

Influence of stereoirregularities on the formation of the γ -phase in isotactic polypropene

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Abstract

Medium to high molar mass isotactic polypropenes with different amounts of stereoirregularities were characterised with respect to their crystallisation behaviour and for comparison a random copolymer of ethene and propene with 5.8 wt% ethene is used. The influence of stereoregularity and crystallisation temperature on the γ -content of the crystallised samples is studied by means of wide angle X-ray scattering, atomic force microscopy and light microscopy. The paper deals also with the temperature rising elution fractionation of an i-PP with large amounts of stereoirregularities and the influence of a nucleation agent on the γ -content. It is shown that effects which render the chainfolding in lamellae more difficult, enhance the formation of the γ -modification. The necessity of chainfolding in isotactic polypropene is discussed in terms of a model that is based on the number of chains that emerge from the lamellae surfaces of the α - and the γ -modification, respectively. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The crystallisation behaviour of isotactic polypropene (i-PP) is very complex. Different crystal modifications are known (α , β , γ and smectic) [1–7]. Calculations of the packing energies of γ - and α -modifications suggest that the γ -modification is slightly more stable than the α -modification [8,9]. The orthorhombic unit cell of the γ -modification is formed by bilayers composed of two parallel helices [10,11]. The direction of the chain-axis in adjacent bilayers is tilted at an angle of 80° [10–12]. At atmospheric pressure the γ -modification is observed as a minor constituent [2,13]. Its content is enhanced when i-PP is crystallised at elevated pressures [14,15], or in low molar mass samples (between 1000 and 3000 g/mol) [16–19]. Also random copolymers of propene with 2.5–20 wt% of other 1-olefins may crystallise preferably in the γ -modification [20–25]. In a previous paper we were able to show that i-PP with stereoirregularities tends to crystallise in the γ -modification [26]. Recently Almao et al. published a detailed work about structural and kinetic factors governing the formation of the γ -modification [27].

In this paper i-PPs with different amounts of stereoirregularities are compared. The influence of stereoirregularities and crystallisation temperature on the γ -content is studied by means of wide angle X-ray scattering (WAXS), atomic force microscopy (AFM), and light microscopy. One sample is fractionated using a temperature rising elution fractionation (TREF) apparatus. The influence of a nucleation agent (NA) on the γ -content is studied for a random copolymer of propene and ethene with 5.8 wt% ethene (P(*P-co-E*)). A model based on the differences in the number of chains that emerge from the lamellae of α - and γ -modification is used for the explanation of the competition during the crystal growth of the two modifications.

2. Experimental

2.1. Materials

The i-PP samples under investigation were synthesised using catalyst systems $\text{Me}_2\text{Si}(\text{Benz}[\text{e}]\text{Ind})_2\text{-ZrCl}_2/\text{MAO}$ (PP1/PP3) and $\text{SiO}_2/\text{MAO}/\text{Me}_2\text{Si}(2\text{-Me-Benz}[\text{e}]\text{Ind})_2\text{-ZrCl}_2$ (PP2/PP4), respectively. All characteristic polymer data are given in Table 1. The molar mass data were obtained by size exclusion chromatography (SEC) of the

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Table 1
Polymer data

Polymer	M_n (g/mol)	M_w/M_n	2,1-Insertion (%)	Mrrm-pentads (%)	\sum Defects (%)	n_{iso}^a	Catalyst ^b
PP1	51 000	2.1	0.4	0.7	1.18	84.6	BI
PP2	117 000	2.7	0.6	1.1	1.74	57.6	Si-BI
PP3	22 000	1.9	0.9	1.4	2.49	40.2	BI
PP4	117 000	2.2	1.0	1.2	2.24	44.7	Si-BI
P(P-co-E)	54 000	4.3	Comonomer content: 5.8 wt%				

^a Catalyst: BI = $Me_2Si(Benz[e]Ind)_2-ZrCl_2/MAO$; Si-BI: $SiO_2/MAO/Me_2Si(2-Me-Benz[e]Ind)_2-ZrCl_2$.

^b $n_{iso} = P_n / (1 + P_n(W_{mrm} + W_{2,1}))$.

i-PP samples or P(P-co-E) dissolved in 1,2,4-trichlorobenzene at 140°C. An IR detector is used and the calibration is done with narrow molar mass i-PP samples characterised by light scattering. P(P-co-E) is a technical propene/ethene copolymer (Novolen MC 3300/BASG AG) with an ethene content of 5.8 wt%.

As a NA, bis(*p*-ethylbenzylidene)sorbitol (commercial name: NC-4) was used. It was kindly supplied by Mitsui Toatsu Chemicals, Japan. The melting point of bis(*p*-ethylbenzylidene)sorbitol is 235°C.

2.2. Sample preparation

The samples used to study the crystalline morphology by light microscopy were produced by melting the powder of the as-prepared and dried polymer between two cover glasses. The layer thickness between the glasses was about 30–50 μ m. The samples were held for 10 min at 180°C and then quenched to the crystallisation temperature. The samples used to study the influence of the NA were prepared by extrusion of P(P-co-E) and 1 wt% NA using the twin-screw extruder ZSK25 (Werner and Pfleiderer) at

processing temperatures between 190 and 230°C. Tensile test specimens were injection moulded using a Ferromatic Milacron K40-DE. From these specimens, pieces were cut and prepared for crystallisation experiments.

2.3. Light microscopy

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 crystallisation.

2.4. Atomic force microscopy

The prepared films were etched to remove amorphous material from the surface. The etching reagent was prepared by stirring 0.02 g potassium permanganate in a mixture of 4 ml sulphuric acid (95–97%) and 10 g orthophosphoric acid. The 30–50 μ m thick films were immersed in the fresh etching reagent at room temperature and held there for 1 h. In the beginning the samples were held in an ultrasonic bath for 30 min. For subsequent washings, a mixture of 2 parts by volume of concentrated sulphuric acid and 7 parts of water was prepared and cooled to near the freezing point with dry ice in isopropanol. The samples were washed successively with 30% aqueous hydrogen peroxide (to remove any manganese dioxide present). Then the samples were washed with distilled water. Each washing was supported with an ultrasonic bath. The AFM experiments were carried out with a 'Nanoscope III' scanning probe microscope (Digital Instruments) at ambient conditions in the height- and amplitude- mode.

2.5. Wide angle X-ray scattering

Samples for WAXS measurements were isothermally crystallised at various temperatures. The measurements were carried out with a Siemens D500 apparatus. For the measurements CuK_{α} radiation of a wavelength of $\lambda = 0.154$ nm was used.

2.6. Temperature rising elution fractionation

TREF was carried out using a preparative TREF apparatus. 4 g of PP4 were dissolved in 400 ml xylene under N_2 at 100°C and then very slowly and steadily

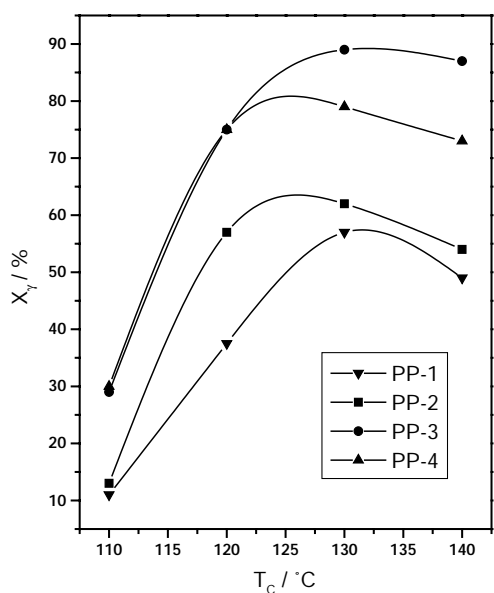


Fig. 1. Content of the γ -modification as a function of the crystallisation temperature for PP1, PP2, PP3 and PP4.

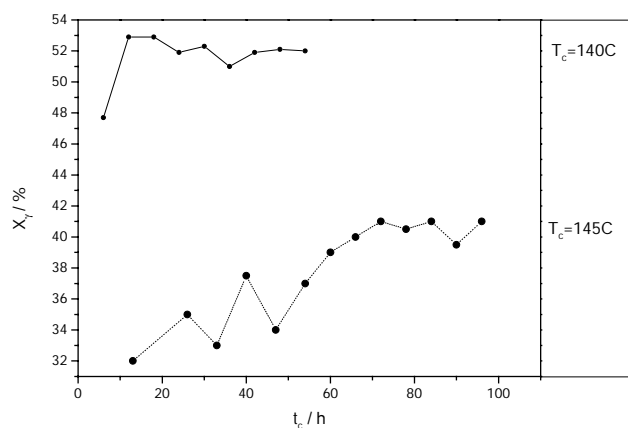


Fig. 2. Content of the γ -modification as a function of the crystallisation time for PP4 taken at $T_c = 140^\circ\text{C}$ (○) and $T_c = 145^\circ\text{C}$ (●).

cooled at a rate of $1.8^\circ\text{C}/\text{h}$ to 25.9°C . At this temperature the sample is precipitated. The precipitate was then dissolved by gradually adding fresh solvent and a step-wise increase of temperature in intervals of about 12°C . For each dissolution step, 400 ml solvent were added. After each temperature increase, the solutions were collected and taken as further fractions. Six fractions were collected.

3. Results and discussion

3.1. X-ray measurements

Fig. 1 shows the amount of the γ -modification in PP1, PP2, PP3 and PP4 as a function of the crystallisation temperature. All measurements are taken at room temperature after isothermal crystallisation and subsequent quenching to room temperature. The γ -content X_γ is calculated

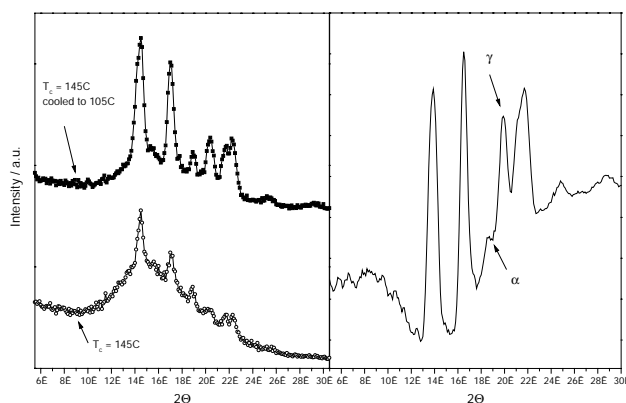


Fig. 3. Left: WAXS traces of PP4 isothermally crystallised at 145°C for 100 h taken at 145°C and after additional cooling to 105°C . Right: WAXS trace calculated by subtracting the WAXS traces given on the left. This WAXS trace represents the crystallisation behaviour of material that crystallises during the cooling process.

according to Turner Jones [13] from the ratio of the heights of the peaks at $2\theta = 18.8^\circ$ (130 peak of the α -modification) and at $2\theta = 20.2^\circ$ (117 peak of γ -modification). It can be seen that the γ -content increases with increasing crystallisation temperatures. Only at very high crystallisation temperatures the γ -content decreases. The γ -content also depends strongly on the amount of stereoirregularities. This behaviour is similar to that of samples published in Ref. [27]. For the samples under investigation the γ -content decreases with decreasing amount of stereoirregularities.

Fig. 2 depicts the content of the γ -modification in the PP4 sample as a function of crystallisation time taken at crystallisation temperatures of $T_c = 140^\circ\text{C}$ (○) and $T_c = 145^\circ\text{C}$ (●), respectively. The γ -content is relatively constant, a small increase with crystallisation time can be observed. The γ -content of the sample crystallised at 145°C is lower than the γ -content of the sample crystallised at 140°C . The sample crystallised at 140°C reaches a constant γ -content and a constant degree of crystallinity after 10 h; the sample crystallised at 145°C arrives at a constant γ -content and a constant degree of crystallinity after 70 h. The γ -content is significantly lower than the values measured after rapid cooling of the samples to room temperature as shown in Fig. 1.

WAXS traces of PP4 measured at 145°C after isothermal crystallisation at 145°C for 100 h (i.e. after reaching a constant degree of crystallinity and a constant content of the γ -modification), and the WAXS trace of the same sample after additional slow cooling to 105°C can be seen in Fig. 3 (left). Upon cooling, the γ -content and the crystallinity increases. Fig. 3 (right) shows a WAXS trace calculated by subtracting the WAXS data taken at 145°C from the WAXS trace taken at 105°C . The resulting WAXS trace shows the crystallisation behaviour of a portion of the sample that was unable to crystallise at 145°C . The peak at $2\theta = 20.2^\circ$ is very intense. The amount of PP4 that crystallises during this slow cooling process shows about 90% of the γ -modification. This indicates that the decrease of the γ -content at high crystallisation temperatures is caused by a fractionation process. Fractions with high contents of stereoirregularities show lower melting temperatures than highly stereoregular fractions. These fractions are able to form high contents of the γ -modification at relatively high crystallisation temperatures above 100°C but they are unable to crystallise at 145°C . This fractionation appears at temperatures above 125°C . With increasing crystallisation temperatures the amount of this non-crystallisable fraction increases. Quenched to room temperature, the non-crystallisable fraction stays amorphous or crystallises in a temperature range where the α -modification is preferably formed. This leads to a decrease of the γ -content compared to samples crystallised at temperatures in the range of 120°C . Very slow cooling of samples that were isothermally crystallised at very high temperatures leads to significant higher amounts of the γ -modification compared to quenched samples. In these samples, the portion that was

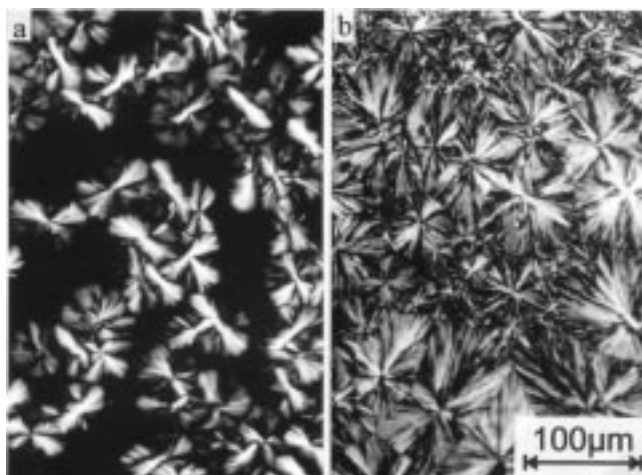


Fig. 4. Light micrographs of TREF fractions 1 (left) and 6 (right) isothermally crystallised at 135°C.

unable to crystallise during the isothermal annealing crystallises in a temperature range where it is able to form the γ -modification. Under these conditions a decrease of the γ -content at high crystallisation temperatures is not observed.

3.2. Temperature rising elution fractionation

To support the results discussed above, TREF was used for the fractionation of PP4. TREF is a special fractionation technique, developed to characterise semicrystalline polymers with respect to their crystallisability. It is especially effective to fractionate copolymers according to their comonomer distribution, because of its direct relation to the crystallisability. The influence of the molar mass on the fractionation is usually negligible for molar masses $>10\,000$ g/mol [28,29]. As shown above PP4 is composed of fractions of different crystallisability. Our TREF experiments resulted in 6 fractions with different stereoregularities determined by ^{13}C NMR spectroscopy according to Ref. [30]. The number of mmmm-pentads differ from 91% (fraction 1) to 96% (fraction 6). Thus TREF can be used to fractionate i-PP according to a distribution of macromolecules with differences in their stereoregularity. Therefore, it is not surprising that the crystallisation behaviour of the fractions is different. Isothermally crystallised at 135°C and then slowly cooled to room temperature, fraction 1 yields a γ -content of about 90%, the more stereoregular fraction 6 forms under identical conditions only 60% of the γ -modification. The behaviour of fraction 1 is hence very similar to the portion of PP4 that is found to be non-crystallisable at high crystallisation temperatures (e.g. 145°C). The influence of the stereoregularity on the supermolecular appearance is shown in the light micrographs of Fig. 4. The less stereoregular fraction 1 forms bundle like structures at a crystallisation temperature of 135°C shown in Fig. 4a (γ -content: 90%). The fraction 6 with the highest

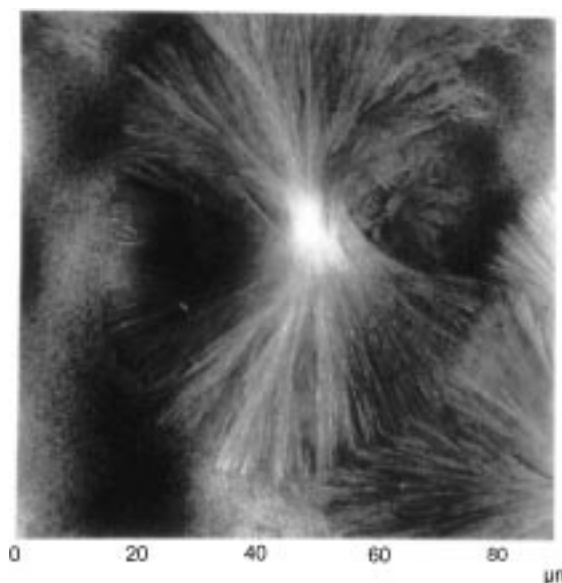


Fig. 5. AFM micrograph of a bundle like morphology formed during isothermal crystallisation of PP4 at 130°C.

stereoregularity crystallised under identical conditions forms spherulites well-known from the crystallisation of i-PP in the α -phase (γ -content: 60%).

3.3. Morphology

Fig. 5 depicts an AFM micrograph of PP4 isothermally crystallised at 130°C. The morphology is different from the spherulites formed by the α -modification. PP4 forms at elevated temperatures, bundle like morphologies known from mixed superstructures of the α - and γ -modification in i-PP of relatively low molar mass [26].

Fig. 6 shows an AFM micrograph of PP3 isothermally crystallised at 125°C. At this magnification the typical triangular morphology of γ -phase single crystal like entities is visible. These single crystal like structures are arranged at an angle of 50° to the completely covered underlying lamellae of the α -modification, forming the superstructure. This angle is exactly the angle of the epitaxial ongrowth of the γ -modification on lamellae of the α -modification that is shown schematically on top of the photograph of Fig. 6.

These morphologies composed of α -lamellae and epitaxial ongrowth of the γ -modification are also observed in PP4 cooled from the melt at 10°C/min (Fig. 7). The bundle like morphology (lower right part of the photograph, marked as γ) is surrounded by the typical cross-hatched structure formed by the α -modification of i-PP (indicated by an arrow as α). This is a clear indication that non-isothermally crystallised samples of i-PP with large amounts of stereoirregularities show a heterogeneous superstructure built up by bundle like structures with high contents of the γ -modification, and of areas formed by the pure α -modification. This heterogeneity might have an influence on the optical and mechanical properties of such samples.

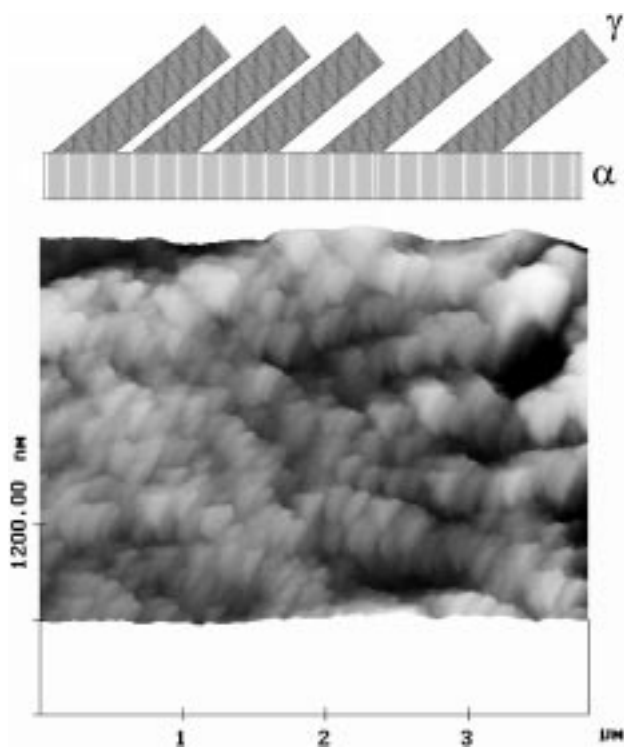


Fig. 6. AFM micrograph of the epitaxial ongrowth of the γ -modification on α -lamellae in PP3 isothermally crystallised at 125°C (bottom); scheme of the epitaxial ongrowth (top).

3.4. Nucleation

It is mentioned above that the amount of the γ -modification depends on the crystallisation temperature. It is well known that NAs are able to raise the crystallisation temperature of *i*-PP during the cooling regime from the melt. Therefore, nucleation should have a significant influence on the amount of the γ -modification formed during non-isothermal crystallisation. The content of the γ -modification as a function of the cooling rate for P(P-co-E) and P(P-co-E) + 1 wt% of NA is shown in Fig. 8. For the very slow cooling rate of 0.2°C/min only differences of about 20% in the γ -contents between the copolymer with and without NA, respectively, are found. For higher cooling rates the γ -content stays relatively high for the nucleated sample but decreases rapidly for the non-nucleated sample.

Under isothermal crystallisation conditions no significant difference in the γ -content is found between the nucleated and the non-nucleated sample (Fig. 9, top). Hence the observed higher γ -content is caused by an increase of the crystallisation temperature in the nucleated sample and not by preferential growth of the γ -modification on the NA. The bottom part of Fig. 9 shows DSC traces of P(P-co-E) and P(P-co-E) + 1 wt% of NA cooled from the melt at 10°C/min. It is demonstrated that the nucleation is effective in order to shift the crystallisation temperatures in a temperature range where large amounts of the γ -modification are formed. Therefore, it can be concluded that the increase of

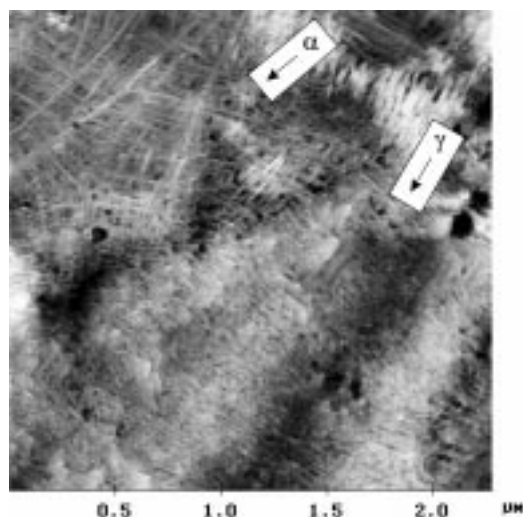


Fig. 7. AFM micrograph of the heterogeneous morphology found in a PP4 sample that was cooled from the melt with 10°C/min. Areas are marked as α and γ with respect to the dominating modification.

the γ -modification in nucleated samples, crystallised under non-isothermal conditions, is only caused by an increase of the crystallisation temperature and not by a special nucleation of the γ -phase.

4. Model

It was shown by Almao et al. [27] that kinetic requirements are important for the formation of the γ -modification. They discussed the fact that the flux of chains that emanate from the 001 plane is reduced in the γ -modification due to the arrangement of antiparallel tilted chains, and that therefore

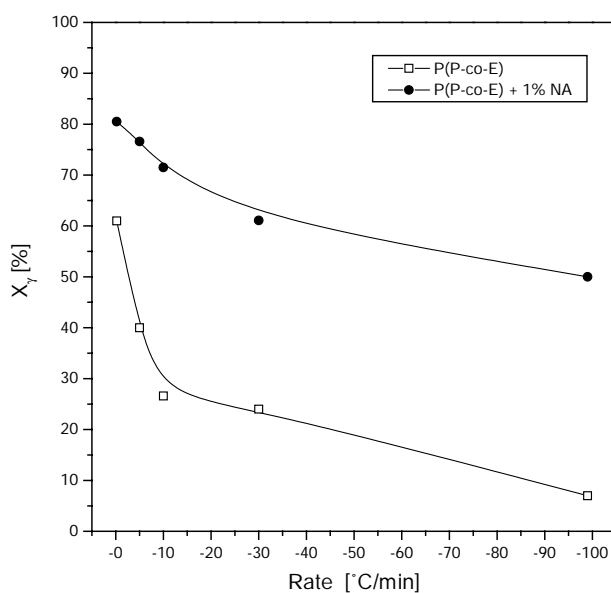


Fig. 8. Content of the γ -modification as a function of the cool rate for P(P-co-E) and P(P-co-E) + 1% of NA.

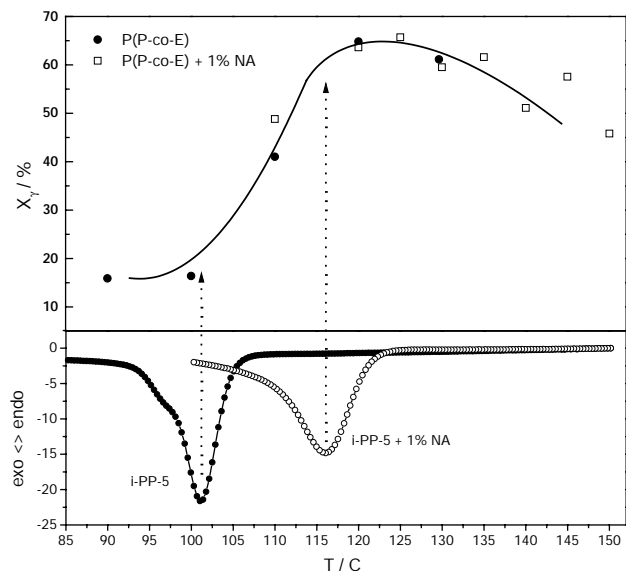


Fig. 9. Content of the γ -modification as a function of the crystallisation temperature for P(P-co-E) and P(P-co-E) + 1% of NA (top), DSC crystallisation traces of P(P-co-E) and P(P-co-E) + 1% NA taken upon cooling with a rate of $10^\circ\text{C}/\text{min}$.

the formation of the γ -phase is a natural consequence of accommodating chain defects outside the crystal.

Fig. 10 schemes the different arrangements of helices in the α - and the γ -modification. In the α -modification (Fig. 10a) the helices are arranged perpendicular to the lamellae surface. The distance between the chains at the lamella surface (d_α) is identical with the chain distance in the lamellae themselves (d_h). Fig. 10b shows the arrangement of helices in the γ -modification. The helices have an angle of 50° to the lamella surface. In this case the distance of the chains at the lamella surface (d_γ) is significantly higher than the chain distance in the lamellae (d_h), and also higher than d_α for an identical d_h . This reduces the number of chains that emerge from the lamellae surface [5.73 chains per nm^2 for the α -modification and 4.39 chains per nm^2 for the γ -modification].

This difference has a remarkable effect on the amorphous phase. Fig. 11 shows two chains of the same length emer-

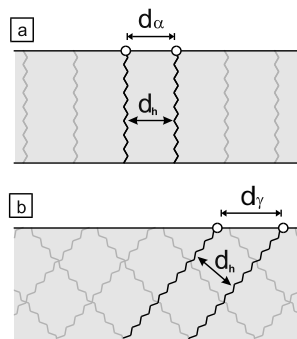


Fig. 10. The arrangement of helices in lamellae: (a) α -modification; (b) γ -modification.

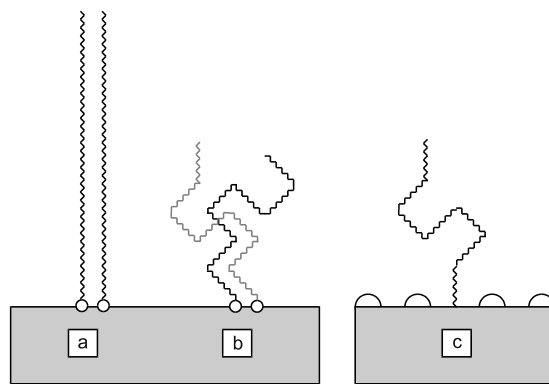


Fig. 11. Helices that emerge from the lamella surface: (a) helical conformation; (b) random walk conformation; (c) lamellae surface with chainfolding.

ging from a lamella: (a) chains in an elongated helical conformation; (b) chains in random coil conformation. In the case that all chains of an α -lamella emerge in the elongated 3_1 -helical conformation (similar to Fig. 11a), the density of the 'amorphous' phase would be 26.46 propene units per nm^3 . This density is identical with that of the crystalline lamella. If all chains adopt random coil conformation (similar to Fig. 11b), the density would be significantly higher than that of the crystalline lamella. A realistic density, lower than that of the crystalline material, cannot be achieved when all chains emerge from the lamella surface. This calculation is one of the main arguments for a chain folding in melt crystallised polymers [31,30]. Therefore, a large amount of chains that emerge from lamellae of the α -modification must fold back (Fig. 11c). For polyethylene it was calculated that 50% of the chains must fold back [32].

The situation is totally different for the γ -modification. As described above the number of chains per unit lamella surface is reduced. If all chains emerge from the lamella in an elongated helical conformation (similar to Fig. 11a), the density of the 'amorphous' phase would be 20.27 propene units per nm^3 . This value is significantly lower than that of the crystalline core, and even lower than that of amorphous i-PP. The density at the lamella surface is thus relatively small so that even a high degree of conformational disorder can appear without the necessity of chain folding. This means, that any factor which suppresses chainfolding makes the formation of α -modification difficult, but promotes the formation of the γ -modification.

Crystallised random copolymers of propene with ethene, 1-butene, 3-methylbutene, 1-octene and other comonomers are known to crystallise in significant amounts in the γ -modification [20–25]. Depending on its size and structure, the comonomer units can be excluded from, or included into the crystal lattice. In general, the exclusion from the crystal lattice is energetically favoured and even if an inclusion is possible the majority of comonomer units are excluded [33]. Because the comonomers are distributed randomly in the chain, it can only happen coincidentally that a comonomer unit is in the right position to be part of a sharp chain folding

connected with adjacent re-entering. In general, the exclusion of comonomers leads to the formation of long loops, or the chainfolding is totally suppressed. As discussed above a large amount of sharp chain folds is necessary to form α -lamellae. For that reason it is easy to understand that the exclusion of comonomer units increases the amount of γ -modification. A very similar effect is caused by stereoirregularities, that leads to imperfections in the 3_1 helices which must be excluded. Similar to comonomer units, the exclusion of stereoirregular units renders the formation of sharp adjacent chain folds difficult and promotes the formation of γ -modification. The smaller lamella thickness of the γ -modification compared to that of the α -modification [26] amplifies this effect, due to an easier collecting of *i*-PP segments of fitting length to form lamellae [34]. In low molar mass *i*-PP samples tapered ends and chemically different end-groups might have a similar influence.

5. Conclusions

Isotactic polypropenes with different amounts of stereoirregularity were compared. It is shown that the γ -content depends on the stereoregularity and on the crystallisation temperature. At high crystallisation temperatures the samples are fractionated in a non-crystallisable fraction with a large number of stereoirregularities and a crystallisable fraction with higher stereoregularity. Upon cooling also, the more stereoirregular fraction is crystallisable. Slowly cooled to room temperature, it forms mainly the γ -modification. TREF on a metallocene *i*-PP sample leads to fractions of different stereoregularity that form different amounts of the γ -modification. These fractions show different types of superstructures, spherulites for low contents of stereoirregularities, bundle like structures for high contents of stereoirregularities. Nucleation increases the crystallisation temperature of P(*P-co-E*). Therefore, nucleation with bis(*p*-ethylbenzylidene)sorbitol is able to increase the γ -content in P(*P-co-E*) significantly during the cooling regime from the melt.

A remarkable difference between the α - and the γ -modification of *i*-PP is the necessity of chain folding in melt crystallised lamellae. Similar to polyethylene a large number of chains that emerge from the surface of α -lamellae of *i*-PP must fold back in order to guaranty that the amorphous has a lower density compared to the crystalline regions. There is no necessity to fold back for chains that emerge from γ -lamellae of *i*-PP. This difference becomes important when the chemical structure of the polypropene chain suppresses the formation of sharp chain folds. In that case the formation of the α -modification is more difficult, and the amount of γ -modification increases. Typical examples are random copolymers of polypropene, polypropenes with regio- and stereoirregularities, and low molar mass samples.

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