

TIME-TEMPERATURE-MISCIBILITY AND MORPHOLOGY OF POLYOLEFIN BLENDS

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Abstract Miscibility and crystallization have been studied for polypropylene-polyethylene and polyethylene-polyethylene blends. In the case of the polypropylene blends the composition of interest is 20% polypropylene. At this composition the polypropylene has been found to be soluble in linear low density polyethylene but insoluble in high, low and very low density polyethylenes. The miscibility has been concluded from the crystallization kinetics and polarised optical microscopy with a hot stage. Polyethylene-polyethylene blends have been formed from polymers with similar average branching content but where they have different melting temperatures. Important consequences are to introduce long branches into a polyethylene that only has short branches, and to modify the morphology of a polyethylenes so that haze, gloss and strain hardening are improved. Polyethylene blends must be developed after careful consideration of the branch content and distribution within each of the constituents. It is not sufficient to simply blend polyethylenes, with the desired range of properties, without regard to the miscibility of the blend composition.

Keywords Polypropylene, Polyethylene, Blend, Miscibility, Thermal analysis, Morphology, Crystallization, Melting

INTRODUCTION

Polyolefins have the simplest chemical structure of all polymers, yet their diversity due to branch concentration and distribution provides a complexity of chain structure that is reflected in their morphology and relative miscibility^[1]. Polypropylenes and polyethylenes are the two main classes of polyolefins considered in this paper. Isotactic homo-polypropylene (PP) is the only type of polypropylene considered. All of the main classes of polyethylenes are considered. These are high density, or linear, polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE) and ultra low density polyethylene (ULDPE). The polyethylenes are characterised by their density, melt flow index (MFI) and the type of catalyst used in polymerization. HDPE has density in the range 0.95–0.97 g cm⁻³, between 0.93–0.95 g cm⁻³ is called medium density polyethylene. LLDPE has density in the range 0.91–0.93. VLDPE has density in the range 0.89–0.91 g cm⁻³ and ULDPE less than 0.89 g cm⁻³. The density is primarily controlled by the branch concentration.

The distribution of branches is controlled by the type of catalyst. Multisite catalysts, such as Zeigler-Natta, Phillip and Unipol, produce a broad distribution of branches both intermolecularly and intramolecularly, Single-site catalysts, such as metallocenes, produce a narrow distribution of branches. The molar mass distribution is also narrower for polymers produced by single site catalysts. Because of their well defined molecular properties the new metallocene polyethylenes provide excellent examples for study of blend miscibility and co-crystallization. Since all of these polymers have the same chemical constitution, they are all compatible^[2].

Another variable is the branch length or structure. Short branches are formed by co-polymerization with alkenes: propene to give methyl branches, 1-butene to give ethyl branches, 1-hexene to give butyl branches,

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1-octene to give hexyl branches, and other branched 1-alkenes to form corresponding branch structures. The distribution of branches in polyethylenes has been studied using temperature rising elution fractionation (TREF) and stepwise crystallization by differential scanning calorimetry (DSC)^[3]. Methyl branches are small enough to be included in the crystal structures while other branch lengths are excluded from crystal^[4] structures except where they are formed under rapid cooling conditions. With the exception of methyl branch type is considered to be of no importance in determining miscibility and crystallization. Crystallization conditions are an important factor in determining the degree of co-crystallinity that can occur in a miscible blend as shown by Galante, Mandelkern and Alamo^[5]. This later research has not considered the proven alternative that some polyolefin blends are immiscible in the melt as shown by Hill, Organ and Barham^[6]. Hill and Barham have also proved that liquid-liquid phase separation occurs when single-site catalysed polyethylenes are used in blends with linear polyethylene^[7].

The crystals of all polyethylenes consist of ethylene units in a chain folded structure. The branches are excluded from the crystals. The segment length of ethylene units will limit the lamella thickness. There will be a distribution of lamella thickness within a branched polyethylene even if the polymer could be crystallized under equilibrium conditions.

There are several paths that a polyolefin blends can follow when it is cooled from the melt. These are shown in Fig. 1. If the components are immiscible in the melt, the two phases will continue to be immiscible on cooling and so they will crystallize independently. This is because polyolefins are expected to exhibit upper critical solution behavior. If the components are miscible in the melt then they may become immiscible on cooling and again crystallize independently. Alternatively, they may continue to be miscible, but crystallize independently, or they may co-crystallize. Because of the dispersity of the branches, mixtures of the above behaviors may occur. Note that when a polyolefin blend forms two phases each phase will consist of a mixture of each component according to the phase rule. Therefore, even if the blend crystallizes as two phases the morphology of each phase will be different to that in the respective component polymer.

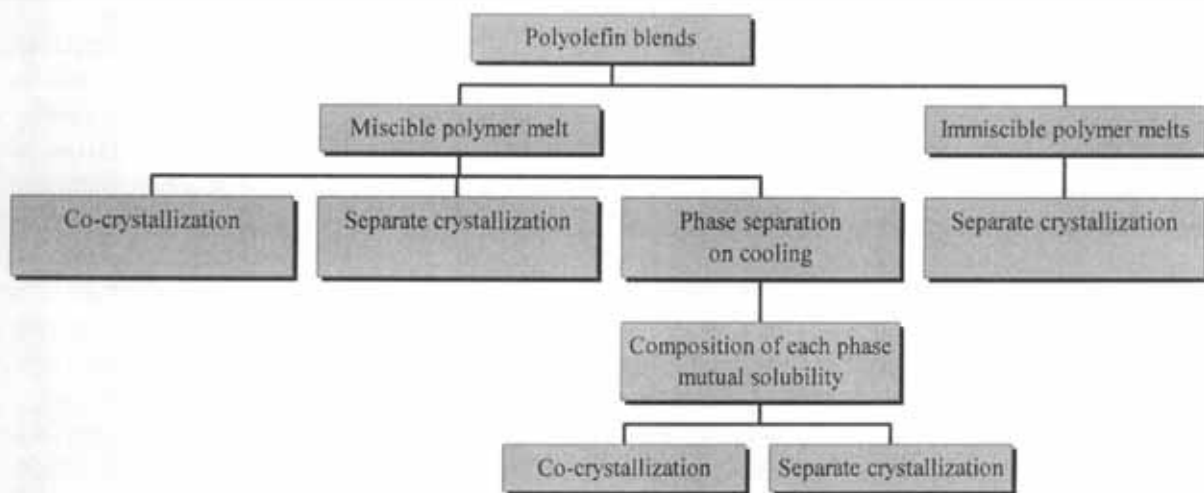


Fig. 1 Time-temperature miscibility and morphology

The morphology of polyethylene blends will affect their thermal properties and mechanical properties. The thermal properties, crystallization and melting, are dependent on the miscibility and thermal history discussed above. The mechanical and dynamic mechanical properties of polyethylenes are determined largely by the crystallinity and so can be modified accordingly^[8].

Polyethylene blends have been shown in many instances to provide an upper critical solution temperature (UCST) phase diagram. The two phase region often covers the half of the composition range with the higher concentration of branched polyethylene^[6]. The miscibility of polymer blends and the UCST curve have been

more fully described by a loop type two-phase region. This has been explained using a treatment of the Flory-Huggins equation by Kammer^[9]. This approach has been extended to account for the microphase separation in miscible polymer blends on the basis of local concentration fluctuations^[10].

The most common blends studied are those in which one of the components is HDPE. Blends of HDPE with single-site catalysed LLDPE in which the comonomer is 1-octene have been studied by varying the concentration of the LLDPE. As the octene level was increased from 0.72 mol% to 4.82 mol% (3.6–24.1 branches /1000C) the blends showed an increasing separation into two crystalline phases^[11]. Similar blends of HDPE with single-site catalysed, octene copolymer containing some long chain branches have been characterised^[12]. The results showed that as the short branch concentration increased the co-crystallization diminished. The long chain branches were not the dominant factor.

The present research reports examples from several blend combinations illustrating the types of miscibility, immiscibility, co-crystallization and independent crystallization as shown in Fig. 1. The single-site catalysed polyethylene copolymers offer many possibilities for blending since they can be chosen with well defined branch distributions that match or partially overlap with the other polyethylene so as to provide a level of co-crystallinity. Co-crystallinity of blended polymers is a means of providing significant modification to the morphology and hence appearance and mechanical properties of polyolefins.

EXPERIMENTAL

Polymers and Preparation of Blends

The polyolefins used in this research are shown in Table 1. Blends were prepared using an Axon extruder with a 12.5 mm Gateway screw with temperature zones set at 150, 200, 200 and 160°C and a screw speed of 70 rpm. Blends were extruded as tapes of 50 × 0.5 mm.

Table 1. Polyolefins and their properties

Polyolefin	Catalyst	Density (g cm ⁻³)	MFI (dg min ⁻¹)	<i>T_c</i> (°C)	<i>T_m</i> (°C)
PP	Z-N	0.905	8.5	119	161
HDPE	Z-N	0.953	0.3	117	130
LDPE	radical	0.919	7	88	107
LLDPE	Z-N	0.920	1.0	106	120
VLDPE	Z-N	0.912	1.0	101	123
VLDPE	M	0.901	27	77	93
VLDPE LB1	M	0.908	1.0	91	106
VLDPE LB2	M	0.915	1.0	97	111
ULDPE	M	0.870	0.5	47	60

Z-N = Ziegler-Natta and M = Metallocene

Differential Scanning Calorimetry

A Perkin-Elmer Pyris 1 DSC was used. Samples of approximately 2 mg were heated to 180°C for 5 min prior to cooling at 10 K/min. Melting scans were performed from 20 to 150°C (or 180°C for the polypropylenes) at 10 K/min. A baseline scan was performed with empty pans for converting the DSC curves into specific heat curves. Isothermal crystallization curves for polypropylene were performed by cooling rapidly, in the DSC, from 200°C to the desired isothermal crystallization temperature, in the range 119–130°C. Data were analysed by the Avrami equation and then the results were used to calculate the crystallization half-times.

Optical Microscopy

A Nikon Labophot II microscope with Mettler FP80 hot stage and temperature programmer was used. Images were captured with a Sony video camera and saved on a Macintosh 7500 computer. Image analyses were performed using IPLab spectrum and image enhancement used Photoshop.

RESULTS AND DISCUSSION

Figure 2 shows isothermal crystallization half-times for polypropylene in 1:4 blends with various polyethylenes.

The crystallization temperatures were chosen so that the polyethylene remained as liquid during the crystallization of the polypropylene. Most of the results show similar half-time values. These data in conjunction with the optical microscopy showed that these blends were immiscible. The polypropylene crystallized as phase separated droplets, which were composed of essentially pure polypropylene. This means that they crystallize at almost the same rate as pure polypropylene. The data for LLDPE show greatly increased half-times or decreased crystallization rates. Optical microscopic images showed a homogeneous solution of PP in LLDPE. Therefore, the PP crystallized from a solution of LLDPE and the crystallization of PP was very slow due to the dilution effect.

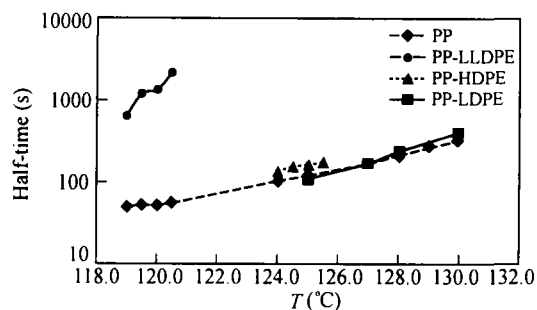


Fig. 2 Crystallization half-time versus temperature for polypropylene and its 20:80 blends with polyethylenes

When PP was blended with HDPE, the PP was present as droplets in the HDPE (Fig. 3). PP is immiscible, but compatible, with HDPE. Upon cooling slowly from the melt in the DSC, the PP crystallized at the higher temperature, then the HDPE crystallized. If the melt was cooled rapidly the HDPE crystallized first at about the same temperature as when it was cooled slowly, then the PP crystallized at a much lower temperature. The DSC curves for melting show the independent melting endotherms for PP and HDPE unchanged from the positions of the pure polymers, whether they were cooled slowly or rapidly. Conversely when HDPE was the minor phase, HDPE droplets were observed in the matrix of PP and the same DSC crystallization and melting peaks were observed. These conclusions were confirmed by optical microscopy. The spherulites of polypropylene can be seen in the dispersed droplets.

When PP in LLDPE (1:4) was crystallized isothermally at a temperature above that where the LLDPE could crystallize, the PP crystallized from the homogeneous solution in LLDPE (Fig. 4). Figure 4 was chosen to illustrate both crystallization from solution in the form of long fibrous crystallites and phase separated droplets. In other LLDPEs crystallization could be observed to occur entirely from solution. The composition of these blends (1:4) was chosen because it appears to be the borderline of miscibility for LLDPE and PP. VLDPEs have been found to be immiscible at this concentration, except at temperatures above 130 °C. ULDPE, density < 0.89 g cm⁻³, is miscible with PP at a concentration of 1:4. The crystallization rate of PP in LLDPE has been found to be dependent on melt flow index (MFI). For low MFI the crystallization rate was found to be slower due to the PP molecules having slower diffusion through the viscous melt of LLDPE.

Blends of polyethylenes have also been studied. The first example is metallocene-catalysed VLDPE blended with LDPE (Fig. 5). The two polymers have been chosen because they have similar melting temperatures. This means that they will have similar sequence lengths between branches and hence similar lamella thickness. The main melting peak shows a continuous decrease in temperature in going from LDPE to VLDPE. This indicates that co-crystallization has taken place between some of the molecules with similar length between branches. A second lower temperature peak is present in all curves, though an actual peak is not evident in pure LDPE as there is a continuous low temperature range melting. The maximum of this lower temperature peak also parallels the main peak, again indicating co-crystallinity. Co-crystallinity requires that the blends be miscible in the liquid state. This type of blend will contain a long chain branch content dependent on the LDPE content. The long chain

branches are not significant in crystallization. The branch point will be excluded from the crystals but there are few long branches compared with short branches.

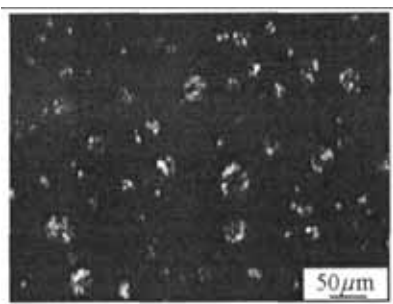


Fig. 3 PP droplets in a blend of PP-HDPE (1:4) at 130°C after 20 min (magnification: $\times 100$)

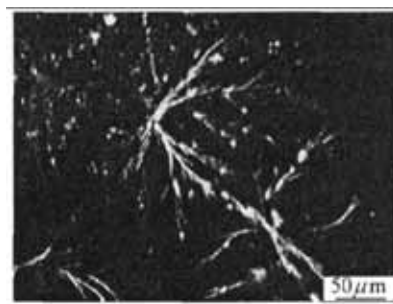


Fig. 4 Diffuse PP spherulites in a blend of PP-LLDPE (1:4) after isothermal crystallization at 130°C for 2 h (magnification: $\times 100$)

VLDPE (ZN type) and VLDPE LB1, with long branches, blends are shown in Fig. 6. The highest melting temperature peak of the VLDPE (ZN) remains almost constant up to about 50%. The lower temperature broad peak remains at the same temperature over the composition range. This shows that the highest melting components of VLDPE (ZN) crystallize independently up to 50% composition of VLDPE LB1. Above 50% VLDPE LB1 the higher melting temperature peaks broaden and decrease in melting temperature. The broad lower melting peak is consistent with co-crystallization of both polymers.

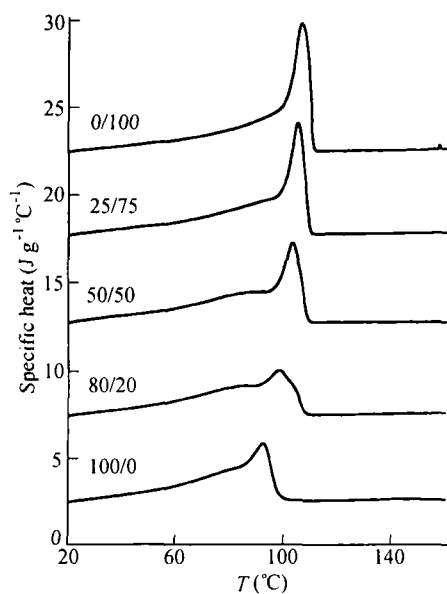


Fig. 5 DSC specific heat curves of very low density polyethylene—low density polyethylene (second number) blends obtained at 10 K/min following crystallization at 10 K/min from 200°C. An adapted scale is drawn by consecutively adding 5 units to each curve.

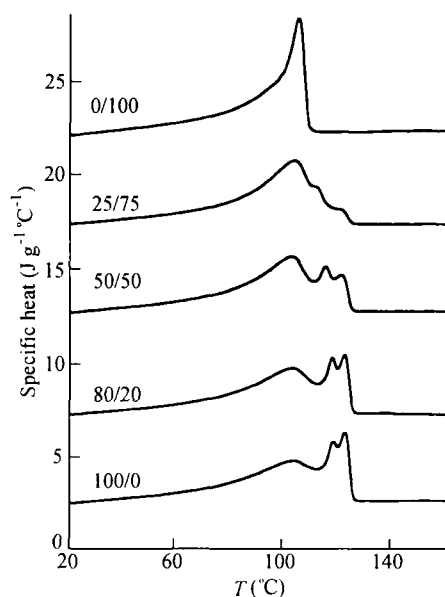


Fig. 6 DSC specific heat curves of linear low density polyethylene (ZN type)—very low density polyethylene with long branches (VLDPE LB1, second number) blends obtained at 10 K/min following crystallization at 10 K/min from 200°C. An adapted scale is drawn by consecutively adding 5 units to each curve.

The next example (Fig. 7) contains two VLDPEs; the first with butene and the second with octene as comonomer, and one is linear, while the other contains long branches. They have been chosen to have slightly

different melting temperatures so that their melting could be resolved by the DSC, yet they would be similar enough to have similar segment lengths between branches in many molecules. The higher melting VLDPE LB1, with long branches, shows the same melting temperature until its concentration is reduced to 50%. A second lower temperature peak appears due to the VLDPE LB1 with only short branches. In this region, the polymers crystallize independently so there may be melt immiscibility. Between 50% and 100% of the lower melting VLDPE LB1 there is a smooth trend where the melting temperatures merge. In this composition range, the melting is indicative of co-crystallization. This type of behavior is characteristic of that observed by others and ascribed to a phase diagram with an upper critical solution temperature^[6].

Thermal fractionation resulting from stepwise isothermal cooling is shown for the blends in Fig. 8. The series of melting peaks define different branch densities, with more branched molecules melting at lower temperatures. Performing this treatment on the polymers more clearly reveals their branch distribution. Performing thermal fractionation on blends can more clearly show regions where they are co-crystallized and regions where they crystallize independently. Two of the blends, 10% and 50% VLDPE LB2 have superimposed calculated specific heat curves. These are calculated from the curves for the pure polymers by adding them in the proportion that they are present in the blend. A comparison of both sets of curves shows that the experimental curves are better resolved in the region where the VLDPE LB2 polymer has its main melting peak. The highest melting peak of the LLDPE is changed in area by the VLDPE LB2 even though the VLDPE LB2 does not melt in the same region. The highest melting fraction will be expected to crystallize first, so it will be crystallising from a liquid containing some of the VLDPE LB2. Even if there is a phase separation, each phase will contain some of the other component, and so the crystallization can be influenced. This is important for controlling the haze, gloss and even strain hardening of polyethylene films.

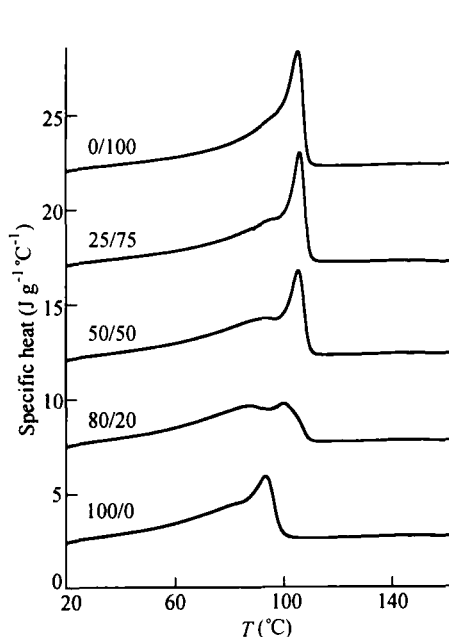


Fig. 7 DSC specific heat curves of very low density polyethylene — very low density polyethylene with long branches (VLDPE LB1, second number) blends obtained at 10 K/min following crystallization at 10 K/min from 200°C

An adapted scale is drawn by consecutively adding 5 units to each curve.

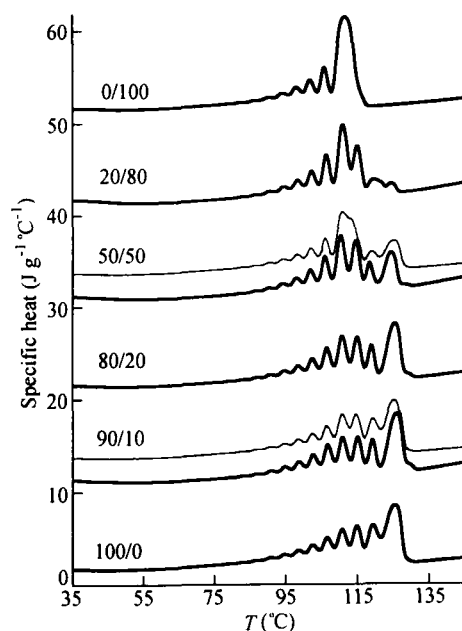


Fig. 8 DSC specific heat curves of LLDPE and VLDPE LB2 (second number) blends after thermal fractionation

Thin solid lines represent the calculated specific heat curves for the 10% and 50% VLDPE LB2 blends. An adapted scale is drawn by consecutively adding 10 units to each experimental curve and 12 units to each calculated curve.

The broad peak at the maximum melting temperature of the VLDPE LB2 in the calculated specific heat curve in Fig. 8 shows that melting does not occur at the same temperature in the DSC curves of pure component. The experimental curve shows sharp melting peaks in this region. This gives evidence for co-crystallization of VLDPE and LLDPE in this region of melting temperatures. The two polymers must have the same segment length between branches in these crystals.

Figure 9 shows very low density polyethylene blends where one of the components has long chain branches. This is similar to the example shown in Fig. 7. For compositions with LLDPE of 50% and above the higher melting temperature peaks are constant, indicating that these components crystallize independently. As the concentration of LLDPE goes below 50% the peaks merge to the VLDPE LB1 peak showing co-crystallization. In the co-crystallization region the two polymers must be miscible, while in the other region they are probably immiscible in the melt. This again is characteristic of the typical upper critical solution temperature phase diagrams found for such blends.

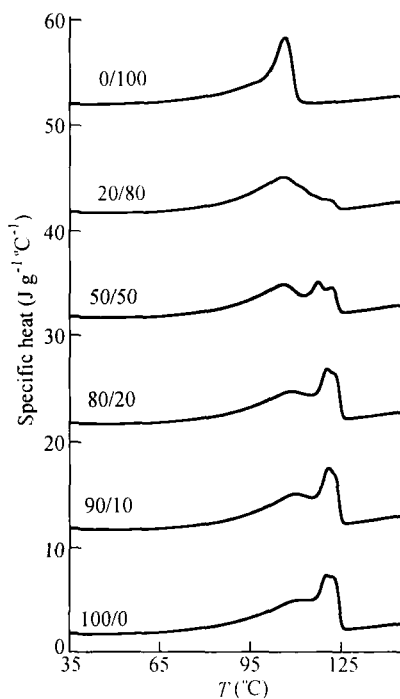


Fig. 9 DSC specific heat curves of linear low density polyethylene – very low density polyethylene with long branches (VLDPE LB1, second number) blends obtained at 10 K/min following crystallization at 10 K/min from 180°C. An adapted scale is drawn by consecutively adding 10 units to each curve.

CONCLUSIONS

Examples have been provided for polyolefin blends that are miscible and immiscible in the melt. Polypropylene-linear low density polyethylene (1:4) is miscible in the melt yet the polymers crystallize separately. They have sufficiently different crystallization temperatures for them to be crystallized independently giving unique morphology with changes in mechanical properties. Polypropylene was immiscible in the melt with each of the other polyethylenes investigated and so they crystallized in the already distinct matrix and dispersed phases. Polyethylenes may be immiscible in the melt, though they do have similar crystalline structures. The ability to co-crystallize requires first that the polyethylenes in the blend are miscible. They then must have similar segment lengths between branches since branches are excluded from the crystals. In the portions of the branch distribution where they are similar they co-crystallize, while in other portions they crystallize independently. In segments

where they do not have similar branch distributions the crystallization of one polyethylene can still be modified by the other. In this way polyethylene blends can modify the transparency, elasticity and gloss of films.

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