Study of Polyethylene Blends by Differential Scanning Calorimetry

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Synopsis

The melting behaviors of linear and branched polyethylene blends were studied using a Perkin-Elmer DSC-1B differential scanning calorimeter. Three endothermic peaks were occasionally observed in the DSC thermogram on polyethylene blends which had not been subjected to any isothermal annealing. The nature of the third intermediate temperature peak is discussed in relation to the prior cooling rate, the blend composition and the molecular structures of both components. The results appear to indicate that the intermediate peak is associated with the fusion of the hybrid crystallites of linear and branched polyethylenes. These hybrid crystallites seem to be formed on the rapid cooling of lean linear polyethylene blends. Blends containing low molecular weight branched polyethylene seem inclined to form the hybrid crystallites.

INTRODUCTION

Melting thermal behaviors of crystalline polymers have been studied by many workers, and several of them have observed and reported multiple peaked melting thermograms of polyethylene, polyethylene blends, and ethylene copolymers.[1–8]

Clampitt[1,2] reported a "cocrystal peak" on the melting thermogram of linear and branched polyethylene blends after isothermal annealing. At about the same time, Gray and Casey[3] demonstrated a multiple-peaked thermogram for the similar system after stepwise annealing.

In the course of our work with similar blends, some interesting melting phenomena were observed, which will be described in this paper.

EXPERIMENTAL

The thermal analyses were carried out by a Perkin-Elmer DSC-1B unit on 0.5–5.0 mg samples in covered sample pans.

Each thermogram was calibrated with indium as internal temperature standard in the reference holder. In general, samples were cut out from melt-pressed films by a cork borer. In order to be free from unknown thermal histories, samples were heated above their melting points and then cooled at various well-defined rates. The samples covered with the

TABLE I
Pertinent Properties of Samples[a]

Sample	Linear polyethylenes				Branched polyethylenes			
	Melt index, dg/min	Density, g/cc	Methyl content, per 1000 carbons	Melting point, °K	Melt index, dg/min	Density, g/cc	Methyl content, per 1000 carbons	Melting point, °K
A	5.9	0.962	5.5	398	19.8	0.923	31.4	379
B	5.9	0.962	5.5	398	5.4	0.922	27.3	379
C	5.9	0.962	5.5	398	1.1	0.923	25.7	381
D	5.9	0.962	5.5	398	0.35	0.922	25.6	380
E	5.9	0.962	5.5	398	20.6	0.926	26.1	382
F	5.9	0.962	5.5	398	1.0	0.931	18.0	384
G	0.41	0.956	1.7	404	5.4	0.922	27.3	379
H	0.75	0.965	1.3	404	5.4	0.922	27.3	379
I	0.39	0.959	3.4	401	5.4	0.922	27.3	379

[a] Melt index and density were measured by ASTM D1238-65T and ASTM D1505-63T, respectively; melting points were measured as the peak of the DSC melting endotherm at a heating rate of 16°C/min for the samples which were cooled down to room temperature from melt at 16°C/min.

aluminum disk were gently pressed while molten to ensure good contact with the detection area.

The samples cooled down to room temperature were then annealed at 45°C for 3 min and then cooled down to room temperature. This annealing was done for the purpose of clearly defining the melting range of branched polyethylene; it was confirmed to have no effect on the occurrence of the third intermediate temperature peak described below.

The melting thermogram was obtained at a heating rate of 16°C/min in nitrogen atmosphere.

Sample blend components were commercially available linear and branched polyethylenes listed in Table I.

Experimental blends were usually prepared by solution blending. A 0.33% by weight solution was prepared by dissolving 2 g of the blend components in 600 ml xylene containing an oxidation inhibitor, 2,6-di-*tert*-butyl-4-methylphenol and stirring for 30 min at 120°C. The polymer
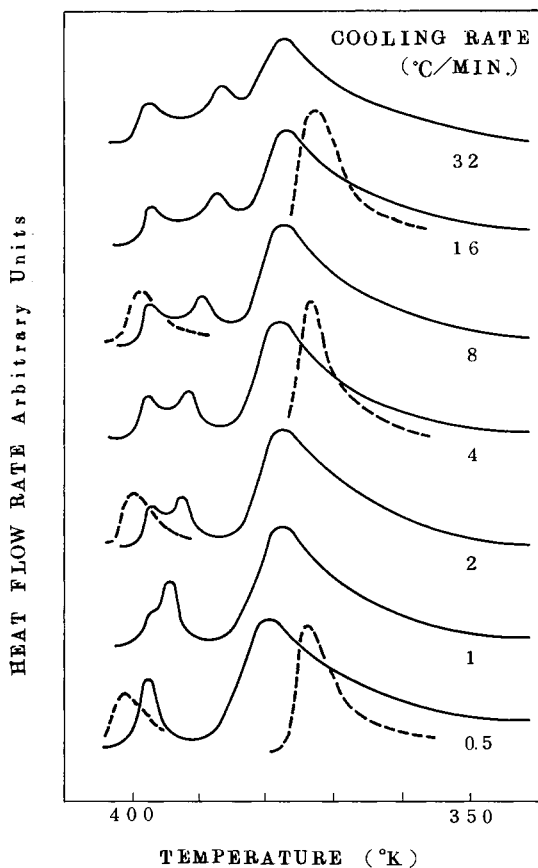

Fig. 1. Melting thermograms for sample A and starting materials at various prior cooling rates: (——) sample A; (– – –) starting materials. Scanning rate 160°C/min.

solution was poured into methanol, then the polymer precipitated from methanol was filtered, washed repeatedly with methanol, and dried in a vacuum oven.

Blends of 5%, 10%, 20%, 30%, and 50% by weight of linear polyethylene with the balances of branched polyethylene were prepared. Some blends were also prepared by melt blending of both components in a Brabender Plastograph (Type PL 3S) at 165° to 170°C for 20 min at 170 rpm. The experimental results with melt blends did not differ appreciably from those with solution blends.

RESULTS

Figure 1 shows the melting thermograms of the experimental blends prepared from 5% by weight of a linear polyethylene having a melt index of 5.9 and from 95% by weight of a branched polyethylene having a melt index
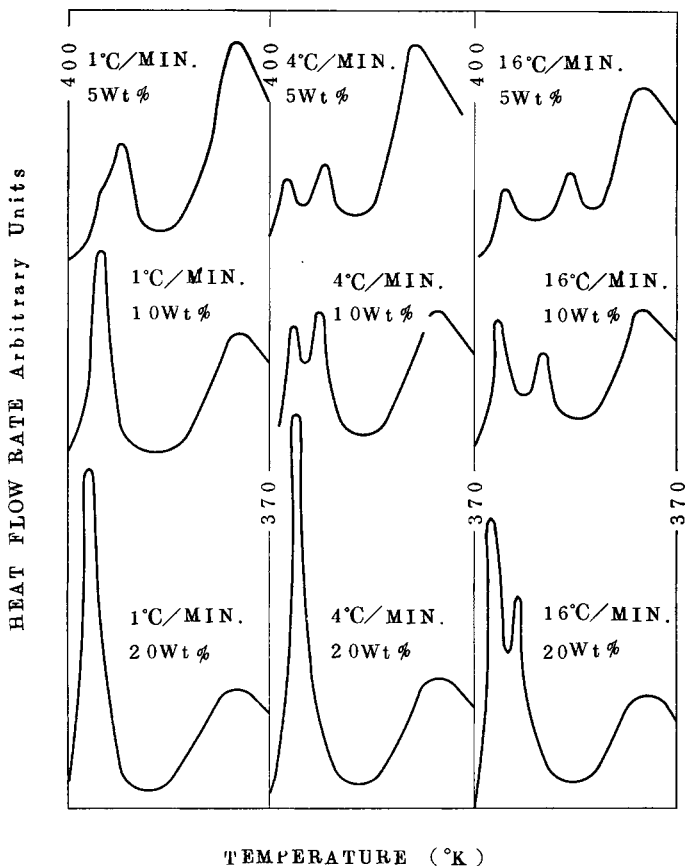

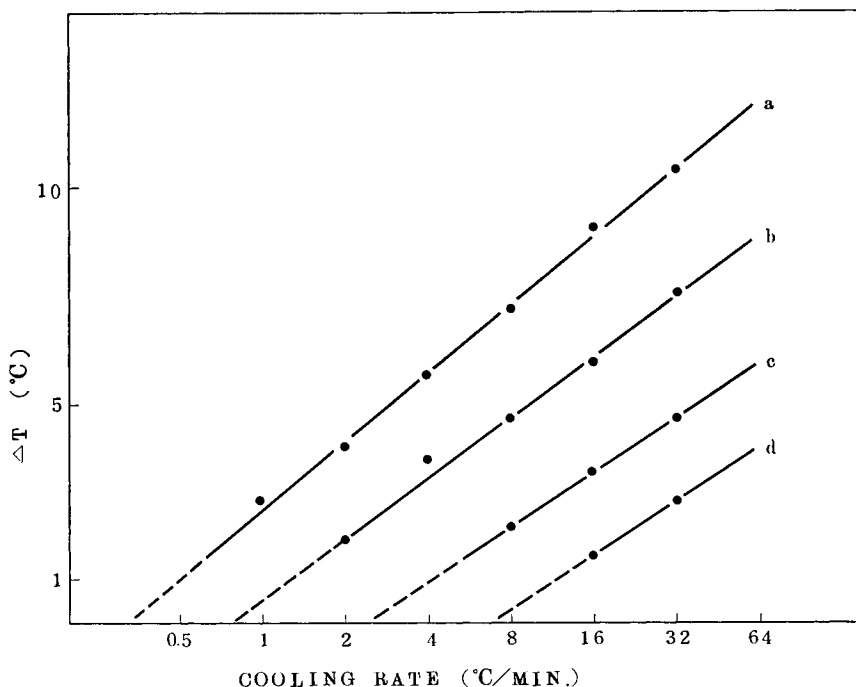Fig. 2. Melting thermograms for sample A at various blend compositions. Scanning rate 16°C/min.

Fig. 3. Plots of ΔT vs. cooling rate: (a) linear PE 5%; (b) 10%; (c) 20%; (d) 30%.

of 19.8. The numerals on the curves indicate the cooling rates to which the samples were subjected prior to the melting. As Figure 1 indicates, polyethylene blends which have been cooled rapidly have three endothermic peaks in the melting thermogram. For instance, the melting thermogram of the polyethylene blend solidified at the cooling rate of 16°C/min has three endotherms, at 397°K, 388°K, and 377°K.

From the relative sizes and positions of these peaks, it may be concluded that the highest temperature endotherm is associated with the fusion of the linear polyethylene crystallites, while the lowest one is associated with branched polyethylene crystallites. The intermediate peak is clearly observed after rapid cooling, and it shifts toward the highest temperature endotherm as the cooling rate is reduced. At the slowest cooling, 0.5°C/min, the intermediate peak is hardly distinguished from the high temperature peak and only two peaks, each of which is associated with linear and branched polyethylene, respectively, can be observed.

Figure 2 shows the change of the melting thermograms with change of prior cooling rates and blend compositions as well. The nature of the intermediate peak will be argued in relation to the prior cooling rate and the linear polyethylene content. As the cooling rate is reduced, the intermediate peak shifts toward the linear peak for each linear content, and so the temperature difference between these two peaks, ΔT, was taken as an
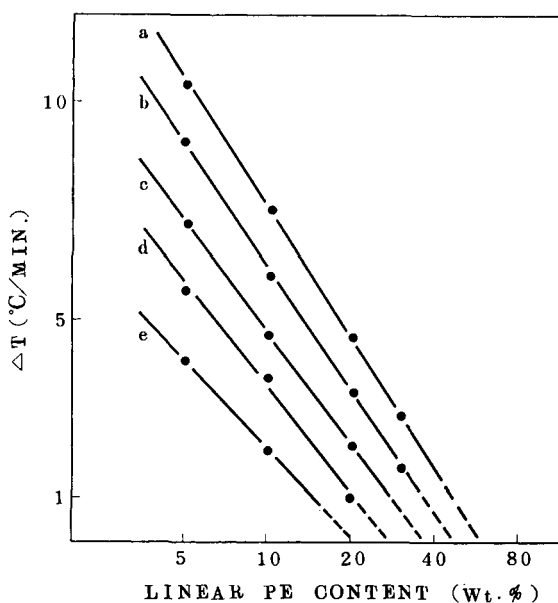
Fig. 4. Plots of ΔT vs. linear PE content: (a) cooling rate 32°C/min; (b) 16°C/min; (c) 8°C/min; (d) 4°C/min; (e) 2°C/min.

apparent index for the nature of the intermediate peak. The observed ΔT is plotted against the logarithm of the cooling rates in Figure 3 and listed in Table II for various blend compositions.

TABLE II
ΔT Data for Sample A

	ΔT at cooling rates of					
	32°C/ min	16°C/ min	8°C/ min	4°C/ min	2°C/ min	R_c, °C/ min
Linear PE content, wt-%						
5	10.4	9.1	7.2	5.7	4.1	0.32
10	7.5	6.0	4.7	3.7	1.9	0.70
20	4.7	3.5	2.2	—	—	2.0
30	2.8	1.7	—	—	—	6.8
X_c, wt-%	58	47	36	27	20	

As observed in Figure 3, when ΔT (°C) is plotted against the logarithm of the prior cooling rate R (°C/min), a family of straight lines results for the four blend compositions studied. Extrapolating each line to zero ΔT, we can get the critical rate R_c, the cooling rate at which the intermediate peak disappears and submerges into the linear peak:
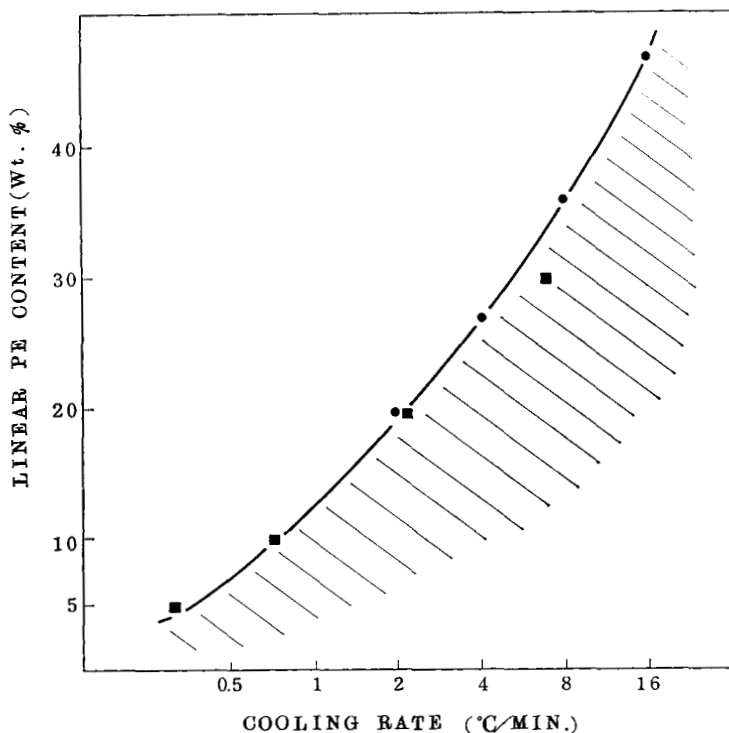
$$R_c = \lim_{\Delta T \to 0} R$$

Fig. 5. The region of occurrence of the intermediate peaks for sample A: (●) critical cooling rate shown in Table II; (■) critical linear PE content shown in Table II.

For instance, a critical cooling rate of 0.32°C/min is obtained for 5% linear blend.   This means that when the cooling rate is lower than 0.32°C/min, the intermediate peak cannot be observed in the melting thermogram for 5% linear blend.

Critical cooling rates are obtained for the four blend compositions and lised also in Table II.

When the ΔT is plotted against the logarithm of the linear content X (wt-%), a family of straight lines results for the five cooling rates studied, as shown in Figure 4.   Similarly, as with the cooling rate, the critical linear content X_c is obtained extrapolating each line to zero ΔT.   For instance, the intermediate peak never appears over 47% linear content at the cooling rate of 16°C/min.   The critical linear contents are also listed in Table II for the five cooling conditions:

$$X_c = \lim_{\Delta T \to 0} X$$

From the critical data X_c and R_c we can get Figure 5.   The hatched region is the region where the intermediate peak can be observed for this blend system.   It is evident that the intermediate peak is much influenced by the prior cooling rate and the linear polyethylene content.   So it may be
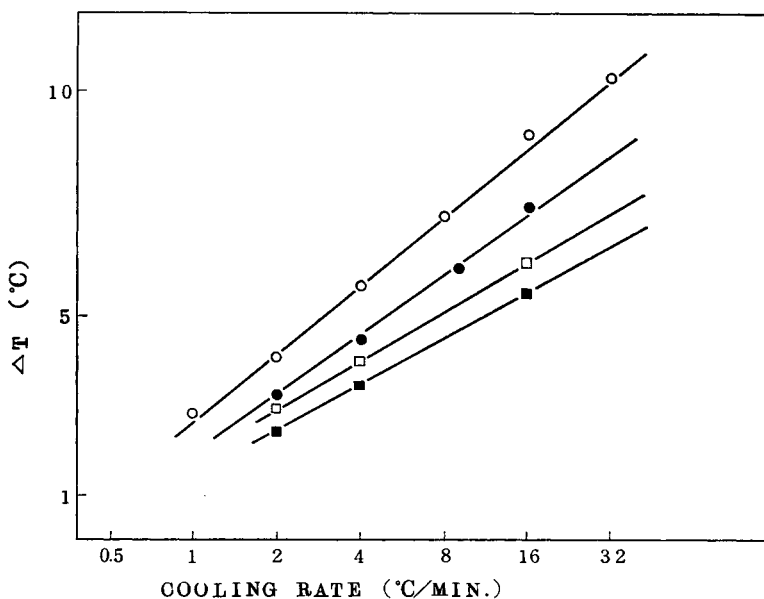
Fig. 6. Effect of melt index of branched PE: (O) sample A; (●) sample B; (□) sample C; (■) sample D.

tenable that this peak is due to the fusion of the hybrid crystallites of linear and branched polyethylene which resulted from the incomplete segregation of both components.

Figure 6 shows the effect of the melt index of branched polyethylene. The apparent ΔT is large for the blend which contains the branched polyethylene having a high melt index. The critical data, R_c at $X = 5$ wt-% and X_c at $R = 16°C/min$, for these blends are given in Table III.

TABLE III
Critical Data for Various Blends

Sample	R_c (at $X = 5$ wt-%), °C/min	X_c (at $R = 16°C/min$), wt-%
A	0.32	47
B	0.43	47
C	0.25	55
D	0.50	30
E	0.23	60
F	0.28	58

For sample D, which contains a branched polyethylene having a melt index of 0.35, the critical cooling rate is 0.50 C/min, and the critical linear content is 30 wt-%. It seems to indicate that sample D has rather limited feasibility for the intermediate peak formation compared with samples A, B, and C, which contain the branched polyethylenes having melt indices of 1.1,
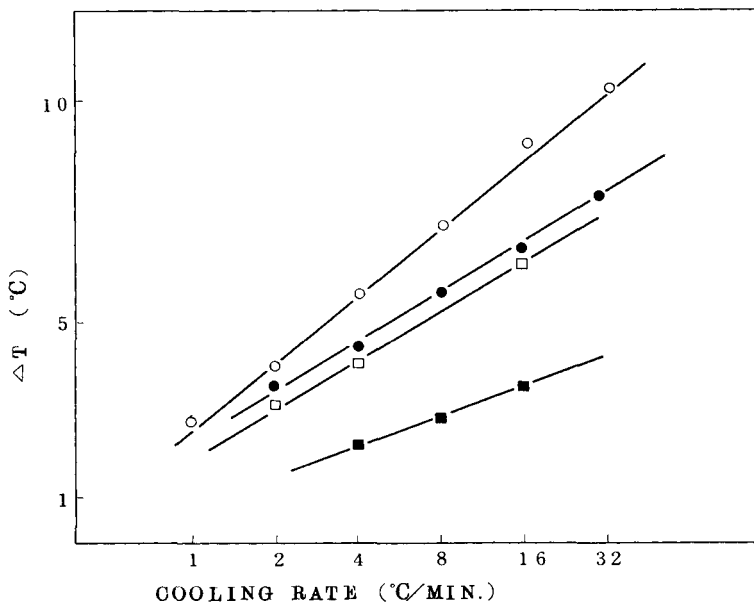
Fig. 7. Effect of methyl content of branched PE: (O) sample A; (●) sample E; (□) sample C; (■) sample F.

5.4, and 19.8, respectively. Samples A, B, and C give similar critical data, but the nature of the intermediate peaks of these samples may be different as is expected from the large differences of the apparent ΔT data.

Figure 7 shows the effect of methyl content of branched polyethylene. The critical data are also given in Table III. Samples A and E contain branched polyethylenes having almost equal melt indices, ca. 20, and different methyl contents. Though the apparent ΔT of sample A and E are fairly different, the critical data do not differ remarkably. Similar results were obtained for samples C and F which contain branched polyethylenes having almost equal melt indices, ca. 1.0, and different methyl contents. It seems that the methyl content of branched PE has some relation with the apparent ΔT, the nature of the intermediate peak, but has little effect on the critical data, the feasibility for the intermediate peak formation.

Figure 8 shows the effect of the linear component, which seems to indicate that the effect of the linear component is rather small although sample I seems slightly unfavorable for the hybrid formation as compared with samples B, G, or H.

DISCUSSION

It is very interesting that polyethylene blends have three endothermic peaks without any isothermal annealing as described above. It may be obvious that the nature of the intermediate peak reported here is different
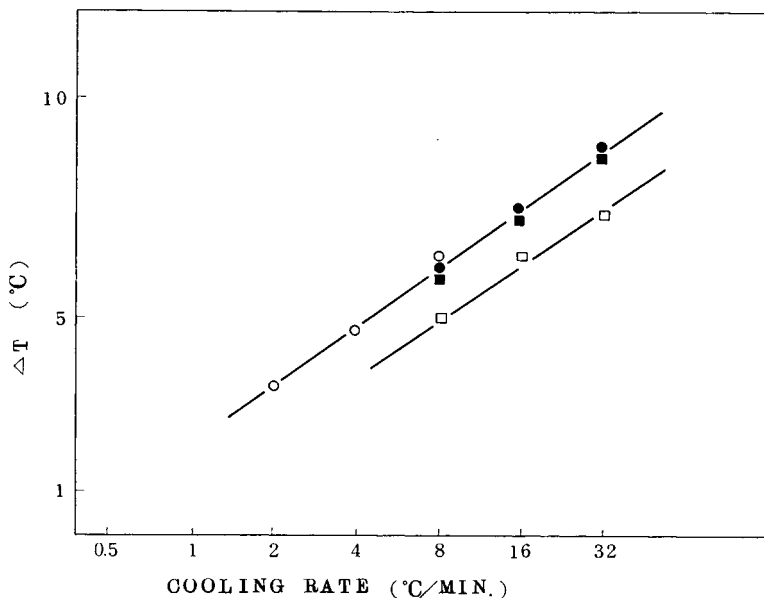
Fig. 8. Effect of linear component: (O) sample G; (●) sample B; (□) sample I; (■) sample H.

from Clampitt's "cocrystal peak"[2] which is undoubtedly due to the limited annealing effect and which results from the bunching of crystallites presumably experienced before melting and recrystallization at the annealing temperature and so having nearly equal or slightly higher melting temperatures as compared with the annealing temperature.

Holden[4] observed multiple peaks on the polyethylene melting thermogram both after isothermal annealing and after rapid cooling from the melt. In the latter case, he interpreted the two observed peaks as being directly due to different mechanisms of crystallization, heterogeneous and homogeneous nucleation. According to him, the rapid crystallization at high supercoolings can lead to appreciable heat buildup in the sample under adiabatic conditions thus giving rise to an annealing effect and further accentuating the two peaks, which are associated with the fusion of crystallites originating from the different nucleations.

In the present case, for the blend system, the different mechanisms of crystallization cannot be excluded a priori, but the heat buildup factor is to be disregarded because, in the DSC-1B instrument, the fact that extremely small, thin samples completely encapsulated in aluminum are used rules out any appreciable heat buildup during crystallization.

Gray and Casey[3] showed, for polyethylene blends and an ethylene–butene copolymer, multiple peaked melting thermograms after stepwise isothermal annealings using a DSC-prototype thermal analyzer. They reported only double peaks on 25% linear to 75% branched polyethylene

blends after cooling at 6°C/min or 2°C/min, concluding that even mod-
derately slow crystallization conditions are sufficient to segregate the linear
portion.   Further, they were inclined to disagree with Holden's interpreta-
tion of the two peaks on the polyethylene melting thermogram after rapid
cooling from the melt and argued that the effectively nonlinear cooling rate
caused by the initial, large exothermic heat of crystallization would result in
a transient annealing of the crystallizing polymer, with resulting dual peaks
in the melting thermogram.

The transient annealing, i.e., the annealing during crystallization, seems
important for the crystallization of linear and branched polyethylene blend
systems, since the crystallization of branched polyethylene following that of
linear polyethylene release a latent heat of crystallization, which is likely
to be used for the annealing of linear polyethylene crystallites.

Stafford[5] applied thermal analysis to determine the compositions of
linear and branched polyethylene blends, and he reported only double peaks
on the whole range of blend compositions after linear cooling at 8°C/hr
(0.13°C/min).   The extremely low rate of crystallization adopted by him
seems sufficient for the complete segregation of both polyethylenes, as is
expected from our experimental results.

Thus, the origin of the intermediate melting peak observed in our work is
considered to be (1) the formation of the hybrid crystallites of linear and
branched polyethylene which have been formed in reality during crystalliza-
tion on account of incomplete segregation of both components; (2) the
fusion of the transiently annealed crystallites which have been formed in
reality during crystallization (the formation of this type of crystallite is
admittedly highly dependent on the not well-defined or nonlinear cooling
rates); (3) the fusion of the crystallites which have premelted, rearranged,
and recrystallized during the heating DSC run.[9]

The rapid heating rate of 16°C/min adopted in this work was felt to rule
out the third hypothesis.   The second hypothesis, the transient annealing
during crystallization, cannot be excluded entirely.   However, the forma-
tion of the intermediate peak reported in this paper is much dependent on
the blend composition as well as on the cooling rate.   This seems to suggest
that the intermediate peak is more likely to be concerned with the hybrid
crystallites of linear and branched components.   So the first hypothesis
appears most tenable in our case.

The intermediate endothermic peaks, which are observed on the melting
thermograms of linear and branched polyethylene blends, may be con-
cluded to be associated with the fusion of the hybrid crystallites of linear
and branched polyethylenes.

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