Cocrystallization and Phase Segregation of Polyethylene Blends between the D and H Species. 5. Structural Studies of the Blends As Viewed from Different Levels of Unit Cell to Spherulite

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ABSTRACT: The structure of polyethylene (PE) blends between deuterated high-density PE (DHDPE) and hydrogeneous PE with various degrees of side chain branching (for example, linear low-density PE (LLDPE)) has been investigated on the basis of wide-angle and small-angle X-ray scatterings, infrared absorption spectra, and small-angle light scattering measured at room temperature. For the blend samples showing an almost perfect cocrystallization phenomenon between the D and H species (DHDPE + LLDPE-(2)), the unit cell parameters, crystallite size, interlamellar spacing, and spherulite size change continuously depending on the relative D/H content. For the case showing phase segregation between the D and H species (DHDPE + LLDPE(3)), lamellae consisting of either D or H chains are stacked together to form a spherulite, the size of which is remarkably larger than those of the pure D or H component.

Introduction

In a series of papers we have investigated the crystallization behavior of polyethylene (PE) blends between deuterated high-density PE (DHDPE) and hydrogeneous PE with various degrees of side chain branching on the basis of measurements of DSC, X-ray diffraction, and infrared spectra as a function of temperature.[1-4] As a result, the crystallization behavior was found to change drastically depending on the degree of branching and the relative content of D and H species. For example, the DHDPE blend with linear low-density PE having ca. 17 ethyl branchings/1000 carbons [LLDPE(2)] shows almost perfect cocrystallization phenomenon, i.e., the D and H species coexist in a common crystallite *even when cooled slowly from the melt*. This cocrystallization occurs for all the blend samples containing an arbitrary content of the D and H species. On the other hand, the blend of DHDPE with LLDPE(3) having ca. 41 branchings/1000 carbons exhibits essentially the phase segregation and the D and H species separately form their own crystalline lamellae. In our previous paper we measured the X-ray scatterings [wide angle (WAXS) and small angle (SAXS)], infrared spectra, and small-angle light scatterings (SALS) for these blend samples with D/H = 50/50 wt % composition and discussed the structure of crystal lattice, lamellar stacking, and spherulite.[2] In this paper, we will describe how these structures change depending on the D/H content as well as the degree of branching.

Experimental Section

Samples. As described in the previous studies,[1-4] DHDPE, which was purchased from Merck Chemical Co., Ltd., was used as one component in the blends. The hydrogenous PE 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. The blends were prepared by dissolving the D and H species of 25:75, 50:50, or 75:25 wt % ratio into 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.

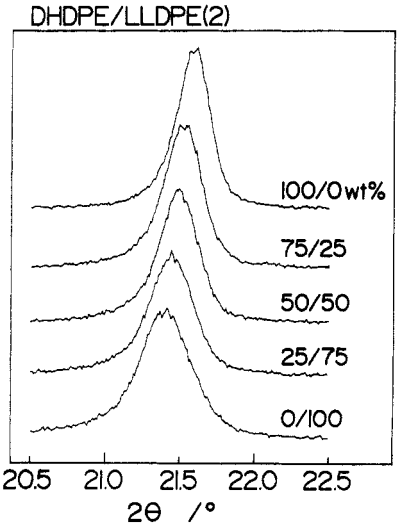

Figure 1. Blend content dependence of the 110 X-ray reflection pattern measured for the DHDPE/LLDPE(2) blend system at room temperature.

Table 1. Characterization of PE Samples

	M_w	M_n	M_n/M_w	branching/1000C
DHDPE	80 000	14 000	5.7	2-3
HDPE	126 000	24 000	5.3	1
LLDPE(2)	75 000	37 000	2.0	17
LLDPE(3)	61 000	20 000	3.1	41

Measurements. Infrared spectra were taken by using a Japan Spectroscopic Co. FT-IR 8300 spectrometer. X-ray diffraction powder patterns were obtained using a Rigaku RAD-ROC diffractometer with a graphite-monochromatized Cu Kα radiation (λ = 1.5418 Å). The SAXS was measured using a Mac Science Imaging Plate System with a sample-to-detector distance of 1 m. The SALS patterns were taken for the samples sandwiched by a pair of cover glass and by using a laser light source of 632.8 nm wavelength under the polarization condition of H_V at room temperature.

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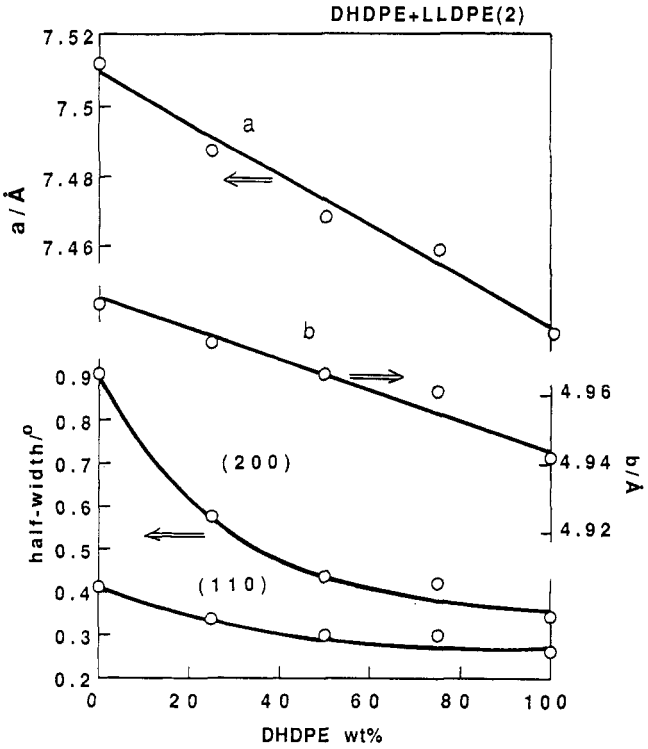

Figure 2. Blend content dependence of the unit cell parameters a and b and half-width of the 200 and 110 reflections evaluated for the DHDPE/LLDPE(2) blend system.

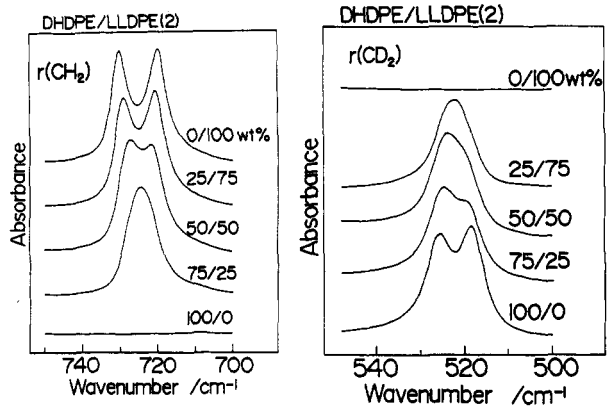

Figure 3. Blend content dependence of infrared spectra measured for DHDPE/LLDPE(2) blend samples at room temperature in the frequency regions of the CH_2 and CD_2 rocking modes.

Results and Discussion

DHDPE/LLDPE(2) Blend System. (A) Structure of Crystalline Lamellae. As described above, this blend shows almost perfect cocrystallization phenomenon in the lamellar crystal. Figure 1 shows the 110 X-ray reflection patterns measured at room temperature for the blend samples with various D/H contents. Depending on the D content the peak shifts continuously between the positions intrinsic of pure DHDPE and LLDPE(2) crystallites. The unit cell parameters (a and b) and the half-width evaluated from the 110 and 200 reflections change as shown in Figure 2 depending on the blend content. Originally, the DHDPE shows a more regularly packed crystal structure compared with the LLDPE(2) having some degree of ethyl branching. In the cocrystallized sample, the D and H chains coexist in the same crystallite and so the regularity of the unit cell decreases gradually as the branched H chains are introduced into the DHDPE lattice.

In Figure 3 is shown the change of infrared spectral pattern of the CH_2 and CD_2 rocking bands measured at room temperature for a series of the samples. In the case

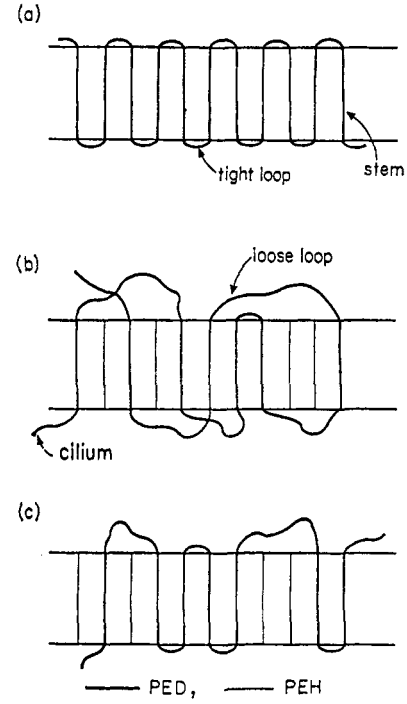

Figure 4. Some illustrations of chain-folding models: (a) regular adjacent reentry model, (b) random reentry model, and (c) central cluster model.

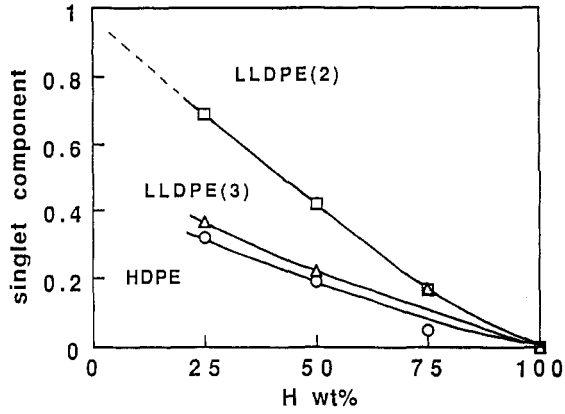

Figure 5. Blend content dependence of the relative intensity of CH_2 rocking singlet band estimated for the blend samples (room temperature).

of the orthorhombic PE crystal, the CH_2 bands split into two components because of intermolecular interactions between the neighboring CH_2 chain stems. If a CH_2 chain stem is surrounded by the CD_2 stems, then the vibrational coupling between the CH_2 groups becomes weaker and the band splitting width decreases correspondingly.[5] A similar situation can also be expected for the CD_2 bands. The spectral change observed in Figure 3 clearly indicates that this occurs in the DHDPE/LLDPE(2) blend system. Krimm et al. measured the CD_2 band splitting width for the HDPE samples containing the highly diluted DHDPE component and analyzed it as a function of the CD_2 cluster size.[6,7] In that analysis they assumed that such a cluster is formed as a result of *regular adjacent reentry* of the folded chains along the (100) and (110) directions (see Figure 4a). The array of chain stems along the (100) direction gives a singlet band, while the array along the (110) direction causes the band splitting. Depending on the relative content of these two types of arrays, the apparent band splitting width or the band profile can change in a complicated manner. The change in the infrared spectral pattern shown in Figure 3 might be also interpreted based on such an idea. In the previous paper[4] we resolved the infrared bands of Figure 3 into several

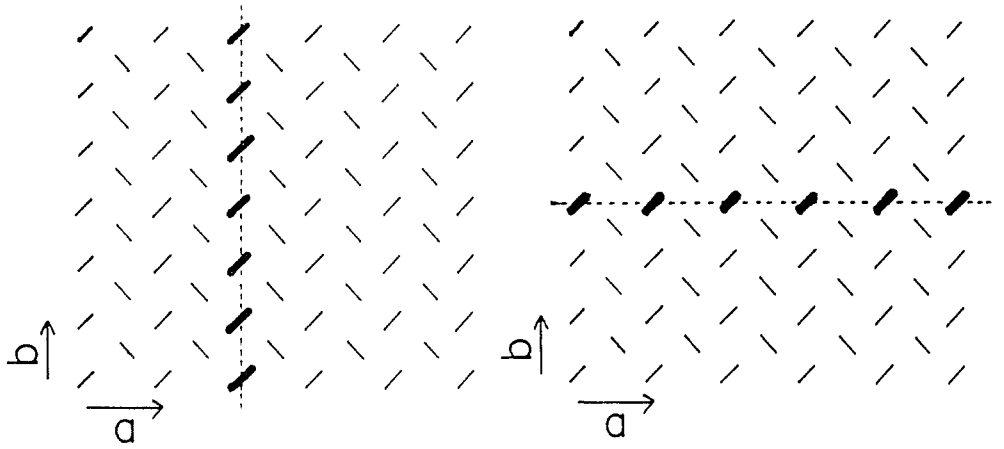

Figure 6. Illustration of regularly adjacent folding of isolated single chain along the (100) plane or (010) plane.

components and found that the band splitting width of the doublet component and the fraction of singlet band component change almost linearly with the D/H content, as reproduced in Figure 5. Being extrapolated to the H content 0%, i.e., in an extremely diluted case, the singlet fraction is considered to reach almost unity. If the above-mentioned adjacent reentry model is persisted even in such an extreme case, we have to imagine that the isolated single chain is folded many times regularly only along the (100) or (010) plane (see Figure 6). Such a folding mode has been said to be possible in the melt-crystallized sample.[8] But the sample used there was a blend of DHDPE and HDPE, and the problem of phase segregation between the D and H species makes the discussion obscure, different from the present cocrystallized system. Besides, the regularly repeated folding structure of an isolated long chain *as a whole* is difficult to imagine from the stereochemical point of view. *n*-Paraffin crystals consisting of the mixture of CH_2 and CD_2 chains behave just as in the DHDPE/LLDPE(2) blend system: the band splitting width changes gradually and an almost perfect single narrow band can be observed for the crystal of $C_{36}D_{74}/C_{36}H_{74}$ (1/20), for example.[7] This spectral change was reasonably interpreted by assuming a statistically mixed crystal of the D and H chains. It may be natural to consider that the DHDPE/LLDPE(2) case is also interpreted by using such a statistically mixed crystalline model (see Figure 4b): the probability of the CH_2 (CD_2) chains neighboring with the CD_2 (CH_2) chains is determined by the D/H blend content.

This conclusion is important in association with the long controversial history of the folding mechanism of PE crystal.[8] Mainly three models have been proposed so far based on the infrared and neutron scattering experimental data collected for the HDPE/DHDPE blend system: (1) the perfectly random reentry model; (2) the regular adjacent reentry model; and (3) the central cluster model in which random reentry occurs in some parts and regular adjacent reentry in other parts. The most natural interpretation of Figure 3 may be made on the basis of the model 2, *the statistically random* positioning of the D and H stems. In other words, it is difficult to apply the *perfectly adjacent* reentry folding model to, at least, this DHDPE/LLDPE(2) system slowly crystallized from the melt. So far the discussion on the chain folding in the HDPE/DHDPE blend system has been limited mainly to the samples which were prepared by rapid quenching from the melt in order to escape from the phase segregation problem.[8] The present result may be useful for clarifying the folding mechanism in the PE sample crystallized under *normal* slow cooling conditions or isothermal conditions. The model discussed here can also be supported by the wide-angle neutron scattering (WANS) measurement,

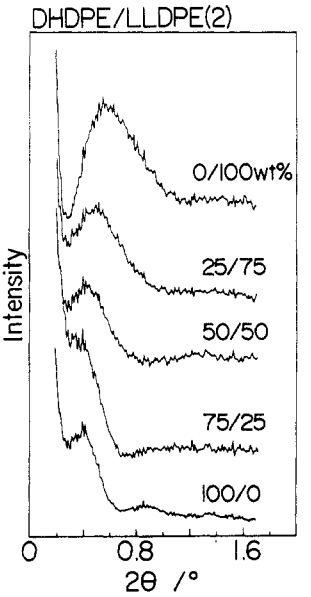

Figure 7. SAXS patterns of a series of DHDPE/LLDPE(2) blend measured at room temperature.

which will be reported in a separate paper with the computer simulation of the infrared band splitting and WANS profile.

(B) Higher Order Structure. The effect of cocrystallization on higher order structure such as the lamellar stacking structure and the spherulite structure may be deduced by measuring the SAXS and SALS (and SANS). In Figure 7 are shown the SAXS patterns of this blend system taken at room temperature. With the change in blend content the peak position shifts continuously between those of the pure samples. The long periods L estimated from these peaks are plotted against the blend content in Figure 9. Figure 8 shows the SALS (H_v) patterns. The spherulite size R estimated form the peak position is plotted in Figure 9. The crystallite size D estimated using Scherrer's equation from the half-width of the WAXS 200 reflection (Figures 1 and 2) is also shown in Figure 9. All these structural parameters, i.e., the lamellar size, long spacing (interlamellar distance), and spherulite size, change continuously and systematically depending on the blend content. Thus, we can notice a good correlation between the inner structure of the lamellae and the higher order morphology: the continuous change in the packing structure of the unit cell reflects on the continuous morphological change.

DHDPE/LLDPE(3) Blend System. (A) Phase Segregation. The phase segregation phenomenon in this blend sample is observed in the X-ray reflection pattern measured at room temperature as in the infrared pattern

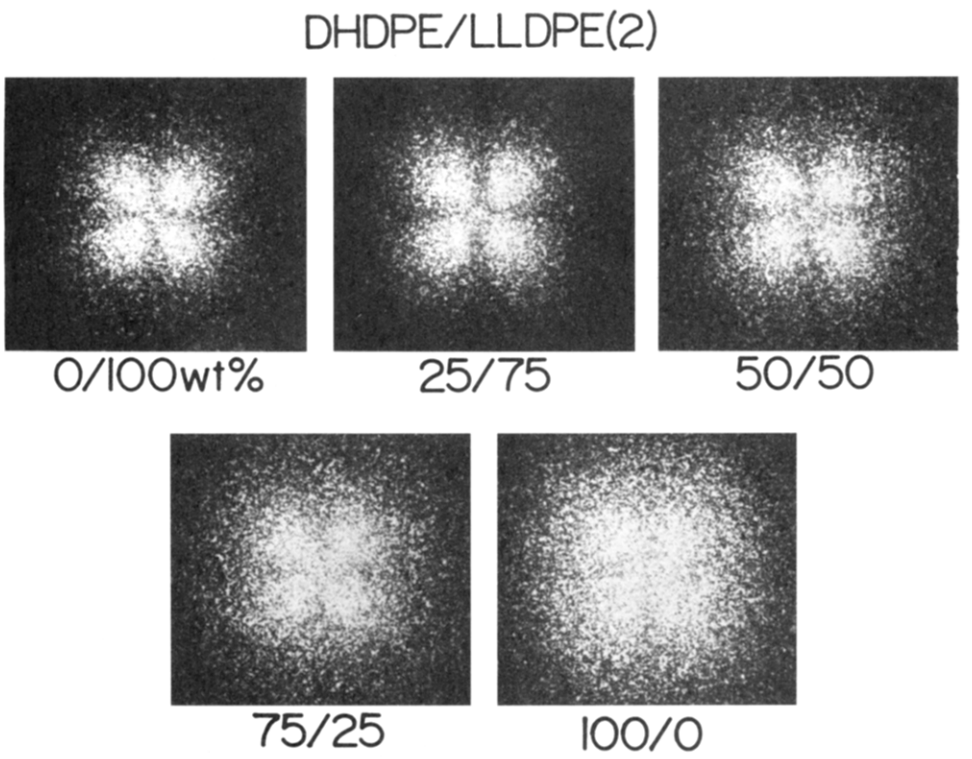

Figure 8. SALS (H_v) patterns of a series of DHDPE/LLDPE(2) blend samples measured at room temperature.

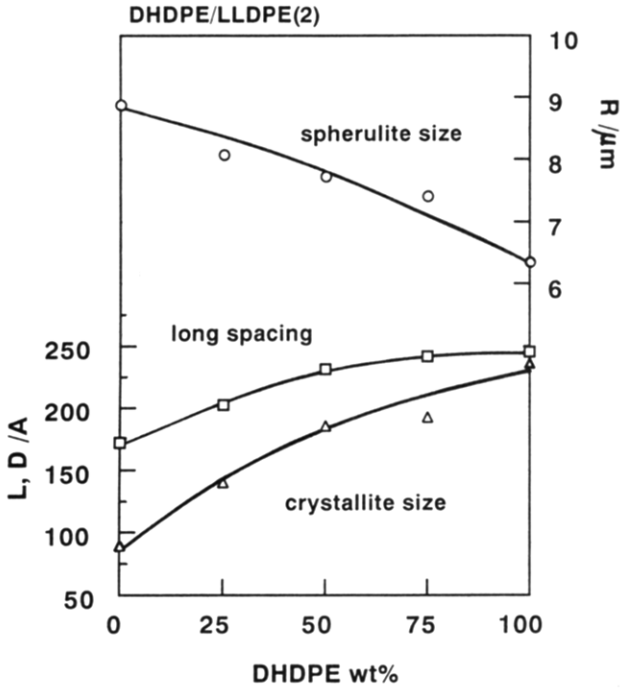

Figure 9. Blend content dependence of spherulite size, long period, and crystallite size estimated from SALS, SAXS, and WAXS data of the DHDPE/LLDPE(2) blend system.

reported already. Figure 10 shows the 110 reflection pattern. It should be noted here that the reflectional intensity is not normalized and thus only the profile should be compared among the samples. Different from the case of DHDPE/LLDPE(2), the peak position of the pure DHDPE component does not shift so much even when the content is changed, although the pure LLDPE(3) originally shows a very broad reflection in this region because of the low degree of crystallinity and, therefore, it is somewhat difficult to detect the change in X-ray profile of the blends. The pattern observed for the D/H 25:75 wt % sample may be assumed as an overlap of those of the pure DHDPE and LLDPE(3).

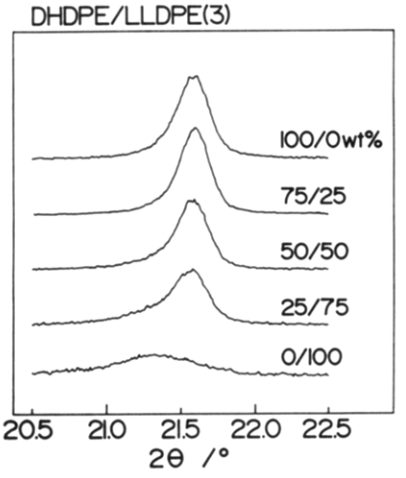

Figure 10. Blend content dependence of the 110 X-ray reflection patterns measured for DHDPE/LLDPE(3) blend samples at room temperature.

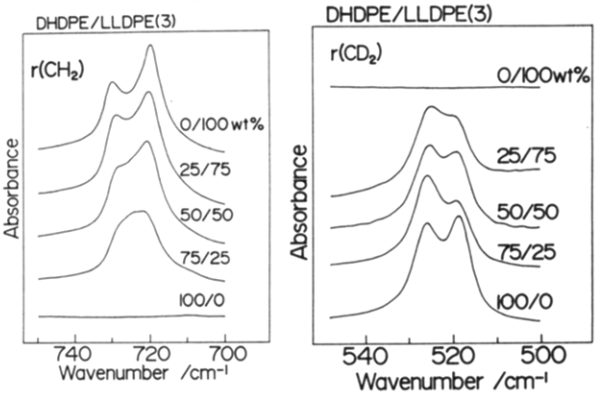

Figure 11. Blend content dependence of infrared spectra of the DHDPE/LLDPE(3) blend samples measured at room temperature in the frequency regions of CH_2 and CD_2 rocking modes. The intensity is not normalized among the spectra shown here.

In Figure 11 are shown the infrared spectra in the CD_2 and CH_2 rocking region. In comparison with the case of

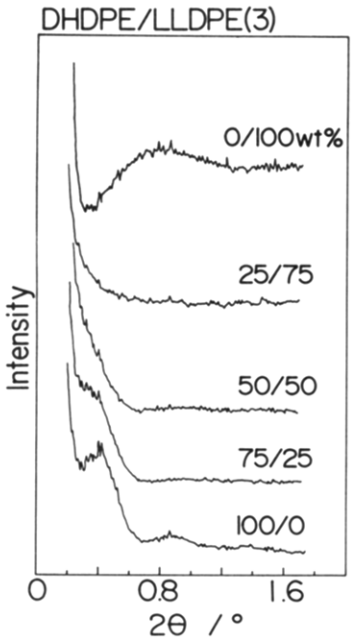

Figure 12. SAXS patterns of a series of DHDPE/LLDPE(3) blend samples measured at room temperature.

the DHDPE/LLDPE(2) blend, the band splitting due to the vibrational coupling is still observed even for the sample with highly diluted H component. But it should be also noticed that some amount of the singlet component is coexistent with such a band pair. Existence of the singlet component suggests some portion of the CH_2 chains is cocrystallized with the CD_2 chains as pointed out in the previous papers.

(B) Higher Order Structure. The SAXS patterns of this blend system are shown in Figure 12. The SAXS profile observed here is not simply interpreted as an overlap of the patterns of the original pure components. As the LLDPE(3) content increases, the peak position becomes difficult to see. One plausible interpretation may be due to the shift of the peak to lower angle side. This is contrast to the DHDPE/LLDPE(2) system where the peak shifts between the positions of the pure components. This suggests that the apparent long period L becomes larger as the LLDPE(3) content increases. But, for the pure LLDPE(3), the broad SAXS peak is observed around $2\theta = 0.8°$, indicating that the long period is decreased again. In Figure 13 are shown the SALS (H_v) patterns of the blends: the spherulite size R estimated from the SALS pattern becomes a few times larger for the blend samples than those of the pure cases (see Figure 14). A combination of the SAXS and SALS data leads us to speculate that the crystalline lamellae characteristic of the individual two components are stacked together in a common large spherulite, resulting in a new long period in the SAXS pattern (Figure 15 model A).[2] But the problem to be solved here is why the long spacing of the blend is larger than that of the pure LLDPE(3) sample. If the spacing between the neighboring two DHDPE lamellae is increased by an invasion of the LLDPE(3) lamellae, as illustrated in Figure 15 model A, the averaged long spacing should shift between the values intrinsic of the pure components as long as the lamellar structure is assumed not to be affected so much even in the blend. One of the ways to interpret the observed behavior of the SAXS long spacing may be as follows. As understood from the broad and low scattering intensity of the SAXS signal of LLDPE(3), the difference in electron density between the crystalline and amorphous regions is not considered to be extremely large. This comes from the low degree of order in the crystalline region because of the existence of bulk ethyl branchings in the cell. On the contrary, the pure DHDPE crystalline phase has a much higher electron density than in the amorphous phase (and also better periodicity of lamellar stacking), reflecting on the high SAXS intensity and the appearance of even the second order reflection. As pointed out already, the crystalline lamellae of the DHDPE and LLDPE(3) are considered to be mixed and stacked together in a common spherulite of the blend sample. Therefore, the distribution of electron density may be illustrated as shown in Figure 16a. This array of the crystalline lamellae of the D and H species may be replaced approximately by the

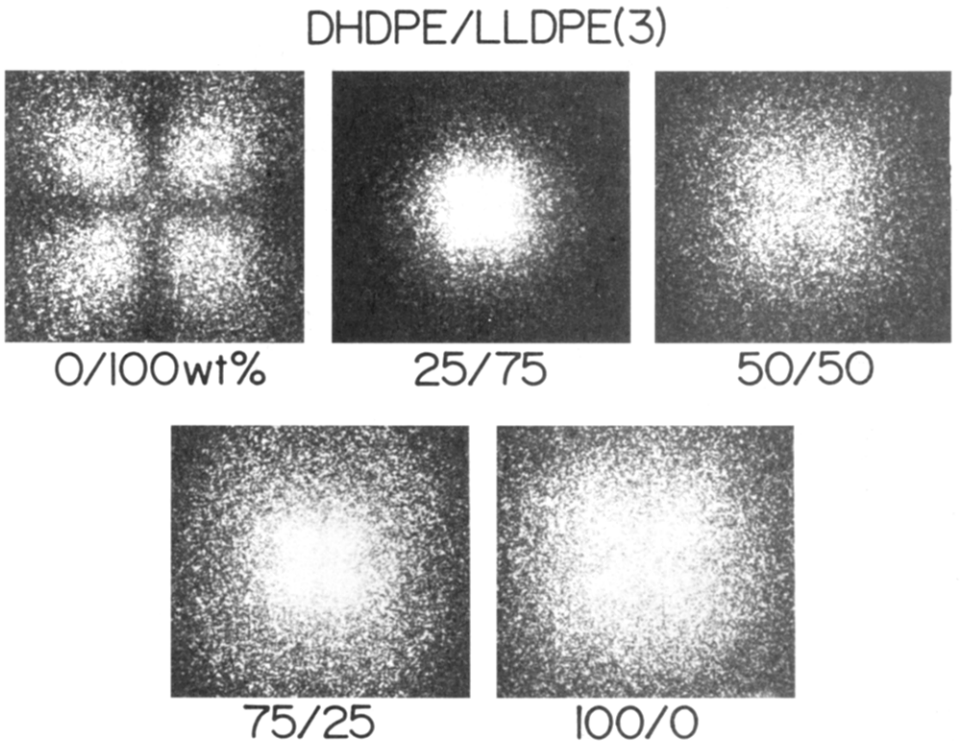

Figure 13. SALS patterns of a series of DHDPE/LLDPE(3) blend samples measured at room temperature.

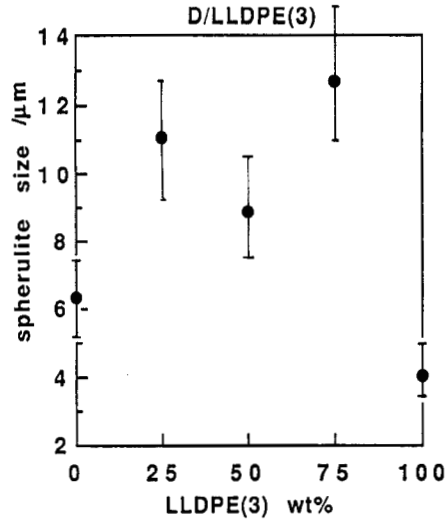

Figure 14. Blend content dependence of the spherulite size R estimated from SALS pattern of DHDPE/LLDPE(3) blend system.

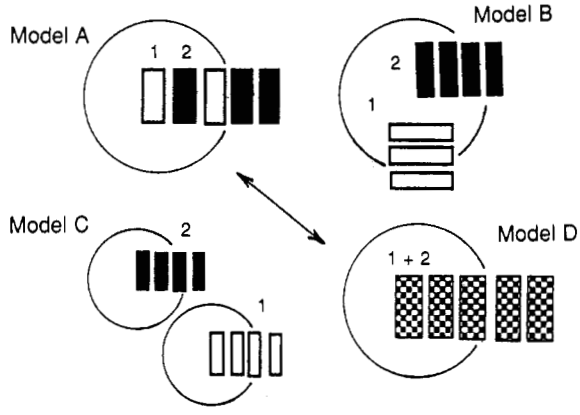

Figure 15. Illustration of lamellar stacking structure of the blend systems. (a) Model of randomly stacked D and H lamellae in a spherulite, (b) a coexistence of stacked lamellae consisted of the same species of the chains in a spherulite, (c) a coexistence of two types of spherulites in the sample, and (d) lamellar stacking model of the species cocrystallized in the common crystal lattice.[2]

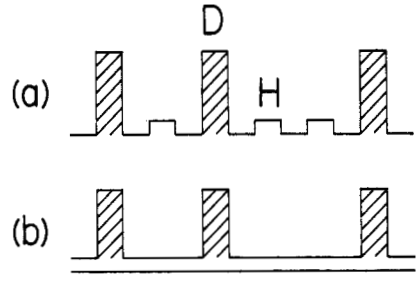

Figure 16. (a) Electron density distribution model of the randomly stacked D and H lamellae and (b) the simplified model under the assumption that the relative electron density of the H lamellae is too low because of the low degree of crystallinity compared with that of the D lamellae.

model in Figure 16(b), where the relatively low electron density of the LLDPE(3) is assumed to be almost the same as that of the amorphous region when compared with the high density of the DHDPE region and is smeared into the background. As a result the apparent long spacing should be longer with an increase of the LLDPE(3) content. But as the H content increases toward 100%, such a situation is not applied any more and the original repetition of the crystalline and amorphous phases is realized, the long spacing being closer to that of the pure LLDPE(3) (Figure 12). The SANS data should be helpful to check this model because the information on the interlamellar spacing between the D crystallites may be obtained more clearly; the results will be reported later.

Conclusions

In this paper, the structure of the crystal lattice and the stacking state of the lamellae in the spherulite were described for the DHDPE/LLDPE (2) and DHDPE/LLDPE(3) blend systems, which are typical examples of the almost perfectly cocrystallizable system and the preferentially phase-segregated system, respectively. In the case of the DHDPE/LLDPE(2) blend, the D and H chain stems are coexistent statistically randomly within the common crystal lattice at the probability determined by the D/H content. This model of random packing of the D and H stems can be deduced reasonably from the quantitative interpretation of the infrared band profiles. The result should be related with the random reentry chain-folding mechanism. Although such a random reentry folding model might be limited only to the present DHDPE/LLDPE(2) case, it gives us important suggestions in the general discussion of the chain-folding mechanism of the PE lamellae.

In the case of DHDPE/LLDPE(3) blend, the D and H lamellae are coexistent within the common spherulite, although some portions of the H chains are considered to be included in the D crystallites as discussed in the previous papers. The averaged interlamellar distance, as viewed from the SAXS data, changes apparently curiously depending on the D/H blend content. But it can be interpreted reasonably based on the model consisting of the randomly stacked D and H lamellae. The size of the spherulite changes drastically after blending of the DHDPE and LLDPE(3), as seen in the change of SALS. This change can be also consistently interpreted on the basis of the above-mentioned stacked lamellar model.

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References and Notes

(1) Tashiro, K.; Stein, R. S.; Hsu, S. L. *Macromolecules* **1992**, *25*, 1801.
(2) Tashiro, K.; Satkowski, M. M.; Stein, R. S.; Li, Y.; Chu, B.; Hsu, S. L. *Macromolecules* **1992**, *25*, 1809.
(3) Tashiro, K.; Izuchi, M.; Kobayashi, M.; Stein, R. S. *Macromolecules*, in press.
(4) Tashiro, K.; Izuchi, M.; Kobayashi, M.; Stein, R. S. *Macromolecules*, in press.
(5) Tasumi, M.; Krimm, S. *J. Polym. Sci., Part A-2* **1968**, *6*, 995.
(6) Bank, M. I.; Krimm, S. *J. Polym. Sci., Part A-2* **1969**, *7*, 1785.
(7) Cheam, T. C.; Krimm, S. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 423.
(8) Special issue on chain folding problem, *Faraday Disc. Chem. Soc.* **1979**, *68*.