Cocrystallization and Phase Segregation of Polyethylene Blends between the D and H Species. 4. The Crystallization Behavior As Viewed from the Infrared Spectral Changes

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ABSTRACT: Through detailed analysis of the temperature dependence of the infrared spectra, the structural change occurring in the cocrystallization and phase segregation processes has been investigated for polyethylene (PE) blends between the deuterated and hydrogeneous species with various degrees of branching. In the blend of deuterated high-density PE (DHDPE) with linear low-density PE (LLDPE(2), 17 ethyl branches/1000 carbons), almost perfect cocrystallization occurs, during which the D and H chains are distributed statistically randomly in crystalline lamellae at a probability determined by the relative content of the D and H species. In the blend of DHDPE with LLDPE (3) (41 ethyl branches/1000 carbons), basically the phase segregation occurs but some portion of the H species cocrystallizes with the D chains. In this case the H chain stems are isolated from each other by the neighboring D chain stems as clarified from the analysis of the infrared band splitting width as a function of temperature.

Introduction

Polyethylene (PE) blend samples, for example, the blend between high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) and so on, are industrially very important, and their properties have been improved progressively. In such improvement of the properties, it is necessary to clarify the crystallization behavior and aggregation state of each component in the PE blends separately and microscopically. It is, however, very difficult to distinguish the components clearly because of the similarity in their chemical structures. As described in the previous papers, we utilized a deuterated high-density polyethylene (DHDPE) as one component and blended it with the normal hydrogeneous PE having various degrees of side chain branching.[1-3] The deuterated sample was used on the basis of such an idea that the infrared spectroscopy, for example, may distinguish the CH_2 and CD_2 groups definitely since the vibrational frequencies of these two groups are different from each other. As the hydrogeneous PE samples, we used mainly three types, i.e., HDPE without side branching, LLDPE-(2) with the ethyl branching content of ca. 17 per 1000 carbons, and LLDPE(3) with the branching content of about 41/1000 carbons (Table 1). By measuring the temperature dependencies of the infrared spectra and X-ray scatterings of these blend samples during slow cooling from the melt, we clarified how the crystallization phenomenon changes depending on the degree of branching and also on the blend content of the CD_2 and CH_2 species. That is to say, for the blend of DHDPE with LLDPE(2), almost perfect cocrystallization occurs for any D/H blend content *even when cooled slowly from the melt*. On the other hand, in the blend samples of DHDPE/LLDPE(3) or DHDPE/HDPE, essentially the phase segregation occurs and the lamellae consisted of CD_2 or CH_2 species are coexistent within the spherulite. Strictly speaking, however, the crystallization behavior of these blends is not as simple as described above but occurs in a more complicated manner. In the present paper this complicated behavior will be described in detail through the analysis of the infrared spectra measured in the cooling process from the melt.

Table 1. Characterization of PE Samples

	M_w	M_n	M_w/M_n	branching/1000 C
DHDPE	80k	14k	5.7	2-3
HDPE	126k	24k	5.3	1
LLDPE(2)	75k	37k	2.0	17
LLDPE(3)	61k	20k	3.1	41

Experimental Section

Samples. As described in the previous papers,[1-3] DHDPE was used as one component in the blends (purchased from Merck Chemical Co., Ltd.). The hydrogeneous polyethylene samples with different degrees of branching, i.e., high-density polyethylene (HDPE) and two types of linear low-density polyethylene [LLDPE(2) and (3)], were supplied from Exxon Chemicals Co., Ltd. For the LLDPE samples the side chain is the ethyl group. The characterization of these samples is listed in Table 1. The blends were prepared by dissolving the D and H species with the contents of 25/75, 50/50, or 75/25 in wt % into boiling *p*-xylene (concentration ca. 2 wt %) and preticipating the solution into methanol at room temperature. Samples were melted and pressed on a hot plate at ca. 150 °C and then cooled slowly to room temperature. The film thickness was ca. 30 μm for infrared measurement.

Measurement. Infrared spectra were taken by using a Japan Spectroscopic Co. FT-IR 8300 spectrometer with a resolution of 2 cm^{-1}. The sample film was sandwiched between a pair of KBr single crystals with a thermocouple embedded as closely as possible to the sample and then it was set into an optical heating cell.

Results and Discussion

Brief Review on the Crystallization Behavior of the Blends. In Figure 1 is reproduced the temperature dependence of the infrared spectra measured for the DHDPE/LLDPE(2) blend with a D/H content of 75/25 wt %.[3] Figure 2 shows the "crystalline" spectra obtained after subtraction of the amorphous component from Figure 1 under the assumption that the bulk spectra are the simple overlap of the crystalline and amorphous spectra[1-3]; i.e., (the bulk spectra) = k_c*(crystalline spectra) + (1 - k_c)*-

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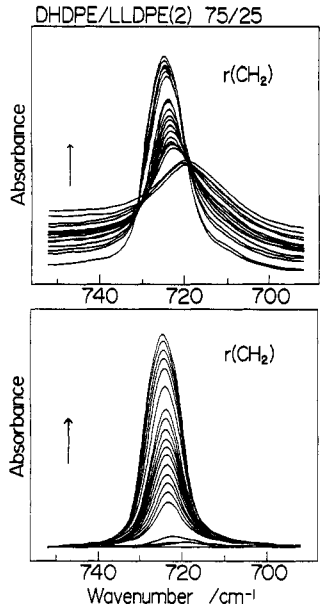

Figure 1. Temperature dependence of the observed FTIR spectra and the corresponding "crystalline" spectra obtained for the DHDPE/LLDPE(2) 75/25 wt % sample. The temperatures are 150, 140, 130, 125, 120, 117, 114, 111, 108, 105, 102, 99, 96, 93, 90, 85, 80, 70, 60, 50, and 40 °C, from the bottom.

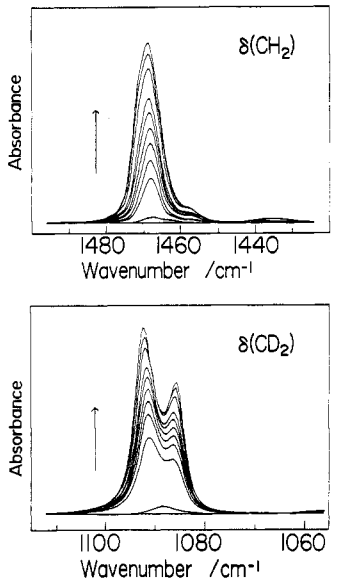

Figure 2. Temperature dependence of the FTIR spectra obtained for the crystalline parts of the DHDPE/LLDPE(2) 75/25 wt % sample in the frequency regions of the CH_2 and CD_2 bending modes. The temperatures are 150, 130, 120, 114, 108, 102, 96, 90, 80, 60, and 40 °C, from the bottom.

(amorphous spectra) Figure 3 shows the temperature dependence of the coefficient k_c evaluated for the CH_2 and CD_2 bands. It was found that for all the blend samples with different blend contents, the CH_2 and CD_2 crystalline bands begin to appear simultaneously at the crystallization temperature characteristic of each blend sample. Combining these data with the wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS) data,[1-3] we concluded that almost perfect cocrystallization occurs in the case of the DHDPE/LLDPE(2) blend *even when cooled slowly from the melt*. The process of "slow cooling" is quite important. For example, in the research on the chain folding structure of PE lamallae, the blend of DHDPE and HDPE components was used frequently and the behavior of the tagged CD_2 chains was traced by neutron scattering measurement and so on. In these cases, however, the sample was found to show the phase

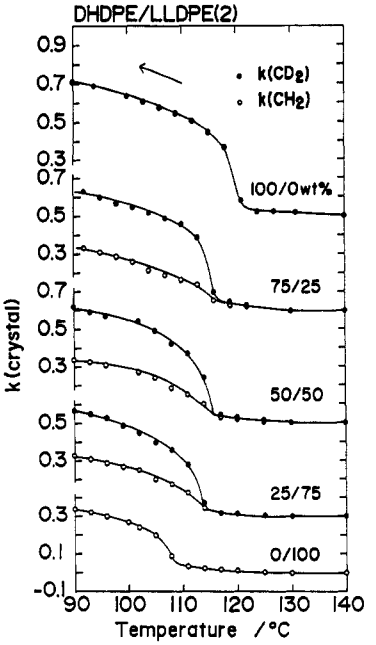

Figure 3. Temperature dependence of the coefficient k_c of the D and H species evaluated for a series of DHDPE/LLDPE(2) blends (cooling process from the melt).

segregation between the CD_2 and CH_2 components when cooled slowly from the melt.[4-7] Therefore, so as to get the homogeneously cocrystallized specimen, the sample was quenched at liq. nitrogen temperature. But this preparation method of quenching is too special and cannot be assumed to give useful information on the general crystallization behavior under such normal conditions as isothermal crystallization or slow cooling from the melt. As described above, the DHDPE/LLDPE(2) blend cocrystallizes almost perfectly even when cooled slowly from the melt and therefore may be utilized effectively as one of the ideal samples for the investigation of the crystallization behavior and the folding structure of PE lamellae. The detailed discussion will be reported in a separate paper.

Figure 4 shows the temperature dependence of the coefficient k_c evaluated for the blend samples of DHDPE/LLDPE(3). In this case the crystalline D bands begin to appear at first(●) and then the CH_2 species crystallize gradually in the lower temperature region (○) where the pure LLDPE (3) crystallizes in a similar way (□). As seen in the case of D/H = 75/25 [Figure 4a], however, some portion of the CH_2 chains crystallize simultaneously with the CD_2 chains in the high temperature region. This indicates that, even in the case of the DHDPE/LLDPE(3) blend (and also for the DHDPE/HDPE blend), cocrystallization is detected to some extent although the degree is not so high.

As already reported, the coexistence of the CD_2 and CH_2 chains in the common lamella reflects on the infrared band splitting width. The infrared band splitting is originally caused by the intermolecular interactions between the neighboring stems of the same species. If the CH_2 chain is isolated by the surrounding CD_2 chains, such intermolecular $CH_2 \cdots CH_2$ vibrational coupling is cut away and the CH_2 band should appear as a singlet.[8-10] The singlet band of the CH_2 bending mode [$\delta(CH_2)$] shown in Figure 1 is a typical example: a singlet band is observed at an early stage of crystallization and then some shoulders are observed after the temperature is decreased furthermore, suggesting an increase of the doublet band component or the number of $CH_2 \cdots CH_2$ coupling pairs.

In this way the degree of band splitting is dependent on the spatial distribution of the D and H chains in the

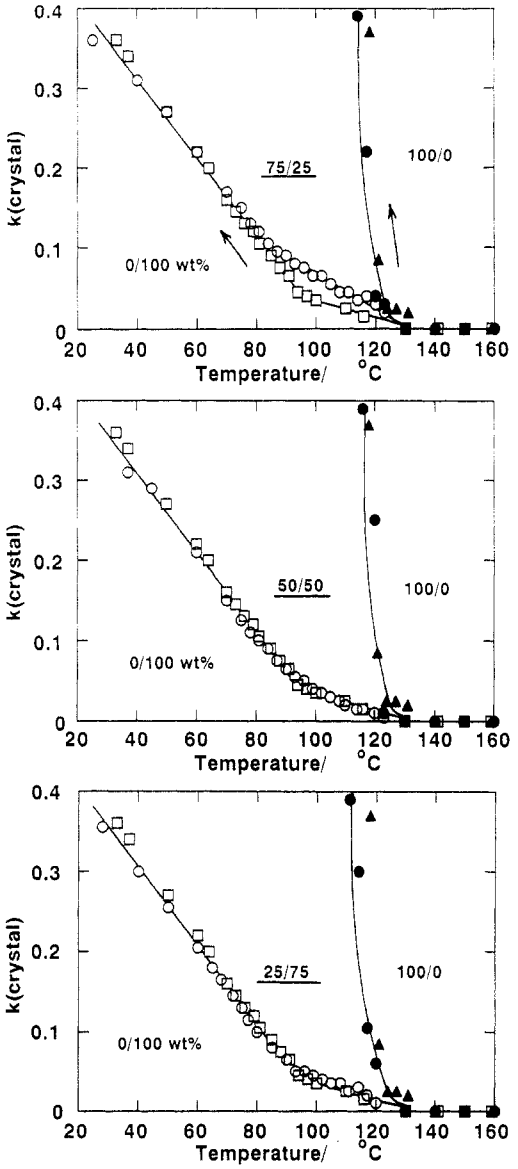

Figure 4. Temperature dependencies of the coefficient k_c estimated for the DHDPE/LLDPE(3) 25/75, 50/50, and 75/25 wt % blend samples. The crystallization of the pure DHDPE sample is indicated by the symbol ▲. Those of the blend samples are indicated by the symbols ○ and ●. The case of the pure LLDPE(3) sample is indicated by the symbol □.

crystalline lamella. Therefore detailed spectral analysis may give us useful information concerning the crystallization behavior of each component, as described in the following section.

DHDPE/LLDPE(2) Blend System. The infrared spectra measured during crystallization from the melt are decomposed in the same way as described in the previous paper.[3] In an approximation the "crystalline" spectra are assumed to be the overlap of three types of bands, as discussed before: (1) the singlet component coming from the CH_2 (or CD_2) stem isolated from eath other by being surrounded by the other isotopic stems or the singlet component originating from the CH_2 (or CD_2) stems arrayed regularly along the (200) or (020) plane,[8-10] (2) the doublet component originating from a coupled pair of CH_2···CH_2 (or CD_2···CD_2) groups in the cocrystallized lamellae, where the splitting width may vary depending on the D/H content, and (3) the doublet component corresponding to the segregated lamellae. Therefore, the spectra may be resolved using at least five band components originating from these three factors. As stated in the previous paper, we aim to clarify the relative content

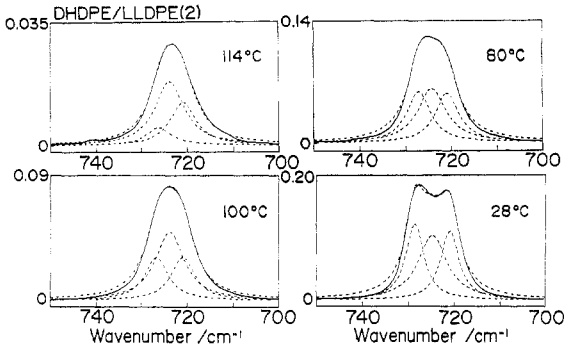

Figure 5. Infrared spectral profiles and their band components obtained for the DHDPE/LLDPE(2) 50/50 wt % sample at the various temperatures: (—) observed; (– – –) calculated.

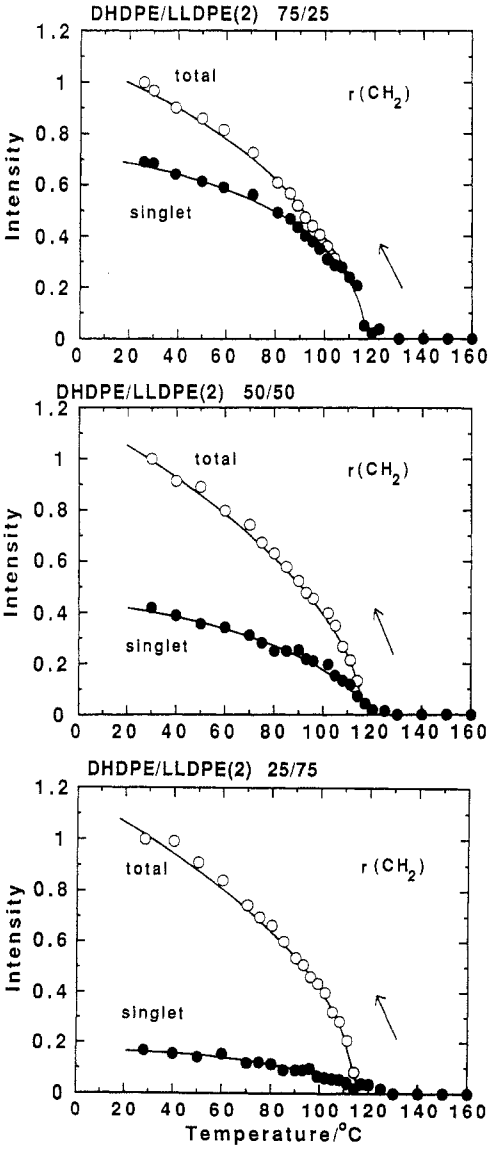

Figure 6. Temperature dependencies of the singlet band intensity and the total band intensity evaluated for the infrared CH_2 rocking mode of the DHDPE/LLDPE(2) blend samples.

of the singlet component (1) originating from the isolated chain stems. In an approximation, therefore, the doublet components due to the factors 2 and 3 are averaged and treated together and thus the observed "crystalline" spectra were separated into three bands, a singlet and a doublet.

Figure 5 shows some examples of curve resolution made for the spectra of the DHDPE/LLDPE(2) 50/50 wt % sample measured at various temperatures. Figure 6 shows the temperature dependencies of the integrated intensity

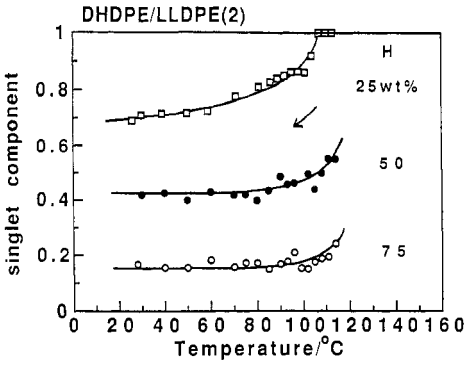

Figure 7. Temperature dependence of the relative intensity of the CH_2 rocking singlet band evaluated for the DHDPE/LLDPE-(2) blend samples.

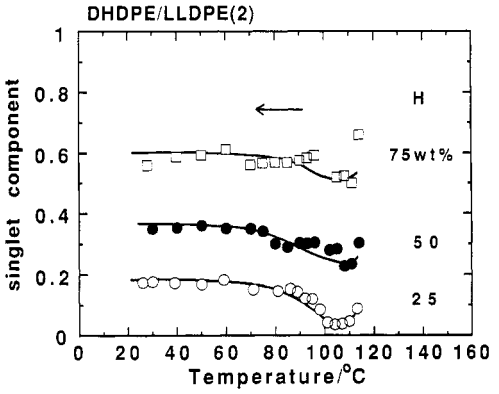

Figure 8. Temperature dependence of the relative intensity of the CD_2 rocking singlet band evaluated for the DHDPE/LLDPE-(2) blend samples.

of the singlet component and that of the whole band. At the crystallization temperature mainly the singlet component begins to appear and then both the singlet and doublet components grow in parallel as the temperature is decreased. In Figure 7 is shown the temperature dependence of the fraction of the singlet band contributing to the total band intensity. For all the samples a similar tendency is observed: the almost pure singlet component is observed at an early stage. In the lower temperature region the singlet and doublet bands grow in parallel and so the singlet component fraction becomes almost constant. The CD_2 chains, on the other hand, behave differently from the CH_2 chain. Figure 8 shows the temperature dependence of the singlet component fraction evaluated for the CD_2 bending band. In the temperature region where the CH_2 band appears as a singlet, the CD_2 band grows with a relatively low fraction of the singlet component. Around 100 °C the CD_2 singlet component begins to increase and, finally, the singlet:doublet ratio becomes constant. From Figures 7 and 8, the following model may be deduced for the crystallization behavior of the DHDPE/LLDPE(2) system. In an early stage of crystallization (110–90 °C), the CH_2 band appears preferably as a singlet and the CD_2 band as a doublet. This indicates that the cocrystallization begins to occur with the H chains isolated from each other by being surrounded by the CD_2 chains. This tendency is most clearly realized in the case of the D/H = 75/25 wt % blend and becomes more ambiguous as the H content increases from 25 to 50 and to 75 wt %. As the temperature decreases further, both the singlet and doublet components increase in parallel, indicating that the CH_2 and CD_2 crystalline stems take their positions in the lattice at the statical probability determined by the D/H blend content. Figure 9 illustrates this crystallization behavior for the D/H = 75/25 wt % blend sample.

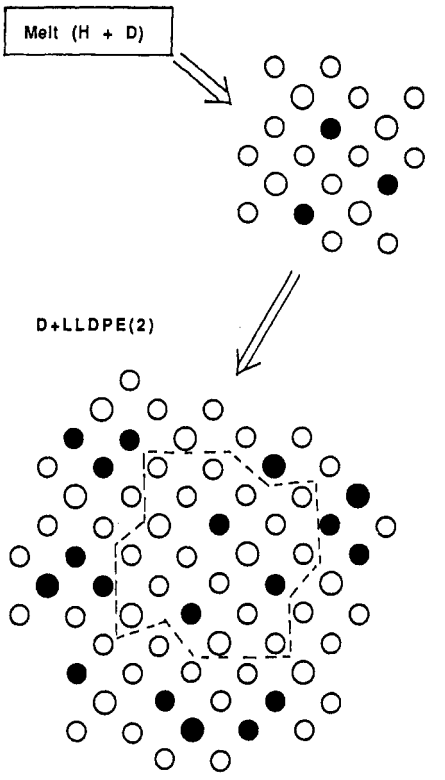

Figure 9. Illustration of the crystallization mechanism of the DHDPE/LLDPE(2) 75/25 wt % blend system: (○) CD_2 stems; (●) CH_2 stems.

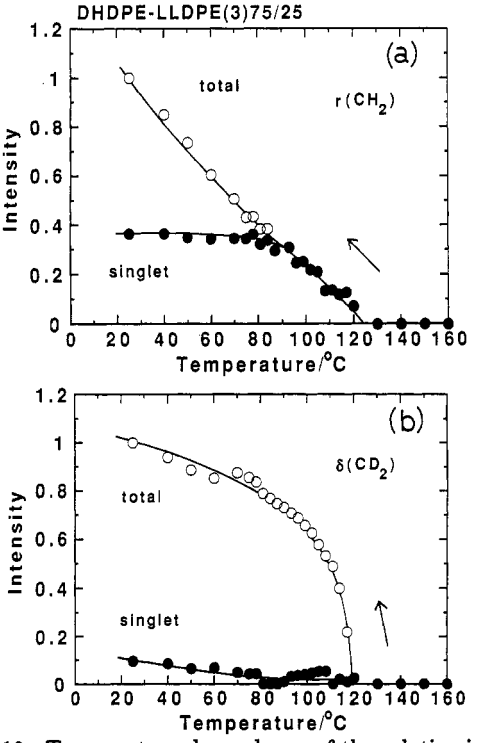

Figure 10. Temperature dependence of the relative intensity of the (a) CH_2 and (b) CD_2 rocking singlet bands evaluated for the DHDPE/LLDPE(3) 75/25 wt % sample.

DHDPE/LLDPE(3) Blend System. In a similar way the infrared band components were separated for the DHDPE/LLDPE(3) 75/25 and 25/75 wt % blend samples. The result obtained for the CH_2 rocking bands is shown in Figure 10a. In Figure 10b is shown the result for the CD_2 bending bands. As already shown in Figure 4 some of the LLDPE(3) crystalline component begins to appear simultaneously with the DHDPE component in the crystallization temperature region of the pure DHDPE. As shown in Figure 10a, the LLDPE(3) begins to appear

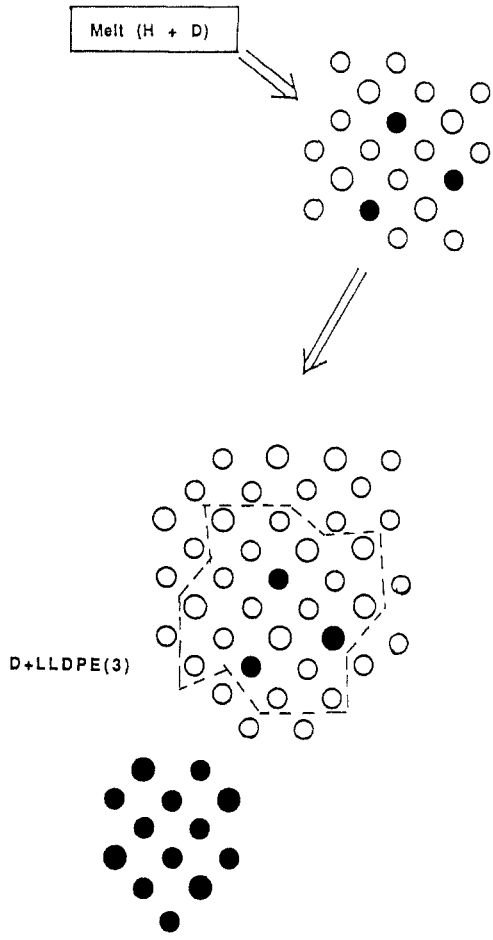

Figure 11. Illustration of the crystallization mechanism of the DHDPE/LLDPE(3) 75/25 wt % blend system: (○) CD_2 stems; (●) CH_2 stems.

as a singlet and increases its intensity. Below 90 °C, where the main part of LLDPE(3) begins to crystallize separately from the CD_2 species, the intensity of the singlet component does not increase but remains constant. The total band intensity, on the other hand, increases gradually in this temperature region. That is, the fraction of doublet component increases when the main part of the CH_2 chains begins to crystallize separately from the CD_2 chains. From such an observation we may say that in the temperature region 120–90 °C where the CD_2 chains begin to crystallize (Figure 10b), some portion of the CH_2 stems is induced to cocrystallize, just when the CH_2 chains are isolated from each other by the surrounding D stems. As the temperature decreases down to ca. 90 °C, the H stems crystallize separately from the growing CD_2 crystals. Figure 11 illustrates this crystallization model for the DHDPE/LLDPE(3) 75/25 blend sample.

In the case of the DHDPE/LLDPE(3) 25/75 wt % sample, too, we can observe a similar phenomenon. The CD_2 component crystallizes at the temperature almost coincident with that of the pure sample. In this temperature region, the small portion of LLDPE(3) cocrystallizes with the CD_2 component, being observed as a singlet infrared band, as shown in Figure 12. This singlet component (●) of the CH_2 chains is relatively low in population compared with that of the case of the D/H = 75/25 wt % sample, originating from a lower concentration of the CD_2 species. As the temperature approaches ca. 90 °C the doublet component of the CH_2 band increases largely, while the singlet component remains almost constant.

DHDPE/HDPE Blend System. Different from the above mentioned blend samples of DHDPE/LLDPE(2)

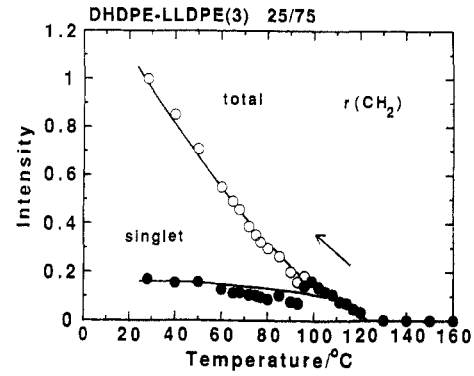

Figure 12. Temperature dependence of the relative intensity of the CH_2 rocking singlet band evaluated for the DHDPE/LLDPE(3) 25/75 wt % sample.

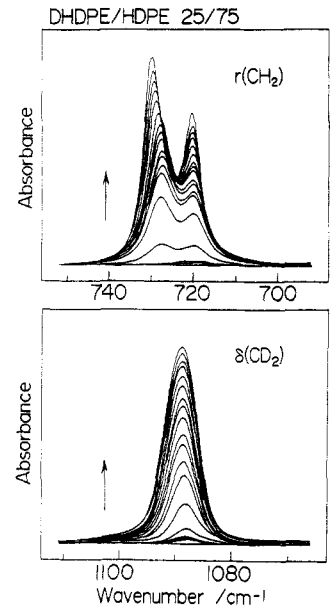

Figure 13. Temperature dependence of the FTIR spectra obtained for the crystalline part of the DHDPE/HDPE 25/75 wt % blend sample. The temperatures are 140, 130, 127, 124, 121, 118, 115, 112, 109, 106, 100, 95, 90, 80, 70, 60, 50, 40, and 26 °C, from the bottom.

and DHDPE/LLDPE(3), the pure HDPE crystallizes at a higher temperature than the pure DHDPE although the difference in the crystallization temperature is not too large. In the sample of D/H 25/75 wt %, as shown in Figure 13, the CH_2 crystalline band begins to appear as doublet, just when the CD_2 band is observed as a singlet. This tendency does not change too much even when the band intensity increases further in the lower temperature region. That is to say, in the DHDPE/HDPE 25/75 blend sample, the CD_2 chains are induced to cocrystallize when the CH_2 chains begin to crystallize in the higher temperature region. The CD_2 stems are considered to be isolated by being surrounded by the CH_2 stems, as deduced from the infrared spectral data. In the lower temperature region the crystallization proceeds further, but the CD_2 stems continue to be isolated (the singlet band in Figure 13). In Figure 14 is shown the result for the D/H = 75/25 wt % sample. When the weak CH_2 band begins to appear as a doublet, the weak singlet CD_2 band is observed simultaneously. In the lower temperature region the CH_2 and CD_2 bands increase the intensity together as a "doublet". In this case of the D/H = 75/25 blend, therefore, we may describe the crystallization behavior as follows. The CD_2 chains are induced to cocrystallize with the CH_2 chains in an early stage of crystallization, but the remaining CD_2

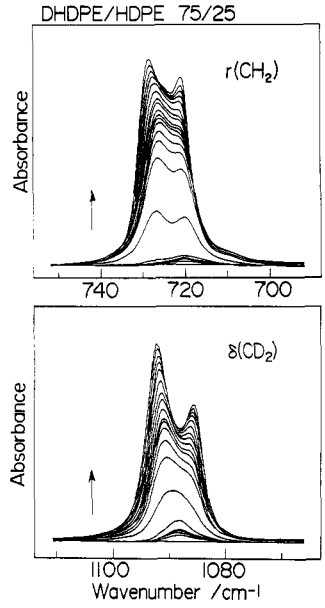

Figure 14. Temperature dependence of FTIR spectra obtained for the crystalline part of the DHDPE/HDPE 75/25 wt % blend sample. The temperatures are 144, 134, 130, 128, 122, 119, 117, 114, 109, 105, 104, 100, 95, 90, 80, 70, 60, 50, 38, and 29 °C, from the bottom.

component crystallizes in a separated lamella in the lower temperature region. In this case, thus, the model illustrated in Figure 11 may be applied also suitably but by exchanging the marks for the CD_2 and CH_2 species.

Combining the results of the DHDPE/HDPE and DHDPE/LLDPE(3) blends, it may be said that the component of originally *higher* crystallization temperature (the CD_2 chains in DHDPE/LLDPE(3) and the CH_2 chains in DHDPE/HDPE) tends to crystallize first, just when some portion of another component begins to *cocrystallize* together, although this cocrystallizable content is dependent on the degree of branching. In the lower temperature region, the still melted component crystallizes separately, as observed as doublet bands in the infrared spectra.

Strictly speaking, even in the case of DHDPE/LLDPE-(2), such a tendency can be observed in an early stage of crystallization: when some portion of the pure CD_2 component begins to crystallize first (as an IR doublet), then the CH_2 component is induced to grow preferably as a singlet (Figures 7 and 8), although not as remarkably as in the above-mentioned two cases. As the temperature decreases further, the cocrystallization occurs and the singlet and doublet components increase in parallel.

Conclusions

In this paper the crystallization behavior of the D/H PE blend samples was investigated through the analysis of infrared spectra as a function of temperature. The singlet band corresponds to the crystalline parts in which chains of one component are isolated from each other by being surrounded by another component. For example, the DHDPE/LLDPE(3) blend case is typical. When the CH_2 chains with the originally lower crystallization temperature cocrystallize with the CD_2 chains in an early stage of crystallization from the molten state, the CH_2 bands are observed preferentially in the form of a singlet and the CD_2 bands as a doublet. This means that the CH_2 chains are induced to cocrystallize by being surrounded by the CD_2 chains. This tendency is more or less detected in all the types of blend samples discussed here and most typically observed in highly diluted cases such as D/H = 75/25 wt % DHDPE/LLDPE(3) etc. As the temperature decreases further, the remaining CH_2 chains crystallize separately from the CD_2 chains to form the segregated crystallites within the same spherulite in the case of the DHDPE/LLDPE(3) blend.[2] In the case of DHDPE/LLDPE(2) with any D/H content and the case of DHDPE/HDPE with D/H = 25/75 wt %, the cocrystallization proceeds even when the temperature reaches room temperature.

In this way the species with the originally lower crystallization temperature (LLDPE(3), for example) has a tendency to be trapped by another species with the originally higher crystallization temperature (DHDPE) in an early stage of crystallization. In other words, when the DHDPE species, for example, begins to crystallize, some portion of the LLDPE(3) species might escape from the molten state by being surrounded by the "host" chains (DHDPE): this CH_2 species cocrystallizes even at such a high temperature that the pure LLDPE(3) cannot crystallize originally. Such a model of cocrystallization, i.e., "pairing" of the CD_2 and CH_2 chains in an early stage of crystallization requires several factors: (1) the CD_2 and CH_2 chains should be thermodynamically miscible; (2) the crystallization rates of the CD_2 and CH_2 species should be as close as possible to each other; (3) the CD_2 and CH_2 chains in the molten state should be almost perfectly miscible. Factor 1 has been already confirmed through the thermal analysis of the blends, the X-ray and infrared measurements, etc.[1-3] The miscibility (3) in the molten state is now being investigated by using neutron scatterings. As for problem 2 we have performed the time-resolved measurement of infrared spectra under temperature jump conditions, the results of which will be reported in a separate paper.

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