Morphology of binary linear polyethylene blends

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(*Received 15 October 1987; accepted 5 January 1988*)

The morphology of binary mixtures of sharp fractions of linear polyethylene (molecular weights: 2500, 11 000, 22 000 and 66 000) has been studied by polarized microscopy and small-angle light scattering. The samples were crystallized under isothermal conditions over a wide temperature range (380–403 K). Three types of supermolecular structure have been observed: axialites, non-banded spherulites and banded spherulites. Data are presented displaying the morphology as a function of both composition and crystallization temperature. The results are discussed with reference to current theories for polymer crystallization.

(Keywords: linear polyethylene sharp fractions; binary mixtures; morphology; optical microscopy; small-angle light scattering)

INTRODUCTION

The morphology of linear polyethylene (LPE), as revealed by optical microscopy or small-angle light scattering (SALS), depends on both molecular weight and crystallization temperature[1,2]. External factors such as pressure and shear or elongational forces acting during solidification also have a major effect on the morphology, but these factors are not dealt with in this paper. A number of possible morphologies may be obtained in abaric, melt-crystallized LPE: (a) banded spherulite, (b) non-banded spherulite, (c) axialite, (d) random-lamellar structure.

The banded spherulite, i.e. spherulite with concentric rings, has been known since the early work by Keller[3]. The periodic changes in the birefringence along the radius of the spherulite were explained by Keller[3,4] and Fischer[5] with reference to a regular smooth twisting of the lamellae along the radius of the spherulite, but more recent studies by Low *et al.*[6] and Bassett[7] reveal results inconsistent with this regular twisting model. Instead, Bassett[7] presents microscopy data showing the presence of relatively untwisted s-shaped (as seen along the b-axis) lamellae in LPE with banded spherulites. The length of these lamellae along the radius of the spherulite is about one-third of the spacing, and it is suggested that the variation in birefringence is caused by localized changes of the lamellar normal along the spherulite radius possibly by screw dislocations[7]. The uncertainty of the exact details of the microstructure and of the origin of the twisting of the lamellae is, however, generally acknowledged[7,8]. LPE samples of molecular weight (M_w) between 20 000 and several hundred thousand crystallized at supercoolings greater than 25 K display banded spherulites[9]. Samples cooled extremely rapidly in this molecular weight range do not, however, display banded spherulites[10]. Within a limited temperature range, the band spacing for several polymers, including LPE, has been found to increase with increasing temperature of crystallization[4,11].

The non-banded spherulite, which is characterized by a spherical symmetry without any periodic change in birefringence along the radius of the spherulite, is the dominant structure in LPE samples of M_w between 20 000 and 120 000 crystallized at a supercooling between 16.5 K and 25 K[1]. LPE of M_w between 7000 and 20 000 also displays non-banded spherulites when crystallized at a greater supercooling[12,13].

The axialite (alternative concepts are 'rod structure', 'sheaf' and 'hedrite') lacks spherical symmetry. The lamellar crystals are instead contained within a peripherally slightly expanded cylinder. Early work by Banks *et al.*[12] showed that LPE samples of $M_w < 7000$ displayed axialites independent of thermal prehistory. According to Hoffman *et al.*[1], samples of M_w between 18 000 and 115 000 exhibit spherulites after crystallization at a supercooling greater than 16.5 K and axialites at a supercooling less than 16.5 K. Samples of M_w between 119 000 and 807 000 display only irregular spherulites. Maxfield and Mandelkern[2] presented a somewhat deviating view; for samples crystallized at temperatures greater than 393 K only axialites were observed in samples with a M_w up to 46 200. For a sample of M_w 80 000, the axialite–spherulite transition was observed after about 6 K more extensive supercooling than that reported by Hoffman *et al.*[1] for samples of this molecular weight. Furthermore, Maxfield and Mandelkern[2] observed both axialites (low supercooling) and spherulites (high supercooling) in samples of M_w between 80 000 and 1 000 000.

For high molecular weight LPE samples ($M_w > 2 000 000$), a random lamellar structure characterized by an azimuthal-angle-independent H_v SALS pattern and an extremely fine-textured structure as revealed by polarized microscopy has been reported[2].

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0032-3861/88/061037-08$03.00

The subject of this paper, the morphology of binary mixtures based on sharp LPE fractions of M_w ranging from 2500 to 66000, has not been reported in the literature so far. The morphology of samples crystallized at different temperatures covering a wide range of supercooling (14–35 K) is reported.

EXPERIMENTAL

Single components and binary mixtures based on sharp fractions ($M_w/M_n = 1.1$–1.3) of LPE, referred to as $LM_w \times 10^{-3}$, received from AtoChemie, France, and Polymer Laboratories Ltd, UK, have been studied. The M_w of the different sharp fractions studied were: 2500, 11000, 22000, 31000 and 66000. Each binary mixture was made by stirring a hot *p*-xylene solution containing both components for at least 20 min, and then rapidly precipitating the polymer by adding an excess amount of cold methanol, followed by centrifugation, decantation and drying in vacuum to constant weight. G.p.c. analysis confirmed the adequacy of this procedure.

Two main crystallization procedures were used in this study. After melting, the samples were either rapidly cooled in air while being kept between object and cover glasses (air-quenching; the cooling rate in the solidification temperature range was about 200 K min^{-1}) or crystallized under isothermal conditions in a Mettler Hot Stage FP 82 (IC treatment). During the IC treatment the crystallization was monitored in an optical microscope equipped with crossed polarizers (Leitz Ortholux POL BK). The morphology of the air-quenched samples was examined at 300 K by both polarized microscopy and SALS, H_v pattern. The morphology of IC-treated samples was examined directly in the microscope at the crystallization temperature.

RESULTS AND DISCUSSION

Figures 1 and *2* show the morphology of air-quenched samples of binary mixtures of L2.5/L66 and L11/L66, respectively. A number of features can be observed in these photomicrographs:

All samples except L2.5/L66 with 0.8/0.2 w/w composition display banded spherulites.

The band spacing (L_b) decreases with increasing content of L66 in both series of binary mixtures.

L_b decreases with increasing radial distance from the spherulite centre. This was also observed in pure L66. Crystallization obviously starts in the centre of the spherulites at the highest temperatures and occurs at progressively lower temperatures in the peripheral parts which, according to the literature[4,11], should give rise to the observed L_b–radial distance relationship. There is no sign of radial segregation of the low molecular weight component in the blends. The adequacy of mixing of the component is also demonstrated by the similarity in band spacing in different spherulites located in different regions of the samples.

Samples with larger L_b values have less well-developed rings, i.e. the rings have circumferential interruptions.

Data for the band spacing are presented in *Figure 3* as a function of composition for air-quenched binary mixtures of L2.5/L66, L11/L66 and L22/L66. The bars associated with each data point indicate the variation in L_b along the spherulite radius. The manner in which L_b changes with composition is however very clear:

The band spacing increases both with increasing content of low molecular weight, *second* component and with decreasing molecular weight of the second component.

The lower w_{L66} limit for the existence of banded spherulites increases with decreasing molecular weight of the low molecular weight component.

The insert figure shows the lack of any unique L_b–M_w relationship for the LX/L66 blends. The band spacing of the binary blends is generally larger than that of a pure LPE sharp fraction of the same molecular weight values.

Thus, the presence of the low molecular weight component does have a significant effect on the morphology of the rapidly cooled L66 blends. The underlying lamellar organization of these banded spherulites can only be speculated on at this stage. However, we shall return to this matter later after presenting and discussing the morphologies obtained at lower degrees of supercooling.

The controlled isothermal crystallization experiments made in the hot stage have focused on the L2.5/L66 mixtures and these results are presented in *Figure 4*. Three types of supermolecular structure are observed. Axialites are formed at the highest temperatures above curve B (*Figure 4*). Non-banded spherulites are formed in the temperature-composition domain between curves B and C. Banded spherulites are formed at even lower temperatures, i.e. below curve C.

The axialite–spherulite transition is well-defined for mixtures in the composition range $w_{L66} = 0.2$–1.0 and is established on the basis of both polarized microscopy and SALS. Spherulites are recognized with polarized microscopy as 'circular' birefringent objects (*Figure 5*) and with SALS (H_v) by a clover-leaf scattering pattern. Axialites appear as rods or sheaves (polarized microscopy, *Figure 5*) and give rise to a SALS H_v pattern lacking a clear clover-leaf. The axialite–spherulite transition is, in agreement with earlier findings of Hoffman *et al.*[1], accompanied by a change in kinetics of crystallization demonstrated by a slope change in the $\log G$ vs. $1/T_c\,\Delta T$ plot (G is the growth rate of the axialites/spherulites, T_c is the crystallization temperature and $\Delta T = T_m^\circ - T_c$, the supercooling). These data are reported in an accompanying paper[14]. A value for T_m° ($M_w = 66000$) equal to 417.7 K[17] is used in this paper. The temperature of the axialite–spherulite transition decreases with increasing content of L2.5 in the mixtures. For pure L66 it occurs at about 400.5 K whereas at $w_{L66} = 0.2$ the transition occurs at 396 K. The transition temperature recorded for L66 is in agreement with that given by earlier data by Hoffman[1]. The significant change in transition temperature with composition of the blends may be associated with a corresponding change in the equilibrium melting of the crystallizable component of the mixture, i.e. L66 at these high temperatures, and possibly with a change in substrate length of the growing crystals.

The melting point (T_m) of crystals of L66 in equilibrium with the melt containing the two miscible components may be calculated according to the equation derived by Nishi and Wang[15] using the Flory–Huggins approximation:

$$1/T_m - 1/T_m^\circ = -R/\Delta H_u[\ln v_2/m_2 + (1/m_2 - 1/m_1)v_1 + \chi v_1^2] \quad (1)$$

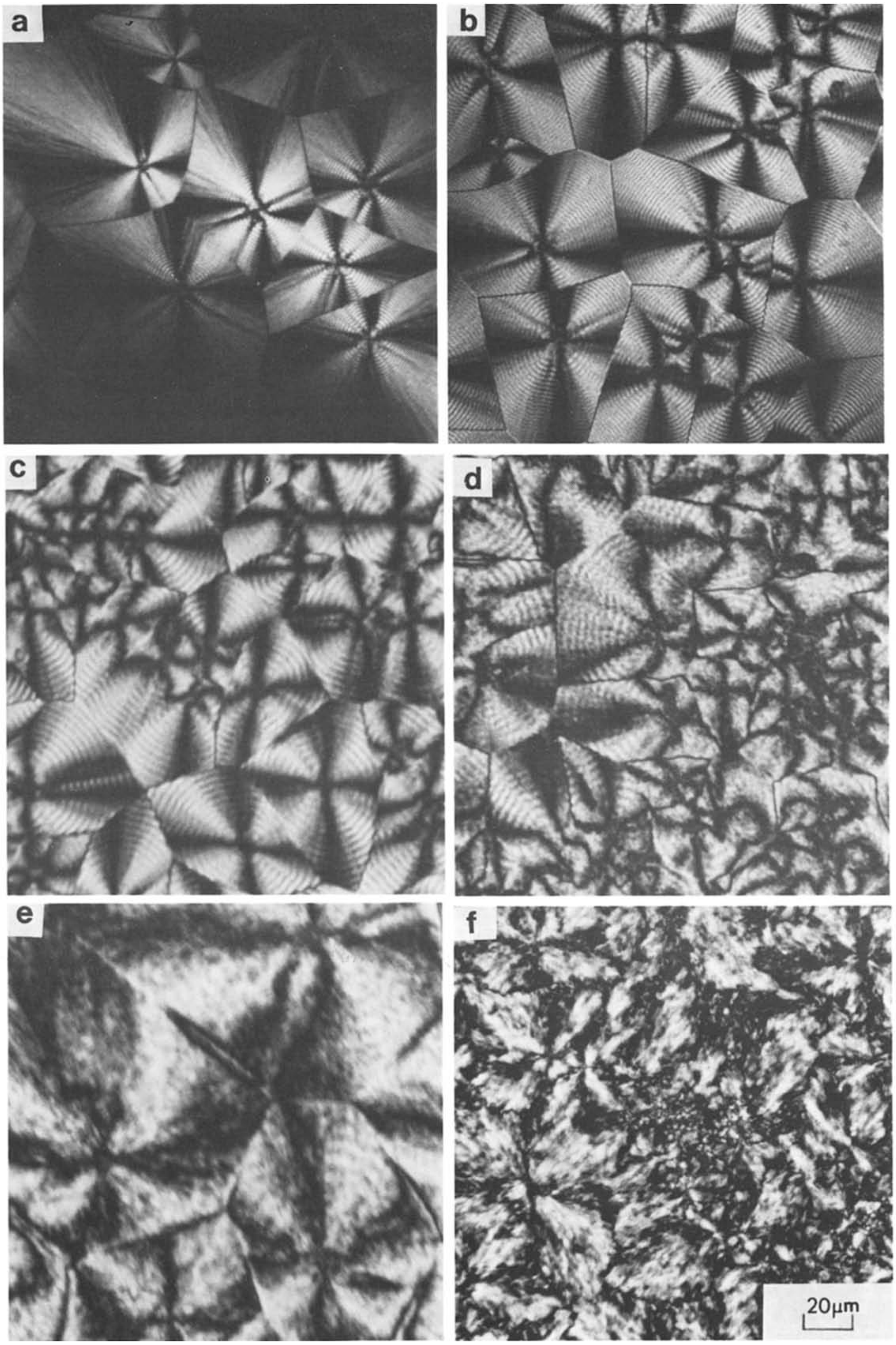

Figure 1 Polarized photomicrograph of air-quenched binary mixtures of L2.5/L66 with the following composition: (a) 0/1, (b) 0.2/0.8, (c) 0.4/0.6, (d) 0.6/0.4, (e) 0.7/0.3, (f) 0.8/0.2

where T_m° is the equilibrium melting point for pure L66, ΔH_u is the heat of fusion per mole of repeating units, v_1 and v_2 are the volume fractions of L2.5 and L66, respectively, m_1 and m_2 are the degrees of polymerization of L2.5 and L66, respectively, and χ is the interaction parameter.

The interaction parameter is calculated from a best fit of crystallization rate data (log G vs. T_c). The curves obtained for the different mixtures are shifted in parallel along the temperature scale. The T_c value corresponding to $\log G(\mu\mathrm{m\,s^{-1}}) = -3$, which is arbitrarily chosen as a characteristic for the equilibrium melting point of the

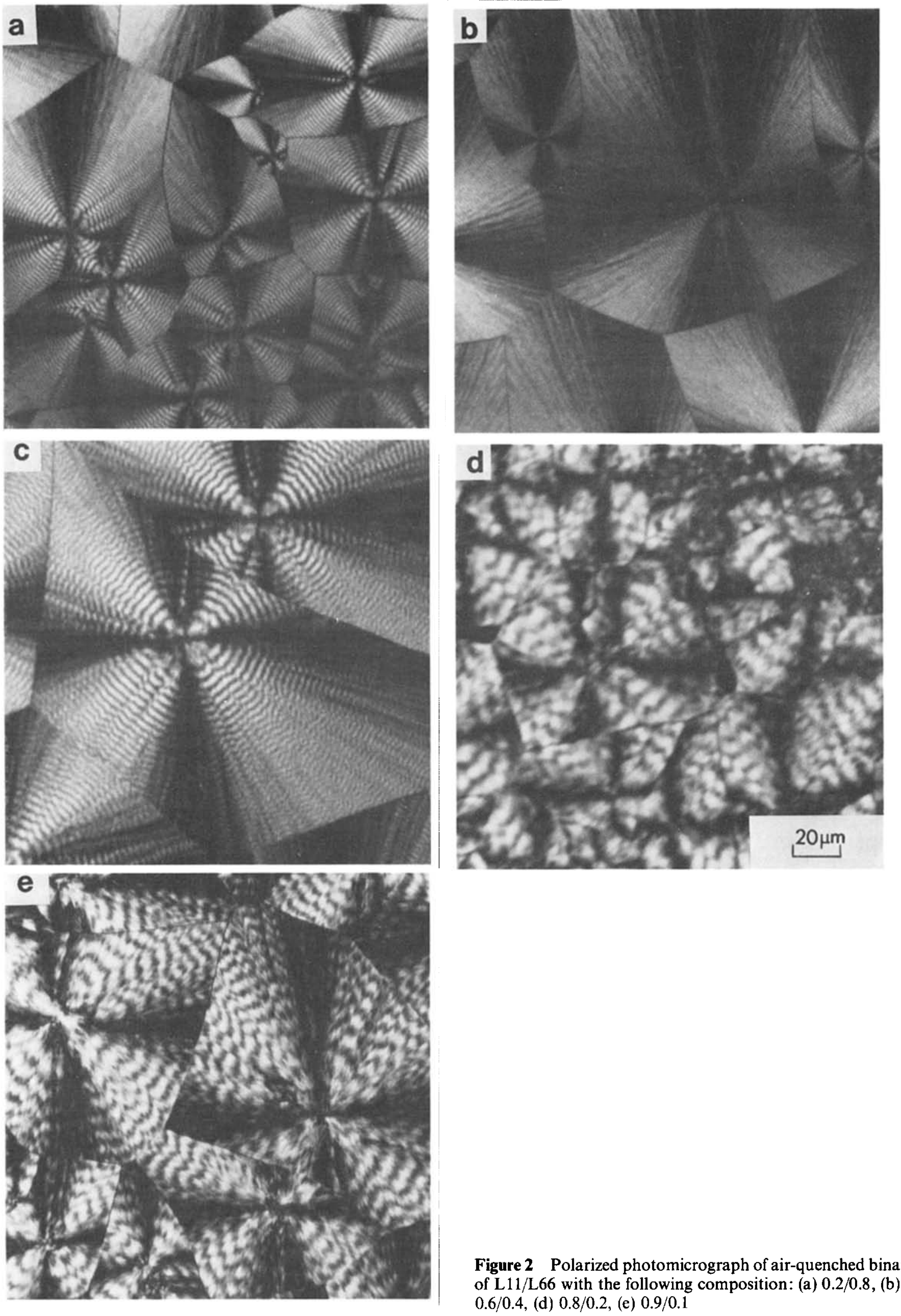

Figure 2 Polarized photomicrograph of air-quenched binary mixtures of L11/L66 with the following composition: (a) 0.2/0.8, (b) 0.4/0.6, (c) 0.6/0.4, (d) 0.8/0.2, (e) 0.9/0.1

blends, is plotted *versus* composition in *Figure 6*. An optimum fit of the curve (*Figure 6*) reveals a χ value of -0.008. Similar, slightly negative values of χ have been reported by Smith and St. John Manley[16].

The axialite–spherulite transition occurs at a greater supercooling (assuming an equilibrium melting point determined according to equation (1) with $\chi = -0.008$) for mixtures rich in L2.5 than for pure L66. The 1 K change in transition supercooling can however be explained by a change in the substrate length of the growing crystals. The axialite–spherulite transition is predicted to occur at a Z-value of about unity[17] where Z is given by:

$$Z = iL^2/4g \qquad (2)$$

where i is the rate of formation of secondary nuclei on the

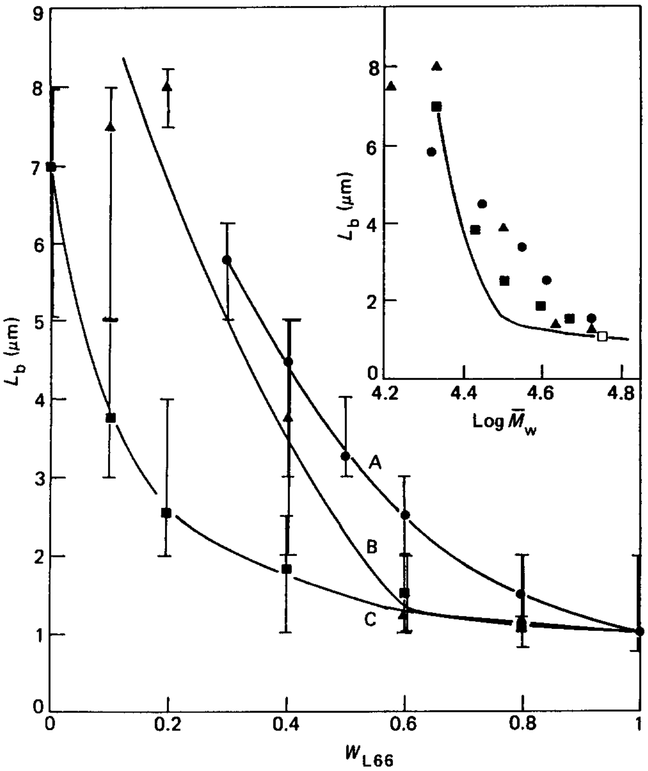

Figure 3 Band spacing (L_b) in air-quenched binary mixtures as a function of weight content of L66: (A) L2.5/L66, (B) L11/L66, (C) L22/L66. The insert figure shows the band spacing as a function of the logarithm of the weight average molecular weight. The solid line refers to data obtained for pure sharp fractions. The symbols ●, ▲, ■ refer to binary mixtures of L2.5/L66, L11/L66 and L22/L66, respectively

substrate, L is the substrate length and g is the substrate completion rate. Calculation by Hoffman[17] shows that the axialite–spherulite transition occurring at $\Delta T = 16.5$ K is consistent with a substrate length of 0.77 μm. The 1 K increase in ΔT recorded for the 0.8–0.2 L2.5/L66 blend can, according to equation (2), be explained on the basis of a 50% decrease in substrate length for this sample with reference to that of pure L66. TEM work is at present being carried out to confirm possible corresponding alterations in the crystal width.

Curves C–F in *Figure 4* are based on samples obtained from both true isothermal crystallization carried out in the hot stage and crystallization during air-quenching. Curve G in *Figure 4* is obtained by extrapolation to 200 K min^{-1} (cooling rate at air-quenching) of solidification d.s.c. data obtained at different cooling rates. By combination of the data presented in *Figure 3* with curve G in *Figure 4*, the low temperature/low w_{L66} parts of curves C–F were obtained. Banded spherulites are formed at temperatures lower than that defined by curve C in *Figure 4*. The non-banded/banded spherulite transition (defined by curve C) does not occur at a constant supercooling with regard to either of the components. The 'iso-L_b' curves (C–F) all have a similar shape and are almost only shifted in parallel along the temperature axis with respect to each other. The band spacing decreases from a maximum of about 10 μm at the highest temperatures near curve C to about a tenth of that at 10–15 K lower temperatures (*Figure 4*). No low-temperature hot-stage work was carried out on the binary mixtures of L11/L66 and L22/L66. However, based on the results presented in *Figure 3* (air-quenched samples) it can be concluded that both the non-banded/banded spherulite transition temperature and the 'iso-L_b' curves should have a qualitatively similar but weaker dependence on w_{L66} than in the case of the data for L2.5/L66.

The basic concepts in the morphological model proposed to explain the observations made in the low temperature crystallized samples are *dominant lamellae* and *subsidiary lamellae*. The dominant lamellae which are formed at relatively high temperatures form 'strings' which radiate out from the centre of the spherulites. The length of an individual dominant lamella is short compared with the length of a dominant lamellar string. The subsidiary lamellae crystallized at low temperature are shorter and thinner than the dominant lamellae and are sandwiched in between the dominant lamellae strings. For simplicity, the individual dominant lamellae are assumed to be planar and to be in either of two states:

Optically isotropic lamellae (I), i.e. the chain axis of the lamella is parallel to the light propagation vector.

Optically anisotropic lamellae (A), i.e. the chain axis of the lamella is perpendicular to the light propagation vector.

In banded spherulites where the two types of lamellae, I and A, exist in concentric ring layers there must exist a mechanism for a 'synchronized' reorientation of the dominant lamellae in the string, i.e. an I–A and A–I transition. It is here proposed that the formation of sharp boundaries between A and I type lamellae in banded spherulites has two causes:

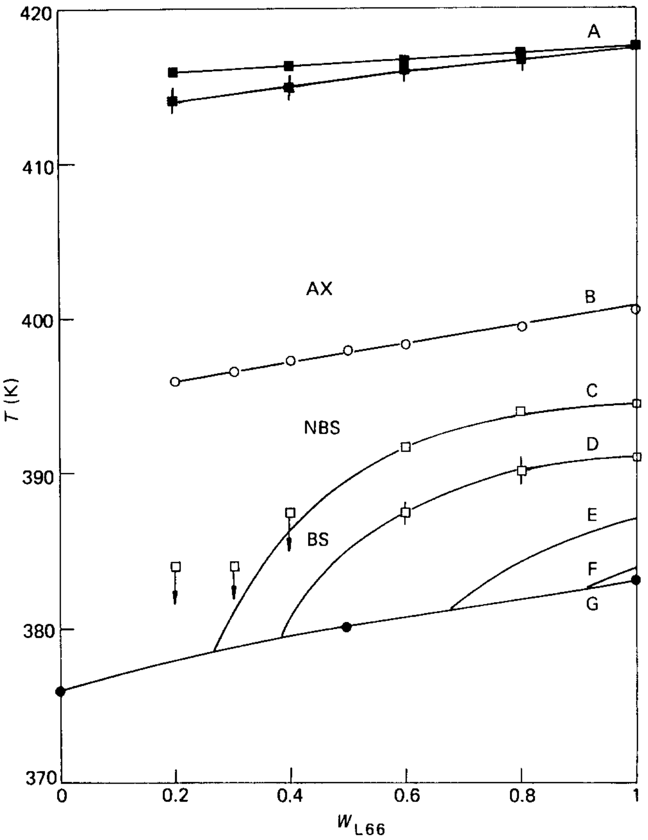

Figure 4 Morphologies existing in binary mixtures of L2.5/L66 as a function of composition (w_{L66}) and crystallization temperature (T). (A) Equilibrium melting point according to equation (1) assuming $\chi = 0$ (■) and −0.008 (⧯). (B) Axialite/non-banded spherulite transition (AX/NBS) (○). (C) Non-banded spherulite/banded spherulites (BS) transition (band spacing = 10 μm) (□). (D) Banded spherulites (band spacing = 5 μm). (E) Banded spherulites (band spacing = 2 μm). (F) Banded spherulites (band spacing = 1 μm). (G) Crystallization temperature of samples during air-quenching (from d.s.c.) (●)

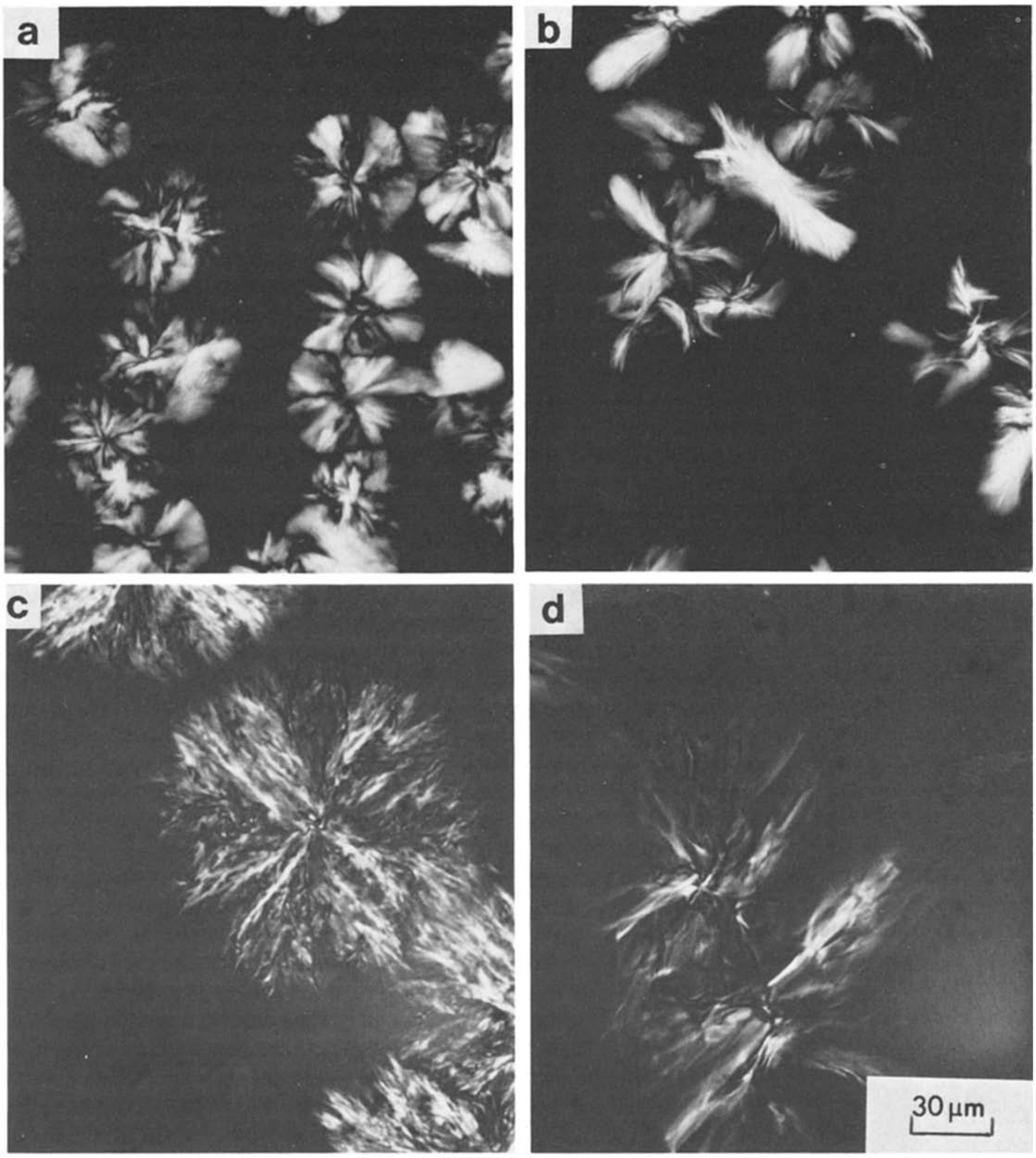

Figure 5 Polarized photomicrograph of isothermally crystallized L2.5/L66 samples: (a) 0.2/0.8, $T_c = 398.4$ K; (b) 0.2/0.8, $T_c = 401.3$ K; (c) 0.7/0.3, $T_c = 392.7$ K; (d) 0.7/0.3, $T_c = 398.3$ K

There are a small number of 'leading' dominant lamellar strings (denoted *leaders*) in a spherulite. The frontiers of the leaders have a slightly more peripheral location with respect to the spherulite centre than the surrounding dominant lamellar strings. There is a certain probability (denoted P_1) that such a string with a sequence ... AAA is transformed into ... AAAI, i.e. for a string reorientation. The probability P_1 is a function of both molecular weight and crystallization temperature.

When a leader is reorienting (e.g. ... AAA to ... AAAI) there is a certain probability (denoted P_2) that the surrounding dominant lamellar strings also reorientate correspondingly. Such a coupled reorientation of the nearby lamellae may be associated with the space filling (or rather space exclusion) caused by the leader.

In a pure LPE, such as L66, crystallized at about 383 K, there is a significant probability for leader reorientation, i.e. a significant P_1. The amount of subsidiary lamellar material in such a sample should be low due to the absence of low melting species. Therefore it is reasonable to assume that there is a high probability for reorientation of the surrounding dominant lamellar strings accompanying a leader reorientation. Introduction of low molecular weight material, such as L2.5, in L66 should have at least two implications. According to evidence by TEM presented in another paper[14], the crystallization at these low temperatures results in only a partial segregation of the components of the blends. It can therefore be assumed that the molecular weight of the material in the dominant lamellar strings is reduced and this should influence the probability of leader reorientation (P_1). Partial segregation of the low molecular weight component results in the formation of a larger proportion of subsidiary lamellar material which increases the distance between adjacent dominant lamellar strings and in turn should lead to a decrease in the probability P_2. The existence of subsidiary lamellar material enriched with low molecular weight material in such a sample is revealed by TEM and presented in an accompanying paper[14]. The 'roughness' in the banding

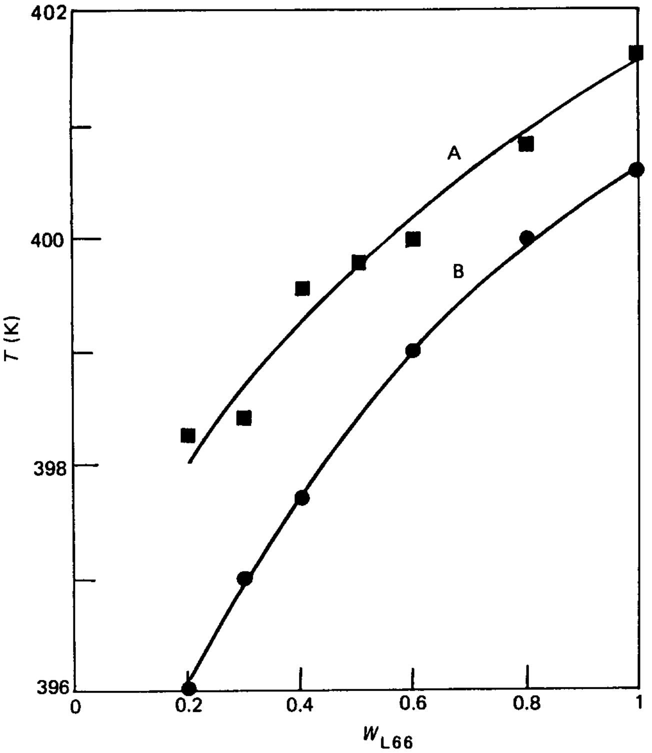

Figure 6 Temperature corresponding to log G (μm s^{-1}) = -3 (A) and to the axialite–spherulite transition (B) for binary mixtures of L2.5/L66 as a function of the composition

observed in the LX/L66 mixtures with a large content of low molecular weight component may also be explained by the proposed model. In such blends, the probability for coupled reorientation of nearby dominant lamellae should be reduced.

The increase of the molecular weight of the first component in the LX/L66 blends has proven to have a significant effect on the low temperature morphologies (*Figure 3*) and it may be explained by the proposed model by the influence of the molecular weight of the first component on segregation and on the amount of subsidiary lamellar material. Both P_1 and P_2 should increase with increasing molecular weight of the first component.

CONCLUSIONS

Binary mixtures based on sharp fractions of linear PE with M_w 2500 (L2.5) and 66000 (L66) crystallized at temperatures between 380 K and 403 K display, depending on temperature, three types of morphologies as revealed by polarized microscopy and SALS. Axialites are formed at the highest temperatures, non-banded spherulites at intermediate temperatures and banded spherulites at the lowest temperatures. For all the samples studied (compositions ranging from 0.2 to 1.0 w/w L66) there is a fairly sharp axialite–spherulite transition occurring at supercoolings ranging from 16.5 to 17.5 K (with respect to the equilibrium melting point of L66 which is the only crystallizing component at these temperatures). L2.5 acts as diluent which merely has the effect of reducing the equilibrium melting point of the crystallizing L66. The axialite–spherulite transition is, in accordance with the literature[1], accompanied by a distinct change in crystallization kinetics. The observed increase in supercooling of the axialite–spherulite transition with decreasing w_{L66} may be explained by an increase in substrate length of the growing crystals with increasing w_{L66}. The axialite–spherulite transition temperature recorded for pure L66 is in agreement with earlier data by Hoffman *et al.*[1]

A relatively distinct transition from non-banded spherulites (high temperatures) to banded spherulites (low temperatures) occurs at temperatures which have no simple relationship to the equilibrium melting point of either L2.5 or L66. A model is proposed which explains in qualitative terms the effect of the low molecular weight component in the LX/L66 mixtures on morphology. The basic features of the model are dominant lamellae which are arranged in radial strings and are formed prior to the shorter and subsidiary lamellae which fill the volume between the dominant lamellae strings. The individual dominant lamella is assumed to be planar and depending on the orientation of the lamellar crystal with respect to the light propagation vector either optically isotropic or anisotropic. A mechanism for reorientation of the dominant lamellar strings which grow somewhat faster than the surrounding dominant lamellar strings (so called leaders) is postulated. The frequency (probability) of such reorientation decreases both with increasing temperature and with decreasing molecular weight. A leader reorientation may or may not be accompanied by a corresponding reorientation of the nearby dominant lamellar strings. The space filling of the leader may very possibly be a factor in favour of such coupled lamellar reorientation. Introduction of low molecular weight material (e.g. L2.5) in L66 may possibly reduce both the tendency for leader reorientation and for coupled lamellar reorientation. The former is due to the change in composition of dominant lamellar material resulting from incomplete molecular weight segregation, i.e. partial cocrystallization of the components and the latter is associated with the formation of a larger proportion of subsidiary lamellar material in samples rich in low molecular weight material. TEM evidence in favour of this view is presented in an accompanying paper[14]. Data from additional low temperature crystallization of binary mixtures based on LPE sharp fractions with M_w 11000 (L11) and 22000 (L22) and L66, i.e. L11/L66 and L22/L66, support the proposed model.

ACKNOWLEDGEMENTS

The reported study has been sponsored by the Swedish Natural Science Research Council (NFR), grant K-RT 1910-100, the Swedish Board for Technical Development (STU), grant 85-3479 and the Swedish Plastics Federation—Plastic Pipe Group. The Spanish scholarship for JMR is gratefully acknowledged.

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