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Blends of Amorphous-Crystalline Block Copolymers with Amorphous Homopolymers. 2. Synthesis and Characterization of Poly(ethylene-propylene) Diblock Copolymer and Crystallization Kinetics for the Blend with Atactic Polypropylene

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ABSTRACT: A symmetric diblock ethylene-propylene copolymer (DEP) was synthesized through hydrogenation of an anionically polymerized polybutadiene-poly(2-methyl-1,3-pentadiene) diblock copolymer (PBD-b-PMPD). IR and NMR measurements showed the hydrogenation to be more than 98% complete. The resultant diblock copolymer consists of an atactic polypropylene block and a polyethylene block (b-PE) containing 3 mol % of ethyl branches. Differential scanning calorimetry (DSC) was carried out for three series of binary blends made from DEP ($M_w = 113 \times 10^3$) and three atactic polypropylene (APP) samples with molecular weights of $M_w = 15, 39, \text{ and } 190 \times 10^3$. Blending did not affect the melting behavior of b-PE but drastically altered the crystallization behavior depending on the molecular weight and composition of the blend. Adding APP to DEP caused the primary crystallization peak to shift to lower temperature. In the composition range of more than 50 wt % of APP, another new crystallization peak appeared around 70 °C for all blends. This feature was especially pronounced for the blends with the lowest molecular weight APP. Isothermal crystallization studies were carried out for the blends and the data were analyzed by the Avrami theory. The analysis indicates that the dimensionality of the crystallization growth geometry was reduced by blending and each crystallization peak could be correlated with a different dimensionality in the growth geometry. These results are consistent with the framework of the currently accepted microphase separation model for homopolymer/diblock copolymer blends.

Introduction

Blends made from a symmetric diblock copolymer (b-AB) and the corresponding homopolymer (h-A) have two stability limits for phase separation,^{1,2} one for microphase separation and the other for macrophase separation. That for microphase separation is mainly determined by the molecular weights of the b-AB blocks and the magnitude of the interaction parameter between A and B segments. This is because the limit on the scale of the microphase separation arises from the connectivity of the chemically different blocks in b-AB. The other stability limit, which is for macrophase separation, is related to the molecular weight difference between b-AB and h-A and, to a lesser degree, the A-B segment interaction.¹ That is usually expressed in terms of the relative molecular weight, which is defined as M_{h-A}/M_{b-A} , where M_{h-A} and M_{b-A} are the molecular weights of h-A and b-A, respectively. When $M_{h-A} > M_{b-A}$, h-A cannot enter the microdomains of A in b-AB and so macrophase separation occurs between h-A and b-AB. If $M_{h-A} \approx M_{b-A}$, the macrophase separation is suppressed and h-A and b-AB tend to mix at a certain level. However, in this case h-A is excluded from the interface and segregates in the center of the microdomain.³ In the case of $M_{h-A} < M_{b-A}$, mixing of h-A and b-A at the molecular level becomes more favorable. Only in this case can blending induce morphological transitions in the microdomains.² If the block copolymer is symmetrical, the transitions usually proceed from a lamellar to a bicontinuous double diamond, then to a hexagonally

packed cylinder, and finally to a spherical structure. The reason for this is that the lower molecular weight homopolymer can enter into the A rich phase in the microdomain and thus change the interfacial free energy. The above mentioned basic principles concerning the micro- and macrophase separation for block copolymer blends have been established experimentally as well as theoretically.^{1,2,4}

Morphological studies of blends of block copolymers with the corresponding homopolymers are of both fundamental and commercial importance. The practical interest is focused on ternary blends of homopolymer A and B with diblock AB. In these cases the block polymers have been shown to be an effective compatibilizer by reducing phase size and improving physical properties when compared to the A/B homopolymer blends.⁵ This is generally done with a low level of added block polymer, usually between 1 and 5%. Many of the basic studies have dealt with binary blends of homopolymer A with an AB diblock and have concentrated on how the addition of the diblock modifies the microphase structure of the block.^{2,6} Some work has also been done on determining the phase diagram of this binary system.⁷ All of these studies have involved blends and blocks where both components are amorphous. It would be interesting to extend such studies to blends in which the block polymer contains a crystallizable block. One might suspect that in such a blend the geometrical constraints existing due to the presence of the microphase separation would influence the order in the crystalline phase. This study involves exploitation of methods to control the supermolecular structure as well as the crystallization kinetics and, it is hoped, will result in the ability to produce blends having

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a wide range of physical properties and mechanical behavior.

The thermodynamics of the blends made from a crystalline-amorphous diblock copolymer and an amorphous polymer involve crystallization as well as macro- and microphase separation.⁸ These various transitions should relate to each other and might cooperatively occur; possibly, one transition can induce another. Therefore, these blends might exhibit very complicated phenomena. On the other hand, it might be possible that such blends would exhibit novel morphologies leading to unusual properties. Although not a block copolymer blend, Inaba *et al.* studied the cooling behavior from the melt for the blend of an isotactic polypropylene and an ethylene-propylene random copolymer.^{9,10} They showed that the blend texture consisted of a modulated structure formed by spinodal decomposition and that this structure was stabilized by the subsequent crystallization of the polypropylene. They also observed that the final morphology could be controlled by changing the demixing time and the crystallization conditions. This is an example of controlling the morphology of polymer blends by using a combination of liquid-liquid phase separation and crystallization.

Even crystalline-amorphous diblock copolymers themselves show complicated phenomena. Cohen *et al.*¹¹ synthesized a polystyrene-polyethylene diblock copolymer and showed that variations in solvent-casting technique and the bulk annealing conditions led to different morphologies for this diblock copolymer. Since the glass transition temperature of polystyrene is close to the melting temperature of polyethylene, they speculated that the structure was kinetically trapped and could not attain a final equilibrium state. Another study was reported by Nojima *et al.*¹² They measured small angle X-ray scattering from ϵ -caprolactone-butadiene diblock copolymer and concluded that the microstructure formed in the melt state was destroyed by the subsequent crystallization of the ϵ -caprolactone. Recently, however, Cohen *et al.* studied a series of hydrogenated poly(1,2-butadiene-*block*-1,4-butadiene) with different molecular weights and showed that the hydrogenated 1,4-butadiene block, which is essentially polyethylene, crystallized within the segregated region defined by the microphase separation in the melt state.^{13,14}

In this series of investigations,^{15,16} we examined the binary polymer blend consisting of an atactic polypropylene (APP) and a diblock poly(ethylene-*block*-propylene) (DEP). For this system, the difference between the glass transition of APP and the melting temperature of polyethylene is about 100 °C, which should be large enough to isolate the crystallization from the influence of the glass transition. Other advantages of this system are that the polyethylene crystal structure and crystallization kinetics are generally well understood,¹⁷⁻¹⁹ that APP and DEP are prepared through hydrogenation of anionically polymerized dienes, so the molecular weight distribution can be narrow, and that both precursor polymers before the hydrogenation are quite soluble in common solvents and so molecular weight determinations and other characterization can be done by conventional methods.^{20,21} This paper will report the synthesis and characterization of DEP and calorimetric studies on the crystallization of the blends with DEP and three APP samples. Here, the molecular weight combinations for DEP and APP's correspond to the three cases of $M_{h-A} < M_{b-A}$, $M_{h-A} \sim M_{b-A}$, and $M_{h-A} > M_{b-A}$.

Figure 1. Schematic illustration of synthesis scheme of diblock poly(ethylene-propylene) copolymer (DEP).

Experimental Section

(1) Samples. (a) Synthesis. Fetters's synthetic method²⁰ was used to prepare poly(2-methyl-1,3-pentadiene) (PMPD) and polybutadiene (PBD), precursor polymers for an atactic polypropylene (APP) and a polyethylene (PE), respectively. As described below in detail and also by the schematic synthetic path in Figure 1, the synthetic procedures for PMPD and PBD were combined and used for the preparation of poly(butadiene-*block*-2-methyl-1,3-pentadiene) (PBD-*b*-PMPD), a precursor polymer for poly(ethylene-*block*-propylene) (DEP).

2-Methyl-1,3-pentadiene (MPD) was purified by stirring with *n*-butyl lithium for 2 h at 0 °C. This treatment did not start polymerization because of the slow propagation reaction of MPD and served to eliminate protic and other diene impurities.²⁰ 1,3-butadiene was purified over triethyl aluminum at -78 °C for 30 min and distilled prior to use. The hexane solvent was dried over polystyrenyllithium and distilled directly into a reactor flask.

Synthesis of PBD-*b*-PMPD was carried out with *n*-butyl lithium in hexane in a conventional vacuum line. A 16.0-g quantity of dry 1,3-butadiene was condensed into a dried reactor flask containing 4.3×10^{-4} mol of *n*-butyl lithium in 200 mL of dried hexane. The reactor flask was warmed to 40 °C and 1,3-butadiene was polymerized at this temperature for 18 h. After that, the reactor flask was degassed to remove residual 1,3-butadiene monomer. The second monomer of MPD was distilled from 34.8 g of MPD containing 6.4×10^{-3} mol of *n*-butyl lithium directly into the reactor flask. The flask was warmed to 40 °C and the polymerization was started again, initiated by living polybutadienyllithium. Reaction was terminated after 5 days by adding degassed 2-propanol. The resultant polymer was stabilized by 2,6-dibutyl-4-methylphenol, precipitated into methanol, redissolved in THF, and reprecipitated into methanol.

PBD, PMPD, and PBD-*b*-PMPD were hydrogenated in cyclohexane solution at 80 °C under 2900–3300 kPa using palladium on calcium carbonate (Strem Chemical Co.) as a catalyst or at 70 °C under 200 kPa with palladium on barium sulfate.^{20,22} It took 2–7 days of such hydrogenation until olefinic unsaturated peaks were no longer detectable by ¹H NMR. After the reaction was complete, the hydrogen was removed, the solution was filtered, and the polymer was precipitated with methanol and dried under vacuum for several days.

Two DEP samples with similar molecular weight, three APP samples with different molecular weights, and one PE sample were prepared by the method described above and identified as shown in Table 1.

Table 1. Nomenclature and Molecular Characteristics

sample	nomenclature	M_w^a	M_w/M_n^a	polyethylene content, ^b wt %	ethyl branch content, ^c mol %	density g/cm ³
ethylene-propylene diblock copolymer	DEP113	113 000	1.12	48	3.0	
	DEP99	99 100	1.07	50	3.0	
				$f = 0.504^d$		
atactic polypropylene	APP15	15 100	1.05	0		0.8500
	APP39	39 300	1.04	0		0.8510
	APP190	190 000	1.10	0		0.8515
polyethylene PE43	PE43	43 000	1.10	100	3.0	0.9145

^a Calculated from unhydrogenated precursors' results which were measured by GPC with low-angle laser light scattering. The calibration was done by standard polybutadiene samples. ^b From ¹³C NMR on unhydrogenated precursors. ^c From ¹³C NMR and FT-IR (in PE block for DEP). ^d Symmetric factor defined as ethylene composition (vol %).

(b) Molecular Characterization. ¹³C NMR measurements were carried out at room temperature in about 20% (w/v) CDCl₃ solutions of PMPD, PBD, APP, PBD-b-PMPD, and DEP using a Varian XL-300 spectrometer. As mentioned above, ¹H NMR was used to keep track of the elimination of olefinic unsaturated peaks during the hydrogenation of the precursor polymers. For both measurements, tetramethylsilane was used as a chemical shift standard. ¹³C NMR spectra for PBD-b-PMPD and PBD were used for determination of copolymer composition and ethyl branch content in b-PE. Infrared absorption was measured for PE, DEP, APP, and a standard of high density polyethylene (HDPE), purchased from Polyscience Inc., using an IBM IR/32 FT-IR spectrometer at a resolution of 1 cm⁻¹ averaged over 30 scans.

The weight average molecular weight and molecular weight distributions were measured for the precursor polymers by gel permeation chromatography using ultra Styragel columns (10³, 10⁴, 10⁵ Å) with low-angle laser light scattering. The instrument was calibrated using standard polybutadienes and the details are described elsewhere.²³ The density measurements were carried out for APP's, PE43, and HDPE utilizing a water-ethanol density gradient column at 25 °C.

(c) Blend Preparation. All blends were made by solution mixing. DEP113 and APP's were dissolved separately in hot toluene at a concentration of about 5-15 wt % and these solutions were mixed to provide a given weight percent of APP in the blend. The mixture was poured onto a water surface at 95 °C and the solvent was evaporated. This procedure prevents inhomogeneity which results from the crystallization of b-PE before the mixing of the two components. After evaporation of the solvent, the blend film was picked up from the water surface and all samples were dried and annealed at 150 °C for 5-7 days under vacuum before the measurement. The annealing temperature did not make any difference in the results of the calorimetry as long as it was in the range of 150-250 °C. However, it was found that long annealing, at least for 3 days, was essential to obtain reproducible thermograms.

(2) Differential Scanning Calorimetry (DSC). Thermograms of cooling and heating cycles at 10 °C/min were obtained using a DuPont differential scanning calorimeter type 2000. The melting temperatures of indium and mercury were used for the calibration of the calorimeter. The sample quantity was always kept within 16-17 mg and the sample was annealed at 180 °C for 30 min before the measurements. The thermograms for both heating and cooling obtained in the second cycle were used for the data analysis, although no significant difference was observed between the first and second cycle.

The calorimetric technique was also used to determine the amount of crystallinity developed as a function of time

Figure 2. ¹³C NMR spectra for hydrogenated poly(2-methyl-1,3-pentadiene) (APP) from CDCl₃ solution.

at a fixed temperature. The samples were first melted in a hot plate control at about 170 °C and quickly transferred to the holder in the calorimeter which was beforehand set at a given crystallization temperature. The measured enthalpy of fusion (ΔH) was converted to the degree of crystallinity (m_c/m_0), by taking 290 J/g to correspond to the enthalpy of fusion for the perfect polyethylene crystal.

(3) Optical Microscopy. Optical microscopy observations of spherulites formed from the blend were done under polarized light. The specimens of the blend and DEP113 were melted at 150 °C and gradually cooled to 50 °C, taking about 2 days.

Results

(1) Characterization. The ¹³C NMR spectra for PMPD samples show aliphatic peaks at 16.2, 20.4-21.1, 23.8, 30.7-31.1, 39.9-40.0, and 48.2 ppm and olefinic peaks at 131.7-133.3 ppm, which are consistent with Fetters's results.²² The results show that there is no appreciable evidence for 1,2- and 3,4-additions in PMPD. An example of ¹³C NMR spectra for a hydrogenated PMPD, that is an APP sample, is presented in Figure 2. The spectrum is the same as that typically observed for atactic polypropylene.^{20,24}

A comparison of the ¹³C NMR spectra between PBD-b-PMPD and DEP is shown in Figure 3 and a magnified spectrum of PBD-b-PMPD in the 110-150 ppm region is also shown Figure 4. By referring to previous work^{20,24} and comparison to the spectra of PBD and PMPD, the peaks of PBD-b-PMPD were assigned, and the results are presented in the figures. As shown in Figure 3, the hydrogenation eliminates peaks due to unsaturated hydrocarbons and provides simplified spectra, indicating that

Figure 3. Comparison of ^{13}C NMR spectra for PBD-b-PMPD (lower) and DEP (upper). The numbers show the peak assignments which are provided in Figure 4.

Figure 4. Magnification of the region for the unsaturated carbon peaks of PBD-b-PMPD.

most of the unsaturated hydrocarbon was hydrogenated. The extent of hydrogenation was confirmed by ^1H NMR, by comparing the peak area between olefinic (4.5–5.0 ppm) and aliphatic (0.6–2.6 ppm) bands. The analysis yielded an extent of hydrogenation of 98%. Figure 3 shows that the spectrum of DEP seemed to consist of a composite of those of PE and APP, although the broad peaks of DEP make the exact assignment of the peaks difficult. The broad peaks were probably caused by the poor solubility of DEP.

As indicated by the assignments in Figures 3 and 4, the PBD-b-PMPD spectra constituted a combination of the corresponding spectra of PBD and PMPD. The PBD block had two microstructures of 1,4-addition and 1,2-addition units. The ratio of 1,4- to 1,2-units was evaluated to be 93:7 from the ratio of the peak area of 128.3–130.8 ppm for the 1,4-unit and 114.2 and 142.7 ppm for the

Figure 5. Comparison of infrared spectra for HDPE, PE43, APP39, and DEP113 in the range of 600–1500 cm^{-1} .

1,2-unit. The ratio was converted to the ethyl branch content in the polyethylene block (b-PE) in DEP. The PMPD block consists of only 1,4-addition units (131.2–132.2, 133.2 ppm) and there are no appreciable peaks from 1,2- or 3,4-addition units. The copolymer composition of PBD and PMPD was determined by comparison of the 131.2–133.2 peaks for PMPD and the 128.3–130.8, 114.2, and 142.7 peaks for PBD, and the results were converted to weight percent of polyethylene block in DEP, assuming that the hydrogenation does not result in chain scission. The results of these analyses are listed in Table 1.

Figure 5 shows a comparison of FT-IR spectra of a high-density polyethylene (HDPE), PE43, DEP113, and APP39 in the range of 600–1500 cm^{-1} . Comparing the spectra of PE43 and HDPE reveals that PE43 exhibited extra peaks around 1380, 966, and 773 cm^{-1} , and these are assigned to be due to ethyl branches.²⁵ From the area of the 773- cm^{-1} band for CH_2 rocking, the ethyl branch content was estimated to be 2–4 mol %, assuming that the extinction coefficient for this band is 0.04 $\text{g}^{-1} \text{cm}^{-1}$.²⁵ The spectrum for DEP113 is a combination of those of PE43 and APP39 and so confirms that DEP113 is a block copolymer of APP and PE. The figure shows a difference in crystalline bands of CH_2 rocking around 730 cm^{-1} and CH_2 bending around 1470 cm^{-1} among samples. HDPE exhibited the more enhanced crystallization peaks compared with that of PE43, indicating higher crystallinity for HDPE than for PE43. This is expected because PE43 has about 3% ethyl branches and it is well known that even such a small amount of branching disrupts crystal formation. Furthermore, the polyethylene block in DEP113 showed less crystallinity than that of PE43, suggesting that the block nature further decreases the degree of crystallinity.

Weight and number average molecular weights were obtained for the precursor polymers and converted to weight average molecular weight and molecular weight distribution of DEP and APP samples assuming 100% hydrogenation. These results are summarized in Table 1 together with densities. The density of APP and the molecular weight and copolymer composition of DEP were used to calculate the symmetrical factor defined as the ethylene volume fraction in the amorphous state. Here, the density of PE in the amorphous state was assumed to be 0.865 g/cm^3 .

(2) Heating and Cooling Thermograms. Heating and cooling thermograms for HDPE, PE43, and DEP113 are shown in Figure 6. Offset temperature for melting (T_m)

Figure 6. Comparison of crystallization and melting peaks of polyethylene for HDPE, PE43, and DEP113. The heat of fusion for PE43 and DEP113 are magnified by three times for comparison. The heating and cooling rate is 10 °C/min.

and onset temperature of crystallization (T_c) were determined by a conventional interpolation method as illustrated in the figure. The values of the enthalpies of the transitions, ΔH_m for melting and ΔH_c for crystallization, were also evaluated from the peak area by taking a base line as illustrated in the figure. Furthermore, the glass transition temperature (T_g) and change in heat capacity (ΔC_p) at T_g were determined. These values are listed in Table 2 together with the results for some blends.

Figure 6 shows a clear difference between HDPE and the other two samples. Both melting and crystallization peaks for PE43 and DEP113 appeared at considerably lower temperatures than those of HDPE, and also showed a very broad shoulder on the lower temperature side. That feature is typically observed for a linear low-density polyethylene (LLDPE) with low branch content.²⁶ According to Seguela and Rietsch,²⁷ even small amounts of branches are not able to enter the crystalline phase, resulting in small crystal size and imperfection. Both of these cause lower melting or crystallization temperatures and also lower crystallinity. The other difference between HDPE and the other polymers is that both PE43 and

DEP113 exhibit a small exothermic peak around 60 °C on cooling. Such a secondary peak is normally observed for LLDPE and is understood to be due to the broad branch distribution which exists both inter- and intramolecularly.²⁶ However, this interpretation is not valid for the case of PE43 and DEP113 because of the homogeneity of the ethylene branch distribution in the PE chain due to anionic polymerization. As far as we know, no interpretation has been given for this second exothermic peak on cooling for anionically polymerized and then hydrogenated polybutadiene samples.

Figure 7 compares heating thermograms obtained for DEP113 and the blend with APP190 in the left panel and with APP15 in the right one. Since the blend with APP39 showed the same features as those in Figure 7, the thermograms are not presented here. The values of T_m and ΔH_m obtained from the thermograms are summarized in Table 2. Comparison of melting peaks for DEP113 and the blends illustrates that blending produces no significant changes in either peak position or shape. This is an indication that blending with different molecular weight homopolymers or with different compositions does not affect the melting behavior of b-PE in DEP. As shown in Figure 7 the glass transition of DEP113 occurs at exactly the same temperature as that of APP, and also each blend exhibits the values of ΔC_p that would be expected from the weight fraction of PE present in the blend. Furthermore, the width of the glass transition for DEP and the blend are the same as that of APP. These facts suggest that microphase separation takes place and the phases are strongly segregated. It should be mentioned that APP has a somewhat higher T_g than the average value reported for atactic polypropylene obtained by solvent extraction. According to Fetters,²⁰ this phenomenon may result from the larger free volume in APP due to the fact that it is "more atactic" than the hexane soluble fraction of polypropylene polymerized by Ziegler-Natta catalysis.

Figure 8 illustrates the composition dependence of the cooling thermograms for the APP190 blends, the highest molecular weight of APP. DEP113 showed a broad crystallization peak with an onset temperature of 94 °C and a small exothermic event around 65 °C. Adding 10 wt % APP190 to DEP113 caused the onset of the crystallization to shift to lower temperature by 8 °C. With increasing APP190 the predominant crystallization peak

Table 2. Results of DSC

sample	APP wt%	heating ^a				cooling ^e			
		T_g , °C	ΔC_p , J g ⁻¹ °C ⁻¹	T_m , °C	ΔH_m , J g ⁻¹	m_d/m_0 , %	peak I T_c , °C	peak II T_c , °C	ΔH_c , J g ⁻¹
HDPE ^d				144	298	100	118		300
PE43				113	107	37	90.6		124
DEP113		-2.0	0.55	111	110	38	94.2		97
DEP99		-2.0	0.58	110	115	40	95.0		99
APP190	100	0.5	0.61						
APP190/DEP113	75	-1.7	0.65	109	137	47	83.5	72.2	115
APP190/DEP113	50	-1.0	0.63	110	137	47	85.9	73.0	138
APP190/DEP113	25	-0.5	0.54	111	135	47	86.5		167
APP39	100	-2.0	0.61						
APP39/DEP113	75	-3.0	0.54	108	94	33	80.5	67.0	98
APP39/DEP113	50	-3.5	0.58	109	90	31	83.0	70.5	88
APP39/DEP113	25	-4.8	0.61	110	114	40	85.8		97
APP39/DEP113	13	-3.0	0.54	110	113	39	86.5		88
APP15	100	-3.0	0.62						
APP15/DEP113	75	-2.0	0.52	107	78	27		73.0	101
APP15/DEP113	50	-2.6	0.51	109	84	29		69.0	83
APP15/DEP113	25	-2.0	0.55	110	106	37	84.0		94
APP15/DEP113	10	-2.8	0.53	111	89	31	87.5		101

^a Final temperature of melting peak. ^b Calculated from polyethylene weight percent in blends and heat of fusion assuming 290 J/g for enthalpy of perfectly crystalline polyethylene. ^c Onset temperature of crystallization peak. ^d Polyscience Inc. standard high density polyethylene $M_w = 53,000$, $M_w/M_n = 3$, and $\rho = 0.958$ g/cm³. ^e Heating and cooling rate is 10 °C/min.

Figure 7. Comparison of heating thermograms between APP190 and APP15 blend. The numbers in the figure show weight percent of APP in the blend. The heating rate is 10 °C/min.

Figure 8. DSC cooling thermograms measured for a series of blends of DEP113 and APP190. The cooling rate is 10 °C/min. The heat of fusion is normalized by total weight of the blend.

gradually shifted to lower temperatures and the 60 °C event disappeared. Above 50 wt % a small second crystallization peak appeared at 70 °C. Figure 9 plots cooling thermograms for the blends with APP39, the middle molecular weight sample. As shown in the figure, the APP39 blends exhibited almost the same features as the APP190 blends as long as the composition was in the 10–40 wt % range. Above 50 wt %, the main peak became broader and finally disappeared and the second crystallization peak became dominant. The difference between Figures 8 and 9 clearly displays the effect of the molecular weight of APP on the crystallization behavior of b-PE.

Figure 9. DSC cooling thermograms measured for a series of blends of DEP113 and APP39.

For the lowest molecular weight of APP, the effect was even more pronounced, as shown in Figure 10. Here, there was no coexistence of the two peaks. In the range of 90–45%, only the first peak was observed, similarly to the other blends. Above 50%, however, the first peak completely disappeared and only the second one was observed. It is surprising that the onset temperature of the second peak above 50% in APP increased with increasing APP content, in strong contrast to the decreasing onset temperature of the first one. This feature suggests that the first and the second peak correspond to different crystallization mechanisms, so we denote them as peaks I and II, respectively. All of these results on the

Figure 10. DSC cooling thermograms measured for a series of blends of DEP113 and APP15.

Figure 11. Plots of onset temperatures of peaks I and II against APP weight percent in the blend.

cooling thermograms are collected in Figure 11 and some of them are in Table 2.

Figure 12. An example of isothermal crystallization experiment: the time course of heat flow and the temperature fluctuation for a blend with 50 wt % of APP15 crystallized at 82.7 °C.

Figure 13. Plots of $\Delta H_t / \Delta H_{ref}$ against crystallization time $t - t_0$ for PE43. The enthalpy of perfect crystalline polyethylene is assumed to be 290 J/g for ΔH_{ref} .

(3) Isothermal Crystallization. Isothermal crystallization measurements were carried out for PE43, DEP113, and the blends, and the data were analyzed using the Avrami theory. Due to the resolution limit of our calorimeter, we could not measure ΔH_C accurately for some of the higher APP compositions. For the same reason, the crystallization temperature had to be chosen in a certain range such that crystallization would be complete within 10–60 min. Figure 12 shows a representative example for the time evolution of the heat flow, the running integral of the heat flow, and the temperature fluctuation during an isothermal crystallization. The curve for the running integral shows a sigmoidal shape typical of isothermal crystallization for polymers and also confirms that the temperature was well controlled within ± 0.1 °C. To estimate a degree of crystallinity (m_c/m_0) as a function of time, t , a straight base line was assumed and an initial time (t_0) was determined by interpolating between the quenching region and the exothermic region as illustrated in the figure. Figures 13 and 14 show plots of m_c/m_0 against $t - t_0$, illustrating examples for PE43 and some blends.

Mandelkern *et al.* extensively studied isothermal crystallization kinetics of hydrogenated polybutadiene over a wide range of both branch content and molecular weight by use of the dilatometric technique.¹⁷ Referring to their data, the isotherms in Figures 13 and 14 exhibit the general features observed by those authors as well as some

Figure 14. Comparison of isothermal crystallization behavior for the blends. The numbers in the figures indicate the crystallization temperature.

additional ones. With increasing crystallization temperature, all isotherms shifted toward longer times, meaning that the crystallization rate decreased with increasing crystallization temperature. This is evidence that the crystallization took place by a nucleation-controlled mechanism. The level of crystallinity that can be attained isothermally is in the relatively low range of 5–20%. However, this is normally observed for hydrogenated polybutadiene.

According to Mandelkern et al.,¹⁷ the low crystallinity is due to the fact that an ethyl branch cannot enter the crystal lattice, so the crystallization is disrupted to a large extent. The temperature over which isothermal crystallization can take place in an experimentally convenient time scale is very dependent on blend composition and molecular weight of the APP. With increasing APP composition, the crystallization temperature range is lower. For example, the crystallization temperature for APP15 blends decreased to around 85 °C, which is about 15 °C lower than that of DEP113 itself. However, for the same blend composition, isotherms seemed parallel to each other and a superposition of the isotherms is possible for the initial stages of crystallization. This indicates that a unique time–temperature variable governs the early stage of crystallization at the same composition and molecular weight, so that the Avrami theory is applicable to analyze the crystallization kinetics.

The Avrami formulation at small degrees of crystallinity is given by¹⁷

$$m_c(t)/m_0 \propto t^n \quad (1)$$

Here, n is the Avrami exponent, which is related to the

Figure 15. Relationship between the Avrami exponent and APP weight percent.

Table 3. Results of the Avrami Analysis of Isothermal Crystallization

sample	APP wt %	crystallization temperature range, °C	Avrami exponent, n
PE43		92.9–97.7	2.8 ± 0.1
DEP113		89.9–92.7	2.4 ± 0.1
+APP190	25	87.3–90.0	2.4 ± 0.1
	50	85.0–87.4	2.3 ± 0.1
	75	83.4–84.4	2.1 ± 0.2
+APP39	13	87.9–90.4	2.3 ± 0.1
	25	83.1–87.1	2.1 ± 0.1
	50	82.6	1.9 ± 0.2
+APP15	10	88.2–90.6	2.0 ± 0.1
	25	85.9–87.3	2.0 ± 0.1
	40	85.0	2.0 ± 0.1
	50	80.5–83.7	1.5 ± 0.1
	60	83.3–84.7	1.5 ± 0.1
	70	84.2	1.5 ± 0.2

type of nucleation mechanism and the geometry of crystal growth. Equation 1 indicates that the initial slope of a plot of $\log(m_c/m_0)$ against $\log(t - t_0)$ is the exponent n . Table 3 summarizes the values of n obtained in this way and Figure 15 is the APP composition dependence of n . For PE43, n is 2.8 ± 0.2 and the value is consistent with the result by dilatometry.¹⁷ DEP113 shows an exponent of 2.3, slightly lower than that of PE43, and blending causes various changes in the exponent depending on the molecular weight and composition of APP. For the APP190 blend, n did not change upon blending. On the other hand, when adding APP15, n decreased in two steps. n was constant between 10 and 40% and decreased abruptly by 0.5 around 45%, remaining constant again between 50 and 70%. For APP39, the data points were between those of APP190 and APP15. The Avrami analysis also shows drastic changes in the APP15 blend, suggesting that the crystallization kinetics of b-PE changed upon blending with APP15.

Comparing Figures 11 and 15 shows a correlation between T_c and the Avrami exponent, especially for the APP15 blends, where the correlation is quite obvious. For the APP15 blends, the peak I region in Figure 11c corresponds to the first plateau where the exponent is about 2 in Figure 15. The transition of T_c took place at the same composition as that in which n abruptly decreased to 1.5. The second plateau of the exponent also corresponded to the peak II region. Since peak II in the APP190 blends was very small (Figure 8) and the isothermal crystallization temperatures were always chosen around T_c , the unchanged exponent of about 2.2 is consistent with the fact that peak I is the major crystallization exotherm for the entire composition range of the

Figure 16. Temperature dependence of crystallization rate.

APP190 blends. Therefore, the above discussion based on the comparison of Figures 11 and 15 leads to the conclusion that the difference in the crystallization kinetics caused the different peaks in the cooling thermograms and that peaks I and II can be characterized as having Avrami exponents of 2 and 1.5, respectively.

The temperature dependence of the crystallization rate is a function of the Avrami exponent and usually a lower exponent provides a weaker temperature dependence.²⁸ Figure 16 is a plot of the time required to develop 1% of crystallinity ($\tau_{0.01}$) as a function of the supercooling depth (ΔT). The equilibrium melting temperature used here is 141 °C.¹⁷ The data exhibit that changing both molecular weight and composition of APP caused drastic changes in the temperature dependence. As mentioned before, in order to maintain the crystallization rate around $\tau_{0.01} = 1$ min, the crystallization temperatures had to be lower with increasing APP composition. Panel a compares the temperature dependence of $\tau_{0.01}$ for various compositions for APP190 and APP39 blends. Each group of data points can be fitted by a straight line and the slope of the lines seems unchanged. On the other hand, blending with APP15 caused completely different behavior from that of APP190 and APP39 when the composition was higher than 50 wt %. As shown in panel b, up to 25 wt % of APP15, the features were the same as for the other blends. However, adding more than 50 wt % APP15 caused the slope to decrease and also the crystallization temperature to shift to higher values. The decrease in the slope is consistent with a lower value of the Avrami exponent in this composition range. This feature indicates that an entirely different crystallization mechanism governs this composition range.

(4) Optical Microscopy. Cross polarized optical microscopy was carried out and a spherulitic crystal texture was observed for DEP113 and some blends. For APP190 and APP39 blends, the Maltese cross pattern was observed up to 75 wt % of APP. For APP15 blends, the cross pattern was observed for less than 50 wt % of APP and was absent above 50 wt %, although the sample is still optically anisotropic. Figure 17 shows examples for the photographs taken through a cross polarized microscope for DEP113, APP39 blends, and APP15 blends.

When the spherulites are nucleated simultaneously, the boundaries between them are straight.²⁸ However, when the spherulites have been nucleated at different times, so that they are different in size when impinging on one another, their boundaries form hyperbolae.²⁸ Our optical

DEP113

DEP113+APP39(50wt%)

DEP113+APP15(50wt%)

Figure 17. Comparison of cross polarized microscope photographs for DEP, APP39 blend (50 wt %), and APP15 blend (50 wt %).

microscopy showed straight boundaries and quite uniform size for spherulites as shown in picture a and b. These facts indicate that the nucleation mechanism for b-PE can be characterized as a simultaneous nucleation.

Discussion

DSC measurements showed that blending APP with DEP113 did not cause any changes in the melting behavior of the b-PE in DEP. It did, however, cause drastic changes in the crystallization behavior. The primary crystallization peak (peak I) shifted to lower temperatures with increasing APP composition and the second peak (peak II) appeared above 50 wt % APP. This feature was more pronounced for APP15 blends, for which only peak I was observed below 45 wt % and then only peak II was observed above 50 wt %. The crystallization kinetics were different for peaks I and II, as indicated by the different Avrami exponents of 2 and 1.5. Furthermore, the optical microscopy examination of the spherulites formed in slow-cooling experiments indicated simultaneous nucleation of these spherulites.

There are several explanations for the reduction of the Avrami exponent for the crystallization from polymer

blends. Miscibility enhancement due to low molecular weight is one of them. One might suspect that, for some of the APP15 blends, b-PE and APP15 are miscible at the molecular level, so that can make a difference in the crystallization kinetics. There has been little direct measurement of miscibility for the blends made from polypropylene and polyethylene. Wignall *et al.* showed that these polymers are immiscible at high molecular weight by small-angle neutron scattering (SANS).²⁹ Other studies on related systems^{30,31} would indicate that the Flory interaction parameter is quite large for polypropylene and polyethylene melts. Moreover, the glass transition temperatures of the blends studied here were not different from those of the pure components (see Figure 7 and Table 2). As described in an upcoming paper,³² a rheological study on this system clearly showed that there was no miscible region for APP15 blends. Furthermore, the rheological study indicated that DEP113 and the blend were microphase separated at any temperature below 280 °C and the microdomains were strongly segregated. Therefore, it is reasonable to assume that APP and b-PE chains are incompatible for the molecular weight range studied here, so miscibility is not the cause for reducing the Avrami exponent. The Avrami exponent is related to the nucleation mechanism and the crystallization growth geometry. As mentioned before, optical microscopy shows a simultaneous nucleation mechanism in the blends for all compositions of APP190 and APP39, as well as those below 40 wt % of APP15. Above 50 wt % of APP15, no spherulites were observed. However, since the lower crystallization temperature caused the simultaneous nucleation, the low crystallization temperature for APP15 blends suggests that, even above 50 wt %, the nucleation mechanism was also simultaneous as in the other blends. Therefore, it is reasonable to suppose that for our case the only possible parameter to change the Avrami exponent comes from the crystallization growth geometry, and the dimensionality of the geometry is decreasing with increasing APP wt % or decreasing molecular weight of APP.

As mentioned in the introduction, in the case that b-AB forms a microdomain structure, the stability limit of the macrophase for the blend with h-A and b-AB is very sensitive to the relative molecular weight which is defined as M_{h-A}/M_{b-A} . In the case of $M_{h-A}/M_{b-A} > 1$, macrophase separation takes place in almost the entire composition range. On the other hand, in the case of $M_{h-A}/M_{b-A} < 1$, blending causes a morphological transition of the microdomain. Winey *et al.* have studied extensively the morphological transition of amorphous block copolymer blends and constructed a morphological diagram.² According to them, the diagram represents a universal trend for amorphous block copolymer blends, regardless of the kinds of polymers involved. Since the rheological study of DEP showed strong segregation in the melt state, this diagram should be applicable to the blends with DEP and APP. Figure 18 shows the copolymer morphological diagram and also indicates the relative molecular weight for each combination of DEP113 and APP. The diagram predicts the phase separation and morphology of the melt state (above the melting temperature of polyethylene) in these blends. Since the symmetric factor of DEP113 is 0.48, DEP113 should form a lamellar type microdomain structure. For APP190 blends, macrophase separation is expected for all composition ranges, so blending does not change the structure of the microdomains of b-PE. For the APP39 blends, APP39 chains can merge into the APP rich domain to the same extent; however, they may not be so miscible that blending induces a structural transition

Figure 18. Comparison of the relative molecular weight of APP blends and the constant copolymer composition morphology diagram reported by Winey *et al.*² Solid lines indicate the boundaries between different microdomain structures and the dashed line indicates boundaries between micro- and macrophase separation. L, C, and S, stand for lamellae, cylinders and spherical structure, respectively.

of the microdomains. In this case, macrophase separation may take place around 25–50 wt % of APP39. For APP15 blends, the molecular weight is low enough to merge APP15 chains into the APP rich phase in the microdomain. Therefore adding APP15 to DEP113 causes the microdomain structure of the b-PE rich phase to change from a lamellar to a cylindrical and finally to a disordered spherical structure.

There is consistency between the crystallization behavior of our blends and the morphological transitions that can be inferred from the morphological diagram. Since the microdomains in the melt state of b-PE provide spatial constraints to the crystallization growth of b-PE, the microdomain structure of b-PE should influence the crystallization growth. Although there may not be a strict correspondence, a lower geometrical dimensionality in the microdomain should give a higher spatial constraint, which means a lower dimensionality in the crystallization growth and therefore a lower value of the Avrami exponent. This hypothesis can explain the observation that the crystallization kinetics of APP15 blends changes at 50 wt %, which is the same composition for the transition from a cylindrical to a spherical structure in the morphological diagram. Furthermore, since the APP190 blend is macrophase separated, blending does not affect the b-PE microdomains, which also agrees with the unchanged T_m and the Avrami exponent. Therefore, it is concluded that different microdomain structures are responsible for the different crystallization behavior, peaks I and II, and the different Avrami exponents.

In fact, according to an upcoming publication,³² by transmission electron microscopy (TEM) on a quenched thin film, APP15 blends form a bicontinuous cylindrical structure below 50 wt % and a discrete cylindrical or spherical structure above 50 wt %. Therefore it is reasonable to expect that the different morphology observed for the quenched samples is related to the different morphology in the melt state. Furthermore, scanning electron microscopy (SEM) indicates macrophase separation of APP190 blends,³² also consistent with Winey's morphological phase diagram.

Figure 11b shows that the onset temperature of peak I decreases with increasing APP weight percent; on the

contrary, the onset of peak II increases with increasing APP. The decreasing onset temperature is understandable because increasing APP content may reduce the continuity of the b-PE phase and so depress the crystallization temperature. On the other hand, the increasing onset temperature of peak II needs more study to be well understood. However, the following argument may give one possible explanation for this behavior. In the microdomains formed by b-AB, the interfacial tension between the different domains elongates the chains perpendicular to the interface. In the case of $M_{h-A}/M_{b-A} < 1$, the interface increases with addition of h-A to b-AB and so the conformations of the block B chains are first deformed back to a more symmetrical form then finally elongated parallel to the interface. Through this change, the conformational entropy of the B block increases and reaches a maximum when the conformation becomes symmetrical and then decreases. Since the composition range of more than 50 wt % of APP15 may correspond to the decreasing conformational entropy region, the above argument is qualitatively consistent with the increasing crystallization temperature as shown in APP15 blends, taking account of the fact that the crystallization temperature is given by $\Delta H_m/\Delta S_m$. This argument also explains the fact that DEP113 shows a higher onset crystallization temperature than that of PE43 (see Figure 6). In order to prove this speculation, it is necessary to evaluate the thickness of the microdomain of b-PE as a function of APP weight percent. This evaluation can be done by measurement of SANS from the melt state of the blend and DEP in which one block is deuterated.³²

Summary and Conclusion

A symmetric diblock ethylene-propylene copolymer of DEP was synthesized through hydrogenation of PBD-b-PMPD. Molecular characterization showed the hydrogenation to be about 98% complete and the b-PE to contain 3 mol % ethyl branches. Three series of blends of DEP113 and APP with different molecular weights were studied by calorimetry. Blending causes enormous changes in the crystallization behavior. The results can be interpreted in the framework of the currently accepted microphase separation model for homopolymer/diblock copolymer blends. We are currently studying the morphology of these blends by TEM, SEM, SAXS, and small-angle neutron scattering. Those results will be presented subsequently.³²

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