Competition between α and γ phases in isotactic polypropylene: effects of ethylene content and nucleating agents at different cooling rates

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Abstract

The influence of ethylene content, nucleating agents and cooling rate upon the formation of γ phase in isotactic polypropylene is investigated. Detailed analysis of wide angle X-ray diffraction shows that some γ phase can appear even in copolymers of very low ethylene content (0.5 mol.%). Differential scanning calorimetry shows a double melting peak. Nucleating agents of different types are found to enhance γ phase crystallization, even in high molecular weight homopolymers. In any of the materials studied the amount of γ phase decreases with increasing cooling rate, going to zero at a cooling rate of about $10°C \, s^{-1}$. We interpret the observations in terms of the kinetics of growth and the phase stability, which shows that: (a) there is a region in which the γ phase has a lower free energy than the α phase; and (b) this region reaches lower temperatures with increasing comonomer content. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Isotactic polypropylene; α and γ phases; Ethylene content

1. Introduction

Isotactic polypropylene (iPP) is on the one hand an 'ordinary' commodity polymer with a very simple chemical structure. On the other hand despite its chemical simplicity it shows a remarkable complexity of crystal structures, and self-assembly behavior [1,2]. Control of the growth of the different polymorphs as a function of material grade and crystallization conditions is of great technological importance.

Many studies have therefore been carried out with the aim of understanding the complex crystallization scenario. Concerning the crystal structures themselves, this work is concerned with the α and γ modifications. The monoclinic α phase is the most prevalent. It is generally the majority phase observed both in melt and solution-crystallized samples prepared at atmospheric pressure. For the γ phase, initially indexed as triclinic [3,4], studies of a form generated at atmospheric pressure from low molecular weight polymer led to a reassignment of the structure as orthorhombic [5] with a unique crossed arrangement of the chains in subsequent growth layers. It has an epitaxial relationship with the α phase such that either can grow onto lamellae of the other phase [6,7]. In general, however, the α

phase is observed to grow first, followed by epitaxial growth of the γ phase, rather than the other way round [8]. The amount of γ phase generated is known to be enhanced by (i) crystallization under high pressure [9,10], (ii) low molecular weight [4,11] (iii) the presence of chain defects or chemical heterogeneity caused by atacticity [12,13], and (iv) ethylene comonomer units in the chain [4,14–16].

The latter effect was first noticed by Turner-Jones et al. [4]. Zimmermann [14] investigated random polypropylene–ethylene copolymers with ethylene contents from 4.3 to 11 mol.%. From the wide angle X-ray diffraction (WAXD) patterns the author determined the amount of γ-phase formed. Although he concluded that γ-phase can first be detected for an ethylene content of 5 mol.%, close inspection of the WAXD pattern of the 4.3 mol.% sample shows a clear sign of the γ phase, namely a small peak at just above $2\theta = 20°$ (as will be explained in Section 3).

More recently, detailed studies on the γ phase have been carried out by Laihonen et al. [16] and Mezghani et al. [15,17]. They confirmed the earlier findings that the amount of γ phase is proportional to the ethylene content, and show that more material crystallizes in the γ phase at low supercoolings and a smaller cooling rate. A maximum in the fractional content of the γ phase reported by Mezghani et al. [15] has recently also been found in an investigation of metallocene catalyzed polypropylenes with different defect concentrations [13]. For homopolymers [17] the amount of

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Table 1
Materials studied and their molecular weight (Mw), molecular weight distribution (Mwd), xylene solubility (Xs), comonomer content and nucleating agent

Material	Mw	Mwd	Xs	% ethylene	Nucleating agent
M7	377 000	4.8	2.3	0.0	–
M7N	379 000	5.3	3.4	0.0	Talc 1000 ppm
M4	268 000	5.0	3.8	0.0	–
M4N	277 000	5.1	4.1	0.0	DBS 2000 ppm
M3	213 000	4.3	2.8	0.0	–
M9	380 000	3.8	5.0	0.5	–
M16	293 000	7.3		3.1	–
M14	293 000	7.3		3.1	DBS

γ phase formed increases with pressure and crystallization temperature, so that it becomes possible at e.g. 125 MPa to grow pure γ phase material. Based on their extensive data, Mezghani and Phillips [17] were able to derive equilibrium melting point data and construct a temperature–pressure phase diagram for the α and γ forms.

This study presents recent results on the influence of ethylene content, nucleating agents and cooling rate upon the γ phase formation. The novelty of this work arises from two factors. Firstly, crystallization was carried out under a wide range of controlled cooling conditions, emulating non-isothermal solidification conditions usually experienced in polymer processing. Secondly, we analyze our observations of the phase behavior, as well as those of previous studies, in terms of the kinetics and size dependent stability of the phases.

2. Materials

The present study encompasses a wide range of iPP, kindly provided by Borealis AS, Norway, within the Brite project BRPR.CT92.0331. The main material characteristics are listed in Table 1.

Considering the data in Table 1, the influence of ethylene content was studied comparing M3, M9 and M16, while that
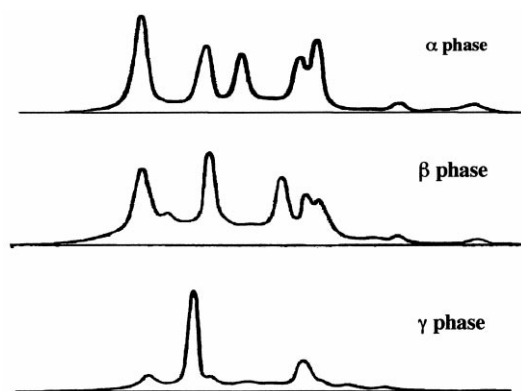

Fig. 1. Templates of typical WAXS patterns of pure α, β and γ crystalline forms of iPP.

Table 2
Assignment of WAXD peaks of the α, β and γ crystalline phases of iPP. For each phase the number at the top is the angle 2θ, and the index (hkl) is given below

	I	II	III	IV	V	VI	VII
α	14.08	16.95	18.5	21.2	21.85	25.5	28.45
	(110)	(040)	(120)	(131)	(041)	(060)	
β	16.1	16.6	21.3	24.7	28.07		
		(008)					
γ	13.84	15.05	16.72	20.07	21.2	21.88	
	(111)	(113)	(008)	(117)	(202)	(026)	

of different nucleating agents was studied comparing M7N and M4N with the respective nucleating agent free polymers (M7, M4). Finally, the effect of a simultaneous presence of ethylene and nucleating agents was studied by comparison of M14 and M16.

All the samples were solidified as thin films from the melt, controlling the cooling rate by an apparatus recently developed [19]. Prior to quenching, the polymer is kept in the melt at 250°C for a period of 30 min in order to erase memory effects. A nitrogen atmosphere prevents degradation [20]. The sample is quenched by spraying a suitable cooling fluid through two opposite spray nozzles onto the sample assembly, whereby the thin polymer film is sandwiched between two copper plates. One dimensional heat transfer is obtained in the thickness direction and, by control of sample thickness, homogeneous cooling conditions can be obtained. These, measured on the copper plates, can be controlled by changing their thickness and the cooling fluid used and its flow rate from 0.1 up to 1000°C s^{-1}. In the present work the cooling rates have been restricted to the range 0.04–30°C s^{-1} since outside this interval no γ phase is observed.

The advantage of our approach over standard methods of thermal analysis is that a wider range of cooling conditions can be explored. Characterization of the final structure can then be related to the thermal history recorded during cooling. While the full thermal history is available (and is used for the validation of models of crystallization kinetics examined elsewhere [19]), here only the cooling rate at 70°C is used as a single parameter characterizing the cooling conditions. The relevance of this parameter has been established elsewhere [19].

3. Characterization methods

Samples were characterized by means of Differential Scanning Calorimetry (DSC) using a Perkin-Elmer DSC7, and Wide Angle X-ray Diffraction (WAXD) on a Philips diffractometer with a Cu Kα tube and wavelength of $\lambda =$ 0.15418 nm. DSC provides melting points, and WAXD was used to identify the phases and their respective amounts. Peak deconvolution was performed using the software program Peakfit, supplied by Jandel Sci.
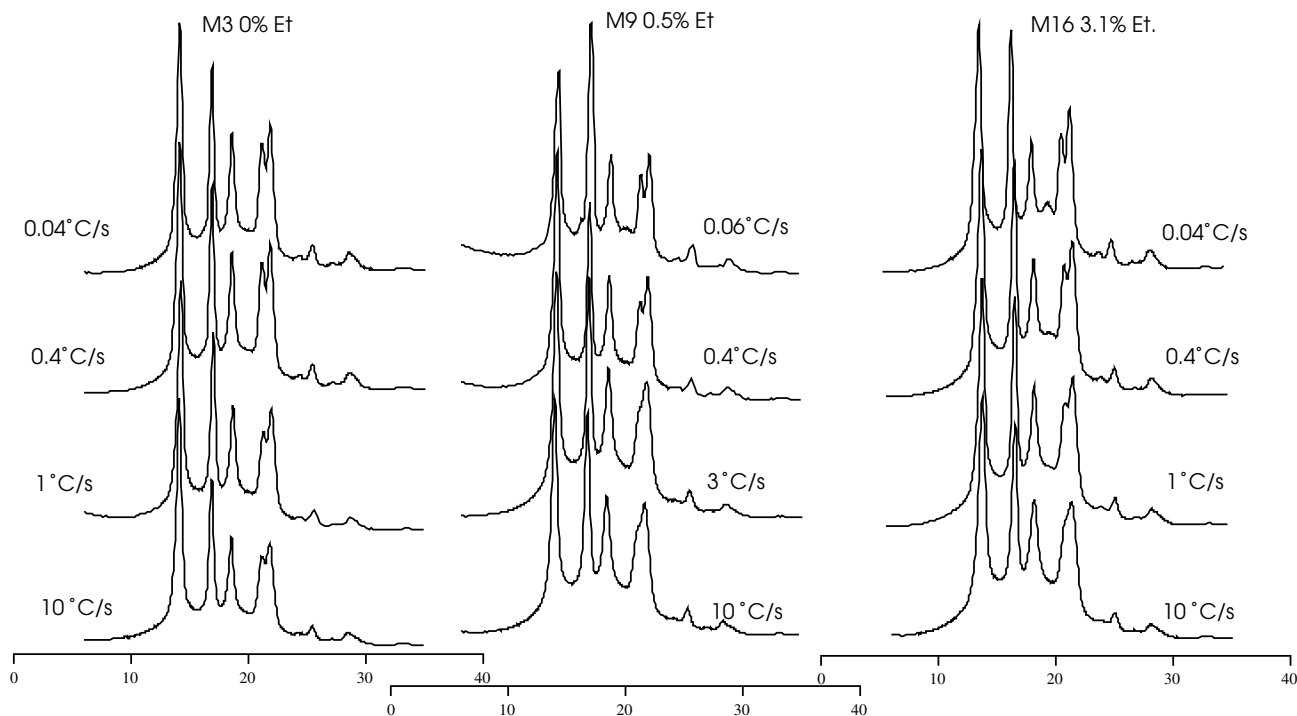
Fig. 2. WAXS patterns of M3, M9 and M16 with ethylene content of 0, 0.5 and 3.1%, respectively for different cooling rates at 70°C.

4. WAXD analysis methods

Each of the α, β and γ crystalline forms has its own distinctive peaks in the WAXD patterns, shown qualitatively in Fig. 1 and quantitatively in Table 2.

In a typical WAXD diffraction pattern of the α phase, the second peak is always smaller than the first one. However, this effect is not observed in samples containing the γ phase; their patterns are characterized by a second peak larger than the first one, which is not surprising considering the location of the strong peak II in the γ phase. Due to the closeness of the α and γ phase peaks in this region, peaks I, II and III are not ideal for an identification of the γ phase. Therefore, the identification of the presence of γ phase usually relies on the peak at $2\theta = 20.07°$. In previous studies [14,15], the γ to α ratio was calculated simply from the relative intensities of the unique γ and α peaks at 20.07 and 18.5°, respectively. Although this ratio provides the correct limits of zero γ and α phase in the absence of the respective peaks, it does not necessarily give the correct ratios in the intermediate regime. Therefore, in the present work the overall intensities in the angular range 10–23° of both phases are determined by means of a WAXD pattern deconvolution procedure. After subtraction of background scattering, for the γ phase the intensity of the unique peak IV is obtained directly from Peakfit. The intensities of all other peaks are then calculated on the basis of the relative intensities proposed by Brückner and Meille [5]. From their interpretation of the γ form, the peaks at $2\theta = 15.05°$ (113) and 20.07° (117) not overlapping with the α form ones, have a constant ratio of ca. 15/85. Moreover, the intensity of the (117) peak at 20.07° divided

by the sum of the intensities of all peaks in the angular range between 10 and 23° is also constant. After subtracting the γ phase intensity so determined, the overall α phase intensity could be determined easily following the peak pattern of Table 2. The relative phase amounts were then given by the relative intensities. This rationale is adopted throughout this work to evaluate quantitatively the amount of γ phase.

The above method fails for very small amounts of γ phase when the (117) peak can no longer be distinguished from the amorphous background. Nevertheless, our observations indicate that the presence of γ phase can still be identified from the relative height of the peaks at $2\theta = 14°$ and $2\theta = 16.8°$. The former is the sum of the α peak at 14.08° and the γ peak at 13.84°, the latter the sum of the α peak at 16.95° and the γ peak at 16.72°. The latter being higher is the signature of the γ phase.

5. Results

5.1. Effect of ethylene content and cooling rate

The WAXD patterns obtained after cooling materials M3, M9 and M16 at increasing rates are shown in Fig. 2. By visual inspection we note that, at the lowest cooling rate, for the three materials, the second peak is either higher or comparable to the first one, and a little additional peak can be found at $2\theta = 20.07°$. This feature is more evident with increasing ethylene content. The same situation can be observed for cooling rates up to $1°C\,s^{-1}$, although less
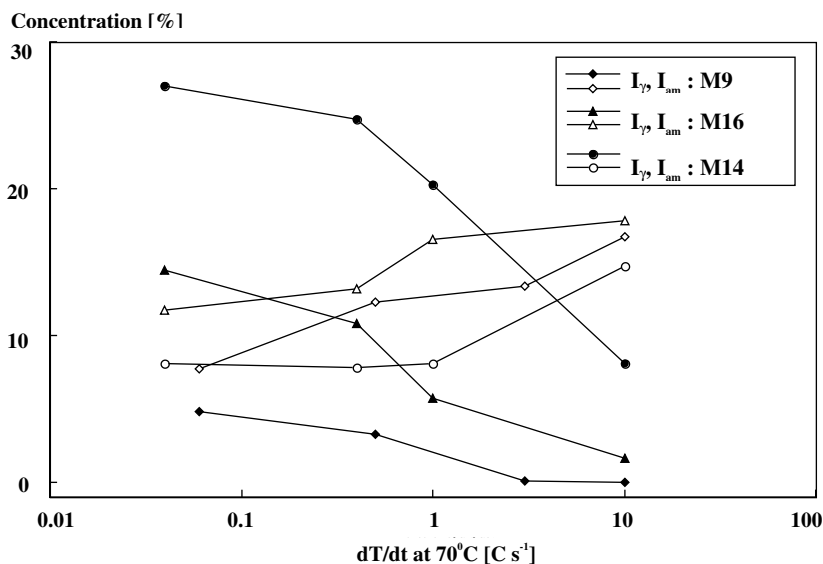
Fig. 3. The γ phase and amorphous content, respectively, as a function of cooling rate for the different copolymers.

evidently. The γ phase seems to have more or less disappeared at a cooling rate of $10°C \, s^{-1}$.

Quantitatively, the amount of γ phase and of the amorphous halo calculated for the copolymers is shown in Fig. 3. For a given cooling rate the amount of γ phase as well as the amorphous halo increase with ethylene content. With increasing cooling rate the content of γ phase decreases, disappearing at higher cooling rate the larger the ethylene content.

The DSC traces of the copolymers M9 and M16, shown in Fig. 4, reveal a double peak over most of the range of crystallization conditions, in contrast to the single melting peak of the homopolymer M3.

There is disagreement about the assignment of the peaks in the literature. According to Mezghani and Phillips [17] the γ phase is preferred at lower cooling rates and lower supercoolings. It therefore is expected to form the first
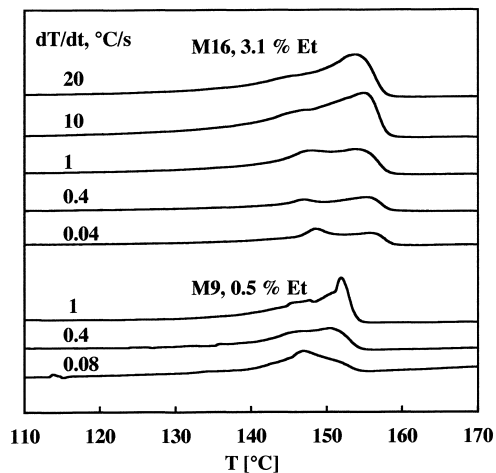
dominant lamellae onto which the α phase crystallizes epitaxially. Due to the tilt of the chains in the γ phase, the stem length of the epitaxial α phase crystals would be reduced by 24% [17]. Hence, on the basis of smaller crystal thickness Mezghani and Phillips assign the lower peak to the α phase. On the other hand, the DSC traces show the lower peak to decrease in strength relative to the higher temperature peak with increasing cooling rate. Melting and recrystallization phenomena will play a role especially for the larger cooling rates, and may result in a smearing out of the lower peak and strengthening of the final melting peak. Although this distortion makes it difficult to discern the effect of the initial phase content, the observed trend in relative peak heights is at least consistent with the WAXD results if we assign the lower peak to the γ phase. This would also be consistent with the γ phase growing onto the α phase [11], hence in our case at lower temperature. The recent work by Alamo et al. [13] corroborates the latter view. WAXD during melting shows a significant portion of the γ phase crystals disappear in the lower peak but some remain until the final melting. This observation is related to two populations of γ phase crystals: one that nucleates initially and independently and one that grows epitaxially onto the α phase. We shall come back to this point in our analysis.

5.2. Effect of nucleating agents and cooling rate

The WAXD patterns obtained for homopolymers with and without nucleating agents (M7,M7N and M4,M4N) are shown in Figs. 5 and 6. Visual inspection and quantitative analysis (Fig. 7) clearly show that the γ phase formation is enhanced by the presence of either nucleating agent, talc or DBS. M4N and M7N are mainly characterized by a second peak much larger than the first one for all cooling rates. In the case of M4N, in addition to the above

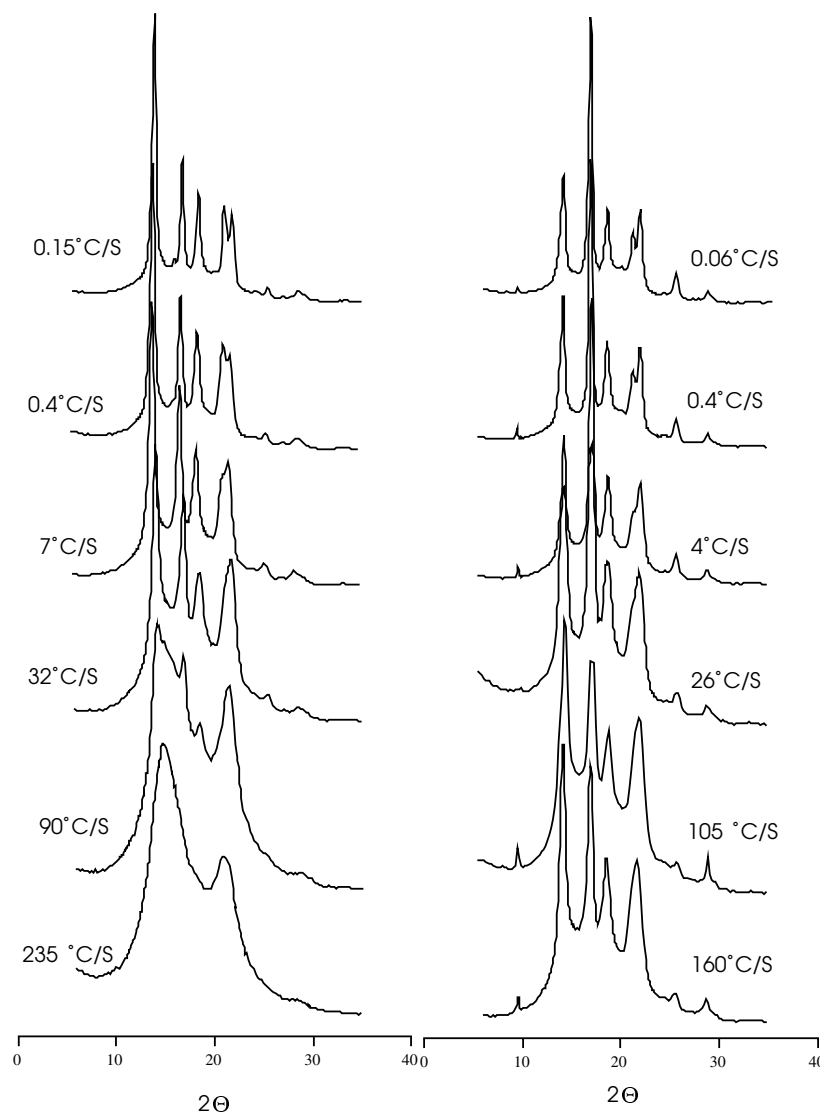Fig. 4. DSC traces of the copolymers M9 and M16.

Fig. 5. WAXS patterns of M7 (left) and M7N (right) for different cooling rates at 70°C showing the influence of the nucleating agent talc on the γ phase content.

observation, the γ phase peak at 20.07° is also observed at low cooling rates. We cannot at present conclude whether this is an effect of the type of nucleating agent or is related to the lower molecular weight in comparison to the talc-filled polymer M7N. However, much lower molecular weights are usually needed to give rise to an increase of the γ phase content [4]. As above, increasing the cooling rate leads to a decreasing amount of γ phase and an increase of the amorphous halo (Fig. 7).

5.3. Combined effect of ethylene content, nucleating agents and cooling rate

We compared the two copolymers, M16 and M14, both with the same ethylene content (3.1%), and the latter including a nucleating agent. The first question to ask is whether the γ phase enhancing effects of the ethylene content and nucleating agents combine. The WAXD of the nucleated copolymer, Fig. 8, shows that this is indeed the case. Hence, for M14 the amount of γ phase is larger, and the cooling rate range in which the γ phase appears is wider, than for M16, as Fig. 3 shows.

The DSC traces of the M14 sample (Fig. 9) show an endothermic 'hump' followed by the main melting peak. The traces are similar to those reported by Mezghani and Phillips for isothermally crystallized samples with a considerable amount of γ phase. However, as noted above it is likely that different γ phase crystals are involved in the whole melting range.

6. Discussion and analysis of phase behavior

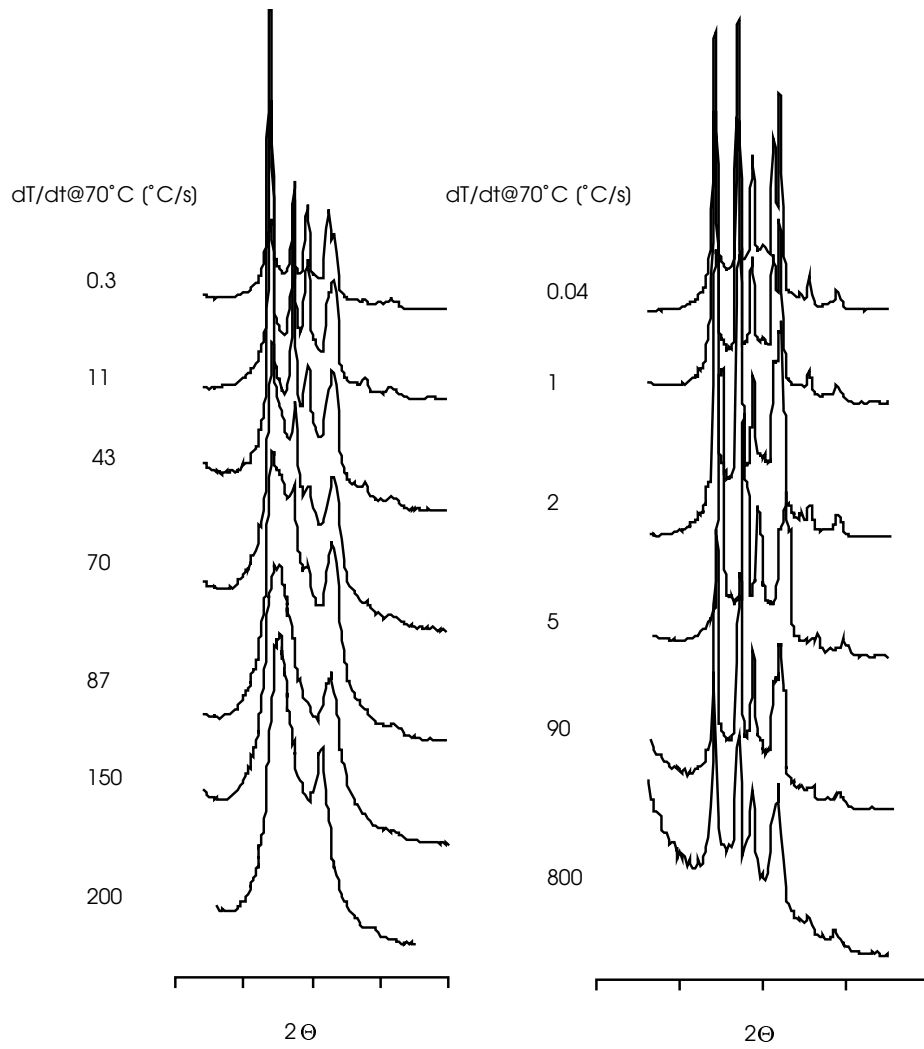An analysis of the phase behavior of isotactic

Fig. 6. WAXS patterns of M4 (left) and M4N (right) for different cooling rates at 70°C showing the influence of the nucleating agent DBS on the γ phase content.
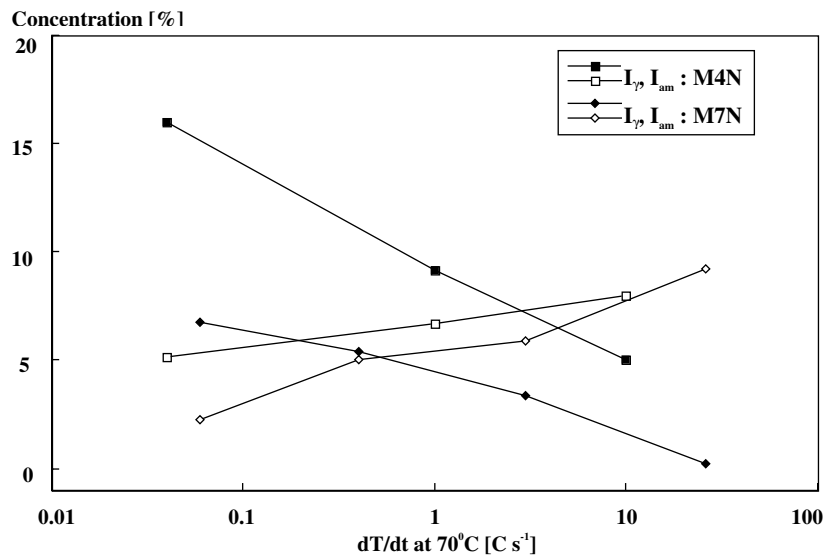

Fig. 7. γ phase and amorphous halo content based on Peakfit deconvolution vs cooling rate for the nucleated iPPs (M4N and M7N).
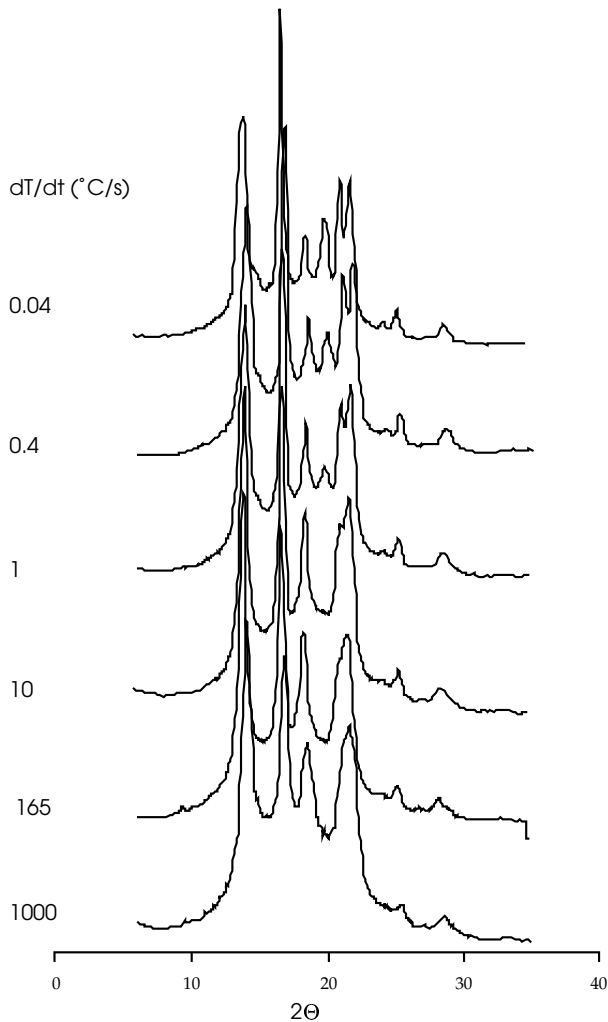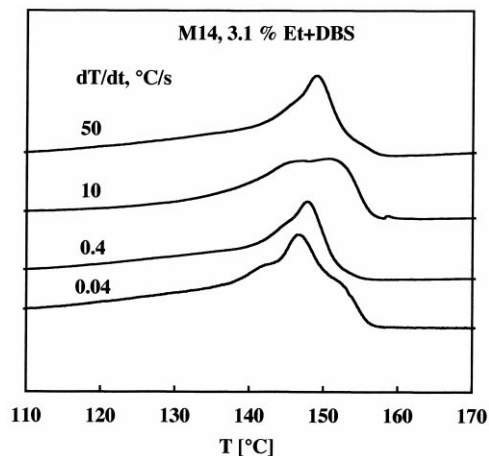
polypropylene was recently carried out by Mezghani and Phillips [17]. They considered mainly the equilibrium melting points of the α and γ phases, and the effect of pressure on the phase behavior. Our concern is to put forward a possible explanation of the observation of phase behavior in copolymers, materials with nucleating agents and their dependence on cooling conditions.

The results above show that ethylene comonomer units, even in small amounts, lead to some γ phase crystallization. Higher cooling rates, hence higher supercoolings, are shown to be less favorable for γ phase growth. The question remains as to why this is so. There are basically two possible factors determining the likelihood of growth of a particular phase: kinetics and thermodynamics. In our discussion of these effects we follow broadly the considerations put forward by Keller et al. [21] in their discussion of the competition between the orthorhombic and hexagonal phases in polyethylene.

Kinetically, most of the evidence suggests that the α phase crystallizes faster than the γ phase. Experimentally it is generally found to crystallize first [11]. From a theoretical view point we would also conclude that the α phase is preferred in a homopolymer. To rationalize this we assume as in [21] that the rate of formation *N* is given by:

$$N = A \exp\left[-\frac{B}{T(\Delta T)^{n-1}}\right] \tag{1}$$

where the value of *n* is either 3 or 2 for primary nucleation or surface growth, respectively. The prefactor *A* contains, apart from transport terms, the frequency with which chain sections ready to crystallize present themselves. We expect this to be larger for the α phase due to its simpler structure. For phases with very similar melting points, the exponential term is mainly determined by the factor *B,* which is basically given by the ratio of surface free energy over heat of fusion [21]. A smaller ratio means faster growth, and this is indeed the case for the α phase, as follows from the thermodynamic data [17] shown in Table 3. For the copolymer we can argue that both factors change in favor of the γ phase. The increased flexibility in the chains should enhance the availability of segments to crystallize in the γ phase structure. Furthermore, the surface free energy will increase considerably more with comonomer content for the α phase structure than for the γ phase structure for the following reasons argued by Alamo et al. [13]. The presence of defects leads to shorter crystallizable sections, and many sections become too short for chain-folded crystallization. The chains will therefore proceed straight into the amorphous phase, which leads to an overcrowding and high surface free energy in the α phase structure, but can be accommodated in the γ phase structure because of the high tilt angle.

Thermodynamically, the relative stability of the different polymorphs may change as a result of growing phase size as well as changing temperature. For very small crystals, i.e. initially, a different phase may be stable to that which is the finally stable one at large size. This concept was discussed

Fig. 8. WAXS patterns of M14 for different cooling rates at 70°C.

Fig. 9. DSC traces of the M14 sample.

Table 3
Thermodynamic parameters for the homopolymer [17]

Phase	T_m^0(°C)	ΔH (J g^{-1})	ρ (g cm^{-3})	σ_e (10^{-7}J cm^{-2})
α	186.1	209	0.936	52.2
γ	187.2	190	0.933	51.7

e.g. by Keller et al. [21] in the context of the competition between the orthorhombic and hexagonal phases in polyethylene, and we shall follow a similar analysis.

Since the β phase is absent in the materials and conditions we studied, we concentrate on the relative stability of the α, γ and melt phases. For this purpose we need to determine the melting lines of the two phases as a function of size, and a line which denotes the transition between the two crystalline phases.

The melting lines are defined by the Gibbs–Thomson relation:

$$T_m(\ell) = T_m^0\left(1 - \frac{2\sigma_e}{\ell\rho\Delta H}\right) \qquad (2)$$

where T_m^0 is the equilibrium melting point, σ_e the fold surface free energy, ρ the density, and ΔH the heat of melting of the respective phase (α or γ). The transition line is defined in principle by a similar equation with the respective quantities in Eq. (1) relating to the transformation between the α and γ phases. As in Ref. [21] it is determined simply by a straight line through two points: (i) the triple point T_Q (at which the melting lines cross), and (ii) the transition temperature T_{tr}^0, which is given by equating the Gibbs free
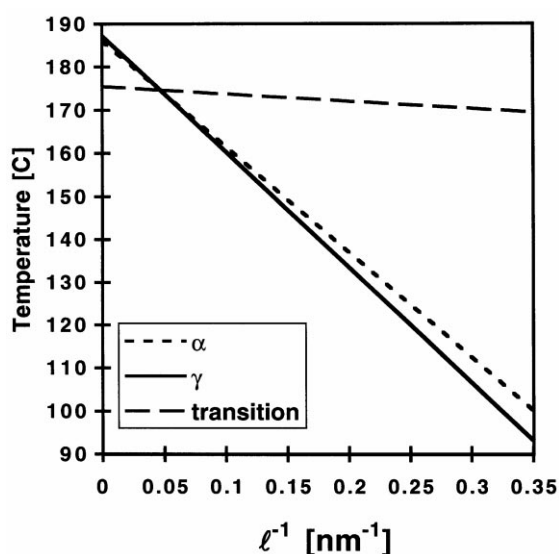

Fig. 10. Schematic phase stability diagram of an iPP homopolymer showing the melting lines of the α phase and γ phase, respectively, and the transition line between the two phases.

energies of the two phases [18]:

$$T_{tr}^0 = \frac{T_{m,\alpha}^0 T_{m,\gamma}^0(\Delta H_\alpha - \Delta H_\gamma)}{T_{m,\gamma}^0\Delta H_\alpha - T_{m,\alpha}^0\Delta H_\gamma} \qquad (3)$$

In combination with Eqs. (1) and (2) and inserting the data from Table 3 we obtain the homopolymer phase stability diagram shown in Fig. 10. We note in particular the transition lines between the two phases that divides the diagram into a region above it where the γ phase is more stable than α, and below it where the α phase is more stable.

Numerically, on the basis of the parameter values given by Mezghani and Phillips, the range of lower free energy of the γ phase in homopolymers is limited to temperatures close to the melting point. The equilibrium transition point is at $T_{tr}^0 = 175$°C, and the triple point is at a temperature $T_Q = 174$°C, and a lamellar thickness of 21.2 nm. Hence hardly any γ phase can be expected for a plain homopolymer. However, the higher the temperature of crystallization, the more likely it becomes that some γ phase is formed. This agrees with the observation of small amounts of γ phase in the nucleated materials (Figs. 5 and 6).

The question now arising is how this scenario changes in the case of copolymers. The melting points of copolymers of similar molecular weight and ethylene content were determined by Mezghani and Phillips [17]. However, their data refer to mixed phase crystals and hence only provide some average melting point of 180°C for a 0.5% copolymer and 166°C for a 3% copolymer. We assume that the melting point of the α phase is still slightly below that of the γ phase and set the melting points to 165 and 166°C, respectively. The density and heat of fusion are reduced due to an inclusion of some of the ethylene in the crystalline phase [18]. The data in Ref. [18] have a considerable uncertainty but suggest that for the 3% copolymer the heat of fusion is reduced by about 10 J g^{-1} and the density decreased by about 2%. As for the surface free energies we assume that σ_e increases somewhat more for the α than for the γ phase due to overcrowding of chains on the α phase fold surface but not on the γ phase crystals [13]. The resulting data set in Table 4 is hence our best estimate for the copolymer M16. In any case it should serve qualitatively to illustrate the expected behavior, and we shall comment on alternative scenarios below. The corresponding phase stability diagram is shown in Fig. 11. The melting lines are shifted downwards in temperature by about 20°C, and the (negative) slope of the α phase melting line is slightly increased. This scenario is in good agreement with experimental observations of the effect of co-units on the equilibrium melting behavior. As an example we quote the study by Cheng et al. [22] on the isotacticity effect on crystallization and melting of polypropylenes.

Fig. 11 shows that the region in which the γ phase has the lowest free energy is significantly larger than in the homopolymer. The melting and transition lines are almost parallel due to similar surface free energy to heat of fusion ratios.

Table 4
Estimated thermodynamic parameters for the copolymer M16

Phase	T_m^0 (°C)	ΔH (J g^{-1})	ρ (g cm^{-3})	σ_e (10^{-7} J cm^{-2})
α	165	199	0.917	57
γ	166	180	0.914	52

The triple point has therefore shifted down to 95°C, and a thickness of about 4 nm. The diagram is an expression of the fact that (a) the thermodynamic driving force for the growth of γ phase crystals is very similar to that of the α phase, (b) some γ phase may form initially as its region of lower free energy is passed, and (c) this region becomes wider at higher temperatures. The phase stability diagram is consistent with our observations that faster cooling leads to less γ phase and with that of isothermal studies [15] showing that the formation of γ phase takes place at lower supercoolings only [17]. Although the material finally, when cooled down, ends up in the region in which the α phase is most stable, such a solid–solid transformation would not be expected to take place during cooling at the given rates nor at room temperature because of the small free energy difference and the large difference in crystallographic structure of the two phases.

The considerable enhancement of γ phase that we observed in the case of copolymer with nucleating agent (M14) can also be understood in the scenario of Fig. 11. We note first that the nucleating agent is expected to be active for both α and γ phases due to their epitaxial relationship. In the presence of nuclei crystallization sets in at higher temperatures, and therefore a much larger part of the transformation will take place in the γ phase 'stability region'.

Finally, we comment on alternative scenarios. The above interpretation relies on the two facts that the γ phase melting point is above that of the α phase, and the slope $S = 2T_m^0 \sigma_e / \rho \Delta H$ is greater for the γ phase. If the order of the

melting points is reversed, two alternative scenarios arise: (i) if the slope S remains in the same order for the two phases; then the α phase is the most stable phase under all conditions; and (ii) if at the same time the order of S is changed, then the whole picture is simply reversed and the γ phase is the most stable phase at lower temperatures.

7. Conclusions

We have observed the crystal structure of isotactic polypropylene homopolymer and ethylene copolymers with and without nucleating agents crystallized at different cooling rates. The results can be summarized as follows: As observed by previous studies, ethylene comonomers lead to the formation of some γ phase, the amount increasing with ethylene content, but decreasing with increasing cooling rate. Nucleating agents also lead to a small amount of γ phase and enhance the amount of γ phase formed in ethylene copolymers. We put forward an interpretation for all of these observation in terms of crystallization kinetics and phase stability diagrams. The phase stability diagram shows a small region where the γ phase has lower free energy than the α phase. It is limited to high temperatures for homopolymers but moves to lower temperatures and increases in size with increasing comonomer content. In addition, the kinetics acts in the same way, favoring the α phase for homopolymers but less so with increasing ethylene content. Therefore on both counts more γ phase is expected to form with increasing comonomer content. As the α phase remains the most stable one at lower temperatures, the amount of γ phase formed will decrease with increasing cooling rate or undercooling. Nucleating agents will hence lead to an increase in the amount of γ phase since crystallization will set in at higher temperatures.

Fig. 11. Schematic phase stability diagram of an iPP copolymer with 3% ethylene. The melting lines of the α phase and γ phase, respectively, and the transition line between the two phases are shown.

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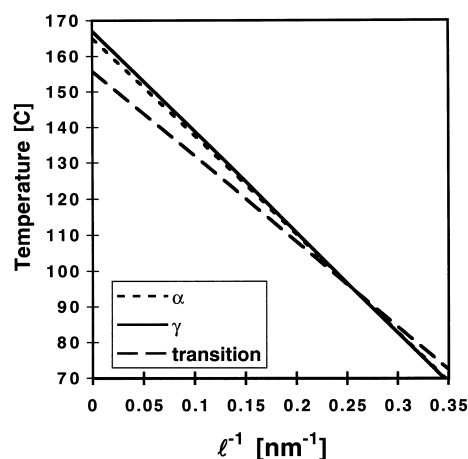[8] Lotz B. Private communication, 1999.

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