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The crystallization of blends of different types of polyethylene: The role of crystallization conditions

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Cocrystallization in blends of linear and branched polyethylenes has been studied under both isothermal and slow-cooling crystallization conditions. Before the more common, polydisperse-type polyethylenes were studied and the results analysed, model systems were investigated in detail. The components used in the model binary blends were molecular weight fractions of linear polyethylene, hydrogenated poly(butadiene) as a model for the ethylene-1-alkene copolymers, and a three-arm star hydrogenated poly(butadiene) as a model for the long chain branched polyethylenes. It was found that a key factor in governing the extent of cocrystallization in these blends is the closeness of crystallization rates of each of the components. The extent of the cocrystallization thus diminishes with increasing concentration of the linear component in the blend. It is found that copolymer composition and molecular structure also have a strong influence on cocrystallization. The amount of cocrystallization is favoured at the lowest isothermal crystallization temperatures and is maximized under quenching conditions. The general features that influence cocrystallization, which have evolved from this study, are discussed. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: blends; cocrystallization; models)

INTRODUCTION

Blends of linear and branched polyethylenes have been widely studied over the past thirty years. Investigations of the morphology, in both the melt and solid state, of such blends, varying in composition and molecular structure of the components, have been reported[1–12]. Most of these works emphasize that the interest in polyethylene blends stems from the need to understand the conditions for phase segregation and miscibility and to improve specific properties relative to one-component systems. Traditionally, different polyethylenes are blended in order to improve processability and the toughness of the final product.

Neutron scattering studies of the melt of blends of high density polyethylene (HDPE) and low density polyethylene (LDPE) conclusively showed melt miscibility of the components over the whole range of concentrations[13]. The studies on blends of HDPE and hydrogenated polybutadienes (HPBDs), which are model ethylene 1-butene linear low density polyethylenes (LLDPEs), pointed out that the changing interaction parameter with increasing branching content of the LLDPE induces liquid–liquid phase separation at a given co-unit content[14–16].

The solid state morphology of blends of HDPE and HPBD, with ethyl branch contents ranging from 2 to 5.5 mol% of branch points, was previously studied using samples that were rapidly crystallized[17]. By using differential scanning calorimetry and solvent extraction techniques it was found that cocrystallization of the linear and branch components occurs up to a branch content of approximately 4 mol%. Our present interest is to study the degree of cocrystallization of such blends after either slow cooling or isothermal crystallization from the melt.

Extensive studies on the crystallization and morphology of solid blends of polyethylenes have been carried out by Stein *et al.*[8–19] and by Tashiro *et al.*[20–27]. In these papers, as well as in the majority of the other literature reports cited, the blends were either rapidly crystallized or slowly cooled from the melt. However, controlled isothermal crystallizations were not studied. A detailed characterization of the samples used in these latter works[20–27] was not given. Thus the LLDPEs studied, which were probably of the Ziegler type, would possess broad molecular weight and comonomer composition distributions. Therefore, the nature of the samples would strongly influence the general conclusions that were made. One of the conclusions of these studies was that blends of HDPE and LLDPE with two or less branches per 100 carbons show complete cocrystallization either under rapid crystallization conditions or when slowly cooled from the melt. This conclusion is contrary to the general tendencies observed by other investigators[2,4,10,12], and at variance with the two melting peaks that are usually found after slow crystallization. The results could also be influenced by the heterogeneity in molecular weight and composition of the LLDPE used. In the present study emphasis is also given on clarifying these aspects of the problem. Thus, blends are first studied with components that have narrow distributions. The results obtained with such

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Table 1 Molecular characterization of blend components

Polymer	M_w (g mol^{-1})	M_w/M_n	Mol% branch points	T_m (°C)[a]
Linear LPE-1	96 000	1.14	0	130.6
Linear LPE-2	76 700	3.33	0	N.D.[b]
Linear LPE-3	115 000	1.12	0	132.0
Linear LPE-4	149 000	3.60	0	N.D.
Hydrogenated polybutadiene (HPBD)	108 000	1.20	2.20	100.0
Ethylene–hexene copolymer (E–H)	121 000	2.19	1.60	107.4
Ethylene–butene copolymer (E–B)	140 000	7.10	1.70	~120
3-arm star hydrogenated polybutadiene (star HPBD)	120 000	1.12	2.20	96.0
Long chain branched polyethylene (LDPE)	136 000	11	1.6	110.0

[a] Peak melting temperatures after rapid crystallization inside the d.s.c.
[b] N.D.: not determined.

systems then serve as a base, or reference, for further studies in which at least one of the components, the polydispersity, is much broader. In changing the polydispersity of the LLDPE, the polydispersity of both the molecular weight and branching composition is changed from narrow to broad. A three-arms star HPBD is used as a narrow model compound to be compared with broad LDPE.

The cocrystallization behaviour of blends of both narrow and broad distributed components, after isothermal crystallization, has been primarily studied here. However, to corroborate previous results, rapid quenching and slow cooling crystallizations were also investigated. The study of mixtures of the different polyethylenes is thus carried out to assess the influence of molecular structure on the solid state properties of mainly isothermally crystallized blends.

EXPERIMENTAL

Materials

The molecular characteristics of the polyethylenes used in this work are listed in *Table 1*. Linear polyethylenes, LPE-1 and LPE-3, are narrow molecular weight fractions obtained from Societé des Pétroles d'Aquitaine (SNPA). Linear LPE-2 and linear LPE-4 are typical commercial whole polymers. The hydrogenated polybutadiene (HPBD) is a random ethylene–butene copolymer obtained from the Phillips Petroleum Company. It is characterized by narrow molecular weight and composition distributions[28]. It thus serves as a model for random ethylene-1-alkene copolymers. The ethylene–hexene copolymer (E–H) was prepared with one of the metallocene-type catalysts following the method of Kaminsky *et al.*[29]. It is characterized by a most probable molecular weight and narrow composition distribution. The ethylene–butene copolymer (E–B) is a commercial whole polymer prepared with a Ziegler–Natta-type catalyst. Thus it has a broad molecular weight and composition distribution. The 3-arms star hydrogenated polybutadiene (star HPBD) is a model compound for low density polyethylene (LDPE).† The long chain branched polyethylene (LDPE) is a whole commercial ethylene copolymer prepared by free radical polymerization under high pressure.

Procedures

The mixtures were prepared by rapidly quenching dilute solutions of the two species involved. Weighed amounts of the pure components (total weight = 40 mg) were dissolved in 30 ml of *o*-dichlorobenzene at 177°C and stirred for 15 min. After mixing, the solution was rapidly quenched into 300 ml of chilled (−60°C) methanol. The quenched solution was allowed to gradually warm up to room temperature. The blend was then filtered and dried overnight in a vacuum oven at 60°C. The pure components were also subject to the same solvent treatment (see Appendix A). Thin films, approximately 100 μm thick, were prepared by compression moulding at 180°C. The sample compositions that are given are based on weight percent. The general designation LPE/ethylene copolymer of 80:20, 50:50 and 20:80 was used for all the blends, except for LPE-3/LDPE; in this blend the concentrations were 10:90, 50:50 and 90:10.

The thermal behaviour was studied by differential scanning calorimetry (d.s.c.) using a Perkin-Elmer DSC-2B that was calibrated for temperature and enthalpy of fusion using indium as a standard. Melting points were obtained at 10 K min^{-1} using 2–3 mg samples. Melting temperatures were taken as the peaks of the endotherms. In a few cases of interest the degrees of crystallinity were calculated by comparison with the heat of fusion of a perfectly crystalline polyethylene, i.e., 289 J g^{-1} [30]. The crystallization exotherms were obtained from the melt by cooling at the rate of 10 K min^{-1}. The onset of the first exothermic peak (T_0), taken as the temperature at which the peak starts to deviate from the baseline, could be identified with the crystallization rate of the sample.

RESULTS AND DISCUSSION

LPE-1/HPBD blends

Since the primary interest of this work lies in establishing the cocrystallization behaviour between linear and branched polyethylenes of different molecular constitutions, we shall discuss the results of the blends of homogeneous narrowly dispersed components separately from those composed of more heterogeneous components. Thus we first consider blends of a linear polyethylene fraction with a copolymer having a narrow molecular weight and composition distribution. As a point of reference, we examine the thermal behaviour of the model blend LPE-1 with HPBD. Before interpreting the results obtained in the solid state we need first to address the melt properties. Studies of the melt properties of the same HPBD with deuterated linear polyethylene, by small-angle neutron scattering, have shown that the melt is homogeneous at all concentrations[13]. This conclusion is corroborated for a series of blends of varying compositions which were rapidly crystallized, i.e. quenched to −78°C. The thermograms that result are plotted in *Figure 1*. Concentrations of LPE of 50% or higher lead to single peaked endotherms that are consistent with a homogeneous melt. The endotherm of the 20/80 blend

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† We wish to thank Prof. B. Crist for providing us with this sample.

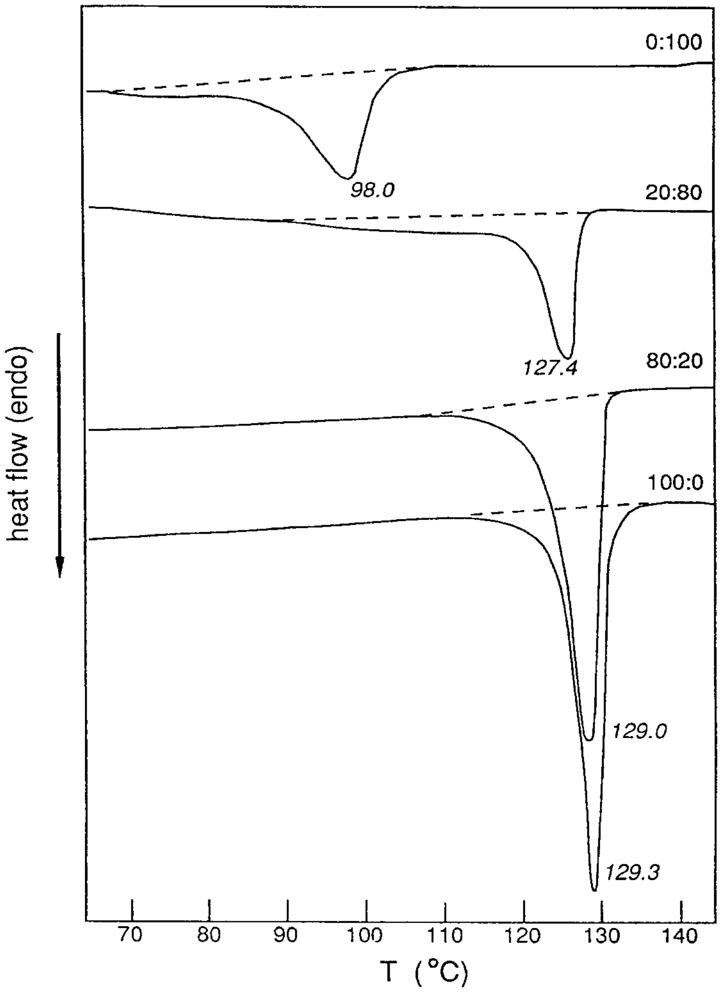


Figure 1 D.s.c. melting endotherms for LPE-1/HPBD blends rapidly quenched to − 78°C from the melt. The blend compositions are indicated

shows a major peak and a broad shoulder at the low temperature side. The shoulder appears at a higher temperature than the melting of the pure branched component. It is most probably associated with the melting of the thinnest crystallites from a broad crystallite thickness distribution. The single endotherms and the decrease of the melting temperature with increasing concentration of HPBD are also indicative of substantial cocrystallization of the two species under these crystallization conditions.

Isothermal crystallizations were also carried out with the same blends to assess the nature of the crystallites that develop. The blends were initially equilibrated in the melt at 150°C in the d.s.c. and then rapidly cooled, at the rate of 30 K min^{-1}, to the crystallization temperature (T_c) and maintained there for a predetermined time. The fusion process was subsequently recorded starting from T_c, i.e. without further cooling. However, in a few experiments the sample was rapidly quenched to 47°C, after isothermal crystallization, and the heating process was initiated from this temperature. Approximately 1 min was found to be sufficient for the melt to reach equilibrium. Longer times (e.g. 5 and 10 min) gave identical results in the subsequent endotherms. *Figure 2* gives the melting endotherms that were obtained for the 20:80 blend crystallized at 120°C for increasing crystallization time. For the endotherms (a), (b) and (c) the fusion was initiated from T_c subsequent to crystallization. In thermogram (d) the sample was cooled to 47°C after crystallization prior to the initiation of fusion. Two melting peaks are observed in the range of 120–130°C, one at approximately 128°C and the other at 125°C. The intensity of the latter increases with the crystallization time. Pure HPBD does not crystallize at this temperature, whereas the pure linear LPE-1 shows a single melting peak, at ~133°C, under the same crystallization conditions. The high temperature peak ($T_m = 127–128$°C) is associated with the melting of pure linear polyethylene crystals. Hence, the peak at 125°C can be attributed to the melting of cocrystals formed between the linear polymer and the copolymer.

A 5–6°C difference between the melting temperatures of the pure linear polyethylene and its value in the blend is observed in *Figure 2*. There are several reasons for this difference. In *Figure 1*, where for a fixed crystallization procedure the composition was varied, there is a 2°C difference between the melting temperature of linear polyethylene and its value in the 20:80 blend. In *Figure 4* (see later text), the melting temperature of the linear polymer in an 80:20 blend ($T_c = 119$°C, 20 min) is 131.4°C, 2 degrees less than the pure species. There is therefore a dilution effect on the observed melting temperature that depends on the melt mixing thermodynamics, as well as possible morphological effects. Further evidence for the influence of morphology and crystallite structure is found by varying the crystallization temperature for a fixed blend composition. For a 20:80 LPE-1/HPBD blend the difference in melting temperature is 5–6°C when crystallized at 120°C. However, after crystallization at 126°C this difference is reduced to 2–3°C. The difference can be attributed to crystallite size and perfection. Thus there are two

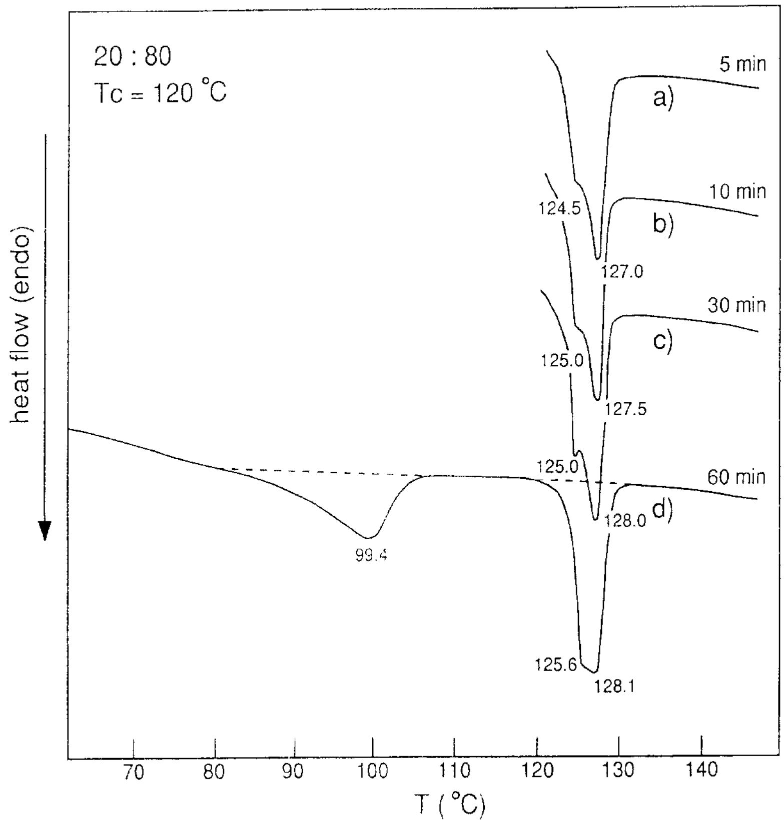


Figure 2 D.s.c. melting endotherms for a 20:80 blend of LPE-1/HPBD crystallized at 120°C for the times indicated. Fusion was started at the crystallization temperature in thermograms (a), (b) and (c) and from 47°C in thermogram (d)

explanations, or combinations thereof, that can explain the apparent discrepancy in the melting temperatures of linear polyethylene.

The endotherm peak at 99.4°C that appears in thermogram *d* corresponds to the HPBD which did not crystallize and, thus, crystallizes on quenching. The degree of crystallinity calculated from the heat of fusion of this quenching peak is ~12%. This value is significantly lower than that calculated on the basis of pure quenched HPBD (20%). This indicates that the amount of HPBD that cocrystallizes with the linear fraction is not negligible.

The possibility that the two endothermic peaks resulted from a partial melting and recrystallization process was also considered. Specifically, a 20/80 blend of the polydisperse linear polyethylene admixed with a long-chain branched polyethylene was crystallized at 116°C for 15 min. The fusion was recorded from the crystallization temperature (without previous cooling). Heating rates of 5, 10 and 20° min^{-1} were used. Two melting endotherms were observed for all heating rates. The relative intensity between the high and the low melting temperature peaks (as measured from their relative heights) remained invariant with heating rate. Thus, melt-recrystallization could be ruled out as a possible cause of the appearance of the two endotherms.

At sufficiently high crystallization temperatures, $T_c >$ 125°C, the distinct multiple peaks are no longer observed. For example, as is illustrated in *Figure 3A*, after isothermal crystallization at 126°C only a single endothermic peak is observed at the different crystallization times. The endothermic peak temperature is now only 2–3° lower than that of the pure linear polyethylene crystallites whose endotherms are shown in *Figure 3B* for comparison. There is no outward indication of cocrystallization in the thermograms of *Figure 3A*. However, the endothermic peaks are broader than those observed for the high temperature peak of *Figure 2* associated with the melting of the pure linear polyethylene crystallite. There is, therefore, the distinct possibility that a weak endothermic peak, representing cocrystals, is buried within the observed broad endothermic peak. Thermogram (d) in *Figure 3A* represents the blend after it was isothermally crystallized for 896 min and then rapidly quenched. The melting peak associated with the fusion of the pure HPBD crystallites formed during quenching also appears at ~100°C. The level of crystallinity corresponding to the quenching peak increases with increasing crystallization temperature. It is 12% for the sample crystallized at 120°C, and increases to 17% for the sample crystallized at 126°C. These values are systematically lower than the 20% crystallinity level found when the HPBD of the 20:80 mixture crystallizes separately under these conditions. They approach the crystallinity level of pure HPBD with increasing crystallization temperature. The results are, therefore, consistent with the presence of a relatively small degree of cocrystallization between the linear and the branched components that takes place in this interval of crystallization temperatures. Conversely, the amount of cocrystallization increases with decreasing crystallization temperature. The experimentally observed melting temperature of the HPBD is well below the 120–126°C interval of crystallization temperatures studied. However, sequences of this copolymer can cocrystallize with the linear polymer since its equilibrium melting temperature is ~137.7°C[31,32]. It is, thus, theoretically possible to crystallize sequences of this copolymer at temperatures below this value.

A similar cocrystallization behaviour with increasing crystallization temperature is found in blends having higher

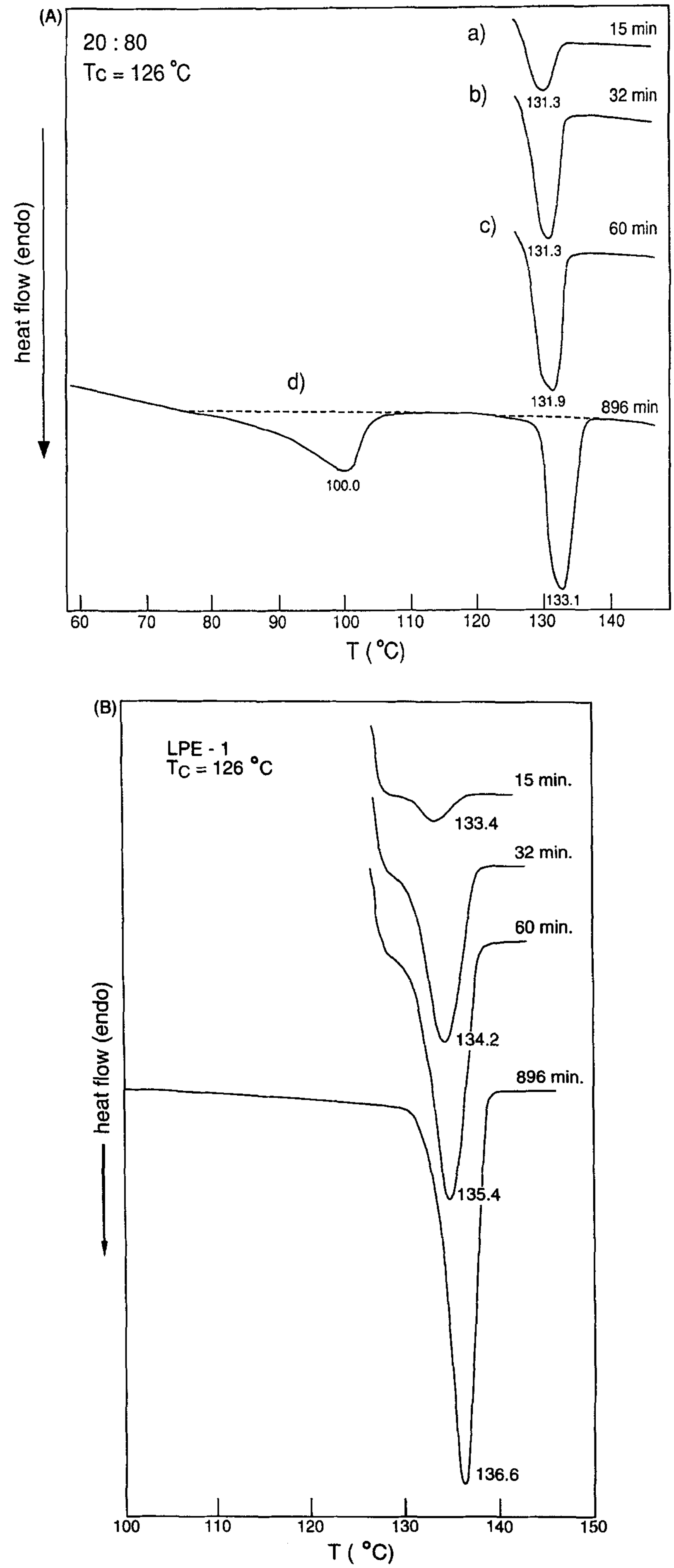


Figure 3 (A) D.s.c. melting endotherms for a 20:80 blend of LPE-1/HPBD crystallized at 126°C for the times indicated. In (a), (b) and (c) melting started from 126°C. In (d) melting started from 47°C. (B) D.s.c. melting endotherms for linear polyethylene crystallized at 126°C for the times indicated

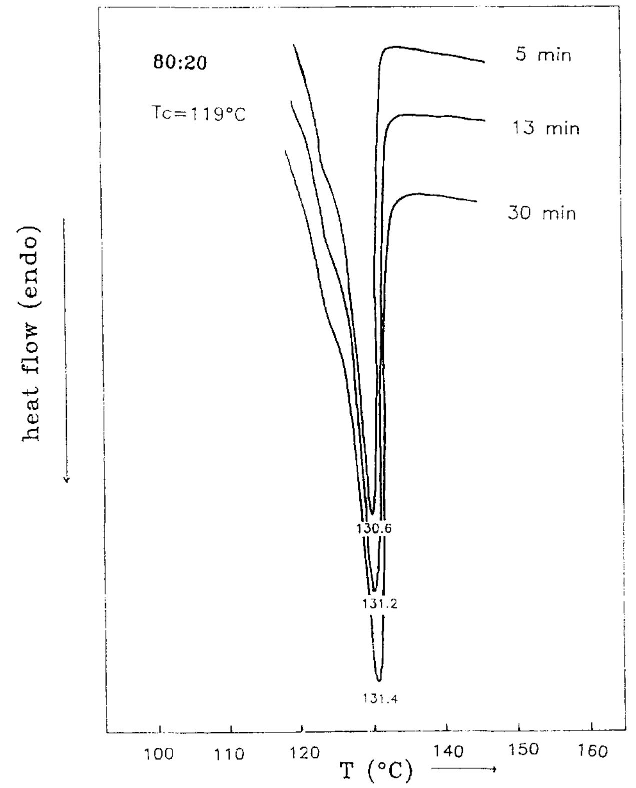


Figure 4 D.s.c. melting endotherms for an 80:20 blend of LPE-1/HPBD crystallized at 119°C for the times indicated. In all cases, fusion was started at the crystallization temperature

concentrations of linear polyethylene. 50:50 blends crystallized at a relatively low temperature, 118°C, clearly show two melting peaks. There is a low temperature peak at ~123°C that can be assigned to the melting of cocrystals and a high temperature peak corresponding to the melting of pure linear polyethylene. The endotherms resulting from crystallization at 124°C follow a similar trend. Single broad endotherms are observed at the beginning of the crystallization. However, a well developed shoulder develops with time, indicating that there is another melting component that can be attributed to cocrystals.

Blends rich in linear polyethylene (80:20) were also crystallized at temperatures intermediate between the melting temperatures of each of the components. A typical set of endotherms is given in *Figure 4* for this blend, which crystallized at $T_c \approx 119$°C. This crystallization temperature is relatively low for isothermal crystallization of this blend. A major, single melting endotherm is associated with the melting of crystals formed mainly from the pure linear species. There is also a weak shoulder appearing in the low temperature side of the thermograms. The intensity of this shoulder decreases with increasing crystallization temperature, following the trend observed in other compositional blends of the sample species. A comparison between the melting temperatures and degrees of crystallinity of this blend and that of the pure linear fraction, crystallized under the same conditions, indicates that, if there is cocrystallization of the components at this composition and temperature, the amount is very small. The pure LPE-1 crystallized at 119°C for the same length of time as that illustrated in *Figure 4* gives single melting peaks at temperatures between 131.6°C and 132.4°C and degrees of crystallinity ranging from 48% to 53%. The 80:20 blend crystallized at 119°C develops a degree of crystallinity of approximately 43%. This is the value expected for the linear component, assuming that only this component has crystallized. Thus the observed endothermic peak in this blend can be assigned primarily to the melting of pure LPE-1 crystals.

A similar behaviour is observed in 80:20 blends crystallized at higher crystallization temperatures. At these temperatures the weak shoulder was no longer observed. We can conclude that blends with a high concentration of the linear component tend to form segregated crystals under isothermal crystallization conditions, especially when crystallized at relatively high temperatures. The conclusion that cocrystallization decreases with increasing LPE concentration is substantiated by the behaviour of the low temperature shoulders at other compositions. An example is found in thermogram (c) of *Figure 2* for the 20:80 blend.

LPE-1/E–H blends

The influence of the molecular weight distribution and the type of copolymer was studied in blends of the same narrow fraction of linear PE with a metallocene-catalysed ethylene–hexene (E–H). This copolymer has a broader molecular weight distribution than HPBD while still maintaining a narrow composition distribution. A set of typical thermograms of different LPE-1/E–H compositions, crystallized at different temperatures, is given in *Figure 5*. The thermogram of pure E–H copolymer brought rapidly from the melt to 47°C inside the d.s.c. is also included in the figure. The shape and peak temperature of the endotherm illustrated for the pure copolymer are very similar to the quenching peaks found in the copolymer-rich blends. When the concentration of the copolymer is decreased, the quenching peak of the uncrystallized copolymers appears only as a shoulder in the thermogram. This effect is quite evident in the thermogram of the 80:20 blend crystallized at 118°C. The quenched peak in the thermogram for 124°C crystallization mainly represents the uncrystallized linear component. In these experiments the blends were crystallized isothermally to complete transformation and then cooled to 47°C prior to commencing the heating cycle. The quenched peaks, marked Q, are easily identified in the thermograms. The pattern of endotherms in this figure is qualitatively very similar to the results of the LPE-1/HPBD blends. At each composition double melting peaks are easily discerned in the blends that were crystallized at the lower T_c; viz. 20:80, 115°C; 50:50, 117°C; 80:20, 118°C. Single broad endothermic peaks are observed for the highest isothermal crystallization temperatures of each blend. Thus, in this type of blend, the amount of cocrystallization also decreases with increased crystallization temperature. However, the widths of the peaks are broader for the higher crystallization temperatures as compared to the high temperature endotherm that results from crystallization at the lower temperature. The broadening of the endotherms is more accentuated for the 20:80 and 50:50 blends. There is, therefore, some indication of small amounts of cocrystallites at these compositions in the high crystallization temperature interval. In the 50:50 blend, crystallized at 123°C, the Q peak area indicates a crystallinity level of 12%, comparable to that of the quenched pure E–H copolymer (13%).

The thermograms in *Figure 5* also show that there is a shift of the quenching peak to slightly higher temperatures when the crystallization temperature increases. This shift can be explained by the fact that the melting temperature of the copolymer is related to the melt composition after the isothermal crystallization. The residual melt composition

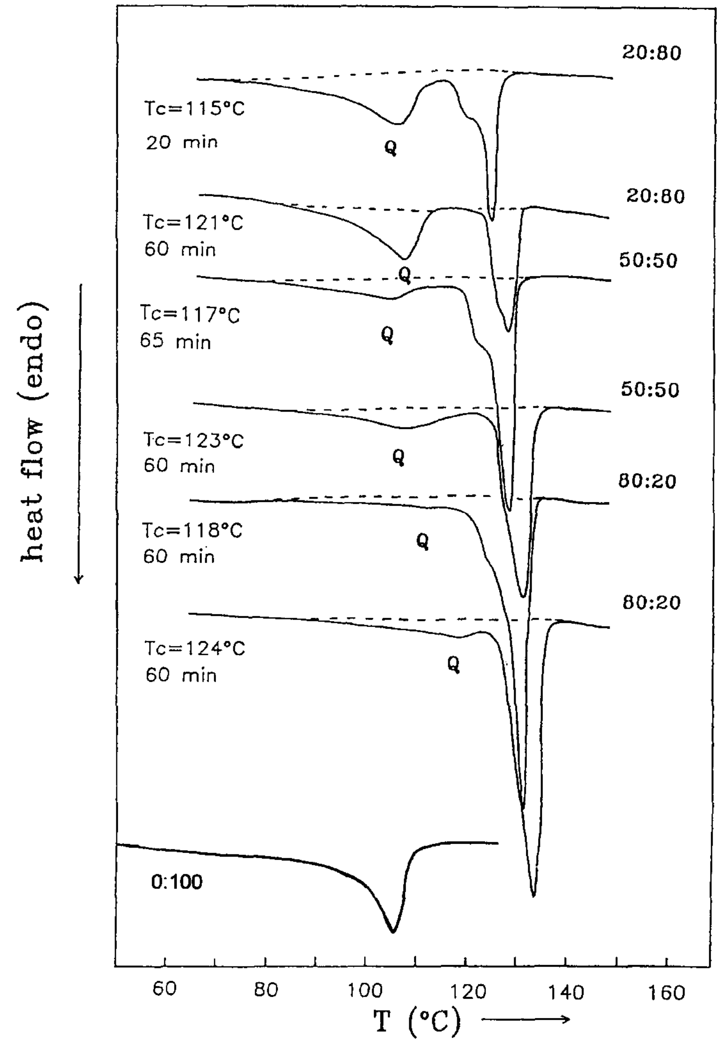


Figure 5 D.s.c. melting endotherms for various compositions of LPE-1/E-H blends. Two different crystallization temperatures are illustrated for each composition. Q indicates the quenching peak. Lower thermograms: pure E-H. All samples quenched to 47°C

depends on the amount of cocrystallization that has occurred. At high crystallization temperatures most of the long sequences of the copolymer, which at low temperatures could form cocrystals, will be unable to cocrystallize because of kinetic requirements. However, they can crystallize during quenching and thus produce the shift of the melting peak to higher temperatures.

LPE-1/E-B blends

We consider next the thermal behaviour of the LPE-1/E-B blend. The E-B copolymer (produced with a Ziegler-Natta-type catalyst) is much more polydisperse with respect to molecular weight and composition than the two copolymers that were discussed previously. As indicated in *Table 1*, this copolymer has a weight-average molecular weight and nominal branching content that are similar to those of ethylene-hexene copolymer and are comparable to that of hydrogenated poly(butadiene). However, LLDPEs prepared with a Ziegler-Natta-type catalyst have very broad molecular weight and composition distributions[33,34]. In particular, the shorter chains have a much higher than nominal comonomer branching content, while the composition of the longer molecular components approaches that of the linear chains[33,34].

Figure 6 gives some representative thermograms of this blend that were obtained after isothermal crystallization at the temperatures indicated and were then cooled prior to heating. The thermogram for the pure copolymer, crystallized in a similar manner to E-B, is also included in the figure. The relation between the blend thermograms and the pure copolymer is very similar to that of the E-B blends. The results are similar to those found in the other copolymer blends studied here. The blends crystallized at the lowest temperatures again show distinct double melting endotherms after isothermal crystallization. The cocrystallization tendency, as manifested by the character of the endotherms, decreases with increasing crystallization temperature and the concentration of the linear component. The quenching peaks are well defined in the thermograms illustrated in *Figure 6*. In spite of the extremes in polydispersity of the LLDPEs studied here, the general trends of isothermal cocrystallization with a linear fraction of the three types of blend are surprisingly similar to one another. On the basis of the character of the melting endotherms, the extent of cocrystallization decreases in the blends richer in the linear component.

This result contrasts with recent studies on slowly cooled blends of a polydisperse deuterated linear polyethylene and an LLDPE (presumably of the Ziegler type)[23,35]. Using mainly infrared techniques, it was concluded that the extent of cocrystallization increased with increasing concentration of the linear component. The conclusion was based on a

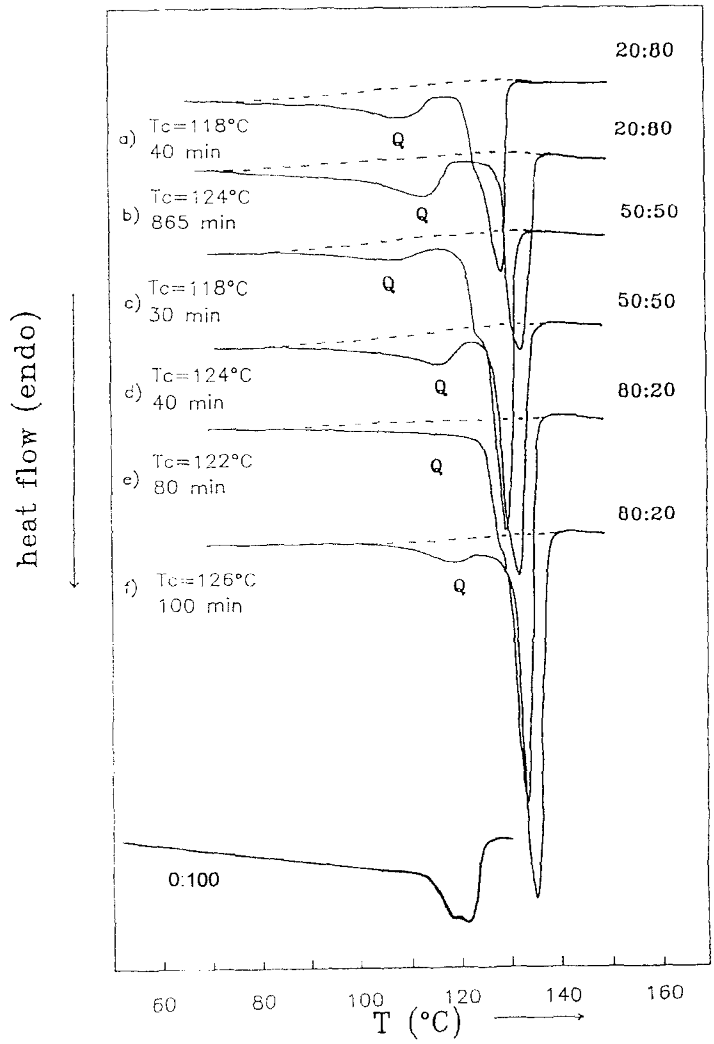


Figure 6 D.s.c. melting endotherms for various compositions of LPE-1/E–B blends. Two different temperatures are illustrated for each composition. Q indicates the quenching peak. Lower thermograms: pure E–B. All samples quenched to 47°C

quantitative analysis of the doublet component from the coupled CH_2–CH_2 or CD_2–CD_2 in the crystalline lamellae or in segregated crystals, as well as from the singlet originating from an isolated D or H stem surrounded by the opposite isotope. A 75/25 linear/LLDPE blend that was slowly crystallized showed a singlet of the rocking CH_2 crystalline mode ($\sim 725\ cm^{-1}$) at room temperature. This result is consistent with a statistical dispersion of the copolymer in a crystalline linear polymer environment. The doublet of the CD_2 rocking band for the same blend suggests the presence of a second population of lamellar crystals formed from the pure deuterated linear component. Due to the limited number of linear crystalline sequences in the copolymer, compared to the linear component, one would expect that the cocrystals would be significantly thinner than the crystals from the pure linear component. There is no indication of this happening[24,35]. As matters stand, there is an apparent discrepancy with blends of this type that have a high concentration of the linear component.

In a subsequent paper isothermal crystallization kinetics were reported using time-resolved SAXS measurements[26]. However, the crystallization temperatures used were not given. Instead, the kinetics of the pure components and those of the 50/50 blends were referred to a fixed, pseudo-undercooling ΔT that was based on the peak crystallization temperature T_c^0, obtained by dynamic cooling of the sample at a constant cooling rate. Since T_c^0 of the blend differs from that of the pure components, the crystallization temperature used to determine a fixed ΔT in the kinetic studies would logically be different. Thus it is difficult to compare Tashiro's kinetic results with those of the present work.

Tashiro *et al.*[26] explained the cocrystallization on the basis of crystallization kinetics and the closeness of the crystallization rates of each component. The important conclusion was reached that a major factor governing cocrystallization of mixtures of linear and branched components is the similarity of the crystallization rates of the pure components. This conclusion agrees with that reached previously with work on mixtures of linear and low density polyethylenes[36]. The proximity of the crystallization rates of the linear and branched polyethylenes will be proportional to the dilution effect of the branched component on the melting temperature of the linear one when crystallized from a homogeneous melt. The effect of this dilution on the initial crystallization temperature of the linear polyethylene, and the type of LLDPE, control the cocrystallization behaviour of slowly crystallized blends.

This point is illustrated in *Figure 7*, in which the temperature of the onset of crystallization (T_o) is plotted against copolymer composition for blends crystallized from the melt in the d.s.c. at $10\ K\ min^{-1}$. T_o can be taken as a measure of the crystallization rate and reflects the behaviour

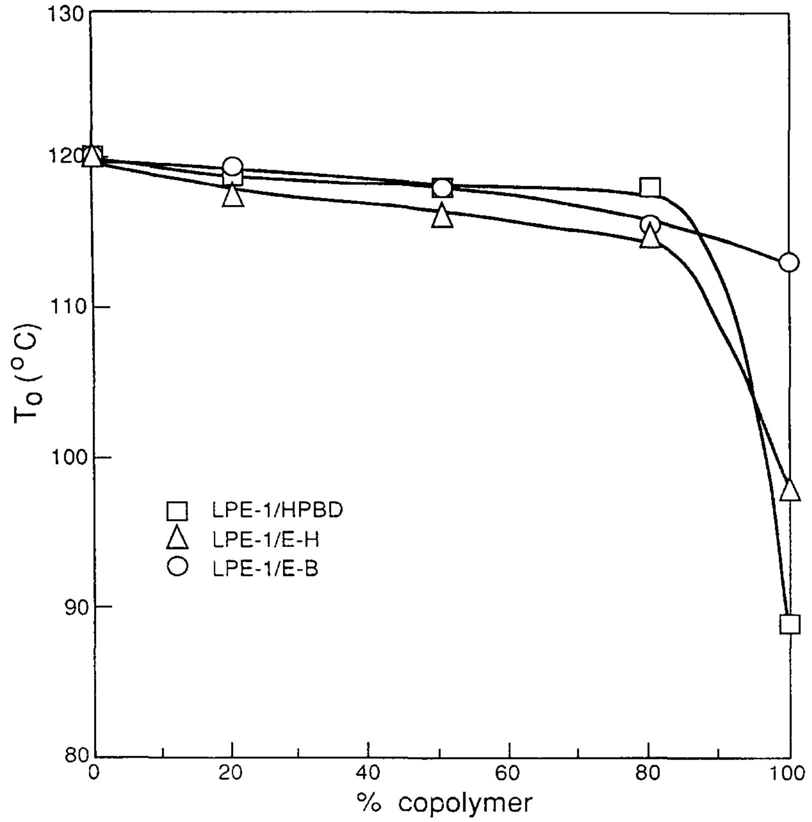


Figure 7 The dependence of crystallization temperatures, T_0, on composition for LPE-1 blends with different types of copolymer. Crystallization was carried out by cooling at 10 K min^{-1} from the melt

of the most rapidly crystallizing entity. The effect of the branched component on T_0 is quite different for the LPE-1/E–B blend than for the others. In this blend, the difference in the rates of crystallization of the pure components is smaller than in the other mixtures. For example, the addition of about 75% of the E–B to the linear component brings the T_0 of the blend to only one degree above that of the branched component. This in effect causes an 85% dilution of the linear PE. On the other hand, only a 6% dilution effect of the melting temperature of the linear component is observed for the HPBD blend of the same composition. The decrease of T_0 with increasing concentration of the branched component should favour cocrystallization, in agreement with the results found after isothermal crystallization. There is also an influence of the E–H metallocene-type copolymer on the crystallization kinetics of the linear polyethylene. T_0 decreases by about 5°, from 120°C to 115°C, for the 75/25 blend. Taking 115°C as the crystallization temperature of the linear in the 75/25 blend, this temperature is obviously well removed from the 98°C crystallization temperature of the pure E–H component. This greater difference in crystallization rates, as compared to the LPE-1/E–B system, hinders extensive cocrystallization under isothermal crystallization.

The LPE-1/HPBD blend presents a more extreme case. Here there is a negligible influence of the copolymer species on the crystallization kinetics of the linear polyethylene when cooled at 10 K min^{-1}. The difference in T_0 between the blends and the copolymer is the largest in the three systems studied. Thus the degree of cocrystallization should be the smallest, as is observed.

The character of the T_0–composition plot of *Figure 7* allows one to scale qualitatively the degree of cocrystallization of these three mixtures on the basis of differences in the T_0 values between the blend and the pure components. Thus, the LPE-1/E–B blend shows the greater degree of cocrystallization, followed by LPE-1/E–H (metallocene) and LPE-1/HPBD. The cocrystallizability is driven by the molecular constitution of the copolymer. For example, the heterogeneity of molecular and composition distribution of the E–B copolymer contrasts with the more homogeneous metallocene sample and the narrow distributions that characterize HPBD. The longer chains, which are lightly branched or even unbranched, of the E–B copolymer are responsible for its high T_0 compared to the E–H copolymer having the same molecular weight and branching content. When crystallization of a linear/E–B blend takes place under slow cooling conditions, the faster crystallizing chains of the E–B copolymer (the almost linear ones) will have the opportunity to match the crystallization rate of the linear chains of the homopolymer, thus forming a cocrystal. This possibility is obviously more restricted in blends with more homogeneous copolymers such as E–H or HPBD, where the chains have a uniform branching content.

LPE-3/star HPBD blends

The crystallization behaviour of isothermally crystallized blends of linear and long-chain branched polyethylenes (LDPE) has also been studied. A three-arm star hydrogenated poly(butadiene) has been taken as a model reference system for the LDPE, since it has a very narrow molecular weight and composition distribution. Except for the junction point of the three arms, the molecular characteristics of the star (see *Table 1*) are virtually identical to those of the hydrogenated polybutadiene previously discussed (HPBD).

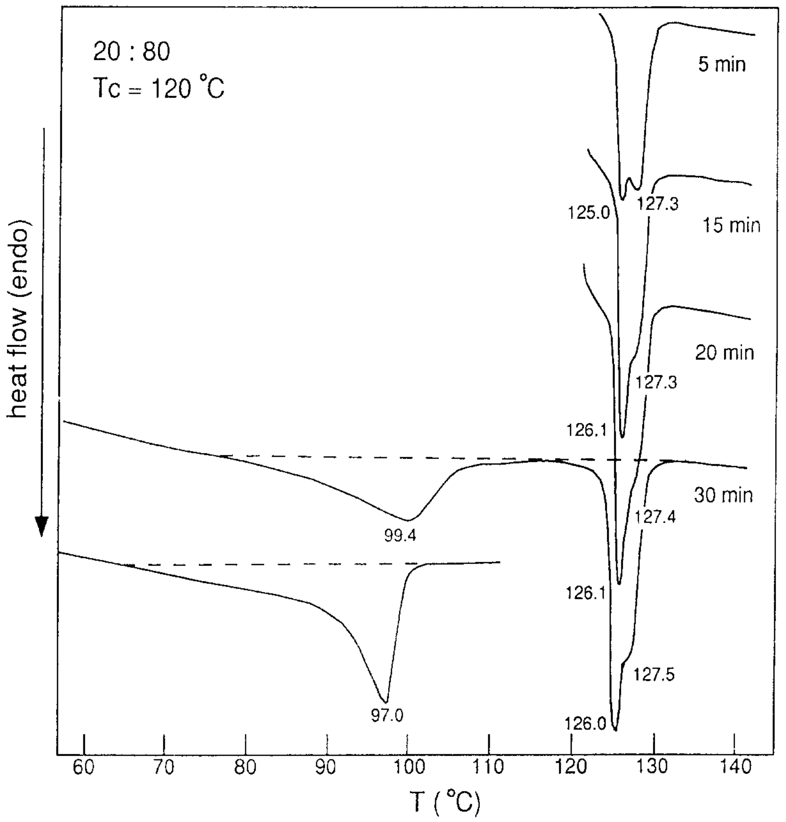


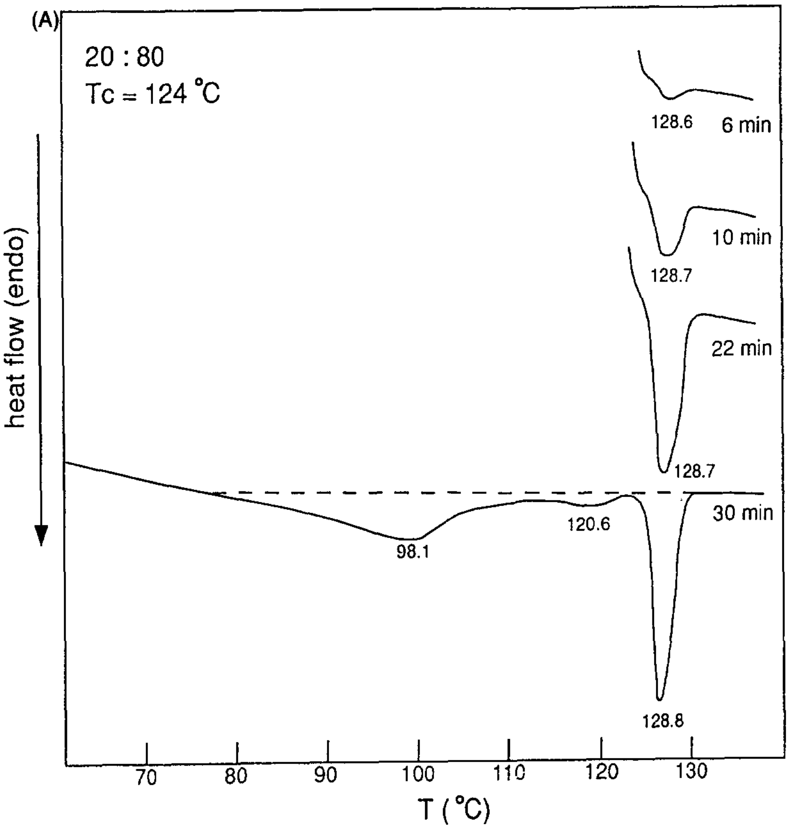
Figure 8 D.s.c. melting endotherms for a 20:80 blend of LPE-3/star HPBD crystallized at 120°C for the times indicated. Melting started either from the crystallization temperature or from 47°C. The melting endotherm of the pure quenched star HPBD is given in the insert

Melting thermograms of the 20:80 LPE-3–star HPBD blend, obtained after isothermal crystallization at 120°C for different times, are illustrated in *Figure 8*. The melting endotherm of the rapidly crystallized star molecule is given in the insert of this figure. Independent crystallization of the pure components at 120°C resulted in single endotherms with peak temperatures between 133°C and 134°C for the linear PE and lack of crystallization for the star species. Once more, two melting peaks are observed in the blends. Thus, we again take the peak at 126°C to result from the melting of cocrystals and that at ~127.4°C from the melting of crystals formed from the pure linear species. The relative intensity of the peak at 126°C, as compared to the peak associated with melting of the linear PE crystals, is greater than that observed for the blends previously described (see *Figures 2, 5 and 6*). This result suggests that a larger amount of cocrystallization takes place between these two species. However, the amount of cocrystallization at this relatively high crystallization temperature is actually small since most of the branched component crystallizes separately in the quenching process, as is illustrated in the figure. Higher crystallization temperatures result in the typical broad single endotherm that is primarily associated with a separate crystallization of the linear component. This point is illustrated in *Figure 9A* for T_c = 124°C for the 20/80 blends. A peculiarity of these blends is the development of a second peak at about 120°C when the sample is quenched to room temperature prior to melting. This peak can be attributed to the melting of cocrystals that are formed from the uncrystallized components during cooling. The existence of such cocrystals can be attributed to the slow diffusion of the star molecule. For comparison purposes, the thermal behaviour of the pure linear component is illustrated in *Figure 9B*. As is indicated in this figure, a peak at ~127°C corresponds to the melting of crystals formed during rapid crystallization.

The peak at 98.1°C in the lowest thermogram of *Figure 9A* corresponds to the crystals formed by the pure star HPBD. A comparison of the degree of crystallinity of this quenching peak (16%) with the theoretically calculated value, assuming complete segregation of the star HPBD crystals (21%), allows for a quantitative measure of the small portion of the copolymer that cocrystallizes with the LPE during cooling. The cocrystallization behaviour of blends with increasing concentration of the linear component follows the trends explained above for the linear PE/branched blends.

LPE-2/HPBD blends

The influence of polydispersity of the linear component on isothermal crystallization was studied in blends of LPE-2 (M_w = 76 700, M_w/M_n = 3.33) and HPBD. The thermal analysis indicates that cocrystallization is slightly favoured by the polydispersity of the linear component. For example, as is shown in *Figure 10*, after crystallization of a 20:80 linear/HPBD blend at 118°C, the thermograms display cocrystal peaks at ~124°C. Pure LPE-2 crystallizes at the same temperature and, for the same length of time, displays single endotherms peaked at 131–132°C. These peaks, corresponding to the cocrystals, are better defined than if the linear component had a narrow molecular weight distribution with approximately the same M_w (see *Figure 2*). The fact that these differences are small is consistent with the crystallization kinetics. The plot in *Figure 11* of T_0 *versus* the HPBD content of the two types of slowly cooled blend shows that there is also a very small difference in rates of crystallization between the two systems. As was found in the previous blends studied here, increasing the crystallization temperature leads to single broad endotherms and



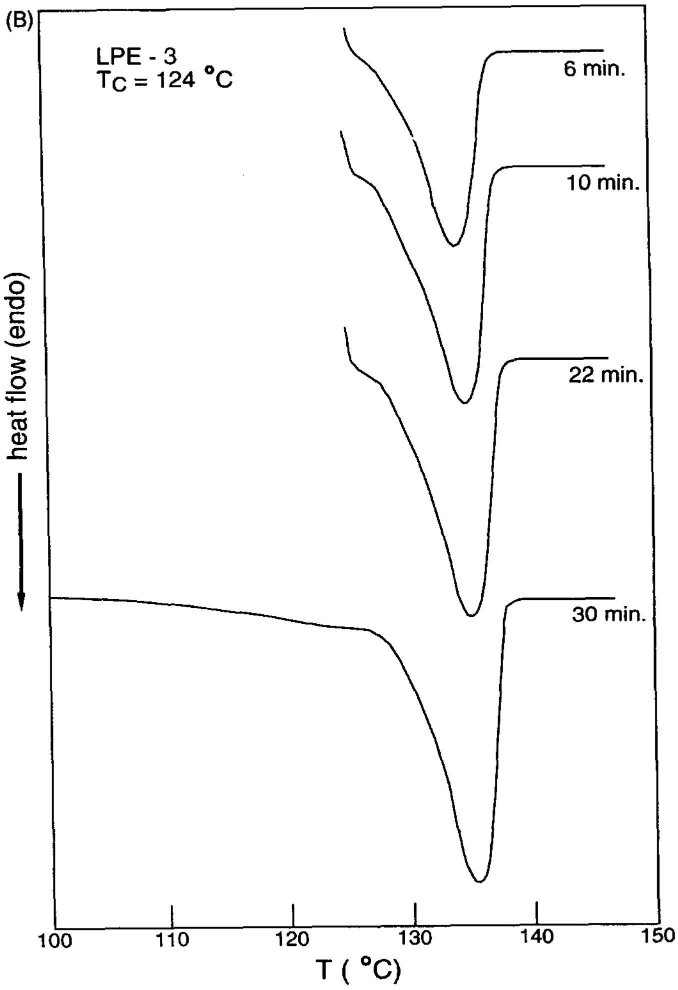


Figure 9 (A) D.s.c. melting endotherms for a 20:80 blend of LPE-3/star HPBD crystallized at 124°C for the times indicated. Melting started either from the crystallization temperature or from 47°C. (B) D.s.c. melting endotherms for linear polyethylene LPE-3 crystallized at 124°C for the times indicated

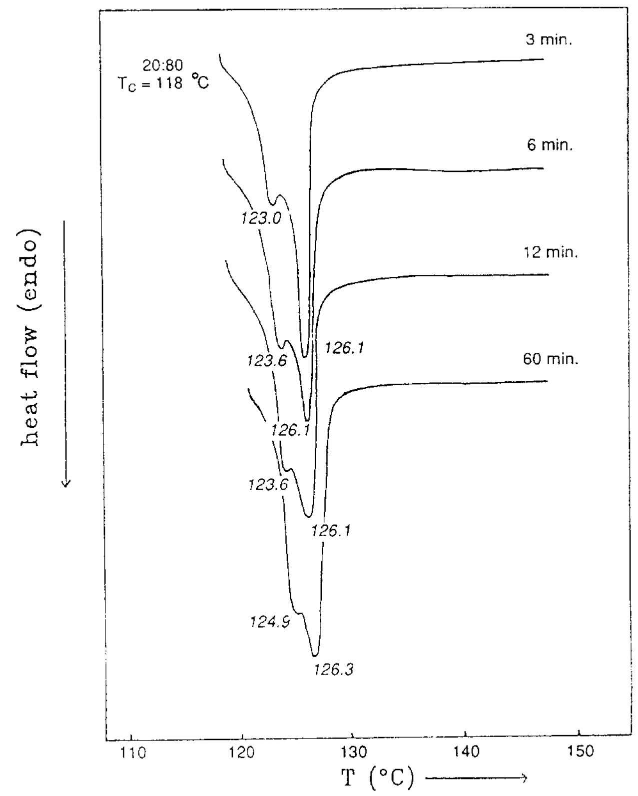


Figure 10 D.s.c. melting endotherms for a 20:80 blend of LPE-2/HPBD crystallized at 118°C for various times. Heating started at the crystallization temperature

thus either to a reduction in, or a lack of, cocrystallization. A diminished amount of cocrystallization is also observed with dilution of the branched component.

LPE-4/LDPE blends

The final blend studied here consisted of a polydisperse linear polyethylene (LPE-4) admixed with a polydisperse long-chain branched polyethylene that was synthesized under high pressure (LDPE). The weight-average molecular weights of each component are effectively the same. The thermograms obtained for the 10:90 blend, crystallized isothermally at 116°C, are given in *Figure 12*. Two well developed melting peaks are observed. The high temperature peak at ~127°C can again be assigned to the melting of the pure linear polyethylene crystals while the low temperature peak at ~124°C is assigned to cocrystals formed from both components. Thus a partial cocrystallization takes place in these blends with a high concentration of LDPE when they are crystallized isothermally at relatively low temperatures. In a recent work using very similar blends[37], the cocrystal peak was attributed to LDPE crystals nucleated on the surface of the LPE crystals.

When the 50:50 blend is crystallized at 119°C then, as is shown in *Figure 13*, only a single melting peak at ~129°C is observed in the samples heated without cooling, subsequent to crystallization. The lowest thermogram in the figure is for a sample cooled to 47°C prior to heating. In this case a second melting peak at 108°C is observed, which is readily assigned to the fusion of the pure LDPE crystals, T_m = 107°C, formed in this process. The degree of crystallinity of this peak is 14%, which agrees quite well with the value of 15% calculated assuming segregated crystals. In contrast, as illustrated in *Figure 14*, the LPE-3-star HPBD blend of similar concentration, crystallized at the

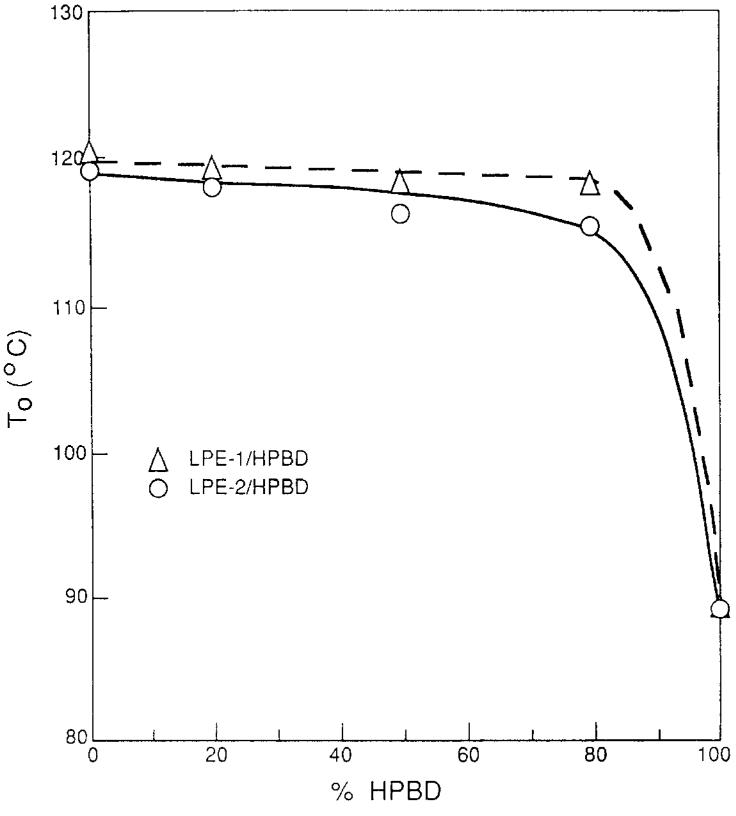


Figure 11 The dependence of crystallization temperature on compositions, for blends of LPEs with HPBD. Narrow (LPE-1) and broader (LPE-2) molecular weight distributions are compared. Cooling rate 10 K min^{-1}

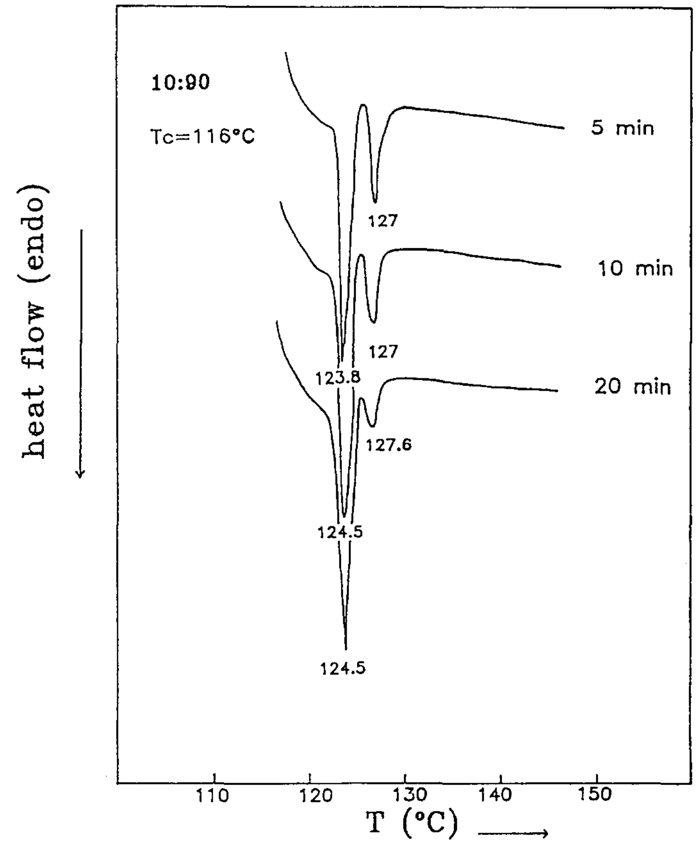


Figure 12 D.s.c. melting endotherms for a 10:90 blend of LPE-4/LDPE crystallized at 116°C for the times indicated. Melting started at 116°C

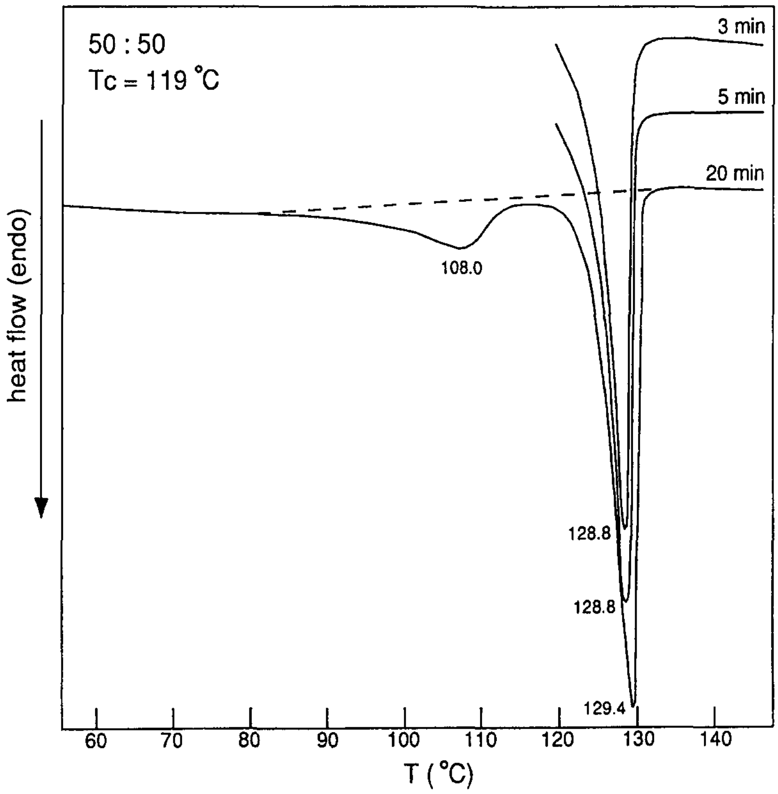


Figure 13 D.s.c. melting endotherms for a 50:50 blend of LPE-4/LDPE crystallized at 119°C for various times. Melting started from either the crystallization temperature or from 47°C

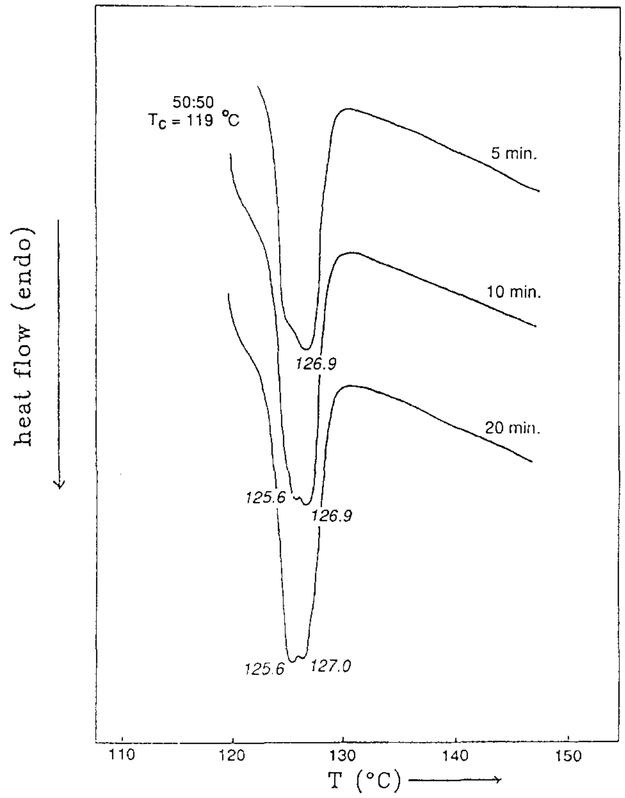


Figure 14 D.s.c. melting endotherms for a 50:50 blend of LPE-3/star HPBD crystallized at 119°C for the times indicated. Melting started at the crystallization temperature

same temperature, shows double melting peaks at ~125°C and 127°C. These results are indicative of a partial cocrystallization. The polydispersity of the long chain branched polymer reduces the tendency for cocrystallization relative to the model monodisperse star HPBD. The latter component produces a higher degree of isothermal cocrystallization in the blend and favours further cocrystallization during quenching.

CONCLUSIONS

The conditions under which isothermal cocrystallization takes place in blends of linear and branched polyethylenes have been determined. The results are based on the analysis of data obtained with model compounds, taking into account the molecular structure of the components. A key factor that governs the extent of cocrystallization is the closeness of crystallization rates of each component. Increasing the copolymer concentration reduces the crystallization rate of a blend and progressively moves it closer to that of the copolymer. Consequently, under these conditions a greater amount of cocrystallization will be achieved. The amount of cocrystallization is favoured at the lowest isothermal crystallization temperatures and is maximized under quenching conditions.

Partial cocrystallization is also found after slowly cooled conditions or isothermal crystallizations. The cocrystallization is also influenced by the branching composition of the copolymer[8,17]. Besides composition, the molecular structure and branching distribution have a definite effect on the cocrystallization. Cocrystallization is slightly favoured in mixtures of unfractionated, polydisperse ethylene copolymers. The polydispersity of the linear component, or that of the long chain branched polyethylene, does not seem to affect the cocrystallization to a measurable degree.

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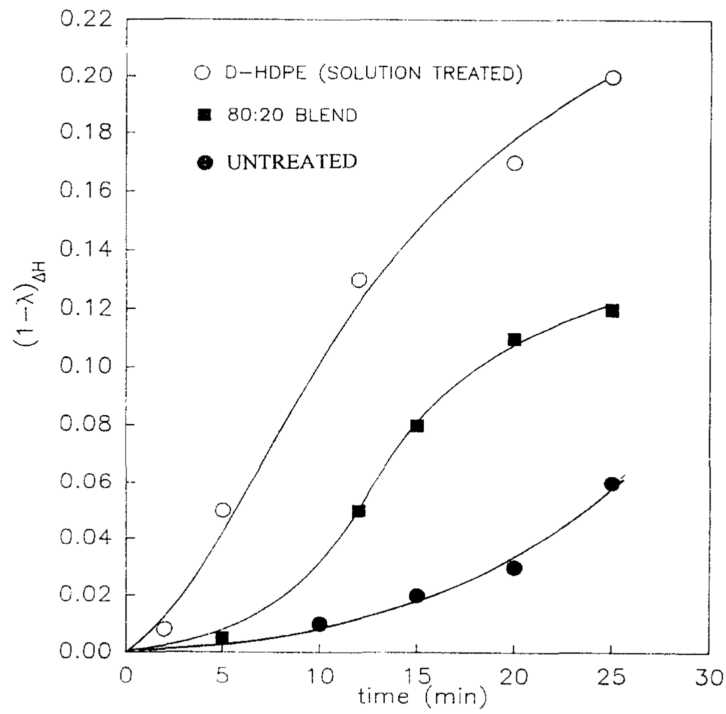

Figure 15 Degree of crystallinity $(1 - \lambda)_{\Delta H}$ as a function of time for isothermal crystallization at 118°C of a polydisperse deuterated linear polyethylene (D-HDPE) and the 80:20 blend of D-HDPE/HPBD. ○, solvent treated D-HDPE; ●, untreated original D-HDPE; ■, blend

experiments. MJG wishes to acknowledge support from the National Research Council of Argentina (CONICET). RGA acknowledges support from the Exxon Education Foundation.

In a recent paper, Tashiro[26,35] reported that the crystallization rates of blends composed of polydisperse linear and branched polyethylenes are appreciably higher than that of the pure components. This unexpected result was explained by invoking the concept that the thermodynamic compatibilities of the components were increased. It should be noted, however, that the blends were prepared from solution whereas the pure components were not given any solvent treatment. In the course of the study of the blends used in this work, we found similar results when the linear component was polydisperse and was not given the same solution treatment as the blend.

A summary of these experiments is illustrated in *Figure 15*. Here the increase in the degree of crystallinity with time is plotted for isothermal crystallization at 118°C. Shown in the figure are data for a polydisperse deuterated linear polyethylene (D-HDPE) ($M_w = 104\,600$; $M_w/M_n = 5.6$) without any solvent treatment and after being dissolved and precipitated in the same solvent as was used to prepare its blend with the branched polymer. The isotherm corresponding to the 80:20 blend of this linear polyethylene and hydrogenated polybutadiene is also shown for comparison. The non-solvent treated polyethylene crystallizes at a much slower rate than the treated sample. It also crystallizes slower than the blend. In fact, the crystallization rate of the blend lies between those of the solvent and non-solvent treated linear polyethylenes. These results explain the observations of Tashiro *et al.*[35,38]. Thus, to avoid the possibility of misinterpreting the kinetic results, it is important that both the pure components and the blends be subjected to the same preparative treatments.

Now that the basis for the apparent differences in rate has been established, it is of interest to consider possible reasons for the role played by solvent treatment. In this connection we have also found that the linear polyethylenes having narrow molecular weight distributions (LPE-1 and LPE-3) did not show this effect. In this case both solvent-treated and untreated polyethylenes had the same crystallization rates. These latter results suggest that some type of molecular weight fractionation probably takes place during the solvent treatment. Removal of the low molecular weight species is very likely to occur under these circumstances. In turn, the change in distribution will influence the crystallization rate.

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