Cocrystallization and Phase Segregation of Polyethylene Blends. 1. Thermal and Vibrational Spectroscopic Study by Utilizing the Deuteration Technique

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ABSTRACT: Crystallization behavior has been investigated by DSC and Fourier transform infrared spectroscopic methods for the 50/50 wt % blends of deuterated high-density polyethylene (DHDPE) with hydrogeneous PE species having different branching content. A utilization of the fully deuterated sample as one component has made it possible to trace the crystallization behaviors of the H and D species separately by measuring the CH_2 and CD_2 vibrational bands as a function of temperature. The blend between DHDPE and linear low-density PE (LLDPE) with a relatively low degree of short-chain branching has been found to exhibit a cocrystallization phenomenon even in the slow cooling process from the melt. For the blend with high-density PE or LLDPE of a high degree of branching, the phase segregation has been observed between the D and H species. In this way the degree of cocrystallizability has been found to correlate with the branching content. The Davydov splitting of the infrared crystalline bands has also been found to be affected by the degree of branching of the H species in the blend.

Introduction

Recently much attention has been paid to the polymer blends from scientific and practical points of view. Polyethylene (PE) blends between the samples with different degrees of branching content have also been widely investigated.[1-10] In these studies, it is very important and useful to get the information of the structure and crystallization behavior of each component separately and at the molecular level. Unfortunately, however, the two components in the usual PE blends have almost the same chemical structure of carbon and hydrogen atoms. Therefore, it is very difficult to distinguish the behaviors of the components separately.[11-12] Then we tried here to use a deuterated PE sample as one component. This idea comes from such a fact that the infrared bands of CH_2 and CD_2 groups appear at different frequency positions. That is to say, by tracing the change in the infrared bands of CH_2 and CD_2 species, we may clarify the crystallization behavior of the H and D species and their correlation. Another interesting point is a problem of the cocrystallization and phase segregation between the H and D species in the PE blend.[13,14] (There have been many discussions on the blends between the H and D species such as high-density and linear low-density PE blends, etc.[1-9]) For example, in the blend between the deuterated HDPE (DHDPE) and hydrogeneous HDPE, the phase segregation was reported to occur when the sample was slowly cooled from the melt,[15-19] but such a segregation has been found not to occur in the blend of DHDPE with linear low-density PE (LLDPE) as described here. In this paper we will measure the differential scanning calorimetry and the temperature dependence of the infrared spectra during the heating and cooling processes from the melt in order to clarify the problem of cocrystallization and phase separation in the PE blend system.

In a study on blends, detailed information is also needed on the relationship between the structure (crystal structure, lamellar structure, and spherulite structure) and crystallization behavior as seen at different levels of viewpoint from molecular dimension to the higher dimension. Then we carried out the experiments of wide-angle and small-angle X-ray scatterings and small-angle light scattering in parallel with the present infrared study. The results will be reported in a separate paper.[20]

Experimental Section

Samples. In this study the deuterated high-density PE (DHDPE) sample was used as one component, which was purchased from Merck Chemicals Co., Ltd. The hydrogeneous PE samples with different degrees of branching were supplied from Exxon Chemicals Co., Ltd. (For the LLDPE samples the side chain is an ethyl group.) They were rinsed carefully by using *n*-hexane to remove the process oil (about 1% content). The characterization results of these samples are listed in Table I, in which the molecular weights were evaluated using GPC and the branching content was estimated from the viscosity measurement. The names of the samples were abbreviated as HDPE for high-density PE, LLDPE for linear low-density PE, and LDPE for low-density PE. The blends were prepared by dissolving the two equiweighted species (50 wt % DHDPE and 50 wt % HDPE, which is equivalent to 0.875 mol of DHDPE/1 mol of HDPE) in boiling *p*-xylene with a concentration of about 2 wt % and by rapidly precipitating into methanol at room temperature. The films for the infrared measurements were prepared by pressing the samples on the hot stage.

Measurements. The DSC thermograms in both the heating and cooling processes were measured using a Du Pont differential scanning calorimeter type 2000, and the data obtained in the second cycle were used in order to eliminate any thermal history. The heating and cooling rates were 10 °C/min. (Sometimes 2 °C/min, etc., was also used in order to investigate the heating/cooling rate dependence of the thermograms, but no essential difference was detected.) The temperature dependences of Fourier transform infrared (FTIR) spectra were measured in both the heating and cooling processes with a rate of ca. 1 °C/min. The used FTIR spectrophotometer was an IBM FTIR type 32 with an instrumental resolution of 2 cm^{-1}.

Results and Discussion

DSC Measurements. In Figures 1 and 2 are reproduced the DSC thermograms measured for the pure PE samples listed in Table I in the heating and cooling processes, respectively. The melting behavior becomes gradually broad as the branching content is increased from HDPE to LLDPE(3). DHDPE has a melting point about

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Table I
Characterization of PE Samples

	M_w	M_n	M_w/M_n	branching[a]
DHDPE	80K	14K	5.7	2-3
HDPE	126K	24K	5.3	1
LLDPE(1)	121K	27K	4.5	18
LLDPE(2)	75K	37K	2.0	17
LLDPE(3)	61K	20K	3.1	41
LDPE	181K	22K	8.2	26

[a] No. of short chains/1000 carbons.

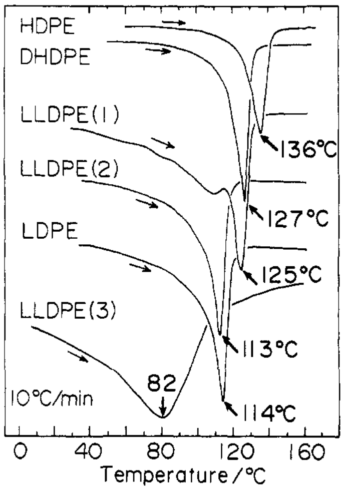

Figure 1. DSC thermograms measured for a series of PE samples in the heating process.

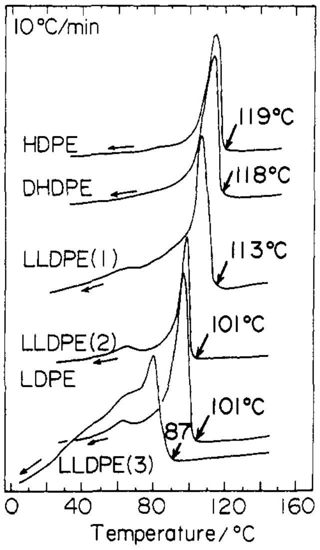

Figure 2. DSC thermograms measured for a series of PE samples in the cooling process.

9 °C lower than that of HDPE (at 10 °C/min), which is not inconsistent with the published data.[14,15] In the cooling process the DSC curves measured for the HDPE and LLDPE(1) and -(2) rise up relatively sharply. In the latter two cases broad shoulders which extend down to the lower temperature region are observed. For the LLDPE(3) an exothermic peak is appreciably broad and consists of at least three components. The subpeak near 65 °C is commonly observed for all the samples of LLDPE and LDPE.

In Figures 3–5 are shown, respectively, the DSC thermograms of the (i) DHDPE + HDPE, (ii) DHDPE + LLDPE(2), and (iii) DHDPE + LLDPE(3) systems in comparison of the following two types of samples: one is a blend obtained by precipitation from the p-xylene solution, and the other one is a simple mixture of the H and D species; i.e., the blocks of the two species were packed into the DSC sampling pan. In the thermogram of the DHDPE + HDPE system (Figure 3), apparently one but actually two overlapping peaks are observed in the heating process:they are slightly different in position from those of the original pure samples. In the cooling process, too, the two overlapping peaks are detected for both the blend and mixture although the peak positions are difficult to read out definitely. (It should be noted that the rising-up temperature of the curve is almost coincident with those of the original pure samples.) For the DHDPE + LLDPE(2) blend system shown in Figure 4, one sharp peak can be clearly observed in both the heating and cooling

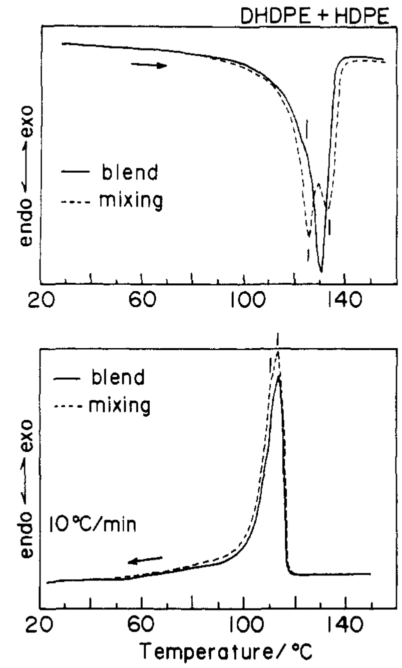

Figure 3. Comparison in the DSC thermogram between the blend and a mixture of the H and D species in the DHDPE + HDPE system: (upper) heating and (lower) cooling processes.

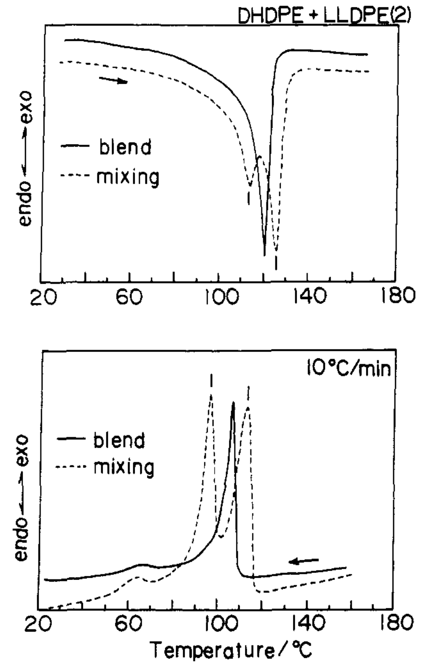

Figure 4. Comparison in the DSC thermogram between the blend and a mixture of the H and D species in the DHDPE + LLDPE(2) system: (upper) heating and (lower) cooling processes.

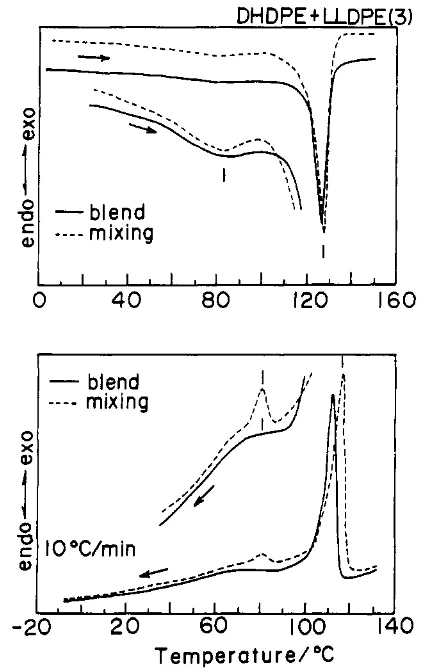

Figure 5. Comparison in the DSC thermogram between the blend and a mixture of the H and D species in the DHDPE + LLDPE(3) system: (upper) heating and (lower) cooling processes.

Table II
Thermal Analyses of PE Blends (Cooling from Melt[a])

			crystallinity, %	
	T_c, °C	ΔH, J/g	DSC[d]	X-ray[e]
DHDPE	117.6	173.4	60.1	68.2
HDPE	118.6	183.0	63.5	
blend	116.0 (+110.3[b])	204.7	71.0	
LLDPE(1)	113.2	110.9	38.5	
blend	109.9	150.3	52.1	
LLDPE(2)	100.8	126.9	44.0	50.2
blend	108.0	153.0	53.1	53.6
LLDPE(3)	86.7	82.5	28.6	34.0
blend	114.4 (+88.3[c])	119.0	41.3	38.6
LDPE	101.4	107.5	37.3	
blend	110.4	144.6	50.1	

[a] 10 °C/min. [b] Shoulder. [c] Subpeak. [d] $\Delta H^{\circ}(CH_2) = 288.4$ J/g which was assumed to be equal to $\Delta H^{\circ}(CD_2)$. [e] Refer to the following paper in this issue.[20]

processes; the rising-up temperature of the curve is quite different from the original ones. For the DHDPE + LLDPE(3) system in Figure 5, two peaks are observed in the heating process which correspond to those of the separated two components in the mixture. In the cooling process, for example, one exothermic peak is observed at the position 4 °C lower than the original one: this is considered to come from the DHDPE component. A very broad peak extending from 100 to 0 °C is common to both the blend and mixture and assigned to the crystallization peak of the LLDPE(3) component although the original sharp peak is smeared into a broad peak in the blend case. In Table II are listed the thermal analysis results made for all the samples.

As seen in Figures 3–5 and Table II, the melting and crystallization behaviors detected in the DSC thermograms are different between the blend and mixture. The degree of such a difference is dependent upon the type of the species included in the samples. Roughly speaking, the system of DHDPE with LLDPE(2) is most remarkably affected by an effect of blending. A disappearance of the two peaks coming from the original species and a simultaneous appearance of one sharp peak may indicate an occurrence of the *cocrystallization* between the two components. Such a cocrystallization is also detected for the blends of DHDPE with LLDPE(1) or LDPE, though the degree is a little lower than in the case of LLDPE(2), as clarified later. The blend of DHDPE with HDPE or LLDPE(3) gives a DSC curve not so much different from that of the simple mixture, although the peak position and profile are affected more or less after blending. Judging from Figures 1 and 2 and Table II, the degree of the cocrystallizability between the two components, detected by the DSC measurement, seems to correlate with the difference in the melting and/or crystallization temperature between the original two components. But, as seen in a later section, the infrared spectral data will show that this speculation is not the case. We must also consider some reasons for the lower shift in the peak position observed even for the blend samples which do not show a very high cocrystallization tendency, i.e., the samples of DHDPE + HDPE and DHDPE + LLDPE(3). Even when cocrystallization does not occur at all, in other words, even when the lamellae of each component exist separately in the blend sample, the melting (and crystallization) point may be influenced by such effects as the lamellar size and the interaction at the boundary between the two lamellae of the different species. The lamellae of one species might be surrounded not only by the amorphous phase of itself but also by the amorphous chains of the other species, resulting in some perturbation on the melting behavior of the species. In order to clarify these circumstances more clearly, the FTIR spectral measurements have been made as described below.

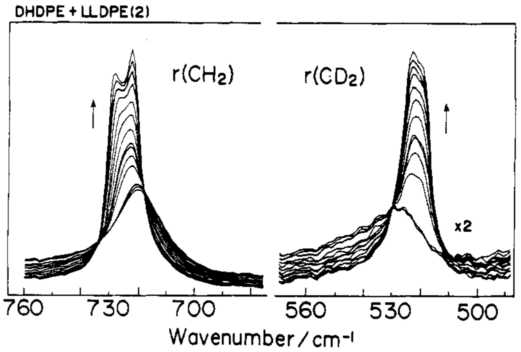

Figure 6. Temperature dependence of the infrared spectra measured for the DHDPE + LLDPE(2) blend sample in the cooling process from the melt. The temperatures are 130, 120, 111, 108, 105, 101, 99, 92, 82, 72, 60, 51, 40, and 30 °C from the bottom.

FTIR Measurements. (1) DHDPE + LLDPE(2) System. In Figure 6 is reproduced the temperature dependence of the FTIR spectra in the region of 800–500 cm^{-1}, which were taken for the blend system of DHDPE + LLDPE(2) during the cooling process from the melt. In Figures 7–10 the temperature dependences of the FTIR spectra are compared between the blend and mixture in the frequency regions of CH_2 rocking [r(CH_2)], CD_2 rocking [r(CD_2)], CH_2 bending [δ(CH_2)], and CD_2 bending [δ(CD_2)] vibrational modes. Quite consistently with the DSC data, the CH_2 and CD_2 crystalline bands have been found to increase their intensity almost simultaneously at about 108 °C or the crystallization temperature of the blend detected in the DSC thermogram. In these spectra the two remarkable phenomena can be noticed. One is the observation of the isobestic points between the crystalline and amorphous bands. Another point is the difference in the band splitting width between the pure H (or D) sample and the corresponding component in the blend. That is to say, the so-called Davydov splitting originating from

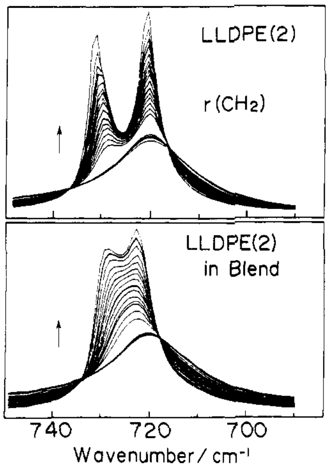

Figure 7. Comparison in the temperature variation of the r(CH_2) infrared band between the pure LLDPE(2) and the DHDPE + LLDPE(2) blend measured during the cooling from the melt. The temperatures are as follows: (upper) 120, 110, 107, 104, 101, 98, 95, 92, 89, 85, 80, 75, 72, 68, 65, 61, 55, 50, 41, and 27 °C and (lower) 120, 117, 114, 111, 108, 105, 101, 99, 96, 92, 88, 82, 78, 72, 65, 60, 51, 40, and 30 °C from the bottom.

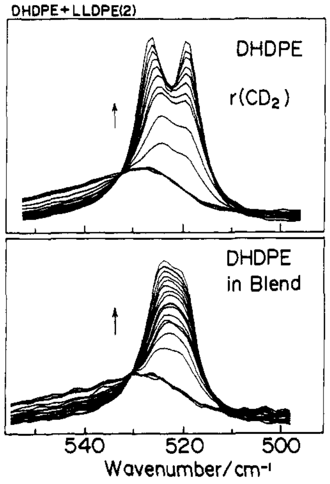

Figure 8. Comparison in the temperature variation of the r(CD_2) infrared band between the pure LLDPE(2) and the DHDPE + LLDPE(2) blend measured during the cooling from the melt. The temperatures are as follows: (upper) 130, 120, 115, 110, 105, 100, 90, 80, 70, 60, 50, 40, and 30 °C and (lower) 120, 117, 114, 111, 108, 105, 101, 99, 96, 92, 88, 82, 78, 72, 65, 60, 51, 40, and 30 °C from the bottom.

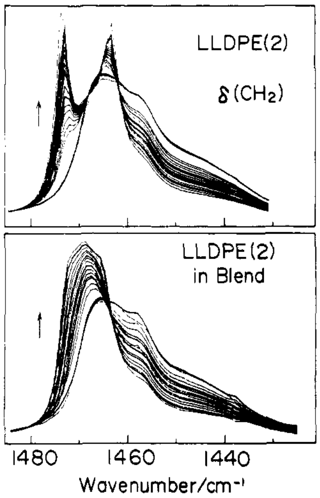

Figure 9. Comparison in the temperature variation of the δ(CH_2) infrared band between the pure LLDPE(2) and the DHDPE + LLDPE(2) blend measured during the cooling from the melt. The temperatures are as follows: (upper) 120, 110, 107, 104, 101, 98, 95, 92, 89, 85, 80, 75, 72, 68, 65, 61, 55, 50, 41, and 27 °C and (lower) 120, 117, 114, 111, 108, 105, 101, 99, 96, 92, 88, 82, 78, 72, 65, 60, 51, 40, and 30 °C from the bottom.

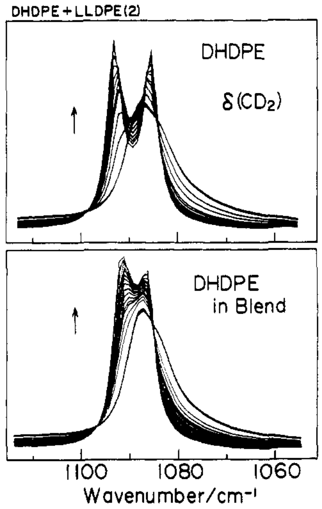

Figure 10. Comparison in the temperature variation of the δ(CD_2) infrared band between the pure LLDPE(2) and the DHDPE + LLDPE(2) blend measured during the cooling from the melt. The temperatures are as follows: (upper) 130, 120, 115, 110, 105, 100, 90, 80, 70, 60, 50, 40, and 30 °C and (lower) 120, 117, 114, 111, 108, 105, 101, 99, 96, 92, 88, 82, 78, 72, 65, 60, 51, 40, and 30 °C from the bottom.

the intermolecular interactions is smaller in the blend than the pure polymer for all the bands of r(CH_2), r(CD_2), δ(CH_2), and δ(CD_2). An existence of the isobestic points suggests that the infrared spectra of the blend can be interpreted in a good approximation as a simple summation of the spectra of the two phases, i.e., the crystalline and amorphous phases, although, strictly speaking, the temperature dependence of molar absorption coefficients of these two phases should be taken into account.[21] Under such an assumption of neglecting the temperature dependence of the molar absorption coefficients, the following equation may be written. When the absorbance spectrum of the pure crystalline sample is represented by C and that of the 100% pure amorphous sample by A, then spectrum B of the semicrystalline sample with a degree of crystallinity k_c is expressed by

$$B = k_c C + (1 - k_c)A$$

Therefore, by performing the subtraction calculation between the observed spectra B and A the crystalline spectrum ($k_c C$) could be obtained. In the actual process of subtraction, the FTIR spectrum of the molten state was used as A. The coefficient k_c was determined so that the broad amorphous band was eliminated completely and reasonably. Thus obtained crystalline spectra are shown in Figures 11–14 in comparison with those for the original pure polymers. The coefficient k_c evaluated in this way is plotted against temperature in Figure 15 for the pure samples. The k_c at room temperature decreases gradually as the branching content is increased from HDPE to LLDPE(3). Figure 16 shows the temperature dependence of the coefficient k_c evaluated for the H and D species of the DHDPE + LLDPE(2) blend system in comparison with those of the original pure polymers. Different from the cases of pure polymers, the k_c's of the CH_2 and CD_2 bands begin to increase *simultaneously* in the vicinity of the crystallization point detected by the DSC measurement, indicating clearly a phenomenon of the cocrystallization. More direct proof of this cocrystallization could be found by the wide-angle and small-angle X-ray scattering mea-

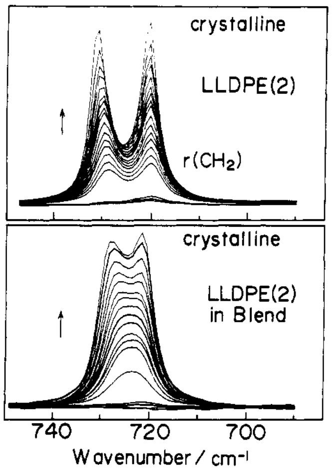

Figure 11. Comparison in the temperature variation of the r(CH_2) *crystalline* band between the pure LLDPE(2) and the DHDPE + LLDPE(2) blend measured during the cooling from the melt. The temperatures are as follows: (upper) 110, 107, 104, 101, 98, 95, 92, 89, 85, 80, 75, 72, 68, 65, 61, 55, 50, 41, and 27 °C and (lower) 120, 117, 114, 111, 108, 105, 101, 99, 96, 92, 88, 82, 78, 72, 65, 60, 51, 40, and 30 °C from the bottom.

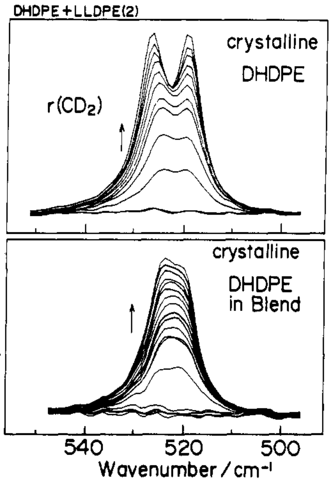

Figure 12. Comparison in the temperature variation of the r(CD_2) *crystalline* band between the pure LLDPE(2) and the DHDPE + LLDPE(2) blend measured during the cooling from the melt. The temperatures are as follows: (upper) 120, 115, 110, 105, 100, 90, 80, 70, 60, 50, 40, and 30 °C and (lower) 120, 117, 114, 111, 108, 105, 101, 99, 96, 92, 88, 82, 78, 72, 65, 60, 51, 40, and 30 °C from the bottom.

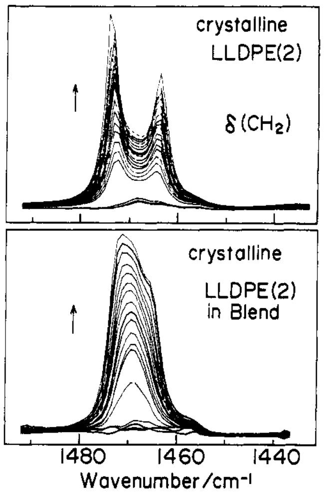

Figure 13. Comparison in the temperature variation of the δ-(CH_2) *crystalline* band between the pure LLDPE(2) and the DHDPE + LLDPE(2) blend measured during the cooling from the melt. The temperatures are as follows: (upper) 110, 107, 104, 101, 98, 95, 92, 89, 85, 80, 75, 72, 68, 65, 61, 55, 50, 41, and 27 °C and (lower) 120, 117, 114, 111, 108, 105, 101, 99, 96, 92, 88, 82, 78, 72, 65, 60, 51, 40, and 30 °C from the bottom.

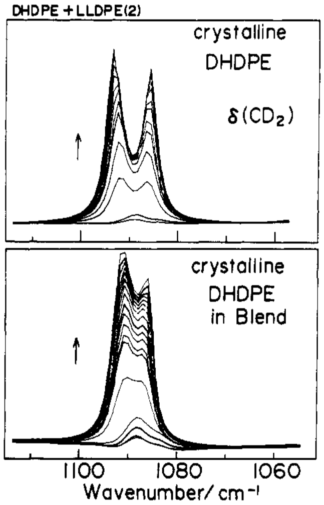

Figure 14. Comparison in the temperature variation of the δ-(CD_2) *crystalline* band between the pure LLDPE(2) and the DHDPE + LLDPE(2) blend measured during the cooling from the melt. The temperatures are as follows: (upper) 120, 115, 110, 105, 100, 90, 80, 70, 60, 50, 40, and 30 °C and (lower) 120, 117, 114, 111, 108, 105, 101, 99, 96, 92, 88, 82, 78, 72, 65, 60, 51, 40, and 30 °C from the bottom.

surements as reported later.[20] In Figures 15 and 16 it should be noted that the $k_c(CH_2)$ and $k_c(CD_2)$ are different from each other. No comparison can be made for the absolute crystallinity between the CH_2 and CD_2 species, although they should be the same if the original definition of k_c is taken into account. This may come from the difference in the ratio (ϵ_c/ϵ_a) of the molar absorption coefficients of the crystalline and amorphous bands between the H and D species. That is to say, even at the stage where the contribution of the CH_2 amorphous band is eliminated from the spectra, the amorphous component of the CD_2 spectra cannot be completely erased away because the relative intensity of the crystalline and amorphous bands is different between the H and D species.

In Figures 11–14 we can also notice that the band splittings are smaller in the blend than the original samples. These differences in the band splitting are considered to reflect the changes in the intermolecular interactions caused by the invasion of CH_2 (or CD_2) stems into the CD_2 (or CH_2) lamellae by cocrystallization.[13,14,18] The detailed discussion will be made in a later section. In addition to these spectral changes the bandwidth of the CD_2 stretching region, for example, is found to be much smaller for the blend than for the DHDPE pure polymer, as shown in Figure 17. This also seems to correlate with the smaller band splitting mentioned above.

(2) DHDPE + LLDPE(3). In Figure 18 is shown the temperature dependence of the r(CH_2) and r(CD_2) bands measured during the slow cooling of the DHDPE + LLDPE(3) blend system. The crystalline r(CD_2) band begins to appear at first around 111 °C, and then the crystalline r(CH_2) band appears in the vicinity of 90 °C and increases quite gradually. The temperature dependence of the coefficient k_c reflects this situation more clearly as shown in Figure 19. The two curves of $k_c(CD_2)$ and $k_c(CH_2)$ are almost coincident with those of the independently measured curves of these two polymer components and quite consistent with the DSC data of Figure 5. Roughly speaking, therefore, we may conclude that the crystallization occurs separately between the CH_2 and CD_2

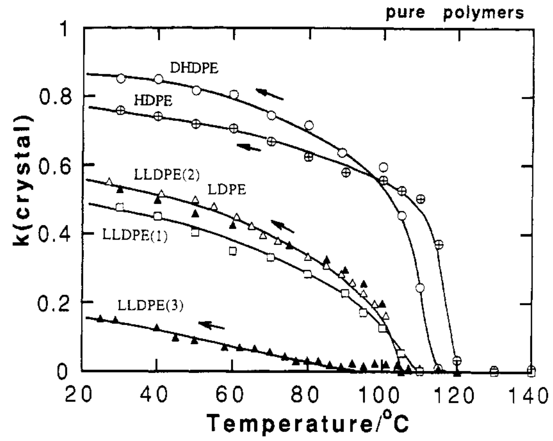

Figure 15. Temperature dependence of the coefficient k_c estimated for a series of the pure polyethylene samples.

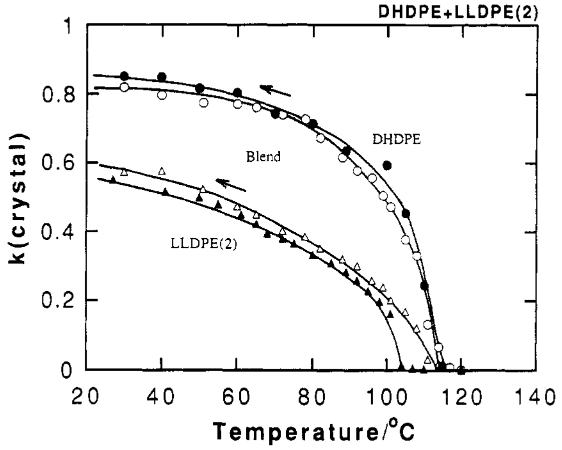

Figure 16. Temperature dependence of the coefficient k_c estimated for the DHDPE + LLDPE(2) system: (open circles and triangles) blend; (filled circles and triangles) pure samples.

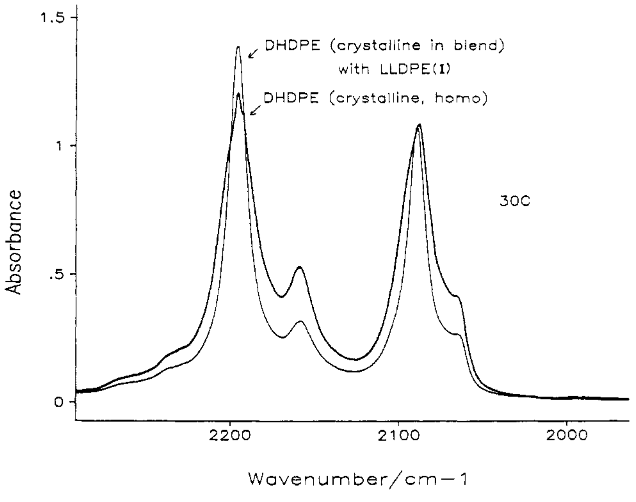

Figure 17. Comparison in the infrared spectral pattern in the frequency region of 2000–2300 cm^{-1} between the blend and pure sample for the DHDPE + LLDPE(1) system where the amorphous contribution is subtracted. (The essential feature is just the same also for the DHDPE + LLDPE(2) system.)

components in this blend system. Strictly speaking, however, some interactions exist between the two components even in this blend system, as judged from the Davydov splitting of the crystalline bands. A detailed discussion is presented in a later section.

(3) Correlation between the CH_2 and CD_2 Species in the Crystallization Process. In order to investigate the strength of the correlation between the CH_2 and CD_2 species in the crystallization process from the melt, the coefficient $k_c(CH_2)$ is plotted against $k_c(CD_2)$ at the corresponding temperature. The results are summarized in Figure 20 for all the blend samples used in this experiment. For example, in the blend of DHDPE + LLDPE(2) (curve c in Figure 20), the crystalline bands of the H and D components begin to appear simultaneously and they increase the intensities in parallel, indicating the cocrystallization phenomenon. The blend systems of DHDPE + LLDPE(1) (curve b) and DHDPE + LDPE (curve d) exhibit also very similar behavior with curve c, although

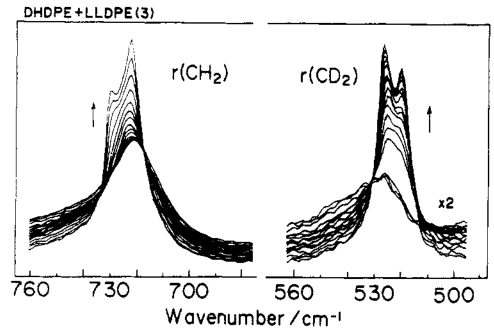

Figure 18. Temperature dependence of the infrared spectra of the DHDPE + LLDPE(3) blend sample measured during the cooling from the melt. The temperatures are 130, 120, 114, 111, 108, 105, 99, 93, 87, 81, 75, 68, 60, 50, 40, and 30 °C from the bottom.

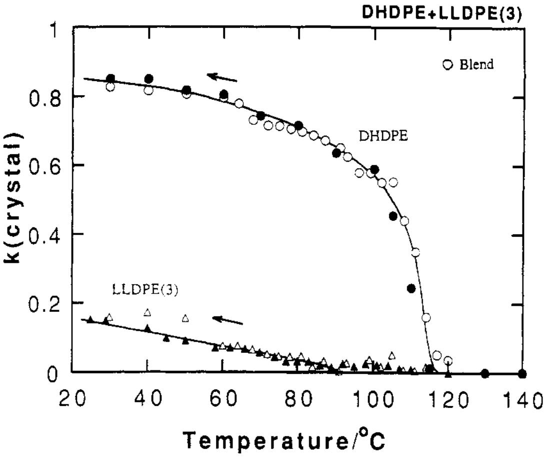

Figure 19. Temperature dependence of the coefficient k_c estimated for the DHDPE + LLDPE(3) system: (open circles and triangles) blend sample; (filled circles and triangles) pure samples.

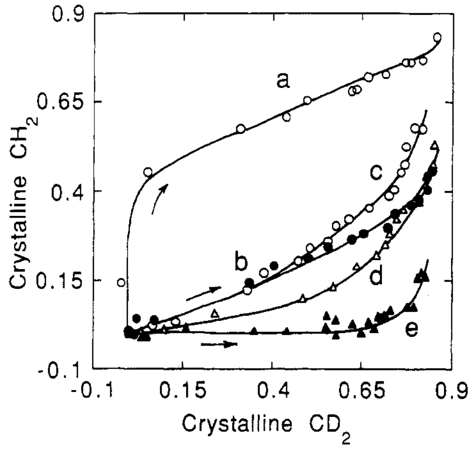

Figure 20. Correlation of the coefficient k_c between the CH_2 and CD_2 crystalline bands for a series of the DHDPE blend samples with (a) HDPE, (b) LLDPE(1), (c) LLDPE(2), (d) LDPE, and (e) LLDPE(3).

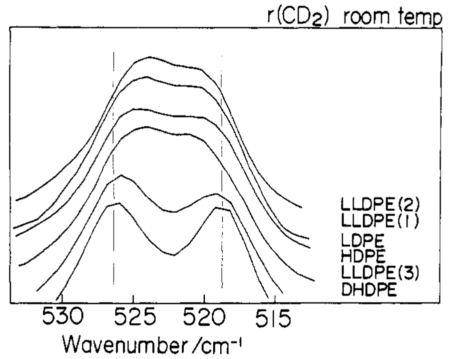

Figure 21. Comparison in the r(CD_2) infrared band profile between a series of the blends and pure DHDPE sample measured at room temperature.

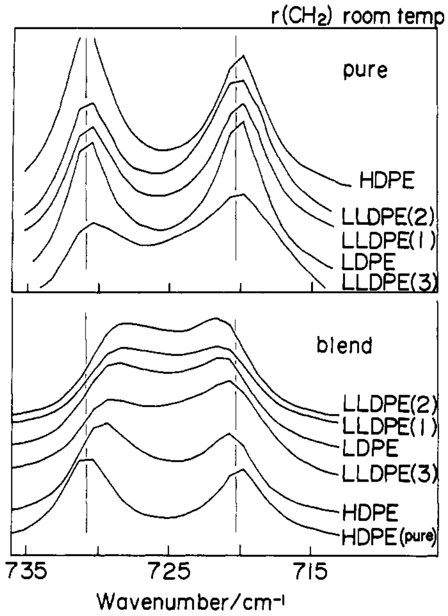

Figure 22. Comparison in the r(CH_2) infrared band profile: (upper) between the pure samples and (lower) between a series of the blends measured at room temperature.

the degree of cocrystallization is lower for the blend DHDPE + LDPE than for the DHDPE + LLDPE(1) blend as noticed from the curves. In the case of the DHDPE + HDPE blend, on the other hand, the CH_2 crystalline phase begins to appear in the higher temperature region, during which the $k_c(CD_2)$ remains zero, and then the CD_2 crystalline phase begins to be observed in the lower temperature region. The DHDPE + LLDPE(3) blend shows the opposite behavior: the CH_2 crystalline bands appear after an appreciable intensity of the crystalline CD_2 bands grows in the higher temperature region. In this way the degree of cocrystallization is found to change remarkably depending upon the relative branching content of the H species. On the basis of the DSC data and Figure 20, the degree of cocrystallization may change in the following order:

LLDPE(2) > LLDPE(1) > LDPE ≫ HDPE, LLDPE(3)

Such a tendency of cocrystallization can also be detected from the difference in the IR band splitting among the various blends. In Figures 21 and 22 are compared, respectively, the Davydov splittings of the r(CD_2) and r(CH_2) bands among a series of the blends at room temperature. Any essential difference cannot be detected between the pure polymers as shown in Figure 22 (top), while the band splitting becomes smaller when these H species are trapped in the blends. The largest change in the band splitting is seen for the blend sample of DHDPE + LLDPE(2). The splitting width is considered qualitatively in proportion to the degree of cocrystallization estimated in Figure 20. It may be interesting to note that even for the blend with HDPE or LLDPE(3), which shows poor correlation between the CH_2 and CD_2 components, the band splitting is still different from the pure polymer cases. According to Krimm et al.,[13,14,18] the band splitting is affected by the aggregation state of the H and D stems in the lamellae. For example, in the crystalline lamella consisting of the CH_2 and CD_2 chain components, a perfect side-by-side arrangement of the CD_2 trans zigzag stems only along the (100) plane does not give any band splitting if the $CH_2...CD_2$ intermolecular interaction is very small. On the contrary, an alternately directed packing of the CD_2 stems along the (110) plane gives the band splitting. A finite size of the CD_2 (or CH_2) crystalline domain (or cluster) included in a lamella affects also the band splitting width.[18] If these ideas may be applied to the present blend cases, then the experimental facts presented in Figures 21 and 22 allow us to speculate that the blend sample has some special arrangements of the CH_2 and CD_2 stems in the lamellae and that such a packing structure is related with the branching content of the hydrogenous species. Additional data of the wide-angle and small-angle X-ray scattering and small-angle light scattering will make it possible to discuss the more detailed structure of the blends.[20]

After getting the above-mentioned conclusions on the cocrystallization and phase segregation, we noticed that Schelten et al. had tried to prepare the blend sample of DHDPE with slightly branched high-density PE by slow cooling.[19] They said, however, that the segregation or clustering effect could not be eliminated completely. This may come from the small degree of branching of the PE sample they used, as judged by Figure 20.

(4) Factors Affecting the Cocrystallization Behaviors. As described above, the blend sample of DHDPE and LLDPE(2) has been found to show the cocrystallization phenomenon, and the degree of cocrystallization (or phase segregation) between the H and D species is affected by the relative branching content of the H species. The branching has been well-known to influence the crystal structure and various physical properties of PE samples. As discussed in the preceding section, the r(CH_2) band splitting can be assumed qualitatively as a measure of the degree of cocrystallizability. In order to clarify the factors determining the degree of cocrystallizability, therefore, the band splitting measured at room temperature is plotted against the difference in such various physical parameters between the D and H species as melting point (T_m), crystallization temperature (T_c), molecular weight (M_w), molecular weight distribution (M_w/M_n), degree of crystallinity (x), etc., where the difference between the D and H species was used because the "closeness" in these physical quantities between D and H species is considered to be related to the cocrystallization behavior. In Figure 23, for example, the difference in T_c between the H and D species is used as a physical parameter. However, no good correlation can be extracted from it. Simply considering, we could speculate that the closer T_c between the two components results in the cocrystallization, but such an idea cannot be applied here as typically seen for the blend of DHDPE and HDPE; the two components exhibit very close T_c to each other (Figure 2) but do not cocrystallize so well. In fact, Figure 23 does not show any good correlation between the band splitting and T_c. Closeness in the M_w/M_n and M_w between the D and H species does

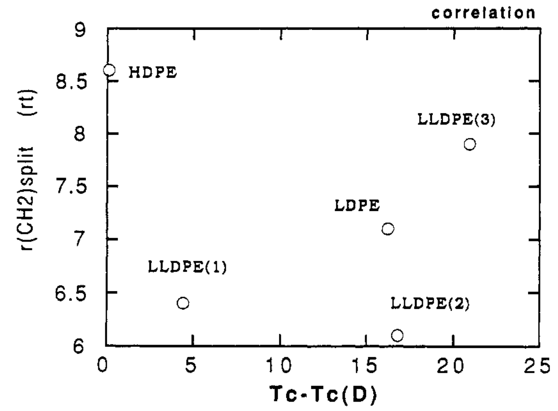

Figure 23. Correlation between the r(CH$_2$) band splitting and the crystallization temperature T_c (the difference from that of the DHDPE sample) estimated for a series of the blend samples.

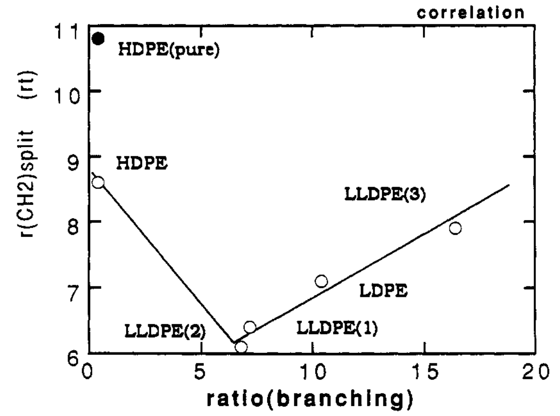

Figure 24. Correlation between the r(CH$_2$) band splitting and the branching content (the ratio to that of the DHDPE sample) estimated for a series of the blend samples.

not also show any good correlation with the cocrystallization.

In Figure 24 is plotted the r(CH$_2$) band splitting against the ratio of the branching content between the H and D species, giving a fairly good correlation. The branching affects not only the T_c, T_m, etc., but also the crystallization rate (R_c) from the melt. The R_c is reasonably speculated to decrease with an increase of the branching content:

$$\text{HDPE} > \text{LLDPE(2)} > \text{LLDPE(1)} > \text{LDPE} > \text{LLDPE(3)}$$

Mandelkern et al. reported that the crystallization rate of DHDPE is lower than that of HDPE in the crystallization process from the dilute solution.[15] If DHDPE is positioned accidentally around LLDPE(2) in the above-mentioned R_c sequence, then the difference in the R_c will be minimal for the blend between DHDPE and LLDPE(2) and increase for the blends with HDPE or LLDPE(3). Such a difference in R_c among LLDPE(2), HDPE, LLDPE(3), and so on might result in the difference in the degree of cocrystallization. In order to prove this speculation, we need to investigate the crystallization behavior or the kinetics of these blend systems.

Concluding Remarks

The high-density PE blend system between the D and H species has been reported so far to show the cocrystallization behavior only for the samples prepared by rapid quenching. Slow cooling from the melt results in the phase segregation phenomenon.[15-19] In this paper, however, the cocrystallization phenomenon was found to occur for the blend samples between the DHDPE and LLDPE *even for the slow cooling process from the melt.* This finding seems very important from the various points of view. For example, in the neutron experiments many efforts have been made to investigate the spatial correlation of the D and H stems in the crystalline lamella of PE, but the samples were limited only to those prepared by quenching as stated above. The DHDPE + LLDPE(2) system, a typical sample of cocrystallization, may be useful for such an experiment. In other words, by investigating the neutron scatterings in the wide- and small-angle regions, we may clarify the local positions of the H and D stems in the crystalline lamella and the influence of branching on such a crystalline structure. As pointed out in Figures 21 and 22, the infrared band splitting is remarkably affected by the degree of cocrystallization. This finding is also important in investigating the chain-folding mechanism, as discussed by Krimm et al.[13,14,18] Through these studies we may clarify the role of branching in the crystallization of PE samples.

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