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Miscibility of Propylene−Ethylene Copolymer Blends

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ABSTRACT: Miscibility of homogeneous propylene/ethylene (P/E) copolymers of relatively narrow molecular weight distribution was studied as a function of constituent comonomer content. Polymers with up to 31 mol % ethylene were blended in pairs in order to vary the comonomer content difference. Binary blends were rapidly quenched from the melt to retain the phase morphology, and the phase volume fractions were obtained from AFM images. Copolymers of molecular weight about 200 kg mol^{-1} were miscible if the difference in ethylene content was less than about 18 mol % and immiscible if the ethylene content difference was greater than about 20 mol %. Blends with constituent composition difference in the range of 18−20 mol % exhibited partial miscibility in the melt as indicated by a phase volume fraction that was different from the blend volume fraction. The temperature dependence of blend morphology confirmed the UCST behavior of P/E copolymer blends. The phase composition and the χ interaction parameter were extracted by using an approach that considered the molecular weight distribution. The compositional dependence of χ conformed to the copolymer equation and depended on comonomer content difference only, not on comonomer content per se.

Introduction

Polypropylene is frequently blended or copolymerized with a rubbery ethylene/propylene copolymer as a method of imparting low-temperature toughness to an otherwise brittle thermoplastic. A relatively high ethylene content ensures that the impact modifier is amorphous, has a low glass transition temperature, and phase separates from the polypropylene matrix. However, some level of compatibility, or interaction with the matrix, is desirable for effective stress transfer and particle size control. In the past, a major barrier to probing the thermodynamic interaction of propylene/ethylene (P/E) copolymers was the broad molecular weight distribution and heterogeneous comonomer distribution of copolymers synthesized with Ziegler−Natta catalysts.

Recent developments in single-site catalyst technology greatly facilitate the study of real olefin copolymers. With homogeneous comonomer distribution and narrow molecular weight distribution, they are excellent vehicles for fundamental studies of copolymer miscibility. The opportunities presented by the new homogeneous copolymers were initially demonstrated with ethylene copolymers.[1,2] However, single-site catalysts also allow for synthesis of propylene copolymers with controlled comonomer content and high levels of isotacticity in the propylene sequences. They offer an excellent model system for studying miscibility behavior of propylene copolymer blends.

The first experiments that directly measured the interaction strengths of isotactic polypropylene and random P/E copolymers relied on small-angle neutron scattering (SANS) and indicated that a P/E with as little as 8 wt % (11.5 mol %) was immiscible with isotactic polypropylene.[3] More recent SANS measurements suggested that blends of isotactic polypropylene with random P/E copolymers containing 19 and 47 mol % ethylene form homogeneous melts.[4] The apparent discrepancy may arise from the low molecular weight of the polymers used in the latter study. The SANS method has the distinct advantage that the phase condition is determined in the melt. However, the impracticality of producing deuterated polymers for SANS experiments limits studies of real propylene copolymers. Another study relied on rapid quenching to preserve the melt morphology in binary blends of isotactic polypropylene with a random P/E copolymer. For polymers having M_w of about 200 kg mol^{-1}, it was found that the critical ethylene content for miscibility was between 16 and 23 mol % (11.3 and 16.6 wt %).[5]

Discussions of polymer miscibility usually start with the Flory−Huggins equation for the free energy of mixing of a binary blend:

$$\frac{\Delta G_m}{RT} = \frac{\phi_1}{N_1}\ln\phi_1 + \frac{\phi_2}{N_2}\ln\phi_2 + \chi\phi_1\phi_2 \qquad (1)$$

where ϕ_1 and ϕ_2 are the volume fractions of constituents 1 and 2, N_1 and N_2 are the respective degrees of polymerization, and χ is the Flory−Huggins interaction parameter. The critical miscibility conditions are obtained by setting the derivatives of eq 1 equal to zero.[6] For the interaction parameter, the critical condition is

$$\chi_c = \frac{1}{2}\left[\frac{1}{\sqrt{N_1}} + \frac{1}{\sqrt{N_2}}\right]^2 \qquad (2)$$

For a blend of two statistical copolymers of the same comonomers, the interaction parameter is often given by[7,8]

$$\chi = \chi_{AB}(\Delta\psi)^2 \qquad (3)$$

where χ_{AB} is the segmental interaction parameter of the comonomer units A and B, and $\Delta\psi$ is the difference in comonomer weight fraction. For a blend of two A/B copolymers to be miscible at any concentration, χ should be less than χ_c.

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Table 1. Characteristics of Propylene/Ethylene Copolymers

polymer designation	ethylene content (mol %)	ethylene content (wt %)	M_w (kg/mol)	M_w/M_n	density (g/cm^3)	crystallinity[a] (wt %)
mPE 0.0	0.0	0.0	282	2.2	0.9062	51
mPE 3.1	3.1	2.1	318	2.0	0.8993	44
mPE 4.9	4.9	3.3	183	2.1	0.8954	41
mPE 11.0	11.0	7.6	150	2.3	0.8887	32
mPE 13.6	13.6	9.5	110	2.1	0.8845	26
mPE 18.8	18.8	13.4	201	2.1	0.8736	16
mPE 25.2	25.2	18.3	219	2.1	0.8607	7
mPE 30.8	30.8	22.9	193	2.0	0.8550	2

[a] Calculated from first heating thermogram.

Combining eqs 2 and 3 leads to an expression for the critical composition difference for miscibility:

$$\Delta\psi_c = \left[\frac{1}{\sqrt{N_1}} + \frac{1}{\sqrt{N_2}}\right]\left[\frac{1}{\sqrt{2\chi_{AB}}}\right] \qquad (4)$$

According to eq 4, miscibility depends on comonomer content difference only, not on comonomer content per se. This has been experimentally demonstrated in some instances.[9,10] For example, studies of homogeneous ethylene/styrene copolymers of different styrene content established the validity of eq 4 for this system and revealed the critical comonomer content difference to be about 9 wt %.[11] Furthermore, these studies demonstrated the role of molecular weight distribution. However, numerous exceptions to eq 4, in which the critical composition difference is a function of comonomer content, have been reported.[12−15] Blends of high-density polyethylene with homogeneous ethylene/octene copolymers,[2] and model polyolefins obtained by hydrogenation of almost monodisperse polydienes,[14,16] exhibit a systematic increase in the quantity $\chi(\Delta\psi)^{-2}$ with increasing $\Delta\psi$. It remains to be determined whether eq 4 holds for P/E copolymer blends.

With the assumption that the interaction parameter is purely enthalpic, χ_{AB} can be written in terms of the solubility parameter difference as

$$\chi_{AB} = \frac{V_{ref}}{RT}(\delta_{PA} - \delta_{PB})^2 \qquad (5)$$

where δ_{PA} and δ_{PB} are the solubility parameters of homopolymer A and homopolymer B, and $V_{ref} = (V_A V_B)^{1/2}$ is the reference volume with V_A and V_B defined as the molar volumes of A and B units, respectively. Combining eqs 4 and 5 provides an estimate of the critical composition difference.

Typically, χ_{AB} is a small number, and therefore it is very sensitive to the choice of δ_A and δ_B. However, for any given polymer, a large range of δ values is often reported due to the relatively large method-to-method variation.[17] To minimize such effects, the difference in solubility parameters of polypropylene and polyethylene, $\delta_{PP} - \delta_{PE}$, was estimated from solubility data provided by a single source. From the solubility parameters of polypropylene (16.37 MPa$^{1/2}$) and polyethylene (17.83 MPa$^{1/2}$) reported by Sperling,[18] and reference volumes V_P = 53 cm^3/mol for the propylene unit and V_E = 36 cm^3/mol for the ethylene unit,[19] the value of $\chi_{P/E}$ was estimated to be 0.0238. From the relative solubility parameters of polypropylene (0.25 MPa$^{1/2}$) and polyethylene (1.48 MPa$^{1/2}$) reported by Lohse,[16] a slightly lower $\chi_{P/E}$ value of 0.0169 was estimated. Using $\chi_{P/E}$ values of 0.0238 and 0.0169, the critical composition difference in ethylene content for copolymers with M_n of 10^2 kg mol^{-1} was calculated to be about 17 and 20 wt % at 200 °C, respectively.

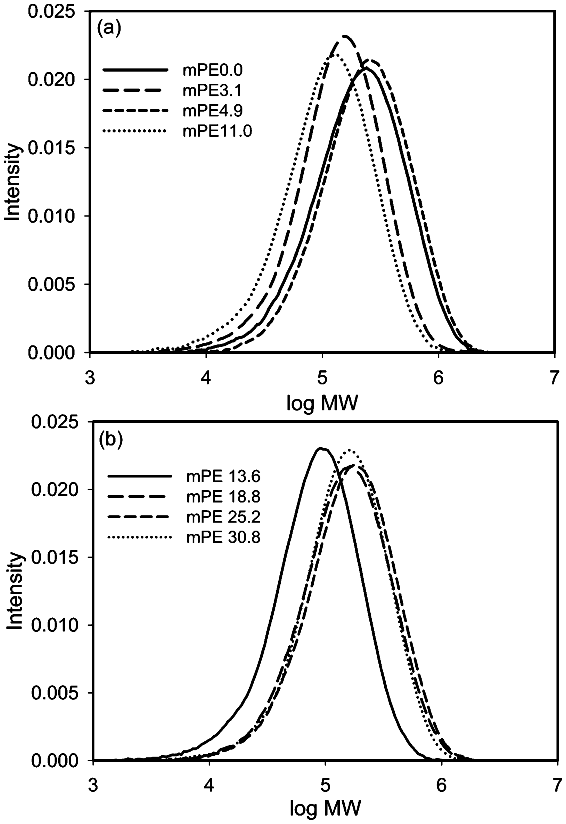

Figure 1. Molecular weight distribution of P/E copolymers as weight fractions. Peak areas are normalized to unity.

The present study tests the miscibility condition for binary blends of polypropylene and P/E copolymers. The study utilizes homogeneous P/E copolymers with a broad range in comonomer content and well-characterized composition and molecular weight distribution as a model system for testing eq 4 and related concepts of copolymer miscibility. Blend morphology is examined using atomic force microscopy (AFM) to image domains of the chemically similar constituents. The power of the AFM technique is exploited to probe the compositional region of

Table 2. Summary of mPE Copolymer Blends Showing Phase Condition Based on Difference in Ethylene Content

constituent 1	constituent 2	ethylene content difference Δ (mol %)	blend composition (w/w)	melt temp (°C)	phase condition
mPE 11.0	mPE 18.8	7.8	70/30; 30/70	200	miscible
mPE 0.0	mPE 13.6	13.6	70/30	200	miscible
mPE 11.0	mPE 25.2	14.2	70/30; 60/40	120, 160, 200	miscible
mPE 3.1	mPE 18.8	15.7	70/30; 30/70	160, 200	miscible
mPE 13.6	mPE 30.8	17.2	70/30; 60/40	120, 160, 200	miscible
mPE 0.0	mPE 18.8	18.8	70/30; 60/40; 40/60; 30/70	160, 180, 200, 220, 240	partially miscible
mPE 11.0	mPE 30.8	19.8	70/30; 60/40; 40/60; 30/70	160, 180, 200, 220, 240	partially miscible
mPE 4.9	mPE 25.2	20.3	70/30; 60/40; 40/60; 30/70	160, 180, 200, 220, 240	partially miscible
mPE 3.1	mPE 25.2	22.1	70/30; 30/70	160, 200, 240	immiscible
mPE 3.1	mPE 30.8	27.7	70/30; 30/70	200	immiscible
mPE 0.0	mPE 30.8	30.8	70/30; 30/70	200	immiscible

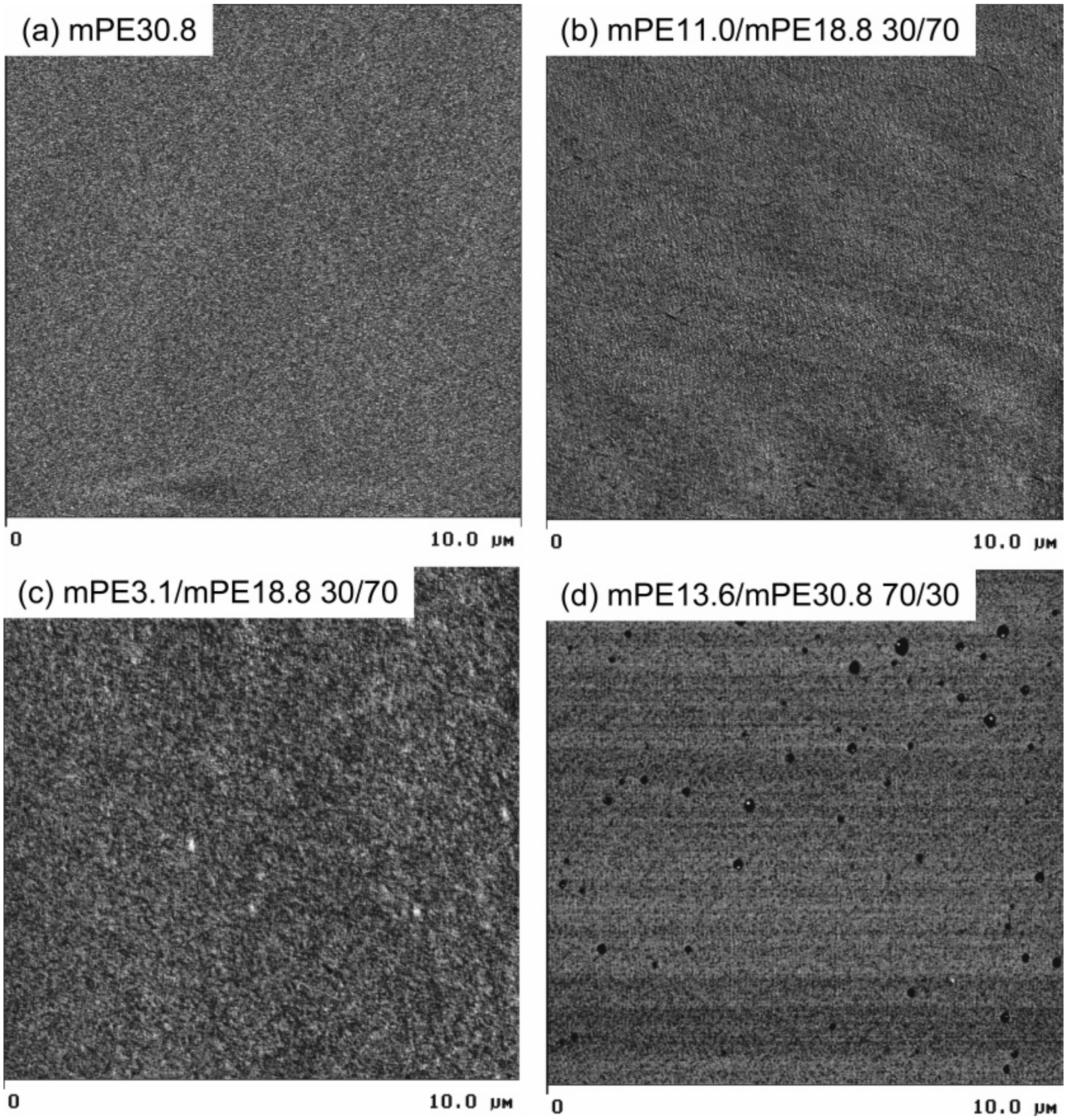

Figure 2. AFM phase images of a P/E copolymer and miscible blends quenched from 200 °C: (a) mPE30.8, (b) mPE11.0/mPE18.8 30/70, (c) mPE3.1/mPE18.8 30/70, and (d) mPE13.6/mPE30.8 70/30.

partial miscibility for the effects of temperature, molecular weight, and molecular weight distribution. The results are compared with more conventional experimental methods that infer miscibility from glass transition and melting behavior.

Materials and Methods

The propylene/ethylene copolymers described in Table 1 were provided by The Dow Chemical Co. The copolymers were prepared using a conventional metallocene catalyst and are identified by the prefix mPE followed by the ethylene content as mole percent. The ethylene content varied from 0 to 30.8 mol %. The comonomer distribution in the mPE copolymers was reported to be homogeneous and close to random.[20] The molecular weight distribution was determined by gel permeation chromatography (GPC) calibrated with polystyrene standards. The equivalent polypropylene molecular weights were deduced using the appropriate Mark−Houwink coefficients for polypropylene and polystyrene.[21,22] The data were provided by Dow and are shown in Figure 1. Most of the copolymers had weight-average molecular weight M_w of about 200 kg mol^{-1}. All the polymers had relatively narrow molecular weight distribution with polydispersity in the range 2.0−2.3.

The density of slowly cooled compression-molded films was determined using a density gradient column. Water and 2-propanol were mixed according to ASTM-1505-85. The error in the density determination was no greater than 0.0003 g cm^{-3}. Crystallinity of the copolymers and their blends was determined using a Perkin-Elmer model 7 DSC. Thermograms were obtained with a heating rate of 10 °C min^{-1}. Crystallinity was calculated using a heat of fusion of 209 J g^{-1} for the polypropylene crystal.[23,24]

The copolymers were blended in solution. The appropriate amounts of the constituents (vol/vol) were weighed and dissolved in 1,2,4-trichlorobenzene at 130 °C, maintaining the total concentration less than 1 wt %. The mixture was stirred continuously for 1 h after a homogeneous solution was obtained. Blends were precipitated by pouring the solution into chilled methanol. The mixture was centrifuged to obtain the solid blend. The blend was washed with acetone and dried in a vacuum at 60 °C for 48 h or until constant weight was achieved. The dried blend was stabilized by spraying with 3000 ppm of Irganox 1010/Irgafos 168 in a 50/50 composition in acetone.

Specimens for AFM imaging were prepared by melting ∼40 mg of the blend in an uncovered pan under nitrogen in a Rheometrics DSC. Specimen size was minimized in order to achieve as rapid a cooling rate as possible during quenching. The specimens were heated to 255 °C for 5 min before they were rapidly cooled to the desired melt temperature. Specimens were held at 160, 180, 200, 220, or 240 °C for 30 min. To freeze in the phase morphology at the melt temperature, the specimens were quenched by rapidly removing the pan from the DSC and plunging it into a dry ice/acetone bath.[25]

Specimens were microtomed at −75 °C to expose the bulk morphology. Tapping mode AFM was performed using a Digital Laboratories Nanoscope IIIa with a multimode head and J-scanner. All measurements were made at ambient temperature, and intermediate to hard tapping was employed to reveal good contrast in both height and phase images. Because the modulus difference between the copolymers was large, AFM phase images provided better contrast for revealing the domain morphology of partially miscible or immiscible blends. Generally, the 20 μm phase images provided a good resolution of the phase morphology and were used to obtain phase volume fractions. The AFM phase images were analyzed using Image-Pro Plus software from Media Cybernetics to obtain the amount of each phase. Results from three unique images were averaged to obtain phase volume fractions.

Results and Discussion

Miscibility Limit. The miscibility of P/E copolymers was examined by blending copolymers that differed in ethylene content. The difference in ethylene content of the blend constituents Δ varied from 7.8 to 30.8 mol %. The blend compositions and the melt temperatures that were studied are summarized in Table 2. A blend was considered miscible if it exhibited a homogeneous texture similar to that of the constituent copolymers. A one-phase texture without well-developed crystalline features typified a copolymer that had been quenched from the melt (Figure 2a). A similar homogeneous texture in AFM phase images of mPE11.0/mPE18.8 (Δ = 7.8) and mPE3.1/mPE18.8 (Δ = 15.7) blends quenched from 200 °C (Figure 2b,c) indicated that these blends were miscible. Additional experiments established that mPE11.0/mPE18.8 (Δ = 7.8), mPE0.0/mPE13.6 (Δ = 13.6), and mPE3.1/mPE18.8 (Δ = 15.7) blends were miscible in all compositions and at all temperatures studied.

The texture of mPE11.0/mPE25.2 (Δ = 14.2) and mPE13.6/mPE30.8 (Δ = 17.2) blends was not completely homogeneous. The phase image of an mPE13.6/mPE30.8 blend after it was quenched from 200 °C showed a small amount of a second phase that appeared as small dark domains about 100 nm in diameter that were dispersed in a bright matrix (Figure 2d). The dark domains were an mPE30.8-rich phase with lower modulus than the harder mPE13.6-rich matrix. The measured phase volume of the dark domains was 1−2%. It was noteworthy that this phenomenon was observed only if both constituents had very low crystallinity, namely mPE11.0/mPE25.2 (Δ = 14.2) and mPE13.6/mPE30.8 (Δ = 17.2) blends, but was not observed with mPE3.1/mPE18.8 (Δ = 15.7) blends which incorporated a constituent with higher crystallinity. This study relied on rapid crystallization during quenching to preserve the phase condition in the melt. However, constituents with higher ethylene content crystallized very slowly.[26] It was speculated that a blend with Δ close to the miscibility limit might be completely miscible at the melt temperature, but only partially miscible at ambient temperature. If the blend constituents did not crystallize during quenching, phase separation could have proceeded when the glassy blend was taken above the T_g to ambient temperature. Slow concurrent cold crystallization halted phase separation at the condition found in the AFM images. In accordance with this speculation, mPE11.0/mPE25.2 and mPE13.6/mPE30.8 blends were catagorized as miscible in the melt.

Examination of the DSC cooling thermogram and the subsequent heating thermogram of an mPE11.0/mPE18.8 blend revealed a single glass transition temperature that was intermediate between the glass transition temperatures of the two constituents (Figure 3). This behavior was characteristic of a miscible blend. Furthermore, the complex melting behavior suggested that the constituent copolymers cocrystallized to some extent.

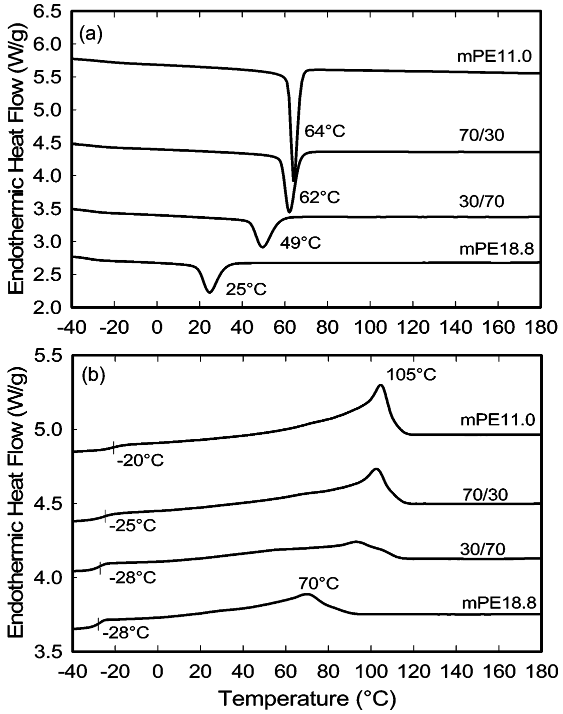

Figure 3. DSC thermograms of mPE11.0/mPE18.8 miscible blends: (a) cooling curves and (b) subsequent heating curves.

The AFM phase images of mPE0.0/mPE18.8 (Δ = 18.8), mPE11.0/mPE30.8 (Δ = 19.8), and mPE4.9/mPE25.2 (Δ = 20.3) blends revealed phase-separated morphologies (Figure 4). The bright phase was enriched in the lower ethylene, higher modulus constituent, and the dark phase was enriched in the higher ethylene, lower modulus constituent. For example, the dark domains in the mPE0.0/mPE18.8 blend with 70/30 composition were the mPE18.8-rich phase whereas the bright matrix was the mPE0.0-rich phase. Reversing the composition to 30/70 inverted the contrast so that the bright dispersed domains were the mPE0.0-rich phase. For blends of these three P/E pairs, the measured phase volume ratio was different from the blend composition, which indicated that the constituents were partially miscible. For example, the measured phase volume ratio of mPE11.0/mPE30.8 70/30 quenched from 200 °C was 85/15.

The DSC thermograms were consistent with a partially miscible, two-phase blend (Figure 5). The crystallization exotherm of mPE11.0 in mPE11.0/mPE30.8 blends broadened and shifted to lower temperatures as the amount of mPE30.8 increased, although the transition enthalpies were proportional to the amount of mPE11.0 in the blend. The subsequent heating thermogram of the mPE11.0/mPE30.8 70/30 blend exhibited a broad T_g region that encompassed the T_gs of the mPE11.0-rich and mPE30.8-rich phases. In the 30/70 blend, the prominent glass transition inflection of the mPE30.8-rich phase was broader and shifted to a slightly higher temperature than the T_g of mPE30.8.

Blends of mPE3.1/mPE25.2 (Δ = 22.1), mPE3.1/mPE30.8 (Δ = 27.7), and mPE0.0/mPE30.8 (Δ = 30.8) formed coarse phase-separated morphologies (Figure 6). The dark matrix was the higher ethylene, lower modulus constituent, and the bright domains were the lower ethylene, higher modulus constituent. The domains of the immiscible blends were much larger than those of the partially miscible blends. The large domain size and correspondence between the measured phase composition

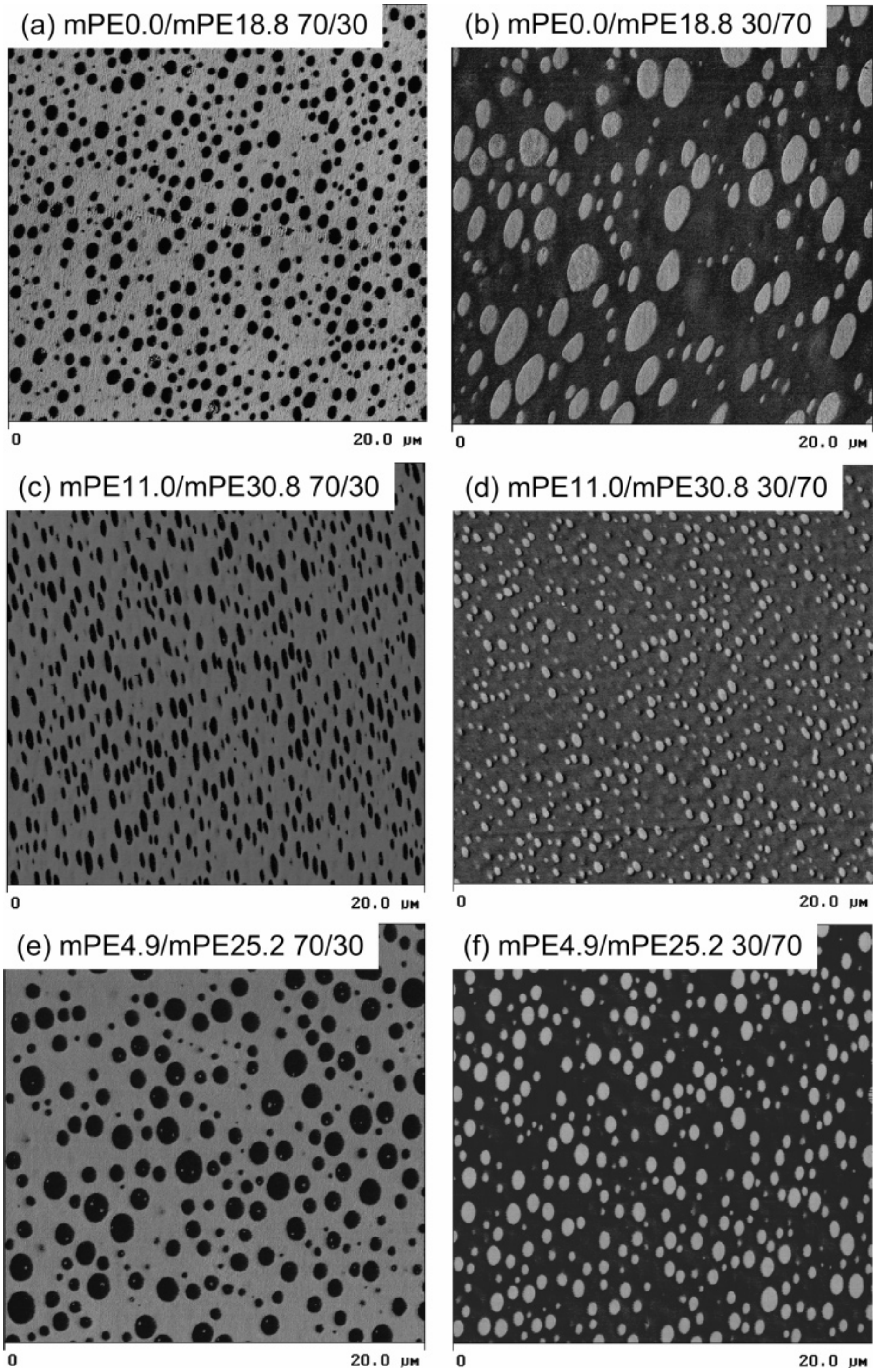

Figure 4. AFM phase images of partially miscible blends quenched from 200 °C: (a, b) mPE0.0/mPE18.8 70/30 and 30/70, (c, d) mPE11.0/mPE30.8 70/30 and 30/70, and (e, f) mPE4.9/mPE25.2 70/30 and 30/70.

and the blend composition indicated that these blend constituents were immiscible. These blends were immiscible at all temperatures and compositions studied.

In DSC thermograms, the crystallization and melting temperatures of mPE3.1 were not affected by blending (Figure 7), and the transition enthalpies were proportional to the amount of mPE3.1 in the blend. The glass transition temperature of mPE30.8 at −37 °C was not altered by blending. It is characteristic of immiscible blends that the thermal behavior is an additive combination of the constituent behavior.

A summary of the phase behavior of propylene/ethylene copolymer blends based on ethylene content difference is given in Table 2. Varying the ethylene content difference of the constituent polymers established the critical difference in comonomer content for miscibility as about 18 mol %, in good agreement with the prediction of 20 mol % for copolymers in this molecular weight range. Furthermore, examination of the phase morphology revealed a very narrow range in ethylene content difference of 18−20 mol % where the blends exhibited partial miscibility. The critical comonomer content difference for P/E copolymers was considerably larger than that found for ethylene/octene (EO) and ethylene/styrene (ES) copolymers of similar molecular weight. Compared to 18−20 mol % for P/E blends, the critical composition of EO for miscibility with HDPE

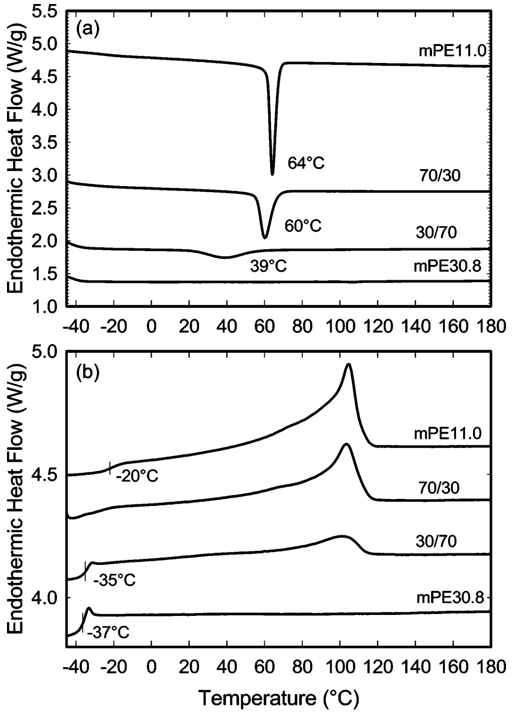

Figure 5. DSC thermograms of mPE11.0/mPE30.8 partially miscible blends: (a) cooling curves and (b) subsequent heating curves.

was 6−9 mol % octene,[2] and the critical composition difference for ES blends was 2−3 mol %.[11]

Phase Behavior of Partially Miscible Blends. The narrow range of partial miscibility was probed further by quenching the partially miscible blends, mPE0.0/mPE18.8, mPE4.9/mPE25.2, and mPE11.0/mPE30.8, of various compositions from melt temperatures between 160 and 240 °C. In all cases, the amount of the dispersed phase decreased as the temperature was raised. The temperature dependence of the blend morphology showed characteristics of upper critical solution temperature (UCST) behavior.

Phase composition (v/v) from the AFM phase images differed from blend composition (Table 3), indicating that these blends were partially miscible at all the temperatures studied. As the melt temperature increased, the volume fraction of the dispersed phase decreased; however, for the compositions studied, the maximum temperature was not high enough to eliminate the second phase completely and achieve complete miscibility.

Given the strong molecular weight dependence of the mixing free energy as expressed in eq 1, it follows that a discussion of real polymers cannot neglect consideration of the molecular weight distribution, even though the molecular weight distribution of homogeneous copolymers is relatively narrow. Solc and co-workers developed a thermodynamic approach to incorporate the molecular weight distribution of the individual blend constituents.[27−29] The analysis follows the mixture through the cloud point and deeper into the two-phase region to access the change in composition of coexisting phases with changing temperature. The application of this approach to partially miscible ethylene copolymers with homogeneous composition and polydisperse molecular weight distribution was demonstrated previously.[1,2]

In the general case of two polydisperse constituents, the free energy of mixing for a blend of composition ϕ_2 is given by

$$\frac{\Delta G}{RT} = \sum_i n_{1i} \ln \phi_{1i} + \sum_j n_{2j} \ln \phi_{2j} + \chi \phi_2 \sum_i n_{1i} r_{1i} \qquad (6)$$

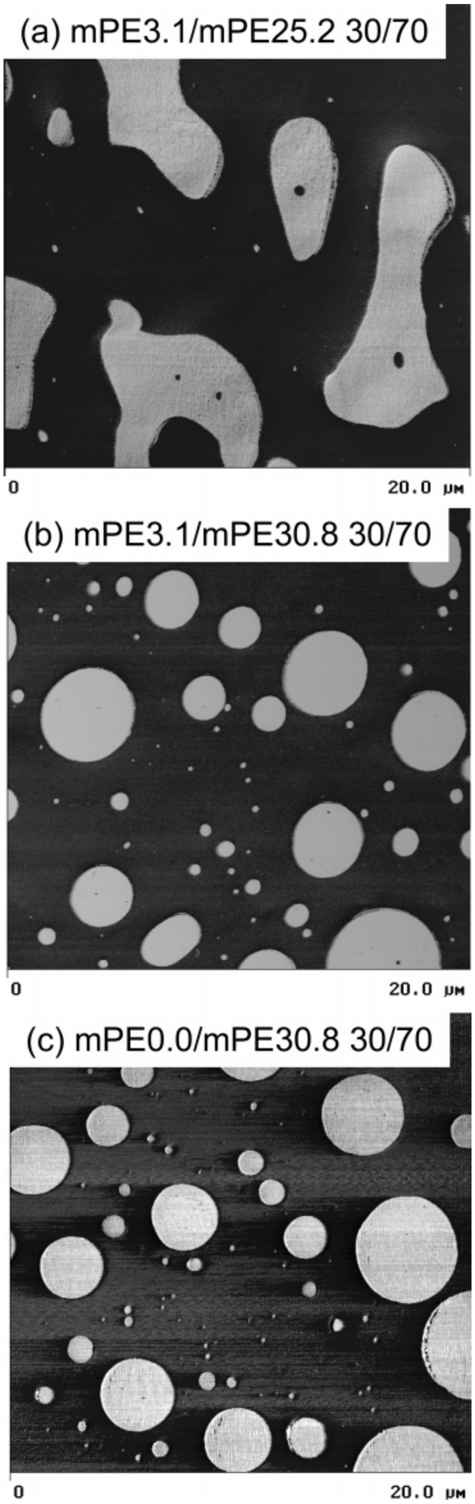

Figure 6. AFM phase images of immiscible blends quenched from 200 °C: (a) mPE3.1/mPE25.2 30/70, (b) mPE3.1/mPE30.8 30/70, and (c) mPE0.0/mPE30.8 30/70.

where n is moles of chains and ϕ is volume fraction in the blend of the monodisperse fractions identified by the subscripts i and j for constituents 1 and 2, respectively. The relative chain length r is defined as the number of basic units in a chain, and the volume fractions of such chains in the blend are $\phi_{1i} = n_{1i}r_{1i}/r_{\text{total}}$ and $\phi_{2j} = n_{2j}r_{2j}/r_{\text{total}}$, where $r_{\text{total}} = \sum n_{1i}r_{1i} + \sum n_{2j}r_{2j}$. Using the average monomer of constituent 1 as the basic unit, $r_{1i} = N_{1i}$ and $r_{2j} = N_{2j}(v_2/v_1)$, where N is the degree of polymerization and v_1 and v_2 are the average monomer volumes of constituents 1 and 2, respectively.

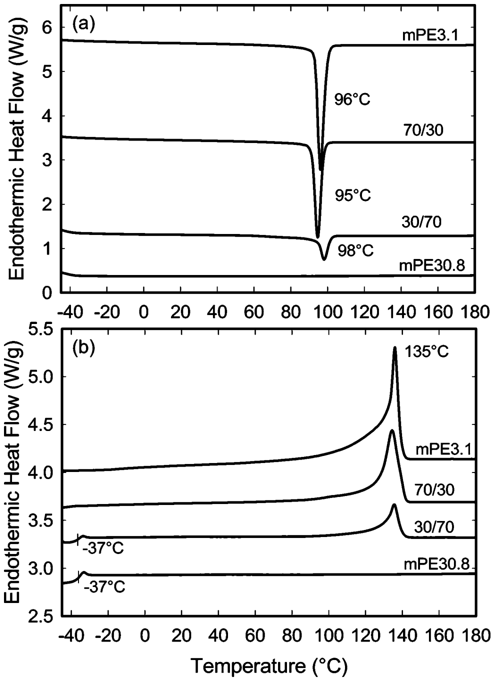

Figure 7. DSC thermograms of mPE3.1/mPE30.8 immiscible blends: (a) cooling curves and (b) subsequent heating curves.

At equilibrium, the chemical potential of each fraction is the same in both phases. Thus, the calculation of equilibrium concentrations involves the solution for a system of equations. However, the number of equations can be reduced dramatically by introducing two separation factors,[30] σ_1 and σ_2, where the partitioning of each constituent between the two phases (indicated by ′ and ″) obeys the relation

$$\sigma_1 = r_{1i}^{-1}(\ln \phi''_{1i} - \ln \phi'_{1i}) \qquad (7a)$$

and

$$\sigma_2 = r_{2j}^{-1}(\ln \phi''_{2j} - \ln \phi'_{2j}) \qquad (7b)$$

for all i and j. Therefore, the system of equilibrium equations is reduced to two equations

$$\sigma_1(\phi'_1 + \phi''_1) + \sigma_2(\phi'_2 + \phi''_2) - 2\left[\left(\frac{\phi''_1}{r''_{n1}} + \frac{\phi''_2}{r''_{n2}}\right) - \left(\frac{\phi'_1}{r'_{n1}} + \frac{\phi'_2}{r'_{n2}}\right)\right] = 0 \qquad (8)$$

and

$$\sigma_2 - \sigma_1 = 2\chi(\phi''_1 - \phi'_1) \qquad (9)$$

where r'_{n1}, r''_{n1}, r'_{n2}, and r''_{n2} are the number-average chain lengths of each constituent in each phase

$$r'_{n1} = \phi'_1\left(\sum_i \frac{\phi'_{1i}}{r_{1i}}\right)^{-1}, \text{ etc.} \qquad (10)$$

Equation 8 is a cloud point function that is independent of temperature, i.e., independent of χ, whereas eq 9 is a difference function that expresses the effect of interactions between the two polymers in terms of χ. Additional mass balance equations are used to compute the phase compositions and χ. Volume additivity upon demixing gives

$$\phi'_{1i} + R_v\phi''_{1i} = (R_v + 1)\phi_{1i} = (R_v + 1)\phi_1 W_{1i} \qquad (11a)$$

and

$$\phi'_{2j} + R_v\phi''_{2j} = (R_v + 1)\phi_{2j} = (R_v + 1)\phi_2 W_{2j} \qquad (11b)$$

where $R_v = V''/V'$ is the volume ratio of the two phases, ϕ_1 and ϕ_2 are the volume fractions of constituents 1 and 2 in the blend, and W_{1i} and W_{2j} are the weights of fractions i and j in constituents 1 and 2, respectively. Combining eq 11 with eq 7, the definition of the separation factor, gives

$$\phi'_1 = \sum_i \phi'_{1i} = (R_v + 1)\phi_1 \sum_i \frac{W_{1i}}{1 + R_v \exp(\sigma_1 r_{1i})} \qquad (12a)$$

and

$$\phi'_2 = \sum_j \phi'_{2j} = (R_v + 1)\phi_2 \sum_j \frac{W_{2j}}{1 + R_v \exp(\sigma_2 r_{2j})} \qquad (12b)$$

Table 3. Phase Volume Percent from AFM Analysis

		70/30			60/40			40/60			30/70		
blend constit[a]	T (°C)	constit 1-rich (vol %)	constit 2-rich (vol %)	error (±)	constit 1-rich (vol %)	constit 2-rich (vol %)	error (±)	constit 1-rich (vol %)	constit 2-rich (vol %)	error (±)	constit 1-rich (vol %)	constit 2-rich (vol %)	error (±)
mPE0.0/	160	80	20	1	67	33	0	38	62	0	17	83	1
mPE18.8	180	82	18	1	69	31	1	37	63	0	16	84	1
	200	83	17	0	70	30	1	35	65	1	13	87	2
	220	85	15	2	73	27	2	34	66	1	11	89	1
	240	88	12	1	78	22	1	31	69	1	9	91	1
mPE11.0/	160	79	21	2	64	36	2	25	75	0	19	81	1
mPE30.8	180	83	17	1	68	32	1	22	78	2	17	83	2
	200	85	15	1	71	29	1	18	82	1	14	86	1
	220	88	12	1	78	22	2	16	84	1	12	88	1
	240	90	10	1	86	14	0	12	88	1	9	91	0
mPE4.9/	160	76	24	0	61	39	0	33	67	1	22	78	1
mPE25.2	180	83	17	1	62	38	1	30	70	1	20	80	1
	200	86	14	1	65	35	0	28	72	1	19	81	0
	220	88	12	2	66	34	1	24	76	1	17	83	1
	240	90	10	2	68	32	2	21	79	2	16	84	2

[a] Constituent.

Table 4. Constituent 1 Phase Compositions and χ Interaction Parameters from Polydisperse Analysis

		70/30			60/40			40/60			30/70			
blend constit[a]	T (°C)	constit 1-rich (ϕ_1')	constit 1-poor (ϕ_1'')	χ (10^{-4})	constit 1-rich (ϕ_1')	constit 1-poor (ϕ_1'')	χ (10^{-4})	constit 1-rich (ϕ_1')	constit 1-poor (ϕ_1'')	χ (10^{-4})	constit 1-rich (ϕ_1')	constit 1-poor (ϕ_1'')	χ (10^{-4})	av χ (10^{-4})
mPE0.0/ mPE18.8	160	0.81	0.22	5.1	0.77	0.22	5.0	0.74	0.17	5.0	0.66	0.21	4.2	4.8 ± 0.5
	180	0.79	0.24	4.7	0.74	0.25	4.6	0.72	0.18	4.9	0.65	0.22	4.1	4.6 ± 0.3
	200	0.78	0.25	4.6	0.73	0.26	4.4	0.70	0.22	4.5	0.62	0.24	3.9	4.4 ± 0.3
	220	0.76	0.27	4.4	0.70	0.29	4.1	0.67	0.24	4.3	0.61	0.25	3.8	4.2 ± 0.3
	240	0.74	0.29	4.1	0.66	0.33	3.8	0.62	0.28	3.9	0.60	0.26	3.7	3.9 ± 0.2
mPE11.0/ mPE30.8	160	0.78	0.42	5.6	0.69	0.35	5.0	0.75	0.27	5.9	0.83	0.16	7.5	6.0 ± 1.1
	180	0.75	0.45	5.2	0.65	0.39	4.8	0.72	0.30	5.5	0.81	0.18	6.9	5.6 ± 0.9
	200	0.74	0.47	5.1	0.64	0.41	4.7	0.70	0.32	5.2	0.78	0.21	6.2	5.3 ± 0.6
	220	0.73	0.49	5.0	0.62	0.42	4.6	0.68	0.33	5.1	0.76	0.23	5.8	5.1 ± 0.5
	240	0.72	0.53	4.9	0.59	0.43	4.5	0.66	0.35	4.9	0.73	0.25	5.5	4.9 ± 0.4
mPE4.9/ mPE25.2	160	0.83	0.26	5.7	0.81	0.24	5.9	0.83	0.17	6.6	0.85	0.13	7.3	6.4 ± 0.7
	180	0.76	0.35	4.7	0.75	0.32	5.0	0.77	0.23	5.6	0.83	0.15	6.8	5.5 ± 0.9
	200	0.74	0.38	4.5	0.71	0.36	4.6	0.75	0.25	5.2	0.81	0.16	6.3	5.2 ± 0.8
	220	0.73	0.39	4.3	0.70	0.37	4.5	0.70	0.29	4.8	0.78	0.19	5.7	4.8 ± 0.6
	240	0.71	0.41	4.2	0.68	0.40	4.3	0.68	0.31	4.6	0.77	0.20	5.5	4.7 ± 0.6

[a] Constituent.

Finally, combining eq 12 with the mass balance expression $\phi_1 + \phi_2 = \phi'_1 + \phi'_2 = 1$ gives

$$\phi_1 \sum_i \frac{W_{1i}}{1 + R_v \exp(\sigma_1 r_{1i})} + \phi_2 \sum_j \frac{W_{2j}}{1 + R_v \exp(\sigma_2 r_{2j})} - \frac{1}{1 + R_v} = 0 \quad (13)$$

Equations 8 and 13 are solved simultaneously to obtain σ_1 and σ_2. A unique solution is obtained in the case of polydisperse constituents because phase composition and phase ratios depend on blend composition. However, if the constituents are monodisperse, phase composition is independent of blend composition, and eqs 8 and 13 are degenerate.

The quantities W_{1i} and W_{2j} were taken from the molecular weight distributions in Figure 1. There were 150 molecular weight fractions provided for each constituent. They were reduced to 15 fractions of equal log M intervals to decrease the calculation time. Although phase compositions and number-average chain lengths were not known, they could be written as functions of σ_1 and σ_2. The Mathematica software was used to solve eqs 8 and 13. Subsequently, eqs 9 and 12 were used to calculate χ and the fraction of constituent 1 in the constituent 1-rich phase ϕ'_1 and constituent 1-poor phase ϕ''_1.

Phase Composition and Interaction Parameter. Phase compositions ϕ'_1 and ϕ''_1 and values of χ from the polydisperse analysis are collected in Table 4. With increasing temperature, the major phase gradually became richer in the minor constituent as it approached the blend composition. The phase composition also depended on the blend composition. As a general trend, blend composition had the most effect on the phase that was rich in the higher molecular weight constituent. For example, the composition of the higher molecular weight mPE0.0-rich phase at 160 °C decreased from 0.81 to 0.66 as the blend composition changed from 0.70 to 0.30, whereas the composition of the lower molecular weight mPE18.8-rich phase remained almost constant at about 0.78. The same compositional trend was observed for the higher molecular weight mPE30.8-rich phase in mPE11.0/mPE30.8 blends and the higher molecular weight mPE25.2-rich phase in mPE4.9/mPE25.2 blends.

The same example of mPE0.0/mPE18.8 revealed that the lower molecular weight constituent was more soluble in the higher molecular weight constituent than vice versa. When higher molecular weight mPE0.0 was the minor phase, the mPE0.0-rich phase contained 0.34 of mPE18.8; however, when lower molecular weight mPE18.8 was the minor phase, the mPE18.8-rich phase contained only 0.22 of the higher molecular weight mPE0.0. This reflected the higher solubility of the low molecular weight fractions of mPE18.8 in mPE0.0. On the other hand, the difference in molecular weight was not large enough to have much effect on the major phase composition, which was 0.81 and 0.79 in these two examples. The same trend was

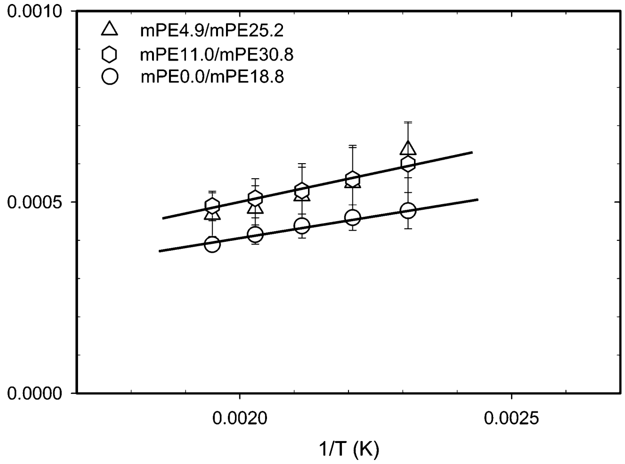

Figure 8. Temperature dependence of the interaction parameter χ.

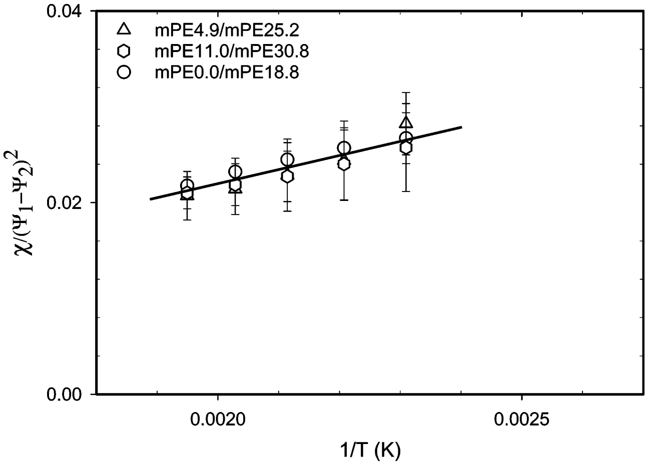

Figure 9. Temperature dependence of the reduced interaction parameter $\chi_{P/E}$.

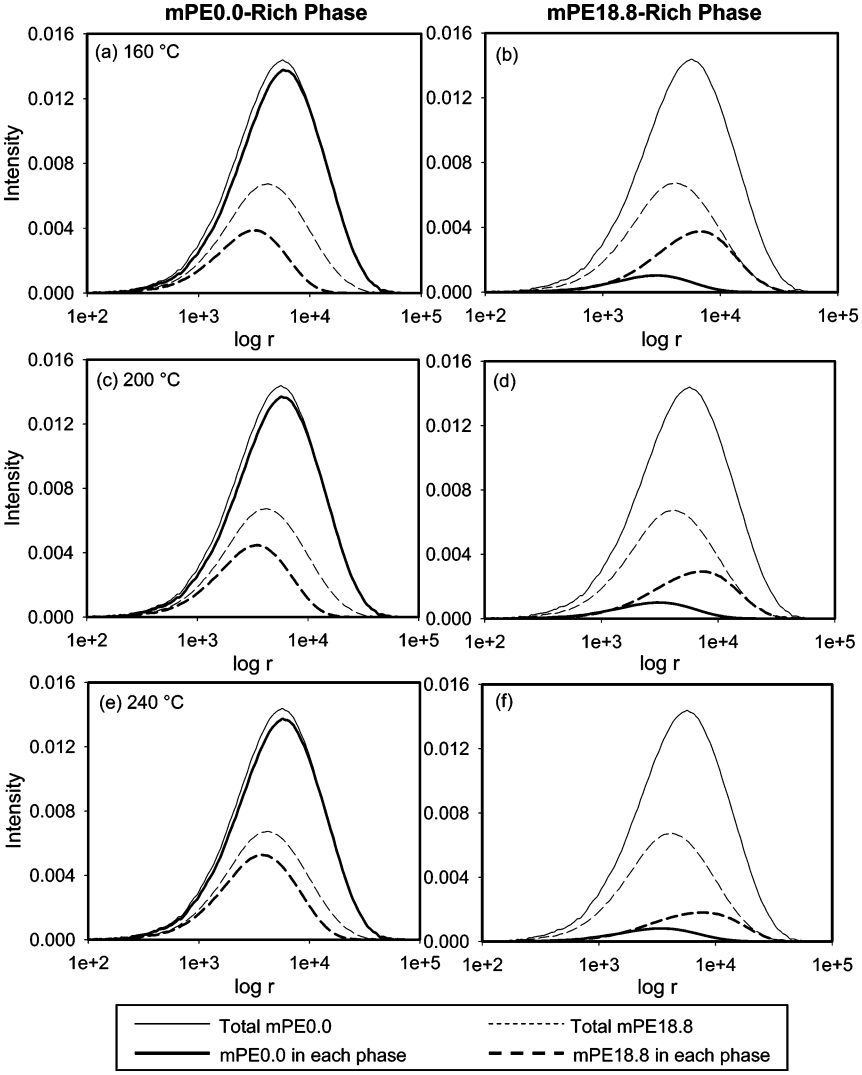

Figure 10. Effect of temperature on the calculated molecular weight distributions in both phases of the mPE0.0/mPE18.8 70/30 blend: (a, b) at 160 °C, (c, d) at 200 °C, and (e, f) at 240 °C.

found in the minor phase composition of the mPE4.9/mPE25.2 blend. In this case, the lower molecular weight mPE4.9 was more soluble in the higher molecular weight mPE25.2 than vice versa, which suggests that this is a general trend and not specific to the mPE0.0/mPE18.8 pair.

The results in Table 4 showed χ to be independent of the blend composition. Although the values of χ scattered, they did not exhibit a systematic change with blend composition. As expected, χ decreased with increasing temperature, indicating a UCST. The temperature dependence of χ usually follows the relationship[6]

$$\chi = a + \frac{b}{T} \tag{14}$$

The parameter a describes the temperature-independent portion and is identified as the entropic contribution to χ whereas the parameter b reflects the temperature dependency and is identified as the enthalpic contribution to χ.[31] Results for P/E blends defined linear relationships in accordance with eq 14 (Figure 8). Linear regression gave $a = -0.00025$ and $b = 0.39$ for mPE4.9/mPE25.2 and mPE11.0/mPE30.8 and $a = -0.00008$ and $b = 0.24$ for mPE0.0/mPE18.8.

The copolymer equation as expressed in eq 3 was tested for P/E blends by plotting the temperature dependence of the reduced interaction parameter as $\chi(\psi_1 - \psi_2)^{-2}$ vs T^{-1}, as seen in Figure 9. The data almost collapsed to a single curve and exhibited a common temperature dependence. A linear relationship satisfactorily accommodated all the data from the polydisperse analysis. The linear regression gave

$$\chi_{\mathrm{P/E}} = -0.0045 + \frac{13.32}{T} \tag{15}$$

The parameters in eq 15 are considerably lower than those for ES copolymer blends (−0.076 and 71 (K))[1] and for blends of linear polyethylene with atactic polybutene (−0.101 and 81 (K)).[32] Equation 15 gives $\chi_{\mathrm{P/E}}$ of 0.0237 at 200 °C, and eq 5 gives $\delta_{\mathrm{PP}} - \delta_{\mathrm{PE}}$ of 1.45, in excellent agreement with values of 0.0238 and 1.46 extracted from the literature.[18]

Molecular Weight Distribution. In blends of polydisperse polymers, lower molecular weight fractions of one constituent are always more miscible with the other constituent than the higher molecular weight fractions. For polydisperse constituents exhibiting partial miscibility, both equilibrium phases consist of higher molecular weight fractions of the major constituent and lower molecular weight fractions of the minor constituent. In other words, the molecular weight distribution of a constituent is not the same in both phases and is not the same as the original distribution. Moreover, the molecular weight distribution in each

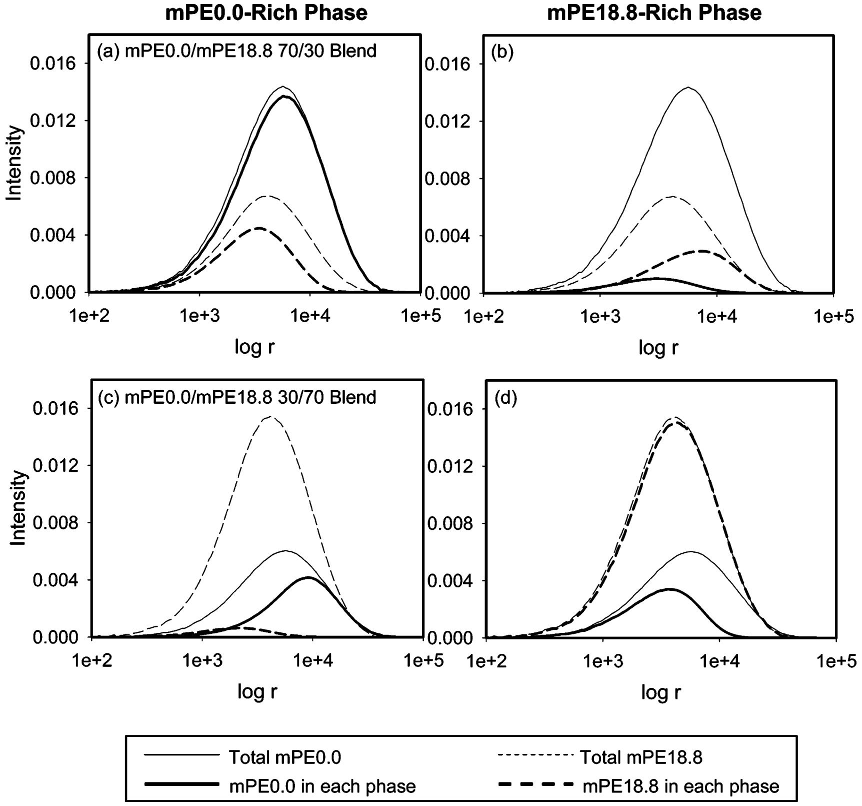

Figure 11. Effect of blend composition on the calculated molecular weight distributions in both phases of mPE0.0/mPE18.8 blends at 200 °C: (a, b) 70/30 blend and (c, d) 30/70 blend.

phase should change with blend composition. As a consequence, phase composition depends on blend composition.

The consequences of polydispersity are demonstrated by calculating the molecular weight distribution of each constituent in each phase. The phase compositions ϕ'_{1i} and ϕ''_{1i} for a given fraction with r_{1i}, and likewise ϕ'_{2j} and ϕ''_{2j} for r_{2j}, were calculated from eqs 7 and 11. The calculation was performed for each of the 150 molecular weight fractions provided. As an example, Figure 10 shows the effect of increasing temperature on the molecular weight distributions of mPE0.0 and mPE18.8 in both phases of a 70/30 (v/v) blend. The original distribution of each constituent is normalized to the blend composition and is presented as the thin lines. The constituent distribution in each phase is normalized to both the amount of the phase and the phase composition and is presented as the thick lines. As is evident from the figure, the constituent distribution in each phase is not the same as the original distribution. Both phases contain lower molecular weight fractions of the minor constituent. With increasing temperature, both phases become richer in the minor constituent as higher molecular weight fractions dissolve, and the amount of the minor mPE18.8-rich phase decreases.

Comparison of the molecular weight distribution of mPE18.8 in the constituent-poor and constituent-rich phases demonstrates the preferential dissolution of lower molecular weight mPE18.8 fractions in the mPE0.0-rich phase. With an increase in temperature from 160 to 240 °C, the distribution of mPE18.8 in the mPE0.0-rich phase broadens to include higher molecular weight fractions as is evident by comparing the mPE18.8 distribution in Figure 10a,c,e. Only the highest molecular weight fractions of mPE18.8 remain in the mPE18.8-rich phase (Figure 10b,d,f).

The minor constituent of the blend most readily demonstrates molecular weight fractionation because it is more or less equally distributed between the two phases. To illustrate this point, constituent molecular weight distributions in the 70/30 and 30/70 blends of mPE0.0/mPE18.8 at 200 °C are compared in Figure 11. Fractionation of mPE18.8 in the 70/30 blend is seen by comparing the thick dashed curves in Figure 11a,b. When mPE0.0 is the minor constituent, as in the 30/70 blend, preferential solution of the lower molecular weight fractions of mPE0.0 in mPE18.8 is immediately apparent by comparing the thick solid curves in Figure 11c,d.

Summary

This study extended the use of homogeneous copolymers prepared with single-site catalysts as models to probe miscibility of real polyolefins. Methodology developed previously with ethylene copolymers was the basis for studying miscibility of isotactic polypropylene and copolymers of propylene with ethylene. Although chemical similarity of the constituents impeded conventional methods for imaging domain morphology of polyolefin blends, the modulus difference between the phases was large enough that the domain morphology could be probed readily using AFM. Copolymers of molecular weight about 200 kg mol^{-1} were miscible if the difference in ethylene content was less than about 18 mol % and immiscible if the ethylene content difference was greater than about 20 mol %. This result confirmed the prediction based on solubility parameters. Blends with constituent composition difference in the range of 18−20 mol % exhibited partial miscibility in the melt as indicated by a phase volume fraction that was different from the blend volume fraction. Further investigation of the partially miscible blends revealed the effects of temperature and molecular weight distribution. The temperature dependence of blend morphology confirmed the UCST behavior of P/E copolymer blends. The phase composition and the χ interaction parameter were extracted by using an approach that considered the molecular weight distribution. The compositional dependence of χ conformed to the copolymer equation and depended on comonomer content difference only, not on comonomer content per se. In this aspect, polypropylene blends with a P/E copolymer differed from polyethylene blends with an ethylene copolymer. In the latter case, the quantity $\chi(\Delta\psi)^{-2}$ increased with $\Delta\psi$. Although the polymers had relatively narrow molecular weight distribution with M_w/M_n of about 2, molecular weight fractionation was readily demonstrated with partially miscible blends. Thus, the phase composition depended on blend composition, and the equilibrium phases consisted of higher molecular weight fractions of the major constituent and lower molecular weight fractions of the minor constituent.

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