polymer papers

A crystallization kinetics study of binary blends of linear and branched polyethylene

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(Received 17 September 1990; accepted 13 December 1990)

The crystallization and morphology of binary mixtures of a low-molecular-mass ($\bar{M}_w = 2500$; $\bar{M}_w/\bar{M}_n = 1.15$) linear polyethylene and a high-molecular-mass ($\bar{M}_w = 166000$; $\bar{M}_w/\bar{M}_n = 6.1$) branched polyethylene grade with 1.5 mol% of ethyl branches have been studied by polarized light microscopy and differential scanning calorimetry. The linear growth rate and the supermolecular structure were found to be highly sensitive to composition. The pronounced increase in linear growth rate with increasing content of the linear fraction may be explained by an increased rate of diffusion of crystallizable segments due to a reduction in chain entanglement. The introduction of the linear polyethylene fraction changed the originally spherulitic structure into a predominantly axialitic texture.

(**Keywords: linear polyethylene; branched polyethylene; binary blends; crystallization kinetics; morphology**)

INTRODUCTION

The morphology and crystallization of binary blends of linear polyethylene (LPE) and branched polyethylene (BPE) have been topics which have received considerable attention during recent years[1–12]. One of the main topics of interest is the compatibility of the constituents in the solid, crystalline state. The similarity in chain structure of LPE and BPE may seem promising to obtain intimate mixing of the two components, but this rarely occurs due to molecular segregation. The concept of molecular segregation takes into account the rejection, during crystallization, of those chains less favoured from a thermodynamic standpoint. This definition covers not only differences in molecular mass but also other aspects of chain structure, e.g. chain branching.

When LPE and BPE are mixed, molecular segregation must be expected depending on molecular features of the two components. Broad molecular-mass grades of BPE and LPE have been found to be largely incompatible in the solid state[1,2,5].

Some authors[3,4,7] have, however, indicated that some blends of low-, medium- and high-density PE can co-crystallize when the two components have similar branch contents. Binary mixtures of an ethyl-branched PE and LPE were reported to co-crystallize, based on data obtained by thermal analysis, X-ray diffraction and Raman spectroscopy[7]. This conclusion was based on the presence of single melting, diffraction and scattering peaks. These results must, however, be considered with caution since, as mentioned in a previous paper[9], unimodal peaks are a necessary but not a sufficient condition for the existence of co-crystals.

Binary mixtures of LPE fractions of different molecular mass have been studied by Gedde and coworkers[13–15] and, depending on crystallization temperature, different degrees of mixing have been found to occur: (a) at high temperatures, only the high-molecular-mass component crystallizes, leaving the low-molecular-mass component in the melt to crystallize at a lower temperature; (b) at intermediate temperatures, the experimental evidence suggests that a parallel but separate crystallization takes place; (c) at low temperatures, partial co-crystallization occurs according to data from transmission electron microscopy (t.e.m.).

An extension of these studies included t.e.m. of chlorosulphonated sections, differential scanning calorimetry (d.s.c.), polarized light microscopy and small-angle light scattering on binary mixtures of low-molecular-mass LPE and higher-molecular-mass BPE[9–11]. A most noticeable effect was the absence of white unstained spots and the presence of a uniform lamellar structure (i.e. thickness of amorphous layer and local crystallinity) in these samples, which constituted major experimental evidence in favour of co-crystallization of the components. The major effect of the introduction of the low-molecular-mass LPE component was a decrease in the average amorphous thickness from about 15 nm in the pure BPE polymer (1.5 mol% ethyl branches) to about 5 nm in the blend consisting of 80% of LPE component, which is clearly evidence in support of co-crystallization of the two components[11]. These effects were quite general and were evident in samples crystallized

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0032-3861/92/030461-06

under different conditions over a broad temperature range[11]. Barham *et al.*[12] have presented convincing evidence by d.s.c. and t.e.m. in favour of a liquid–liquid phase separation in LPE/BPE blends. These samples differ, however, in molecular mass from the samples studied in ref. 11. The higher molecular mass of the LPE ($\bar{M}_w = 98\,000$; $\bar{M}_w/\bar{M}_n = 3.5$) used in ref. 12 is possibly of crucial importance for the liquid–liquid phase separation. The present paper presents data relating to crystallization kinetics and morphological studies carried out on the same blends as those dealt with in a parallel paper[11] reporting t.e.m. data. Special attention is paid to the influence of composition.

EXPERIMENTAL

Binary mixtures of an LPE sharp fraction ($\bar{M}_w = 2500$, $\bar{M}_w/\bar{M}_n = 1.15$), referred to as L2.5, purchased from Polymer Laboratories Ltd, UK, and a BPE sample containing 1.5 ± 0.1 mol% of ethyl branches (according to ^{13}C n.m.r.) and with $\bar{M}_w = 166\,000$ and $\bar{M}_n = 27\,200$ (according to size exclusion chromatography, s.e.c.), provided by Neste Polyethylene AB, Sweden, have been prepared by a solution mixing technique[13,14] in the following proportions (L2.5/BPE): 0.8/0.2, 0.6/0.4, 0.4/0.6 and 0.2/0.8. S.e.c. of the mixtures showed that the content of each component was the required one.

Crystallization kinetic studies have been carried out by polarized light microscopy (Leitz Ortholux POL BK II equipped with crossed polarizers and a temperature-calibrated Mettler Hot Stage FP 82) by measurement of the linear growth rate (G) of the spherulites/axialites and by d.s.c. (Perkin–Elmer DSC-7, temperature- and energy-calibrated according to standard procedures). Further details concerning these experiments, including the analysis of data, are given in ref. 13. The morphology of the crystallized samples was studied by polarized light microscopy.

The crystallization kinetics data for the pure components were treated according to the Hoffman–Miller (HM) theory[16]:

$$G = G_0 \Delta T \exp\left(\frac{-Q_D^*}{RT}\right) \exp\left(\frac{-Kb\sigma_e\sigma T_m^\circ}{kT\Delta T\Delta h_f}\right)$$

$$= G_0 \Delta T \exp\left(\frac{-Q_D^*}{RT}\right) \exp\left(\frac{-K_g}{T\Delta T}\right) \qquad (1)$$

where G_0 is a constant related to the number of repeat units; Q_D^* is the activation energy for reptation; K is a constant depending on the crystallization mechanism ($K = 2$ for regime II and 4 for regimes I and III); σ_e is the fold surface free energy; σ is the lateral surface free energy; T_m° is the equilibrium melting point; T is the crystallization temperature; $\Delta T = T_m^\circ - T$ is the degree of undercooling; and Δh_f is the heat of fusion. The latter is represented approximately by:

$$\Delta h_f = \Delta h_f^\circ \left(\frac{2T}{T_m^\circ + T}\right) \qquad (2)$$

where Δh_f° is the heat of fusion at the equilibrium melting point.

Thermodynamic data are as follows: $\Delta h_f^\circ = 293$ kJ kg^{-1} (ref. 17); $T_m^\circ = 398 \pm 1$ K for L2.5 (ref. 9); $Q_D^* = 24.015$ kJ mol^{-1} (ref. 18); $\sigma = 11.8$ mJ m^{-2} (ref. 16); $b = 0.415$ nm (ref. 19).

RESULTS AND DISCUSSION

Figure 1 shows the variation in the radial growth rate (G) as a function of the crystallization temperature (T) for both the pure constituents and the binary blends. The rate of crystallization of the pure components is very similar at temperatures of 390–392 K, whereas, at temperatures lower than 390 K, L2.5 crystallizes more rapidly. These data suggest *a priori* that L2.5 and BPE are potentially good candidates for co-crystallization. Evidence has been obtained by t.e.m.[14] indicating co-crystallization between L2.5 and BPE (see 'Introduction'). As shown in *Figure 1*, the rate of crystallization of the blends increases continuously with increasing content of L2.5. This is surprising since the equilibrium melting point is significantly greater for BPE than for L2.5. This will be shown later. A feasible explanation can be found by applying the reptation theory to our polymers. The motions of chains in the melt are strongly retarded as a consequence of chain entanglement. One compulsory condition for crystallization is the motion of the chains towards the crystallizing substrate. Entanglement delays the onset of crystallization. The addition of the low-molecular-mass L2.5 may reduce the effective number of chain entanglements and thus reduce the frictional force towards short-chain diffusion. The linear growth rate data are discussed in more detail later in this paper.

Different supermolecular structures—banded and non-banded spherulites and axialites and in some cases mixtures of these structures—were observed by polarized light microscopy. The morphology map presented in *Figure 2* clearly shows that the presence of the linear component favours the formation of axialites. This finding appears to contradict the earlier observations made on L2.5/LPE blends[13]. The introduction of the same low-molecular-mass polymer (L2.5) in blends with higher-molecular-mass LPE ($\bar{M}_w = 66\,000$) affected the morphology to only a minor extent[9]. A small temperature shift, 2–3 K, in the axialite–spherulite transition was observed for these blends[13]. The difference in morphology between L2.5/LPE and L2.5/BPE blends indicates that there is a major difference in crystallization mechanism between the two series of blends. The high-molecular-

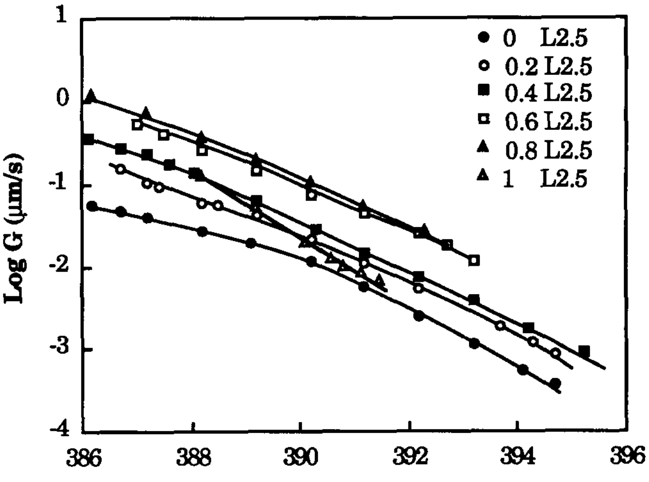

Figure 1 Linear growth rate as a function of crystallization temperature. The mass content of L2.5 in the different samples is shown adjacent to each symbol

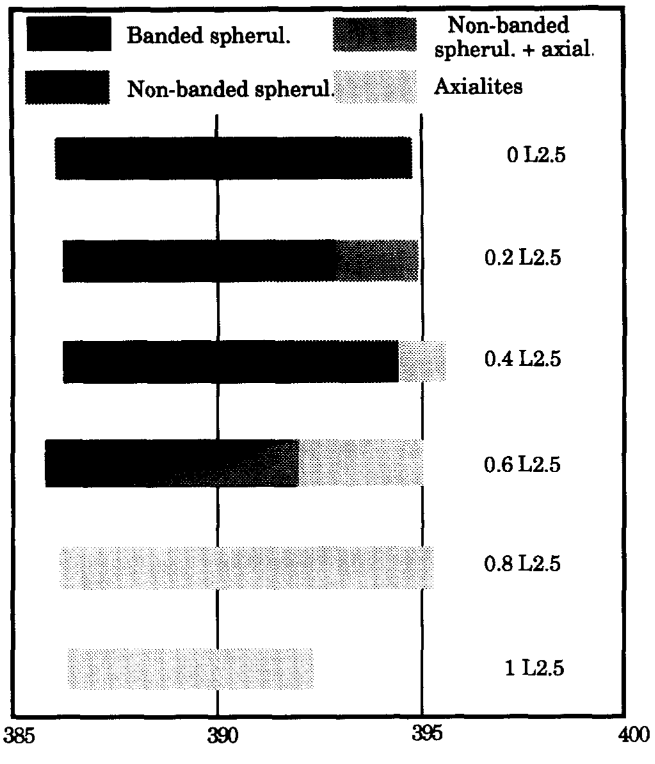

Figure 2 Morphology map of samples studied

mass component in the L2.5/LPE blends crystallizes first, forming the dominant lamellae and hence essentially controls the morphology as revealed by polarized light microscopy[13]. In the L2.5/BPE blends, on the other hand, both components crystallize in the same lamellae[11,12]. This specific issue is discussed in more detail later.

In *Figure 3*, which presents data for the melting point plotted as a function of crystallization temperature, it is evident that the melting point for samples crystallized at a given crystallization temperature increases with increasing content of L2.5 up to 60%. It is worth noting that the melting thermograms of all samples except L2.5/BPE (0.8/0.2) exhibit only two peaks. The high-temperature peak corresponds to the material crystallizing under isothermal conditions and the low-temperature peak is due to rejected species crystallizing during the cooling phase. The fact that only one melting peak is displayed for the isothermally crystallized material suggests that the two components co-crystallize. The L2.5/BPE (0.8/0.2) mixture displays three melting peaks. Two of these are associated with the material that has crystallized under isothermal conditions. Of these, the high-temperature peak occurs still at a higher temperature than that of the corresponding BPE sample. The low-temperature peak occurs at a lower temperature than that associated with L2.5 and the peak temperature increases more strongly with crystallization temperature than that of L2.5.

The melting points of the blends crystallized at the higher temperatures are significantly higher than that of L2.5 (398 ± 1 K). The early growing dominant lamellae in these samples must therefore be enriched in BPE. For almost 10 years it has been an established fact that the thickness of the first formed crystals is controlled only by the degree of undercooling at which the crystallization is performed[20–22]. The branched polymer (BPE) with a supposedly statistical distribution of chain branches has inherently a multicomponent nature with regard to crystallization. The longest linear chain segments tend to crystallize first. It is reasonable to assume that the low-molecular-mass polymer (L2.5) will act as a diluent with respect to these chains and thus decrease their equilibrium melting temperature. These chains will thus crystallize at a lower degree of undercooling, resulting in a thicker initial crystal in the blends than in the pure BPE. Crystal thickening has also to be considered. *Figure 4* shows that the variation in crystallization time, i.e. in the crystal thickening time, is always less than 0.5 decade and that no 'systematic' trend with regard to composition exists. It is therefore suggested that the compositional dependence of the melting point is related to the aforementioned diluent effect.

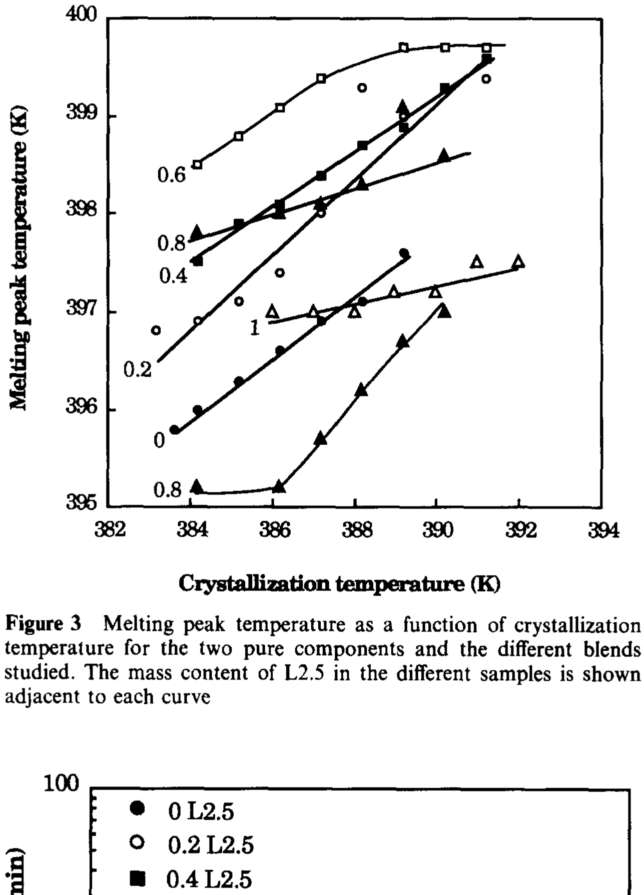

Figure 3 Melting peak temperature as a function of crystallization temperature for the two pure components and the different blends studied. The mass content of L2.5 in the different samples is shown adjacent to each curve

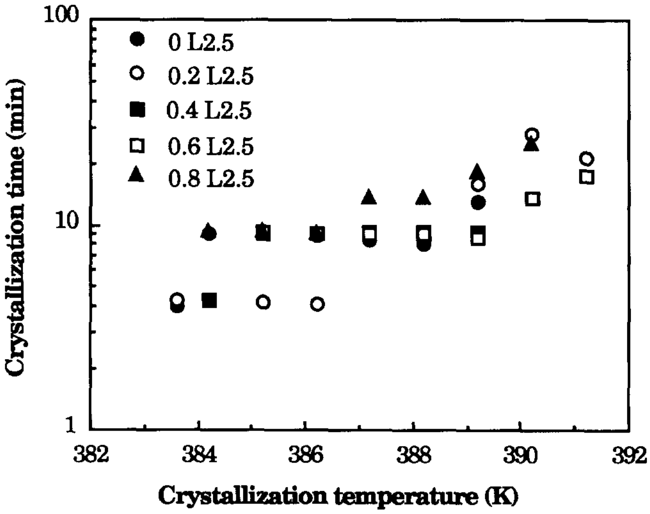

Figure 4 The crystallization time (logarithmic scale), the time period between the occurrence of the maximum in crystallization rate and the termination of the isothermal phase, as a function of crystallization temperature

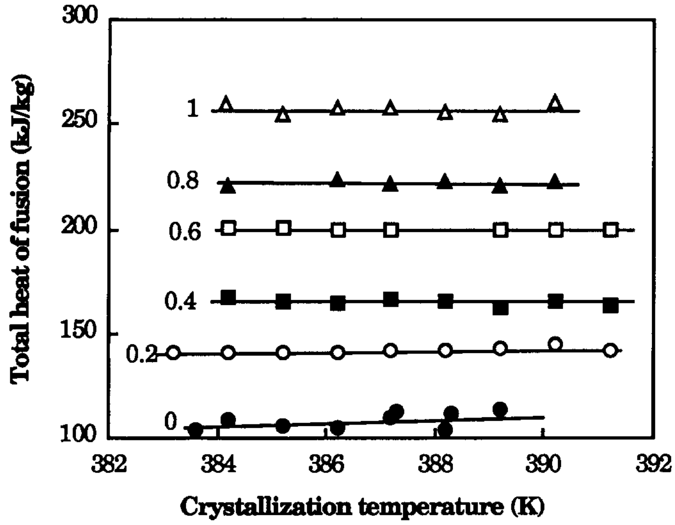

Figure 5 Total heat of fusion plotted as a function of crystallization temperature. The mass content of L2.5 in the different samples is shown adjacent to each line

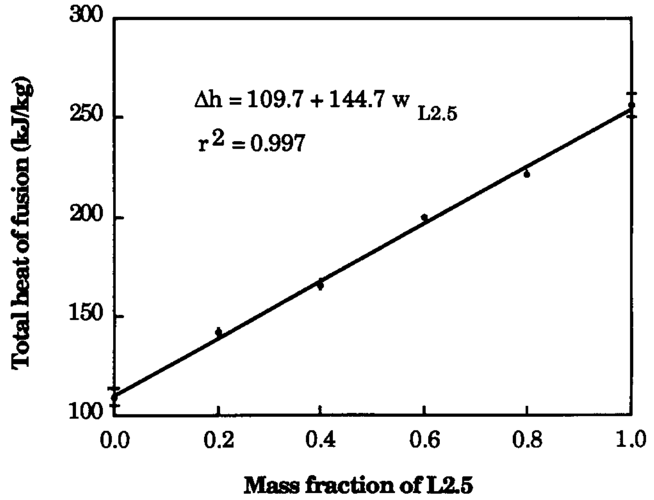

Figure 6 Total heat of fusion plotted as a function of the mass fraction of L2.5. The bars indicate the standard deviation for the different samples crystallized at the different temperatures

The presence of the two high-temperature melting peaks in the blend consisting of 80% of L2.5 is another point of interest. A particularly important observation was made by d.s.c. Two clearly separate crystallization peaks were observed in this blend crystallized at the two highest crystallization temperatures. Separate crystallization and segregation seems to be confirmed in this case of this sample. For the other blends, the crystallization exotherms were always unimodal, which, together with the simple melting behaviour, indicates intimate mixing and potential co-crystallization of the components.

Figures 5 and *6* present data for the total heat of fusion (Δh) as functions of crystallization temperature and composition. It is clearly seen in *Figure 5* that, for a given sample, Δh is approximately independent of crystallization temperature. The rectilinear graph shown in *Figure 6* demonstrates the fact that Δh, i.e. the mass crystallinity ($w_c = \Delta h/\Delta h_f^\circ$), of the blends is a simple additive function of the contributions of the pure constituents. The mass crystallinity increases linearly with increasing content of L2.5 from 45% for pure BPE to about 90% for pure L2.5. The composition of the isothermally crystallized material may, however, be quite different. *Figure 7* shows that the fraction of the crystalline material crystallizing under isothermal conditions is strongly dependent on the crystallization temperature. At the lower temperatures (<388 K) there is a monotonic increase in crystallized fraction with increasing content of L2.5. Above 390 K, the trend seems to be the reverse despite the significant scatter in the presented data. This is consistent with the data for the pure components: L2.5 exhibits a much stronger decrease in crystallized fraction with increasing temperature than BPE, and above 392–393 K essentially no crystallization of L2.5 occurs. The composition of the components in the dominant lamellae cannot be determined from these data. In the blended samples crystallized at high temperatures it is, however, probable that the BPE component constitutes the major part. This specific point is referred to later in connection with the interpretation of the crystal growth rate data.

For a further analysis of the linear growth rate data, it is necessary to estimate the equilibrium melting temperature (T_m°) for the two samples. The value given in the '*Experimental*' section for the linear polymer should be correct within 1 K. For the branched polymer, on the other hand, it is difficult to determine T_m°. The statistical distribution of the chain branches gives this polymer a multicomponent character. The cumulative distribution of linear chain segments of n carbon atoms, each terminated by two chain branches, is given by the equation:

$$W(n) = \int_0^n n(1-p)^2 p^{n-1}\,\mathrm{d}n \qquad (3)$$

where p is the probability that a main-chain carbon atom is not attached to a branch group. The cumulative distribution is shown in *Figure 8*. The abscissa in this plot may be transformed to an equilibrium melting temperature scale by considering the Thompson–Gibbs equation:

$$T_m^\circ(n) = T_m^\circ(n=\infty)\left(1 - \frac{2\sigma_e}{\Delta h_f^\circ \rho n l_{cc}\langle\cos\theta\rangle}\right) \qquad (4)$$

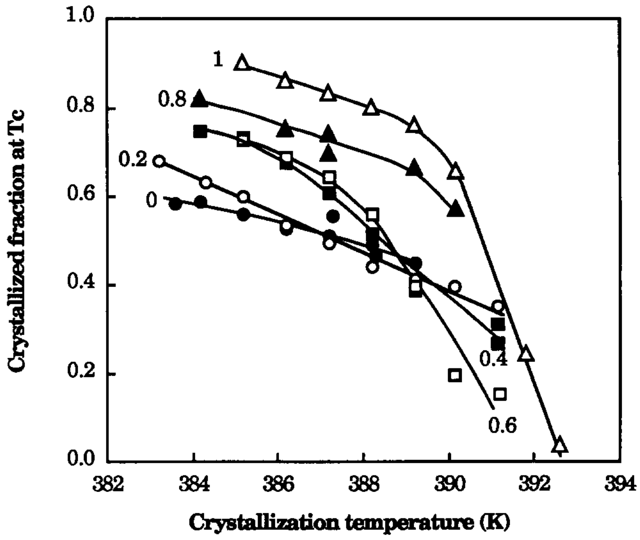

Figure 7 Fraction of the sample crystallized under isothermal conditions relative to the final degree of crystallinity at room temperature plotted as a function of the crystallization temperature

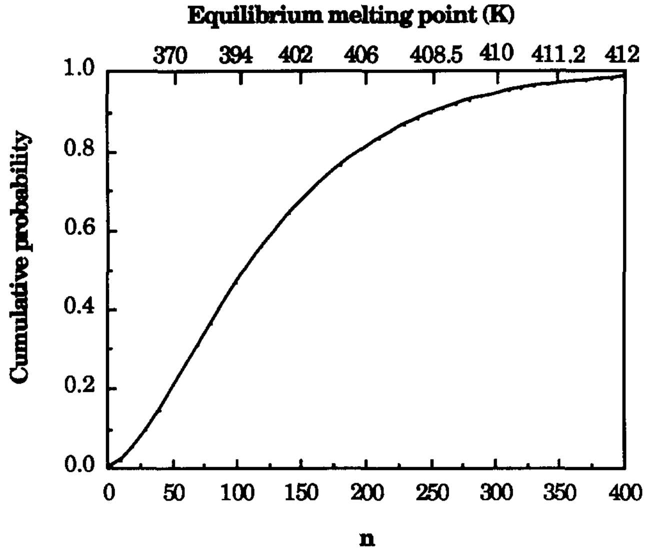

Figure 8 Cumulative distribution function $W(n)$ (mass fraction of linear chains shorter than n) for BPE (1.5% of ethyl branches)

where $T_m^\circ(n = \infty) = 418.1$ K (ref. 19), the crystal density $\rho = 1000\,\mathrm{kgm^{-3}}$ (ref. 23), l_{cc} is half of the crystallographic $c = 0.127$ nm (ref. 23), and θ is the chain tilt angle, which is set to 30° (ref. 24). Thus, the thickness of the equilibrium crystal is determined by the length of the linear segments, and the equilibrium crystals are assumed to contain no chain branches. The task is now to select a level that corresponds to the dominant lamellae which are growing at the highest rate and thus represents the linear growth rate. Let us assume that only 10% of the material participates in this process. The equilibrium melting temperature of this material is 410 ± 2 K. This preliminary T_m° value is used here.

The crystallization kinetics data of the pure components were treated according to equation (1) and the following equations were obtained:

$$G(\mu\mathrm{m\,s^{-1}}) = 7.561 \times 10^3 \Delta T \exp\left(\frac{-2890}{T}\right) \times \exp\left(\frac{-22\,132}{T\Delta T}\right) \quad r^2 = 0.992 \quad \text{(L2.5)}$$

$$G(\mu\mathrm{m\,s^{-1}}) = 6.42096 \times 10^4 \Delta T \exp\left(\frac{-2890}{T}\right) \times \exp\left(\frac{-87\,350}{T\Delta T}\right) \quad r^2 = 0.996 \quad \text{(BPE)}$$

The data showed a linear trend when $\log G - \log \Delta T + Q_D^*/(2.303RT)$ was plotted against $1/(T\Delta T)$. By inserting proper thermodynamic values (see '*Experimental*') and considering that L2.5 crystallizes according to regime I forming axialites ($K = 4$) and BPE exhibits regime II crystallization and spherulite formation ($K = 2$), the fold surface free energy (σ_e) was found to be 12.5 mJ m^{-2} for L2.5 and 87 mJ m^{-2} for BPE. The latter value is similar to values obtained for linear PE of the same molecular mass[19]. The suggested T_m° value for BPE, 410 K, thus seems to be a reasonable choice.

The linear growth rate data of the blends exhibited the same curve shape as that of BPE (*Figure 1*). The different curves are essentially shifted along the ordinate. This was further examined by applying equation (1) to the linear growth rate data (*Figure 9*). The lines are of essentially the same slope, i.e. the different samples exhibit practically the same K_g value (80 000–90 000), but they are shifted vertically. The factor G_0 (equation (1)) increases monotonically with increasing content of L2.5 (*Figure 10*).

The factor G_0 is closely related to the rate at which the crystallizing segments are transported to the crystal surface. A more than 10-fold increase in this rate for the blend with 80% of L2.5 compared with that for the pure BPE is indicated in *Figure 10*.

The linear growth rate data of the blends thus indicate that the crystal lamellae in the growth front consist of the longest linear chain segments of the BPE component. *Figure 7* confirms, however, that a significant part of the linear polymer (L2.5) also crystallizes under the isothermal conditions. The presence of only one melting peak, observed in all the blends except in L2.5/BPE 0.8/0.2, associated with the isothermal crystallization of the material is another observation that seems to contradict the above conclusion that only 'perfect' BPE chain segments participate in the crystallization in the growth front. The dramatic change in morphology from spherulitic to axialitic shown in *Figure 2* which occurs on blending with the linear polymer is another observation that seems at first sight to be inconsistent with this view.

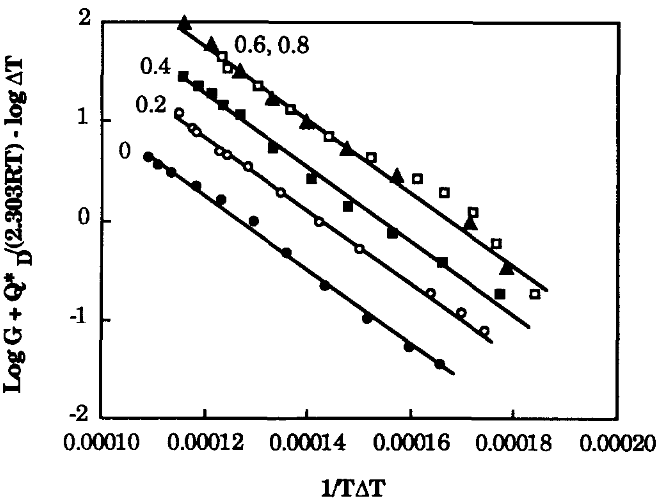

Figure 9 Growth rate data for binary blends according to equation (1)

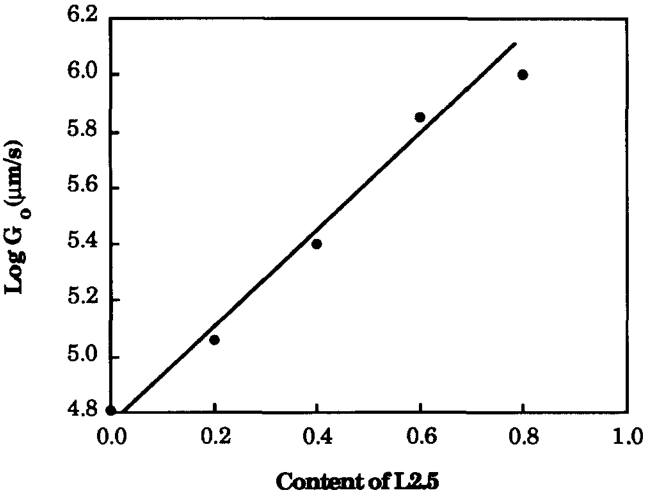

Figure 10 The intercept ($\log G_0$) of the plots presented in *Figure 9* plotted as a function of composition

We believe, however, that all these observations may be true and that the most perfect chain segments of BPE crystallize separately first and thereby control the growth rate. Co-crystallization of L2.5 and the shorter linear chain segments of BPE occurs almost in parallel and affects the morphology by preventing the crystals enriched in the longer linear chain segments from branching and forming spherulites. The morphology thus becomes controlled by this 'second' phase, which constitutes a much larger portion of the isothermally crystallizing material.

CONCLUSIONS

Binary blends based on low-molecular-mass linear polyethylene (L2.5) and high-molecular-mass ethyl-branched (1.5%) polyethylene (BPE) have been examined with regard to their crystallization and morphology as revealed by polarized light microscopy and differential scanning calorimetry.

The isothermal crystal growth rate, i.e. the linear rate by which spherulites/axialites growth, was found to increase strongly with increasing content of L2.5. The growth rate data were treated according to the Hoffman–Miller theory by considering that the linear growth rate was determined by the longest chain segments of the branched polymer. The equilibrium melting point used in the analysis was 410 K. The low-molecular-mass polymer affected only the factor (G_0) related to short-distance diffusion of the crystallizable segments; G_0 increased by more than one order of magnitude when the content of L2.5 was increased from zero to 80%.

The morphology changed from spherulitic to dominantly axialitic when BPE was blended with L2.5. The presence of only one melting peak associated with the material crystallized under isothermal conditions strongly suggests co-crystallization. Data by transmission electron microscopy presented in a parallel paper[11] further strengthen this view. To resolve this apparent contradiction—the linear growth rate data suggest separate crystallization of the longest linear chain segments of BPE whereas co-crystallization is confirmed by the other studies—the following scheme is suggested. A minor fraction of BPE, of the order of 10%, consisting of relatively long linear chain segments crystallizes at the highest rate and determines the propagation rate of the spherulite/axialite boundary. The major fraction of the isothermal crystallization involves, however, co-crystallization of BPE chain segments of lower perfection and L2.5. This second crystallization mechanism, which occurs at a rate comparable with the first, controls the morphology as revealed by polarized light microscopy.

ACKNOWLEDGEMENTS

This study has been sponsored by the Swedish Board for Technical Development (STU), grant 89-02294P, the National Energy Administration of Sweden (STEV), grant 656 109-1, and by the Swedish Plastics Federation. The PE grade was supplied by Neste Polyeten AB, Sweden. The scholarship from the Department of Education, Universities and Research of the Basque Country Government, for JII is gratefully acknowledged.

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