellae, separated from one another by non-crystalline regions. Unlike similarly shaped objects grown from 100% iPS, non-crystalline inclusions are clearly evident throughout the structure. The blend shown in (b) contains only 20% iPS (blend: BPS/210 1) and the overall morphology shows little evidence of lamellae being arranged into sheaf-like structures

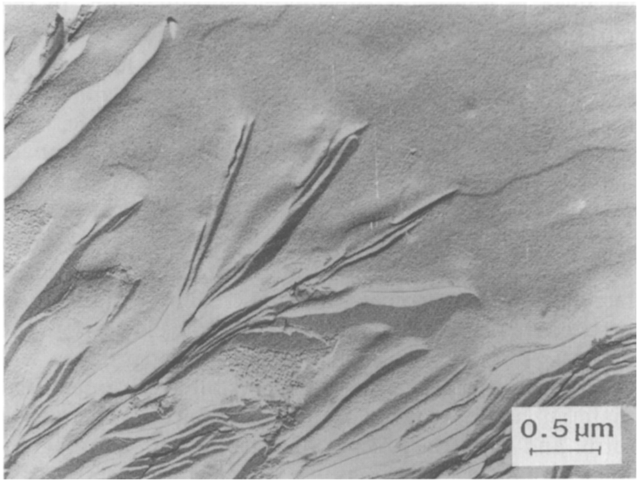

Figure 3 Lamellar growth tip in BPS/210 5. Individual dominant lamellae are evident at the tips of the structure; subsequent subsidairy crystallization is limited by the presence of the non-crystallizable component, such that bundles of lamellae are formed

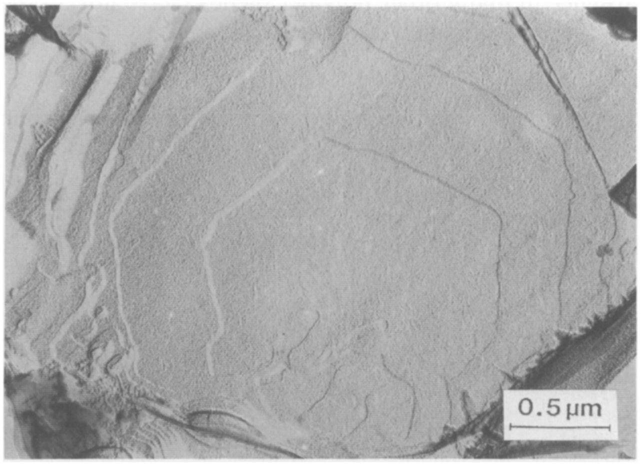

Figure 4 Hexagonal lamellar habit in a blend containing 20% iPS crystallized at 210°C (blend: BPS/210 1)

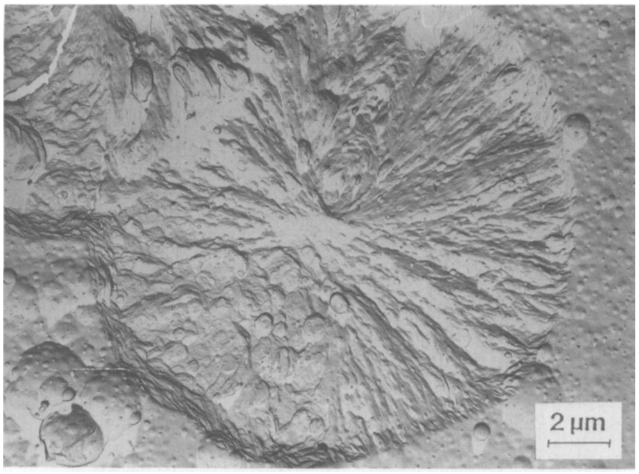

Figure 5 Isotactic polystyrene spherulite grown at 190°C (IPS/190 A)

Ultimately, the mechanism by which this morphology develops is entirely determined by the process of subsidiary crystallization. On the basis of the micrographs shown, the growth of subsidiary lamellae along existing lamellar surfaces is a process that is strongly favoured in polystyrene. This process of development, from single lamella to lamellar stack, can be seen in *Figure 3*. As in the purely isotactic case, the lamellae that develop within these blends show clear evidence of hexagonal symmetry, as shown by *Figure 4*. Thus, in summary, the overall morphological pattern seen in the polystyrene blends considered thus far comes about as a natural consequence of (i) dominant subsidiary crystallization and (ii) the inability of the atactic component of the blend either to crystallize or to diffuse away completely ahead of the advancing interface. This latter point, of course, is supported by the linearity of spherulite growth rates[15], a fact that implies that the melt conditions ahead of the interface are not changing appreciably with time.

Reducing the crystallization temperature of iPS to 190°C results in a dramatic change in morphology, from sheaf-like axialites to fully developed spherical structures (see *Figure 5*). As at higher temperatures, addition of aPS to the melt results in the clustering of lamellae into bundles, these being separated from one another by amorphous, atactic-rich regions. Such a morphology is shown in *Figure 6*. From this it is evident that, typically,

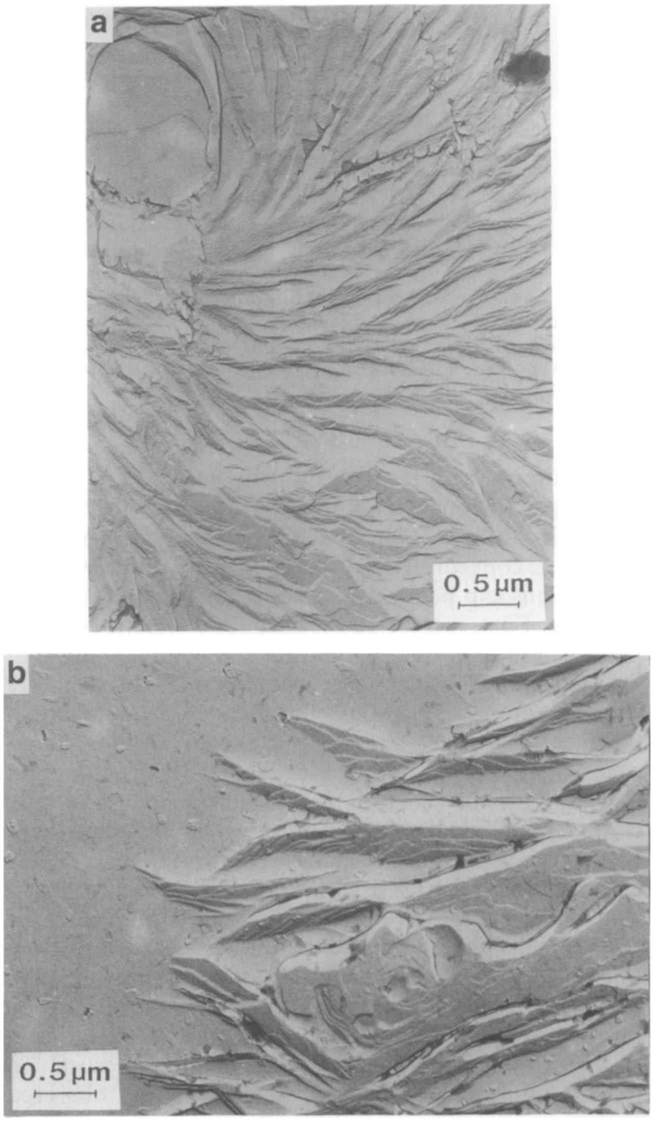

Figure 6 Details of spherulitic structure in BPS/190 5 (190°C, 50% iPS), showing a radiating texture composed of alternating crystalline and non-crystalline regions. In (a) the centre of a spherulite is shown whilst in (b) growth tips can be seen

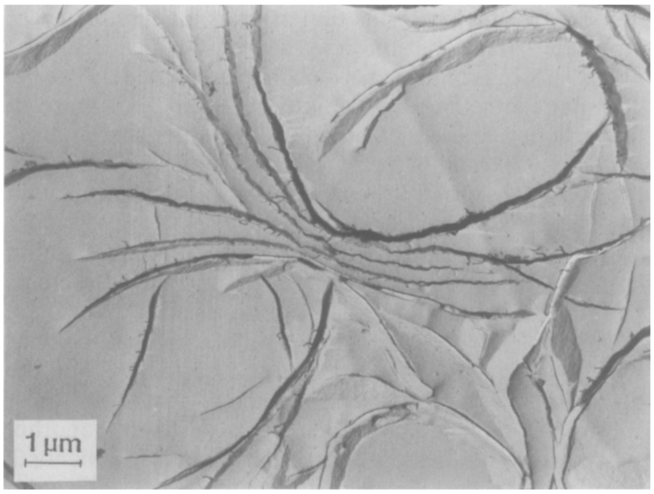

Figure 7 A very open sheaf-like structure grown at 190°C from a blend containing 20% iPS (blend: BPS/190 1)

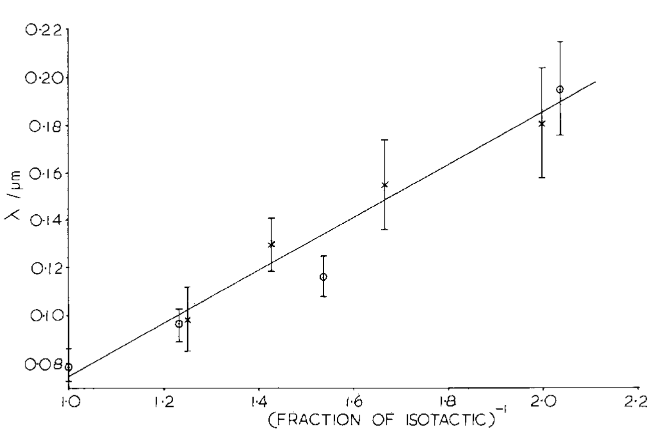

Figure 8 Plot showing the variation of dominant lamellar separation (λ) with blend composition at 190°C: (○) blends of iPS-D and aPS-2; (×) blends of PS-BI and PS-BA. Error bars indicate 99% confidence limits

each bundle is about 0.1 µm in thickness and contains about eight lamellae. In addition, lamellar bundles and intervening non-crystalline regions appear to be of a comparable thickness, as would be anticipated in a 1:1 blend, assuming complete miscibility and steady-state conditions at the interface.

Increasing the concentration of aPS further eventually results in the formation of less mature sheaf-like architectures, as shown in *Figure 7*. Thus, varying the composition has the same qualitative effect as at higher temperatures; that is, high aPS concentrations result in the growth of more simple morphological forms.

However, as discussed above, blending also provides an opportunity to vary some important crystallization parameters independently of one another and to explore the resulting morphological consequences. Whilst a full discussion of such matters is not possible here, it is interesting to consider the variation of one structural parameter, namely the separation between adjacent dominant lamellae (λ) with melt composition. *Figure 8* shows a plot of λ against melt composition for a series of iPS/aPS blends. In all these samples, the isotactic and atactic components were chosen such that the molecular mass of each was comparable and, as a result, the melt diffusion coefficient D would not be expected to change dramatically from one sample to the next. Indeed, even large changes in D are found, experimentally[9,16], to manifest themselves in comparatively small changes in λ. Thus the observed variation in interfacial periodicity may be considered solely in terms of variations in melt composition or, alternatively, spherulite growth rate.

From *Figure 8* it can be seen that λ increases monotonically with increasing atactic content. Indeed, reducing the isotactic component from 100% to 50% of the blend results in an approximate doubling of the dominant interlamellar separation. This again implies that, to a first approximation, the overall composition of the material within the envelope of a spherulite is not too different from that of the melt outside it. This is not to say that fractionation and accumulation of impurities does not occur at the spherulite boundary, but rather that such effects are relatively small in the samples studied here.

A further reduction in crystallization temperature to 162°C results in structures that, at optical resolutions, appear little different to the spherulites previously considered at 190°C. However, crystallization at 162°C differs from that at higher temperatures in one important respect. Whereas all the samples discussed above reveal clear evidence of wide lamellar sheets and an intrinsically hexagonal habit, this is not the case at 162°C. Rather, when lamellae are viewed along a direction close to the molecular chain axis, their appearance is as shown in *Figure 9*. The reason for this apparent radial elongation is, however, unclear since the lateral scale of the elongated lamellae shown in *Figure 9* is markedly greater than current estimates of diffusion lengths of high molecular mass polystyrene at 162°C[17,18].

Addition of atactic diluent does little to clarify matters concerning the underlying lamellar habit. *Figure 10* shows a micrograph of a blend BPS/162 1R, containing 20% iPS and 80% aPS. Whilst there is evidence of radially extended structures, there is also clear evidence of wide lamellae. This apparent contradiction may well

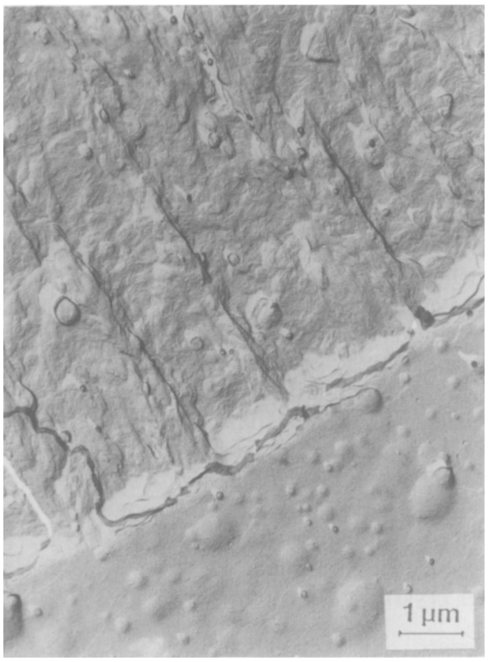

Figure 9 Edge of a spherulite grown from isotactic polystyrene at 162°C (IPS/162 A)

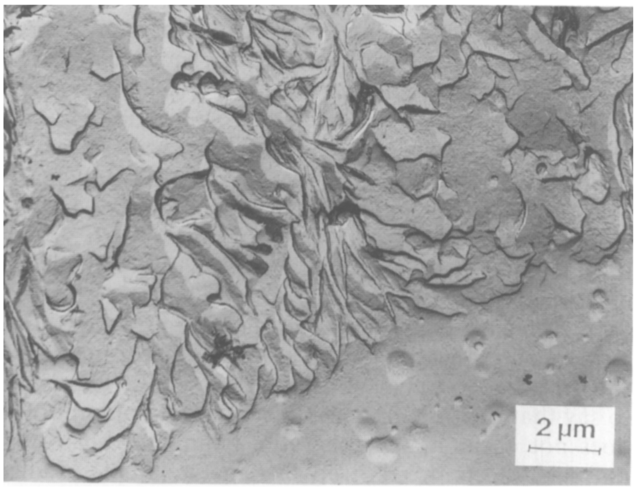

Figure 10 Spherulitic morphology in BPS/162 1R (162°C, 19% iPS)

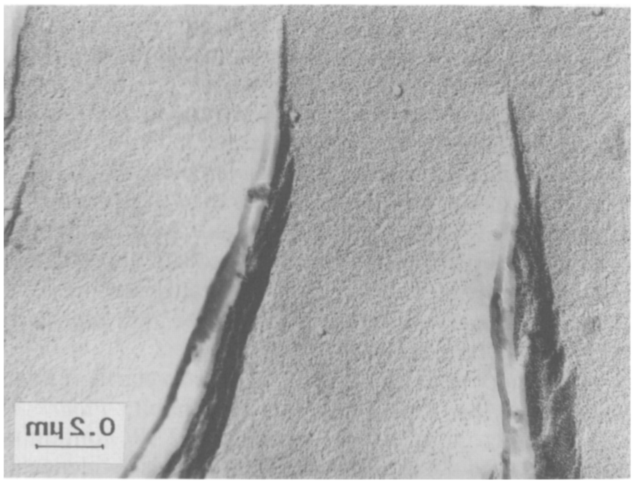

Figure 11 Spherulite growth tips in BPS/162 1R showing individual leading dominant lamellae. Subsequent subsidiary crystallization results in the formation of the compact lamellar bundles shown

be associated with the process of dominant/subsidiary crystallization, since dominant lamellae would be isolated and growing in relatively pure melt whereas, as subsidiary crystallization proceeds within the existing dominant framework, depletion of potentially crystallizable isotactic molecules would tend to favour radial development and may, as a result, lead to the formation of radially extended subsidiary lamellar structures. Nevertheless, whatever the mechanism behind the apparently ribbon-like morphologies seen at 162°C, be it impingement of neighbouring crystallites in the dense array of lamellae that form from isotactic melts or depletion of crystallizable molecular species in blends, the underlying mechanism of growth is the same dominant/subsidiary process that occurs at higher temperatures, other morphological features merely being superimposed onto this. *Figure 11* shows an individual lamella at the growth tips of a spherulite and subsidiary lamellae growing around it to form a lamellar stack of the type described at higher crystallization temperatures.

Blends of linear and branched polyethylene

Figure 12 shows a sample of Sclair 2907 crystallized isothermally at 125°C. This morphology contains a number of lamellar forms that arise as a consequence of molecular fractionation and segregation effects. The object shown is made up of a framework of widely spaced dominant lamellae that radiate out from the centre of the structure and which stand proud of the surrounding material as a result of their greater resistance to etching[19]. In *Figure 12* some of the dominant lamellae have been labelled D.

Between the dominant lamellae, subsidiary crystallization has resulted in the formation of a complex hierarchical structure. For example, at R, the dominant lamellae are separated from one another by a set of apparently planar lamellae that are inclined at an angle of about 30° to the dominants. The interstitial regions between these subsidiary lamellae are themselves filled by another subset of crystallites that are either planar and inclined, or ridged in form. Detailed studies of the crystallization of linear polyethylene[20–22] have clearly demonstrated the subtlety of the process and demonstrated the relationships between crystallization temperatures, molecular mass and lamellar habit and the way in which molecular segregation effects may result in a lamellar hierarchy of the type described briefly above. Thus the pattern of crystallization indicated by the morphology shown in *Figure 12* is broadly in line with expectations.

However, addition of even a relatively small amount of branched polymer changes the morphology quite markedly, as can be seen in *Figure 13*. These micrographs show two samples, both of which were crystallized at 125°C; that is, at a temperature at which the low-density polyethylene is unable to crystallize. Under these crystallization conditions, growth proceeds to give sheaf-like objects, which are surrounded by a banded texture that developed on quenching. Unlike the morphology shown in *Figure 12*, this structure reveals no evidence of the lamellar hierarchy that is so typical of linear polyethylene. Also, the lamellar array appears very compact, with no evidence of distinct dominant and subsidiary lamellar populations, or of inclusions containing branched material that was unable to crystallize prior to quenching. However, examination of such structures in an orthogonal projection reveals that these morphological features do exist. *Figure 14* shows a sheaf as seen when viewed along its radial growth direction, and, from this projection, it is clear that the lamellae can be subdivided into dominant and subsidiary

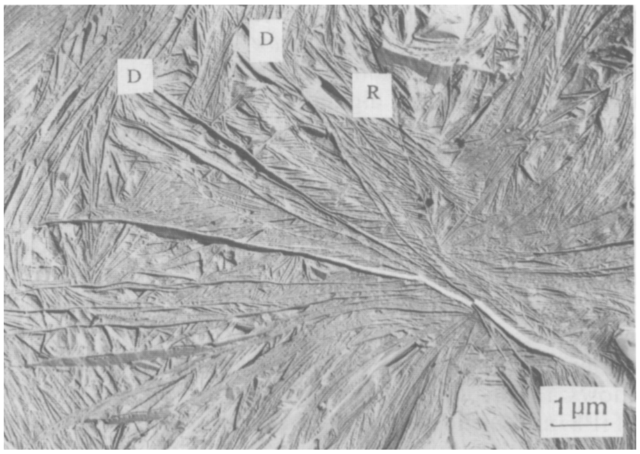

Figure 12 Morphology of Sclair 2907 crystallized at 125°C. Dominant lamellae and a number of subsidiary lamellar populations are evident

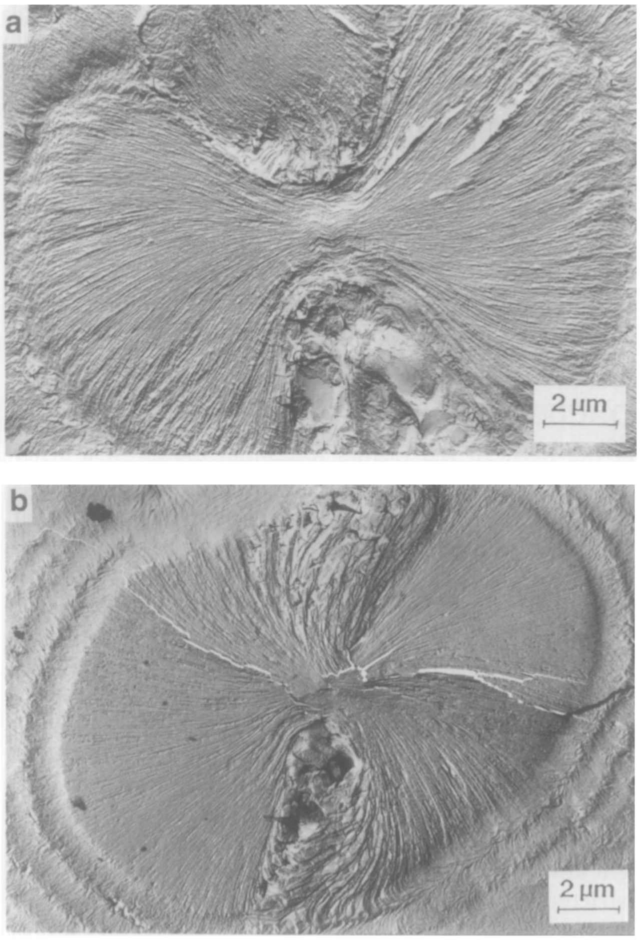

Figure 13 Sheaf-like structures in polyethylene blends crystallized at 125°C: (a) blend BPE/125 C, 61% linear polyethylene; (b) blend BPE/125 E, 23% linear polyethylene

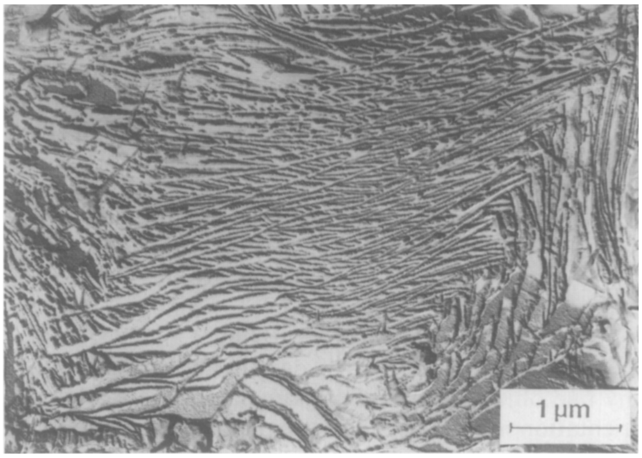

Figure 14 Sheaf-like structure grown at 125°C from BPE/125 B, viewed down the radial growth direction (i.e. crystallographic *b* axis). Extensive dominant lamellae are seen edge-on, oriented from top right to bottom left. Inclined subsidary lamellae are evident between the wide, dominant sheets

populations. The morphology shown is made up of wide, planar or mildly S-shaped dominant lamellae that sweep across the structure and, between these, there is a second set of subsidiary lamellae that are inclined at an angle of $\sim 25°$ to the dominants. Thus, the mechanism of crystallization again involves the initial formation of dominant lamellae together with subsequent in-filling crystallization. However, in discussing *Figures 13* and *14*, it is interesting to consider the role that the branched component of the melt is playing in the crystallization process. First, the most obvious differences between the morphology shown in *Figure 12* and those seen in *Figures 13* and *14* is the reduced extent to which subtle molecular segregation effects appear to occur in polyethylene blends. Clearly, without additional molecular extraction data this assertion is somewhat speculative, but just by 'reading' the morphology it would seem to be the case. But perhaps of more interest in the context of polyethylene blends and their general morphology is the following question: Where is the branched polyethylene in *Figures 13* and *14*?

Figure 15 shows an object, viewed in a similar projection to that of *Figure 14*, but now grown from a blend containing 23% linear and 77% branched polyethylene. Once again wide, sweeping S-shaped dominants are evident together with inclined subsidiary lamellae. However, in this sample there are clearly inclusions between the subsidiary lamellae, within which little or no lamellar structure is evident. These regions presumably contain highly branched molecular segments that were rejected from the growing lamellae and were subsequently unable to crystallize to any great extent. Similar conclusions concerning the location of the least crystallizable components of the blend have been reached from scattering experiments[23]. In addition, other morphological studies of polyethylene blends have revealed a similar pattern of lamellar organization to that described here, although Norton and Keller[24] characterized the structures they observed in terms of isothermally formed dominant lamellae interspersed with finer-scale quenched lamellae. Thus, on the basis of the results presented here, the crystallization of polyethylene blends proceeds by the following mechanism. Initially, an array of dominant lamellae are formed. These grow into the melt, forming interstitial regions within which subsidiary crystallization begins. Subsidiary crystallization then results in the formation of a second set of lamellae

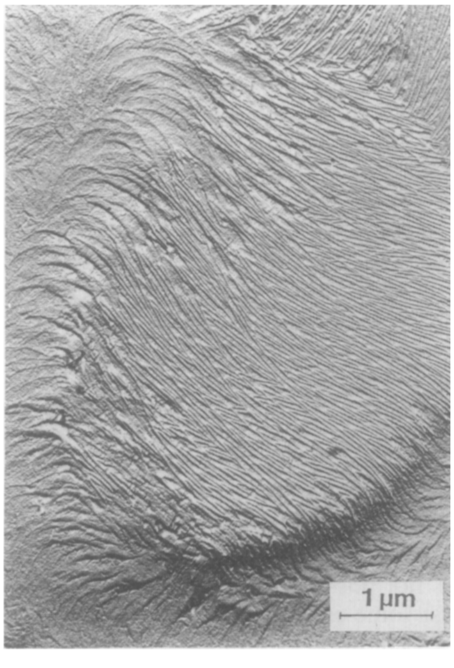

Figure 15 Crystallographic *b*-axis projection of a sheaf in BPE/125 E, i.e. in a blend containing only 23% linear polyethylene

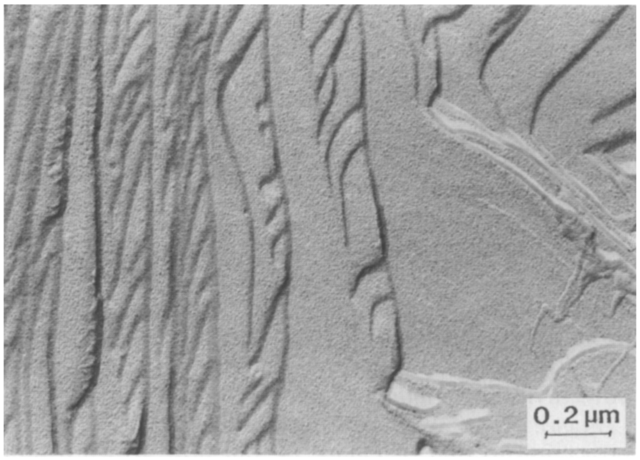

Figure 16 Dominant/subsidiary morphology in BPE/128 E as revealed when dominant lamellae are viewed flat on

that grow at approximately 25° to the existing dominant array (see *Figure 16*). As a consequence of subsidiary crystallization, branched molecular segments become trapped between lamellae such that, in highly doped systems, subsidiary lamellae are separated from one another by quenched regions. However, whilst this interpretation of the micrographs is qualitatively reasonable, it is unclear whether, quantitatively, the quenched interstitial regions seen in *Figure 15* can be integrated to account for the branched component of the blend (77%). Certainly, visual inspection would suggest that this is not the case. Other studies have similarly revealed an apparent discrepancy between the overall composition of polyethylene blends and that of lamellar aggregates grown from the melt, and it has been proposed that a degree of liquid–liquid phase segregation may occur prior to crystallization[25,26].

Comiparison of the polyethylene and iPS/aPS blend morphologies shown here initially suggests that the process of crystallization is fundamentally different in the two cases. In iPS/aPS the morphology is based upon interleaved lamellar bundles and broad non-crystalline regions, whereas in polyethylene blends segregation occurs on the individual lamellar level. However, as outlined above, this apparently different behaviour may be explained solely in terms of the way in which subsidiary lamellae develop between neighbouring dominant lamellae. In polyethylene it has been proposed that S-shaped dominants and their associated subsidiary lamellae share a near common *c*-axis orientation[27]. This idea is appealing as far as the objects considered here are concerned since, although the relative orientation of dominant and subsidiary lamellae varies from object to object, within a given structure, the sense of the inclination is fixed (see *Figures 14* and *15*). Thus the relative inclination of dominant and subsidiary lamellae may indeed have its origin in the inclination of the molecular stems within polyethylene lamellae, although the observed value of 25° is difficult to reconcile quantitatively with accepted values of chain inclination in polyethylene lamellae[28,29]. To consider this point further is not possible without detailed diffraction data, or at least some estimate of chain inclination within the lamellae seen here. Although TEM techniques based upon etching and replication are not generally suitable as a means of obtaining crystallographic data by electron diffraction, as previously mentioned, the multicomponent nature of polymer blends may be exploited experimentally, in this case enabling extraction replicas to be prepared that contain both morphological and crystallographic information. The crystallography of polyethylene blends will be considered in a forthcoming publication. Conversely, in polystyrene, the chain axis is normal to the lamellae[13]. In this system, subsidiary lamellae grow parallel and adjacent to the existing dominant sheets, such that any atactic material that is enclosed within the expanding envelope of a spherulite eventually becomes concentrated between bundles of lamellae.

CONCLUSIONS

On the basis of the results presented above, it is clear that blending can be a valuable aid in understanding the morphology of semicrystalline polymers, and that transmission electron microscopy may be a useful technique for the study of polymer blends. In general, addition of a non-crystallizable diluent results in the formation of less complex, more open textures that are often more amenable to interpretation than are the more compact morphologies that develop from less impure melts. For this reason alone, blending can often be a useful experimental expedient. In the case of iPS, addition of aPS results in the formation of morphologies that are based upon alternating crystalline and non-crystalline regions, the crystalline regions typically containing about eight lamellae. However, in width, these lamellae are not restricted to dimensions comparable to the bundle thickness, since this 'fibrous' morphology comes about through dominant/subsidiary growth and not as a consequence of diffusion-related processes. In blends where the isotactic content is only ~20%, more simple morphological forms are observed than in less dilute systems (i.e. at 210°C multilayered crystals are formed in place of axialites, whilst at 190°C sheaves form rather than more mature spherulites).

At first sight the morphologies seen in polyethylene blends are very different from those described above. Initially, the effect of adding branched material is to suppress fractionation within the linear, crystallizing component of the blend, such that the observed morphologies may be characterized simply in terms of one dominant and one subsidiary lamellar population. On viewing along their crystallographic *b* axis the dominant lamellae appear planar or mildly curved in profile. Subsidiary lamellae are planar and inclined at ~25° with respect to the local dominant lamellae. Within any one object all subsidiary lamellae share a common orientation relative to the dominant lamellar population. Despite the differences, this structural pattern can nevertheless still be understood in terms of the same morphological principles expounded in analysing the polystyrene blends. Whereas in the iPS/aPS case, subsidiary lamellae grow adjacent and parallel to the dominant lamellae, in polyethylene, subsidiary lamellae develop at an angle to the dominants, such that lamellar bundles do not form. Thus, in polystyrene blends, non-crystalline regions are situated between relatively thick crystalline bundles, whilst in polyethylene blends segregation occurs at the lamellar level, i.e. non-crystallizing material is located between neighbouring dominant and subsidiary lamellae, or between adjacent subsidiaries.

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REFERENCES

1 Paul, D. R. and Newman, S. 'Polymer Blends', Academic Press, New York, 1978, Vols 1 and 2
2 Briber, R. M. and Khoury, F. *Polymer* 1987, **28**, 38
3 Khoury, F., personal communication
4 Keith, H. D. and Padden, F. J. *J. Appl. Phys.* 1964, **35**, 1270
5 Keith, H. D. and Padden, F. J. *J. Appl. Phys.* 1984, **35**, 1286
6 Keith, H. D. and Padden, F. J. *J. Polym. Sci. (B) Polym. Phys.* 1987, **25**, 2371
7 Khambatta, F. H., Warner, F. P., Russell, T. and Stein, R. S. *J. Polym. Sci., Polym. Phys. Edn* 1976, **14**, 1391
8 Tung, L. H. *J. Polym. Sci.* 1962, **61**, 449
9 Vaughan, A. S., PhD Thesis, University of Reading, 1984
10 Olley, R. H. and Bassett, D. C. *Polymer* 1982, **23**, 1707
11 Bassett, D. C. and Vaughan, A. S. *Polymer* 1985, **26**, 717
12 Vaughan, A. S. and Bassett, D. C. *Polymer* 1988, **29**, 1397
13 Keith, H. D., Vadimsky, R. G. and Padden, F. J. *J. Polym. Sci. (A-2)* 1970, **8**, 1687
14 Warner, F. P., MacKnight, W. J. and Stein, R. S. *J. Polym. Sci., Polym. Phys. Edn* 1977, **15**, 2113
15 Yeh, G. S. Y. and Lambert, S. L. *J. Polym. Sci. (A-2)* 1972, **10**, 1183
16 Vaughan, A. S., Bassett, D. C. and Olley, R. H. in 'Morphology of Polymers', Walter de Gruyter, Berlin, 1986
17 Vaughan, A. S. and Bassett, D. C., to be published
18 Keith, H. D. and Padden, F. J. *J. Polym. Sci. (B) Polym. Phys.* 1987, **25**, 229
19 Freedman, A. M., Bassett, D. C., Vaughan, A. S. and Olley, R. H. *Polymer* 1986, **27**, 1163
20 Bassett, D. C. and Hodge, A. M. *Proc. R. Soc. Lond. (A)* 1981, **377**, 25
21 Bassett, D. C., Hodge, A. M. and Olley, R. H. *Proc. R. Soc. Lond. (A)* 1981, **377**, 39
22 Bassett, D. C. and Hodge, A. M. *Proc. R. Soc. Lond. (A)* 1981, **377**, 61
23 Song, H. H., Stein, R. S., Wu, D.-Q., Ree, M., Phillips, J. C., Le Grand, A. and Chu, B. *Macromolecules* 1988, **21**, 1180
24 Norton, D. R. and Keller, A. *J. Mater. Sci.* 1984, **19**, 447
25 Monks, A. W., M.Sc. Thesis, Univeristy of Bristol, 1983
26 Barham, P. J., Hill, M. J., Keller, A. and Rosney, C. C. A. *J. Mater. Sci. Lett.* 1988, **7**, 1271
27 Bassett, D. C. in 'Principles of Polymer Morophology', Cambridge University Press, Cambridge, 1981
28 Labaig, J.-J., Ph.D. Thesis, l'Université Louis Pasteur de Strasbourg, 1978
29 Bassett, D. C., Olley, R. H. and Al Raheil, I. A. M. *Polymer* 1988, **29**, 1539