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Polymer 48 (2007) 5753–5766

polymer

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Experimental verification on UCST phase diagrams and miscibility in binary blends of isotactic, syndiotactic, and atactic polypropylenes

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Received 19 April 2007; received in revised form 10 July 2007; accepted 10 July 2007
Available online 15 July 2007

Abstract

Issues in blends of polymers of the same chemical repeat unit but with different tacticities were addressed by investigating on the phase behavior and interaction strength of binary blends of three polypropylenes of different tacticities, i.e., isotactic polypropylene (iPP), syndiotactic polypropylene (sPP), and atactic polypropylene (aPP) using polarized optical microscopy (POM) and differential scanning calorimetry (DSC). Although blends of polypropylenes have been widely studied in the past, there are still on-going debates on true phase behavior (miscibility vs. upper critical solution temperature (UCST) or immiscibility). Except for several earlier theoretical predictions based on the Flory–Huggins mean field theories, UCST behavior had not been experimentally proven for blends of sPP/iPP or aPP/sPP, owing to interference from PP crystallinity. In addition, interaction strength of the blends of different tactic polypropylenes is yet to be established. Using the method of equilibrium melting points, the Flory–Huggins interaction parameter of the aPP/iPP blend was shown to possess a significantly negative value ($\chi_{12} = -0.21$), which proves that the blend is indeed miscible in the melted amorphous as well as semicrystalline states as previously reported in the literature. However, the interaction parameters for the sPP/iPP and aPP/sPP blends were found to be nearly zero ($\chi_{12} = -0.02$ and -0.0071, respectively, at $T = 150-180$ °C), indicating that the interactions in two blends are weak and that the corresponding phase behavior for them borders on immiscibility at ambient temperature. This study also utilized novel approaches in constructing UCST phase diagrams by separating the amorphous phase domains from the crystalline spherulites, yielding data plausible for experimentally determining the UCST in iPP/sPP blend vs. aPP/sPP blend.

Keywords: Syndiotactic polypropylene (sPP); Isotactic polypropylene (iPP); Atactic polypropylene (aPP)

1. Introduction

Although blends of polypropylene (PP) of different tacticities have been intensively studied in the past, several issues are not yet totally settled and some interpretations offered by different investigators contradict. Blends of stereo-isomers have been of interest, and phase behavior in blends of polymers differing in configurations has attracted a lot of studies. Blends of two isomeric and amorphous polymers usually yield straightforward results in phase behavior. Blends of two amorphous isomeric polymers, such as poly(vinyl acetate) (PVAc) and poly(methyl acrylate) (PMA) have been widely reported with conclusive results. The PVAc/PMA blend system is miscible with a stable homogeneous phase [1,2], where PVAc differs from but is a structural isomer to poly(methyl acrylate) (PMA). Another example comprising structural isomeric polymers can be given by miscible blend of poly-(α-methyl styrene) (PαMS) with poly(4-methyl styrene) (P4MS) exhibiting a lower critical solution temperature (LCST) behavior [3].

On the other hand, semicrystalline polymers with different tacticities (i.e., stereo-isomers) are not all miscible, which is a peculiar phenomenon considering that tactic polymers

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doi:10.1016/j.polymer.2007.07.015

possess identical chemical units differing merely in configurations. It has been an intellectually interesting quest that intrigues many investigators probing for answers. A debate is on-going: will two semicrystalline polymers of different tacticities (in crystalline state) be miscible in the amorphous state? Further compounded the problem is that it is usually difficult to assess precisely the phase behavior or miscibility in mixtures of polymers differing only in tacticity but with closely-spaced, or almost the same, glass transition temperatures. Phase behavior in melt-state binary blends of tactic polypropylenes (iPP, sPP, and aPP) has long been a difficult subject because the constituents all possess same chemical units with same physical properties other than different crystals at solid state. Note that the blend of two isomers, such as PVAc/PMA, differs from the blend system of two tactic polymers, such as iPP and sPP, in that the former is polar and amorphous but the latter is non-polar and semicrystalline. Earlier, Thomann et al. have claimed that blends of iPP/sPP are immiscible [4,5]. In addition, Maier et al. [6] have concluded that polypropylenes (PPs) of different tacticities (a, i, or s) are not all miscible with each other. They have concluded that aPP/iPP blend system is miscible, but aPP/sPP system is incompatible with separate phases. Silvestri and Sgarzi [7] have concluded that aPP is partially miscible with sPP but immiscible with iPP, which contradicts with that found by Maier et al. and Thomann et al. Later, Philips [8] also conducted a study on morphology of tactic polypropylene mixtures, and reported that the iPP/aPP blend has upper critical solution temperature (UCST) below 155 °C and is miscible at melt state, while iPP/sPP mixtures exhibit a phase-separated texture at crystallization temperatures. This result of Philips agrees with that of Maier et al., but directly opposes that of Silvestri and Sgarzi. These findings illustrate unsettled issues on blends of PP. Phase behavior in the iPP/sPP blends may be difficult to deal with owing to extremely fast crystallization of both constituent polymers (iPP and sPP). Interpretation of miscibility or phase behavior at melt state of the tactic PP mixtures based on morphology information of the annealed crystals at crystallization temperature may be misleading, and conflicting views have been generated [4–6,9,10].

By comparison, blends of polystyrenes of three different tacticities (aPS, iPS, and sPS) and phase or miscibility issues have also been widely studied. By contrast, iPS/sPS blends, with much lower crystallization rates and higher T_gs than those of PP blends, can be quenched to a fully amorphous state, and preserved at ambient for convenient characterization of phase behavior of the blends at amorphous state. Yeh et al. [11] proposed miscibility in the aPS/iPS blend system based on results of a crystallization kinetic study; they, however, did not provide more direct evidence other than an analysis of the crystallization kinetics of the blend. Syndiotactic polystyrene (sPS) [12] and its blends have been an intensive focus of various studies. Ermer et al. [13] have tentatively proposed that sPS and aPS might be at least partially miscible based on the results of solvent diffusion behavior in the blends. A study in this laboratory has followed up some points and positively proven miscibility in the aPS/sPS blend by utilizing examination of the interaction parameter from measurements of the equilibrium melting point from the thermodynamics point of view [14]. Interactions between isomeric polymers, even being miscible, are expectedly low. Earlier, Runt [15] investigated a classically known miscible blend system of aPS/iPS (M_w ca. 50,000 g/mol for both) and found that the polymer–polymer interaction parameter (χ) for the aPS/iPS pair is about −0.003, which essentially is zero. An earlier study has shown that the interaction parameter in the aPS/sPS system [14] is similarly a small negative, but slightly higher value ($\chi = \sim -0.1$) than that for the aPS/iPS system studied by Runt [15]. Phase behavior of blends of different tactic polymers is influenced by structural parameters such as tacticity, chain polarity, size of pendant groups, etc. It is of interest to compare the phase behavior and miscibility in various blend systems of polymers differing only in types of tacticities. For the case of polystyrenes with a relatively bulky pendant group, miscibility in blends of tactic polymers has been proven to be independent of tacticity. On the other hand, for polypropylenes with a less bulky pendant group (i.e., lower T_g and faster crystallizing), less polarity, and higher crystallinity (than polystyrenes), the miscibility and phase homogeneity in binary PP blends are influenced by tacticity in PP. In general, there seems no rule for predicting the phase behavior in blends composed of polymers of same chemical structures differing only in tacticity.

This study aimed at furnishing positive evidence proving UCST, partial miscibility, or miscibility phase behavior in respective iPP/sPP, aPP/sPP, or aPP/iPP blends. Interaction strength was compared and ranked among the three blends at elevated temperatures. Crystallinity hindered phase-separated domains; thus, phase diagrams were constructed for partially miscible and/or UCST blend systems via microscopy techniques excluding the crystallinity domains in blends.

2. Experimental

2.1. Materials and blend preparation

Polypropylenes of three different tacticities were used. Atactic polypropylene (aPP) was obtained from Scientific Polymer Products, Inc. (USA), with T_g: −27.2 °C (measured with DSC), M_w: 12,000 g/mol, density: 0.85 g/cc. Isotactic polypropylene (iPP), Scientific Polymer Products, Inc. (USA), with T_g: −26 °C (measured with DSC), T_m: 160 °C (measured with DSC), density: 0.9 g/cc. Syndiotactic polypropylene (sPP), Aldrich Chemical Company, Inc. (USA), with T_g: −4.3 °C, T_m: 126 °C, M_w: 127,000, M_n: 54,000 g/mol, density: 0.9 g/cc.

To avoid effects from solvents on phase results, melt mixing at ca. ~200 °C was used for preparing binary blend samples composed of any two of aPP, sPP, or iPP in this study. The constituent polymers of intended compositions were, respectively, ground into fine powder, dried, and pre-mixed. The mixed polymers were then placed into the miniature chamber (a small cylindrical cavity: ca. 2-g capacity) inside a laboratory-designed aluminum mold preheated to ~200 °C. Temperature control was provided by placing the mold-chamber assembly on a hot plate with controlled heating (set at

200 °C). Blending of the polymers (small quantities, ca. 1 g) could be easily accomplished in a short time (5–10 min) by manually hand-stirring the mixtures within the chamber. The viscosity of the blend samples decreased as the temperature increased, and liquid mixtures of a small quantity were easily blended well for 5–10 min. During melt blending, a continuous purge of dry nitrogen was maintained to provide an inert-gas blanket on the mixing chamber in order to minimize possible thermal degradation/oxidation at high temperatures. Blend samples so prepared were examined to be homogeneous and no discernible thermal degradation.

2.2. Apparatus and procedures

A polarized optical microscope (Nikon Optiphot-2, POM) with a digital camera, charge-coupled device (CCD), was used for characterizing optical homogeneity and/or crystalline morphology of the blends. Non-polarized light optical microscopy (OM) was also used for better discerning phase-separation domains in presence of crystalline regions. A small quantity of the melt-blend samples was transferred to micro-glass slides, heated and pressed into thin film on a heating stage, and examined using the optical microscope.

Additionally, for greater magnification (up to 6000×), phase morphology (fracture surface) of blends in quenched amorphous state was examined by scanning electron microscopy (SEM). Blend samples were examined using a scanning electron microscope (HITACHI S-4100) for confirming homogeneity or revealing sub-micrometer phase domains. Quenched samples (amorphous glassy solids) were used for SEM characterization because crystals, if present, might obscure observation of phase morphology of blends. The quenched film samples were fractured across thickness and coated with gold by vapor deposition using vacuum sputtering.

T_g or T_m transitions of the blend samples were measured with a differential scanning calorimeter (DSC-7, Perkin–Elmer) equipped with an intra-cooler. Prior to DSC runs, the temperature and heat of transition of the instrument were calibrated with indium and zinc standards. During thermal annealing or scanning, a continuous nitrogen flow in the DSC sample cell was maintained to ensure minimal sample degradation. For determining the T_g temperatures, a heating rate of 20 °C/min (or 40 °C/min) was used unless otherwise specified; but for measurements of the melting points, a heating rate of 10 °C/min was used instead.

3. Results and discussion

The binary blend pairs, sPP/iPP, aPP/sPP, or aPP/iPP (rapidly quenched into amorphous state) of several compositions, were first examined using optical microscope and scanning electron microscope. Optical microscopy (OM) results revealed that the blends, when kept above the melt temperatures, appeared visually transparent, homogeneous, and free of any heterogeneity or domains (at ca. 800×). All three blend pairs, (1) aPP/iPP, (2) aPP/sPP, and (3) sPP/iPP blends of at least three compositions (10/90, 50/50, and 90/10) were carefully examined using OM to reveal that at above melt (180–300 °C), no discernible phase domains were seen. For brevity, the results of numerous OM graphs are not shown here. However, below melting of the crystals, any phase domains, if present, were difficult to be identified owing to crystallinity of sPP or iPP. Special techniques had to be used to separate the crystalline phase from amorphous domains.

A small glass transition difference from almost zero to only ∼20 °C between polypropylenes of different types of tacticity may make it inconclusive regarding criteria of single T_g. The T_g of sPP differs from that of iPP or aPP by about 20 °C; but T_g of iPP is almost identical with that of aPP. All blend samples for T_g characterization were initially heated to 200 °C for melting the crystals and then quenched from the melt state before DSC scanning. Owing to rapid crystallization, quenching might have brought the blend samples to various residual crystalline states. DSC traces show a single T_g in blends, although the closely-spaced T_gs of these two neat polymers might make it uncertain as evidence of phase homogeneity.

3.1. aPP/iPP blend system

Thermal evidence based on melting temperature of neat polymers and blends in mixture states is known to yield useful information for estimation of interaction strength between polymers. When crystallized at certain T_c, the lamellar crystals in iPP or sPP, however, are known to show complex multiple melting peaks, which make it tricky and uncertain in attempting for extrapolation for equilibrium melting temperature. Thus, in this study, careful thermal schemes were designed to ensure that data of extrapolation were based on a more resolved single melting peak (at 10 °C/min). Fig. 1 shows the DSC thermograms revealing clearly one single T_m in iPP or sPP when crystallized at or above 120 or 100 °C, respectively. At increasingly higher T_c, crystallization would be much slower, but invariably, the crystallized iPP or sPP would exhibit a single melting peak upon scanning. Fig. 2 shows the melting peaks of the aPP/iPP blend system of compositions (w/w ratio): (A) 20/80, (B) 30/70, (C) 35/65, and (D) 40/60, isothermally crystallized at various temperatures. T_c was kept between 120 and 130 °C. Within this selected T_c range, only a single melting peak in the aPP/iPP blends was found when scanned in DSC at 10 °C/min. Note that in this pair, only iPP is crystalline, and aPP remains amorphous and acts as a diluent to the crystalline species. Being of the same chemical unit, the segmental interactions between iPP and aPP may not be particularly specific, or any stronger than those between the pairs of iPP/iPP or aPP/aPP. Nevertheless, the thermal characteristics of melting peaks in neat form or mixtures could be used to assess the interactions between the pair. Table 1 also lists numerical values of measured T_m for each T_c imposed on the aPP/iPP blend samples. These values were used for constructing plots of T_c vs. T_m, as discussed in following sections.

Fig. 3(A and B) shows equilibrium melting temperatures and interaction strength for aPP/iPP blends: (A) equilibrium melting temperatures (of four compositions) by Hoffman–Weeks plots, (B) interaction strength according to the

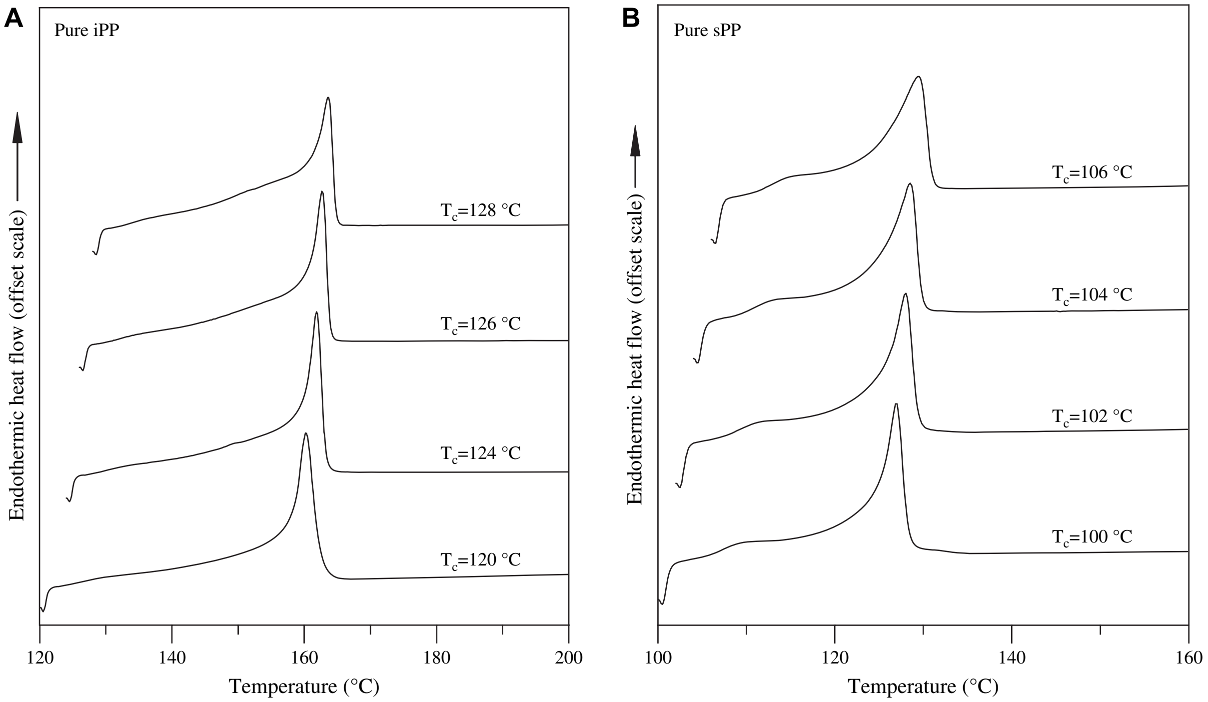


Fig. 1. DSC traces in regimes of single melting peak for: (A) iPP crystallized at T_c equal to or greater than 120 °C; (B) sPP crystallized at T_c equal to or greater than 100 °C.

Flory–Huggins equation Measurement of the equilibrium melting temperature of aPP/iPP blend by using standard extrapolation based on the Hoffman–Weeks plots. Similar extrapolation has also been performed on the aPP/iPP blend by other investigators [4–8]; however, owing to multiple melting peaks in crystallized iPP, quite inconsistent results with significant scattering in data have been reported in the literature [4–8]. In this study, proper range of T_c was selected for minimizing scattering. Only the range of T_c leading to a single melting peak was chosen to ensure consistency in extrapolation. The plots yielded, within experimental accuracy, values of T_m^* for the aPP/iPP blends of all compositions investigated. For convenience, Table 2 lists the values of extrapolated T_m^o or T_m^* for neat iPP and aPP/iPP blends of various compositions investigated.

With the equilibrium melting temperatures determined for the iPP/aPP blends of sufficient composition, interaction strength was further estimated. Fig. 3(B) shows plots according to the Flory–Huggins equation for determining the interaction parameter of aPP/iPP blend. The widely used Flory–Huggins equation is [16]:

$$\frac{1}{T_m}-\frac{1}{T_m^o}=-\frac{RV_2}{\Delta H_f V_1}\chi_{12}\phi_1^2 \qquad (1)$$

or

$$\left(\frac{1}{T_m^*}-\frac{1}{T_m^o}\right)=-\left(\frac{RV_2}{\Delta H_f V_1}\right)\left[\frac{\ln\phi_2}{n_2}+\left(\frac{1}{n_2}-\frac{1}{n_1}\right)\phi_1+\chi\phi_1^2\right] \qquad (2)$$

Eq. (2) is used if entropic effects are to be taken into account. The first two terms in the right-hand-side bracket of Eq. (2) are due to entropic contribution to melting point depression, while the last term is enthalpic contribution to melting point depression. It can be expected that the contributions from the first two terms are small due to relatively large n_1 and n_2. For high-molecular-weight blends, the first two terms (entropic contribution) drop out and Eq. (2) can be approximated to Eq. (1) already discussed earlier. In the equations, notations or subscripts are as noted as following. 1 = aPP (amorphous), 2 = iPP (crystal), $R = 1.987$ (cal/mol K), and V_1/V_2 was assumed to be nearly unity = 1. n_1 and n_2 are degrees of polymerization of these two polymer components, respectively. ΔH_f is the heat of fusion (melting) of the fully crystalline polymer (iPP) per mole repeat unit. The enthalpy of fusion for iPP has been reported to be $\Delta H_f = 2.1 \times 10^3$ cal/mol (or 8.7 kJ/mol) [17]. The plot yielded a slope $= 2.009 \times 10^{-4}$, from which the interaction parameter was calculated to be $\chi = -0.210$ for iPP/aPP blend. This is a quite significant negative value, suggesting that aPP and iPP are likely miscible within the range of the equilibrium melting temperatures (172–190 °C) of the blends. Whether aPP/iPP blend is also miscible much below the T_m may require further clarification; but apparently, the aPP/iPP blend does exhibit significant interaction strength at the temperature of measurement (T_m of iPP). Similar procedures were performed on two other PP blends, as discussed in following sections.

3.2. sPP/iPP and aPP/sPP blend systems

Although both components in the sPP/iPP blends are semicrystalline and crystallizable, the classical Flory–Huggins theory on melting point depression for miscible polymers can

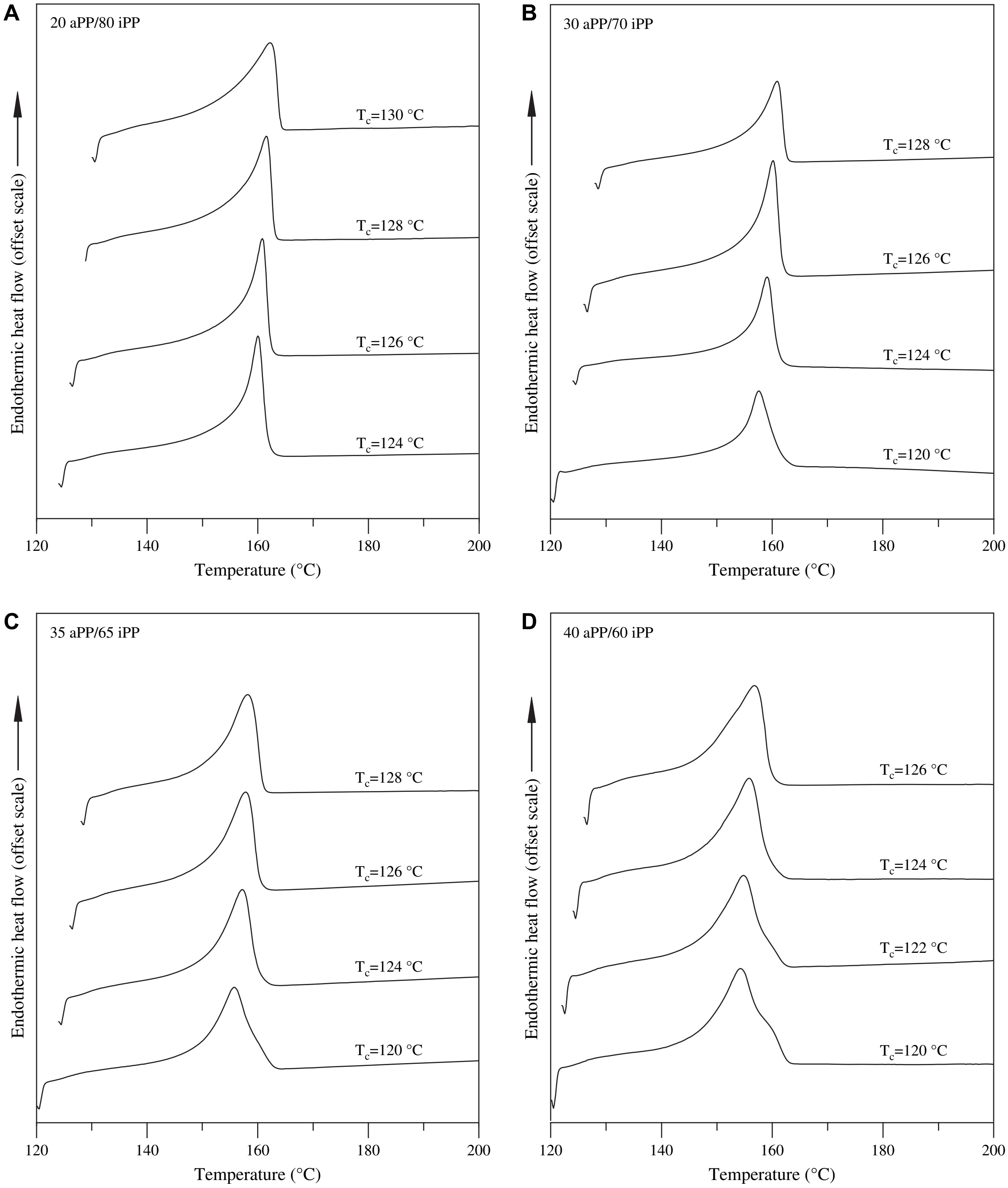


Fig. 2. DSC traces in regimes of single melting peak for aPP/iPP blend system: (A) 20/80, (B) 30/70, (C) 35/65, and (D) 40/60, isothermally crystallized at various temperatures. $T_c = 120–130$ °C.

also be used to estimate the intermolecular interaction strength. This is owing to the fact that at T_c where the iPP constituent would crystallize, the lower-melting sPP constituent remains essentially amorphous liquid in the blend. That is, T_c was chosen for the blends where co-crystallization of both constituents would not exist, and iPP exhibits only a single melting peak for easier extrapolation. Melting point depression was performed on the higher-melting constituent, iPP. Similarly, the second system, sPP/iPP blend, was dealt with the same procedures and analyses, but with properly adjusted thermal schemes to ensure consistence and meaningful comparison. Fig. 4 shows the sPP/iPP blend system of four compositions (w/w ratio): (A) 30/70, (B) 40/60, (C) 45/55, and (D) 50/50, isothermally crystallized at various temperatures (T_c kept between 124 and 128 °C). Note that at the chosen T_c, only one constituent polymer (iPP) is capable of crystallizing. A relative narrow temperature range was chosen for crystallization so that only a single melting peak was

Table 1
T_m (°C) for aPP/iPP blend of various compositions crystallized at different T_cs

T_c (°C)	aPP/iPP (wt/wt)				
	0/100	20/80	30/70	35/65	40/60
120	160.18	– (N.A.)	157.70	155.60	154.35
122	–	–	–	–	154.84
124	161.84	160.00	159.01	157.18	155.85
126	162.67	160.80	160.17	157.87	156.84
128	163.70	161.50	160.90	158.96	–
130	–	162.45	–	–	–

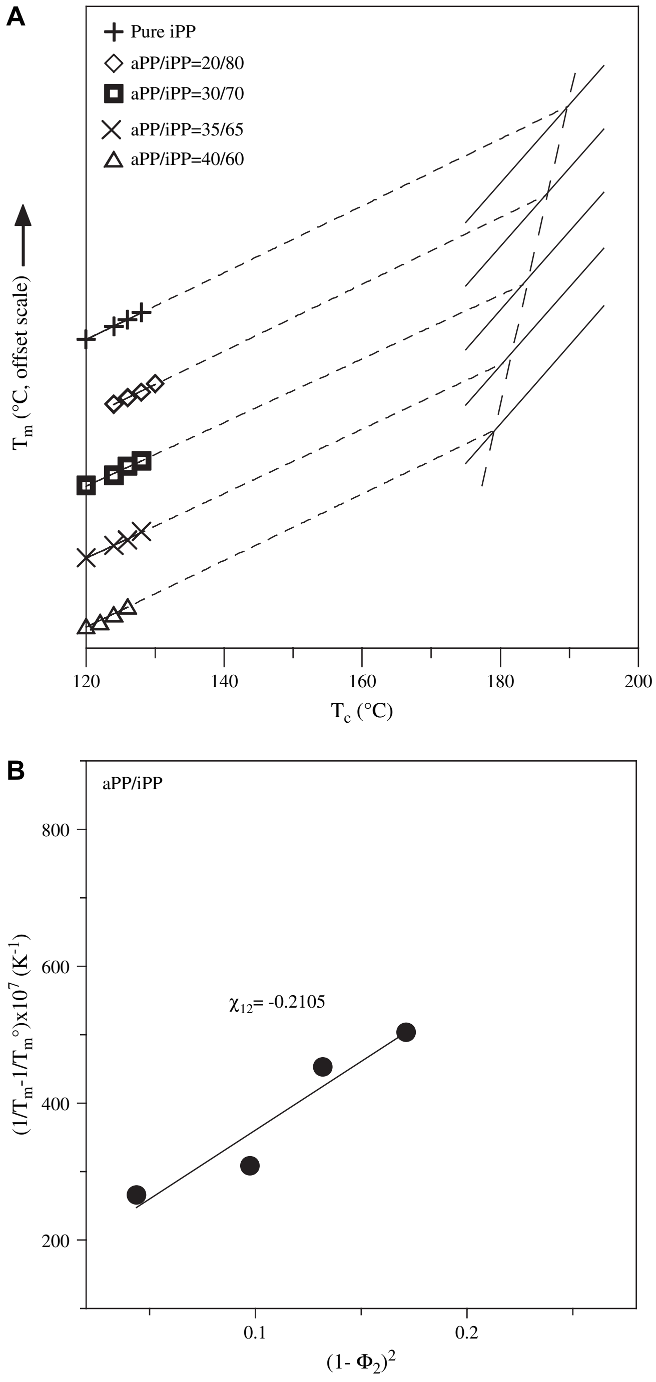


Fig. 3. aPP/iPP blends: (A) equilibrium melting temperatures (of four compositions) by Hoffman–Weeks plots and (B) interaction strength according to the Flory–Huggins equation.

Table 2
Equilibrium T_m^o (°C) for neat iPP, neat sPP and three blend systems ((I) aPP/iPP, (II) sPP/iPP, and (III) aPP/sPP) of various compositions

wt/wt	aPP/iPP	sPP/iPP	aPP/sPP
0/100	189.85	189.85	145.18
20/80	186.52	–	145.17
30/70	183.33	189.79	145.07
35/65	180.34	189.76	–
40/60	179.30	–	144.94
45/55	–	189.55	–
50/50	–	189.10	144.90

detected in the crystallized blends. Table 3 lists the numerical values of measured T_m for each T_c imposed on the sPP/iPP blends. These values were used for constructing plots of T_c vs. T_m, as discussed in the following sections. Fig. 5 shows the aPP/sPP blend system of four compositions (w/w ratio): (A) 20/80, (B) 30/70, (C) 40/60, and (D) 50/50, isothermally crystallized at various temperatures. T_c was kept between 100 and 106 °C to ensure single melting peak in sPP and its blends. Table 4 lists the numerical values of measured T_m for each T_c imposed on the aPP/sPP blends. These values were used for constructing plots of T_c vs. T_m.

Extrapolation of T_m from each T_c led to the equilibrium melting temperature of the aPP/sPP blend system using Hoffman–Weeks plots. Owing to similarity, the plots are shown together for comparison. Fig. 6 shows the extrapolation leading to equilibrium melting temperatures of (A) sPP/iPP blends and (B) aPP/sPP blends by Hoffman–Weeks plots. The procedures are standard and discussion is abbreviated here. However, note that the extrapolation for most blend compositions intersects at roughly the same temperature position, indicating that the equilibrium melting temperatures do not differ much for all compositions investigated. That is, little or negligible depression in the melting points is seen in the blends. Same results are observed for both blend systems. Nature of interactions between PP segments likely has something to do with the configuration (i.e., tacticity) of PP. The interaction between PP is mainly van der Waals force originating from contacts between chain segments. The isotactic configuration (CH_3 arranged on the same side of zigzag C–C plane) in iPP provides the most intimate contact with aPP, in comparison to those between the aPP/sPP or sPP/iPP pairs.

From these analyses, interaction strength in aPP/sPP and sPP/iPP blends could be assessed at near T_m of sPP. Although the interaction strength was not compared at ambient temperature, the difference in the obtained values could be used for interpreting the observed morphology at lower temperatures. Results of final procedures are summarized in a superimposed plot for comparison of trend of variation in the interaction strength for three pairs of blends composed of any two of iPP, sPP, and aPP. Fig. 7 shows superimposed plots for determination of the interaction parameters for iPP/aPP blend in comparison with iPP/sPP and sPP/aPP blends. All lines are linear with little scattering and they more or less go through the origin, indicating little effects from entropic contribution in estimating the parameters. The significant difference among the slopes of the lines indicates that the interaction parameters for aPP/iPP, aPP/sPP and

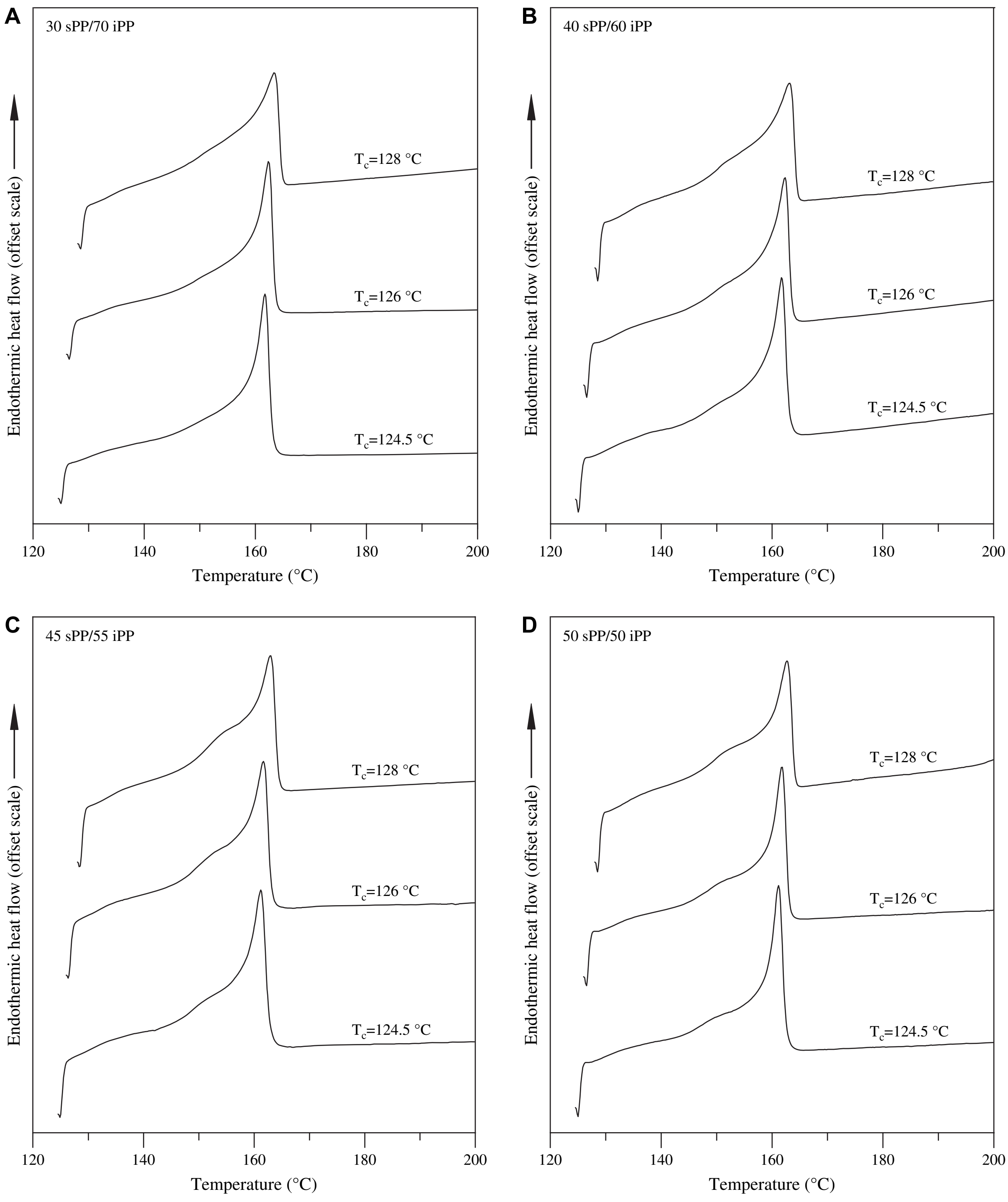


Fig. 4. DSC traces in regimes of single melting peak for sPP/iPP blends of four compositions: (A) 30/70, (B) 40/60, (C) 45/55, and (D) 50/50, isothermally crystallized at $T_c = 124–128$ °C.

sPP/iPP are significantly different. The widely different interaction strengths (at elevated temperatures) would imply significant difference in the phase behavior of these blend systems. Then, from the T_m^* of each blend composition, the interaction parameter (χ) between aPP and sPP was estimated from the Flory–Huggins relationship as discussed earlier [16]. The subscript "1" now indicates the non-crystallizing polymer aPP, at the chosen T_c, and "2" the crystallizing polymer (sPP). ΔH_f is the heat of fusion (melting) of the fully crystalline polymer

Table 3
T_m (°C) of neat iPP and sPP/iPP blend of various compositions crystallized at different T_cs

T_c (°C)	sPP/iPP (wt/wt)				
	0/100	30/70	40/60	45/55	50/50
120	160.18	– (N.A.)	–	–	–
124	161.84	–	–	–	–
124.5	–	161.69	161.69	161.15	161.19
126	162.67	162.34	162.35	161.69	161.80
128	163.70	163.20	163.20	162.67	162.70

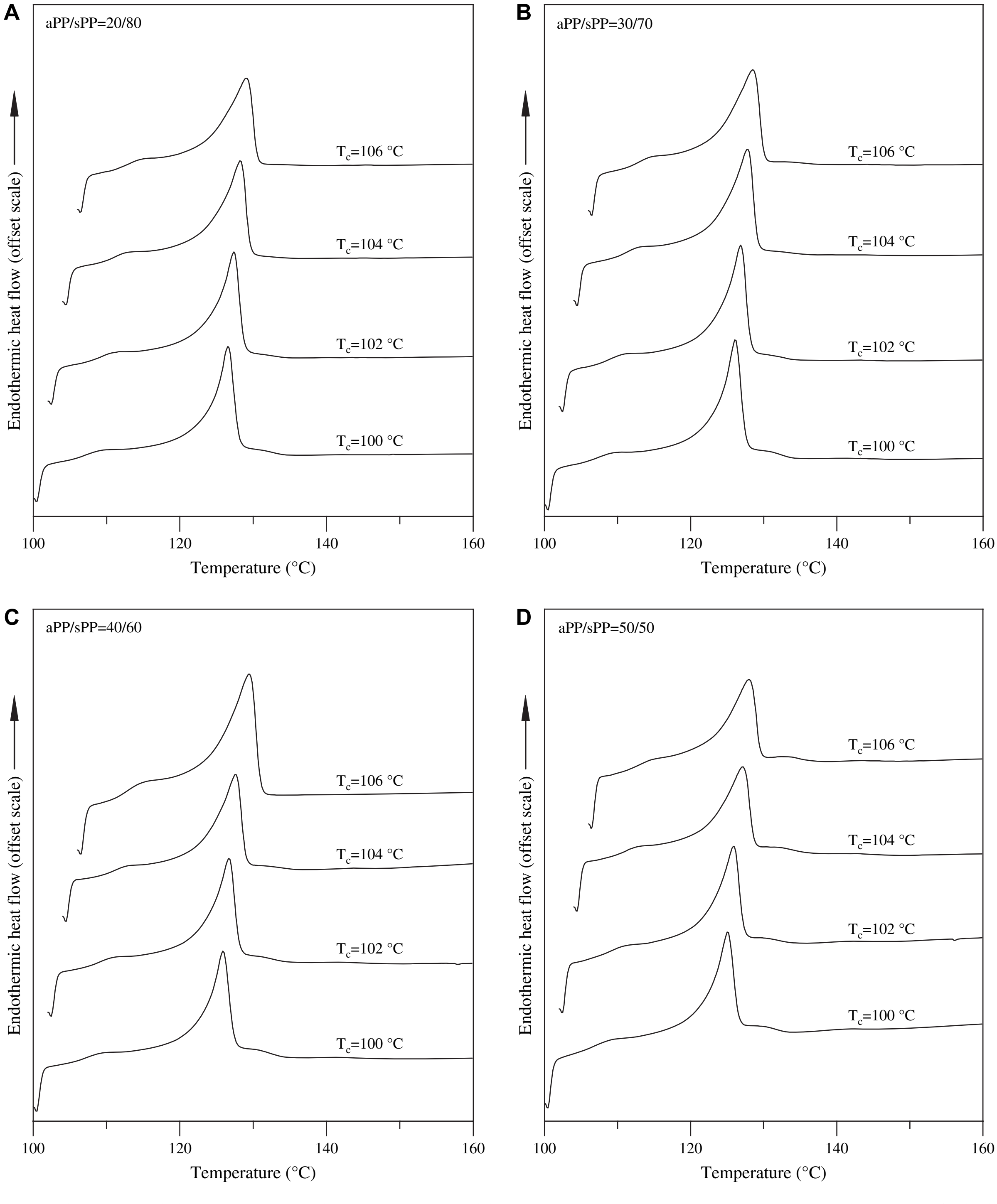


Fig. 5. DSC traces in regimes of single melting peak for aPP/sPP blends of four compositions: (A) 20/80, (B) 30/70, (C) 40/60, and (D) 50/50, isothermally crystallized at $T_c = 100–106$ °C.

(sPP) per mole repeat unit. The enthalpy of fusion for sPP has been reported to be $\Delta H_f = 2.0 \times 10^3$ cal/mol (or 8.3 kJ/mol) [18]. ϕ_1 is the volume fraction of the non-crystallizing polymer (aPS), which is same as the weight fraction if the density of aPP and sPP is assumed to be approximately equal (both in amorphous state), i.e., $V_1/V_2 = 1$. From the extrapolated values of equilibrium melting points for the neat polymer (iPP) or blends of various compositions, Eq. (2) could be utilized to obtain the interaction parameter χ. The numerical values of T_m^o or T_m^* of sPP in aPP/sPP blends of three compositions are also summarized in Table 2. These values were used in next-step plotting for estimation of interaction strength for this blend system. One then would inquire about the third blend system, i.e., aPP/sPP, on which similar procedures and analyses were performed. A plot of the left-hand-side of Eq. (2) vs. ϕ_1^2 yields a fairly linear line for the sPP/iPP blend, which led to $\chi = -0.02$. The numerical values of T_m^o or T_m^* of iPP in three compositions of sPP/iPP blends are also summarized in Table 2.

Table 4
T_m (°C) of neat sPP and aPP/sPP blend of various compositions crystallized at different T_cs

T_c (°C)	T_m (°C) of aPP/sPP (wt/wt)				
	0/100	20/80	30/70	40/60	50/50
100	127.02	126.53	126.03	125.86	125.36
102	128.02	127.34	126.84	126.70	126.36
104	128.53	128.18	127.85	127.52	127.13
106	129.53	129.00	128.50	128.40	128.00

Interaction parameter for the blend system could be estimated. Similarly, plot of the left-hand-side of Eq. (2) vs. ϕ_1^2 yielded a fairly linear line for the aPP/sPP blend system, with a slope = 7.08×10^{-6}. Calculation led to $\chi = -0.007$ for aPP/sPP blend, which is even smaller than that found for the sPP/iPP blend ($\chi_{12} = -0.02$). By comparison, the values of interaction strength for either sPP/iPP or aPP/sPP ($\chi = -0.02$ or -0.007) are order of magnitude smaller than that for aPP/iPP blend ($\chi = -0.21$). Thus, the values of interaction parameter for both sPP/iPP and aPP/sPP blends are essentially zero, indicating a state of free energy approaching phase separation. For practical reason, this nearly nil value can be regarded as quite slight interaction strength approaching zero, and it may represents a state of uncertain phase behavior if one takes into account some inevitable experimental deviations and possible uncertainty in extrapolating the lamellar thickness to infinite. The nearly nil value of χ indicates that the molecular segments of aPP and sPP or those of sPP and iPP are less likely favored to form a miscible state. Although at above the melt state, the sPP and iPP molecular moiety of different configurations are comparable regardless of tacticity, at the melt equilibrium temperature at which χ is measured, the chain segments of sPP and iPP may not be fully miscible by judging from the extremely small value.

From above analyses, a nearly zero but quite small negative value of χ_{12} was obtained as -0.02 and -0.007 for the iPP/sPP and sPP/aPP blends, respectively, which confirms weak interaction strength in these two PP blend systems even at above T_m. By comparison, the iPP/aPP blend exhibits a much larger negative value, which affirms miscibility between the constituents (iPP and aPP). Quantitative interaction strengths as represented by the χ parameters were then compared among the three pairs of polypropylene blends: aPP/iPP ($\chi = -0.21$) $\gg$ sPP/iPP ($\chi = -0.02$) > aPP/sPP ($\chi = -0.007$). The interaction parameters $\chi = -0.21$ for the aPP/iPP blend would suggest that it is the most favorable interaction leading to miscibility among the three blend systems (aPP/iPP, sPP/iPP, and aPP/sPP). The interaction strength for the aPP/iPP blend agrees with the result of the OM characterization on phase behavior at or above the melt state of this blend system. However, on the other hand, the interaction parameter for the aPP/iPP blend is a significantly greater negative than either sPP/iPP or aPP/sPP blends. For the sPP/iPP and sPP/aPP blends, the interaction strengths are nearly zero (-0.02 and -0.007, respectively, at $T_m \sim 180$ °C), indicating that the interactions in these two latter blends may be too weak to maintain a miscible phase; or perhaps, the latter two blend systems (sPP/iPP and aPP/sPP) display a phase behavior that borders on miscibility–immiscibility characterized by a UCST behavior. If the phase behavior of the sPP/iPP and sPP/aPP blends is deemed immiscible, this conclusion, however, contradicts with the OM characterization showing phase homogeneity at or above the melt states of these blends. There seems dilemma in the experimental results. Thus, a plausible postulation is that an UCST exists at certain temperatures

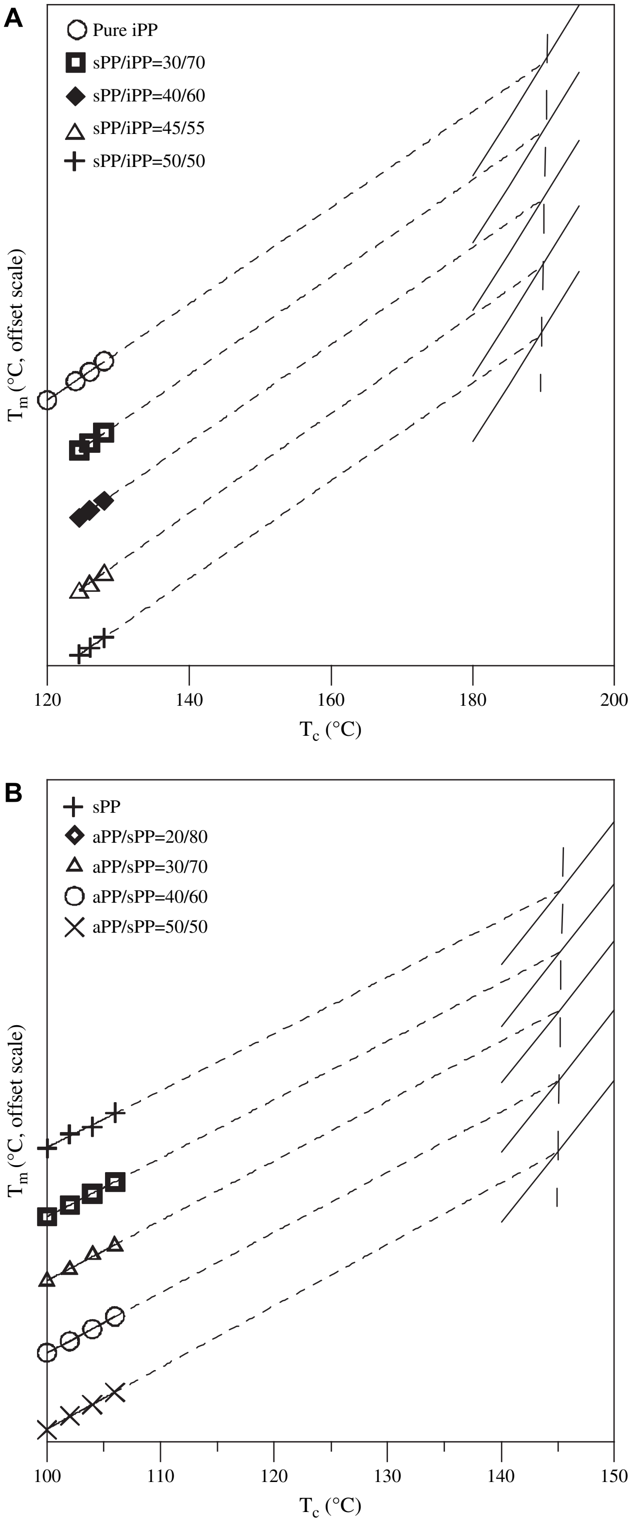


Fig. 6. Equilibrium melting temperatures of (A) sPP/iPP blends and (B) aPP/sPP blends by Hoffman–Weeks plots.

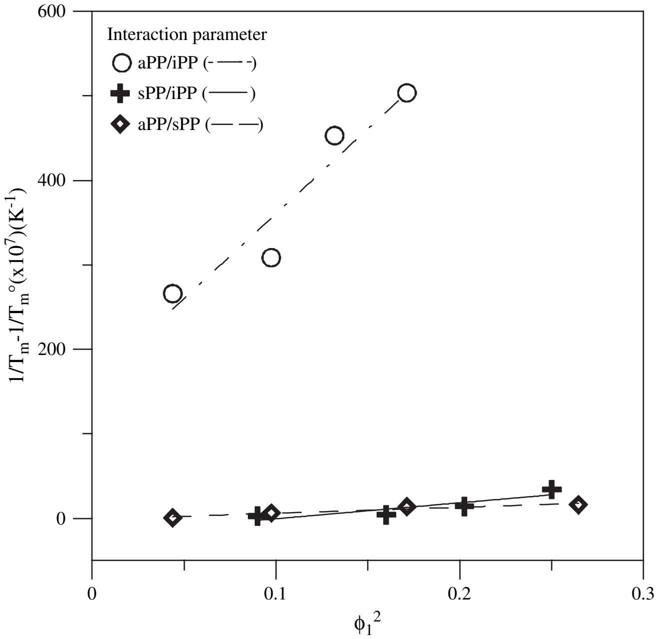


Fig. 7. Comparison of interaction strength according to the Flory–Huggins plots for aPP/iPP, sPP/iPP, and aPP/sPP blends.

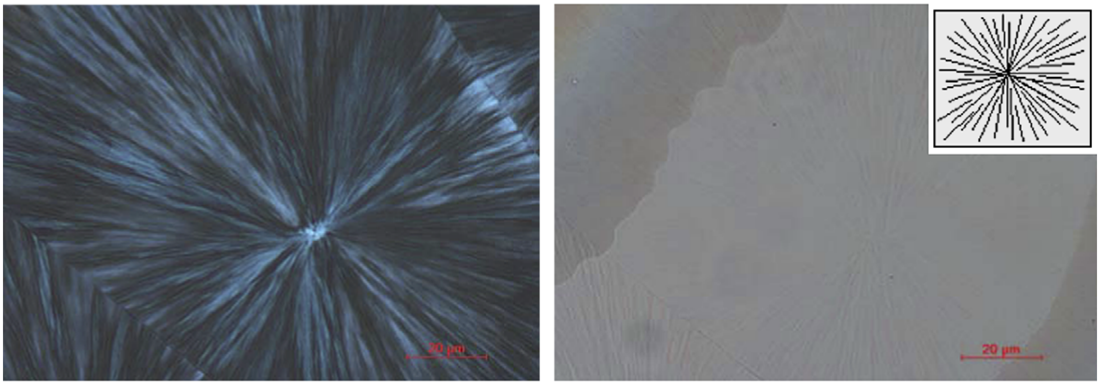
near T_m of the crystal in the sPP/iPP and sPP/aPP blends. Experimental difficulty would be encountered in attempting to prove this postulation because the crystal phase(s) would mask observation of amorphous phase domains, if present. Experimental OM characterization was done by removing the interfering crystalline domains using non-polarizing light.

3.3. Morphology evidence for miscibility or UCST in polypropylene blends

Neat iPP and sPP exhibited quite different patterns in spherulites when crystallized. Fig. 8 shows POM and OM photographs of neat iPP crystallized at $T_c = 128$ °C and neat sPP crystallized at $T_c = 106$ °C. Inset photographs on right-hand-side are morphology of neat iPP or sPP taken under non-polarized light OM. The scheme set in the corresponding photograph shows drawing of enlarged domain pattern for better details of morphology. The crystallized iPP in thin-film forms displays large Maltese-cross-type spherulites (up to 100 μm) with impingement, while the crystallized sPP morphology is filled with tiny crystals (1–2 μm) and in this morphology no pattern could be discerned.

Blends of aPP/iPP of various compositions were similarly characterized using polarized and non-polarized microscopy. Blends of several compositions were examined, which all displayed similar spherulite morphology. For brevity, only a blend of aPP/iPP (30/70) isothermally crystallized at 130 °C was used as an example for discussion. Fig. 9 shows the aPP/iPP (30/70) blend (sample crystallized at $T_c = 128$ °C), with crystalline Maltese-cross spherulites that are typical of iPP crystals. The micrograph on the right-hand-side shows no

Neat iPP isothermally crystallized at 128 °C



Neat sPP isothermally crystallized at 106 °C

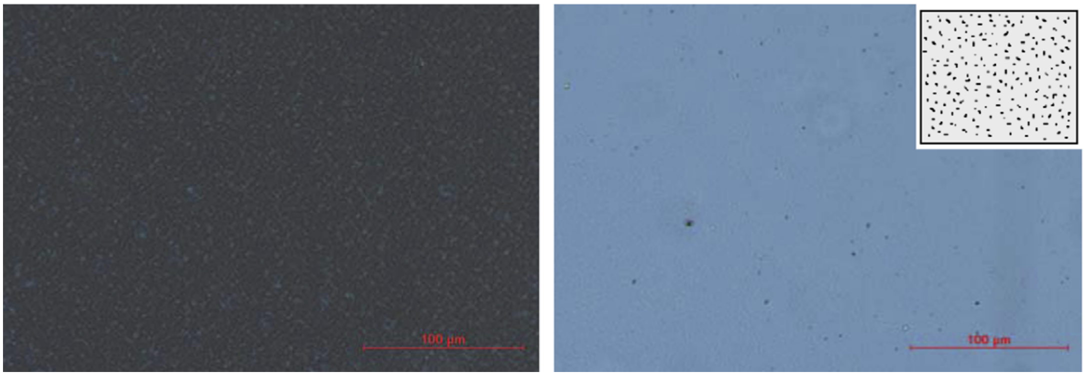


Fig. 8. POM vs. OM graphs showing (left) crystal spherulites vs. (right) crystals in absence of polarized light for: neat iPP crystallized at $T_c = 128$ °C, neat sPP crystallized at $T_c = 106$ °C.

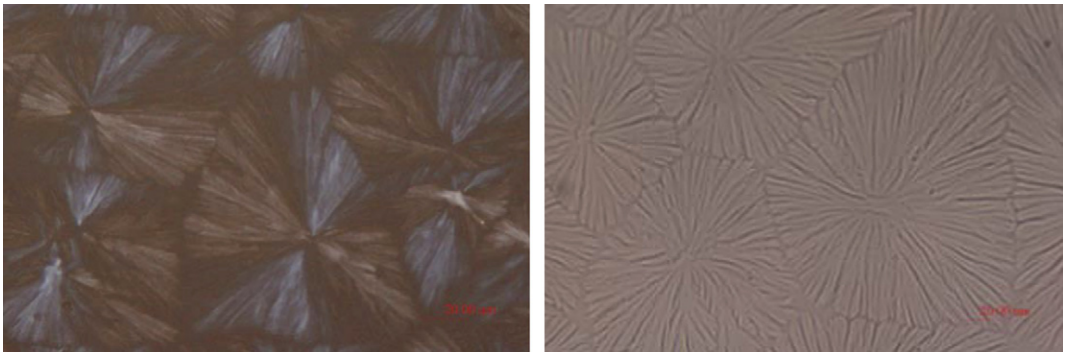


Fig. 9. Micrograph showing phase homogeneity in aPP/iPP (30/70) blend at $T_c = 128$ °C: (left) POM showing crystal spherulites and (right) non-polarized image showing homogeneity with no phase-separation domains.

phase-separated domains in the blend when viewed in non-polarized light, which positively confirms miscibility in the aPP/iPP blend system showing a large negative $\chi = 0.21$.

On the other hand, the other two blend systems, sPP/iPP and aPP/sPP, with interaction parameters nearly zero ($\chi = -0.020$ and -0.007, respectively), are likely immiscible at lower temperatures (below crystal melting). As crystal phase under POM might overwhelmingly mask the phase separation, a special technique was adopted by viewing both POM vs. OM results, which showed distinctly a heterogeneous morphology exposing phase-separation domains under non-polarized optical microscopy (OM). Fig. 10 shows micrographs at $T = \sim 130$ °C in sPP/iPP (30/70) blend: (left) POM revealing crystals interference on phase domains and (right) non-polarized image showing phase-separation domains. Similarly, the aPP/sPP blend with near nil interaction parameter was characterized using the same POM vs. OM technique. Fig. 11 shows micrographs at $T = 106$ °C in aPP/sPP (30/70) blend: (left) POM revealing crystals interference on phase domains and (right) non-polarized image showing phase-separation domains. Note that a few more blend compositions for both blend systems were examined; however, for brevity, only a selected blend composition is demonstrated and discussed here. In both Figs. 10 and 11, the micrographs on right-hand-side show the phases/spherulites under non-polarized light for the corresponding blend samples. The scheme (inset) set in the micrographs shows drawing of enlarged domain patterns for better details of morphology. For the crystalline/crystalline sPP/iPP blend system, the microscopic (non-polarized light) evidence reveals distinct phase-separation domains of spinodal decomposition characteristic at 110–130 °C. For the sPP/iPP blend system, the microscopic (non-polarized light) evidence reveals distinct phase-separation domains of spinodal decomposition characteristic at 130 °C. Note that neat sPP exhibits only tiny spherulite crystals (Fig. 8(B)), but the aPP/sPP blend (30/70) displays much larger spherulites than neat sPP, indicating effect of partial miscibility between aPP and sPP on the crystalline phases. For the amorphous/crystalline aPP/sPP blend system, the phase-separation domains are not as distinct as those in the crystalline/crystalline sPP/iPP blend. However, the inset micrographs (non-polarized light) still reveals phase-separation domains resembling spinodal decomposition characteristic at 110 °C.

Thus, for the aPP/iPP blend, with large negative interaction parameter (−0.21), the homogeneous morphology agrees with the thermodynamic favorable interactions. The other two blend systems (i.e., sPP/iPP and aPP/sPP), with nearly zero interaction parameters, are immiscible at 110–130 °C (below the melting temperature); however, they become homogeneous and approached miscibility at temperature near or above T_m. Thus, the later two blend systems might undergo phase transition from immiscibility to miscibility as they were heated up, which, in thermodynamic sense, is a UCST behavior. As noted earlier, experimentally it would be difficult to distinguish phase domains of immiscibility vs. crystals under polarized light

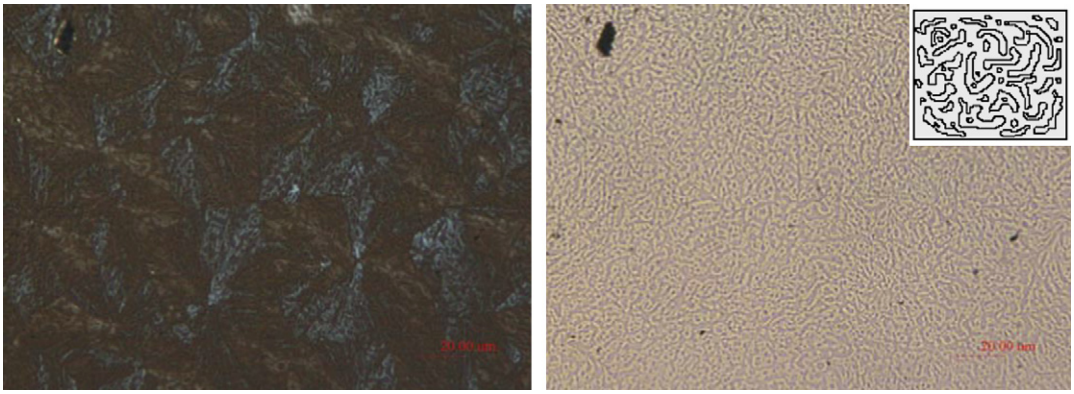


Fig. 10. Micrographs at $T = \sim 130$ °C in sPP/iPP (30/70) blend: (left) POM revealing crystals interference on phase domains and (right) non-polarized image showing phase-separation domains.

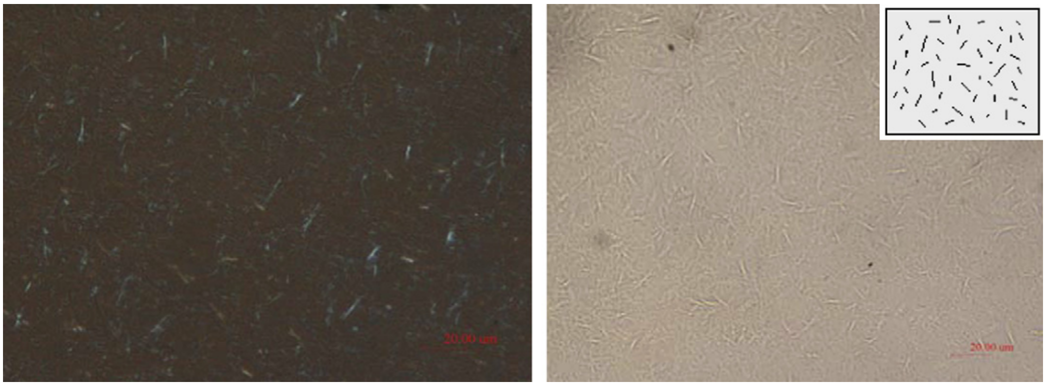


Fig. 11. Micrographs at $T = 106$ °C in aPP/sPP (30/70) blend: (left) POM revealing crystals interference on phase domains and (right) non-polarized image showing phase-separation domains.

if both co-existed. But by using non-polarized OM, phase domains in crystalline blends could be more clearly discerned. Table 5 shows the results of clarity points by heating (10 °C/min) on sPP/iPP and aPP/sPP blends. The experimental result revealed that upper critical solution temperature (UCST ∼ 140–160 °C) likely existed in the sPP/iPP and aPP/sPP blends, which means that they are immiscible at or below 140 °C, but can become miscible and homogeneous above it. The UCST in the blends is either slightly above or nearly overlapped with T_m of polypropylenes. T_ms of iPP and sPP differ significantly, with the apparent T_m of iPP (163 °C) being much higher than that of sPP (129 °C). The clarity point of the sPP/iPP blend was found to be below or near the melting point of iPP. On the other hand, the clarity point for the aPP/sPP blend was found to be ∼15 °C above the apparent melting point of sPP ($T_m = 129.0$ °C). That is, UCST phase transition is located above, not below, the sPP crystal melting; thus the crystalline phases did not mask the amorphous UCST phase transition in the aPP/sPP blends. As a result, clarity points with UCST (∼140 °C) for the aPP/sPP blend could be more positively discerned as being located above T_m of sPP.

Thus, the weak interaction parameters for both sPP/iPP and iPP/sPP blend systems measured at above T_m suggested that there might exist a temperature at which phase was transformed from immiscibility to miscibility upon heating. That is, both sPP/iPP and iPP/sPP blend systems might exhibit UCST behavior. As discussed earlier, heterogeneity with phase domains at below crystal melting was evidenced by a comparative technique of POM vs. OM characterization. Although UCST theoretical prediction has been performed for PP blends [6], experimental verification is yet to be confirmed. This work attempted to construct an experimental phase diagram for the sPP/iPP and iPP/sPP blend systems, respectively. First of all, for the crystalline/crystalline sPP/iPP blend, phase diagram must consider the higher-melting component (iPP). Fig. 12 shows experimental UCST and clarity points for the sPP/iPP blends, in comparison with the theoretical UCST curve adapted from the literature. Crystal melting points (for higher-melting iPP) are indicated in graph for reference. The UCST in the blends nearly overlaps with T_m of polypropylenes, which makes justification of UCST somewhat difficult or less certain. Inset blocks show schematic drawings for the corresponding micrographs taken at the designated temperatures. Theoretical UCST curve (— - - - —) based on Flory–Huggins mean field theories, reported earlier by Maier et al. [6], was adapted from the literature and re-plotted here in the same graph for comparison, for sPP/iPP blend of a closest molecular weight of 25,000 g/mol. Theoretical UCST curves for PP blends are highly dependent on MW. In this figure, the closest MW was chosen for comparison with the experimental UCST. Although the general shapes differ between the experimental data and the theoretical calculations, the values of UCST (maximum of curves) agree. Note that the immiscible sPP/iPP blend might exhibit partial miscibility at extreme compositions (such as 5/95 or 95/5 w/w compositions, etc.). Thus, experimentally it was difficult to verify the phase diagram at compositions away from the middle range. Nevertheless, for the first time, UCST behavior in sPP/iPP is experimentally observed and proven.

Similarly, a phase diagram was constructed for the amorphous/crystalline aPP/sPP blend. Fig. 13 shows experimental UCST and clarity points for aPP/sPP blends in comparison with theoretical UCST curve. Crystal melting of sPP must

Table 5
Clarity points (UCST curve) as determined by heating (at 1–2 °C/min) on sPP/iPP and aPP/sPP blends

wt/wt	sPP/iPP			aPP/sPP		
	Phase transition	Crystal transition		Phase transition	Crystal transition	
	Clarity point (°C)	Apparent T_m (°C) (at $T_c = 128$ °C)	T_m^o (°C)	Clarity point (°C)	Apparent T_m (°C) (at $T_c = 106$ °C)	T_m^o (°C)
20/80	–	–	–	143	129.0	145.2
30/70	163	163.2	189.8	144	128.5	145.1
40/60	163	163.2	189.8	143	128.4	144.9
45/55	162	162.7	189.6	–	–	–
50/50	162	162.7	189.1	143	128.0	144.9

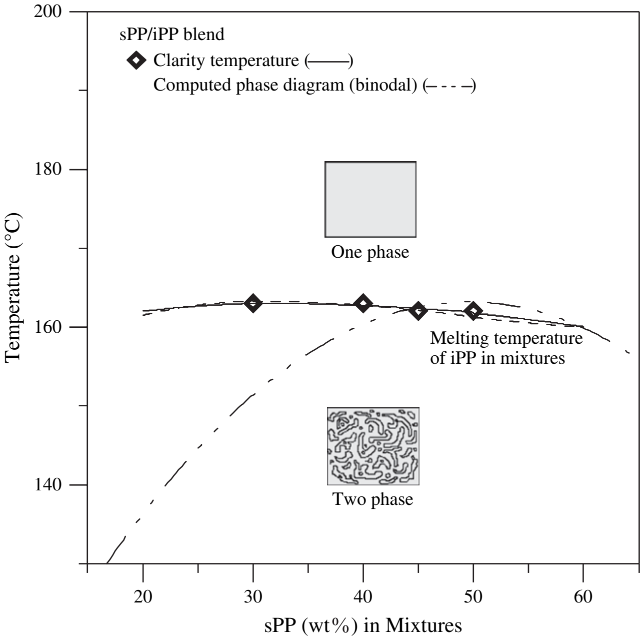


Fig. 12. Experimental UCST diagrams for sPP/iPP blends in comparison with theoretical UCST prediction [6]. Crystal melting points (for higher-melting iPP) plotted in graph for reference.

be shown in relation to UCST transition. Crystal melting points (sPP) are indicated in graph for reference. Again, theoretical UCST curve (— - - - —) based on Flory—Huggins mean field theories, reported earlier by Maier et al. [6], was replotted here in the same graph for comparison, for aPP/sPP of a closest molecular weight of 25,000 g/mol. Although the values of experimental data do not fully match the theoretical UCST curve, it must be pointed out that UCST behavior in aPP/sPP is experimentally justified.

There may be some concern whether or not the Hoffman—Week plots for UCST blend systems may be applicable, as the crystallization temperatures for the Hoffman—Week plots are below UCST of sPP/iPP or aPP/sPP blend. As an originally immiscible (or partially miscible) aPP/sPP or sPP/iPP blend (e.g., slow-cooled from melt) is heated up, indeed it is phase separated at 120—140 °C, until it reaches UCST. However, once it is brought above UCST to a homogeneous phase and rapid-quenched back to 120—140 °C, it remains locked in a "quasi-miscible" state. The Hoffman—Weeks procedure in this study involved heating the blend samples at 160—170 °C (which is above respective UCST), then rapid-quenched to designated T_c (120—140 °C). At this stage, the blend was locked into a "quasi-miscible" state, for which its equilibrium melting temperatures were assessed. Indeed, it should be noted that there might be some uncertainty in data as there was some extent of slow phase separation from the homogeneous phase to tiny domains when held at the selected T_c. This partially accounts for the fact that the measured values of interaction parameters were nearly zero for the aPP/sPP and sPP/iPP blends.

The experimental evidence, by removing the interfering crystalline domains, reveals that upper critical solution temperature (UCST ~ 160 °C) does exist in the sPP/iPP and aPP/sPP blends. By judging from the nearly zero interactions and proven UCST transition in sPP/iPP and aPP/sPP blends, it is clear that these two blends are immiscible at or below ca. 160 °C, but they can become miscible and homogeneous above UCST temperature. By comparison, other than crystal melting, UCST transition is not found in the aPP/iPP blend. By judging from the significantly large negative value ($\chi = -0.21$) of the interaction strength, miscibility is quite well expected in the aPP/iPP blend, which agrees with most of the reported results in the literature.

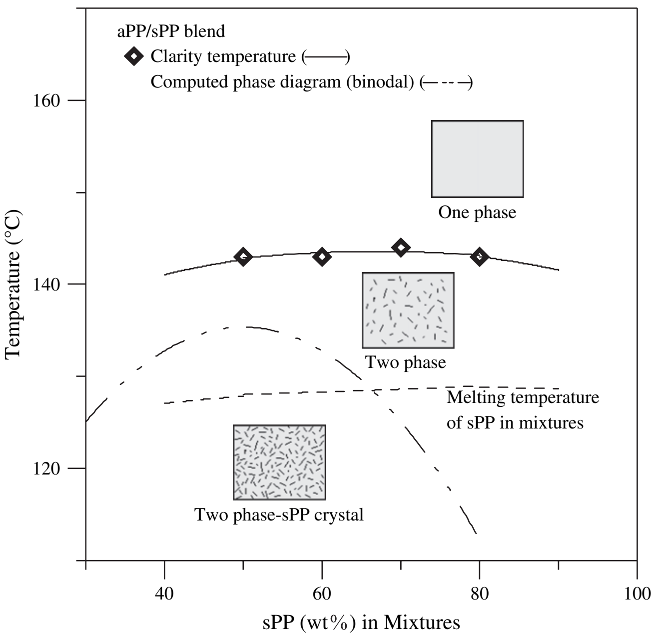


Fig. 13. Experimental UCST diagrams for aPP/sPP blends in comparison with theoretical UCST prediction [6]. Crystal melting points (sPP) plotted in graph for reference.

4. Conclusion

Blends of two semicrystalline polymers but of different tacticities have been the subjects of studies for some time with hard-to-resolve conflicting interpretations, owing to complexity in experimental validation of phase behavior. This study provides timely clarification on confusing issues in binary blends of PP of different tacticities. Unlike amorphous blends of isomeric polymers that typically are miscible, blends of two stereo-isomeric semicrystalline polypropylenes of different tacticities can be miscible or immiscible with UCST (i.e., turning miscible upon heating). Critical clarification has been advanced in this work on interpreting the true phase behavior of blends of polypropylenes differing in tacticity (a, s or i). For the first time, quantitative interaction parameters for three binary pairs of polypropylenes, i.e., blends of aPP/iPP (amorphous/crystalline), sPP/iPP (crystalline/crystalline), and aPP/sPP (amorphous/crystalline), respectively, were assessed, compared, and correlated to the observed phase behavior that had puzzled many investigators for a long time. Quantitative interaction strengths as represented by the χ parameters were then compared among the three pairs of polypropylene blends: aPP/iPP ($\chi = -0.210$) $\gg$ sPP/iPP ($\chi = -0.020$) $>$ aPP/sPP ($\chi = -0.007$). The aPP/iPP is miscible at ambient temperature and no UCST transition exists in the blend. For the latter two blend systems, the interaction strength is essentially zero, suggesting a state of mixture bordering on phase separation. These interaction parameters for the polypropylene blends were measured at or near the respective melting points of iPP (or neat T_m of sPP for the aPP/sPP blend), whose values could be expected to correlate with the variation in trend of the phase behavior of the blends at temperatures between ambient and T_m. The blends of sPP/iPP and aPP/sPP, however, may be on immiscibility at ambient temperature, which, upon heating, can go into miscibility with a UCST transition at or near 140 °C.

Except for theoretical prediction, UCST behavior for blends of sPP/iPP or aPP/sPP had never been proven, owing to interference from PP crystallinity. This study pioneered approaches in discerning UCST experimentally for crystalline/crystalline polypropylene blends by separating the amorphous phase domains from the crystalline spherulites. UCST in the iPP/sPP blend was found to be near T_m of iPP (= 163 °C); as a result, determination of UCST for the sPP/iPP blend was dependent on a feasible technique of removing the crystal from phase-separation domains. On the other hand, UCST for the aPP/sPP blend was found to be ~15 °C above the apparent melting point ($T_m = 129.0$ °C) of sPP. Clarity points with UCST (~140 °C) for the aPP/sPP blend could be more positively discerned as being located above T_m of sPP, whose UCST phase transition was free from interference by the crystal phase.

Acknowledgment

This work was financially supported by a basic research grant (NSC-94 2216 E006 003) in consecutive years from *National Science Council* (NSC) of Taiwan.

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