

# Miscibility and Crystallization of Metallocene Polyethylene Blends with Polypropylene

Jun Li,<sup>1</sup> Robert A. Shanks,<sup>1</sup> Yu Long<sup>2</sup>

<sup>1</sup>Department of Applied Chemistry, CRC for Polymers, RMIT University, GPO Box 2476V, Melbourne, Victoria, Australia

<sup>2</sup>CSIRO Manufacturing Science and Technology, Clayton, Victoria, Australia

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**ABSTRACT:** The crystallization and morphology of very-low-density polyethylene (VLDPE) and ultra-low-density polyethylene (ULDPE) blends with isotactic polypropylene (PP) were studied by differential scanning calorimetry (DSC) and hot-stage optical microscopy (HSOM) with polarized light. In particular, the isothermal crystallization of PP in molten PE was investigated. A polypropylene homopolymer was melt-blended with six types of VLDPEs and ULDPEs, with variations in branch content and length and in molecular weight. All the blends contained 20% PP by mass. It was found that the crystallization temperatures of PP and PE changed in the blends, and the crystallization of PP was affected by branch length and content and by the molecular weight of the PE, indicating a certain degree of miscibility between PP and PE. The isothermal crystallization rate of PP decreased in the blends; in particular, the crystallization rate of PP was slower in the ULDPE with

lower MFI, suggesting that crystallization of PP was hindered by PE and that its rate was regulated by the viscosity of ULDPE. HSOM images showed that a portion of the PP crystallized from molten PE, although phase separation was obvious, providing additional information on the miscible behavior between PP and VLDPEs (or ULDPEs). Furthermore, the miscible level between the PP and the ULDPEs was higher than that between the PP and the VLDPEs because the degree of change in the crystallization behavior of the PP and PE was greater in the PP-ULDPE blends. This was possibly a result of the higher branch content in the ULDPE. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1179–1189, 2003

**Key words:** metallocene polyethylene; poly(propylene) (PP); morphology; miscibility

## INTRODUCTION

Metallocene-catalyzed very-low-density polyethylene (VLDPE) and ultra-low-density polyethylene (ULDPE) are new members of the polyethylene family. They are synthesized by single-site metallocene catalysts. In contrast with traditional Ziegler–Natta catalysts, where multiple active sites exist with different reactivities toward the monomers, a single site with very high activity is present during polymerization in metallocene catalysts.<sup>1</sup> Metallocene catalysts allow high degrees of comonomer incorporation and more uniform or homogeneous distribution of branches in copolymers. This suppresses the crystallinity of these polyethylenes to the elastomer region (density < 0.89 g cm<sup>-3</sup> for ULDPE and, 0.90–0.915 for VLDPE). The metallocene-catalyzed VLDPE and ULDPE fill the gap between traditional polyethylenes and elastomers (e.g., ethylene–propylene rubber, EPR).

Because of their low crystallinity, metallocene ULDPE and VLDPE offer good low-temperature properties such as toughness. They serve primarily as mod-

ifiers for brittle materials, particularly as impact modifiers for isotactic polypropylene (PP).<sup>2</sup> The addition of ULDPE to PP improves impact strength, flexibility, tear strength, and low-temperature heat-sealing characteristics.<sup>2</sup>

Metallocene polyethylenes can take on large volume applications via blending, coextrusion, and modification.<sup>3</sup> The VLDPE and ULDPE have gained their place in the market above that of rubbers because of their relatively low prices and their good performance. However, their low moduli and relatively higher prices than conventional PEs preclude their use alone for most applications.

Blends of PP and metallocene VLDPE and ULDPE have attracted broad attention because of their performance importance and economical value. Several researchers<sup>4–9</sup> have investigated the impact properties of PP blended with ULDPEs. Wu et al.<sup>4</sup> found that ULDPEs were superb impact modifiers for PP at a subambient temperature at 25% of ULDPE. They also found that the lower the density of ULDPE, the better was the performance of the blends. Based on melt flow-rate suppression, impact, knit-line, and miscibility considerations, Yu<sup>5</sup> compared the properties of PP blends with EPR rubber and with butene–ethylene, propene–ethylene, and octene–ethylene copolymers.

Correspondence to: J. Li (jun.li@rmit.edu.au).

TABLE I  
Characteristics of the Polymer

Polymer	Branch length	Branch content <sup>a</sup> (mol %)	Density <sup>a</sup> (g cm <sup>-3</sup> )	MFI <sup>c</sup> (g [10min] <sup>-1</sup> )	Source
PP	homopolymer	—	0.905	28	Orica
VLDPE1	butene	6.3 <sup>b</sup>	0.901	27	Kemcor
ULDPE2	butene	20	0.865	10	Kemcor
VLDPE3	octene	7.5	0.915	1.0	Dow
VLDPE4	octene	9.5	0.908	1.0	Dow
ULDPE5	octene	24	0.87	1.0	Dow
ULDPE6	octene	24	0.87	5.0	Dow

<sup>a</sup> Supplied by manufacturers.

<sup>b</sup> According to reference Hill et al. (1997).

<sup>c</sup> Supplied by manufacturers refer to ASTM D1238, 2.16 kg load at 230°C for PP and 190°C for PE.

It was found that the ethylene–butene copolymer was the best overall impact modifier, even though PP and EPR seemed more miscible according to the calculated Flory–Huggins interaction parameter,  $\chi$ .<sup>6</sup> Westphal and coworkers<sup>7</sup> studied the phase morphology [by scanning electron microscopy (SEM)] and thermal behavior of PP–ULDPE blends. They found that an amorphous shell of PP around ULDPE particles, which retarded the crystallization of ULDPE in the blends significantly and reduced the crystallinity of ULDPE. In addition, modification of PP–ULDPE blends could be further optimized by adding a third component, such as a high-density polyethylene (HDPE).<sup>8</sup> The toughening occurred through the development of crystalline microfibrils of the PE, which connected ULDPE and the PP matrix.

Lee et al.<sup>9</sup> studied the morphology, thermal, rheological, and mechanical properties of the blends of PP with two types of ULDPE of different viscosities. They also found that the impact strength of PP was significantly improved by ULDPE addition. The thermal and rheological results showed some partial miscibility between PP and ULDPE, although the SEM presented a clean phase separation. Furthermore, the closer match of viscosities of PP and ULDPE displayed better performance of properties and less obvious phase separation. A study on the blends of ULDPE with PP copolymer was also reported by the same group.<sup>10</sup> Enhanced compatibility of ULDPE with PP block copolymer over PP homopolymer was ascertained.

However, all studies on PP–VLDPE and PP–ULDPE blends have concentrated on the impact properties, and PP was used as the major component in all the above cases. Little research has been undertaken on the miscibility and crystallization of PP–VLDPE and PP–ULDPE blends. To understand the relationship between mechanical properties and microstructure, the crystallization and morphology of PP and VLDPEs (or ULDPEs) were investigated in this work. A polypropylene homopolymer was blended with six types of VLDPE and ULDPE with variations in branch

length and content and molecular weight. The PP was 20% by mass in all blends, as our previous work found that 20% is a critical composition ratio for miscibility.<sup>11</sup> Crystallization and morphology of the blends were investigated by differential scanning calorimetry (DSC) and hot-stage optical microscopy (HSOM) with polarized light. Particularly, the isothermal crystallization of PP in the presence of molten VLDPE (or ULDPE) was studied. Miscibility of the PP and the VLDPEs (or ULDPEs) will be discussed. As far as we know, this is the first report on crystallization of VLDPE–PP and ULDPE–PP blends by HSOM.

## MATERIALS AND METHODS

### Materials and blends preparation

An isotactic polypropylene was blended with six types of VLDPEs and ULDPEs. The characteristics of the polymers are listed in Table I. The blends were mixed in an Axon BX-12 single-screw extruder (Axon Australia Pty. Ltd., Australia) with a screw diameter of 12.5 mm and a L/D ratio of 26:1, operating at a screw speed of 80 rpm. The temperatures for feeding zone, melting zone, compression zone, and die were 170°C, 200°C, 200°C, and 170°C, respectively. The blends were extruded with a four-hole die and pelletized prior to sampling. All the blends were made with a PE:PP mass ratio of 80:20.

### Differential scanning calorimetry

A Perkin-Elmer DSC-7 with nitrogen purge was used to analyze the thermal properties and overall crystallization kinetics of the PP. Samples of around 5 mg were accurately weighed and sealed in aluminum pans. Crystallization and melting temperature measurements were performed by melting samples at 200°C for 2 min followed by cooling to 20°C and subsequent reheating to 200°C. A program rate of 10°C min<sup>-1</sup> was applied. For isothermal crystallization, samples were melted at 200°C for 5 min and

quenched to the isothermal crystallization temperature. The selected isothermal crystallization temperatures were between 108°C and 130°C. Samples were kept at these temperatures for the necessary time for complete crystallization of PP. The heat evolved during isothermal crystallization ( $\Delta H_c$ ) was recorded as a function of time. The crystalline conversion ( $X_t$ ) at constant temperature is related to the generated heat ratio at time  $t$  and at infinite time  $t_\infty$  according to the equation:

$$X_t = Q_t/Q_\infty = \int_0^t (dH/dt) / \int_0^\infty (dH/dt) dt \quad (1)$$

in which  $dH/dt$  is the rate of heat evolution.

The isothermal crystallization was analyzed using the Avrami equation<sup>11</sup>:

$$\ln(-\ln(1 - X(t, T))) = \ln k(T) + n \ln t \quad (2)$$

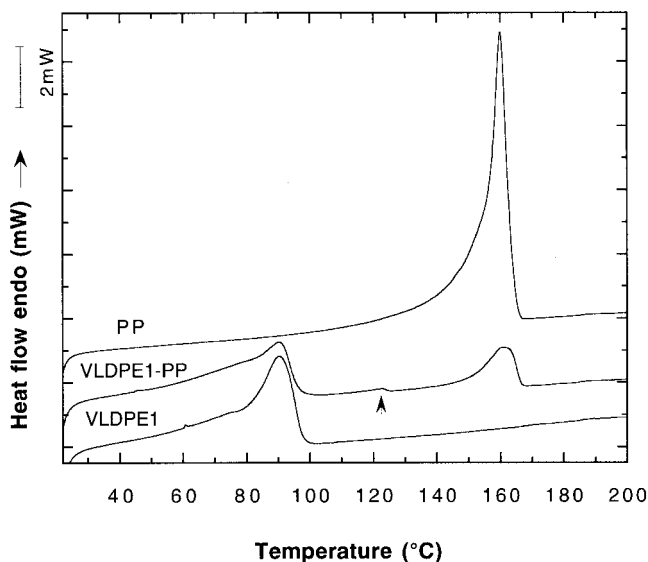
in which  $X(t, T)$  is the volume fraction of crystalline material at time  $t$  and isothermal crystallization temperature  $T$ ,  $n$  is the Avrami exponent that is related to nucleation type and crystal growth geometry; the crystallization rate coefficient,  $k$ , is a parameter of crystallization growth rate and related to the nucleation type, crystal growth geometry, and crystallization temperature.

From graphic representation of  $\ln[-\ln(1 - x)]$  versus  $\ln t$ , the Avrami exponent (slope of the straight line) and the crystallization rate coefficient (intersection with the  $y$  axis) were calculated. Based on these two values, the crystallization half-time, which is a measure of crystallization rate, was obtained from the equation:

$$t_{1/2} = \ln 2 / (k^{1/n}) \quad (3)$$

### Hot-stage optical microscopy

A Nikon Labophot II microscope with polarized light equipped with a Mettler FP90 hot stage was used to study the morphology and crystallization of the blends. Images were captured using a Sony camera and video monitor connected to a Macintosh 7500 computer with IPLab image analysis software. Specimens were prepared by pressing the samples between aluminum foils in a hydraulic hot press at 200°C. The thickness of film was tested by an Elcometer eddy current meter (Elcometer, Australia). Only the films with thicknesses in the range of 15–20  $\mu\text{m}$  were kept for microscopy study. The films were heated between glass slides and cover slips in the hot stage to 200°C for 5 min prior to rapid cooling to the isothermal



**Figure 1** DSC melting curves of PP, VLDPE1, and their blends, showing a small third peak between melting peaks of PP and VLDPE1 in the blend.

crystallization temperature. The crystallization of PP in molten VLDPE or ULDPE was analyzed.

## RESULTS AND DISCUSSION

### Effect of blending on thermal behavior of PP and PE

#### Melting

The melting temperature of PP increased more than 2°C in the blends with ULDPEs, indicating there was some interaction between the PP and the ULDPEs. However, the melting behavior of PP was not affected by the VLDPEs in the PP-VLDPE blends. Also, the melting temperatures of both VLDPEs and ULDPEs did not change after blending with the PP.

In a miscible blend a melting temperature depression would be expected. However, an increase in the melting temperature of PP was observed in the EPR-PP,<sup>9</sup> PP-LLDPE,<sup>11</sup> ULDPE-PP,<sup>13</sup> and blends. Such behavior was interpreted as a partial dissolution of the defective molecules of PP in the EPR, ULDPE, and LLDPE. In this study it was found that the PP might form large and more regular lamellae because of a narrower molecular weight distribution and fewer defective molecules. It was the presence of larger lamellae and more perfect crystals that led to the observed higher  $T_m$ .

An additional, third endotherm appeared at 122.5°C in the VLDPE1-PP blend (Fig. 1), which was not observed in either the pure PP or the pure VLDPE1. A similar endotherm (122.4°C) was also observed in the ULDPE2-PP blend (Fig. 2). In addition, a fourth endotherm, which was weak and broad, appeared at

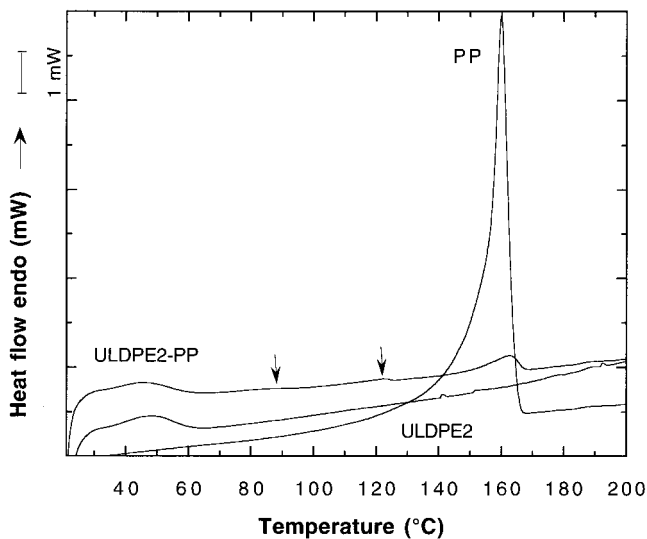


Figure 2 DSC melting curves of PP, ULDP2, and their blends, showing a weak PP peak and two additional peaks.

86°C in the ULDP2-PP blend (Fig. 2). These additional endotherms have resulted from the melting of less branched VLDPE1 and ULDP2 molecules, which dissolved in the PP during blending and in the molten state. On cooling the less branched molecules crystallized independently; on subsequent heating they appeared as additional peaks. Another possible cause for the additional peaks is that more than one type of crystals formed because of the influence of PP on the crystallization of PE.

The melting curves of VLDPE3-PP and ULDP5-PP blends were just simple additive curves of their pure polymers (Figs. 3 and 4). The melting curves of VLDPE4, ULDP6, and their blends with the PP were similar, respectively, to those of VLDPE3, ULDP5,

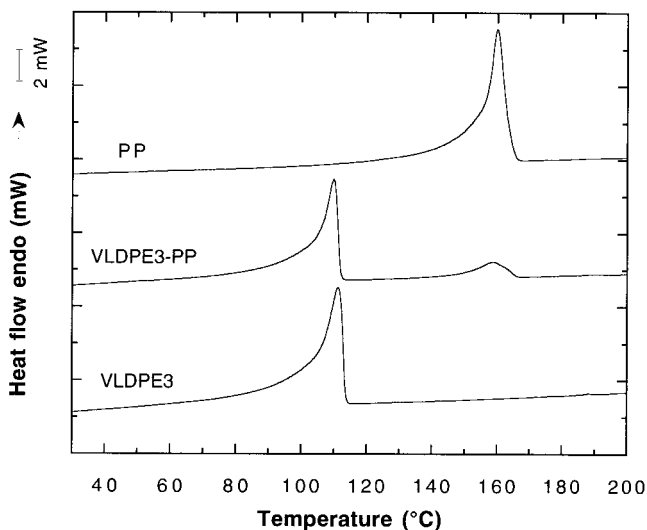


Figure 3 DSC melting curves of PP, VLDPE3, and their blends.

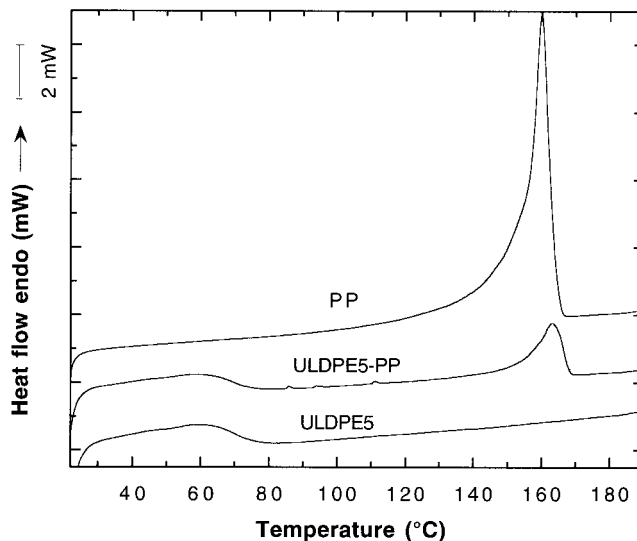


Figure 4 DSC melting curves of PP, ULDP5, and their blends.

and their blends with the PP; so they are not shown here.

Crystallization

The crystallization of the blends was complex compared with melting behavior. The crystallization peak of PP shifted to a lower temperature (2°C lower) and that of VLDPE1 shifted to a higher temperature (approximately 9°C higher) in the VLDPE1-PP blend (Fig. 5). As a change in crystallization temperature is a typical indication of the partially miscible behavior, it can be postulated that the PP was miscible with VLDPE1 at elevated temperatures.

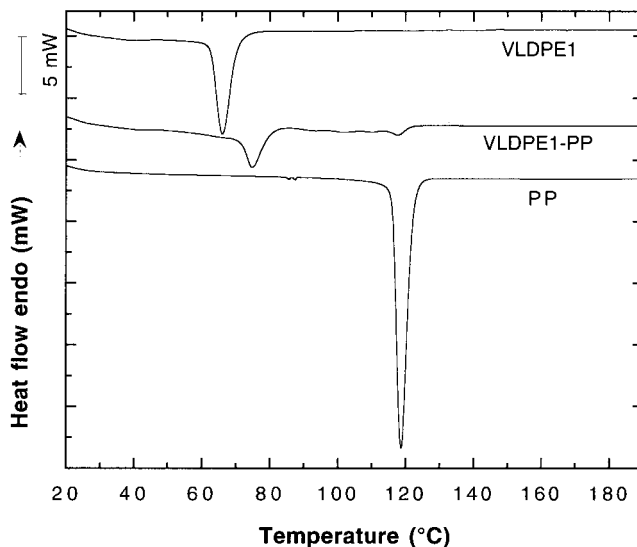
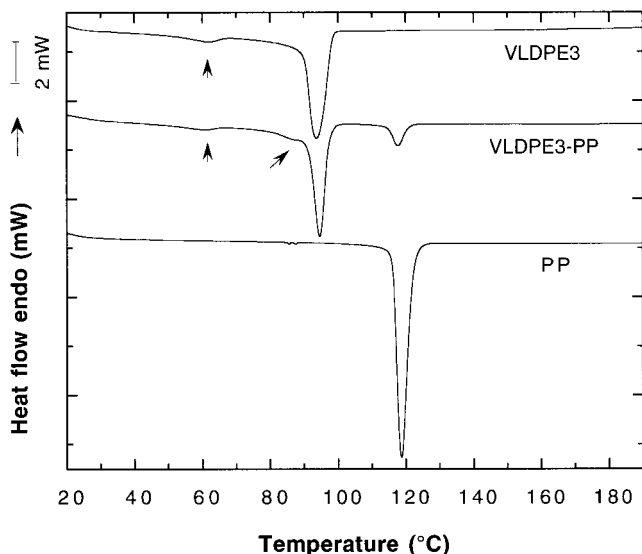


Figure 5 DSC crystallization curves of PP, VLDPE1, and their blends showing shifts in peak positions in the blend.



**Figure 6** DSC crystallization curves of PP, VLDPE3, and their blends.

Another possibility causing changes in crystallization temperatures could be the migration of nuclei from the PP to the VLDPE1.<sup>14,15</sup> Because of the lack of nuclei, the PP could only crystallize at the lower temperature compared with pure PP. On the contrary, VLDPE1 was able to crystallize at a much higher temperature because of abundance in heterogeneous nuclei, which migrated from the PP phase to the VLDPE phase during blending.

The crystallization of VLDPE3 also changed after blending with the PP. The pure VLDPE3 displayed two peaks (Fig. 6), a strong peak at 94°C and a weak peak at 62°C, indicating a bimodal branch distribution. After blending with the PP, the strong peak shifted to a higher temperature (approximately 2°C higher), and a small shoulder appeared in the lower temperature region. However, the weak peak remained in its original position, and the crystallization temperature of PP was not affected by the VLDPE3. The crystallization of VLDPE4 and VLDPE4-PP were similar to those of VLDPE3 and VLDPE3-PP, respectively. These results also indicated that there was interaction between the PP and VLDPE3 (and VLDPE4), although it was not as strong as that between the PP and VLDPE1.

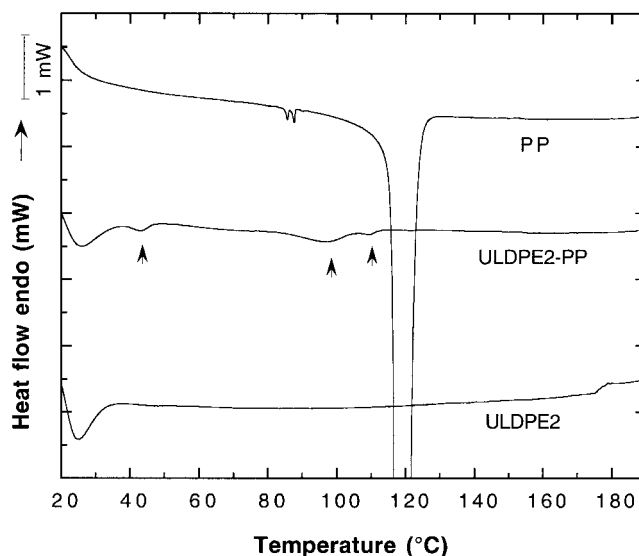
Double peaks were observed for PP crystallization in the ULDPE2-PP blend (Fig. 7), and they were at much lower temperatures (109°C and 97°C), compared with the crystallization temperature of pure PP (119.5°C). This occurred possibly because the PP dissolved in the ULDPE2, which hindered the crystallization of PP. Only after the temperature was further decreased could PP be liberated out of the ULDPE phase and then crystallized at a lower temperature. An additional exotherm also appeared in the higher

temperature region of the normal crystallization exotherm of ULDPE2. This could be caused by the dissolution of ULDPE2 in the PP, as discussed previously. The above results again indicate that the PP was partially miscible with the ULDPE2 in the melt.

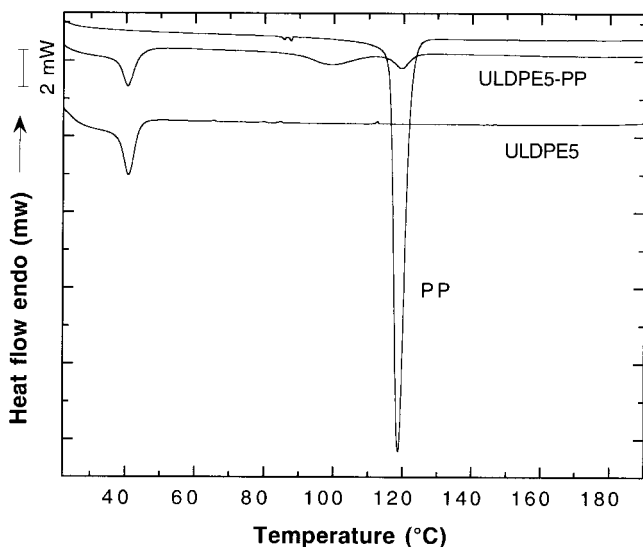
The double PP peaks in the ULDPE2-PP blend may be caused by the different solubility of fractions of PP molecules in the ULDPE2, which are separated by either an isotacticity difference or variations in the molecular weight distribution. The ULDPE2 may dissolve the less isotactic (or smaller PP) molecules more easily than the more stereoregular (or larger) molecules during blending and in the molten state. On cooling the PP molecules with more stereoregular (or larger) molecules can crystallize first; whereas the less isotactic (or smaller) molecules would only crystallize at a lower temperature after they were released by the ULDPE2.

Similar double PP exotherms were also observed in the ULDPE5-PP and ULDPE6-PP blends (Fig. 8). However, the higher temperature exotherms were 10°C above that in the PP-ULDPE2 blend, and the two exotherms were farther apart. Furthermore, the higher exotherms in the ULDPE5-PP and ULDPE6-PP blends were at 119°C, at which the pure PP crystallized.

Different positions of higher-temperature PP exotherms in the ULDPE-PP blends could be caused by the solubility level of PP in the three ULDPEs. Twenty percent of PP may dissolve substantially in the ULDPE2, whereas a much smaller amount may dissolve in the ULDPE5 and ULDPE6 in the molten state. The undissolved fraction of PP in the ULDPE5-PP and ULDPE6-PP blends crystallized at the same tempera-



**Figure 7** DSC crystallization curves of PP, ULDPE2, and their blends, showing weak PP peaks, shifts in peak positions and additional peaks in the blend.



**Figure 8** DSC crystallization curves of PP, ULDPE5, and their blends, showing double PP peaks in the blend.

ture as pure PP. The dissolved PP molecules could only crystallize after the temperature was decreased further. The results imply that the PP was more miscible with ULDPE2 than with the ULDPE5 and ULDPE6.

The lower-temperature PP exotherms in the three ULDPE-PP blends were at approximately the same temperature (between 97°C and 99°C), indicating that these exotherms were from the crystallization of the same PP fraction. Hence, the dissolution level of this fraction of PP molecules in three ULDPEs was the same.

The above observations show that the crystallization and melting behavior of PP changed at a greater degree in the ULDPE-PP blends than that in the VLDPE-PP blends, indicating that the ULDPEs were more miscible with the PP than the VLDPEs. The branch content (comonomer amount) was most likely the predominant cause of the miscibility difference between the VLDPE-PP and ULDPE-PP blends, as the branch contents of ULDPEs are generally higher than those of VLDPEs (Table II).

#### Effect of branch length on miscibility of blends

The branch length (type of comonomer) affects the miscibility level. Both VLDPE1 and ULDPE2 have butene as a comonomer, whereas other VLDPEs and ULDPEs have octene as a comonomer. The branch length of the butene copolymer (C2) is shorter than that of the octene copolymer (C6), providing greater similarity in structure with the PP (C1 branch length). The more miscible behavior between the PP and the butene-ethylene copolymers than between the octene-ethylene copolymers was expected. This explains why the ULDPE2 was more miscible with the

PP than the ULDPE5 and the ULDPE6. It may also account for the stronger interaction between the PP and the VLDPE1 than that between the PP and the VLDPE3 (and VLDPE4).

The effects of branch length on the miscibility level of blends were also studied by other authors. Hill and coworkers<sup>16</sup> studied phase separation in blends of HDPE with a metallocene-catalyzed ethylene-hexene (EH) copolymer and ethylene-butene (EB) copolymers. They found that the liquid-liquid phase separation region in the HDPE-EH blend was wider than that in the HDPE-EB systems, although the shapes of their phase diagrams were very similar. Yu and Wagner<sup>6</sup> calculated the Flory-Huggins interaction parameter,  $\chi$ , between PP and copolymers with various comonomer types.<sup>18</sup> Their results showed that the  $\chi$  values increased with branch length in copolymers from propene, butene, and hexene to octene.

#### Effect of melt flow index on miscibility of blends

The melt flow index (MFI) may also influence the miscibility of the blends. There are significant differences in the MFI of VLDPE1 and VLDPE3 and of ULDPE2 and ULDPE5. Generally, PP and PE with a closer match in MFI should be more miscible.<sup>9</sup> Because VLDPE1 and ULDPE2 have a higher MFI (low viscosity), which are closer to the MFI of PP, more miscible behavior between the PP and the VLDPE1 (and ULDPE2) than between the PP and the VLDPE3 (and ULDPE5) is expected. However, the melting and crystallization behavior of the ULDPE6-PP blend was the same as that of the ULDPE5-PP blend but different from that of ULDPE2-PP blend, although the MFI of ULDPE6 was in between those of ULDPE2 and ULDPE5. Therefore, branch length may be more important in making a difference here.

#### Effect of blending on crystallinity of the PP and PE

Figures 1-4 also show smaller melting endotherms for PP in the ULDPE-PP blends than those in the VLDPE-PP blends. In particular, in the ULDPE2-PP blend a very small PP peak was present, indicating smaller crystallinity of PP in the PP-ULDPE blends.

The enthalpies of melting were used to calculate crystallinity. Values of 209 J g<sup>-1</sup> and 287 J g<sup>-1</sup> corresponding to 100% crystallinity were used for PP<sup>19</sup> and PE,<sup>20</sup> respectively. The crystallinities of ULDPEs were less than 10% (Table III). ULDPE2 displayed the smallest crystallinity (4%), indicating its amorphous character. The crystallinities of VLDPEs were much larger than those of ULDPEs, ranging from 29% to 39%.

After blending, the crystallinity of both PP and the VLDPEs (and ULDPEs) decreased. The crystallinity of PP decreased more in the ULDPEs than in the VLDPEs. Particularly, the crystallinity of PP reduced

TABLE II  
Melting and Crystallisation Temperature (°C) of the PP, VLDPEs, and ULDPEs as Pure Polymers and in the Blends

Sample	T <sub>m</sub>		Additional T <sub>m</sub>		PP	T <sub>c</sub>		Additional T <sub>c</sub>	
	PP	PE	1	2		PE 1	PE 2	1	2
PP	159.4				119.5				
VLDPE1		90.0				66.5	40.8		
ULDPE2		46.2				24.1			
VLDPE3		111.2				94.1	62.2		
VLDPE4		105.9				87.4	56.6		
ULDPE5		58.4				41.1			
ULDPE6		59.9				39.2			
VLDPE1-PP	160.6	90.1	122.5		117.7	75.0	40.6		
ULDPE2-PP	162.4	44.3	122.4	86.3	109.1	26.2	97.2	109.1	43.0
VLDPE3-PP	159.6	110.5			118.6	95.8	61.8	87.5	
VLDPE4-PP	160.2	105.6			118.1	90.8	56.1	81.1	
ULDPE5-PP	163.0	58.7			119.6	40.6		99.4	
ULDPE6-PP	162.3	60.1			118.4	41.1		97.0	

drastically in the ULDPE2-PP (a decrease of 63%). These results were in accordance with the melting and crystallization results.

Due to the hindrance from the VLDPEs and ULDPEs, the PP was unable to crystallize to the same extent as in the pure PP. Some crystallizable segments of PP molecules in the pure PP became amorphous after blending with the VLDPEs and ULDPEs. The crystallization of PP was retarded more by the ULDPEs than by the VLDPEs, presumably because the solubility of PP in the ULDPEs was greater. In particular, in the PP-ULDPE2 blend, the decrease in PP crystallinity was the most significant, indicating that miscibility between the PP and the ULDPE2 was the greatest amongst the metallocene PEs studied.

#### Effect of type of metallocene PE on crystallization rate of PP

The isothermal crystallization of PP in the ULDPE2-PP could not be detected by the DSC at a tem-

TABLE III  
Crystallinity (X<sub>c</sub>) of the PP, VLDPE, and ULDPE and its Percentage Decrease in the Blends

Sample	X <sub>c</sub> of PP	Decrease of PP X <sub>c</sub> (%)	X <sub>c</sub> of PE	Decrease of PE X <sub>c</sub> (%)
PP	0.48			
VLDPE1			0.29	
ULDPE2			0.04	
VLDPE3			0.39	
VLDPE4			0.35	
ULDPE5			0.09	
ULDPE6			0.09	
VLDPE1-PP	0.46	-4.2	0.22	-24.1
ULDPE2-PP	0.18	-63.0	0.037	-7.5
VLDPE3-PP	0.37	-22.9	0.37	-5.1
VLDPE4-PP	0.41	-14.6	0.31	-11.4
ULDPE5-PP	0.36	-25.0	0.07	-22.2
ULDPE6-PP	0.35	-27.1	0.08	-11.1

perature as low as 90°C, although it can be observed by optical microscope. Therefore, no half-time is available for the ULDPE2-PP blend. We previously reported that the crystallization half-time of PP can be used as a measure of the miscibility of PP and PE.<sup>21</sup> When PP and PE were immiscible, the half-time of PP in the blend was similar to that of pure PP, although PP was the minor component. This was because PP crystallized in phase-separated droplets. In these droplets the concentration of PP was close to 100% of PP. When PP was miscible or partially miscible with PE, the crystallization half-time of PP in the blend was slow compared with pure PP because PP crystallized from a dilute solution.

Table IV shows Avrami exponents and Figure 9 displays crystallization half-times for PP. The crystallization behavior of PP in the VLDPE-PP blends was close to that of pure PP (Fig. 10) at lower crystallization temperatures, as shown by both Avrami exponent values and half-times. The Avrami exponents are around 5 in PP and in three VLDPE-PP blends at lower temperatures, indicating that secondary crystallization occurred after a long annealing time, as the DSC technique cannot separate primary and secondary crystallization. The difference in crystallization emerged when the crystallization temperature increased. In particular, in the VLDPE1-PP blends, the half-time increased dramatically at 130°C (Fig. 9), and the Avrami exponent reduced to less than 2, indicating that PP crystals grew in two dimensions at this temperature in the VLDPE1, whereas PP started to show miscible behavior with the VLDPE1.

The PP crystallized much slower in the ULDPE5-PP and ULDPE6-PP blends than in the VLDPE-PP blends (Fig. 9), and the Avrami exponents were around 3 in these two blends, indicating that the growth of PP crystals in these blends was in a three-dimensional spherulitic pattern and that the secondary crystallization did not take place under experi-

TABLE IV  
Avrami Exponent of PP Crystallization in the Blends

Temperature (°C)	PP	VLDPE1-PP	VLDPE3-PP	VLDPE4-PP	ULDPE5-PP	ULDPE6-PP
114					3.0	3.0
115		5.3				
116					3.1	3.0
118		5.1			3.0	2.8
119	5.1					
120	5.2	5.1			2.9	3.1
121	5.3					
122		4.9			3.0	2.6
124		5.3		5.1		
125		5.0				
126		4.8	5.4	4.5		
127	5.2					
128	5.3		5.3	4.1		
129	4.9	4.4				
130	5.0	1.4	4.4	3.5		

mental conditions. The slower crystallization rate in the ULDPE-PP blends again indicated that the PP was more miscible with the ULDPEs than with the VLDPEs. In particular, with the ULDPE2 the isothermal crystallization was not detectable by DSC, implying that the PP showed substantial miscibility with the ULDPE2. It may be that the PP partially dissolved in the ULDPE2 and that the concentration of PP was too low to crystallize. Another possibility is that the PP may disperse in the ULDPE2 with very fine droplets, not all of which contain nuclei. Only after further cooling (e.g., room temperature) could homogeneous nucleation be activated and the crystallization of PP accelerated.

It can also be seen from Figure 9 that the rate of crystallization of PP in the ULDPE6-PP blend was

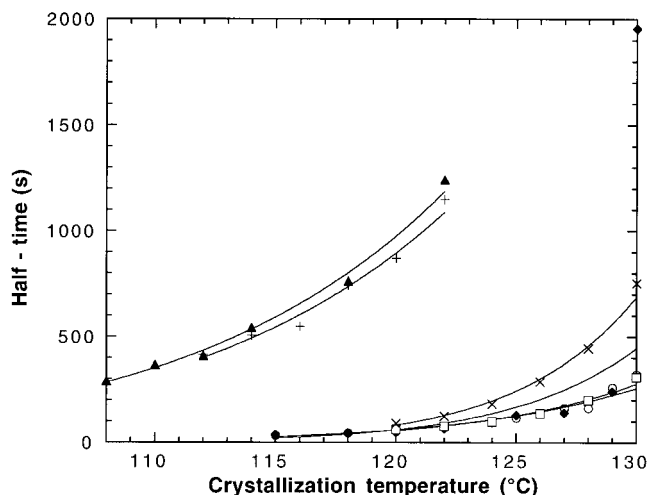


Figure 9 A plot of crystallization half-time of pure PP and the PP in the blends with VLDPE (or ULDPE) versus isothermal crystallization temperature. ○: PP; □: VLDPE1-PP; ◆: VLDPE3-PP; ×: VLDPE4-PP; +: ULDPE5-PP; ▲: ULDPE6-PP.

slower than that in the ULDPE5-PP blend. This may be attributed to the MFI difference between the ULDPE5 and the ULDPE6, as this is the only difference between them. This phenomenon was also observed in the PP-LLDPE blend systems.<sup>22</sup>

#### Morphology of blends under controlled crystallization

The blend morphologies varied with the crystallization temperature and time and the type of PE used in the blends. In the VLDPE1-PP blend the PP crystallized in droplets at 124°C [Fig. 11(a)]. When the crystallization temperature increased to 130°C, the PP grew out of the PP phase and diffused into the VLDPE1 phase [Fig. 11(b)], indicating that the VLDPE1 and the PP were miscible at 130°C or higher. This observation was in agreement with the half-time and Avrami exponent values.

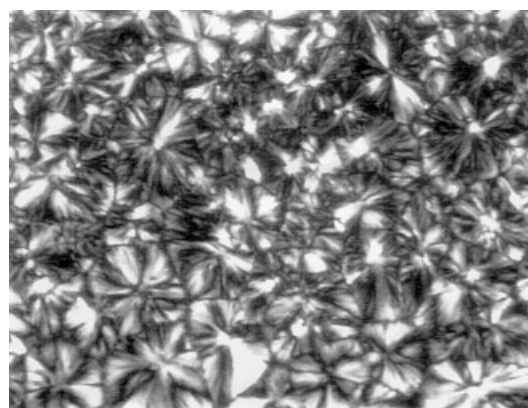
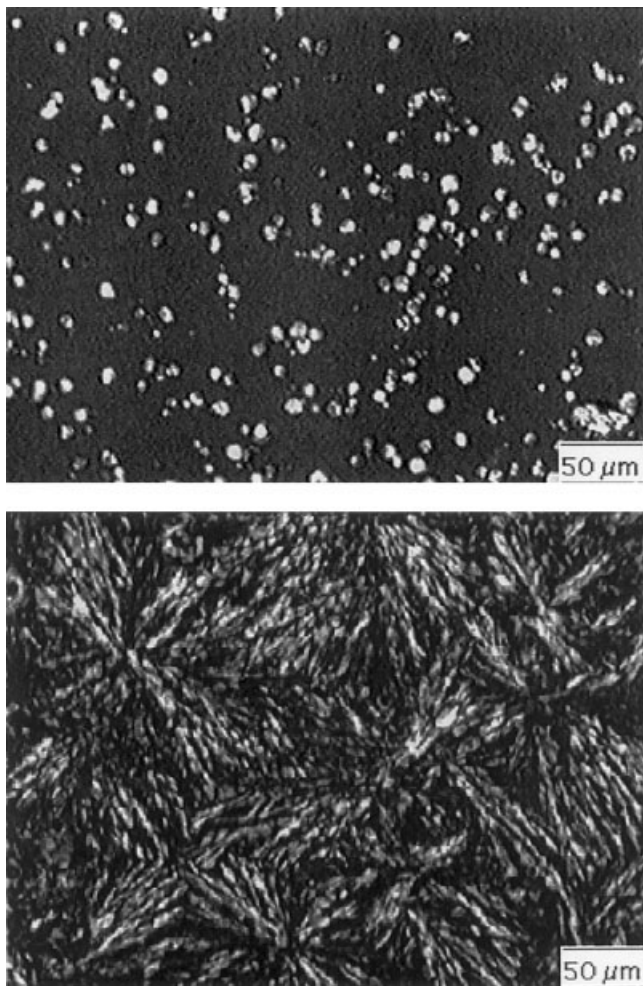


Figure 10 PP spherulites after isothermal crystallization at 130°C for 90 min (magnification × 100).



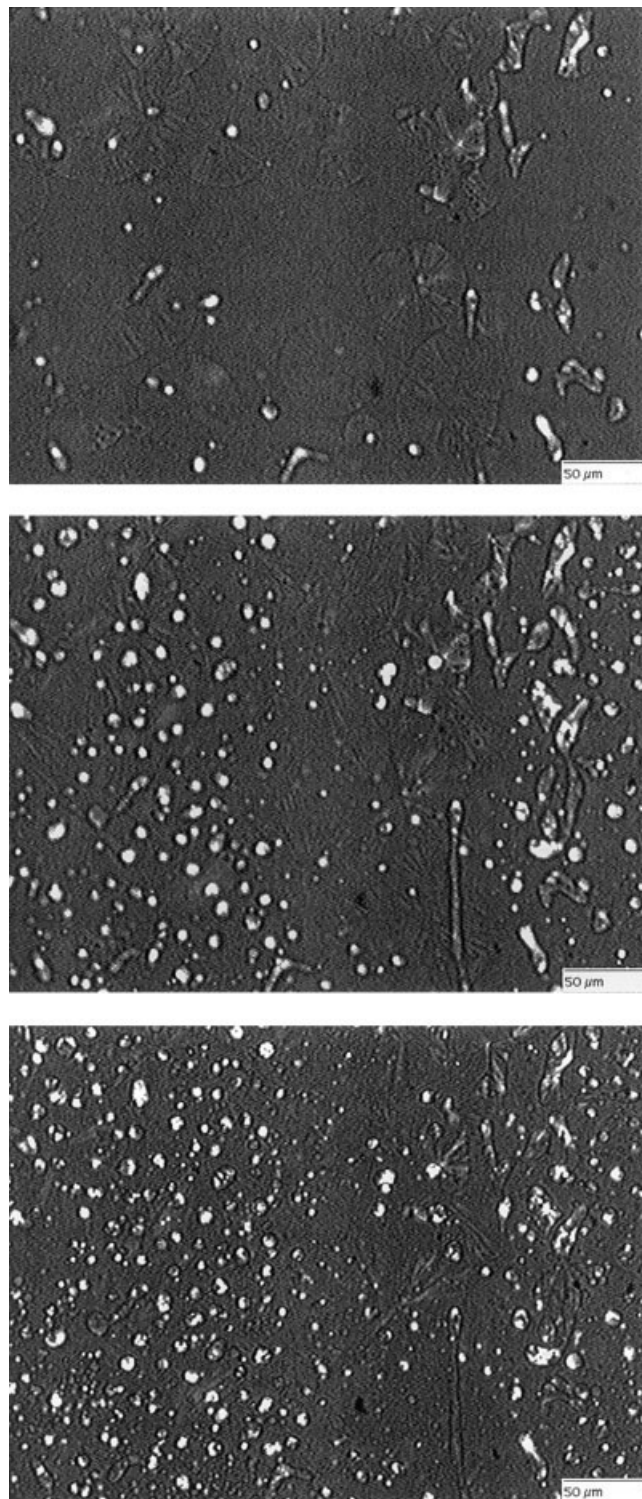


**Figure 11** (a) PP droplets in the VLDPE1-PP at 124°C; (b) PP spherulites in the VLDPE1-PP after isothermal crystallization at 130°C for 5 h; image was captured at ambient temperature (magnifications  $\times 100$ ).

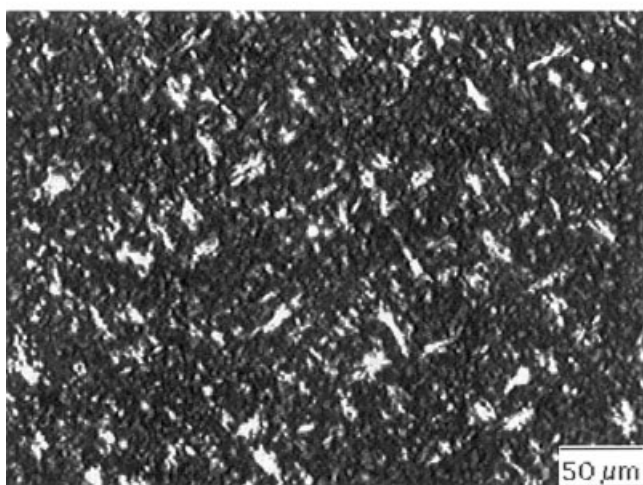
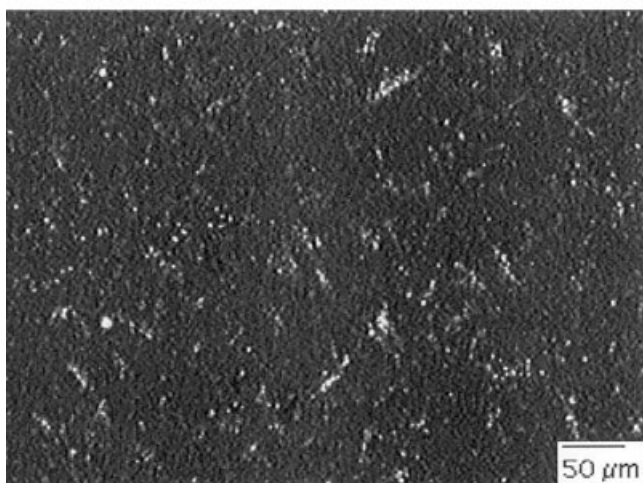
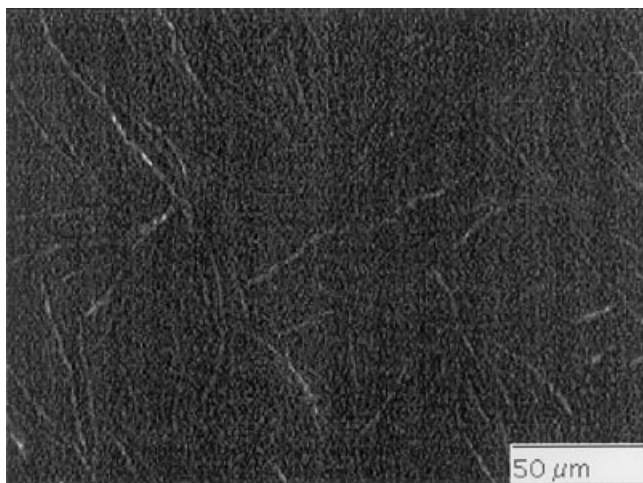
Figure 12 presents three images of the VLDPE4-PP blend at different times during isothermal crystallization at 130°C. Both droplets and solution-grown PP crystals were present at a crystallization time of 15 min [Fig. 12(a)]. With an increase in the crystallization time, the number of droplets increased and the solution-grown spherulites became less distinguishable [Fig. 12(b)]. After 115 min the solution-grown spherulites were not observable, and more droplets appeared, as shown in Figure 12(c). The increase in the number of droplets with time indicated that the degree of phase separation increased with time. The isothermal crystallization behavior of the PP-VLDPE3 blend was similar to that of the PP-VLDPE4.

Twenty percent of PP must be partially dissolved in the VLDPE3 and VLDPE4 above the melting temperatures. On cooling to 130°C, the PP separated from the VLDPE3 and VLDPE4 slowly with time. In addition, there was competition between phase separation and the crystallization because the PP started to crystallize

at 130°C. At an early stage of annealing, the crystallization of PP dominated over phase separation. With an increase in time, the phase separation dominated.

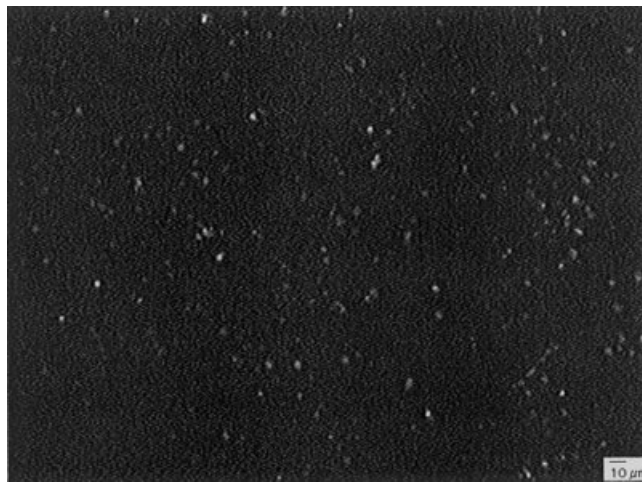


**Figure 12** (a) PP crystallized both in droplets and in the solution of PP and VLDPE4 melt after isothermal crystallization at 130°C for 15 min; (b) more PP droplets phase-separated from the solution of the VLDPE4-PP at 25 min; (c) only PP droplets observable at 115 min (magnifications  $\times 100$ ).



**Figure 13** (a) Fine and weak PP fibrillar crystal in the ULDPE2 at 115°C after 198 min (magnification  $\times 200$ ); (b) PP crystals in ULDPE2 after isothermal crystallization at 126°C for 22 h (image was captured at 126°C, magnification  $\times 100$ ); (c) PP spherulites in ULDPE2 after isothermal crystallization at 126°C for 22 h (image was captured at ambient temperature, magnification  $\times 100$ ).

This phenomenon was also observed in the LLDPE (70%)–PP (30%) blend at 130°C.<sup>13</sup> From the difference in crystal appearance of PP in the VLDPE1–PP and



**Figure 14** Fine dispersion of PP particles in the ULDPE5 (magnification  $\times 100$ ).

VLDPE4–PP blends at 130°C, we can also deduce that the PP dissolved more in VLDPE1 than in VLDPE4. The results were also consistent with the results of crystallization half-time, crystallization, and melting temperatures.

The crystallization of PP in the ULDPE2 was able to be observed by the HSOM, although it was too slow to be detected by DSC. The crystals of PP in the ULDPE2–PP at 115°C after 198 min were fine and fibrillarlike and not bright enough to present a clear image [Fig. 13(a)]. After isothermal crystallization at 126°C for 22 h, the PP crystals were still fine and not very clear [Fig. 13(b)]. It was also observed that for temperatures between 90°C and 126°C, the rate of crystallization of PP was too slow for PP to complete crystallization at these temperatures. When the temperature decreased to room temperature, the crystallization rate of PP increased. Figure 13(c) shows much brighter and coarser PP crystals at ambient temperature, indicating a larger volume of crystalline phase.

Figure 14 shows a fine dispersion of PP in the ULDPE6–PP blend at 130°C. The dispersion of PP in the ULDPE5–PP blend was the same as that in the PP–ULDPE6 blend. The solution-grown spherulites were not observed in these blends. However, the size of the PP phases in the PP–ULDPE5 and PP–ULDPE6 blends was significantly smaller. A finer dispersion of the minor component is also an indication of more miscible behavior between the two components.

The HSOM results confirmed that there was some degree of miscibility between the PP and the PEs studied. The PP was more miscible with the ULDPEs. These findings are in accordance with the DSC results.

## CONCLUSION

At a concentration of 20%, PP was found to be miscible with the VLDPEs and ULDPEs at elevated temper-

atures. The branch content and branch length of VLDPE and ULDPE affected the miscibility level of the blends. The PP was more miscible with the ULDPE than with the VLDPE because of the higher branch content of ULDPE. A decrease in branch length promoted the miscibility of PP and VLDPE (and ULDPE). The molecular weight of PE influenced the crystallization rate of PP and may also influence the miscibility of the blends. The crystallization rate of PP was lower in ULDPE that had a larger molecular weight. This was further proof of miscibility between PP and the ULDPEs, as the diffusion speed of chain segments of PP was reduced at a great level in the more viscous ULDPE melt.

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