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Phase separation in polyethylene melts

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Two-component blends of differing polyethylenes (PE), one fully linear (high density, HDPE) and the other branched (low density, LDPE) are discussed. We show that these systems can display certain prominent thermal and morphological effects in the solid (crystalline) state, which we can only explain in terms of preceding liquid → liquid phase segregation whilst in the melt. Parallel work elsewhere [1], undertaken with different objectives has, unexpectedly, led to similar conclusions. In view of the many previous communications between the two groups, the two mutually reinforcing works are presented here in sequence.

Our work stems from a continuation of previous studies of the morphology of HDPE/LDPE blends [2–5]. In these earlier works we were concerned with the crystallization of the linear component from a homogeneous (single phase) melt of the blend. Evidence for both complete mixing in the melt and subsequent crystallization-induced phase segregation, was obtained from thermograms. Thus after rapid quenching the subsequent melting endotherms showed a single peak situated at a temperature intermediate between those of the pure components. In contrast, when the melt was held for a long time at an appropriate "crystallization" temperature (i.e. a temperature low enough for the HDPE to crystallize but high enough that the LDPE would remain molten before cooling), the subsequent endotherms showed two peaks with melting points characteristic of the individual components. Such behaviour is strongly indicative of liquid → solid phase segregation from an initially homogeneous melt. The accompanying electron microscope studies of the underlying morphology, which often yielded spectacular micrographs (see example, [6]), were also strongly supportive of this conclusion.

Subsequently, however, we found that the above behaviour was not followed by blends of all PE pairs in all compositions. Such a blend forms the subject of the present letter.

In this study the blend components used were low-density polyethylene (LDPE): BP PN220, density 0.918. $M_w \simeq 208\,100$, $M_n \simeq 25\,300$ (long branch content ten per thousand), and high-density linear polyethylene (HDPE): Sclair 2907, $M_w \simeq 98\,000$, $M_n \simeq 28\,200$. As before [2], blending was carried out by coprecipitation from solution, supplemented in some cases by hot evaporation of mixed solutions to ensure removal of all possible memory of the preceding crystal morphology. There was no difference in behaviour of the blends prepared in the two different ways confirming that the prehistory and the preparation method had no influence on the effects described. The starting point for what is to follow was the observation that the blends displayed distinctly different behaviour on subsequent thermal treatments according to concentration regimes. In particular, the following effects were seen after quenching from the molten state at 160° C.

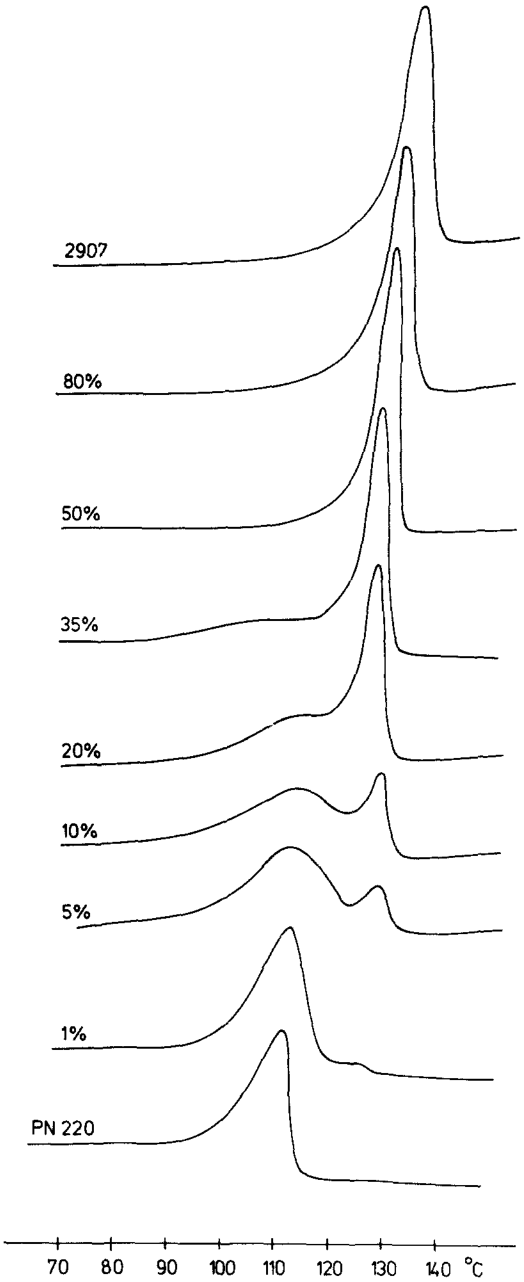

Figure 1 DSC traces obtained by heating blends of HDPE (Sclair 2907) and LDPE (BP PN 220) and 10° C min^{-1} after quenching from 160° C into acetone at freezing point. The percentage figure refers to the percentage HDPE in the blend. Note that blends with 50% or more HDPE show a single endotherm whose position varies with composition. At lower HDPE contents there are two endotherms; one at ~ 130° C and the other a broad peak at ~ 114° C.

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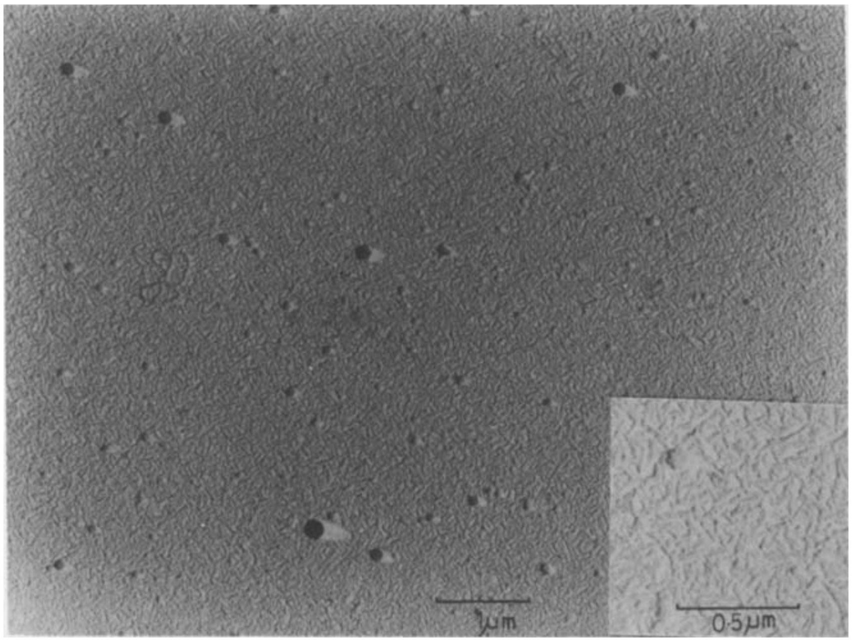

Figure 2 Electron micrograph of a 50% blend of HDPE and LDPE quenched from 160° C. Preparation by permanganic etching followed by shadowing and replication. The insert shows detail at a higher magnification.

At high HDPE concentrations (100 to 50%) all the previously mentioned effects, which in the past we associated with complete mixing in the melt, were seen, notably the single peak endotherm after quenching (which was not dependent on quenching conditions). This is illustrated by the endotherms marked 100 to 50% in Fig. 1.

However, distinctly different behaviour was displayed by blends of HDPE for concentration of 40% and below. Here, after quenching, the samples displayed double-peaked melting endotherms on subsequent reheating (curves for 35% and below in Fig. 1). This peak multiplicity could not be removed even by the most rigorous quenching. This change over in thermal properties within a narrow concentration range of blend composition is remarkable in itself, and clearly must be of significance for blend behaviour, irrespective of its possible cause. The sudden appearance of the effect at a specific composition and its insensitivity to quenching conditions strongly suggests that the origin of the double peak lies not in the possible crystallization events during cooling but in the texture of the melt itself. This in turn leads to the postulate of liquid → liquid phase segregation within the melt.

It is true that so far we have not detected inhomogeneities attributable to liquid–liquid segregation *in situ* within the melt itself (no doubt due to the minute differences in properties, e.g. refractive index, of the distinct phases postulated). Nevertheless, all further observations made on the product after solidification are strongly suggestive of liquid → liquid phase segregation prior to crystallization. A few will be listed below.

Consider first the position of the melting peaks in Fig. 1. Here from HDPE 100 to 50%, the peak melting point decreases gradually. This indicates increasing amounts of LDPE incorporated in the crystals, consistent with homogeneous cocrystallization from a single phase melt. From 40 to 0% the position of the sharper, more accurately locatable high-temperature peak, remains unaltered down to the

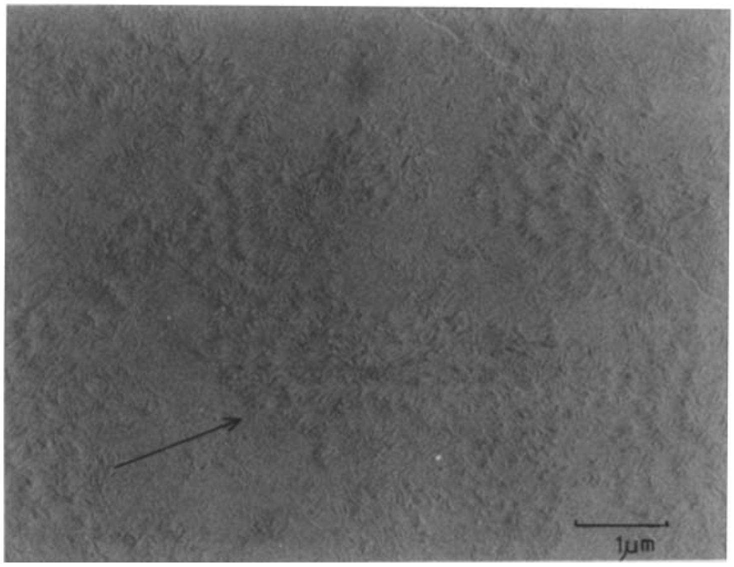

Figure 3 Electron micrograph of a replica of a 10% blend of HDPE with LDPE quenched from 160° C into acetone at freezing point. The arrow indicates morphology typical of the HDPE-rich phase.

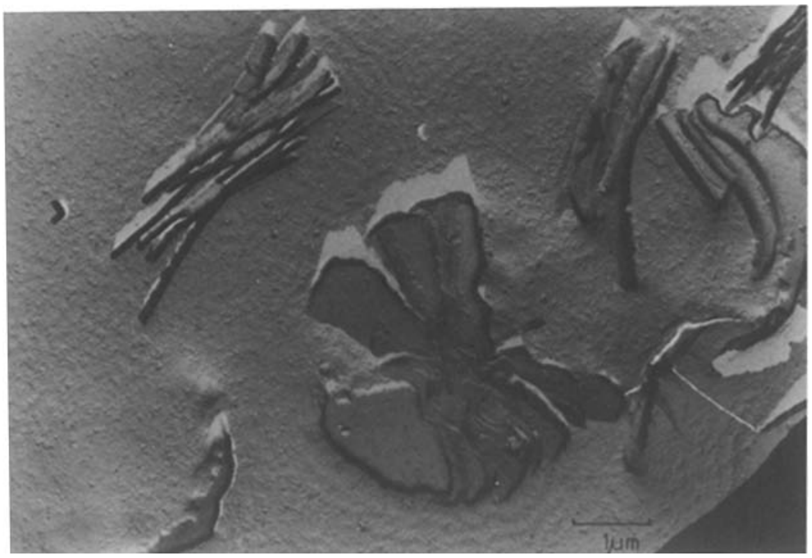

Figure 4 Electron micrograph of a replica of a 1% HDPE with LDPE held at 126° C for 1 week (in argon) and then quenched into acetone at freezing point.

lowest concentration at which it is still detectable (0.2%). This is fully consistent with the expectation that the segregated, HDPE-rich phase crystallizes homogeneously on quenching where the melt composition remains invariant with concentration corresponding to that at the HDPE-rich end point of the appropriate tie line in a binary liquid–liquid phase diagram. The same is upheld for the lower (and much broader) peak which in this picture corresponds to the LDPE-rich phase.

Further support is provided by the electron microscopic morphology, here revealed by using the combined permanganic acid etching–replication technique [7]. The 50% blend quenched from 160° C reveals a totally uniform fine-grained texture (Fig. 2) consistent with the homogeneous cocrystallization from a single-phase melt. In all lower (HDPE) concentrations, on quenching from 160° C a broadly circular "domain" structure is apparent (Fig. 3) the "domains" displaying distinct "spherulitic" features. This is fully consistent with a pre-existing domain structure in a phase-segregated melt, where the more strongly textured regions, such as arrowed domain in Fig. 3, would correspond to the HDPE-rich phase; HDPE and blends of above 50% HDPE concentration show a banded structure when quenched.

Now that we can use morphological criteria such as those described above to assess liquid → liquid phase segregation we are currently in the process of mapping out a rudimentary liquid–liquid "phase diagram" to be published in due course. In the meantime we shall select a few, instructive features for further illustration below.

1. There is a highly asymmetric biphasic region situated at the low HDPE composition. We have seen above that at 160° C the upper concentration boundary of the biphasic region is close to 40%. The lower boundary, by present criteria, must be close to 0% HDPE. This is apparent from DSC traces (Figs 1 and 7 to follow) and can also be inferred from electron micrographs. Fig. 4 is a micrograph of a 1% HDPE blend held isothermally at 126° C (a temperature at which HDPE, but not LDPE, can crystallize). Here liquid–solid transformation, i.e. crystallization, has occurred within the initial melt-phase-segregated HDPE-rich domain, with the LDPE-rich "matrix" crystallizing homogeneously on quenching. While the expected smooth melt domain boundaries are broken up by the large-scale lamellar crystals the additional liquid–solid phase segregation has served to enhance the contrast of the HDPE-rich region, making it strikingly apparent. Of course sheaf-like entities such as those in Fig. 4 could be looked upon as direct products of crystallization from a homogeneous melt (as indeed it has been previously [2–6]). However, in line with representing only 1% of the material, such sheaves are isolated units widely separated in a fine-textured matrix, which would require long-range diffusion of the HDPE molecules within the polymeric, essentially LDPE, melt in comparatively short times. The latter, even by cursory estimate, would require quite unrealistically high chain mobility a problem which is obviated if, as it supported by much other evidence, the melt already consists of HDPE-rich and HDPE-poor phases. The same point is brought out even more strongly by the crystal aggregates formed in the even more dilute (0.2%) HDPE system in Fig. 5.

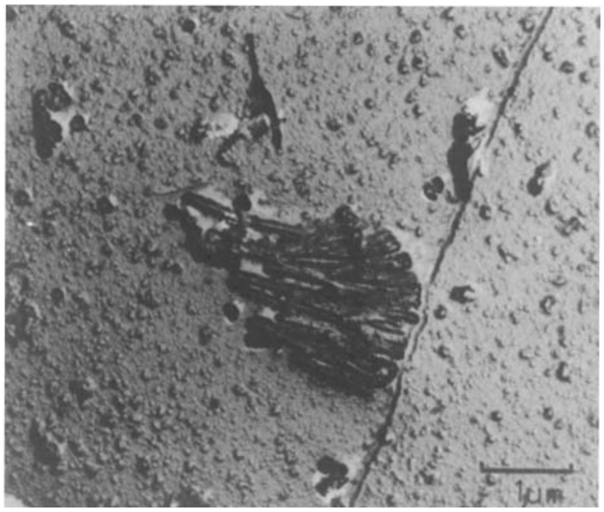

Figure 5 Electron micrograph of a replica of a 0.2% blend of HDPE with LDPE crystallized for 1 week (in argon) at 128° C then quenched into acetone at freezing point.

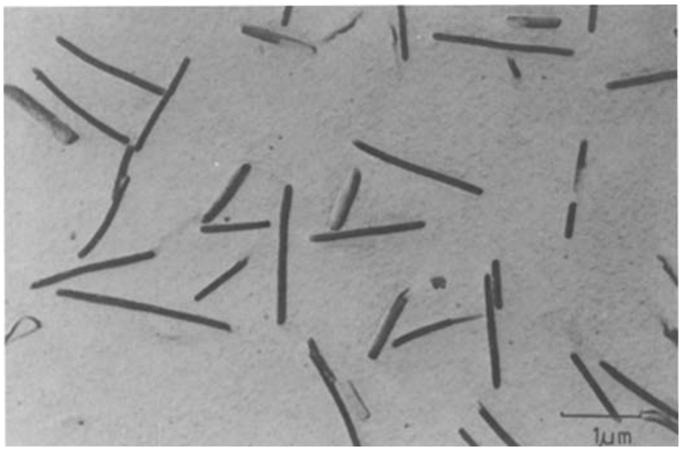

Figure 6 Electron micrograph of a replica of the same blend as in Fig. 5, but with the sample held for 1 week at 122° C prior to quenching.

It follows that the low end of the biphasic coexistence curve must indeed be close to 0% HDPE.

2. The biphasic coexistence curve is of lower critical temperature (LCT) type, where the parabolic apex is truncated by the intervention of liquid → solid transformation. This point is strikingly brought out by morphological evidence. Fig. 6 is a 0.2% blend as in Fig. 5, but crystallized at the lower temperature of 122° C. We see that, in contrast to Fig. 5, the crystal lamellae are single and uniformly dispersed (the same is also true for the 1% blends crystallized at 122°C). We infer that in Fig. 6 (again in contrast to Fig. 5 where we believe the crystals grow within a phase-segregated HDPE-rich melt) they grew from a homogeneous melt. This would mean that (for 1% and 0.2% HDPE) there is an LCT between 128 and 122° C.

We can also deduce from Figs 5 and 6 that the initial phase-segregated melt must have remixed before or during crystallization at 122° C. While at first sight improbable (because quite high diffusion rates are required) this is strongly supported by DSC studies. Fig. 7 shows melting endotherms of melts of a 1% HDPE blend which were held at 122° C for progressively longer times and subsequently quenched. On direct quenching (zero holding time), two peaks are clearly present indicative of a two-phase melt. As seen, the small higher temperature peak, which by our interpretation originates from the HDPE-rich melt phase, becomes "consumed" during storage at 122° C, consistent with remixing before crystallization sets in;

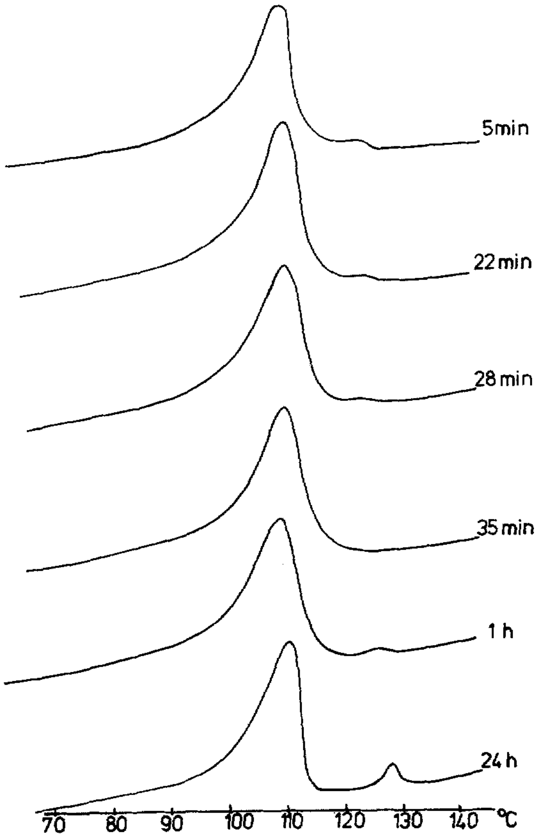

Figure 7 DSC traces of the 1% blend of HDPE with LDPE held at 150° C for 30 min and then held at 122° C for the times indicated, prior to quenching into acetone at freezing point (heating rate 10° C min^{-1}). Note the diminution of the higher melting peak with time; it has vanished after 35 min at 122° C. By 1 h a new high-temperature peak appears, due to isothermal crystallization of HDPE at 122° C.

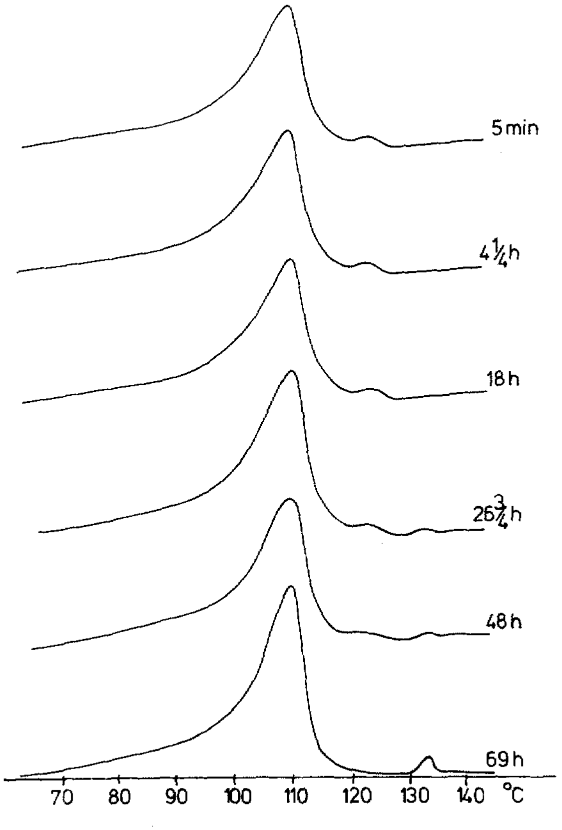

Figure 8 DSC traces from 1% blend samples as in Fig. 7, but held at 128° C for the times indicated prior to quenching (heating rate 10° C min^{-1}). Note that there is no diminution of the high-temperature peak prior to the onset of isothermal crystallization after 20 h.

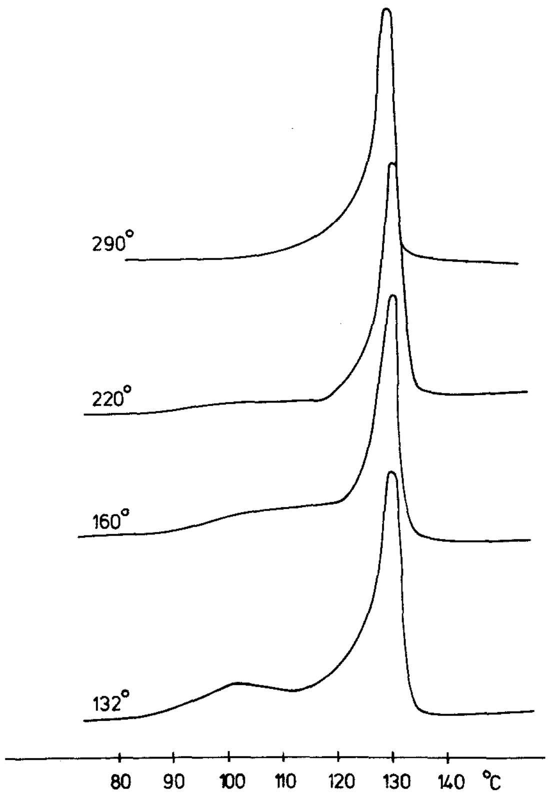

Figure 9 DSC traces of a 35% HDPE blend in LDPE obtained by heating at 10° C min^{-1}. All the samples were held for 30 min at the temperatures indicated prior to quenching into acetone at freezing point. (Heating rate 10° C min^{-1}.)

this is in contrast with storage at 128° C, where this peak remains unaltered until crystallization takes over (Fig. 8), consistent with a stable biphasic melt.

3. There are also some indications of the existence of an upper critical temperature (UCT), i.e. that the biphasic melt region may be a closed loop. This, rather surprising, possibility is suggested by DSC results which show that for the same HDPE composition the biphasic segregation (as assessed by the double endotherm criterion after quenching) is reduced, and in fact can be eliminated when quenching from higher melt temperatures. An example is shown by Fig. 9 (see caption). Again, the experimental fact that the subsequent thermal behaviour of the melt is affected by the temperature at which the melt had been kept is notable in its own right. If the double peak is interpreted as a consequence of melt-phase segregation, the narrowing of the biphasic region with melt temperature, hence the existence of a UCT (not yet fully mapped), follows.

In summary, although no direct evidence from the molten state has been obtained so far, a variety of self-consistent observations on blend samples obtained in their subsequently solidified form (all notable in their own right), are strongly supportive of liquid–liquid phase segregation in the melt with some specific information on features of the underlying phase diagram. If such phase separation, as induced by branch content, may appear surprising, it must be remembered that polyethylene and polypropylene are generally recognized to be incompatible, the ultimate distinction being differences in methyl branch content. While the PE–PP pair is no doubt an extreme case, the question as to where the boundary is to be drawn clearly arises. The present work would indicate that this boundary in branch content may well lie within the limits which by conventional classification are "polyethylenes".

Finally, the parallel work in the following letter [1] has produced strong morphological support for phase segregation (by a different sample preparation and contrasting method) in an unblended PE which, however, had an unusually wide branch content distribution. This raises the further important issue as to the limit when a polymer with chains of differing molecular lengths and isomeric perfections can be regarded as a single- or multi-component system. This issue, common to all synthetic polymeric materials, has already arisen in the past in connection with liquid → solid phase transformation (fractionating crystallization [8–10]) and as we have just noted, is now emerging also for the molten state with fundamental implications for basic polymer science and applications.

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