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Morphology and phase behaviour of blends of syndiotactic and isotactic polypropylene: 2. Differential scanning calorimetry, light transmission measurements, and PVT measurements

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Blends of isotactic and syndiotactic polypropylene were studied by differential scanning calorimetry (d.s.c.), light transmission measurements and pressure–volume–temperature (PVT) measurements. D.s.c. measurements show the absence of any kind of melting point depression in the blends. Furthermore, the change of the ratio of crystallized i-PP and crystallized s-PP in the blends as a function of crystallization temperature is discussed. PVT and light transmission measurements reveal that the rate of crystallization depends stronger on the crystallization temperature for i-PP than for s-PP. Thus at higher degrees of supercooling the crystallization of i-PP is faster and at lower supercoolings s-PP is able to crystallize faster. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

In the first part of this contribution, it has been shown that blends of isotactic polypropylene (i-PP) and syndiotactic polypropylene (s-PP) crystallize separately and that they are also immiscible in the melt[1]. This was demonstrated by X-ray measurements and different microscopic techniques. This part deals mainly with the calorimetric and dilatometric properties of the blends of i-PP and s-PP during the crystallization process. Additionally, light transmission measurements are carried out in order to study the kinetics of the melting and crystallization processes.

EXPERIMENTAL

Materials and blend preparation

The materials, their characteristic data, and the blend preparation were described in full detail in the first part of this work[1].

Light microscopic measurements

The samples for measurements of the relative light intensity between crossed polarizers were made by melting the powder between two cover glasses. The layer thickness was about 40 μm. The samples were held for 10 min at 180°C and then quenched to the crystallization temperature with a rate of 30°C min^{-1}. The light microscopic investigations were carried out with an Olympus-Vanox AH2 microscope and a Linkam TMS 90 hot stage that allows observation during isothermal crystallization. The light intensity between crossed polarizers was measured with a photocell in the microscope, and normalized. This means that the constant light intensity after long crystallization times was taken as 100% and the initial value as 0%. A video camera was used in order to measure the spherulite radius of i-PP as a function of crystallization time. This resulted in straight lines and the slope is the spherulite growth rate.

Differential scanning calorimetry

D.s.c. measurements were carried out with a Perkin Elmer DSC 7 apparatus. The isothermally crystallized samples were quenched to room temperature and then heated to 200°C with heating rates of 10°C min^{-1}, 20°C min^{-1} and 30°C min^{-1}.

Pressure–volume–temperature measurements

The PVT data were obtained using a Gnomix PVT apparatus[2]. The sample cell was filled with 1 g of the neat polymers and with 1 g of the blend, respectively, and mercury. The cell was closed on one end by flexible bellows, and the volume change as a function of time was measured at 10 MPa and isothermally at 140°C.

RESULTS AND DISCUSSION

Figure 1 shows a hysteresis curve of the melting and crystallization process of neat i-PP, neat s-PP and

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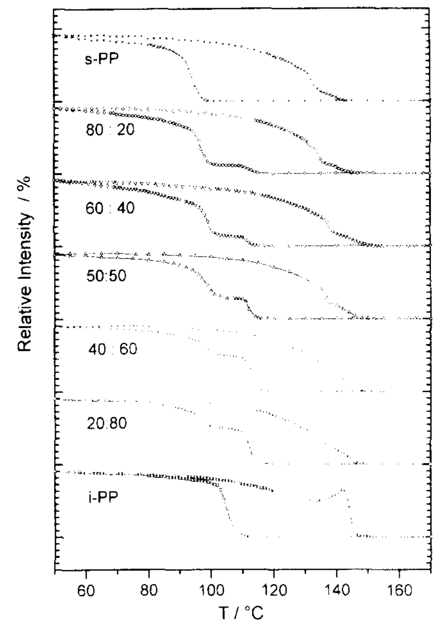

Figure 1 Hysteresis curves of the melting (upper curves) and crystallization (lower curves) of i-PP/s-PP blends having different compositions and the corresponding neat polymers obtained by measuring the relative light intensity in an optical microscope using crossed polarizers. The heating and cooling rate was 10°C min^{-1}

different blends obtained by measurements of the relative light intensity of the samples between crossed polarizers applying heating and cooling rates of 10°C min^{-1}. For the neat s-PP the melting and crystallization is reflected in a continuous decrease and increase, respectively, of the relative light intensity. The change in the intensity is caused by the crystallization and melting process, respectively, which yields or erases chainfolded crystallites able to change the plane of the polarized light^3. The upper curves always represent the melting process and the lower curves the crystallization process. The i-PP sample shows a different behaviour. Shortly before the melting process is finished, an increase in the relative light intensity occurs. This increase can be explained by a transition from type I to type II spherulites^4. The transition is connected with the melting of daughter lamellae, i.e. the cross hatching disappears, and the formation of more perfect lamellae forming the type II spherulite^4. The stepwise transition in the crystallization curves depends on the blend ratio and is discussed below.

Figure 2a shows d.s.c. traces for a 50:50 wt% blend isothermally crystallized at different temperatures. The heating rate was 20°C min^{-1}. At crystallization temperatures of 115 and 120°C the d.s.c. traces show a single melting peak with a small shoulder at higher temperatures. Applying higher crystallization temperatures (ranging from 125 to 135°C), this shoulder shifts towards higher temperatures and finally appears as a second peak. It is possible to simulate all these d.s.c. traces using d.s.c. traces of the neat polymers, crystallized at the same

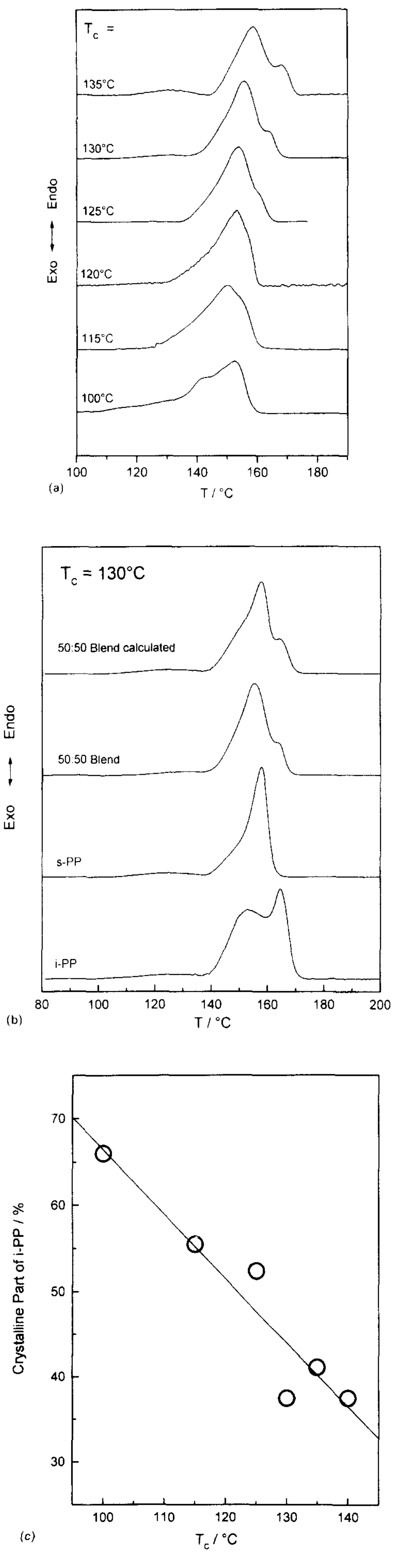

Figure 2 (a) D.s.c. heating curves of i-PP/s-PP 50/50 (wt%) blends isothermally crystallized at different temperatures; (b) d.s.c. traces of the neat polymers and a 50/50 (wt%) blend isothermally crystallized at 130°C. The upper trace is calculated (for detail see text); (c) measured crystalline fraction of i-PP in 50/50 (wt%) blends after crystallizing at different temperatures and reaching the plateau value in the light intensity measurements

temperature. An example for a blend, isothermally crystallized at 130°C, is shown in *Figure 2b*. It is clearly demonstrated that the discussed second peak originates from the crystallization of i-PP. Using the Hoffmann–Weeks procedure[5,6] for the determination of equilibrium melting points and the maximum temperature of the second peak yields the same temperature for neat i-PP and the i-PP in the blend. The absence of any melting point depression is also an indication for the complete immiscibility of i-PP and s-PP[7].

Quantitative evaluation of the simulated peak areas of the d.s.c. traces provides information on the ratio of crystallized i-PP and s-PP in the blend. For these calculations, the peaks of the neat polymers are weighted and fitted to the peak of the blend. *Figure 2c* shows that the amount of crystallized i-PP in the blend is a function of the crystallization temperature. The blend ratio in the as-prepared material is 50/50 (wt%) but the crystalline material in blends, isothermally crystallized at 100°C, contains e.g. 66% i-PP. The crystallized material at $T_c = 140$°C contains 40% of crystalline i-PP. This is also supported by the measurement of the heat of fusion of the neat components and a 50/50 (wt%) blend in dependence on the crystallization temperature as shown in *Figure 3a*. For the neat polymers, the heat of fusion increases as expected with increasing crystallization temperature. The heat of fusion of the i-PP is clearly larger than the heat of fusion of s-PP. This is mainly caused by the lower degree of crystallization of the s-PP. Different values for the heat of fusion of a 100% crystalline s-PP are reported[8–10]. Using the highest reported value of 196.6 J/g[8], the degree of crystallization is 32.5% for s-PP isothermally crystallized at a temperature of 140°C, and 50% for i-PP with the same thermal history (using the value for 100% crystalline i-PP of 209 J/g[11]). The decrease of the melting enthalpy with increasing melting temperature for the 50:50 (wt%) blend seems to be surprising. *Figure 3b* shows the linear regression line taken from *Figure 3a* (dotted line) and the calculated values assuming that the crystallized material contains 50% i-PP and 50% s-PP (full line). Thus the assumption that the crystallized material contains equal amounts of i-PP and s-PP is obviously wrong as already discussed. The explanation can be given by keeping in mind the ratio of the polymers in the crystallized material (see *Figure 2c*). At high crystallization temperatures the s-PP dominates in the crystalline material. As already discussed the heat of fusion (i.e. the measured value and not the value of 100% crystalline material) of the s-PP is also much lower than the heat of fusion of i-PP. The amount of the polymer in the crystalline material with the lower heat of fusion increases with increasing crystallization temperature. Thus the decrease of the heat of fusion with increasing crystallization temperature as shown in *Figure 3a* can be interpreted. The dashed line in *Figure 3b* represents the calculated heat of fusion of the blends, using the heat of fusion of the neat polymers and the real amount of crystalline s-PP and i-PP taken from d.s.c. data. This line is in a reasonably good agreement with the regression line of the measured blend (dotted line).

The phenomenon described above can be explained with different temperature dependencies of the crystallization rates for the two neat polymers. *Figure 4* shows

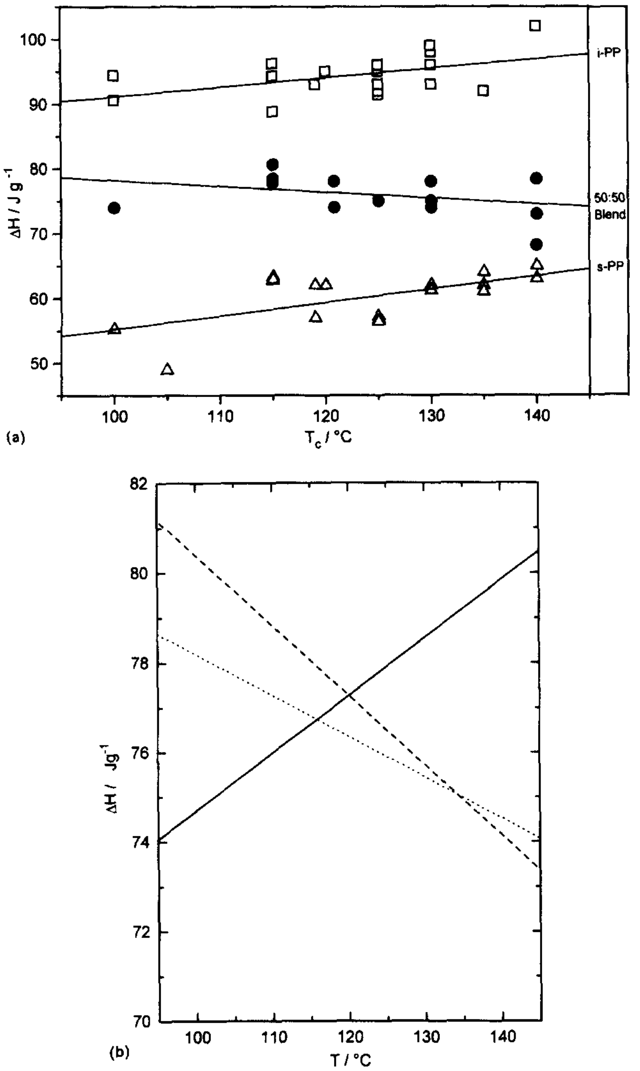

Figure 3 (a) Enthalpy of fusion (ΔH) for neat i-PP, s-PP and a 50/50 (wt%) blend isothermally crystallized at different temperatures measured by d.s.c.; (b) ΔH_M *versus* crystallization temperature for 50/50 (wt%) blends; measured (dotted line), calculated assuming 50/50% i-PP and s-PP in the crystalline state (full line) and calculated assuming weighted fraction of crystallized i-PP and s-PP as discussed in the text (dashed line)

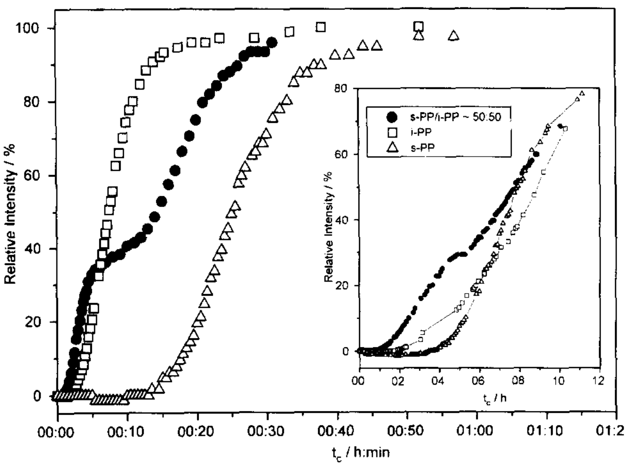

Figure 4 Relative light intensity measured in an optical microscope with crossed polarizers as a function of crystallization time for i-PP, s-PP and a 50/50 (wt%) blend isothermally crystallized at 120 and at 135°C (inset)

the relative intensity of the transmitted light as a function of crystallization time when the i-PP, the s-PP and a 50/50 (wt%) sample is placed between crossed polarizers. The crystallization temperature is 120°C. The curve of the 50/50 (wt%) blend shows a clear step. The initial increase is in agreement with that one of neat i-PP and the second part of the curve starts to increase at the same time when s-PP starts to crystallize. Thus the curve of the blend can be considered to be composed of the two separate crystallization processes of the neat polymers. It has been shown in *Figure 1* that the position of the step is a function of the blend composition. The beginning of the step in the curve of the blend in *Figure 4* is also identical with the occurrence of space filling spherulites of i-PP as could be detected by optical microscopy. In the first part of this contribution it has been explained that the i-PP spherulites were space filling before the s-PP crystallization started (at a crystallization temperature of 120°C). At a crystallization temperature of 135°C, this behaviour is changed completely. The typical s-PP structures appear before the i-PP spherulites fill the space completely. The inset in *Figure 4* shows the relative light intensity as a function of crystallization time at a crystallization temperature of 135°C. The s-PP crystallizes approximately as fast as the i-PP and the step in the blend curve almost disappeared. A comparison of both relative intensity measurements shows unambiguously that the decrease of the crystallization rate of s-PP with increasing crystallization temperature is smaller than the crystallization rate decrease of the i-PP. It can be assumed that in regions already filled with structures of one polymer, the crystallization of large amounts of the second polymer is hindered simply by sterical reason. This causes also the increasing amount of crystallized s-PP in the blends annealed at lower supercoolings. Furthermore, it can be seen that the relative intensity of the 50/50 (wt%) blend increases in the initial stage faster with the crystallization time than the curves of the respective neat polymers. This behaviour might be caused by two different phenomena. Firstly, it is possible that the spherulite growth rate of i-PP in the blends is faster than for the neat i-PP. But a comparison of both spherulite growth rates at different crystallization temperatures shows that they are nearly identical (see *Figure 5*). Secondly, the faster increase of the light intensity for blends compared to the neat components might be caused by a higher nucleation density in the blends. The inset of *Figure 5* shows the relative number of growing spherulites for different blend ratios. 'Relative' means that the number of spherulites per unit area is related to the number of spherulites in the same area in pure i-PP having the same thermal history. There are up to 20 times more spherulites per unit area in the blends compared to neat i-PP. Thus s-PP is a nucleation agent for i-PP as already discussed in the first part of this contribution.

The hindered crystallization of a polymer in areas where a different polymer already formed supermolecular structures has also implications on the melting behaviour of polymer blends containing two semicrystalline polymers. The observed melting behaviour of the blends is thus not simply the opposite process of the crystallization. Due to the phase separation of the blends in the liquid state, the re-melting of the crystallized samples occurs separately for s-PP and i-PP, respectively. During the re-melting of samples, isothermally crystallized at relatively large supercoolings (crystallization temperatures < 125°C), the phases cannot be distinguished. Observed between crossed polarizes, these samples become continuously darker during the re-melting. In samples crystallized at lower

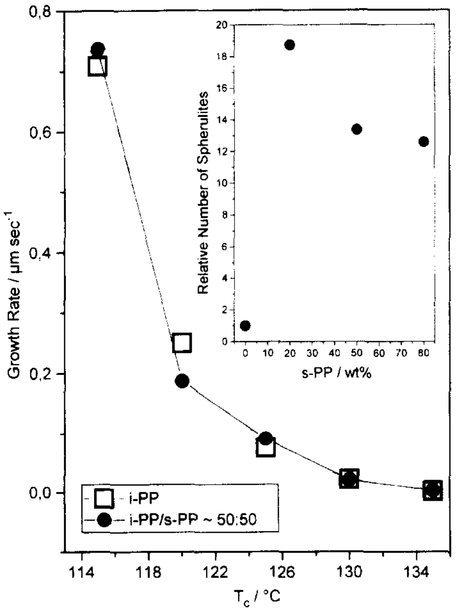

Figure 5 Spherulite growth rate as a function of crystallization time for neat i-PP and for i-PP in a 50/50 (wt%) blend of i-PP and s-PP. The inset shows the relative number of spherulites in i-PP/s-PP blends relative to the number in neat i-PP isothermally crystallized at 125°C

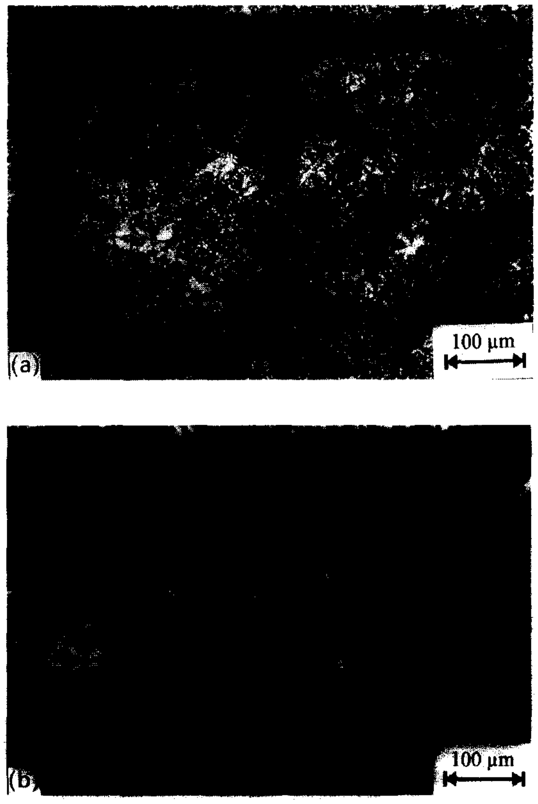

Figure 6 Light micrographs of i-PP/s-PP 50/50 (wt%) blends: (a) isothermally crystallized at 135°C; (b) the same sample but then slowly heated with 0.2°C min^{-1} to 159°C

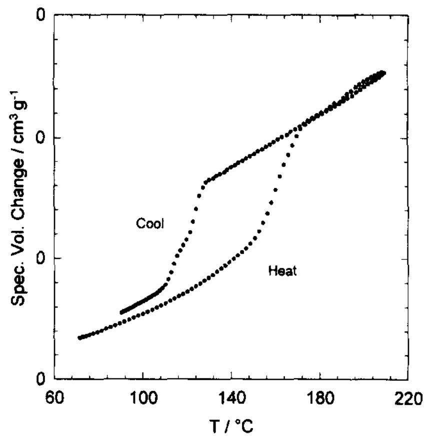

Figure 7 Hysteresis curve for the melting (lower curve) and crystallization (upper curve) of an i-PP/s-PP 50/50 (wt%) blend obtained by PVT measurements at $p = 10\,\mathrm{MPa}$

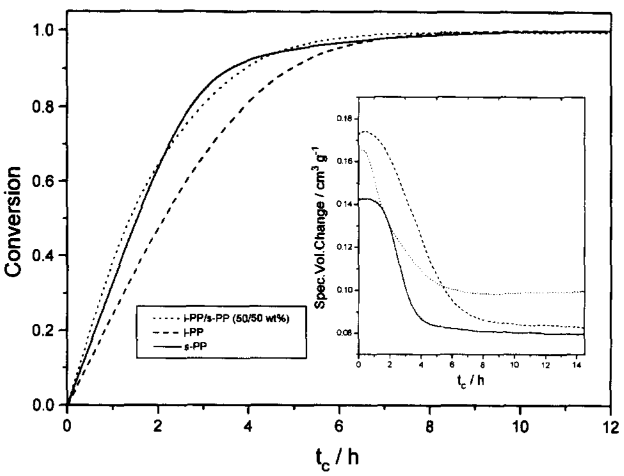

Figure 8 Conversion as a function of time for the isothermal crystallization at 140°C and $p = 10\,\mathrm{MPa}$. The inset shows the decrease of the specific volume during isothermal crystallization in a PVT apparatus at $p = 10\,\mathrm{MPa}$ and 140°C

supercoolings and re-melted with a heating rate of 0.2°C, the different polymers can clearly be observed separately as can be seen in *Figures 6a* and *b*. The melting point of s-PP is 12°C lower compared to i-PP when isothermally crystallized at 135°C. Therefore, the syndiotactic mosaic structures melt first, and the spherulites remain unaltered. Additionally, the spherulites of i-PP seem to grow and become more ordered than before. This is in agreement to the described sterical problem to form large regular spherulites of i-PP in the blends. Therefore, it can be assumed that the i-PP included in domains which contain mainly s-PP is able to crystallize after the s-PP is molten. This is only possible in the case that the i-PP in the s-PP rich phase has a lower melting point compared to the i-PP in the i-PP rich domains or that a large amount of amorphous i-PP is present in the s-PP rich domains. The re-crystallization or reorganization process of i-PP during the heating below the melting point is suppressed when fast heating rates are applied as already observed for a number of different polymers[12–14].

In order to confirm the results obtained by light microscopy and d.s.c., PVT measurements are carried out. The PVT apparatus is able to detect the volume change during crystallization. *Figure 7* shows the hysteresis curve of an i-PP/s-PP 50/50 (wt%) blend. In agreement with the hysteresis curves obtained by light microscopy (*Figure 1*), a step in the cooling run and a smooth transition in the heating run can be observed. Again, this can be assigned to the separate crystallization of i-PP and s-PP in the blend. The change of the specific volume as a function of crystallization time for the neat polymers and a 50/50 (wt%) blend isothermally crystallized at 140°C is shown in the inset of *Figure 8*. It can be seen that at this crystallization temperature the s-PP and the i-PP/s-PP 50/50 (wt%) blend crystallize significantly faster compared to neat i-PP. This is in agreement with microscopic measurements carried out at a crystallization temperature of 135°C (see inset of *Figure 4*). The small maximum of the specific volume as a function of crystallization time in the initial stage might be an artefact of the PVT measurement. A possible reason could be the overshooting during the cooling to the crystallization temperature before reaching the isothermal state. Finally, the conversion *versus* crystallization time is shown in *Figure 8*. Here, the conversion is defined as the relative volume change in dependence on the crystallization time. The area below the curves, shown in the inset of *Figure 8*, indicating the volume change is normalized to 1. Again, the main conclusion of the experiments concerning the crystallization kinetics is proved. At lower supercoolings the s-PP is able to crystallize faster than the i-PP and acts simultaneously as a nucleation agent for i-PP.

CONCLUSION

Again, it can be shown that blends of i-PP and s-PP are completely phase separated. The morphology of the blends is widely influenced by the crystallization kinetics. The rate of crystallization of i-PP is higher compared to s-PP at large supercoolings and vice versa at low supercoolings. At low supercoolinigs much more s-PP nuclei are formed which are able to act as nucleation agents for i-PP. Therefore, the whole blend crystallizes faster at low supercoolings compared to neat i-PP.

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REFERENCES

1 Thomann, R., Kressler, J., Setz, S., Wang, Ch. and Mülhaupt, R. *Polymer* 1996, **37**, 2627
2 Zoller, P., Bolli, P., Pahud, V. and Ackerman, H. *Res. Sci. Instrum.* 1976, **49**, 948
3 Sawyer, L. C. and Grupp, D. T. 'Polymer Microscopy', Chapman and Hall, London, 1987
4 Viehweg, Schley and Schwarz 'Polyolefine', Carl Hanser, Munich, 1969
5 Wunderlich, B. 'Macromolecular Physics', Vol. 3, Academic Press, New York, 1980
6 Hoffmann, J. D. and Weeks, J. J. *J. Res. Natl Bur. Stand., Sect. A* 1962, **66A**, 13
7 Nishi, T. and Wang, T. T. *Macromolecules* 1975, **8**, 909

8 Hafka, S. and Könnecke, K. *J. Macromol. Sci.* 1991, **B30**, 319
9 Galambos, A., Wolkowicz, M., Ziegler, R. and Galimberti, M. *Polym. Mater. Sci. Eng.* 1991, **64**, 45
10 Balbontin, G., Dainelli, D., Galimberti, M. and Paganetto, G. *Makromol. Chem.* 1992, **193**, 693
11 Antberg, M., Dolle, V., Haftka, S., Rohrmann, J., Spaleck, W., Winter, A. and Zimmermann, H. J. *Makromol. Chem., Macromol. Symp.* 1989, **30**, 428
12 Flory, P. J. 'Principles of Polymer Chemistry', Cornell Univ. Press, Ithaca, New York, 1953
13 Hobbs, S. J. and Pratt, C. F. *Polymer* 1975, **16**, 462
14 Groeninckx, G., Reynaers, H., Berghmans, H. and Smets, G. *J. Polym. Sci., Polym. Phys.* 1980, **16**, 261