

Effect of Blending High-Pressure Low-Density Polyethylene on the Crystallization Kinetics of Linear Low-Density Polyethylene

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ABSTRACT: It is well known that the addition of a small amount of high-pressure low-density polyethylene (HP-LDPE) to linear low-density polyethylene (LLDPE) can improve the optical properties of LLDPE, and LLDPE/HP-LDPE blend is widely applied to various uses in the field of film. The optical haziness of polyethylene blown films, as a result of surface irregularities, is thought to be as a consequence of the different crystallization mechanisms. However, not much effort has been directed toward understanding the effect of HP-LDPE blending on the overall crystallization kinetics (k) of LLDPE including nucleation rate (n) and crystal lateral growth rate (v). In this study, we investigated the effect of blending 20% HP-LDPE on the crystallization kinetics of LLDPE polymerized by Ziegler-Natta catalyst with comonomer of 1-butene. Furthermore, by combining depolarized light intensity measurement

(DLIM) and small-angle laser light scattering (SALLS), we have established a methodology to estimate the lateral growth rate at lower crystallization temperatures, in which direct measurement of lateral growth by polarized optical microscopy (POM) is impossible due to the formation of extremely small spherulites. This investigation revealed that HP-LDPE blending leads to enhanced nucleation rate, reduced crystal lateral growth rate, and a slight increase in the overall crystallization kinetics of pure LLDPE. From the estimated crystal lateral growth rate, it was found that the suppression in v from HP-LDPE blending is larger at lower temperatures than at higher temperatures. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3673–3678, 2007

Key words: LLDPE; HP-LDPE; crystallization kinetics; nucleation rate; crystal lateral growth

INTRODUCTION

In the recent two decades, linear low-density polyethylene (LLDPE) has been widely used in the polyolefin industry as a substitute of the conventional high-pressure low-density polyethylene (HP-LDPE) due to its superior mechanical and thermal properties. Unlike HP-LDPE, the LLDPE molecules have linear sequences of polyethylene interspersed by the unit of α -olefin comonomer such as 1-butene, 1-hexene, 1-octene, or 4-methyl-1-pentene. This allows the properties of LLDPE to be engineered to a great extent by varying the type and amount of comonomer in the main chain.¹ The mechanical properties of LLDPE are practically controlled by the type and concentration of α -olefin, though its intermolecular composition distribution largely affects the mechanical strength of LLDPE.² However, the other properties such as processability like bubble stability during the inflation processing and optical properties

such as transparency and film gloss are also essential factors for the polyethylene blown film products. It is difficult to control the processability and optical properties only by the above molecular parameters such as α -olefin type. As for the processability, the difference of bubble stability between LLDPE and HP-LDPE is considered to be due to the difference of the melt tension.³ As for the optical properties, a series of studies^{4–8} have shown that surface roughness of LLDPE caused by the formation of spherulite-like superstructures is the major contributor for the transparency of the blown and cast films while that of HP-LDPE is mainly caused by die-flow surface roughness due to the high melt elasticity.

It is well known that the addition of a small amount of HP-LDPE to LLDPE can improve not only the processability but also the optical properties of LLDPE balanced with the mechanical strength,⁷ and LLDPE/HP-LDPE blend is widely applied to various uses in the field of film applications, which require processability and good optical properties. Furthermore, it is also known that the effect of HP-LDPE blending on the optical property improvement of LLDPE is optimized when the ratio of LLDPE/HP-LDPE is around 80/20, and then we focused on

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the blend of this blend ratio in this study from the practical viewpoint. To clarify the mechanism of optical property improvement by HP-LDPE, various investigations have been vigorously done. Some reports showed that the addition of low levels of HP-LDPE resulted in a decrease of spherulitic superstructures, thereby decreasing the surface roughness and improving the optical properties of the base LLDPE.^{9–11} It was found that the HP-LDPE component acts as a nucleating agent for the crystallization of LLDPE in which nucleation rate is enhanced and spherulite size is thus reduced.⁹ In particular, Cooke and Tikuisis suggested that the complex branching structure and broad molecular weight distribution of HP-LDPE disrupt the LLDPE crystallization by introducing more disorder or randomness into the LLDPE matrix and reduces the mobility of the matrix molecules, thereby effectively reducing the extent of spherulites developed.¹⁰ In addition to the reduced spherulite size, it was found that HP-LDPE also led to the development of fibril row-nucleated type texture such as shish-kebab on the surface of the blown film.^{11–14} In either case, the degree of surface roughness was diminished, thereby lowering the total haze of the film.

Optical properties of polyethylene blown films, as a result of surface irregularities, are thought to be as a consequence of the different crystallization mechanisms. However, only a small number of works were reported with respect to the effect of HP-LDPE blending on the overall crystallization kinetics of LLDPE including nucleation rate and crystal lateral growth rate.^{15–17} In this study, we investigated the effect of blending 20% HP-LDPE on the crystallization kinetics of LLDPE polymerized by the Ziegler-Natta catalyst with the comonomer of 1-butene. Detailed comparison between the nucleation rate and crystal lateral growth rate, as well as the overall crystallization rate, of pure LLDPE and LLDPE/HP-LDPE blend are made by microscopy and light scattering. Furthermore, by combining depolarized light intensity measurement (DLIM) and small-angle laser light scattering (SALLS), we tried to estimate the lateral growth rate at lower crystallization temperatures, in which direct measurement of lateral growth by polarized optical microscopy (POM) is impossible due to the formation of extremely small spherulites.

EXPERIMENTAL

Materials and blend preparation

Commercial grades of pure LLDPE and its binary blend with HP-LDPE were used for this study. LLDPE used was an ethylene-1-butene copolymer produced by a Ziegler-Natta catalyst. The LLDPE/

TABLE I
Characterization Data for LLDPE, HP-LDPE, and LLDPE/HP-LDPE Blends

Polymer Name	Density (g/cc) ^a	T_m (°C)	T_c (°C)	MFR (g/10 min) ^b
LLDPE	0.920	121	107	2.0
HP-LDPE	0.922	108	97	5.0
LLDPE/HP-LDPE (80/20)	–	108,122	108	–

^a Measured at room temperature.

^b Measured at 190°C.

HP-LDPE binary blend used was composed of 80% LLDPE and 20% HP-LDPE. Table I summarizes the properties of these three polyethylene grades. The melting temperatures were measured by differential scanning calorimetry (DSC). Samples for DLIM was prepared by pressing stacked blown film samples at 150°C. Blown films were obtained by inflation molding process at 200°C. Sheet products after pressing had thickness of 100 μm. Samples for POM measurement had thickness of 5 μm, which were prepared by inflation processing with high take-up speed.

Polarized optical microscopy

Blown films of LLDPE and LLDPE/HP-LDPE binary blend with thickness of 5 μm were examined under polarized optical microscopy (POM; Olympus BX50 BX-CSS). A hot stage (Linkam THMS600) linked with a small liquid nitrogen tank was coupled to the microscope for melting and cooling the films. Small square-shaped film samples were carefully prepared by using gloves and tweezers to prevent contamination, and isothermal crystallization was observed under three different temperatures: 113, 115, and 117°C. Each sample was heated up to 200°C at a rate of 130°C/min, held at 200°C for 10 min, and cooled down to its isothermal crystallization temperature at a rate of 130°C/min. During isothermal crystallization, videos and images were captured at different time points for the analysis of crystal lateral growth rate.

Depolarized light intensity measurement

Pressed films of LLDPE and LLDPE/HP-LDPE binary blend with thickness of 100 μm were examined by depolarized light intensity measurement (DLIM; MK-710, Shimadzu). Under crossed polarizers, the isotropic melt transmit no light whereas a portion of the incident light is transmitted through the spherulites because of the birefringence of lamella crystal. Therefore, the magnitude of the light transmission is proportional to the degree of crystallinity of the system. Various isothermal crystallization temperatures

tested were given as follows: 100, 105, 108, 109, 110, 112, 113, 115, and 117°C. Each sample was annealed for 20 min in a 200°C air bath. Subsequently, the sample was quenched to the crystallization temperature by dropping it into a silicon oil bath, and the transmitted light intensity was measured by photomultiplier and recorded during isothermal crystallization.

Small-angle laser light scattering

The LLDPE and LLDPE/HP-LDPE samples used for DLIM measurement were examined under SALLS for the determination of distribution of spherulite size. It is very important to use the same sample between SALLS and DLIM, because we can complementarily use the information obtained from both methods. The validity is shown in Results and Discussion section for the measurement of the spherulite lateral growth rate. The SALLS apparatus is composed of a He-Ne laser light ($\lambda = 633$ nm), a polarizer, an analyzer, a sample holder, and a detector/computer controlling system. Power source, amplifier, pulse generator, digital voltage meter, and a set of computers are connected to the machine in which measurement was performed by running the SALLS program software. Post-DLIM sample was attached to the sample holder so that the laser beam shines through its center where the scattered light showed a clear four-leaf clover pattern around the center of the beam. The scattering data were acquired with the interval of 0.1° in the angle range of 0°–20°. The scattering angle of obtained data was corrected by assuming that PE's refractive index is 1.5. Each SALLS curve at different crystallization temperatures was fitted with a Gaussian distribution curve to obtain the scattering angle ($2\theta_{\max}$) at the highest scattering intensity.

RESULTS AND DISCUSSION

Methodology

Because of the spatial resolution of optical microscopy, it was necessary to perform the experiment at high temperatures for observing slow, clear spherulite formation, and data acquisition for POM experiments at temperatures lower than 112°C could not be performed. On the other hand, the light scattering experiments such as DLIM and SALLS have no temperature constraints, allowing us to determine the overall crystallization rate (k) and nucleation rate (n) at various temperatures. Therefore, an estimation method for the crystal lateral growth rate (v) was established by combining the data acquired from POM, DLIM, and SALLS experiments. The detailed procedure is shown below.

The Avrami eq. (1)¹⁸ was applied to the data obtained from DLIM for calculating the crystal growth dimensionality called as Avrami growth dimension (m) and the overall crystallization rate (k).

$$I(t) = 1 - \exp(-kt^m) \quad (1)$$

Since the overall crystallization process occurs through concurrent nucleation and growth of different portions of the polymer system, the relationship between k , n , and v can be described as in eq. (2):

$$k \propto nv^m \quad (2)$$

The determination of n involved applying Bragg's Law (3), where $\lambda = 633$ nm for the wavelength of laser light.

$$\lambda = 2d \sin \theta \quad (3)$$

where d is the size of the periodic structure and 2θ is the scattering angle. Bragg's Law allowed the determination of average spherulite diameter ($2r$), which in turn led to the determination of volume occupied by one spherulite and thus the nucleation rate according to eq. (4).

$$n \propto \left(\frac{4\pi r^3}{3} \right) \quad (4)$$

Consequently, v at different temperatures was relatively estimated and the predicted value of v at lower temperature was easily obtained by matching the estimated value with the measured values. Figure 1 shows the measured and estimated crystal lateral growth rates (v) of pure LLDPE and LLDPE/HP-LDPE at different isothermal crystallization temperatures. The continuity and the overlap between measured and estimated v in Figure 1 strongly signify the high reliability of this estimation method.

Crystal lateral growth

Figure 1 clearly shows that the lateral growth rate of pure LLDPE spherulite is higher than that of LLDPE/HP-LDPE blend. This suggests that suppression in the lateral growth rate of LLDPE is a result of adding the HP-LDPE component. The suppression of the lateral growth may be due to the strong entanglement between crystallizable LLDPE and HP-LDPE, which are a miscible polymer blend.^{9,14,15,19–22} At the temperature for which isothermal crystallization experiment was performed, HP-LDPE cannot easily crystallize and it may be excluded from LLDPE lamellae to the interlamella^{19,20} or interfibril^{21,22} region like other miscible blend. Since it takes a long time to exclude HP-

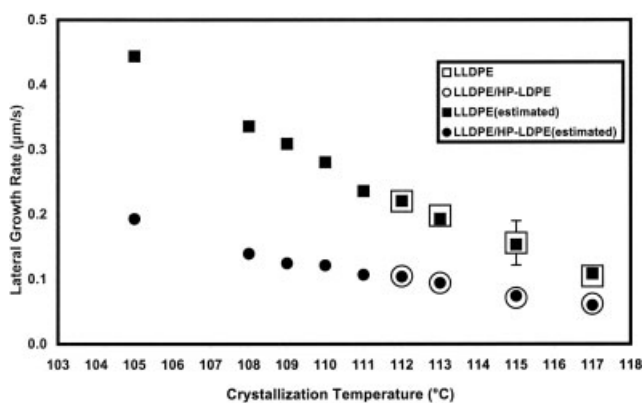


Figure 1 Crystal lateral growth rate for 5 μm LLDPE and LLDPE/HP-LDPE blend at different isothermal crystallization temperatures. (\square) measured LLDPE, (\circ) measured LLDPE/HP-LDPE, (\blacksquare) estimated LLDPE, (\bullet) estimated LLDPE/HP-LDPE.

LDPE to the interlamella or fibril region through the disentanglement process and to arrange the crystallizable LLDPE into rows, a slower lateral growth rate is resulted.

The suppression in crystal lateral growth rate seems to be dependent upon the crystallization temperature. In the lower temperature region, the lateral growth rates of the LLDPE/HP-LDPE blend are only half the rates of the pure LLDPE system. However, as the crystallization temperature increases, the lateral growth rate of the LLDPE/HP-LDPE blend becomes closer to the value of the pure LLDPE system. This may be caused by the increase of molecular movement at the higher temperature. Faster molecular movement at higher temperature may accelerate the disentanglement between HP-LDPE and LLDPE or the exclusion of HP-LDPE and LLDPE that cannot crystallize at the measured temperature, which are followed by the ordering of the crystallizable components. Consequently, the lateral growth rate of the LLDPE/HP-LDPE blend approaches the rates of the pure LLDPE at higher temperatures.

Induction time and nucleation rate

Figure 2 shows the induction time (t_o) for pure LLDPE and LLDPE/HP-LDPE blend at different crystallization temperatures. A clear rising curve trend in induction time is observed with increasing crystallization temperature for both pure LLDPE and LLDPE/HP-LDPE blend systems. As temperature increases, the energy barrier that the nuclei must overcome to reach stable nucleus size also increases. To form stable nuclei, the polymer melt must first form ordered assemblies of chain segments that are larger than a critical size. At higher temperatures,

the critical size becomes larger, which results in a slower rate of formation of the stable nuclei and hence a longer t_o .

The addition of HP-LDPE to pure LLDPE causes a decrease in t_o . This suggests that the HP-LDPE component may be serving as a nucleating agent for the crystallization of pure LLDPE. It is reasonable that addition of HP-LDPE to LLDPE would lead to the reduction of polymer chain motion as a consequence of introducing the complex branching system from HP-LDPE, because LLDPE and HP-LDPE is partially^{23,24} or completely miscible^{9,14,15,25,26} and their molecular motion must be strongly influenced by each other like other blends.^{27–29} By introducing complex long chain branches to the pure LLDPE system, the relaxation time for chain entanglement is increased, thereby restricting molecular movements, which is similar to the molecular movement at the lower temperature, thereby resulting in a faster nucleation rate.

The reduction in t_o as a result of HP-LDPE blending also seems to be temperature-dependent. Although t_o for pure LLDPE and LLDPE/HP-LDPE blend are far apart at higher temperatures, the difference decreases as crystallization temperature decreases. The reason may be due to the increased viscosity at lower temperatures, which impede the overall molecular movement. Thus, the effect of the long chain branching on reducing the molecular movement of LLDPE may be smaller than the temperature effect.

Figure 3 shows typical SALLS patterns of LLDPE and LLDPE/HP-LDPE blend isothermally crystallized at 113°C. Figure 4 shows the average spherulite radius (r) for pure LLDPE and LLDPE/HP-LDPE blend at different crystallization temperatures analyzed from peak position of SALLS data. Clearly, r increases with increasing temperature for both pure

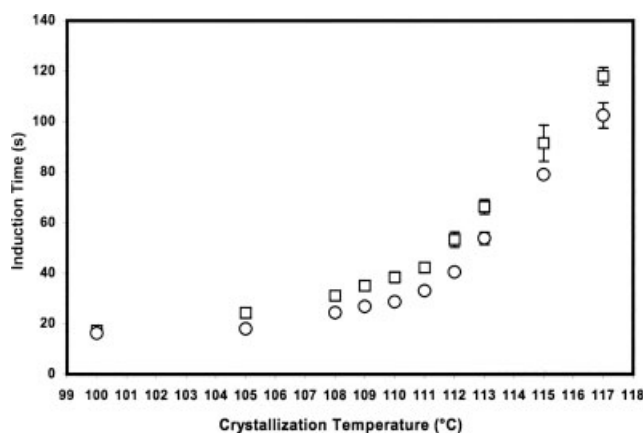


Figure 2 Induction time for 100 μm LLDPE and LLDPE/HP-LDPE blend at different isothermal crystallization temperatures. (\square) LLDPE, (\circ) LLDPE/HP-LDPE.

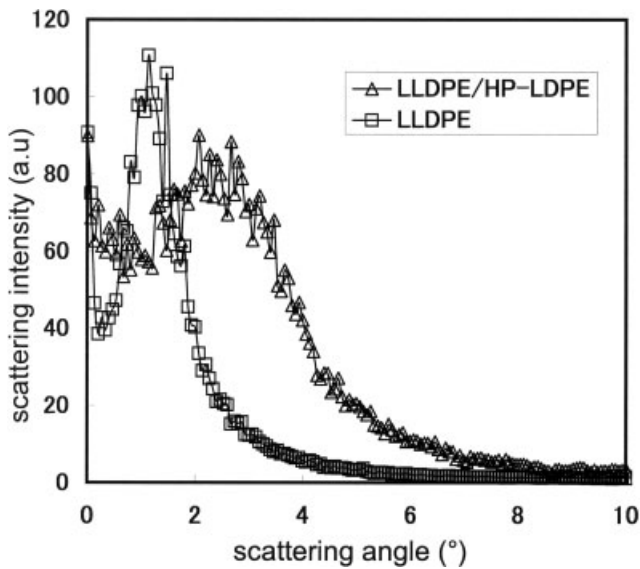


Figure 3 The typical SALLS curve of LLDPE (□) and LLDPE/HP-LDPE (Δ) binary blend isothermally crystallized at 113°C.

LLDPE and LLDPE/HP-LDPE blend, and LLDPE/HP-LDPE blend has much smaller r than the pure LLDPE. Consequently, in Figure 5, both polymer systems show a decreasing trend in their nucleation rate (n) with increasing temperature, and a significant increase in n is resulted from HP-LDPE blending. Good correspondence exists between the results for induction time, average spherulite radius, and nucleation rate, which can well explain the role of HP-LDPE as a nucleating agent for LLDPE crystallization. The enhancement of nucleation rate leads to a higher number of nuclei formed per unit volume. Thus, impingement reaches very rapidly and smaller spherulites are formed.

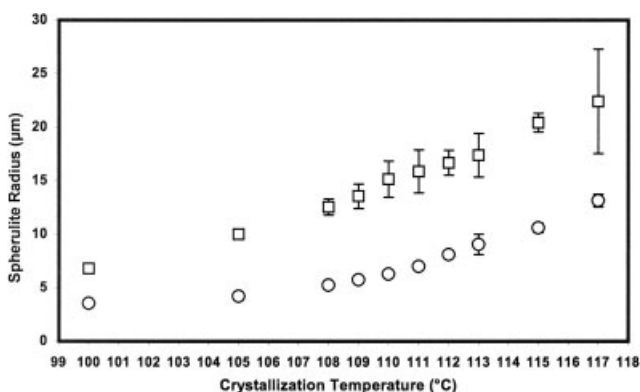


Figure 4 Average spherulite radius for 100 μm LLDPE and LLDPE/HP-LDPE blend at different isothermal crystallization temperatures. (□) LLDPE, (○) LLDPE/HP-LDPE.

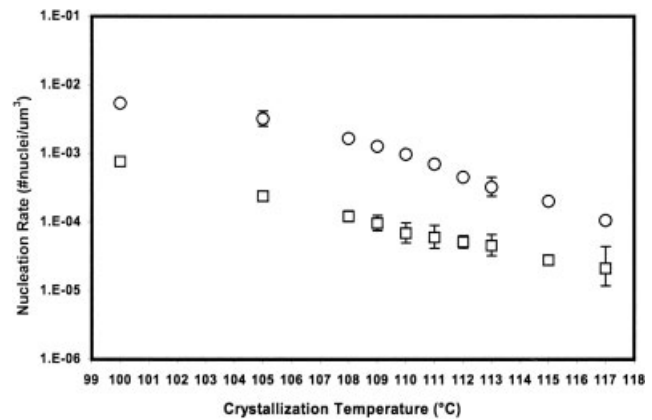


Figure 5 Nucleation rate for 100 μm LLDPE and LLDPE/HP-LDPE blend at different isothermal crystallization temperatures. (□) LLDPE, (○) LLDPE/HP-LDPE.

Overall crystallization kinetics

Figure 6 shows the kinetic constant (k) at various isothermal crystallization temperatures for pure LLDPE and LLDPE/HP-LDPE blend. With suppressed lateral growth rate and enhanced nucleation rate as discussed earlier, the overall crystallization kinetics of the LLDPE/HP-LDPE blend is only slightly faster than the pure LLDPE.

This study revealed that the lateral growth rate of LLDPE decreases as a result of blending HP-LDPE. On the other hand, the nucleation rate of LLDPE is highly enhanced by the HP-LDPE blending. According to (4), it can be said that the slightly higher k for the LLDPE/HP-LDPE blend indicates that the increase in n is far more dominant than the decrease in v^m . It was found that m also varied with crystallization temperature in which it displays an increasing trend at lower temperatures and a decreasing trend at higher temperatures when the measured tempera-

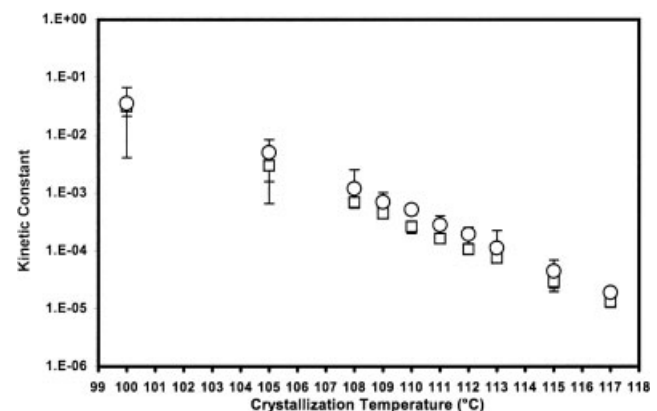


Figure 6 Kinetic constant for 100 μm LLDPE and LLDPE/HP-LDPE blend at different isothermal crystallization temperatures. (□) LLDPE, (○) LLDPE/HP-LDPE.

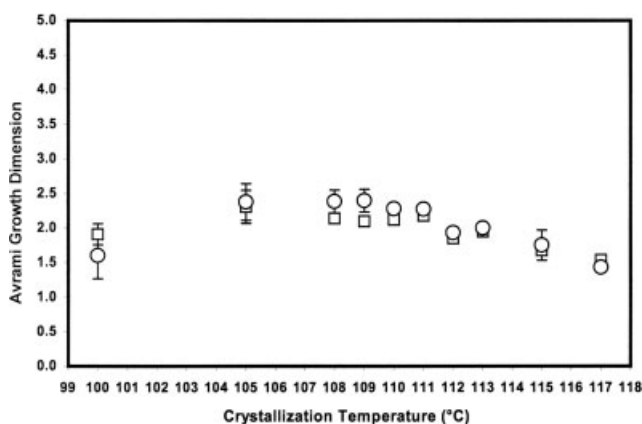


Figure 7 Avrami growth dimension for 100 μm LLDPE and LLDPE/HP-LDPE blend at different isothermal crystallization temperatures. (□) LLDPE, (○) LLDPE/HP-LDPE.

ture was gradually increased as shown in Figure 7. Maximum m for pure LLDPE and LLDPE/HP-LDPE blend hit at 111 and 110°C, respectively. The possible reason of decreasing trend in m at the higher temperature when increasing the crystallization temperature may be the appearance of sample thickness effect. At the higher temperature, the spherulite size ($\sim 50 \mu\text{m}$) is very large and the supposition that the film thickness ($\sim 100 \mu\text{m}$) is much thicker than the spherulite size is no longer reasonable. Therefore, some of the growing spherulites will be impinged by the cover glass immediately, resulting in a decrease in m . As for the low m at 100°C, there may be ambiguity in the observed data since a fair amount of time is necessary for the sample to be quenched to the desired crystallization temperature and at such low temperature, induction time is extremely short. As a result, error from the determination of induction time by the DLIM instrument may be responsible for such low m and data at this temperature is not certain enough to draw any conclusion for the low temperature range.

CONCLUSIONS

The following conclusions were made from this investigation:

1. Crystal lateral growth rate of pure LLDPE is suppressed by HP-LDPE blending.
2. Nucleation rate of pure LLDPE is enhanced by HP-LDPE blending.
3. Overall crystallization kinetics of pure LLDPE is slightly enhanced by HP-LDPE blending.

4. The crystal lateral growth rate can be estimated by combining optical microscopy and light scattering with the relationship between k , n , and v being $k \sim nv^m$ where m is the Avrami growth dimension.
5. Suppression in the crystal lateral growth rate as a result of blending HP-LDPE is larger at lower temperatures than at higher temperatures.

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