Cocrystallization and Phase Segregation of Polyethylene Blends between the D and H Species. 3. Blend Content Dependence of the Crystallization Behavior

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ABSTRACT: Cocrystallization and phase segregation phenomena of polyethylene (PE) blends between the deuterated and hydrogenous species with various degrees of branching were investigated as a function of the D/H blend content on the basis of the measurements of DSC and temperature dependence of FTIR spectra. For the blend samples between the deuterated high-density PE (DHDPE) and the hydrogenous linear low-density PE [LLDPE(2), branching content ca. 17 ethyl groups/1000 carbons] the almost perfect cocrystallization phenomenon was found to occur for all the samples with different blend contents from 0 to 100% *even when cooled slowly from the molten state to room temperature.* The blends of DHDPE with LLDPE(3) (branching content ca. 41 ethyl groups/1000 carbons) or HDPE (ca. 1 branching/1000 carbons) were found to show basically the phase segregation phenomenon between the D and H species but partly the cocrystallization was also found to occur when the dilution of the D or H component was high. A concrete relationship between the degree of cocrystallization and the branching and D/H content was discussed on the basis of infrared band profile analysis.

Introduction

Polyethylene (PE) blends have been widely investigated from scientific as well as industrial interests. One of the most important problems to be solved is the phenomenon of phase segregation between the components of the blends. For example the blend of high-density polyethylene (HDPE) with low-density polyethylene (LDPE) shows segregation between these two components when cooled slowly from the melt.[1-3] Only the quick cooling or quenching of the melt gives a uniformly mixed crystalline sample, or a cocrystallized sample. But this phenomenon is limited to the samples with high HDPE content[4] or to those with a low degree of branching in LDPE.[5-7] For the blend of LDPE with linear low-density PE (LLDPE) a formation of separated crystals or a phase segregation was suggested.[8] For the blend between HDPE and LLDPE the cocrystallization was reported to occur even under the condition of slow cooling.[9] In this way the crystal segregation and cocrystallization are dependent in a complicated manner upon the couples of the selected PEs, the crystallization condition, etc.[10,11]

Most of these studies, however, are based only on bulk observation such as thermal analysis, electron microscopy, and so on. Therefore it is still controversial to give a clear answer for the factors governing the phenomena of cocrystallization and phase segregation in PE blends from the molecular level viewpoint. One of the reasons may come from such a situation where it is difficult to distinguish each component of the normal PE blends at the molecular level because they have almost the same chemical structures consisting of carbon and hydrogen atoms. As was already reported, one of the useful methods to clarify this situation may be use of deuterated PE species as one component. For example, in order to evaluate the radius of gyration of a single PE chain in the solid state, Schelten et al.[12,13] measured the small-angle neutron scattering for the blends with the deuterated PE component highly diluted in the normal PE. In such an experiment it is essentially important to use the samples in which the tagged PE chains are isolated from each other by being surrounded by the H species. In order to satisfy this condition, they could not escape from using the sample rapidly quenched from the melt. Another example, in which PE blends between the deuterated and hydrogenous species were used, is seen in the vibrational spectroscopic study by Krimm et al.[14-16] Their idea was based on a situation where the crystalline bands of the CH_2 and CD_2 groups appear at the different vibrational frequency positions. They analyzed the correlation splitting of the CD_2 bands so as to get information on the chain folding structure. But in their study, too, a highly diluted CD_2 component was used because of the problem of phase segregation. In this way, when we attempt to use the blends between deuterated and hydrogenous PEs to get information on the microscopic aggregation structure, we always encounter the problem of incomplete cocrystallization between the D and H species.

Recently, we investigated the blends of deuterated HDPE (DHDPE) with hydrogenous PE having various degrees of branching and found that the LLDPE with a proper degree of branching exhibits an almost perfect cocrystallization phenomenon with the DHDPE *even when cooled slowly from the melt.*[17,18] We also found that the blend of DHDPE with hydrogenous PE having higher or lower branching shows to a high extent the phase segregation phenomenon. The DHDPE/LLDPE blend system showing the almost perfect cocrystallization phenomenon is considered to be quite useful for investigating the above-mentioned various themes: for example, to clarify the spatial distribution of the H and D stems in the crystalline lamella. This problem is associated intimately with the problem of the chain folding mechanism, which has been discussed for a long time but is still in a controversial stage.

In the previous papers we treated the blend samples of the content D/H = 50/50 wt % and investigated the effect of branching on the degree of phase segregation and

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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

cocrystallization. In order to understand the cocrystallization and phase segregation phenomena in more detail, it is also necessary to clarify how they are affected when the D/H blend content is changed, as discussed here in this paper on the basis of DSC data and the temperature dependence of the infrared spectra measured for many blend samples with various D/H blend contents and degrees of branching.

Experimental Section

Samples. As likely as in the previous studies,[17,18] the deuterated high-density polyethylene (DHDPE) was used as one component in the blends and was purchased from Merck Chemical Co., Ltd. The hydrogenous polyethylene samples with different degrees of branching, i.e., high-density polyethylene (HDPE) and two types of linear low-density polyethylene (LLDPE), were supplied from Exxon Chemicals Co., Ltd. For the LLDPE samples the side chain is an ethyl group. The characterization results of these samples are listed in Table 1, in which the molecular weight was evaluated using GPC and the branching content was estimated from the viscosity measurement. The blends were prepared by dissolving the D and H species of 25:75, 50:50, or 75:25 in wt % ratio in boiling *p*-xylene with a concentration of about 2 wt % and by precipitating 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.

Measurements. The DSC thermograms in both the heating and cooling processes were measured using a SEIKO Industry Inc. DSC Type 20. The heating and cooling rates were 10 °C/min. Infrared spectra were taken by using a Japan Spectroscopic Co. FT-IR 8300 spectrometer equipped with a DTGS detector. The sample film was sandwiched between a pair of KBr single crystals with a Chromel-Alumel (CA) thermocouple embedded as closely as possible to the sample and then it was inserted into an optical heating cell.

Results and Discussion

DHDPE/LLDPE(2) Blend System. As was reported in the previous papers,[17,18] the DHDPE/LLDPE(2) 50/50 wt % blend sample exhibits an almost perfect cocrystallization phenomenon even when cooled slowly from the melt. In order to investigate the effect of blend content on this cocrystallization phenomenon, the samples with D/H = 75/25, 50/50, and 25/75 wt % were prepared. In Figure 1a are compared the DSC thermograms measured for a series of blend samples in the cooling process. In Figure 1b the blend content dependence of the crystallization point is plotted. For all the samples, only one sharp exothermic peak can be observed. The crystallization point (and the melting point) shifts *continuously* depending on the blend content. These DSC data suggest an occurrence of the cocrystallization of the D and H species for all the blend samples. The infrared spectral data confirmed this idea reasonably. That is, the temperature dependence of the infrared spectra was measured in the course of crystallization from the melt. As already discussed in the previous paper,[17] the observed band profiles can be assumed, to a good approximation, as a simple overlap of the crystalline and amorphous bands, i.e.,

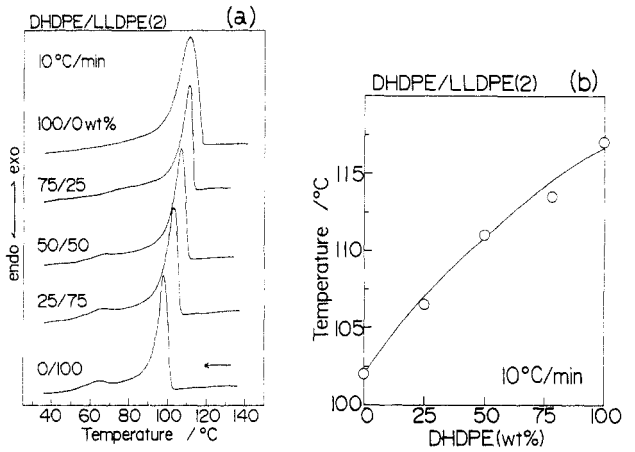

Figure 1. Blend content dependence of the (a) DSC thermograms and (b) crystallization temperatures measured for a series of DHDPE/LLDPE(2) blend samples (cooling process from the melt).

$$\text{(bulk spectra)} = k_c^*\text{(crystalline spectra)} + (1 - k_c)^*\text{(amorphous spectra)}$$

Following the procedure described in ref 17, the amorphous band component was subtracted from the observed spectra, where the spectra of the molten state were used as a standard for the amorphous bands. (Strictly speaking, the temperature dependence of molar absorption coefficients should be taken into account.[17,19]) The thus evaluated coefficient k_c, a measure of the degree of crystallization, is plotted against temperature in Figure 2. For all the samples, the CD_2 and CH_2 bands begin to appear *simutaneously* at a temperature just corresponding to the DSC peak (Figure 1). It should be noticed here that in the blend samples the CH_2 crystalline bands appear in such a high temperature region that the pure LLDPE(2) cannot crystallize originally (ca. 110–120 °C). That is to say, the LLDPE(2) component is induced to crystallize due to the coexistence of the DHDPE component even above its intrinsic melting temperature. These observations indicate definitely an occurrence of cocrystallization of the D and H species in this blend system.

DHDPE/HDPE and DHDPE/LLDPE(3) Blend Systems. In contrast to the DHDPE/LLDPE(2) system, the DHDPE/HDPE and DHDPE/LLDPE(3) blends (50/50 wt %) exhibit phase segregation.[17,18] This phase segregation can be detected also for the samples with other D/H contents. For example, as shown in Figure 3, the DSC thermograms (the heating process) of the DHDPE/LLDPE(3) samples show two peaks at the temperatures corresponding to those of pure DHDPE and LLDPE(3) components, although the melting points shift to some extent depending on the blend content. The temperature dependencies of the infrared spectra were measured for the samples with D/H = 25/75, 50/50, and 75/25 wt %, and the coefficient k_c was evaluated for the CH_2 and CD_2 bands. The temperature dependence of these coefficients is plotted in Figure 4. When the temperature is decreased down to the crystallization point (ca. 121 °C) of the pure DHDPE sample (▲), the crystalline CD_2 component in the blends begins to appear and grow steeply (●). As the temperature decreases further to about 90 °C, i.e., the region of slow crystallization of the pure LLDPE(3) sample (□), the CH_2 component begins to crystallize gradually (○). This tendency of phase segregation is observed for all the samples with different blend contents. Viewing the data in more detail, however, some portion of the CH_2 crystalline band is found to appear already in the

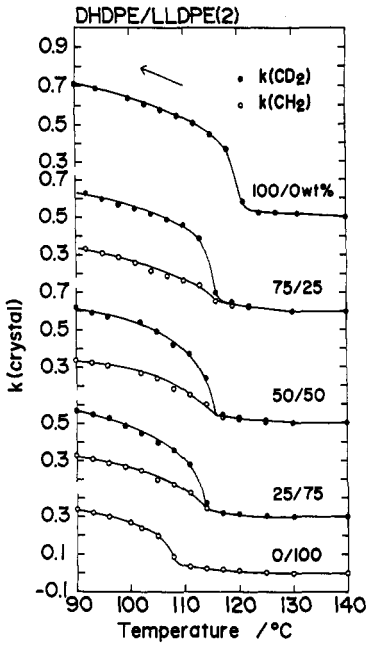

Figure 2. Temperature dependence of the coefficient k_c of the D and H species evaluated for a series of DHDPE/LLDPE(2) blends (cooling process from the melt).

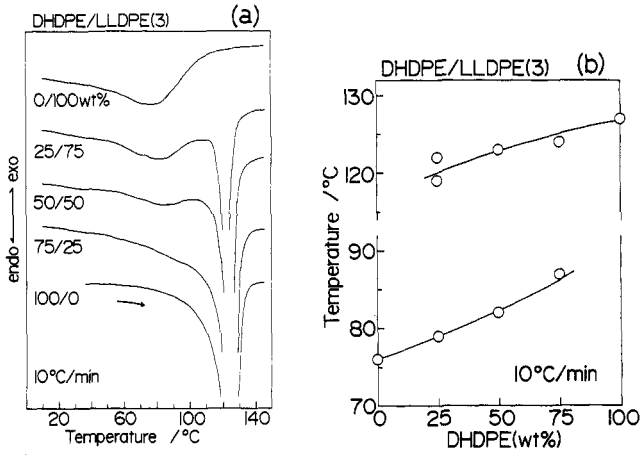

Figure 3. Blend content dependence of the (a) DSC thermograms and (b) melting points measured for a series of DHDPE/LLDPE-(3) blend samples (heating process).

crystallization temperature region of the CD_2 component (this is clearly observed particularly for the D/H 75/25 sample, as shown Figure 4). As will be reported in more detail in the following paper, this CH_2 band increases the intensity in parallel with the growth of the CD_2 crystalline band. All these behaviors of the CH_2 and CD_2 components may indicate an occurrence of some degree of cocrystallization even for the DHDPE/LLDPE(3) system.

The crystallization behavior of the DHDPE/HDPE blend is similar to that of the DHDPE/LLDPE(3) sample. In Figure 5 are shown the DSC thermograms taken in the heating process of the DHDPE/HDPE system. The melting points of the pure CH_2 and CD_2 components are originally close to each other. In the blends the two peaks are detected except for the case of D/H = 25/75 wt %. Figure 6 shows the temperature dependence of the crystalline coefficient k_c plotted for the samples of D/H = 75/25, 50/50, and 25/75 wt %. On the basis of these plots it is difficult to clarify to what extent the phase segregation occurs because of the closeness in the crystallization temperatures of the two components. But the infrared pattern itself is different among the samples with different D/H contents. For example, as shown in Figure 7, the case of the D/H = 25/75 wt % sample, the CD_2

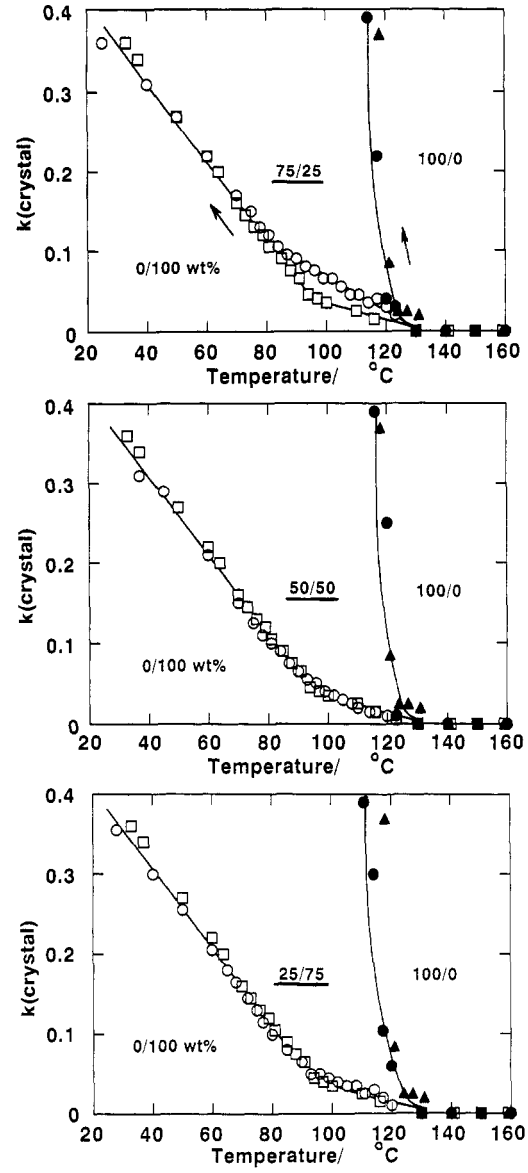

Figure 4. Temperature dependencies of the coefficient k_c estimated for DHDPE/LLDPE(3) 25/75, 50/50, and 75/25 wt % blend samples. The crystallization of the pure DHDPE sample is indicated by the symbol ▲. Those of the blend samples are indicated by the symbol (● and ○). The pure LLDPE(3) sample is indicated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

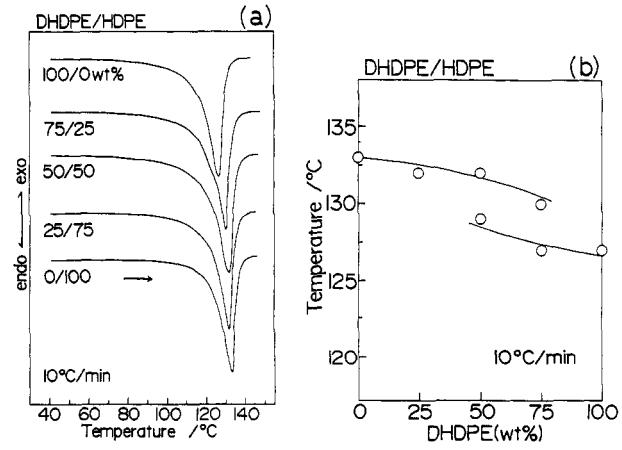

Figure 5. Blend content dependence of the (a) DSC thermograms and (b) melting points measured for a series of DHDPE/HDPE blend samples (heating process).

crystalline band is observed as a singlet, contrary to the case of D/H = 75/25 wt % (Figure 8). This suggests an occurrence of cocrystallization in the D/H 25/75 sample.

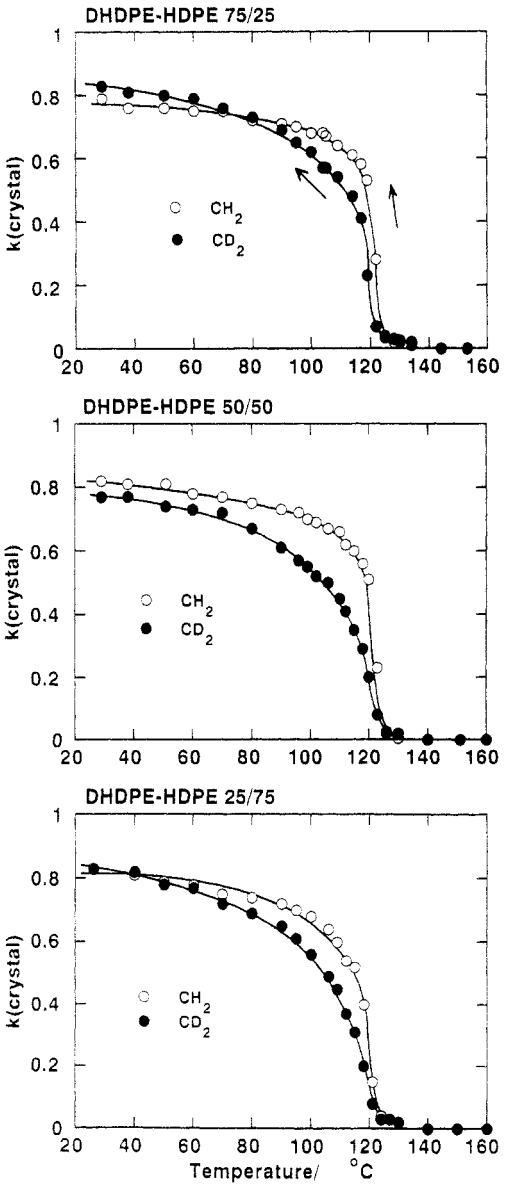

Figure 6. Temperature dependencies of the coefficient k_c estimated for DHDPE/HDPE 75/25, 50/50, and 25/75 wt % blend samples.

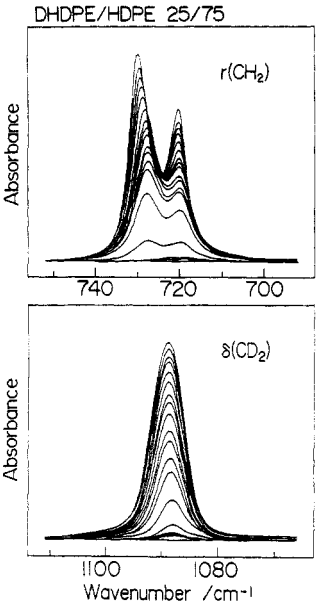

Figure 7. Temperature dependencies of the crystalline infrared spectra obtained for the DHDPE/HDPE 25/75 wt % blend. The temperatures are 140, 130, 127, 124, 121, 118, 115, 112, 109, 106, 100, 95, 90, 80, 70, 60, 50, 40, and 26 °C, from the bottom.

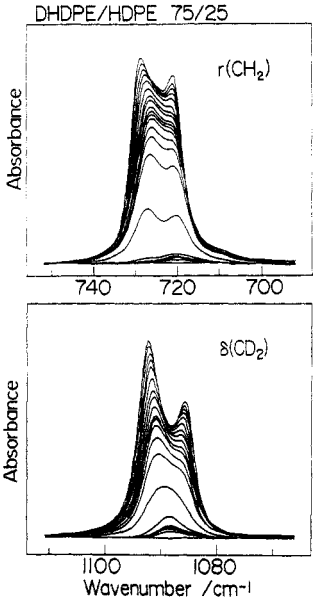

Figure 8. Temperature dependencies of the crystalline infrared spectra obtained for the DHDPE/HDPE 75/25 wt % blend. The temperatures are 144, 134, 130, 128, 125, 122, 119, 117, 114, 109, 105, 104, 100, 95, 90, 80, 70, 60, 50, 38, and 29 °C, from the bottom.

That is to say, the tendency of cocrystallization increases as the D component is diluted by the H component, although the degree of cocrystallization is not as high as that in the DHDPE/LLDPE(2) case. More detailed discussion will be made in a later section.

As discussed here, the crystallization behavior of the D/H blends is quite sensitive to the variation in the degree of branching and in the blend content. For the DHDPE/LLDPE(2) sample almost perfect cocrystallization occurs through all the D/H contents. The DHDPE/LLDPE(3) blend shows basically the phase segregation but some portion of the H component can cocrystallize with the D component when the H component is highly diluted. This can be seen also for the case of the DHDPE/HDPE blend although the role of the D and H components is reversed.

Thermal Stability of the Blends. Annealing the hydrogenous PE blends (HDPE/LDPE) at a high temperature between the melting points of the pure components, Norton and Keller found that these blends were not stable but separated into the components during annealing.[10] Even the *n*-paraffin blends are not thermally stable but transfer into the separated phases when the chain lengths are not so well matched (in other words, the blends consisting of the chains with almost the same lengths are stable as solid solution).[20-24] In such a sense, therefore, the PE blend samples discussed in this paper might be also thermally unstable. Then the blend samples were annealed at the various temperatures and their thermal stabilities were checked by DSC, X-ray, and IR measurements.

For example Figure 9 shows the DSC thermograms measured for the DHDPE/LLDPE(2) 50/50 blend which was annealed at the various temperatures T_a for 1 h and quenched at liquid nitrogen temperature. The thermograms change remarkably: the subpeaks are observed in the T_a region and shift toward the melting temperature of the main peak. In Figure 10 is plotted the relation between the DSC peak temperature and T_a. This phenomenon is frequently observed for the annealed crystalline polymers: the small crystallites of the size intrinsic of T_a are generated when the sample is annealed at T_a. In the heating process these small crystallites melt in the

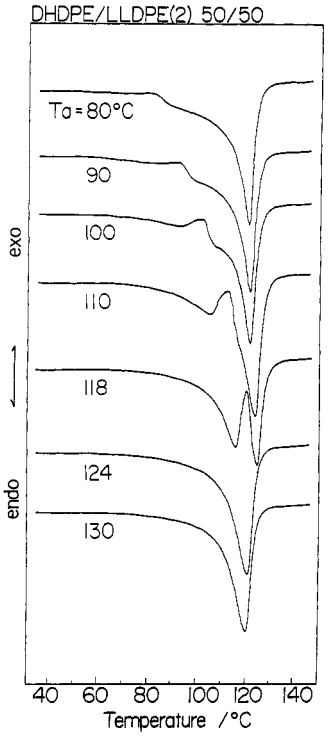

Figure 9. DSC thermograms measured for DHDPE/LLDPE(2) 50/50 wt % blend samples annealed at the various temperatures.

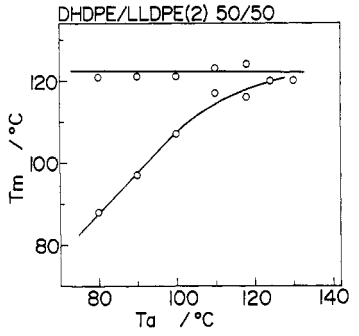

Figure 10. Annealing temperature (T_a) dependence of the melting point (T_m) measured for the DHDPE/LLDPE(2) 50/50 wt % blend sample (refer to Figure 9).

temperature region close to T_a and recrystallize into a larger crystallite of the main melting point. In other words, the subpeaks in Figures 9 and 10 are not considered to come from the melts of the phase-separated lamellae of different components. This can be checked by the X-ray and IR measurements. The original pure H and D samples show the X-ray reflection peaks at positions different from each other. Therefore a change in the pattern should be detected if any change in crystalline state occurs in the tentatively cocrystallized sample. The actually observed result is negative for this prediction, and no change in the X-ray pattern is detected before and after annealing. This can be said also for the infrared spectra: the band profile as well as the splitting width do not show any change before and after annealing.

In order to check an effect of annealing time on the cocrystallized structure, the samples were annealed for a longer time period (24 h at 100 °C) and compared with those treated for 1 h. But no change was still detected in the DSC, X-ray, and IR patterns. The same heat treatment was made also for other types of blend samples such as DHDPE/LLDPE(3) 75/25 and DHDPE/HDPE 75/25, but essentially no change was detected in the infrared patterns. Therefore we may say that, at least for the present blend samples which were obtained by slow cooling from the melt, the crystallites are thermally stable and do not

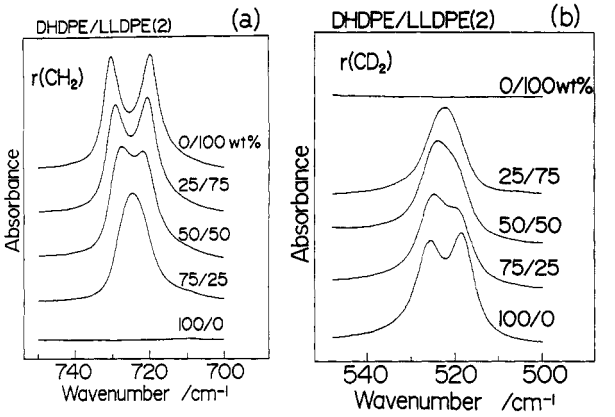

Figure 11. Blend content dependencies of the infrared spectra of a series of DHDPE/LLDPE(2) blend samples measured at room temperature: (a) CH_2 rocking region and (b) CD_2 rocking region.

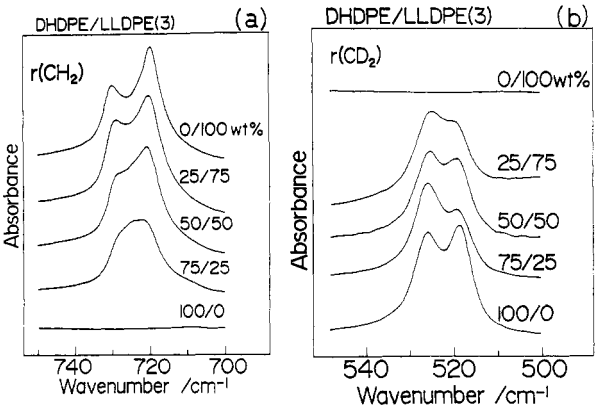

Figure 12. Blend content dependencies of the infrared spectra of a series of DHDPE/LLDPE(3) blend samples measured at room temperature: (a) CH_2 rocking region and (b) CD_2 rocking region.

experience any change in the crystal structure even after long annealing times, although small crystallites intrinsic of the annealing temperatures may be observed in some cases.

Analysis of IR Spectra Measured at Room Temperature. Figures 11 and 12 show a series of infrared spectra measured at room temperature for the blend samples of DHDPE/LLDPE(2) and DHDPE/LLDPE(3), respectively. As already mentioned, the infrared band splitting of the CD_2 and CH_2 groups is a proper indicator for qualitatively estimating the degree of cocrystallization and phase segregation phenomena. Then the band profiles are analyzed in detail, from which concrete information on the aggregation state of the CD_2 and CH_2 species is obtained as below.

At first the amorphous component was separated from the whole infrared profile in a manner similar to that mentioned above. The thus extracted crystalline band profile was then resolved into several band components. As discussed in the previous sections, the CH_2 and CD_2 stems may coexist in the same crystalline lattice or be separated from each other to exist as independent crystalline lamellae. The completely separated crystallites give the band splitting width close to that of the original pure samples. The coexistence in the same lamella will give a complicated pattern depending on the spatial distribution of the CH_2 and CD_2 stems. In the present analysis, however, the process is simplified and the band profile is resolved into three or five components: (1) singlet component originating from an isolated H (or D) stem surrounded by the other isotopic stems or originating

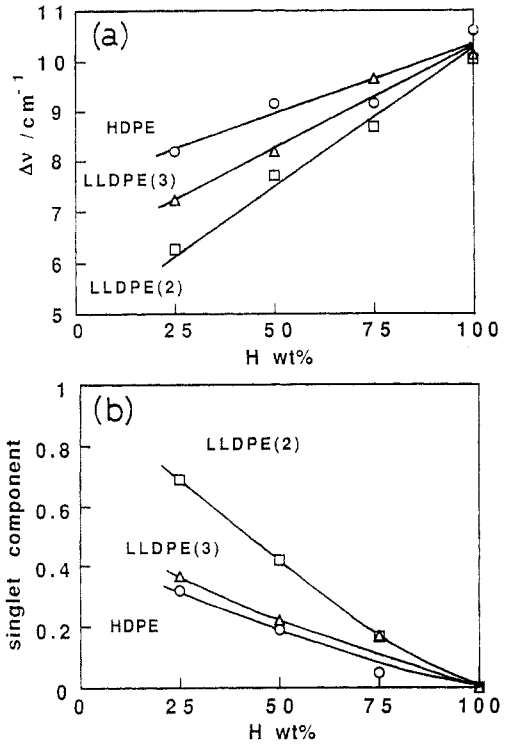

Figure 13. (a) Band splitting width and (b) ratio of singlet band intensity to the total intensity of the infrared CH_2 rocking band plotted against the blend content of the samples with various degrees of branching.

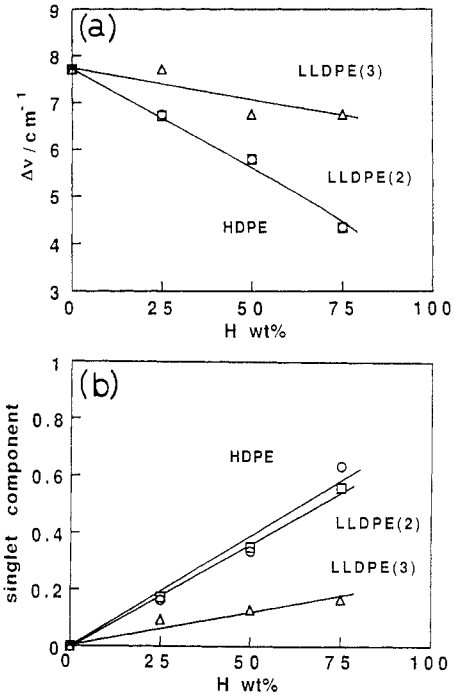

Figure 14. (a) Band splitting width and (b) ratio of singlet band intensity to the total intensity of infrared CD_2 rocking band plotted against the blend content of the samples with various degrees of branching.

from a series of H (or D) stems arrayed regularly along the (200) or (020) direction;[14-16] (2) doublet component originating from a coupled pair of CH_2···CH_2 (or CD_2···CD_2) groups in the crystalline lamellae, where the splitting width may vary depending on the D/H content because the distribution of these chain stems is considered to be determined *statistically randomly* as a function of the content; (3) doublet component coming from the segregated lamellae. Among all these three possibilities, the contribution of case 3 may be negligibly small in the DHDPE/LLDPE(2) blend. For DHDPE/LLDPE(3) and DHDPE/HDPE, factors 1-3 should be taken into consideration. In general the resolution of the profile into many components is so complicated as to yield a systematic change of states. In the present discussion we aim to clarify the relative content of the singlet component originating from the isolated chain stems. Thus, in an approximation, the spectra were separated into three components, a singlet [component 1] and a doublet. The thus evaluated doublet component may be assumed as an average of components 2 and 3, and in this sense, therefore, the estimated band splitting width of the doublet may be an overestimation for case 2 and an underestimation for case 3.

Figure 13 shows the blend content dependence of the $r(CH_2)$ band splitting width $\Delta\nu$ and the contribution of the singlet band intensity in the total band intensity. Figure 14 shows the results for the $r(CD_2)$ band. The splitting width and the singlet fraction change almost linearly with the H content for all the blend samples. The DHDPE/LLDPE(2) blend gives the smallest splitting width and the highest singlet component, compared with the other two cases of DHDPE/HDPE and DHDPE/LLDPE(3). The large splitting width and low singlet fraction are observed for all the D/H contents of the DHDPE/LLDPE(3) sample, indicating the high degree of phase segregation tendency between the D and H components. In this case the fraction of the singlet component is higher for the CH_2 band than for the CD_2 band. This may come from such a situation that the CH_2 chains, which are induced to cocrystallize in an early stage of crystallization of the D chains, are observed as a singlet band in the infrared spectra. The DHDPE/HDPE blend system is in a situation similar to that of DHDPE/LLDPE(3) but the role of the D and H components is reversed. The $r(CH_2)$ band of DHDPE/HDPE blend shows the large splitting width and the low singlet component compared with those of the $r(CD_2)$ band. The DHDPE chains crystallize originally in a temperature region lower than that of the HDPE chains. As mentioned above, some portion of DHDPE is considered to cocrystallize with the HDPE component during cooling from the melt, just when the CD_2 chains are isolated from each other by the surrounding CH_2 chains (the typical example is seen for the D/H = 25/75 sample in Figure 7, where the CD_2 band appears as almost pure singlet).

We may summarize these results as follows. Isolation of one component by being surrounded by another component is considered to occur in the following ways:

DHDPE/LLDPE(2): D and H components are randomly arranged.

DHDPE/LLDPE(3): The H component (with the originally lower crystallization temperature) is preferably surrounded by the D chains in the cocrystallized lamellae.

DHDPE/HDPE: The D component (with the originally lower crystallization temperature) is preferably isolated by the H chains in the cocrystallized lamellae.

That is, the component with the originally *lower* crystallization temperature tends to be isolated more easily by the counter component with the originally *higher* crystallization temperature. On the other hand, in the blend system showing almost perfect cocrystallization phenomenon, the D and H components are statistically randomly distributed in the lamellae. The detailed discussion will be made in a separate paper.

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