On the State of Miscibility of Isotactic Poly(propylene)/Isotactic Poly(1-butene) Blends: Competitive Liquid-Liquid Demixing and Crystallization Processes

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ABSTRACT: The miscibility behavior of blends of high molecular weight isotactic poly(propylene) (it-PP) and isotactic poly(1-butene) (it-P1B) has been investigated by a combination of optical and scanning electron microscopies, differential scanning calorimetry, and dynamic mechanical analysis. The results of these investigations demonstrate that for the molecular weights investigated, it-PP and it-P1B form blends that are partially miscible in the liquid state. Liquid-liquid demixing is observed by optical microscopy at temperatures above the melting temperature of the it-PP component and is also inferred from scanning electron micrographs of the freeze fracture surface of quenched blends after extraction of the it-P1B component with cyclohexane. It-PP spherulites grow through both liquid phases at relative rates that depend markedly on the crystallization temperature. The complex multiple-melting behavior of the isotactic poly(propylene) component in the blend is explained in terms of a bimodal distribution of it-PP lamellar crystals which results from crystal growth in the phase-separated liquid. The heterogeneous nature of the mixed liquid is consistent with the upper critical solution temperature behavior observed in our previous study of blends of atactic poly(propylene) and atactic poly(1-butene). Finally, the dynamic mechanical analysis data are explained in terms of a liquid-liquid demixing process that results in a significant degree of phase mixing.

1. Introduction and Background

Miscibility studies of it-PP/it-P1B mixtures have been reported in the literature for quite some time but have not provided a definite answer as to the conditions under which these mixtures are miscible at the molecular level in the liquid state.[1-11] Examination of the pertinent literature clearly demonstrates the controversial nature of this subject. For example, Boor and Mitchell,[1] on the basis of dilatometric data, reported that when small amounts of isotactic poly(propylene) are added to isotactic poly(1-butene), the crystallization rate of the latter is significantly increased but that this behavior is not highly reproducible, thereby suggesting the difficulty in obtaining a truly homogeneous mixture of the two polymers. Piloz and Decroix[2] using dynamic mechanical analysis and dilatometry infer from the observed variation in glass transition temperature with blend composition that the mixture is "compatible". Berticat et al.[3] using differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and dilatometry suggest these blends to be incompatible. However, one should note that their conclusion is not based on an unambiguous observation of two distinct glass transition temperatures but on a statistical analysis of their data that favors a two-phase model. Siegmann[4,5] observed a depression in the observed melting temperature and in the crystallization rate of the it-PP component with added P1B, a crystallinity in each component that is lower than that expected on the basis of the linear rule of mixtures and morphological variations of the it-PP spherulites with small amounts of the it-P1B component. From these observations, he concluded that the poly(1-butene) acts as a miscible diluent which is rejected from the it-PP spherulites during crystallization and that the two components are highly compatible in their amorphous phase. Gohil and Petermann[6] using transmission electron microscopy and differential scanning calorimetry suggest the blends to be miscible for it-PP content >80% or <20% and immiscible in the intermediate composition range. They also confirmed Siegmann's observation of a melting temperature depression for the it-PP component in blends containing <30% P1B and observed a complex melting behavior for poly(propylene) in blends containing >30% P1B. Finally, Hsu and Geil[7] studied the glass transition, crystallization and melting behavior, and the morphology of it-PP/it-P1B blends prepared by a combination of compression molding at 235 °C and quenching either in air or with isopentane. While some of their specific conclusions, such as the invariance of the it-PP melting point with changes in blend composition and the observation of two separate glass transition temperatures in ultraquenched blend samples, differ from those of Siegmann's work, they concluded that "there is a considerable degree of compatibility, possibly even miscibility, of it-PP and it-P1B in the melt but that miscibility is difficult to obtain by ordinary melt mixing processes".

Physical properties of polymer blends depend markedly on the supercrystalline morphology and the level of phase segregation that result from crystallization and potential phase separation processes. The variation of mechanical properties with blend composition has been used in the past to characterize the level of compatibility in polymer blends.[12] However mechanical compatibility and molecular-level miscibility must be clearly differentiated. As pointed out by Hsu and Geil,[7] low-strain properties such as the modulus are not able to differentiate compatible blends from miscible ones. The composition dependence of large-strain properties such as the elongation at break or the toughness may be more significantly related to the molecular-level homogeneity of a given material. Siegmann[4,5] and Hsu et al.[7] showed that it-PP/it-P1B blends exhibit a linear variation of the modulus and yield strength with blend composition but a nonlinear variation of tensile strength and ultimate and yield elongations with blend composition. It was suggested that the efficient stress transfer between the two components of a compatible blend arises from a good adhesion between their amorphous

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phases. As will be apparent in the discussion section, we would like to suggest a different point of view to account for the mechanical properties of these polyolefin blends that will be based on consideration of phase mixing and on the observation of competing phase separation and crystallization processes. Noting that many of the previous investigations of the state of miscibility in these blends relied either on room temperature measurements or on analyses carried out on samples that had been crystallized under nonisothermal conditions and were subsequently heated during the analysis, we first need to investigate the state of miscibility of this blend in the liquid state prior to crystallization and then study the influence of crystallization of the poly(propylene) component on the extent of liquid–liquid demixing.

It is generally accepted that miscibility in high molecular weight polymer blends must rely on the existence of specific interactions between the repeat units of each component, since the favorable entropic contribution becomes vanishingly small as molecular weights become large.[12] For polyolefin blends such as it-PP/it-P1B, the absence of favorable specific interactions implies that miscibility can only occur when the balance of dispersive interactions and entropic driving force toward mixing is favorable, i.e., at sufficiently low molecular weights of the polymeric components. In such systems, the Flory–Huggins–Hildebrand theory can provide a qualitative description of miscibility criteria.[12] In a related study,[13] this theory was used to estimate the effect of molecular weight on the miscibility of atactic poly(propylene) (at-PP) and atactic poly(1-butene) (at-P1B) blends. We showed that such materials exhibit an upper critical solution temperature behavior, as has been reported for mixtures of deuterated and protonated polyolefins.[14] If we follow the arguments presented by Walsh et al.[15] that tacticity does not affect markedly the dispersive interactions and the entropy of mixing in poly(propylene)/poly(1-butene) blends, we would predict that blends of commercial it-PP and it-P1B materials (i.e., of molecular weight above 10^5 g/mol) would be immiscible and exhibit a UCST above their respective degradation temperatures. Reports have appeared in the literature which show that for blends such as poly(vinyl methyl ether) (PVME)/polystyrene (PS),[16] poly(methyl methacrylate) (PMMA)/poly(vinyl chloride) (PVC),[17] and poly(methyl methacrylate) (PMMA)/poly(vinylidene fluoride) (PVF_2),[18] tacticity can have a significant effect on miscibility. In these blends, the specific interactions are very directional and their magnitude does depend on the respective tacticity of the interactive groups along the polymer chain. More recently, Trask and Roland[19] indicate that the χ interaction parameter for mixtures of *cis*-1,4-polyisoprene and poly(vinylethylene) increases significantly with the tacticity of the poly(vinylethylene). Although in the latter case the absolute variation of χ with tacticity is small, it suggests that the general prediction of critical temperatures for blends of isotactic materials from data on atactic polymers may be inaccurate.

Experimentally, miscibility in polymer blends is generally demonstrated by the observation of a single, composition-dependent glass transition temperature by, for example, differential scanning calorimetry (DSC) or dynamic mechanical analysis (DMA). For systems with either a single or both crystallizable components, such techniques are always ambiguous unless the crystallizable component(s) can be quenched to the amorphous state. Observation of a melting temperature depression for the highest melting component in the blend is also viewed as a good indication of miscibility. However, such studies should be viewed with caution, as a depression in the observed melting temperature can also result from mere kinetic or morphological effects.[20,21] Establishing the miscible character of a semicrystalline polymer blend using the concept of melting point depression is only valid if the composition dependence of the equilibrium melting temperature is investigated through extrapolative techniques such as the Hoffman–Weeks or the Gibbs–Thompson methods.[22] The Flory–Huggins χ interaction parameter of the mixture can then be determined by the treatment proposed by Nishi and Wang.[23] Rim and Runt[21] correctly pointed out that this method is fairly inaccurate for systems exhibiting a small χ. If we assume that the value of χ for the it-PP/it-P1B blends is of the same magnitude as that obtained from the solubility parameter difference between at-PP and at-P1B through determination of the critical temperature (i.e., $\Delta\delta = 0.14$ or $\chi = 0.0012$ at 85 °C),[13] we can predict that the equilibrium melting temperature depression for it-PP crystals grown from it-PP/it-P1B blends will be negligibly small (much less than 1 °C for a 5/95 w/w it-PP/it-P1B blend). In view of the problems associated with the determination of T_g for these materials and the expected lack of significant equilibrium melting point depression, we will investigate the miscibility character of it-PP/it-P1B blends by direct observation of their morphology. One should note that such an approach can only prove the blends to be immiscible since the observation of a homogeneous morphology may result either from true molecular-level miscibility or from the lack of spatial resolution of the microscopic technique utilized.

In this paper, a 30/70 w/w it-PP/it-P1B blend will be examined as a function of residence time in the melt state using optical microscopy, since it is believed that the indices of refraction of amorphous it-PP and it-P1B are sufficiently different. Such experiments will allow us to show that the blend is in a heterogeneous state in the liquid. To study the interplay between crystallization and liquid–liquid demixing, the spherulite growth behavior of the it-PP component will be observed under isothermal conditions for different residence times in the melt prior to crystallization. This study will not address the crystal growth behavior of the isotactic poly(1-butene) component. We will also investigate the morphology of quenched blend samples using scanning electron microscopy. The latter set of experiments will be carried out on samples which are freeze fractured and whose fracture surface is treated with cyclohexane so as to remove the it-P1B component. Such treatment is necessary to evidence the surface topology as previous scanning electron microscopic (SEM) studies on untreated fractured surfaces failed to show any distinguishable morphological features.[7,24] We will then discuss the complex melting behavior of the it-PP component in such blends and propose a correlation between this multiple-melting behavior and the blend morphology resulting from competitive liquid–liquid demixing and crystallization processes. Finally, we will discuss results obtained from dynamic mechanical analysis in the context of phase-separated blends.

2. Experimental Section

Isotactic poly(propylene) (it-PP) was kindly provided by Amoco, and isotactic poly(1-butene) (it-P1B) was purchased from Scientific Polymer Products, Inc. The molecular weights of these two materials were determined by viscometric techniques using *p*-xylene at 85 °C ($K = 9.6 \times 10^{-4}$ dL/g, $a = 0.63$)[25] for isotactic poly(propylene) and *n*-heptane at 35 °C ($K = 4.73 \times 10^{-4}$ dL/g, $a = 0.80$)[26] for isotactic poly(1-butene). Molecular weights are $M_n = 111000$ for it-PP and $M_w = 285000$ for it-P1B. A Haake

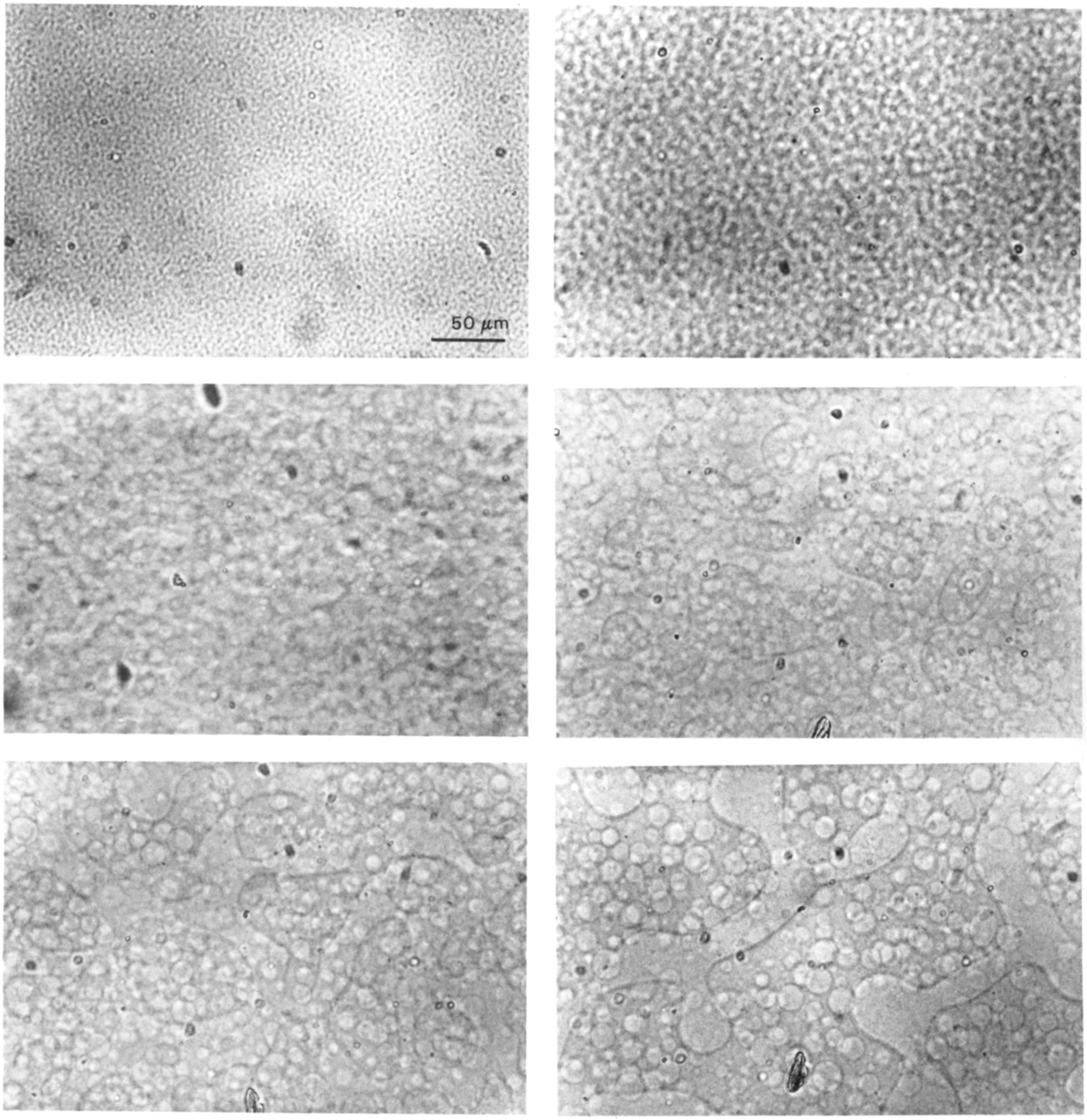

Figure 1. Optical micrographs of a 30/70 it-PP/it-P1B blend at 200 °C for various residence times in the melt: (a) 5, (b) 15, (c) 35, (d) 65, (e) 90, and (f) 180 min.

rheomixer operated at 190 °C with a 5-min mixing time and a rotation speed of 45 rpm was used to prepare the various it-PP/it-P1B blends from the as-received homopolymers. The samples were taken out of the rheomixer and air-quenched to room temperature.

For the optical microscopy study, a thin film of the 30/70 blend was melted at 200 °C in a Linkam THMS 600 heating stage where it was allowed to reside for up to 3 h under a dry nitrogen purge. Optical micrographs were recorded after various residence times in the melt at 200 °C using a Carl Zeiss Axioplan light microscope. In another series of experiments, we observed the isothermal crystallization of the it-PP component in the 30/70 blend at 145 °C after a residence time of 3 min in the melt at 180 °C. These experiments enabled us to observe simultaneously macrophase separation and crystallization of the it-PP component. The crystallization temperature was such that the rates of liquid–liquid demixing and of crystallization were of about the same magnitude. In a third series of experiments, the 30/70 blend was crystallized isothermally at 130, 135, or 145 °C after a residence time of 5 h in the melt at 180 °C. Since the liquid was kept under dry nitrogen, we believe the extent of degradation undergone by the sample was minimized. Such experiments allowed us to observe the isothermal crystallization of the it-PP component from a macroscopically phase-separated melt. These same isothermally crystallized 30/70 it-PP/it-P1B samples were subsequently heated at a rate of 5 °C/min in the microscope hot stage, and the melting of the it-PP spherulites was recorded photographically at different temperatures. In the latter three series of experiments, optical micrographs were recorded so as to observe simultaneously the macrophase-separated morphology and the birefringence of it-PP spherulites. Such simultaneous observations were made possible by slightly rotating the analyzer away from the crossed polarization condition. The temperature scale of the microscope hot stage was calibrated using the melting temperature of indium.

For the SEM study, 30/70 it-PP/itP1B blend samples were melted at 200 °C for various periods of time and quenched directly from the melt to liquid nitrogen temperature and fractured. The fractured samples were kept in cyclohexane at room temperature for 24 h to remove the it-P1B component at the fracture surface.[27] Samples were then again washed with fresh cyclohexane, dried, and coated with gold. The morphology of the fracture surface

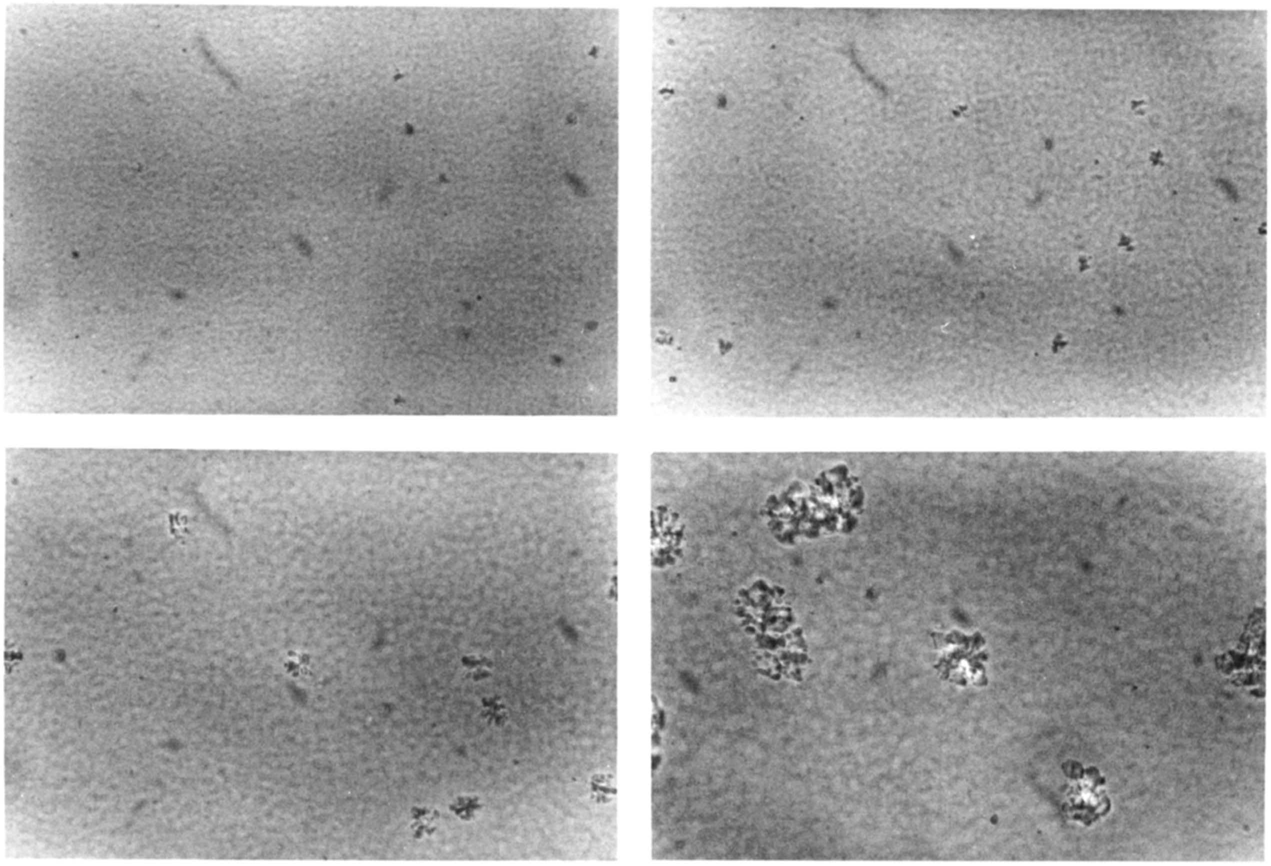

Figure 2. Optical micrographs of a 30/70 it-PP/it-P1B blend at 145 °C for various crystallization times after melting at 190 °C for 3 min: (a) 10, (b) 15, (c) 30, and (d) 62 min (same magnification as in Figure 1a).

was examined in an International Scientific Instruments SI SX40 scanning electron microscope operated at 15 kV.

The melting behavior of the it-PP component in the blend was examined with a Perkin-Elmer Model DSC-2C differential scanning calorimeter at a heating rate of 10 °C/min after isothermal crystallization in the DSC. The sample weight was kept at 4 mg in all DSC studies to minimize the effect of sample weight variation on thermal lag. In all cases, the heating scans were started from the crystallization temperature so as to prevent any crystallization of the it-P1B component.

A DuPont dynamic mechanical analyzer (DMA) Model 983 was used to record the variation of the loss modulus as a function of temperature and blend composition. Samples with dimensions of 40 × 13 × 3 mm^3 were compression molded in a Carver laboratory press at 190 °C for 5 min. They were quenched in liquid nitrogen and kept below their glass transition temperature during transfer to the precooled DMA to preserve the morphology and minimize crystallization. The dynamic mechanical analysis experiments were carried out from −150 to +80 °C at a rate of 1 °C/min, at a frequency of 1 Hz, and with an oscillation amplitude of 0.31 mm.

3. Results and Discussion

Optical Microscopy. Optical micrographs of the 30/70 it-PP/it-P1B blend at 200 °C are shown as a function of residence time in the melt state in Figures 1a–f. The grainy texture observed in Figure 1a clearly indicates that even after a very short residence time in the liquid state, the blend is already phase separated (note that the morphological observations made here did not depend on time in the melt rheomixer for mixing times longer than 3–5 min). For longer residence times in the melt at 200 °C (Figure 1b–f), coarsening of the phase-separated morphology is unambiguously observed. Identical observations were made in a 30/70 it-PP/it-P1B blend prepared by the freeze-drying process of a solution of it-PP and it-P1B in *p*-xylene, indicating that sample preparation had little effect on this conclusion (i.e., the freeze-drying and the melt-mixing processes yield a material that is unstable in the liquid state). However, optical microscopy does not provide us with any information on the difference in the initial level of heterogeneity at 200 °C for samples prepared by these two methods. The morphological evolution of the blend in the liquid state undeniably implies that the 30/70 blend is undergoing a process of liquid–liquid demixing at this temperature. From the observation of interconnected domains (see Figure 1a), one might conclude that the liquid–liquid demixing occurs by a process of spinodal decomposition followed by a breakup of the cocontinuous structures and coarsening.

Similar experiments carried out on the 30/70 it-PP/it-P1B blend at other temperatures (i.e., 180, 220, and 250 °C) and on 50/50 and 80/20 it-PP/it-P1B blends at 180 °C yielded the same morphological evolution, suggesting that the UCST is located far above the melting temperature of the it-PP component.

In the second series of experiments, the blend was first melted at 190 °C for 3 min and then cooled to 145 °C where optical micrographs were recorded as a function of time. In this temperature range, differential scanning calorimetric observations indicate that the it-PP component crystallizes to its fullest extent over a period of a few hours. Micrographs 2a–d show the evolution of the blend morphology as a function of residence time at that temperature. Two observations can be made: first, the same grainy structure which was observed in the same blend at higher temperature (Figure 1) is evident at 145 °C (the length scale of these heterogeneities is observed to increase as a function of residence time at 145 °C); second, irregularly shaped spherulites are observed to grow at this temperature in the phase-separated liquid. From

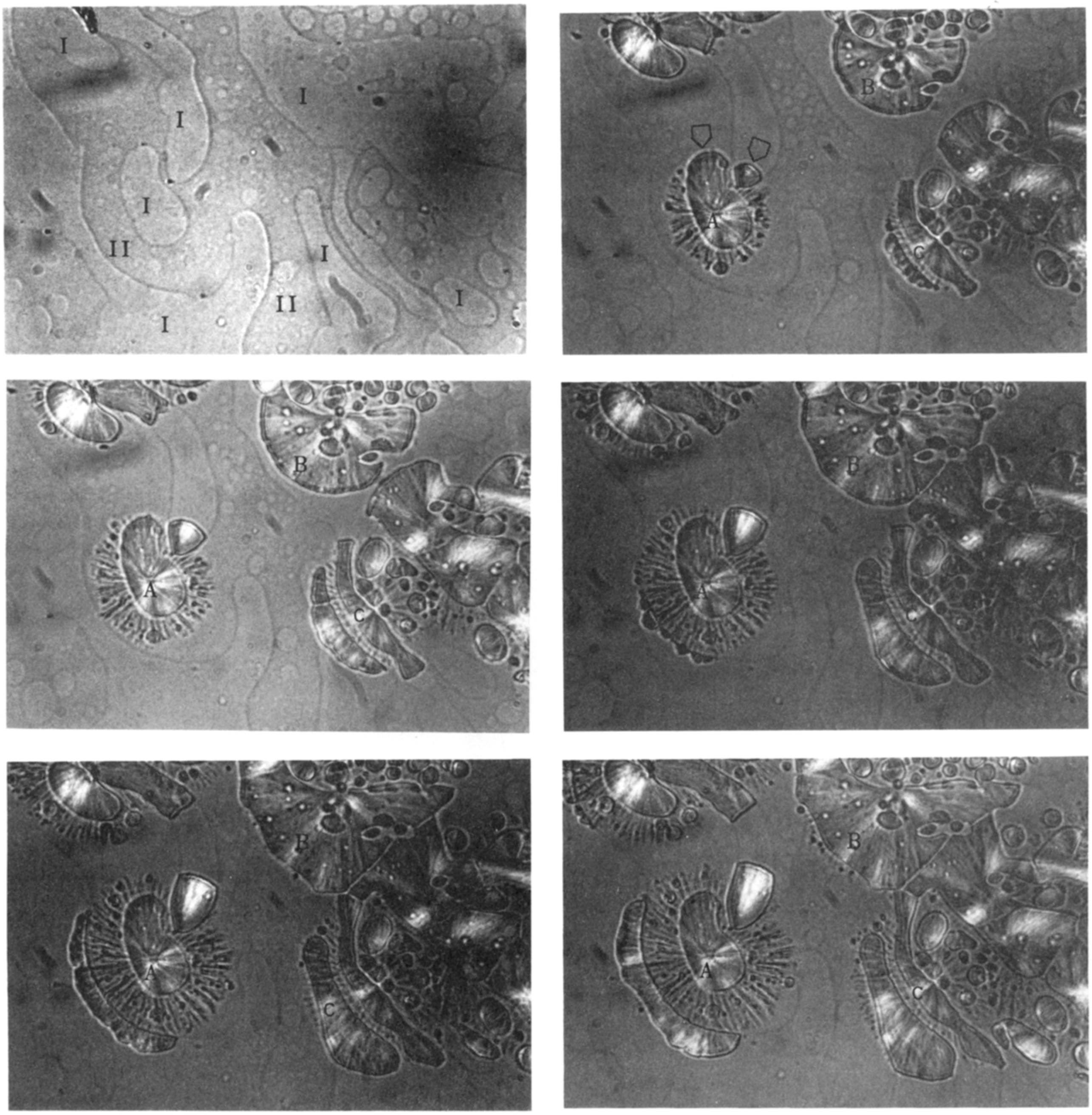

Figure 3. Optical micrographs of a 30/70 it-PP/it-P1B blend (a) after melting at 180 °C for 5 h and (b–f) for various crystallization times at 145 °C after melting at 180 °C for 5 h: (b) 130, (c) 150, (d) 175, (e) 195, and (f) 210 min (same magnification as in Figure 1a).

these observations, one can conclude that liquid–liquid demixing occurs simultaneously to crystallization and that the patchy nature of the it-PP spherulites, which had been previously observed by Siegmann[4] and Hsu et al.,[7] results from the crystal growth of the it-PP component through a partially phase-separated liquid.

More detailed observations of the crystal growth process of the it-PP component in the phase-separated liquid are obtained in the next two series of optical microscopy experiments. First, the blend was allowed to undergo demixing at 180 °C for 5 h prior to quenching to 145 °C where isothermal crystallization was carried out and optical micrographs were recorded as a function of crystallization time between 130 and 210 min (Figures 3b–f). The 5-h residence time in the melt was chosen so as to obtain large enough phase-separated domains, while a crystallization temperature of 145 °C was selected so as to minimize nucleation density and to observe crystal growth through multiple liquid phases. Micrograph 3a represents the same region in the same sample as observed after cooling to 145 °C and should be fairly representative of the morphology of the phase-separated liquid prior to crystallization. To identify the phase-separated domains of similar compositions, we made use of the spatial variation in the contrast with composition in this micrograph and we also relied on the observation of the resulting semicrystalline morphologies shown in the subsequent micrographs of this series. Two different liquid phases are observed and denoted by I and II (see Figure 3a). Let us focus our attention on the growth process for the three spherulites marked A, B, and C on the various micrographs. Comparison of micrograph 3a with micrographs 3b–f indicates that the it-PP spherulites always nucleated in the same phase (liquid phase I on micrograph 3a). When crystal growth occurs within this phase (regions of spherulite A in micrographs 3b–f indicated by the arrows and spherulite B in micrographs

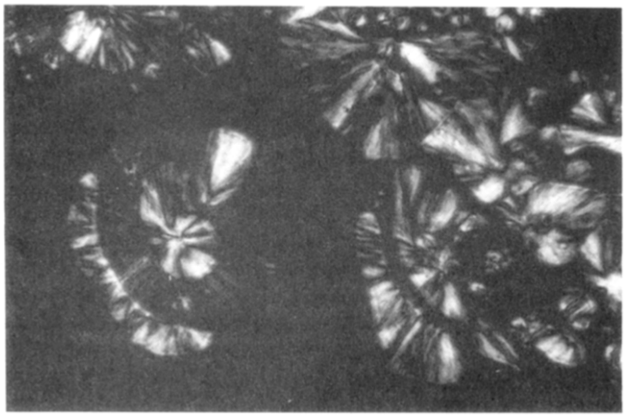

Figure 4. Polarized optical micrograph of a 30/70 it-PP/it-P1B blend crystallized at 145 °C for 210 min after melting at 180 °C for 5 h (same area as in Figure 3f and same magnification as in Figure 1a).

3b–e), the texture of the spherulite is almost identical to that observed for pure it-PP. On the other hand, when crystal growth occurs within the liquid phase II, a much more open spherulitic texture is observed and the crystal growth rate is slightly lower than that in liquid phase I (the ratio of the spherulitic growth rate in phase I to that in phase II at 145 °C is equal to 1.4 ± 0.2). In micrographs 3b–f, spherulite A is observed to grow successively through liquid phases I, II, and I. Spherulite C is observed to cross three I ↔ II liquid–liquid interfaces.

Furthermore, observation of the same region of this sample under cross polarization conditions (Figure 4) indicates that crystal growth within the liquid phase I results in a morphology that produces more optical retardation than the morphology obtained by crystal growth in liquid phase II.[28] Examination of Figure 4 also suggests that, at 145 °C, the average radial direction of crystal growth is preserved during the crossing of the various liquid–liquid interfaces. Since spherulitic growth of the it-PP component proceeds continuously through both liquid phases without a large change in the growth rate, one must conclude that both liquid phase I and liquid phase II contain a nonnegligible volume fraction of the it-PP component. The observation of higher nucleation density, slightly faster crystal growth, and higher optical retardation in liquid phase I than in liquid phase II strongly suggests that liquid phase I is the it-PP-rich phase whereas liquid phase II is the it-P1B-rich phase. This statement finds further support from the observation that the overwhelming majority of the small droplets observed in Figure 3a are of the liquid phase I type, as would be expected for the minor component (it-PP) of a 30/70 (it-PP/it-P1B) blend. One should also note that the crystal growth rate through these phases is linear, indicating that there is no significant rejection of the it-P1B component in the interspherulitic liquid. The melting behavior of the sample crystallized at 145 °C for 210 min (Figure 3f) is shown through a succession of optical micrographs taken during heating at a rate of 5 °C/min (Figure 5a–f). This sequence of micrographs clearly indicates that the it-PP crystals grown from the it-P1B-rich liquid phase melt about 8–10 °C below those formed in the it-PP-rich liquid phase. This observation will be further discussed in the context of our DSC studies.

Spherulitic growth has also been studied at a crystallization temperature of 130 °C after a 5-h residence time in the melt at 180 °C. Optical micrographs recorded at various crystallization times are showed in Figure 6a–d. The it-PP crystallization behavior is similar to that

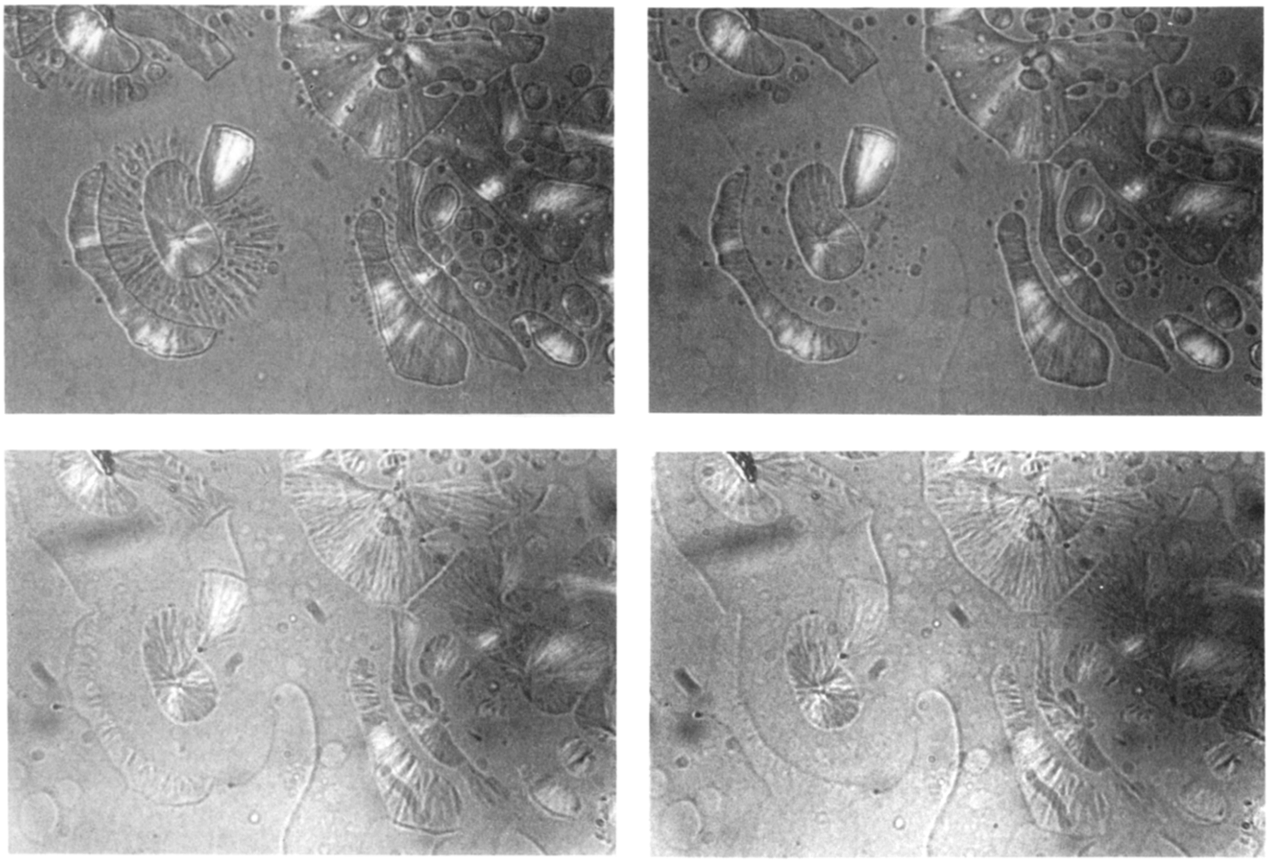

Figure 5. Optical micrographs of a 30/70 it-PP/it-P1B blend at various temperatures during heating from 145 to 180 °C at a rate of 5 °C/min. This sample was isothermally crystallized at 145 °C for 210 min after residing at 180 °C for 5 h (same region as on Figures 3 and 4): (a) 155, (b) 165, (c) 172, and (d) 173 °C (same magnification as in Figure 1a).

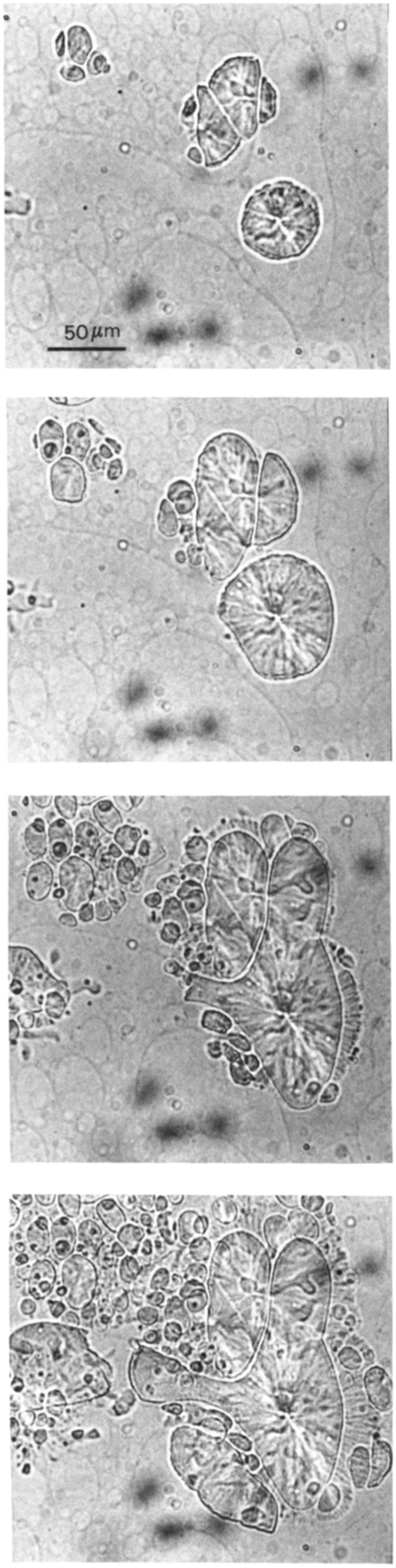

Figure 6. Optical micrographs of a 30/70 it-PP/it-P1B blend as a function of crystallization time at 130 °C after a 5-h residence time in the melt at 180 °C: (a) 3.25, (b) 5.25, (c) 8.75, and (d) 12 min.

observed at higher crystallization temperature, with the difference that crystal growth rates in the two liquid phases are now of different magnitude. The spherulitic growth rate is estimated to be 4.4 ± 0.4 times faster in the it-PP-rich phase than in the it-P1B-rich phase at 130 °C. Note that for the same residence time and temperature in the melt, crystallization at 135 °C is 2.6 ± 0.6 times faster in the it-PP-rich phase than in the it-P1B-rich phase. These observations indicate that the difference in it-PP crystal growth rate between the it-PP-rich phase and the it-P1B-rich phase increases with decreasing crystallization temperature. Furthermore, at a crystallization temperature of 130 °C, the population of it-PP crystals growing in the it-P1B-rich phase is smaller than that observed at the higher crystallization temperature. This observation is consistent with reports of a lower crystallinity for the it-PP component in blends crystallized at lower temperatures or under rapid cooling conditions.[4,5,7] It is also consistent with predictions from the solidification (Erstarrung) model proposed by Fischer and co-workers[29,30] or from crystal growth processes in regime III,[31,32] in which the crystallization of the it-PP component does not result in large-scale reorganization or long-range diffusion of the it-P1B molecules at the crystal growth front. Variation in the blend morphology during heating of the 30/70 it-PP/it-P1B blend crystallized at 130 °C is shown in Figure 7a–c for different temperatures above the crystallization temperature. As mentioned above, the population of it-PP crystals is smaller in the it-P1B-rich phase than in the it-PP-rich phase, and observation of the melting of the former crystals is thus more delicate. Inspection of micrographs 7a–c however suggests that crystals formed in the two liquid phases melt at approximately the same temperature.

Scanning Electron Microscopy. We will now turn our attention to the morphology of fracture surfaces observed for the 30/70 blend after quenching and cyclohexane extraction of the it-P1B component. Figure 8 shows SEM micrographs of three samples that were prepared under similar conditions with the exception of increasing residence time in the melt. Comparing micrographs 8a–c, one is compelled to observe an increase in the coarseness of the fractured surface. Such an increase in coarseness must be associated with an increase in the size of the it-P1B phase that is extracted. This observation confirms the occurrence of phase separation in the liquid state at temperatures above the melting of the it-PP component. The phase sizes determined by examination of the SEM micrographs compare very well with those observed in the optical microscopy study (Figure 1a–f). This observation also suggests that under quenching conditions, no significant long-range diffusion or rejection of either component is brought about by the rapid crystallization process. It also indicates that the morphology produced by liquid–liquid demixing in a relatively thin film (ca. 50 µm thick) is similar to that observed in bulk samples, as long as the average phase size is less than the film thickness. In later stages of demixing, the phase-separated morphology observed by optical microscopy (Figure 1d–f) seems to evolve more slowly, probably as a result of surface tension effects at the film/substrate interface.

Differential Scanning Calorimetry. Figures 9 and 10 show the melting behavior observed by differential scanning calorimetry for the pure it-PP and for the it-PP component in the 30/70 it-PP/it-P1B blend after isothermal crystallization at 130 and 145 °C, respectively. In previous reports,[10,13,24] we discussed observations of the

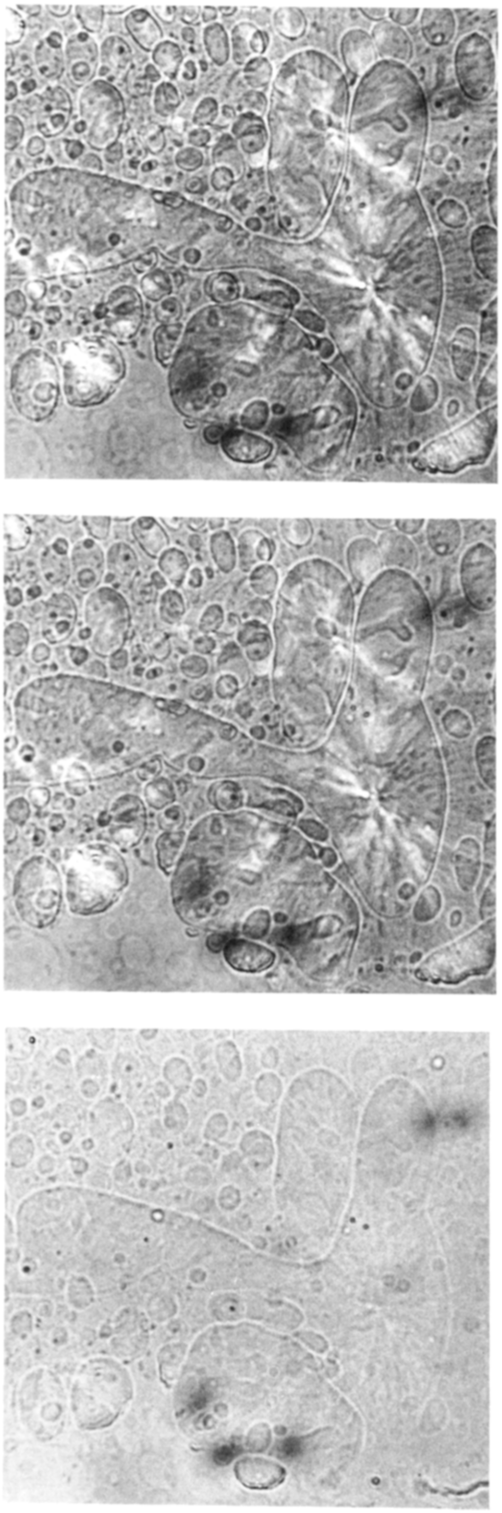

Figure 7. Optical micrographs of a 30/70 it-PP/it-P1B blend during heating at 5 °C/min from a crystallization temperature of 130 °C (a) 156, (b) 159.5, and (c) 164.5 °C.

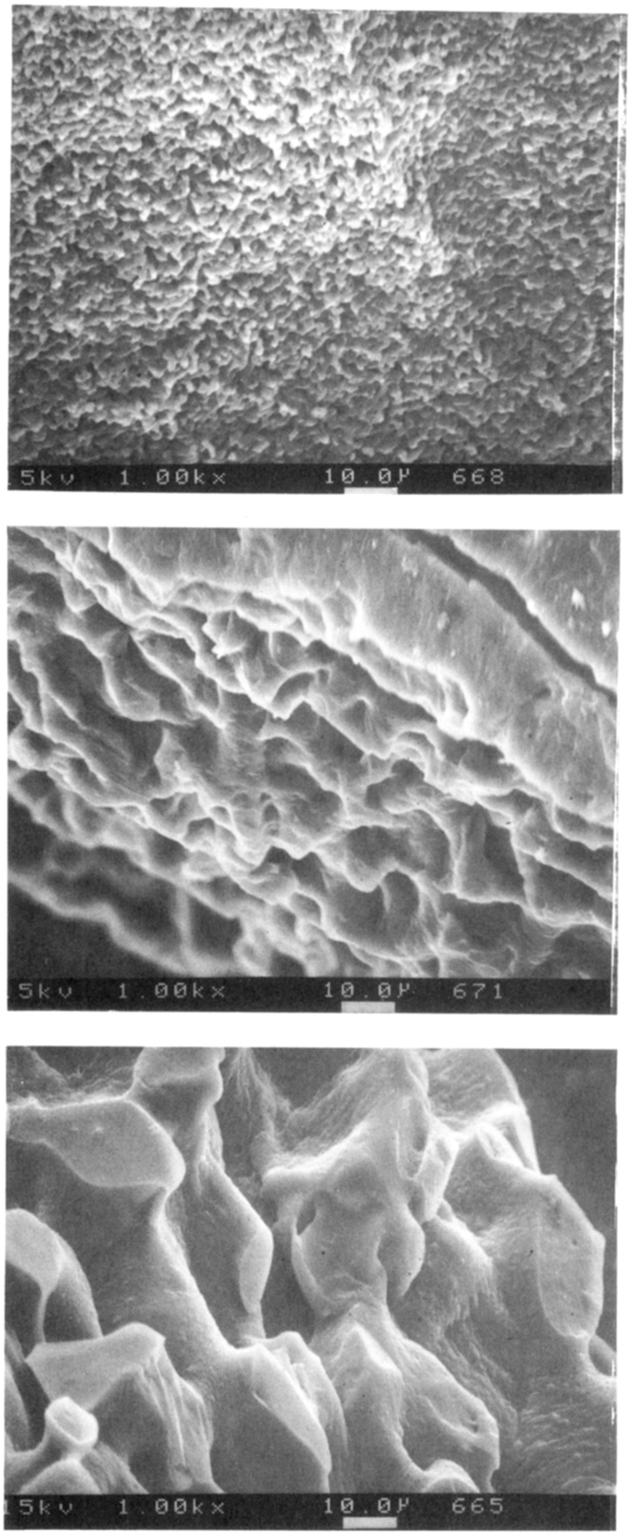

Figure 8. Scanning electron micrographs of the freeze fracture surfaces of it-PP/it-P1B blends quenched from the melt after various residence times in the melt: (a) 1, (b) 30, and (c) 60 min.

melting behavior of it-PP in blends of various compositions but we will only dwell here on the 30/70 blend. Although the melting curves for the pure it-PP and the blend crystallized at 130 °C exhibit the same general shape, some slight but significant differences must be noted. Specifically, the DSC heating trace for the blend is characterized by a broader endotherm and a slightly lower melting temperature than that of the pure it-PP homopolymer. The slight depression in the observed melting temperature and the broadening in the endotherm of the blend sample may be interpreted as arising from the melting of a distribution of lamellar it-PP crystals formed from liquid phases of various compositions. Recalling the morphological findings for the 30/70 blend crystallized at 130 °C, we expect (1) a smaller contribution to this endotherm from the melting of crystals formed within the it-P1B-rich phase and (2) crystals formed in these two liquid phases to melt at about the same temperature.

On the other hand, heating traces of samples crystallized at 145 °C exhibit very notable differences in the shape of the melting endotherm. The multiple-melting behavior

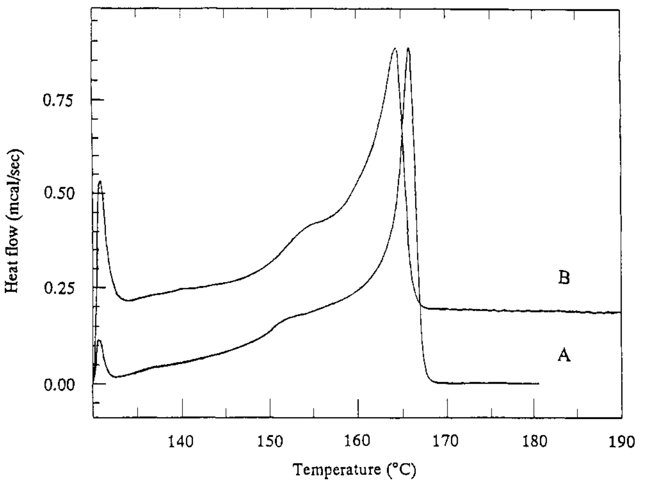

Figure 9. Heating traces (A) of pure it-PP and (B) of a 30/70 it-PP/it-P1B blend isothermally crystallized at 130 °C for 30 min after residing for 3 min in the melt at 180 °C.

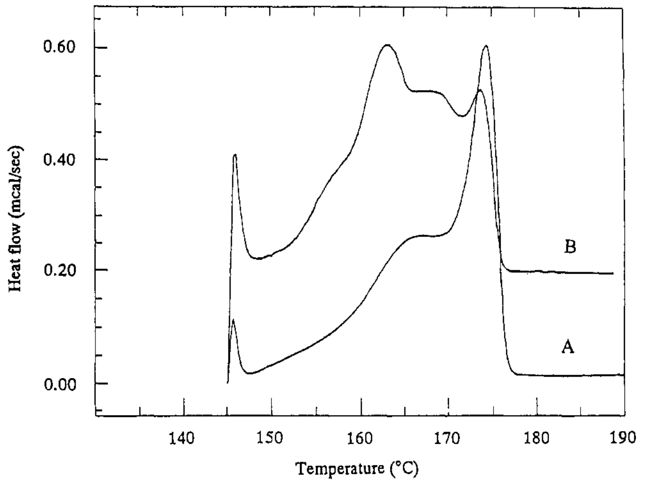

Figure 10. Heating traces (A) of pure it-PP and (B) of a 30/70 it-PP/it-P1B blend isothermally crystallized at 145 °C for 4 h after a 3-min residence in the melt at 180 °C.

exhibited by the 30/70 blend crystallized at 145 °C is consistent with the optical microscope observation of clearly distinct melting temperatures for it-PP crystals formed in the it-PP- and it-P1B-rich liquid phases, respectively. The temperature interval between the two main endothermic peaks in the DSC thermogram is determined to be 10 °C, which is very close to that observed visually by optical microscopy. One should also note that the temperature interval between these two melting transitions is approximately independent of either crystallization time or residence time in the melt. Also note that the relative ratio of these two endotherms is qualitatively consistent with the volume fraction of crystals formed in the it-PP- and it-P1B-rich phases (Figure 3f).

One must now attempt to explain the observed variation in the population of it-PP crystals in the it-P1B-rich phase with crystallization temperature. First, at 145 °C the crystal growth process is slower than at 130 °C and may provide enough time for the growing front of a given it-PP lamella to extract it-PP chains from the it-P1B-rich liquid phase. The observation of a linear but different growth rate in each phase indicates that the it-P1B component is rejected into the interlamellar or interfibrillar regions of the growing spherulites and not in the interspherulitic melt. At lower crystallization temperatures, the thermodynamic driving force toward crystallization is higher and it is likely that only the it-PP chains in the direct vicinity of the lamellar crystal front are able to crystallize. This diffusion-controlled process has been previously reported for semicrystalline polymer blends exhibiting miscibility in the liquid state.[33,34] The variation in the population of it-PP crystals in the it-P1B-rich phase may also be partially accounted for by considering the UCST character of this polymer blend. Since crystallization processes are studied at temperatures well below the spinodal, one may anticipate that at the time of crystallization, the liquid phases have already reached the compositions given by the binodal points. Consequently, at 130 °C the it-P1B-rich domains are more depleted in the poly(propylene) component than at 145 °C, and the variation in it-PP crystal growth rate with temperature in the two liquid phases reflects differences in melt composition. We note here that in mixtures of immiscible polymers such as poly(ϵ-caprolactone)/atactic polystyrene,[35-37] phase separation results in a very low degree of phase mixing and prevents the crystallization to proceed through the liquid–liquid interfaces.

One should also point out that the difference between the observed melting temperatures or the spherulitic growth rates for the it-PP crystals grown in the it-P1B- and the it-PP-rich liquid phases cannot be accounted for by the thermodynamic argument of an equilibrium melting temperature depression but must be related to different morphological features of the lamellar crystals growing in different environments. As mentioned earlier, using the Flory–Huggins theory with a χ parameter value of 0.0012 yields a depression in the equilibrium melting temperature of it-PP crystals much less than 1 °C, even when assuming that the it-P1B-rich phase contains only 5 wt % it-PP. It is interesting to note that in previous studies of the crystallization behavior of isotactic poly(propylene) from miscible blends of isotactic poly(propylene) with either atactic poly(1-butene) or atactic poly(propylene),[13] similar melting temperature depressions were observed for the it-PP component. Hoffman–Weeks analyses of it-PP/at-P1B blends, however, suggested that the depression was due to morphological effects since the T_m' vs T_x curves for various blend compositions appeared to merge at the highest crystallization temperatures. One should further point out that the multiple-melting behavior in the it-PP/it-P1B system cannot be accounted for by a melting–recrystallization behavior, as rates of crystallization become exceedingly low in the temperature range where the initial melting is observed. On the basis of X-ray diffraction studies by us and others, one can also rule out the possibility for various crystal structures[24] or even cocrystallization between poly(propylene) and poly(1-butene) to be at the origin of the multiple-melting behavior.[7,24]

Dynamic Mechanical Analysis. Finally, in view of the above findings and of the existing controversy in the literature, we decided to carry out dynamic mechanical analyses for the pure it-PP and it-P1B homopolymers and for the 30/70 it-PP/it-P1B blend. Quenched samples were used for this study so as to minimize the degree of crystallinity and to maximize the variation in loss modulus in the glass transition region. DMA traces for the pure it-PP, the 30/70 it-PP/it-P1B blend, and the pure it-P1B are shown in Figure 11. The loss peak for the it-PP/it-P1B blend is clearly located between those of the pure polymers. The glass transition temperatures for the it-PP/it-P1B blend and the it-P1B and it-PP homopolymers are determined at the maximum of the loss modulus peak and have values of −11, −19, and +6 °C, respectively. On this basis alone, one might have concluded, in agreement with previous studies,[2,4,5] that these two polymers form a

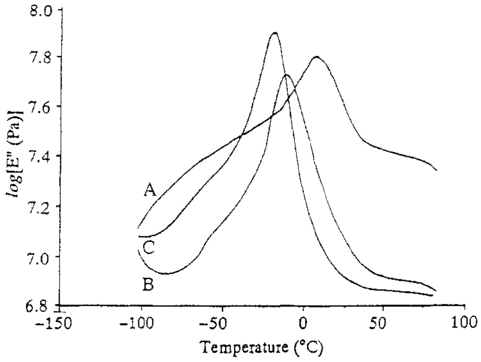

Figure 11. Dynamic mechanical analysis of (A) it-PP, (B) a 30/70 it-PP/it-P1B blend, and (C) it-P1B.

miscible mixture. Since the above morphological observations prove that they are partially miscible, we must reexamine the DMA data from a different point of view. In a heterogeneous blend, each phase should exhibit an individual glass transition temperature whose value may be estimated by the Fox equation[12,38] using values for the phase composition and for the T_g of each homopolymer. The fact that a single glass transition is observed for the blend in the plot of loss modulus vs temperature may then be interpreted as follows. Recalling that crystal growth was observed for the it-PP crystals through both liquid phases, one concluded that there must be a significant degree of molecular-level mixing within each liquid phase. The glass transition temperature of each phase may then be intermediate between those of the pure components, with a temperature slightly lower for the it-P1B-rich phase than for the it-PP-rich phase. Noting that the glass transition temperatures of the pure homopolymers only differ by 25 °C, those of the phase-separated regions will be even less distant from one another and may not be readily resolvable by the DMA technique. One may further add that in the quenched blend used for the DMA study, liquid–liquid demixing was allowed to proceed for much shorter times than in the optical microscope study from which we inferred a significant degree of phase mixing. One may also envision that for very short residence times in the melt (5 min), the liquid–liquid demixing process produces liquid phases that may not have yet reached their equilibrium binodal concentrations. If such is the case, the liquid phases would exhibit a higher degree of phase mixing than predicted from the binodal values and their glass transition temperatures would be even closer and more difficult to resolve than in blends that would undergo a larger extent of demixing.

Finally, these observations provide an impetus to study the origin of the appealing mechanical properties of these blends. Studies of the crystal growth and melting behavior of the it-PP component in these blends and examination of the dynamic mechanical properties suggested high degrees of molecular-level mixing within each of the two liquid phases. It would be of interest to compare the dynamic mechanical or the tensile behavior of blends crystallized at a given temperature but after different residence times in the melt. One would predict that for longer residence times in the melt, further demixing would occur and the interphase boundary would become sharper. In blends that have undergone larger extents of demixing, one may also be able to resolve two individual glass transitions by DMA as is suggested from a simple superposition of the loss modulus curves for the pure homopolymers.

4. Further Discussion

Having discussed the various observations made in this study of it-PP/it-P1B blends and proposed a plausible interpretation of our data, we should examine these results in the light of similar experiments carried out by Hashimoto et al.[39,40] They studied the liquid–liquid demixing in 50/50 and 70/30 w/w mixtures of it-PP and ethylene–propylene copolymers (EPR) by a combination of polarized and depolarized light scattering and optical microscopic techniques. Hashimoto et al.[39,40] showed that rapidly crystallized blends exhibit a memory of the liquid–liquid demixing process occurring before crystallization. The "structure memory" was characterized as a function of demixing time in the liquid by a time-dependent wavelength, Λ_m, for the periodic spatial concentration fluctuation resulting from the spinodal decomposition and the subsequent coarsening processes. Under conditions of rapid crystallization, the liquid–liquid phase-separated structures obtained by melt demixing are locked in by the crystallization process. Spherulitic growth of the it-PP component after a 3-min residence time in the melt at 200 °C was observed to take place linearly as a function of crystallization time at low temperature (140 °C) but nonlinearly at a higher crystallization temperature (145 °C). Furthermore, identical spherulitic growth rates for the 70/30 and the 50/50 blends were measured at 140 °C and suggest that each domain in the demixing mixtures already reached the equilibrium concentration determined by the binodal points at 200 °C. The experimental observation of liquid–liquid demixing and locking in of the liquid–liquid phase-separated morphology by the crystallization process described in this paper for the 30/70 it-PP/it-P1B blend are consistent with the conclusions drawn by Hashimoto et al. on it-PP/EPR blend.

However, differences are noted in the crystallization behavior of the it-PP component in these two different blends. Whereas we observed the effect of crystallization temperature on the crystal growth behavior of poly(propylene) in both liquid phases, Hashimoto et al. only described the crystallization of it-PP in the poly(propylene)-rich phase (the major phase in their 50/50 or 70/30 blends). In contrast with their observation of a nonlinear spherulitic growth behavior at 145 °C, our observations indicate that the crystal growth behavior is linear throughout, until impingement. Furthermore, we feel that the decrease in crystal growth rate for the it-PP component with increasing it-P1B content in a given liquid phase is not due to a depression of the it-PP equilibrium melting temperature but simply to the lower concentration of crystallizable polymer chains at the lateral melt/crystal interface. From our observation of a temperature dependence of the ratio of crystal growth rates in the two liquid phases, we suggest that the composition of the liquid phases is given by the binodal curve at the crystallization temperature and not at the melting temperature. Whether these equilibrium concentrations are reached before the crystallization is initiated or at early stages during the crystallization process will certainly depend on the crystallization temperature and the associated rates of crystal nucleation and growth. We believe that our position is supported by the fact that the experimental range of crystallization temperatures is located at least 100 °C below the spinodal temperature. Under such demixing conditions, the early and intermediate stages[41] of phase separation must be relatively fast[39] and should lead to a rapid establishment of the equilibrium composition within each phase. One should further note that the scaling exponent appearing in the power law between the scattering vector, q_m, associated with the dominant fluctuation, Λ_m, and the demixing time is reported by Hashimoto et al. to vary between $^1/_3$ and $^2/_3$. Such an exponent value indicates that the demixing has already entered the transition stage[41] for residence times in the melt as short as a few seconds and has already resulted in liquid phases exhibiting equilibrium compositions.

These observations lead us to ask the following questions about the level of phase mixing achieved during the blending process. How does the shearing process during the blending affect the UCST, and what is the time scale necessary to achieve equilibrium compositions within the phase-separated liquid? What is the time scale for the readjustment of the composition of each phase after a deep quench from the melting temperature to a crystallization temperature located at least 100 °C below the spinodal temperature? Our studies suggest that the composition within each liquid phase depends on the temperature reached after the deep quench, but we did not observe further liquid–liquid demixing upon reaching the various crystallization temperatures. What is the temperature dependence of this "relaxation" process? Although we do not yet have answers to these questions, ongoing model studies with blends of isotactic poly(propylene) and atactic poly(1-butene) which exhibit an upper critical solution temperature in the vicinity of the poly(propylene) melting temperature may shed some light on some of these issues.

5. Conclusions

Optical microscopic observations of a 30/70 w/w it-PP/it-P1B blend in its liquid state indicate that this mixture is not fully miscible at the molecular level at temperatures as high as 80 °C above the it-PP melting temperature. These observations were confirmed by SEM studies of the fracture surface of quenched blends. At a crystallization temperature of 145 °C, the spherulitic growth of it-PP spherulites is observed to proceed continuously, with a slightly decreasing rate (1.4 times slower), from the it-PP-rich liquid phase into the it-P1B-rich liquid phase. Crystals formed in the it-P1B-rich phase are observed to melt about 8–10 °C below the crystals formed in the it-PP-rich phase. This fact is consistent with the complex multiple-melting behavior of poly(propylene) in it-PP/it-P1B observed by calorimetric measurements by us and others. For a lower crystallization temperature (130 °C), the rate of crystal growth in the it-PP-rich phase is about 4.4 times greater than in the it-P1B-rich liquid phase. A similar melting behavior for pure it-PP and the it-PP component in the blend is observed which is partially accounted for by a decrease in the population of it-PP crystals formed in the it-P1B-rich phase at lower crystallization temperatures. The observation of a single DMA loss modulus peak in quenched it-PP/it-P1B blends is explained in terms of a process of macrophase separation which results in retention of a notable degree of phase mixing and which may not have reached the stage where the composition of the liquid phases becomes invariant. Our studies suggest that the excellent mechanical properties of it-PP/it-P1B mixtures arise primarily from the high degree of phase mixing in the macrophase-separated blend.

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