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Crystallization and morphology of the trigonal form in random propene/1-pentene copolymers

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ABSTRACT

The melting and crystallization behaviour of a series of isotactic propene/1-pentene random copolymers, with 1-pentene contents up to 50 mol%, was investigated by DSC and temperature resolved WAXD/SAXS. The role of the 1-pentene comonomer in the development of the trigonal modification (δ-form) of *i*-PP was studied and the results were compared with those reported in the literature for PP copolymers with 1-hexene. The crystallizing capability of the δ-form, which develops in the composition range between *ca.* 10 and 50 mol% of 1-pentene content, only slightly decreases with concentration of 1-pentene. This result is correlated with the limits imposed to cell expansion by the crystal density. The crystallinity degree calculated from the deconvolution of the WAXD patterns is in fair agreement with the results of the DSC analysis, from which the value of the melting enthalpy of the perfect *i*-PP δ-form has been estimated to be around 140 J/g. The crystallization kinetics of the trigonal modification is characterized by a composition-dependent induction time followed by a relatively fast development of structural order. The sharp WAXD reflections combined with the SAXS data suggest that, notwithstanding the intrinsic intrachain structural disorder, thin and wide lamellae characterize the morphology of the δ-form crystallites.

1. Introduction

The interest in polyolefin copolymers has grown in the last years due to the possibility of tailoring their properties by controlling chain composition and microstructure [1–9]. A systematic investigation on random propene copolymers containing higher even and odd carbon-numbered 1-olefins has been recently tackled in our group in order to clarify the effect of type and amount of comonomer, as well as the influence of the metallocene catalyst, on microstructural, structural and morphological features of the resulting polymers and on their thermal properties [10–15].

It is well known that the crystallization and melting behaviour of isotactic polypropylene and of its random copolymers with ethylene or other 1-olefins is largely affected by nature and content of constitutional and configurational defects as well as by the details of chain microstructure [7,14–19]. The monoclinic α modification is predominant in highly isotactic samples crystallized from the melt at moderate cooling rates [20,21]. Ultra-fast cooling, at cooling rates above *ca.* 100 °C/s [22,23], leads to the formation of the smectic mesophase [24,25]. When crystallization is performed in isothermal conditions at relatively low undercooling, considerable amounts of the orthorhombic γ-form develops [26], particularly if the length of isotactic sequences is short [15,27–29]. The other crystalline structure, the hexagonal β modification [30], preferentially forms in the presence of specific nucleating agents and by crystallizing deformed melts [31,32].

Crystallizability of the copolymers decreases on increasing the concentration of co-units, either if they are included or excluded from the crystal lattice. In the first case, this is due to the enthalpy penalty the crystal has to pay to host the mistaken units [33–35]; in the latter, it is a consequence of the reduced crystal thickness, which must be commensurate with the average distance of the defective units along the chain [36].

Due to the nonspecific effect related to the shortening of the average length of isotactic sequences, the development of a larger fraction of γ-form crystals on increasing the content of randomly distributed defective units is expected if their entrance in the crystalline lattice of the α-form is forbidden. However, the effective length of the regular sequences increases when the defects are, at least partly, hosted into the α crystals or into some other crystalline

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modification different from γ-form. In the case of *i*-PP copolymers, this is mainly associated to the size of the side group. For example, the replacement of the methyl group with hydrogen in ethylene co-units make it unfavourable their inclusion because of the resulting lattice distortion due to the decrease of density in the α-unit cell; the consequence is that the copolymer crystallizes in the γ-form already at low ethylene contents [28,29]. On the other hand, 1-butene and, to lower extent, also 1-hexene units can enter the α-lattice of *i*-PP and, therefore, the development of the γ-form is less favoured [37].

Contrary to the typical behaviour of random copolymers, for what concerns the copolymers of propene with higher α-olefins obtained from metallocene catalysts, and particularly 1-hexene, it has recently been found that the level of crystallinity keeps relatively high up to compositions containing over 25 mol% of co-units [38–40]. Indeed, inclusion of bulky 1-hexene co-units into the crystal lattice, destabilizes the α-form, but favours the slow formation of a new modification, which significantly differs from the well-known structures of isotactic polypropylene (α, β and γ polymorphs), and is isomorphous to Form-I of *it*-poly(1-butene) [39–41]. The crystal structure of this polymorph, that has been found in propene/1-hexene copolymers containing from *ca.* 9 to 30 mol% of 1-hexene and in which the chains are packed in a trigonal unit cell while maintaining the classical 3/1 helical conformation of α-polyolefins is an example of density-driven polymer structure. In the following, we refer to this polymorph as δ-form.

On the basis of these evidences, De Rosa et al. [39] inferred that other random copolymers of propene with higher 1-olefins should develop the trigonal modification when the crystal density and the average composition approach those of *i*-PB. Indeed, De Rosa et al. [42] recently reported clear evidences of δ polymorph formation in propene/1-pentene copolymers in a wide range of compositions, up to 55 mol%.

In this study, attention is focused on a series of propene/1-pentene random copolymers synthesized from a different metallocene catalyst and containing up to around 50 mol% of 1-pentene units. DSC and simultaneous WAXD/SAXS are employed to investigate crystallization and melting behaviour as well as the morphology of the trigonal modification.

2. Experimental section

The studied copolymers are samples with different 1-pentene contents which were synthesized by varying 1-pentene amount in the feed and using a methylaluminoxane (MAO) activated *ansa*-zirconocene catalyst, namely *rac*-$Et(Ind)_2ZrCl_2$, in a hydrocarbon solvent at 30 °C. The corresponding propene homopolymer was as well synthesized for reference purpose. All the experimental details concerning the synthetic procedure as well as molecular (GPC) and microstructural (^{13}C NMR) characterization were reported in a previous contribution [10]. Irrespective of composition, all samples exhibit comparable isotacticity index ($[mmmm] = 0.90 \pm 0.03$) and similar molecular weight ($M_W = 50 \pm 10$ kg/mol). Polydispersity around 2 and reactivity ratio products close to 1, indicative of the random distribution of 1-pentene co-units along the polymer chain, are consistent with the single site nature of the metallocene catalytic system.

2.1. Characterization techniques and procedures

Melting and crystallization curves were recorded on a Mettler DSC 821^e calorimeter (scanning rate 20 °C/min, under nitrogen). All samples were treated as follows: after destroying the nascent crystallinity at 220 °C, the specimens were cooled under controlled conditions down to −60 °C. A second heating run was imposed to acquire information on the melting behaviour. This step was followed by quenching the DSC pan in liquid nitrogen. The quenched samples were aged during 1 month at room temperature and then re-heated to obtain information on their structural and morphological evolution. Low temperature isothermal crystallization experiments, in the range between 0 and 20 °C, were also performed to investigate the effect of composition on the crystallization kinetics. Samples were fast cooled to the desired temperature and held there for different times before a heating run was imposed. This was done directly in the DSC oven, in the case of relatively short crystallization times, or in a thermostated oil bath, for long crystallization times.

Room temperature wide-angle X-ray diffraction (WAXD) measurements were carried out on samples that were molten for a few minutes at 220 °C, quenched to room temperature and then aged for different times to develop the maximum crystallinity. A Siemens diffractometer model D-500 equipped with a Siemens FK 60-10, 2000 W Cu tube (Cu K_α radiation, $\lambda = 0.154$ nm) was used and reflections were collected in the 2θ range between 5 and 35°. To better develop the trigonal form, sample Pe10 was thermally fractionated through a successive self-nucleation and annealing (SSA) procedure [43] and then further analyzed by WAXD (Pe10a). Self-nucleation and annealing steps (duration 5 min) were imposed at decreasing temperatures (ΔT between successive steps 5 °C) in the temperature range 100–30 °C.

Room temperature, temperature- and time-resolved 1-D WAXD and small angle X-ray scattering (SAXS) patterns were collected at beamline A2 of the HASYLAB-DESY synchrotron facility of Hamburg, using a radiation of $\lambda = 0.15$ nm on samples that were quenched from the molten state and aged at room temperature during at least one week. The WAXD 2θ axis was calibrated against PET, the SAXS q axis against wet rat-tail tendon. Samples were placed in a temperature controlled oven and were heated at 10 °C/min. Diffraction data were collected in the 2θ range from 9 to 23° in the wide angle region and in the 0.02–0.1 nm^{-1} range of the scattering vector in the small angle domain. Sampling time was fixed at 15 s, thus enabling us to collect diffraction patterns every 2.5 °C.

The integrated area values were obtained from WAXD patterns by deconvolution of the crystalline and amorphous fraction diffraction peaks using Peak Fit V.4.0 software.

3. Results and discussion

3.1. Thermal behaviour

At the light of the discovery of the δ-form [39–42], our attention is here focused on the propene/1-pentene series previously studied [14,15] which has been integrated with additional samples, to evenly cover the composition range up to 50 mol%.

Table 1, in which the new samples are evidenced in italics, summarizes the relevant thermal features of the copolymers and of the corresponding propene homopolymer.

The DSC traces obtained on heating the samples immediately after cooling at 20 °C/min are shown in Fig. 1a. A progressive shift of the single melting endotherm towards lower temperatures is observed on increasing comonomer content up to about 7 mol%. Copolymers containing between 10 and 25 mol% of 1-pentene barely crystallize on cooling, while exhibit a cold crystallization in the subsequent heating run; at the same time a decrease of the melting enthalpies is observed (Table 1). Further increase of the 1-pentene content fully inhibits the crystallization during cooling and, consequently, only the signal corresponding to the glass transition temperature (T_g) is detected.

The DSC profiles obtained on heating aged samples are shown in Fig. 1b. It is evident that, in addition to the crystallinity which

Table 1
Thermal properties of propene/1-pentene copolymers.

Sample	1-Pe (mol-%)	Heating after controlled cooling			Heating after 1 month aging at room temperature			
		T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_m (I) (°C)	ΔH_m(I) (J/g)	T_m (II) (°C)	ΔH_m (II) (J/g)
PP	0	−10.2	136.1	94	138.0	~75	50.2	~20
Pe1	1.1	−9.7	134.4	76	134.5	71	53.5	11
Pe7	*7.5*	*−13.1*	*98.7*	*54*	*99.7*	*67*	–	–
Pe10	10.6	−17.0	74.2[a]	27	74.5	12	48.8	29
Pe15	*14.7*	*−19.0*	*61.9*[a]	*32*	–	–	*45.9; 61.8*	*50*
Pe18	18.0	−19.1	59.5[a]	26	–	–	48.1; 60.5	44
Pe23	*23.6*	*−21.3*	*59.9*[a]	*8*	–	–	*43.8; 56.6*	*45*
Pe27	*27.7*	*−24.0*	–	–	–	–	*52.0*	*42*
Pe30	*31.2*	*−22.0*	–	–	–	–	*47.8*	*35*
Pe32	32.0	−21.6	–	–	–	–	46.1	31
Pe36	36.4	−22.5	–	–	–	–	46.2	25
Pe40	40.7	−22.7	–	–	–	–	47.9; 56.8	35
Pe48	*48.8*	*−27.0*	–	–	–	–	*46.2*	*15*

[a] Cold crystallization.

develops during fast cooling, resulting in the endotherm labeled T_m(I), all samples undergo further slow ordering upon aging. This is testified by the appearance or the increase of the endothermic signal at about 50 °C, T_m(II); the associated enthalpy values are given in Table 1.

In our previous investigations [14,15], on the basis of preliminary WAXD experiments carried out on samples containing up to 10 mol% of comonomer, the low temperature endotherms were generically ascribed to the melting of less perfect crystals hosting shorter isotactic propene sequences, mostly in the γ modification, which develop and reorganize during the slow secondary crystallization occurring at room temperature. At the light of the evidences found in the recent literature [39–42], we reconsider the thermal behaviour exhibited by 1-pentene rich copolymers and deduce that the low temperature endotherms appearing in the DSC traces of aged samples must be ascribed to the trigonal modification of isotactic polypropylene, as proved by the temperature-resolved WAXD experiments that will be later described. This implies that the 1-pentene co-units enter a different crystalline modification, which slowly develops at room temperature and in which the bulkier co-units can easily be hosted by the crystal lattice without strong destabilizing effects.

The melting temperatures of the samples quenched and aged for one month at room temperature are reported in Fig. 2 as a function of the 1-pentene content in the copolymer.

In line with the typical behaviour of random copolymers, a remarkable decrease of the melting temperature of the α-form crystals is observed already for the samples containing relatively small amounts of C5 co-units: less than 10 mol% of co-units decreases T_m of more than 70 °C. According to this trend, completely amorphous materials are expected to be observed at slightly higher comonomer concentration. Instead, from *ca.* 10 up to *ca.* 50 mol%, aged C3/C5 copolymers exhibit a quite sharp endothermic signal at *ca.* 50 °C. As shown in the inset of Fig. 2, also the melting enthalpy exhibits a similar dependence on composition. Contrary to what it is generally observed in random copolymers, which readily become completely amorphous, all copolymers with 1-pentene content between *ca.* 10 and ca 40 mol% exhibit melting enthalpies in the range 25–50 J/g, indicating that the extent of crystallization only slightly decreases with C5 content. Only sample

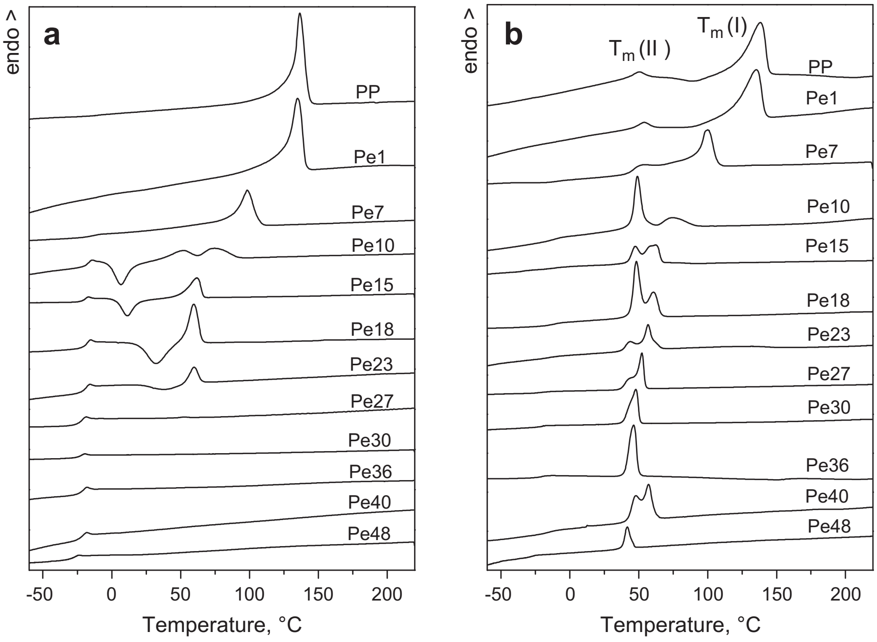

Fig. 1. Normalized DSC traces of propene/1-pentene copolymers on heating: (a) immediately after cooling from the melt to −60 °C at 20 °C/min; (b) after 1 month aging at room temperature of quenched samples.

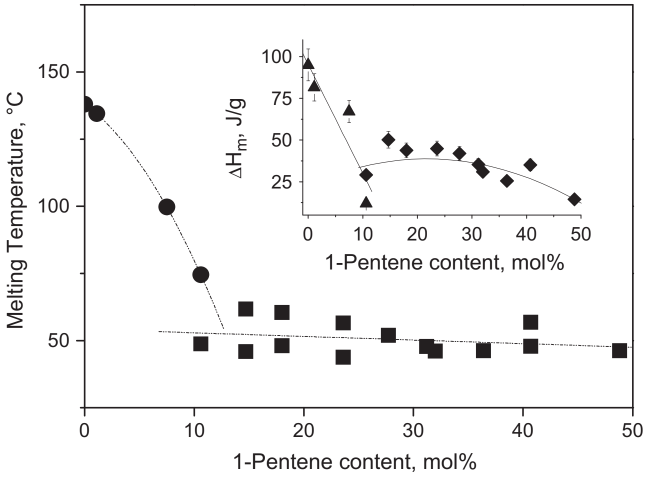

Fig. 2. Peak melting temperatures of propene/1-pentene copolymers quenched and aged at room temperature for 1 month as a function of 1-pentene content; ●, ■ refer to T_m(I) and T_m(II), respectively. In the inset the corresponding melting enthalpies are reported; ▲: ΔH_m(I), ◆: ΔH_m(II).

Pe48 shows a much lower melting enthalpy, thus suggesting that the limit of composition at which the system is capable of crystallizing is approached.

3.2. *WAXD and SAXS analysis*

Development of high levels of crystallinity in random copolymers of propene with higher 1-olefins implies that co-units enter into the crystal lattice, which, to host increasingly amounts of bulky co-units, must expand in one or more directions. This can be assessed by analysis of WAXD patterns. In Fig. 3 the patterns collected at room temperature on well aged samples at various contents of 1-pentene are shown. For the homopolymer and the copolymers with 1-pentene contents up to 7.5 mol% the characteristic reflections of the α-form at $2\theta = 14.2$, 16.9 and 18.6° corresponding to planes (110), (040) and (130), respectively, dominate the pattern; however, a small signal at $2\theta = 20.1°$, indicative of the presence of γ-form, is also detectable. As expected, crystallinity rapidly drops by increasing the comonomer content in this composition range. In the WAXD pattern of sample Pe10, together with the diffraction peaks typical of the α modification, a weak reflection at $2\theta \sim 10.6°$ can be appreciated. With the aim of enhancing the overall level of crystallinity, this sample was also thermally fractionated by applying the successive self-nucleation and annealing (SSA) procedure [43]. The WAXD diffraction pattern obtained after this thermal treatment, which implies step-wise crystallization at high temperature, is also reported in Fig. 3 (trace Pe10a); with the increase of the overall level of crystallinity the reflections at $2\theta \sim 10.6°$ and 20.1° become now well evident, showing that a mixture of α-, γ- and δ-forms is present.

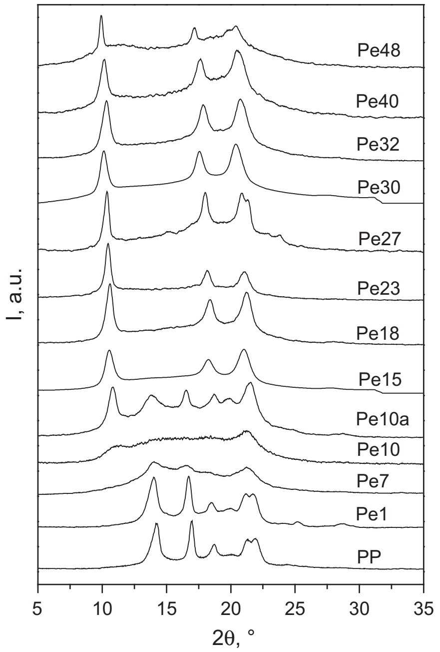

Fig. 3. Room temperature WAXD profiles of propene/1-pentene copolymers aged at room temperature.

For samples with 1-pentene contents higher than 10 mol%, only the three strong reflections at $2\theta =$ *ca.* 10.5, 17.5 and 20.5° appear in the WAXD patterns in the explored 2θ-range.

These reflections characterize the trigonal modification, which is isomorphous to Form I of *it*-poly(1-butene), correspond to Miller indices (110), (300) and (220)+(221), respectively [39–42].

A closer examination of the positions of the diffraction maxima reveals that there is a gradual shift of the reflections towards smaller angles on increasing the percentage of comonomeric units. The values of the corresponding cell parameters are shown in Fig. 4. While the *c* axis value keeps constant at the classical 0.65 nm of the 3/1 helices, the $a = b$ lattice constant linearly increases on increasing the molar content of 1-pentene co-units. This is directly related to the expansion of the lattice in the plane normal to the molecular axis required to host increasingly numerous units bearing the bulkier side groups. In Fig. 4, the data reported by De Rosa et al. for C3/C6 [40] and C3/C5 [42] random copolymers are also plotted.

It is clear that the extent of lattice expansion depends on the size of the substituent: at a given composition the values of *a* and *b* axes of the trigonal unit cell are larger for the copolymers with 1-hexene than for those with 1-pentene. In agreement with the hypothesis of inclusion of comonomeric units into the crystal lattice, which has recently been corroborated by evidences in copolymers with 1-hexene [44], the slope is smaller for the less bulky 1-pentene co-unit. Both lines extrapolate to a value of the lattice constant which corresponds to the hypothetical cell dimension of a propene homopolymer if it could crystallize in the δ-form. Actually, only when the cell density is sufficiently high (*ca.* 0.89 g/cm^3) formation

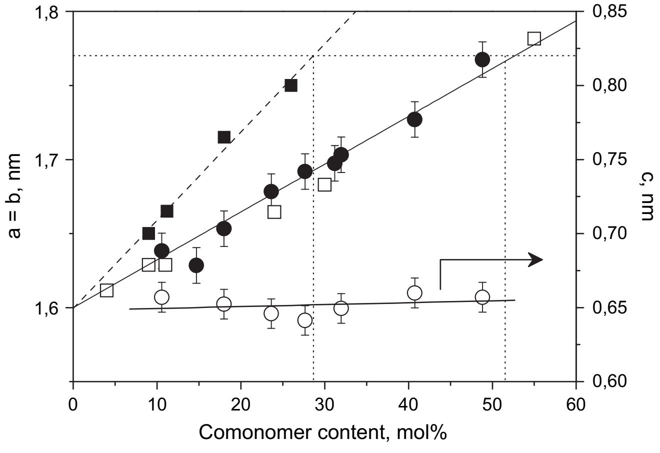

Fig. 4. Cell parameters of the trigonal modification in C3/C5 random copolymers: ● $a = b$ axis (this work), □ $a = b$ axis (from ref. [42]); ○ *c* axis (this work); and ■ $a = b$ axis in C3/C6 random copolymers (from ref. [40]). The dotted line at $a = b = 1.77$ nm corresponds to the cell parameters of Form I of *it*-poly(1-butene) (from ref. [45]).

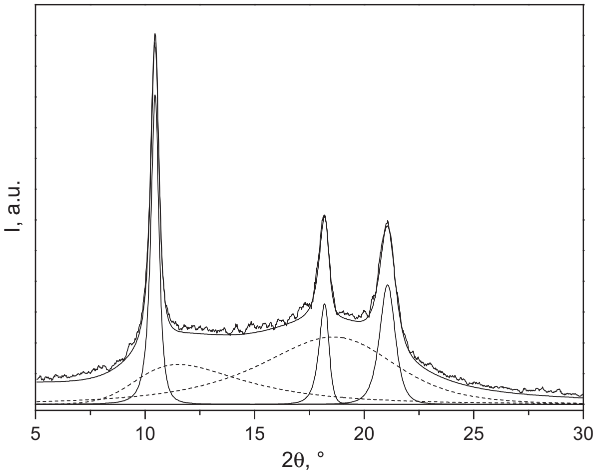

Fig. 5. Example of deconvolution of the WAXD trace of sample Pe18.

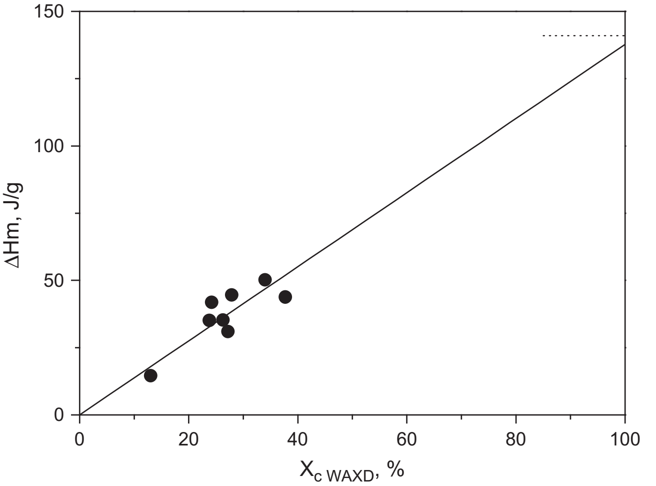

Fig. 6. Melting enthalpy of the α and δ modification in propene/1-pentene copolymers as a function of X_{WAXD}; $\Delta H°_m$ of *it*-poly(1-butene), Form I = 141 J/g (from ref. [50]).

of the trigonal crystals can occur (around 10 mol% for both 1-pentene and 1-hexene co-units). The horizontal line at $a = b = 1.77$ nm drawn in Fig. 4 corresponds to the cell dimensions of *it*-poly-(1-butene), Form I [45]; the intersection of this line with the experimental ones, relative to the two copolymer families, roughly corresponds to the maximum amount of comonomeric units which can enter the trigonal cell: about 30 and 55 mol% for 1-hexene and 1-pentene, respectively. At higher comonomer concentrations the crystalline cell is not longer capable to host the bulky side groups and the material becomes fully amorphous.

To evaluate the degree of crystallinity, the WAXD patterns need to be properly deconvoluted. Several attempts of describing the contribution of the amorphous fraction by a single curve resulted unfruitful, invariably leading to fittings with poor correlation coefficients. Thus, also supported by the WAXD patterns acquired at the synchrotron facility on the molten copolymers, we have used two asymmetric Pearson IV curves, with maxima at *ca.* 12 and 19° 2θ, to fit the signal associated to the amorphous phase. As an example, the deconvolution of the WAXD pattern of sample Pe18 is reported in Fig. 5. The values of the crystallinity degree obtained from WAXD, $X_{C\ WAXD}$, corresponding to δ-form crystals, are reported in Table 2.

The trend of $X_{C\ WAXD}$ as a function of the percentage of C5 is fully consistent with that of the melting enthalpy already shown in the inset of Fig. 2. As shown in Fig. 6, a linear correlation between the melting enthalpy and the degree of crystallinity obtained from the deconvolution of WAXD patterns exists for the aged copolymers containing only the δ modification. By extrapolating to 100% crystallinity, the value of melting enthalpy of the trigonal modification can be estimated to be around 140 J/g. This value is substantially lower than that reported in the literature for the α-form, which ranges from the most reliable $\Delta H°_m = 209$ J/g [46] to $\Delta H°_m = 165$ J/g [47–49]. Instead, it is very close to the melting enthalpy of form I of *it*-poly(1-butene), $\Delta H°_m = 141$ J/g [50], which corresponds to the dotted line in Fig. 6.

Table 2
Morphological features of propene/1-pentene copolymers from WAXD and SAXS analysis.

Sample	$X_{C\ WAXD}$ (%)	D_{110} (nm)	L (nm)	L_C (nm)
Pe10	12[a]	–	9.3	2.5
Pe15	34	13.5	12.0	4.1
Pe18	38	23.5	11.2	4.2
Pe23	28	32.3	9.7	2.7
Pe27	24	–	12.0	2.9
Pe30	26	41.3	12.8	3.3
Pe32	27	27.1	13.4	3.6
Pe40	24	38.1	16.5	4.0
Pe48	13	90.2	–	–

[a] *ca.* 2% δ-form + *ca.* 10% α + γ forms.

As already observed, the formation of δ crystals in C3/C5 random copolymers is a relatively slow process, strongly dependent on comonomer concentration. In Fig. 7 the progress of crystallization in isothermal conditions at 20 °C is shown for a series of samples with different composition, from *ca.* 10 to 40 mol% of 1-pentene, *i.e.* in the range in which the δ-form is favoured.

Since the crystallization of this polymorph is slow, the time-dependent relative crystallinity, ε, was obtained by measuring the melting enthalpy of samples isothermally crystallized for different times from the relationship:

$$\varepsilon(t) = \frac{\Delta H(t)}{\Delta H_\infty} \tag{1}$$

where $\Delta H(t)$ is the melting enthalpy of the sample after crystallization time t, and ΔH_∞ is the value corresponding to the limiting crystallinity attained at long times.

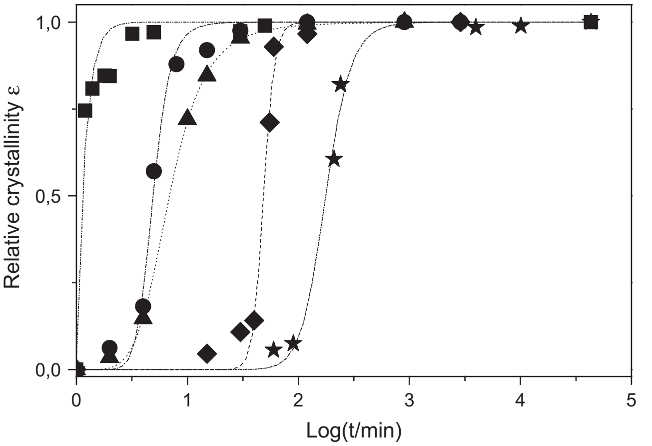

Fig. 7. Crystallization kinetics of the δ-form for various propene/1-pentene copolymers from DSC at 20 °C; ■: Pe 10.6; ●: Pe 18; ▲: Pe 23.6; ◆: Pe 32.0; ★: Pe 40.6.

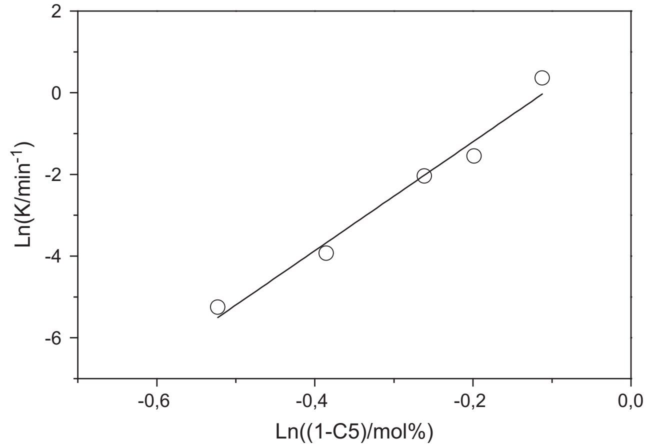

Fig. 8. Overall crystallization rate constant of the δ-form at 20 °C as a function of copolymer composition.

The obtained sigmoidal curves show that, after a composition-dependent induction period, crystallization takes place and quickly reaches a relatively high degree of conversion. As it is common with polymers, the crystallization kinetics slows down in the late stages in which secondary crystallization provides the major contribution. The same trend was obtained by calculating the relative degree of crystallinity from time-resolved WAXD patterns (not shown) collected in isothermal conditions at 0 and 10 °C. The induction time and, consequently, also the overall crystallization rate of the δ-form are strongly dependent on copolymer composition. This is illustrated in Fig. 8, in which the crystallization rate constant, as expressed by the reciprocal of the crystallization half-time, exhibits a power law dependence on comonomer content:

$$K = \frac{1}{t_{0.5}} = K_0(1-[C5])^n \tag{2}$$

with $n \approx 12$.

We suggest that this very strong dependence of crystallization kinetics on the copolymer composition is related to the reduced chance that a chain segment with proper concentration and distribution of branches attaches to the already formed crystalline substrate. Its compositional features must be adequate to fulfil the density constrains required for the formation of the δ-phase along the whole sequence of lattice cells in a lamellar stem. In other words, depending on the local composition of the segments lying on the exposed crystal surface, an arriving segment will contribute to the growth of the crystal only if its constitution enables the density of all cells along the lamellar thickness to lie in the existence range of the δ-form. The difficulty to match this demanding criterion results in frequent failed attempts in which the segments are reshuffled; crystallization will take place only when, through sliding diffusion along the contour length of the chain, a segment with suitable composition is found.

The DSC study on the thermal behaviour of the δ-form in propene/1-pentene copolymers was integrated by temperature-resolved WAXD experiments carried out at beamline A2 of the HASYLAB-DESY. An example of the sequence of WAXD patterns collected on heating at 10 °C/min is shown in Fig. 9, which refers to the sample containing 18 mol% of 1-pentene. The results provide the clear evidence that only δ crystals develop in copolymers with 1-pentene content between *ca.* 15 and 50 mol%. Therefore, the endothermal DSC signals appearing at temperatures around 50 °C must be fully ascribed to melting of crystals in this structural modification. From the series of temperature-resolved WAXD patterns, it can be appreciated that the intensity of all reflections begins to decrease as early as at around 40 °C and that the last traces of crystalline order disappear at *ca.* 60 °C. It has been observed that, after aging at room temperature, all copolymers with 1-pentene content in the range between 15 and 50 mol%, melt in the same wide temperature range, with no clear dependence on composition.

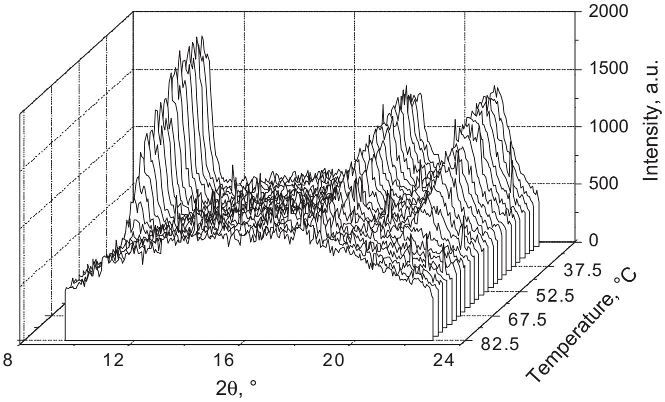

Fig. 9. Temperature-resolved WAXD of sample Pe18. Heating rate: 10 °C/min.

These data are consistent with the broad melting endotherms detected by DSC. This is well evidenced by the comparison of the curves shown in Fig. 10. The intensity of the reflection at $2\theta \sim 10.6°$ is plotted as a function of temperature in part (a) of this figure; the derivative of the smoothed curve fitting the data points in (a) is plotted in part (b); and in part (c) the corresponding DSC signal is also reported. While the melting range detected by DSC seems to be slightly sharper than that derived from the intensity of the (110) reflection in the WAXD patterns, the peak temperature obtained by the two different techniques is coincident.

For the first time, SAXS patterns of polypropylene copolymers crystallized in the δ-form were also collected at the same beamline. In temperature-resolved experiments, the SAXS signal progressively decreases in the same melting range in which the intensity of the WAXD reflections varies. As an example, in Fig. 11 the traces obtained on heating the copolymer Pe32 are shown.

The signals appearing in the SAXS patterns of samples containing the δ-form are weaker than those corresponding to samples in which the α-form is present. This should be ascribed to the lower

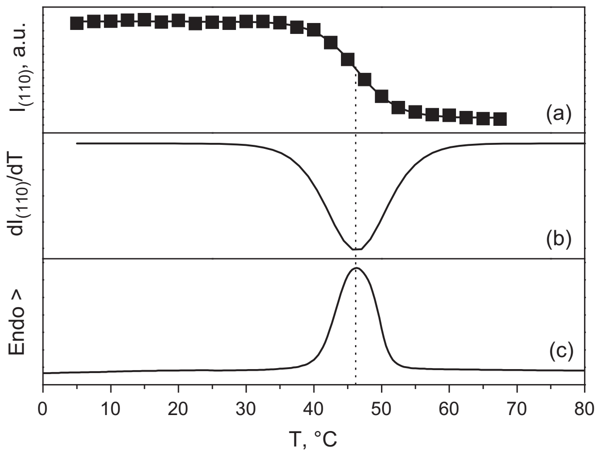

Fig. 10. Comparison between the melting behaviours of the δ-form in copolymer Pe32 as obtained by temperature-resolved WAXD and DSC: (a) temperature dependence of the intensity of (110) reflection; (b) derivative of the curve in (a); (c) DSC signal acquired on heating at 20 °C/min.

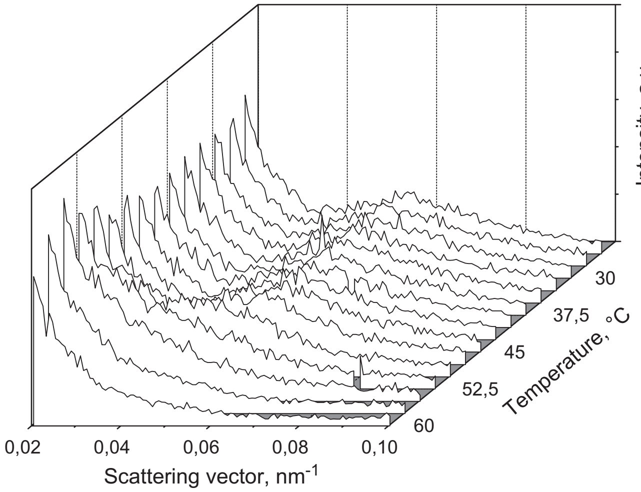

Fig. 11. Temperature-resolved SAXS of copolymer Pe32. Heating rate: 10 °C/min.

electronic contrast between the amorphous phase ($\rho_a = 0.854$ g/cm^3) [39,47] and the crystallites in the low density trigonal modification ($\rho_c(\delta) \approx 0.92$ g/cm^3) [42] in respect to that of the α-form ($\rho_c(\alpha) = 0.95$ g/cm^3) [39,47]. In addition, the existence of wide interphasic regions along the normal to the basal plane of the lamellae and large fluctuations in lamellar thickness due to the wide distribution of the length of crystallizable sequences may also contribute to reduce the intensity of the scattered radiation at small angles.

The raw SAXS data were background subtracted and Lorentz corrected by plotting Iq^2 *vs.* q to enhance the evidence of the peak maximum. The long periods, L, were directly calculated from the position of the maxima and the thickness of the assumed lamellar morphology, L_C, was obtained by considering a two-phase model according to the relationship:

$$L_C = L \cdot X_C \tag{3}$$

The data reported in Table 2 show that the long period of δ-form crystals grown at room temperature progressively increases from *ca.* 9 nm, for sample Pe10, to *ca.* 16 nm for the copolymer with 40 mol% of 1-pentene units. On the other hand, the thickness of the lamellar core keeps constant at $L_C = 4 \pm 1$ nm in the whole range of compositions in which the δ-form exists. This implies that, independent of composition, the lamellae are formed by chain segments around 20 units long packed into the crystal lattice of the trigonal modification and that the amorphous interlayer becomes progressively thicker on increasing the mole fraction of 1-pentene units in the copolymer. This morphological feature is well in line with the previously mentioned problem of finding chain segments with a composition suitable to be incorporated into the crystallites.

It is quite surprising that, notwithstanding the intrinsic disorder associated to the random distribution of 1-pentene co-units, the WAXD diffraction peaks of the δ-form are very sharp, particularly the one corresponding to the (110) plane at *ca.* 10.5° 2θ. In Table 2, the size of the crystallites in the direction normal to the (110) plane, D_{110}, calculated from the Scherrer equation with a correction factor of 0.9 and neglecting the broadening due to lattice distortion, is reported. D_{110} values are in the range 20–40 nm up to 1-pentene content of about 40 mol%. Copolymer Pe48 is characterized by even sharper (110) reflection, which corresponds to a D_{110} value of around 90 nm. By combining the information obtained from SAXS with those from line broadening analysis, one deduces that the δ-form crystallites are thin lamellae which spread laterally over long distances.

4. Conclusions

Notwithstanding the randomness of the insertion of 1-pentene units along the isotactic polypropylene chains, C3/C5 copolymers are capable of crystallizing up to surprisingly high comonomer contents. The resulting structure is the low-melting trigonal modification, δ-form, recently found also in C3/C6 copolymers. The composition range in which this polymorph develops with C3/C5 copolymers is wider than that found for copolymers with 1-hexene and extends up to slightly above 50 mol%.

The melting temperature of the δ-form crystals, which slowly develop upon aging at room temperature, is around 50 °C, substantially independent of the composition and of the bulkiness of the side branch. The melting enthalpy of the pure trigonal modification has been estimated to be around 140 J/g, lower than that of the other polymorphs of *i*-PP, but almost coincidental to that of Form I of *it*-poly(1-butene).

WAXD analysis demonstrates that, in order to host increasing number of the 1-pentene co-units, the lattice expands in the *ab* plane and that the cell expansion depends linearly from the composition. However, the expansion for the studied random copolymers is less pronounced than that observed for analogous *i*-PP copolymers containing the bulkier 1-hexene co-units. It is worth noting that, despite the expected intrinsic structural disorder associated to the randomness in the insertion of the comonomeric units along the chains, the trigonal form exhibits sharp WAXD reflections which indicate a large lateral dimension of the δ-form crystallites.

The long period obtained by SAXS increases on increasing the comonomer content while the thickness of the lamellae keeps constant, at around 4 nm, over the whole range of compositions in which the δ-form develops, thus indicating that the interlamellar amorphous layer becomes thicker on increasing the content of 1-pentene units. The resulting morphological features are consistent with the composition-independent melting temperature and with the strong dependence of crystallization kinetics on copolymer composition.

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